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HYDROBIOTITE FROM THE DĚTAŇ OLIGOCENE TUFFS (DOUPOVSKÉ HORY Mts.)

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ABSTRACT

Oligocene tuffs in the quarry near Dětaň (Doupovské hory Mts.) contain short columns of dark mica reaching up to 15 mm in diameter. X-ray diffraction study revealed that their original phlogopite crystal structure was transformed during weathering processes into phlogopite-vermiculite structure. The dark mica from Dětaň, in comparison to the dark mica from the nearby Oleška locality, shows much simpler X-ray diffraction scheme. X-ray diffraction has found here only phlogopite and vermiculite components joined in mixed-layered forms, irregularly or regularly (hydrobiotites) arranged, beside preserved phlogopite parts of $2M_1$ structural type. DTA curve is similar to that of vermiculite. Thermogravimetry, however, exhibits lower amount of water in respect of this mineral, confirming the presence of the mixed-layer structure. Computer program Newmod simulated the arrangements with regular mixed-layer structure in hydrobiotite beside irregular interstratification of phlogopite and vermiculite sheets.

KEYWORDS: hydrobiotite, Dětaň, oligocene, mixed-layer structure

1. GEOLOGICAL SETTING

The locality Dětaň (an abandoned kaolin quarry) is unique by its set of subaerial and subaquatic tuffitic rocks with a rich palaeontological, sedimentological and mineral context. The locality is situated at the southern margin of the Doupovské hory Mts.,western Bohemia. The area of Doupovské hory Mts. contains the geological record of a polyphase Oligocene volcano (Plate 1A). The volcanic rocks overlie mostly the Upper Carboniferous continental sandstones and arkoses. The volcanites are mostly basaltic, with non-olivine rock types (i.e. tephrites and foidites) prevailing over the olivine ones. The ratio between solid rocks and volcaniclastites is about 1:4. Some pyroclastic accumulations are developed in situ as ash layers and pyroclastic flows, certain part (over 50 %) was re-transported by volcanic mudflows (lahars) and by fluvial processes (river and lacustrine environments). Large part of the pyroclastic rocks has been influenced by secondary carbonation. The lowermost exposed layers at Dětaň, i.e. Carboniferous kaolinised arkoses and sandstones, were subjected to the former exploitation. Overburden layers reach up to 50 m in thickness; of all, 30-40 m of the profile is represented by tuff and tuffite layers usually several decimetres thick. More than 90 individual layers were distinguished. The layers typically differ in colour (grey, brownish, reddish and violet nuances), grain size, lateral extent (lentils, quickly nipping layers, stable layers), presence of lamination, and in palaeontological content. Lower 15-20 m of the volcaniclastic sequence is composed of non-laminated tuff layers gradually passing one to another. Some layers contain frequent angular lava shreds or, less frequently, lapilli. The tuff layers are overlapping by laminated, in places cross-bedded tuffites.

Radiometric and palaeontological data point to the conclusion that all the volcaniclastic series appeared in a relatively short time during the Lower Oligocene. From the point of view of pedology, numerous layers seem to represent paleosols, because of rich root structures and insect traces. However, micromorphological study of individual layers has not approved any stage of soil development.

Lower part of the tuff section of the Dětaň quarry is characterized by the presence of the clinopyroxene phenocrysts, whereas the upper part (Plate 1B) contains short columnar phenocrysts of dark mica (up to 15 mm in diameter) which reflects the growing water content of the parental magma.

Conspicuous dark brown crystals are small whereas the larger crystals are bronze-coloured in margins reflecting alteration process. The small crystals are presumably non altered. The flakes originated by disintegration of large crystals form up to 15 vol.% of certain beds. Similar transformed dark mica phenocrysts were described from the phlogopite-bearing tuff at Oleška, near Doupov (Melka et al.

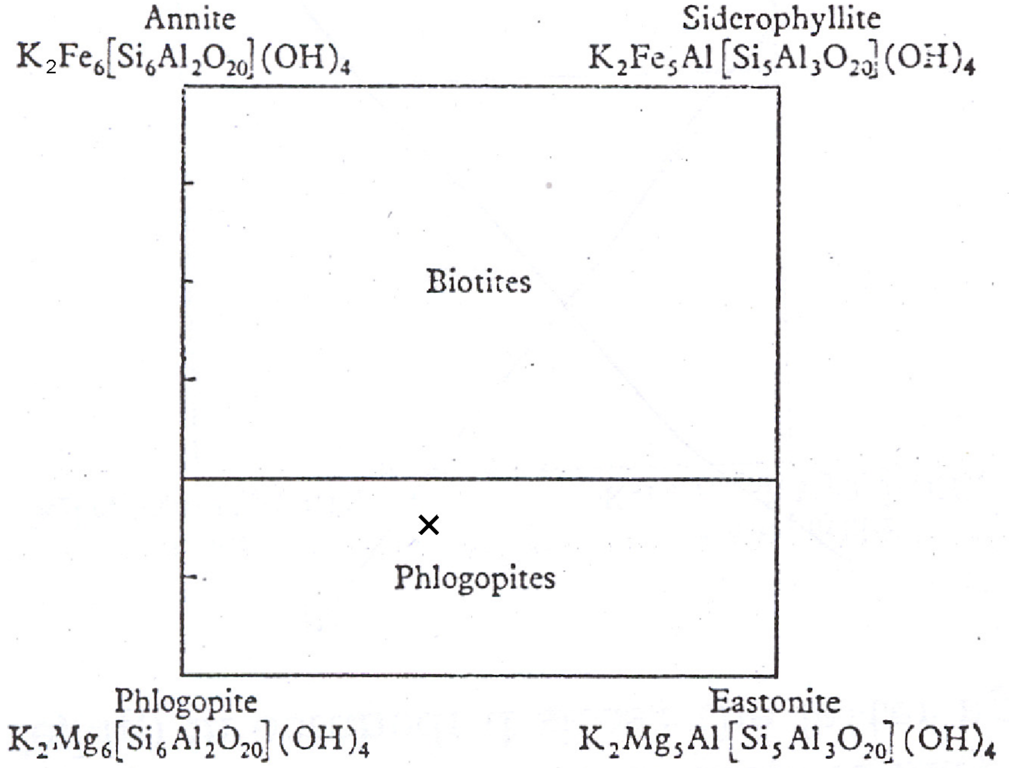

Fig. 1 The composition range between biotite and phlogopite after Deer et al. (1962).
* The position of phlogopite from Dětaň in the diagram is marked by a cross.

2000). Pozzuoli et al. (1992) and Ruizamil et al. (1993) described similar weathering of biotite and its transformation into vermiculite from volcaniclastites in central Italy, including the presence of hydrobiotite interstratified phase with a strong tendency towards regularity. Hydrobiotites were also determined by X-ray diffraction from a number of localities before: North-western and North-eastern Transvaal (South Africa), the Enoree area of South Carolina (USA)-materials studied and published by Brindley et al. (1983), near Křemže (Southern Bohemia) in serpentinites-described by Götzinger (1986) and from a pegmatite body at Stupná (close by Křemže) near the original occurrence-subjected to single-crystal examination by Weiss (1980).

2. CHEMICAL COMPOSITION

Chemical analyses of phlogopites and hydrobiotites were performed by means of the electron microprobe analyzer JEOL JXA-50A equipped with energy dispersive spectrometer EDAX PV 9400. The original dark mica corresponds to phlogopite in classification of Deer et al., see Fig. 1. Adopted nomenclature differentiates phlogopite from biotite on the basis of the Mg:Fe molar proportions: phlogopite (>2:1) and biotite (<2:1).

The main difference between hydrobiotite and phlogopite (Table 1) from chemical point of view is in the amount of potassium and water. The values of *100% - Σ* give some information on water content for hydrobiotites. *Σ* presents the sum of determined components.

$$\underbrace{K_{1.80}Na_{0.18}}_{1.98}\underbrace{(Mg_{4.34}Fe^{2+}_{0.93}Ti^{4+}_{0.49}Mn_{0.02})}_{5.78}\underbrace{Si_{5.45}Al_{2.53}Ti^{4+}_{0.02}}_{8.00}O_{20}(OH)_{4.00}$$

Table 1 Chemical analyses of the studied representative samples from Dětaň.

	hydrobiotite mass % (1)	hydrobiotite mass% (2)		phlogopite mass% (3)
SiO_2	33.55	34.57	SiO_2	37.99
TiO_2	4.21	4.10	TiO_2	4.74
Al_2O_3	13.05	13.21	Al_2O_3	14.99
CaO	2.28	1.96	CaO	-
*FeO	7.33	7.49	*FeO	7.79
MgO	18.10	17.92	MgO	20.30
MnO	0.15	0.20	MnO	0.18
Na_2O	0.98	0.80	Na_2O	0.66
K_2O	**6.36**	**6.31**	**K_2O**	**9.84**
Σ	86.01	86.56	H_2O	4.15
100% - Σ	**13.99**	**13.44**	**Total**	**100.64**

* Total iron content as FeO

Σ Sum of determined components

From the chemical analysis No.3, the empirical formula of phlogopite based on 24 (O,OH) ions in the unit cell was calculated by Mincalc software (Melín and Kunst, 1992). The amount of H_2O for phlogopite in the Table 1 (analysis No.3) results from the use of the mentioned program.

3. MINERAL COMPOSITION

Differential thermal analysis (DTA) of the pulverized mica flakes (Dětaň – Doupovské hory Mts.), containing hydrobiotite beside the original phlogopite, exhibits very intensive endothermic peak (Fig. 2) in the low temperature range with its minimum at 100 °C. It documents the release of molecular water. This peak is doubled and the second minimum occurs at 200 °C.

The DTA curve has the similar appearance like the curve of vermiculite. This component forms a part of the hydrobiotite crystal structure and is responsible for its behaviour during heating.

The thermogravimetric (TG) curve exhibits about 6 % loss in mass, which belongs mainly to the release of water from interlayer positions of the vermiculite part of the hydrobiotite crystal structure, contained in the pulverized mica flakes beside prevailing phlogopite. Standard vermiculite includes roughly 20 % of water while the pure hydrobiotite should have ~ 14 % of water.

Philips automatic apparatus X´pert APD with the graphite monochromator was used for the diffraction analysis. A region from 2θ CuKα 2° to 75° of the X-ray pattern was run by using scanning speed 1°/min. X-ray beam was demarcated by ½° divergence slit, 0.1mm receiving slit and ½° scatter slit. Electric conditions on the X-ray tube were as follows: 40kV/40mA.

The diagram in Fig. 3 compares two X-ray patterns of samples from the locality Dětaň with the third one from Oleška (Melka et al. 2000).

The first analysis was carried out on the separated crystal flake, 1 cm in size, which was mounted directly on the glass slide with a trace of adhesive. The material was not ground. Only basal diffractions of hydrobiotite and phlogopite appeared in the recorded pattern. Individual peaks are indicated by signs belonging to these two mineral phases (Fig. 3, *HB*-hydrobiotite, *P*- phlogopite) together with their Miller indices and the respective spacings. Hydrobiotite has here distinct diffractions.

The second X-ray diagram in Fig. 3 was obtained from the crystal that was ground and its powder pressed into the holder. The surface of the sample was then smoothed. Phlogopite is in this case the prevailing component and it can be subtracted from the first diagram. Besides, a separate preparation was prepared with a side packing for enhancing non-basal diffractions to facilitate the polytype determination. Phlogopite is present in $2M_1$ modification. Its pattern is not reproduced here. Diffraction data are given in Table 2.

The third pattern gives the possibility to compare mica flakes of Dětaň with the material from Oleška which is composed of smectite (*Sm*), vermiculite (*V*) and kaolinite (*K*) beside hydrobiotite (*HB*) and phlogopite (*P*) occurring as main components.

4. HYDROBIOTITE MIXED-LAYER STRUCTURE

Our attention was directed especially to hydrobiotite. It has mixed-layer crystal structure formed of regularly alternating phlogopite and vermiculite sheets in the proportion 1:1. The term hydrophlogopite could be also applied for the studied regular interstratification. But due to the structural

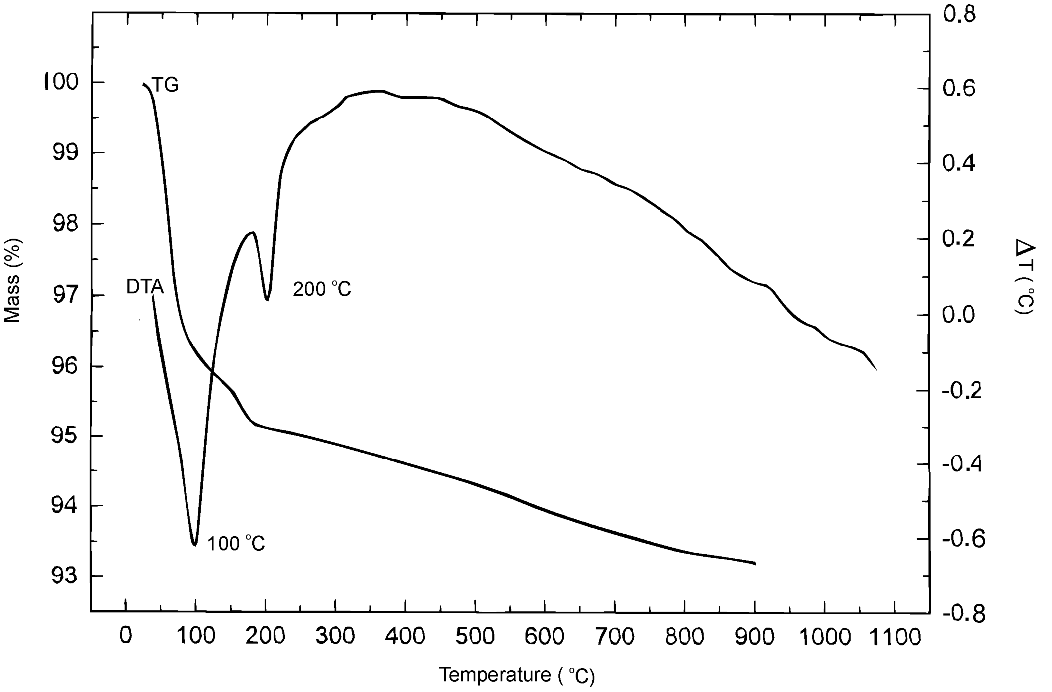

Fig. 2 DTA and TG curves of pulverized mica flakes containing hydrobiotite from Dětaň.

identity and close chemistry between biotite and phlogopite we apply the priority term hydrobiotite for Bi-Ve regular interstratification introduced by Veniale and van der Marel (1969).

Trioctahedral character of mica (phlogopite) and hydrobiotite was determined from *060* diffractions. Value 1.539 Å was obtained from the separate scan in the range of 57° - 63° 2θ for copper radiation. Divergence slit 4°, receiving slit 0.2 mm and scatter slit 4° were used.

On the basis of *00ℓ* basal diffractions mean d_{001} for hydrobiotite from Dětaň was calculated: 24.29 ± 0.92 Å, compared to 24.51 ± 0.051 Å from Oleška (Melka et al. 2000).

For the interpretation of mixed-layered minerals from Dětaň the computer program Newmod-for-windows (Reynolds Jr. and Reynolds III, 1996) was used.

In Fig. 4 a part of X-ray diffraction pattern of the separated crystal flake is reproduced. It represents a mechanical mixture of two mineral phases, of phlogopite and hydrobiotite. Hydrobiotite can be considered to be the intimate mixture of two components, in which phlogopite and vermiculite layers regularly alternate. It is characterized by high value of its basal diffraction, higher orders of which can be derived after dividing by whole numbers. The lower curve represents the real structure. The upper curve was calculated by means of Newmod program. The agreement between these two patterns is apparent. Decimal fraction of *phlogopite* (P_A) : *vermiculite* (P_B) in this case equals 0.5. Numerical value for the range *R* (Reichweite), which determines the probability of *A*-layer following *B*, $(P_{B.A})$, is here 1, whereas probability of *B*-layer following *B*-layer, $(P_{B.B})$, is zero.

Sequential layer probabilities are related by these connections:

$$P_{A.A} + P_{A.B} = 1$$
$$P_{B.B} + P_{B.A} = 1$$

In hydrobiotite layers *A* and *B* are combined according to the following scheme: ABABABAB, it means that *A* (phlogopite) layer is surrounded with *B* layer (vermiculite) from each side.

After crushing and pulverizing a crystal flake, the oriented aggregate of crystallites on the glass slide was prepared. The X-ray diffractogram is reproduced in Fig. 5. Contrary to the previous sample, the mixed-layered mineral phase is composed of the same components, but with the irregular arrangement. The crystal structure of the irregular interstratification of phlogopite-vermiculite (P-V) is registered. It cannot be spoken on hydrobiotite, as this name is reserved for the regular interstratification of phlogopite and vermiculite.

Lower X-ray pattern in Fig. 5 belongs to the real structure. The upper one was calculated. The good agreement of traces belonging to mixed-layer structures is observable. The range *R* (Reichweite) 0.0 was installed in the program to define the ordering type. The decimal fraction of the most abundant

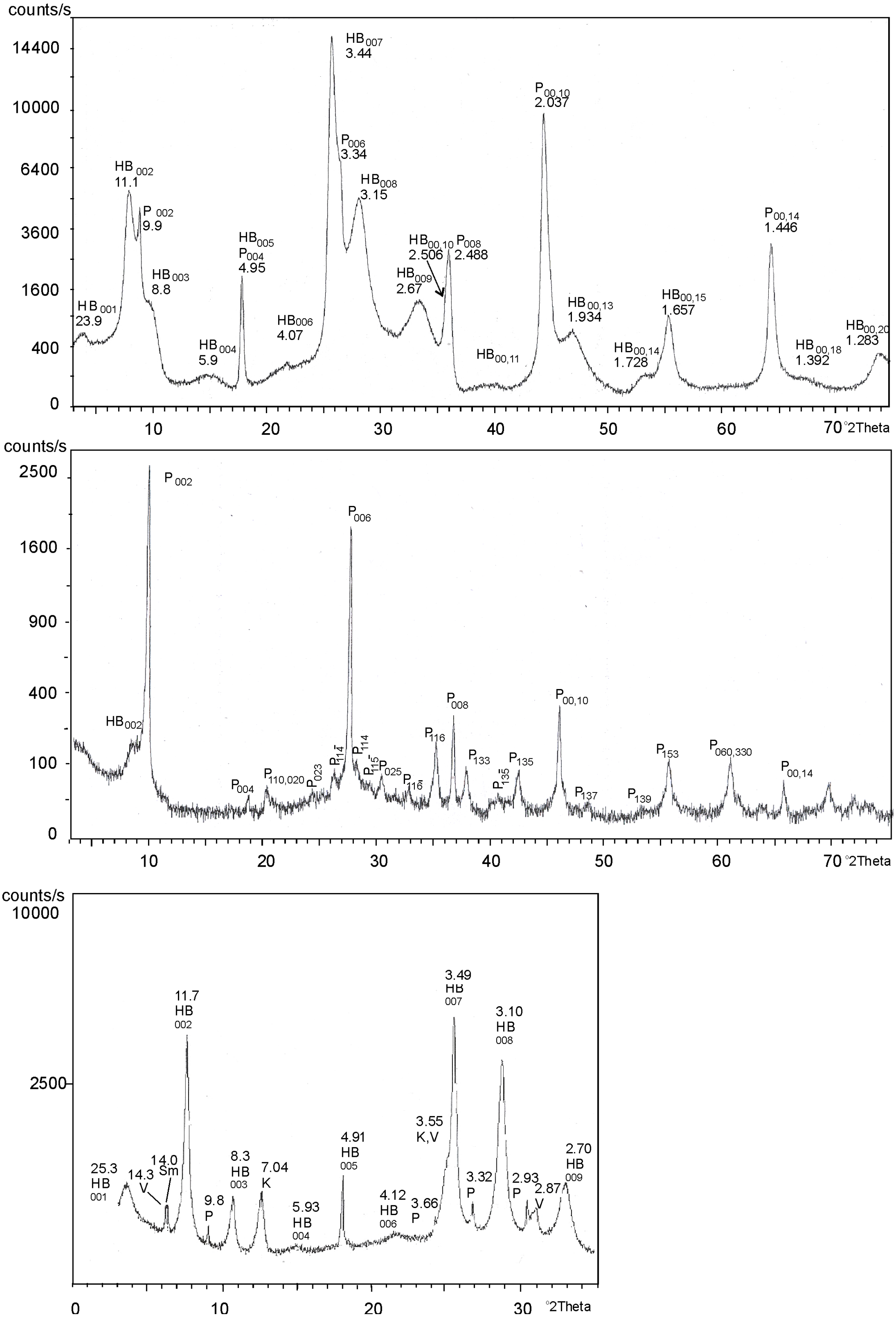

Fig. 3 X-ray diffraction patterns of samples from the locality Dětaň and Oleška:
upper: separated crystal flake (Dětaň),
middle: pulverized sample (Dětaň),
lower: sample from Oleška (Melka et al. 2000).
Diffraction peaks of mineral phases are marked as follows: *HB* - hydrobiotite, *P* - phlogopite, *Sm* - smectite, *V* - vermiculite, *K* - kaolinite. *d*-values in Å and *hkℓ* indices for individual diffraction peaks are indicated.

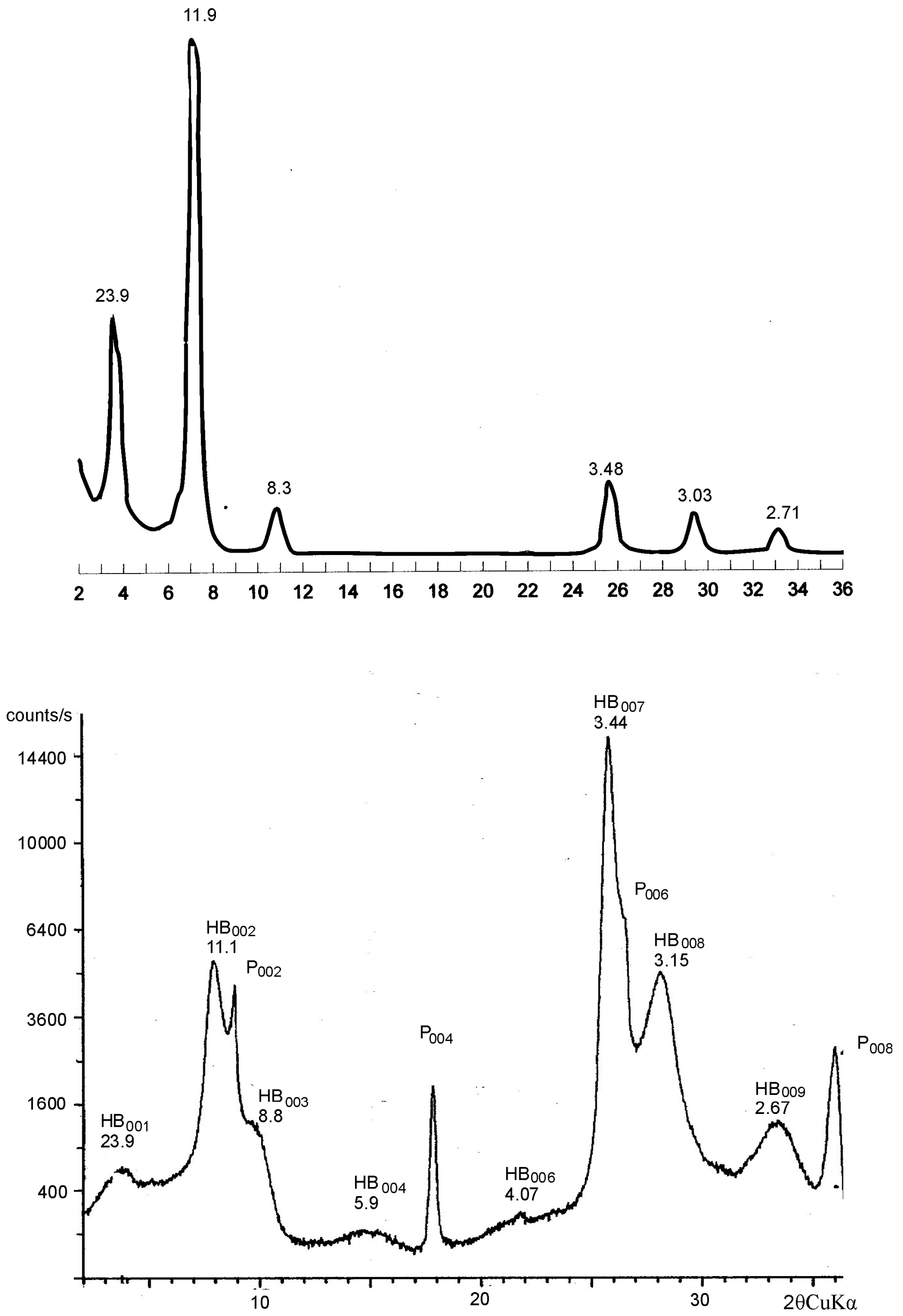

Fig. 4 A part of the real X-ray diffraction pattern of the separated crystal flake from Dětaň (at the bottom) compared with the simulated pattern for the regular mixed-layer structure of the hydrobiotite, i.e. phlogopite-vermiculite 1:1, according to the computer program Newmod-for-windows (upper pattern).

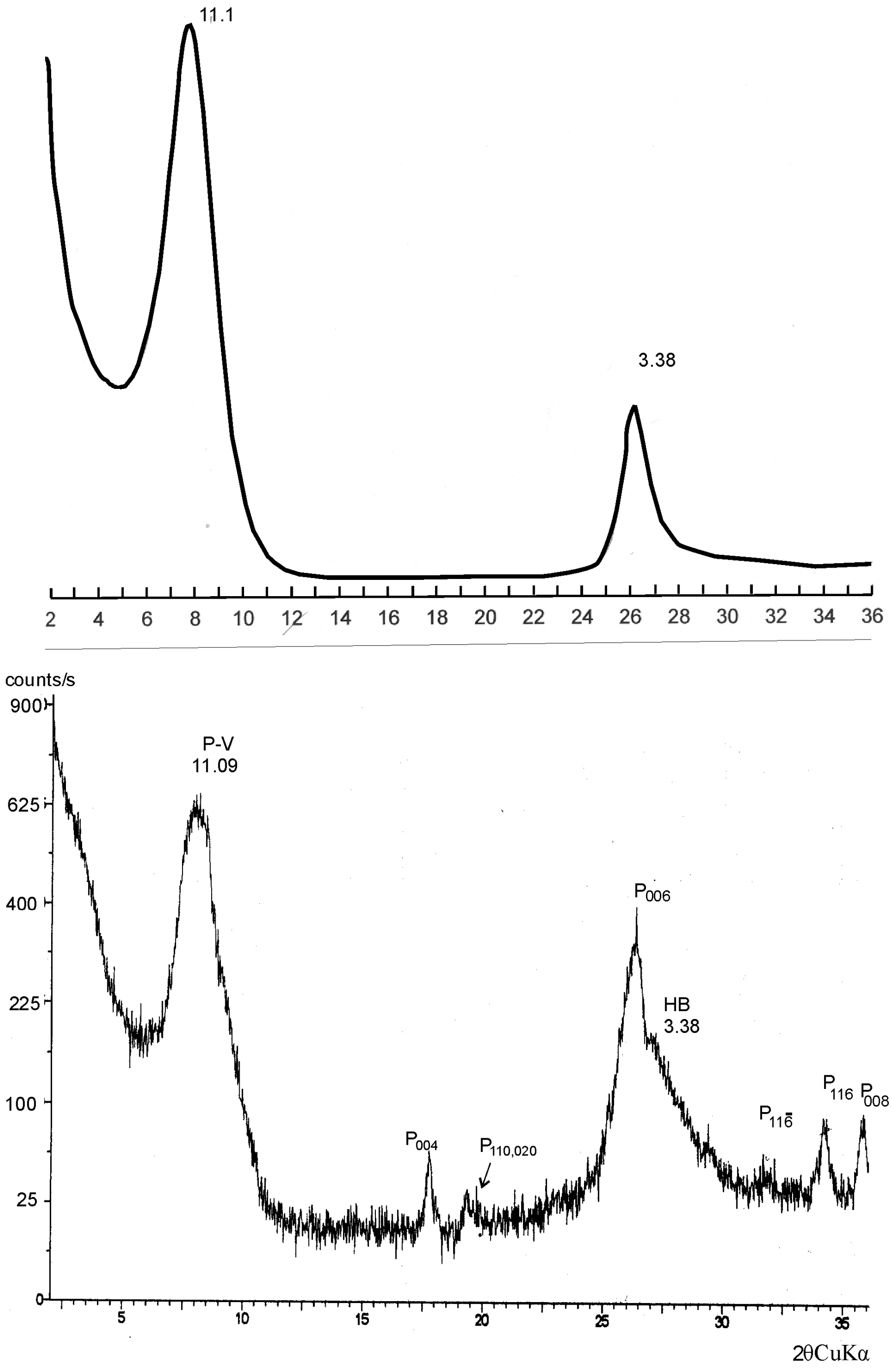

Fig. 5 A part of the real X-ray diffraction pattern of the crushed and pulverized crystal flake (at the bottom) showing the irregular interstratification of the same components as shown on Fig.4 compared with the simulated pattern using computer program Newmod-for-windows (above).

Table 2 X-ray diffraction powder data for phlogopite $2M_1$ from Dětaň (side packing of the sample).

dÅ	I	hkl	Component
11.8	9	002	HB
10.03	100	002	P
5.02	1	004	P
4.61	9	110, 020	P
4.50	4	021	P
4.07	4	112	P
3.805	6	023	P
3.536	12	$11\bar{4}$	P
3.364	48	006	P
3.278	13	114	P
3.158	6	$11\bar{5}$	P
3.045	8	025	P
2.920	4	115	P
2.820	5	$11\bar{6}$	P
2.627	35	116	P
2.514	9	008	P
2.439	17	133	P
2.307	3	220, 040	P
2.267	6	$13\bar{5}$	P
2.177	13	135	P
2.016	9	00,10	P
1.910	2	137	P
1.746	2	139	P
1.675	8	153	P
1.537	18	060, 330	P
1.519	4	062	P

P - phlogopite, HB - hydrobiotite

component (i.e. of phlogopite) was changed step by step untill the good conformity was achieved. This was at the P_A value of 0.73.

A variation of the probability $P_{B.A}$ from zero to 1 describes a series that starts as a *mechanical mixture* and becomes more intimate until at $P_{B.A} = P_A$ (decimal fraction of phlogopite). *A* and *B* in this interval are *randomly interstratified*. Further increase in $P_{B.A}$ enhances the tendency of the *partial ordering* and the ordering is complete at $P_{B.A} = 1$.

When our study of the mica flake from the Dětaň locality is recapitulated, the question to the explanation is remaining, why the crystal flake of hydrobiotite with the *regular interstratification* of phlogopite and vermiculite components has changed after grinding into the *irregular interstratification* of these components. It could be explained by a strong dehydration and shrinkage of the vermiculite phase during dry grinding. A point temperature on individual fragments, namely, can reach up to several hundred degrees centigrade.

5. CONCLUSION

Original phlogopite phenocrysts in tuffs from Dětaň were transformed during weathering processes into mixed-layer compositions formed by phlogopite and vermiculite components. Computer program Newmod was used for the interpretation of these mixed-layer crystal structures. X-ray patterns of real mineral flakes were compared with calculated patterns. As a result regular mixed-layer structure of hydrobiotite (or hydrophlogopite) was determined. After grinding and pulverizing of original flakes a new material was obtained that exhibited irregular interstratification of phlogopite and vermiculite sheets.

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Plate 1A

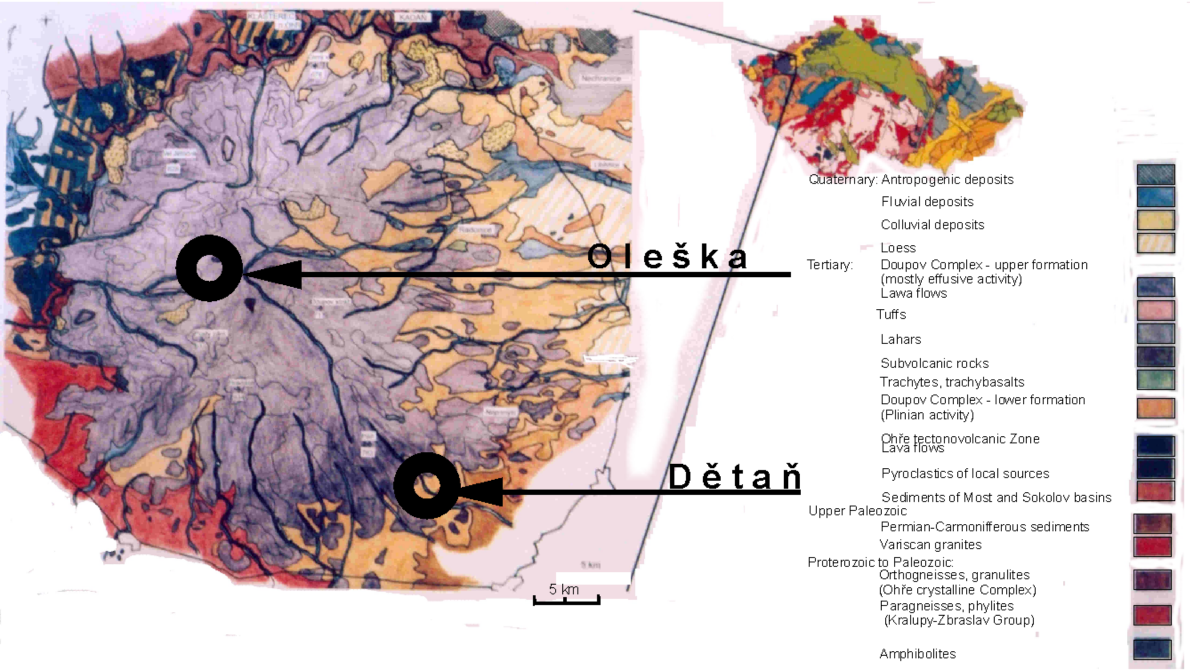

Plate 1B

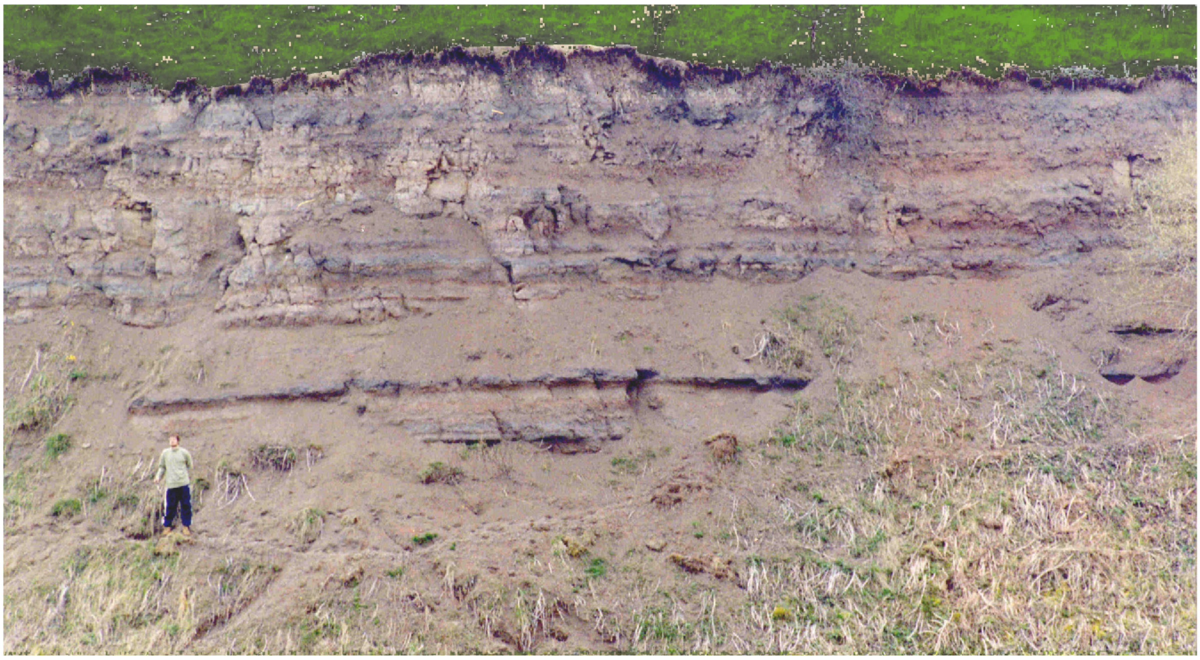

Plate 1A Geological sketch of the Doupovské hory Mts., western Bohemia, showing the location of rocks containing hydrobiotite. Adapted from Hradecký and Rapprich (2002).

Plate 1B Lower part of the volcaniclastic section at Dětaň. Chiefly non-laminated tuff layers show alteration of greyish, brownish and reddish colours. The grey layers contain often large amount of dark mica phenocrysts.