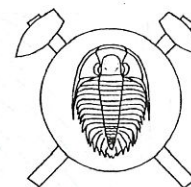


## Crystal chemistry of apatite in tourmaline-bearing alkali-feldspar orthogneiss near Hluboká nad Vltavou, southern Bohemia



### Krystalochemie apatitu v alkalicko-živcových ortorulách s turmalínem u Hluboké nad Vltavou v jižních Čechách (Czech summary)

(3 text-figs.)

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Accessory fluorapatite from three samples of tourmaline-bearing alkali-feldspar orthogneiss was analyzed by methods of wet analysis; rare earth elements were also determined. MnO contents range from 2.11 to 2.84 wt.%, FeO from 0.86 to 2.38 wt.%, REE oxides from 0.36 to 1.02 wt.%, and Na<sub>2</sub>O from 0.54 to 1.20. The chemical composition of apatite including its fluorine content indicates primary magmatic crystallization. The increased contents of Fe, Mn, and REE, and the relative concentrations of Mn – Mg – Fe and La – Ce – Y in these fluorapatites correspond to those of apatites from pegmatites. Apatite is deformed and no post-deformation growth was observed.

### Introduction

The existence of several types of substitutions in apatite make this mineral a useful petrogenetic indicator. We turned our attention to the composition of apatite hoping to characterize the mode of origin of its parent orthogneiss.

The orthogneiss north of Hluboká nad Vltavou is a sheet-like body 7 by 2 km in outcrop size, with a true thickness of about 1 km. It is emplaced conformably to semi-conformably in a sillimanite-biotite paragneiss and belongs to the largest of about ten bodies of similar orthogneisses scattered over the Bohemian part of the Moldanubian Zone (Němec 1980, Klečka et al. 1992). The Hluboká orthogneiss was first mapped and studied by Ambrož (1935) and later mapped in detail (Vrána et al. 1980). About sixty orthogneiss samples have been studied in thin sections, twelve samples were analyzed for trace elements (XRF) and two samples were analyzed for major elements. The results show that the Hluboká orthogneiss is a metamorphosed tourmaline-biotite-muscovite alkali-feldspar granite which is remarkably homogeneous throughout the central and western part of the body. It contains no pegmatite dykes and exhibits a composition corresponding to that of a tourmaline pegmatite (Table 1). Following the geochemical study by Slabý (1991), Hluboká orthogneiss can be compared to granites derived from a crustal source in a syncollisional geotectonic setting. Both the REE in orthogneiss (Slabý 1991) and relative concentrations of accessory minerals indicate that apatite is the major REE carrier; monazite and zircon contents are very low.

Several nests of a poorly foliated aplitic rock up to several meters across are known to occur in the uniform orthogneiss, but they have not been studied in detail. Inclusions of two-mica paragneiss mantle rocks are very rare; relicts of former K-feldspar phenocrysts up to 3 cm long are extremely rare. The rock is medium-grained, has a distinct foliation and more or less prominent linear fabric, sometimes accentuated by oriented tourmaline crystals up to 3 cm long.

### Samples and methods

Heavy mineral concentrates from three samples, each 30 kg in weight, served for the identification of accessory minerals and for separation of apatite. The localities of the samples are as follows:

- #3 roadcut near the road from Hluboká nad Vltavou to Poněšice, near the confluence of Libochovka brook and Vltava,
- #30 disused quarry, 700 m ENE of the elevation Velký Kameník (575 m),
- #85 outcrop in the saddle between Malý Kameník and Velký Kameník, 250 m NW of the elevation 505 m.

The mineral composition of orthogneisses is shown in Table 2. Apatite, frequently amounting to 1 vol. %, forms equant, anhedral and slightly turbid grains evenly distributed in the rock. Few examples of apatite concentration along certain laminae in the foliated fabric have been noted.

The apatite concentrate is grey-green in colour.

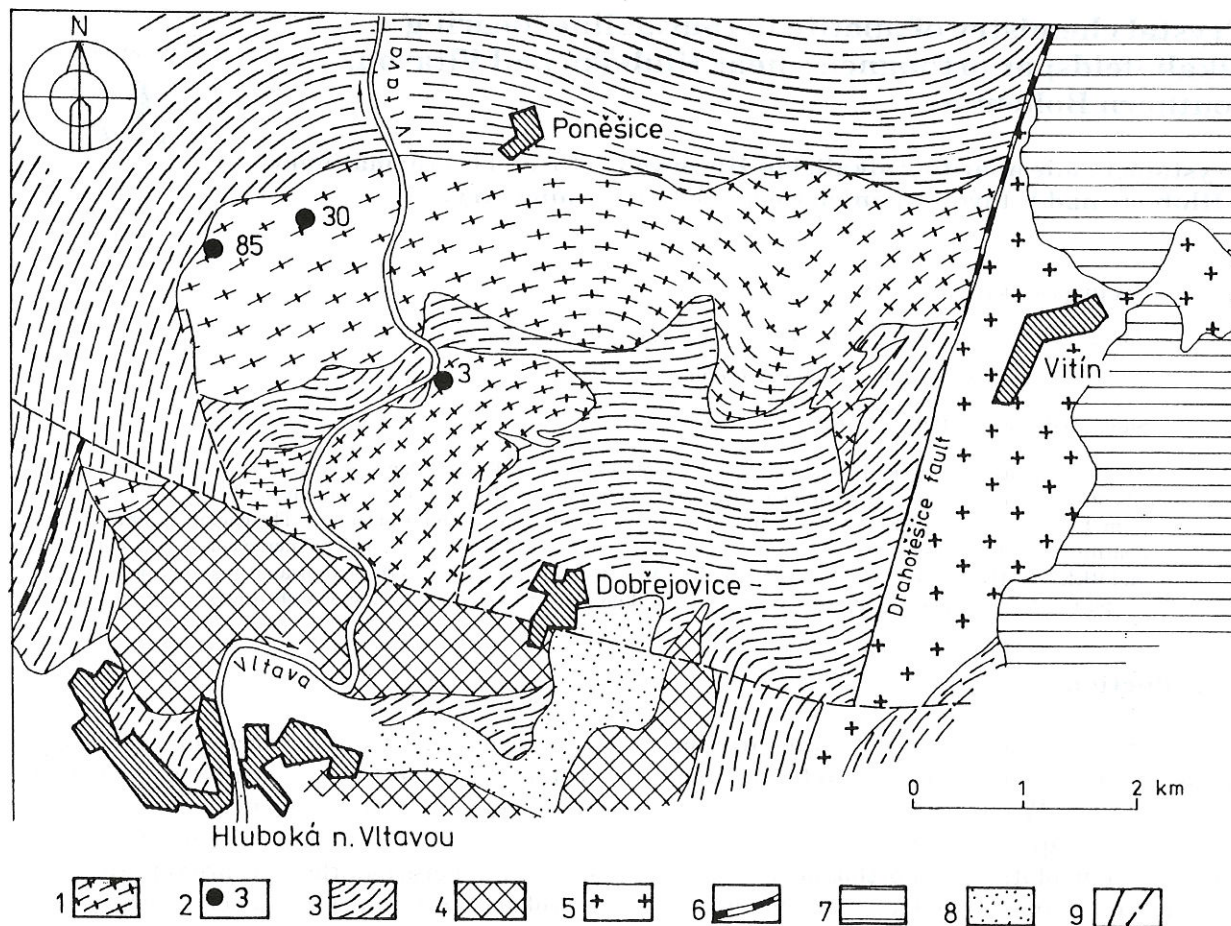


Fig. 1. Simplified geological map of the tourmaline-bearing alkali-feldspar orthogneiss near Hluboká nad Vltavou, showing location of samples. Geology based on 1:50 000 map sheet 22-24 Hluboká nad Vltavou, Czech Geological Survey, Prague. 1 - tourmaline-bearing alkali-feldspar orthogneiss, 2 - sample location, 3 - sillimanite-biotite paragneiss, 4 - gneissified biotite migmatite, 5 - muscovite-biotite granite (Ševětín type), 6 - hydrothermal quartz vein, 7 - Upper Cretaceous sediments, 8 - Miocene sediments, 9 - Faults

Unit-cell parameters measured on one single crystal apatite from sample # 85, using an automated Syntex P2<sub>1</sub> diffractometer gave a = 9.359 (1), c = 6.844 (1) Å. A polycrystalline subsample from the same sample # 85 was measured independently on a powder diffractometer and gave a = 9.361 (1), c = 6.852 (1) Å (Povondra, in press).

Separated apatite was dissolved in diluted HCl and analyzed by wet chemical techniques (Povondra, in press). REE separated from apatite were determined by OES-ICP in the laboratory of the Czech Geological Survey, Prague (V. Sixta, chief chemist).

## Results and discussion

### Crystal chemistry

Contents of the main components in the apatites are similar to those in apatites from other metamorphic rocks. Calcium is the main ele-

ment (89-91 %) in position (vi), showing only a very minor substitution Ca → Sr (0.03 %). The distribution of octahedral cations, shown in Fig. 3 as Mn-Mg-Fe and La-Ce-Y relations, is interesting. The Mn-Mg-Fe relative concentrations show that apatites # 3 and # 85 are close to each other; sample # 30 is notably richer in Fe<sup>2+</sup>. Al three samples plot in the field of apatite from pegmatites and the Příbyslavice peraluminous granite (Povondra, in press) and far from apatites from metamorphic rocks of the Bohemian Massif, such as gneisses, amphibolites, and skarns. The very low contents of Mg in our apatites are also comparable to the contents in pegmatite apatites.

The content of the rare earth elements (REE) - 0.4 to 1.0 wt. % of total oxides - is relatively high. Although REE contents in individual samples are rather variable, the ratios between La, Ce, and Y are similar, and the Hluboká orthogneiss samples, again, plot in the field of apatites from pegmatites and the Příbyslavice

Fig. 2. Distribution pattern of REE in the analyzed apatites

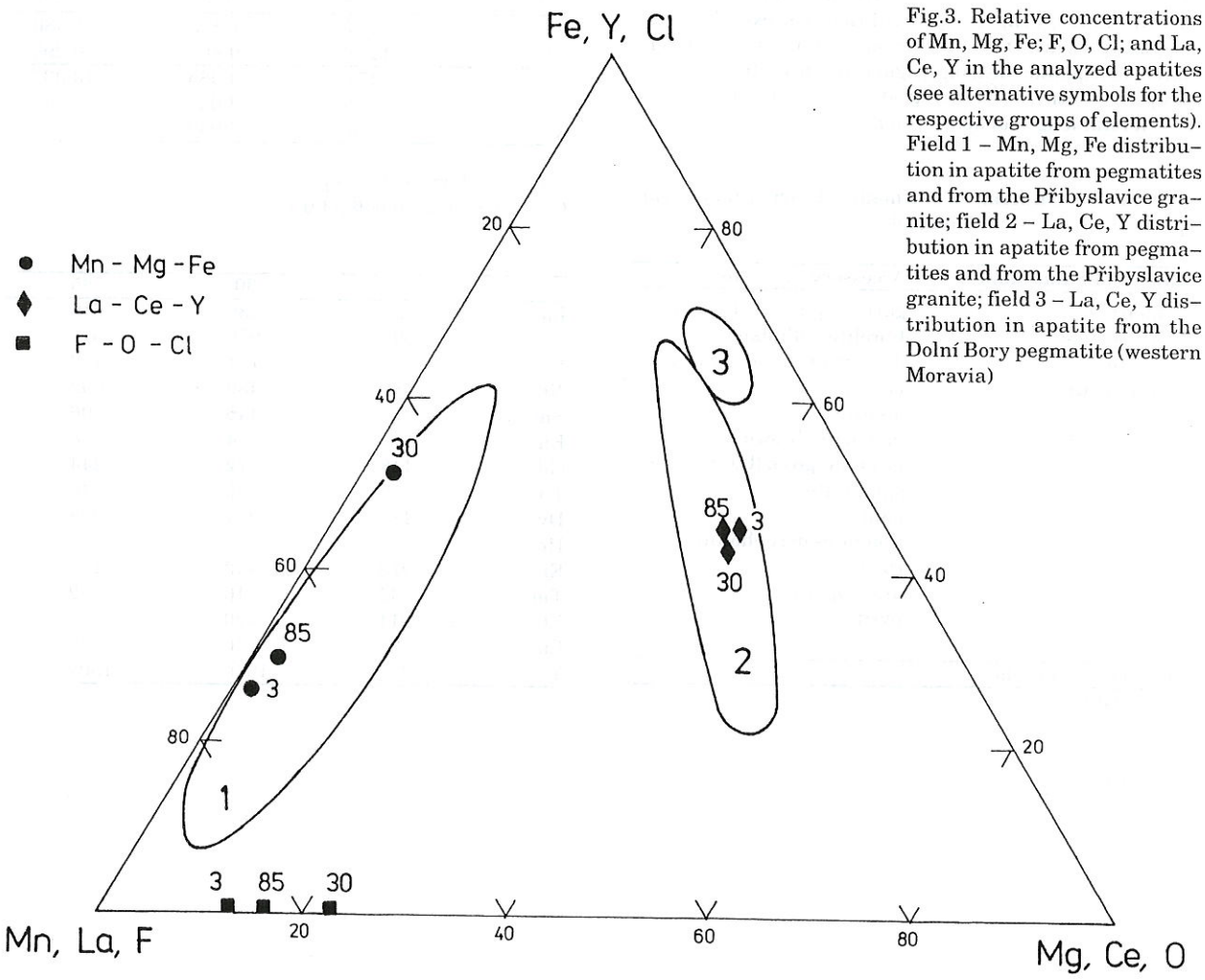
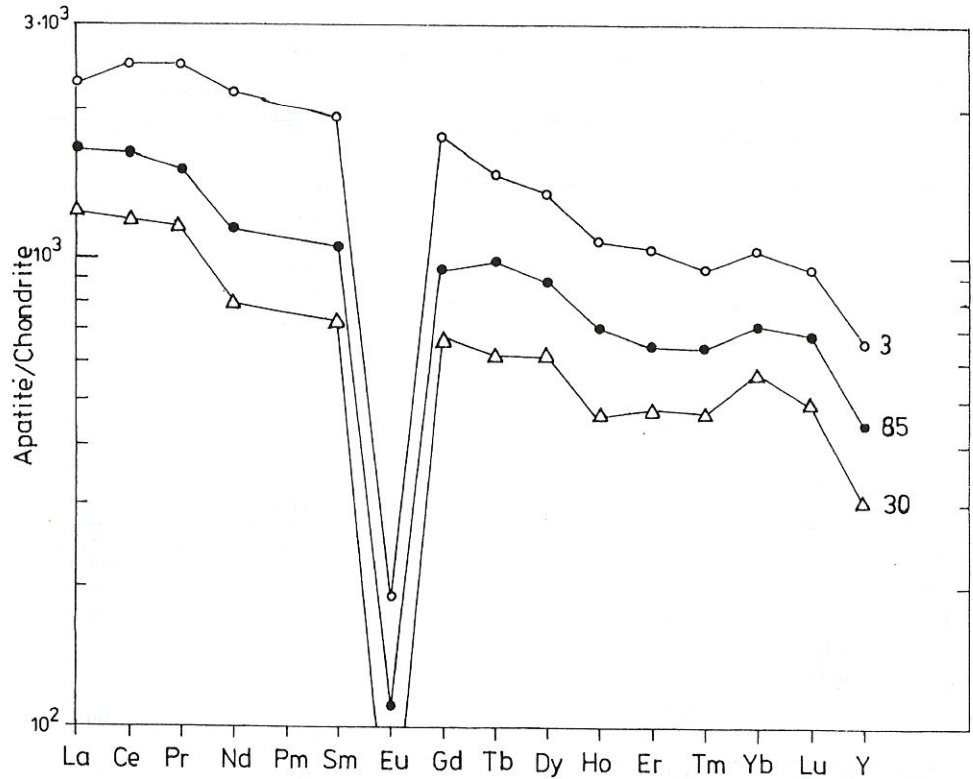


Fig.3. Relative concentrations of Mn, Mg, Fe; F, O, Cl; and La, Ce, Y in the analyzed apatites (see alternative symbols for the respective groups of elements). Field 1 - Mn, Mg, Fe distribution in apatite from pegmatites and from the Příbyslavice granite; field 2 - La, Ce, Y distribution in apatite from pegmatites and from the Příbyslavice granite; field 3 - La, Ce, Y distribution in apatite from the Dolní Bory pegmatite (western Moravia)

Table 1. Composition of tourmaline-bearing alkali-feldspar orthogneiss from Hluboká, compared to an undifferentiated pegmatite

	orthogneiss, Hluboká		Keystone pegmatite
	#3	#30	SouthDakota, U.S.A.
SiO <sub>2</sub>	71.98	74.23	74.2
TiO <sub>2</sub>	0.16	0.07	-
Al <sub>2</sub> O <sub>3</sub>	15.04	14.18	15.0
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.15	0.3
FeO	1.33	1.03	0.3
MnO	0.02	0.02	-
MgO	0.27	0.06	-
CaO	0.51	0.29	0.3
Na <sub>2</sub> O	3.73	3.96	4.6
K <sub>2</sub> O	4.97	3.83	4.2
Li <sub>2</sub> O	0.021	0.039	-
P <sub>2</sub> O <sub>5</sub>	0.48	0.54	0.3
CO <sub>2</sub>	0.025	0.05	-
H <sub>2</sub> O <sup>+</sup>	0.61	0.61	0.6
F	0.17	0.16	0.1
S	0.01	0.01	-
H <sub>2</sub> O <sup>-</sup>	0.21	0.28	-
others	-	-	0.1
Total	99.486	99.219	100.0

Analyses # 3 and # 30 by J.Štícha et al., 1976, Czech Geological Survey, Prague. For localities see text. Keystone pegmatite, South Dakota (Norton 1970) is an undifferentiated tourmaline-bearing pegmatite about 100 m across, sampled continuously using drill cores from two holes with a total length of about 130 m.

Table 2. Minerals in tourmaline-bearing alkali-feldspar orthogneiss from Hluboká

Major and minor minerals	Accessory minerals
quartz	garnet Sp 14-21, Py 3-6, Grs
microcline	fibrolitic sillimanite
albite	dumortierite (very rare)
muscovite	zircon
biotite	apatite
tourmaline	monazite, brown
	monazite, green (U,Ca-bearing)
	sphalerite
	gahnite
	ilmenite-pyrophanite
	rutile
	arsenopyrite
	pyrite
<b>Secondary minerals</b>	
chlorite	
sericite	
anatase	
goethite	

Table 3. Analyses of apatite and crystallochemical formulas

Sample	3*	30	85
CaO	49.90	48.76	50.31
SrO	0.012	0.032	0.032
FeO	0.86	2.38	1.28
MnO	2.42	2.11	2.84
MgO	0.038	0.055	0.034
Li <sub>2</sub> O			0.003
Na <sub>2</sub> O	1.20	0.97	0.54
K <sub>2</sub> O	0.076	0.089	0.023
Al <sub>2</sub> O <sub>3</sub>	0.11	0.15	0.07
REE <sub>2</sub> O <sub>3</sub>	1.02	0.357	0.65
P <sub>2</sub> O <sub>5</sub>	40.94	40.59	41.21
F	3.18	2.88	2.94
H <sub>2</sub> O	0.20	0.40	0.26
insol.	1.02	1.77	0.48
-O=2F	-1.339	-1.213	-1.238
Total	99.637	99.330	99.434
Ca	9.182	9.019	9.195
Sr	0.001	0.003	0.003
Fe	0.124	0.343	0.182
Mn	0.352	0.308	0.410
Mg	0.008	0.015	0.008
Li			0.002
Na	0.399	0.325	0.178
K	0.017	0.020	0.005
Al	0.023	0.030	0.014
RE	0.064	0.023	0.040
PO <sub>4</sub>	5.952	5.932	5.951
F	1.727	1.572	1.586
OH	0.229	0.461	0.296
A	10.171	10.085	10.037
Z	1.956	2.033	1.882
X	5.952	5.932	5.951

\*CO<sub>2</sub> - 0.02 wt. % (0.005 p.f.u.)

Cl<sub>2</sub> - 0.02 wt. % (0.006 p.f.u.)

	3	30	85
La	694	386	516
Ce	1998	970	1318
Pr	302	124	182
Nd	1280	480	692
Sm	378	146	206
Eu	14	4	8
Gd	448	172	244
Tb	70	30	46
Dy	436	204	288
Ho	78	34	50
Er	218	102	138
Tm	32	16	22
Yb	214	120	150
Lu	30	16	22
Y	2234	1040	1502

granite. The chondrite-normalized distribution of REE is shown in fig. 2. The REE distribution pattern of all three samples is identical. The LREE show a slight enrichment compared to HREE, a slight enrichment in Yb, decreased Y and a strong negative Eu anomaly. The ratios LREE/HREE: apatite # 3 – 1.24, apatite # 30 – 1.22, apatite # 85 – 1.19, are near to the average value of 1.4, found in apatites from metamorphic rocks (Povondra, in press).

A surprisingly high content of alkalis (Z – 0.183, 0.345, and 0.416 p.f.u.) compared to the content of  $R^{3+}$  cations and a very minor  $CO_3/PO_4$  substitution indicates the existence of the substitution  $Ca$ , vacancy  $\rightarrow 2R^+$ . The presence of this vacancy could be tested by a detailed study of the crystal structure of our apatites.

The tetrahedral sites ( $XO_4$ ) are fully occupied. The content of  $CO_3$  in apatite sample # 3 (0.005) confirms the known low substitution  $CO_3/PO_4$  and leads to an increase of occupancy in position (iv) to the value of 6.000 p.f.u. The practically equal numbers of  $PO_4$  indicate a homogenous distribution of  $CO_2$  in fluids during the crystallization of apatite.

The anion group X (theoretically 2.000) is nearly fully occupied; fluorine – the dominant anion – occupies 75–85 % of the position. The distribution of F and O is shown in fig. 3. Again, samples # 3 and # 85 are similar, while sample # 30 plots apart. The amount of chlorine, analyzed in the apatite sample # 3 (0.005 p.f.u.), indicates near – absence of this element in the system from which the apatites crystallized.

### Petrology

The presence in a metamorphic rock, an orthogneiss, of apatite displaying compositional characteristic of apatite from granite pegmatite requires a discussion. The orthogneiss, together with the enclosing paragneiss complex, has an amphibolite-facies mineral assemblage corresponding to the sillimanite–muscovite zone. The occurrence of gneissified leucocratic migmatite in close proximity and data on the polyphase deformation – recrystallization history of the paragneisses (Vrána et al. 1980) indicate that the orthogneiss too experienced a polyphase, rather than a single-phase, amphibolite facies metamorphic history. Microscopic study of the orthogneiss in thin sections shows apatite as

anhedral, equant grains which are often deformed and broken, and partly clouded; no obvious indications of apatite recrystallization were observed. Examples of the persistence of primary apatite in various meta-igneous rocks metamorphosed under amphibolite facies are numerous and indicate that apatite in such rocks behaves as a relatively refractory phase.

In our opinion, the refractory tendency of apatite and the fact that the samples analyzed included relatively larger grains corresponding to 0.1–0.3 mm size fraction make it probable that the apatite analyzed essentially corresponds to the primary igneous apatite. Also, we observe in our data no indication of a variable fraction of recrystallized and compositionally distinct apatite populations. Microprobe study may be better suited for a search of indications of compositional trends in apatite, possibly associated with the superimposed metamorphism or recrystallization.

The difference in the Mn/Fe ratio between apatite # 30 and samples # 3 and # 85 indicates a modest evolution/differentiation trend in the orthogneiss body, in spite of the prevailing petrographic and geochemical uniformity.

Povondra et al. (1987) and Klečka et al. (1992) dealt with the Přebyslavice granite and Blaník orthogneiss, respectively. In view of a widespread evidence of the involvement of the enclosing paragneiss mantle rocks in the generation of the Přebyslavice granite, a granitization origin was suggested. Klečka et al. (1992) suggested a late boron metasomatism as a significant process in the evolution of the Blaník orthogneiss. Compared to these two examples of the wider series of Blaník type orthogneisses, the orthogneiss near Hluboká nad Vltavou features a notable petrographic and geochemical uniformity. It could be interpreted as a strongly deformed and regionally metamorphosed intrusion having the composition of a tourmaline-bearing granite pegmatite. Since several significant tectonic events, such as a major crustal stacking in the Moldanubian Zone and D 3 regional deformations postdate the Blaník-type rocks intrusion, it is likely that individual bodies represent different exposure levels without an obvious relation to the original intrusion levels. It is suggested that future comparative studies of these orthogneisses should recognize this complexity.

*Translated by the authors*

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### Krystalochemie apatitu v alkalicko-živcových ortorulách s turmalínem u Hluboké nad Vltavou v jižních Čechách

Práce podává analýzy akcesorického fluorapatitu ze tří vzorků muskovit-biotitické alkalicko-živcové ortoruly s turmalínem, získané klasickou analýzou. Chemicky separované oxidy prvků skupiny TR a Y byly analyzovány metodou ICP. Apatity obsahují 2,11–2,84 hmot.% MnO, 0,86–2,38 hmot.% FeO, 0,36–1,02 hmot.% oxidů TR a 0,54–1,20 hmot.% Na<sub>2</sub>O. Chemické složení apatitů včetně obsahu fluóru svědčí o jejich primární magmatické krystalizaci. Zvýšené obsahy Fe, Mn a TR, jakož i relativní koncentrace Mn – Mg – Fe a La – Ce – Y, odpovídají obsahům v apatitech z pegmatitů. Apatit je deformovaný, bez projevu růstu a rekrystalizace. Zjištěné údaje umožnily využít minerální chemismus jako petrogenetický indikátor, dokládající vznik hluboké ortoruly deformací a metamorfózou výchozího muskovit-biotitického alkalicko-živcového granitu, jehož složení odpovídá jednoduchým pegmatitům.