PHONOLITE WEATHERING PROFILES AT MARIÁNSKÁ HORA HILL, ČESKÉ STŘEDOHOŘÍ Mts., AND SORPTION PROPERTIES OF CLAY RESIDUES

Jiří K. NOVÁK [1]*, **Karel MELKA**[1], **Jaromír ULRYCH**[1] **and Zdeněk ŘANDA**[2]

[1] *Institute of Geology, Academy of Sciences CR, Rozvojová 135, 165 02 Praha 6, +420/233087241, fax +420/220922670*
[2] *Institute of Nuclear Physics, Academy of Sciences CR, 250 68 Řež u Prahy, +420/266173156, fax +420/220941130*
Corresponding author´s e-mail: novak@gli.cas.cz

ABSTRACT
Two exposed but incomplete paleoweathering profiles (without lateritic nodular crust and fossil topsoil cover), developed on phonolite at Mariánská hora Hill in Ústí nad Labem (U-II) and Ryzelský vrch Hill near Most in NW Bohemia, were studied by available laboratory methods. The special attention was paid to the sorption properties of weathering products. Their decolouring ability was used for practical purposes at the beginning of the last century. The saprock and green-coloured saprolite from the bottom part of both profiles host smectitic pseudomorphs after clinopyroxene, while the dominant feldspar components, such as anorthoclase and Na-sanidine, remained resistant to weathering. The cation exchange capacities (CEC) of green-coloured saprolite show high values. The uppermost white saprolite occurs as a result of kaolinitic replacement of feldspars and of the smectite-to-kaolinite transformation, with low CEC values. The additional importance of weathering processes is demonstrated by the mobility of REEs, e.g. of Ce in a white horizon ((Ce/Ce*=1.21).

KEYWORDS: phonolite, weathering, saprolite, smectite, sorption, Mariánská hora Hill, NW Bohemia

1. INTRODUCTION

Perhaps no other subject has attracted as diverse multidisciplinary attention as paleoweathering profile with saprolite pseudo-stratified horizons due to relations to paleoclimatology, landscape evolution, and economic geology. The term saprolite is generally used for the mantle of unconsolidated or secondarily re-cemented rocks, which originated by weathering *in situ* and cover the bedrock (saprock). Beside clay minerals saprolite contains also weathering-resistant components. With sufficient saprolite reserves, weathering processes produce secondary mineral deposits, most importantly those bearing lateritic bauxite, clays such as kaolinite, smectite (bentonite), and Ni-silicate–smectite types, weathering resistates such as supergene Au, Th and Cu, and/or lateritic Au. Conversely, the past bio-climatic and drainage conditions as well as relations to ancient landscape can be studied. Paleoweathering profiles on syenitic and phonolitic bedrocks are widerspread not only in the present-day tropical and subtropical terrains (Brazil: Valeton et al., 1991; Schumann, 1993; Boulangé and Colin, 1994; Cameroon: Bilong, 1988; Braun et al., 1990; Ivory Coast: Boulangé et al., 1975), but also in some places within the Ohře/Eger Rift, NW Bohemia. Our study is mainly focused on the weathering profile at Mariánská hora Hill in Ústí nad Labem. A re-exposed or exhumed type of the paleoweathering profile is also preserved at Ryzelský vrch Hill (Most area) and represents a remnant of earlier landscape. Some of the weathered phonolite bodies, buried beneath the Most Basin and covered by Miocene sediments, have been studied in open cast lignite mines. They were affected not only by argillization, but also by burial diagenesis. Therefore, no saprolite zoning has been preserved.

An attempt has been made to resolve the following questions: 1) Why does the green-coloured saprolite possess some sorption properties? 2) Were the saprolite/cement mixtures utilized as a suitable substitute for cement powder (so-called "cemolite") during World War II? 3) What was the redistribution of fractionated REEs and other trace elements during weathering *in situ* ?

2. PREVIOUS WORKS

The phonolite-derived weathering profile on the southern slope of the Mariánská hora Hill, forming overburden of an active phonolite quarry, first attracted serious interest in about 1957 (Strnad in Krutský et al., 1964). Such profile was reported as a result of lateritic weathering and its uppermost "white laterite" was characterized as gibbsitic-kaolinitic one based on the bulk analyses (34.10 wt. % SiO_2, 43.47 wt. % Al_2O_3) and by DTA analyses. The laboratory work of Cornu and Schuster (1907) on saprolite from Kamenný vrch Hill (Ústí nad Labem-Střekov) and the Lelov area (Teplice area) mentioned its decolouring effect on aniline paints. In order to explain the nature of this property, cation exchange capacities were tested within the present study.

Argillized phonolite bodies buried beneath the Most Basin have received greater attention in the past century (Kavka, 1962, 1977; Holý and Kavka, 1962; Šindelář, 1965) after their exposure by lignite mining. There were two reasons for this interest: (i) a potential for non-bauxitic alumina or (ii) utilization as ceramic raw material (Bárta and Srbek, 1954; Žemlička, 1958; Kavka, 1961, 1967; Kavka and Šindelář, 1963; Šindelář, 1965). Nevertheless, the reserves were sub-economic only and the exploitation was governed by lignite mining imperatives only (Konta and Kühnel, 1999). The clay residues consisted of dominant kaolinite, minor gibbsite, siderite, and/or goethite. Moreover, the argillization processes may not be consistent from profile to profile and have long been the subjects of controversial opinions. Poor agreement regarding differences in detail was due to a limited availability of modern analytical methods in the 1970´s. This raises a question as to which scenario is likely to have generated the clay residues before and after burial conservation. No sorption properties should be expected, as the obvious constituents are dominant kaolinite, minor siderite and/or goethite (Šindelář, 1965). The climatic weathering hypothesis received support from Vachtl and Žemlička (1959), while Kavka (1977, 1978) prefers kaolinization caused by the volcanothermal interaction between hot phonolite lava and wet lacustrine sediments.

3. VERTICAL DIFFERENTIATION OF THE PALEOWEATHERING PROFILES

1. Mariánská hora Hill in Ústí nad Labem

Geologic setting: The surface exposure of the profile U-II is limited to the southeastern slope of Mariánská hora Hill, above the active quarry. Its exposure is explained by tectonic uplift after phonolite emplacement into the Upper Cretaceous sandstone and marlstone and by the Quaternary incision of the Elbe River (Růžičková and Smolíková, 1977). A crucial aspect is the acceptance of the Middle Oligocene weathering process (Domácí, 1976, Kužvart and Konta, 1968), which shows inherited features from the past bio-climatic and hydrogeologic regimes. An important time constraint for the weathering process is the age of phonolite emplacement (26 Ma). It is an open question yet, whether similar weathering profiles are buried beneath volcaniclastic rocks and lava flows of the Děčín Formation (Cajz, 2000; Ulrych et al., 2001). Bentonite residues replacing basaltic tuffs of the Ústí Formation and buried beneath a basanitic lava flow were revealed by drilling operations in the Stebno-Podlešín area, south of Ústí nad Labem (Vlčková, 1986). The presence of the bentonitization process in the Ústí nad Labem area clearly demonstrates pre-Miocene paleosurface and weathering.

The bedrock of the profile U-II is a marginal analcime-phyric facies of the phonolite laccolith that grades into amygdaloidal natrolite-sodalite phonolite in the laccolith centre. This body was affected by post-emplacement hydrothermal fluids and the vesicles were mostly filled with zeolites, analcime, apophyllite, and calcite (Kavka, 1965; Ulrych et al., 2000). Anorthoclase, Na-sanidine, salite pyroxene and analcime, in decreasing volume proportions, are the major mineral phases. They form not only individual phenocrysts but also fluidally arranged groundmass. Titanian magnetite and sphene are ubiquitous accessory minerals clustered around pyroxene. In broad view, a slight degree of bedrock weathering is characterized by ferruginous staining on hard-rock surfaces and fractures.

Saprock: Isolated clinopyroxene phenocrysts, as constituents most sensitive to weathering, are altered along cracks to smectite and/or calcite at the base of the profile. Other primary minerals, such as Na-sanidine and anorthoclase were well-preserved.

Saprolite horizons: With the increasing intensity of weathering, the greenish-grey saprolite (2-3 m thick) is a site for the replacement of clinopyroxene by smectite, while feldspar phases are partly kaolinized (sample U-II/3). This kind of saprolite is unusual in its higher sorption and decolouring abilities (see below). It grades into ferruginous saprolite, rusty-yellow in colour and 0.5 m thick. Goethite coatings are mainly concentrated in smectite pseudomorphs and Ti-magnetite clusters (sample U-II/2). The highest intensity of kaolinization occurs in the well-drained *white horizon* (U-II/4). It resulted from partial pseudomorphic replacement of feldspars and from the transformation of smectite to kaolinite. These clay minerals increase in abundance reaching the values of about 40 vol%. No major fabric changes were documented in the first 8 m above the interface with phonolite, which indicates a gradual weathering *in situ*. Nodular crust and fossil topsoil (with destroyed fabrics) are missing.

A subrecent soil horizon, 20 cm thick, forms the limit between unconformably lying dump material and the weathering profile (see Fig. 1).

2. Ryzelský vrch Hill in the Most area

Geologic setting: A similar phonolite-derived weathering profile with a direct transformation of phonolite into its weathering product is observed in Most-Čepirohy and on the eastern slope of the Ryzelský vrch Hill.

The saprock and the greenish-grey saprolite from the lowermost part of the profile show relatively abundant smectite patches after clinopyroxene clusters, while residual primary minerals, such as anorthoclase, Na-sanidine, and accessories remain preserved.

In the greyish-white clayey saprolite, the proportion of kaolinite increases and minor smectite pseudomorphs are intimately intergrown with kaolinite clay. Although areas of higher porosity are visible in some samples (after weak smectite aggregates), the pre-existing phonolite fabric can still

be recognized. An upper limitation of the profile is the recent soil complex and vegetation cover.

4. EXPERIMENTAL WORKS AND RESULTS

The identification of primary minerals and their weathering products was performed on polished thin sections using (1) optical microscopy and (2) CAMECA SX 100 electron microprobe, particularly for the identification of rock-forming minerals and pseudomorphozed phases. Semi-hard and friable saprolites were mounted into resin and polished. Micrographs of general texture and of selected mineral phases were made using a combined JEOL JXA-50A electron microprobe and the EDAX-equipment for energy dispersive elemental analysis. The energy-dispersive patterns of selected minerals in phonolite weathering profiles are reproduced in Fig. 2.

Mineralogical identification of saprolite samples was carried out by means of powder X-ray diffraction (XRD), which was supplemented in some cases by the thermal analyses (DTA and TG). XRD analyses employed Philips X'Pert APD unit equipped with graphite monochromator. CuKα radiation was used. The X-ray pattern was run using scanning speed of 1°/min. in the range of 2θ from 2° to 75°. Only parts of the patterns (up to 40° 2θ) are shown in Fig. 3 for each saprolite horizon examined in profile U-II. The X-ray beam was restricted by divergence slit ½°, receiving slit 0.1 mm, and scatter slit ½°. The following electric conditions were on the X-ray tube: 40 kV/ 40 mA.

Original natural samples and samples separated below 25 μm and above 25 μm were irradiated with CuKα X-rays and their patterns were evaluated for individual weathering profiles. Preparations were placed on the one hand in commercial sample holders and on the other hand they were mounted on a slide in the form of oriented aggregates. Air-dried and ethylene glycol-saturated samples were X-rayed.

Thermal analyses were performed in the Thermal Laboratory of the Technical University, Prague (analyst Ederová). In case of the diferential thermal analysis (DTA) the sample was continuously heated to 1 000 °C at the heating rate of 10 °C/min. The thermogravimetric analysis (TG) was carried out in the device TG-750 of the firm Stanton–Redford and the heating rate was the same as in the case of DTA.

X-RAY DIFFRACTION ANALYSES
   <u>Profile U-II (Mariánská hora Hill)</u>

(a) Anorthoclase, sanidine and analcime were determined as the main components of the U-II/1 saprock horizon, beside a small amount of smectite (Fig. 3a). Kaolinite and calcite occur as accessories. The amount of clinopyroxene is below the detection limit of XRD but some relics were determined using a microprobe.

(b) Saprolite sample U-II/2: Ferruginous saprolite contains a higher amount of smectite and iron pigmentation is probably bound to this mineral phase (Fig. 3b)

(c) The saprolite horizon U-II/3: green-coloured saprolite possesses smectite as the main component beside residual anorthoclase and sanidine. Smectite is present in the form of: /i/ beidellite and /ii/ montmorillonite, which is observable in electron micrograph as inherited zoning after pyroxene (Fig. 4). Aluminous beidellite prevails over montmorillonite. Kaolinite is present in a negligible amount on feldspar cracks (Fig. 3c).

(d) The uppermost saprolite horizon U-II/4, white in colour, contains mainly disordered kaolinite (Fig. 3d). Some amount of smectite is indicated by differential thermal analysis (Fig. 6) – endothermic reaction at 100 °C. Potential mixed-layer structure kaolinite-smectite was not found out after the ethylene-glycolation test. Smectite is present here as an independent phase. It is supposed that the origin of kaolinite is connected with the smectite-to-kaolinite transformation (?).

THERMAL ANALYSES AND RESULTS

Differential thermal analysis (DTA) together with thermogravimetric analysis (TG) gave additional information on the mineral composition of the weathering horizons. Thermal behaviour of the separated fine-sized fraction (<25 μm), derived from green-coloured saprolite (U-II/3), characterizes two varieties of smectite (Fig. 5). The diagnostic endo-thermic effects appearing at 550 °C (together with dehydroxilation of smaller amount of kaolinite) and at 700 °C are associated with the partition of beidellite and montmorillonite, respectively. Beidellite prevails over montmorillonite. Endothermic effects at 110 °C and 180 °C are responsible for the loss of water in interlayer positions of their crystal lattices. Exothermic peak at 950 °C is caused by the recrystallization to anhydrous phases after a break down of smectite structures. The TG curve displays total loss in weight of 11 %. This is a lower value than in completely weathered material (clays), because of the presence of residual feldspars in the sample.

Differential thermal analysis of white saprolite (fraction below 25 μm) – Fig. 6 – displays an endothermic peak not only at 560 °C belonging to the dehydroxilation of kaolinite, but also at 100 °C. The latter is caused by the presence of some amount of smectite. The exothermic peak at 980 °C is ascribed to the recrystallization of new phases after a collapse of the kaolinite structure. Due to the smectite admixture, the weight loss is higher than that for pure kaolinite, i.e. close to 15.5 % in this case.
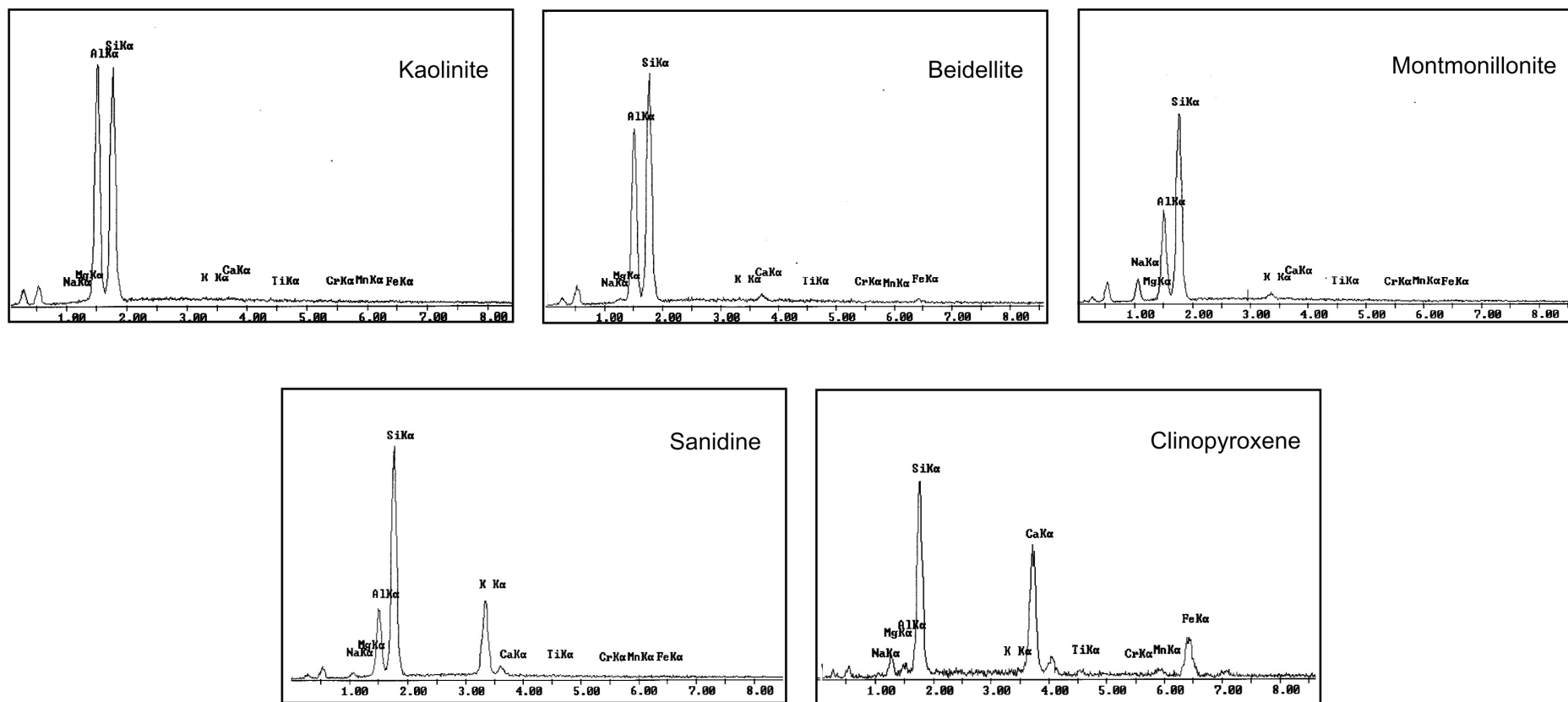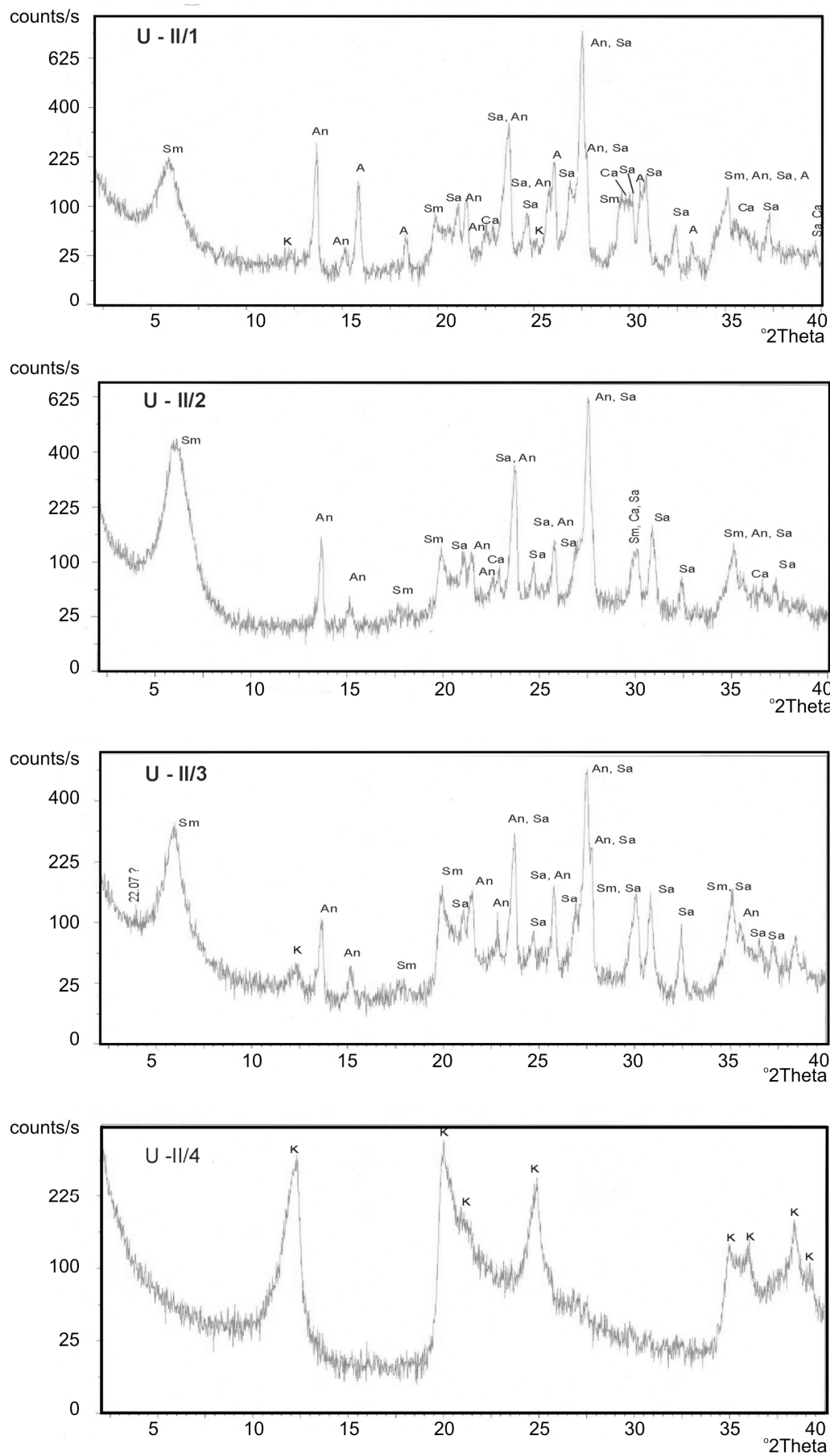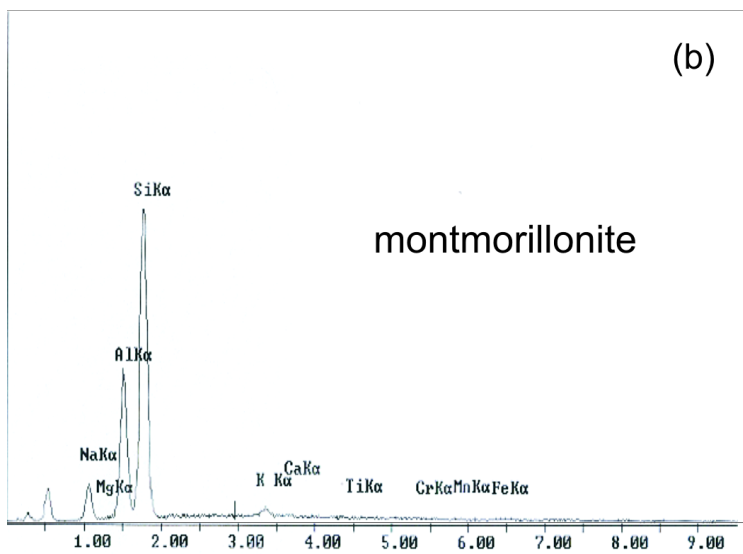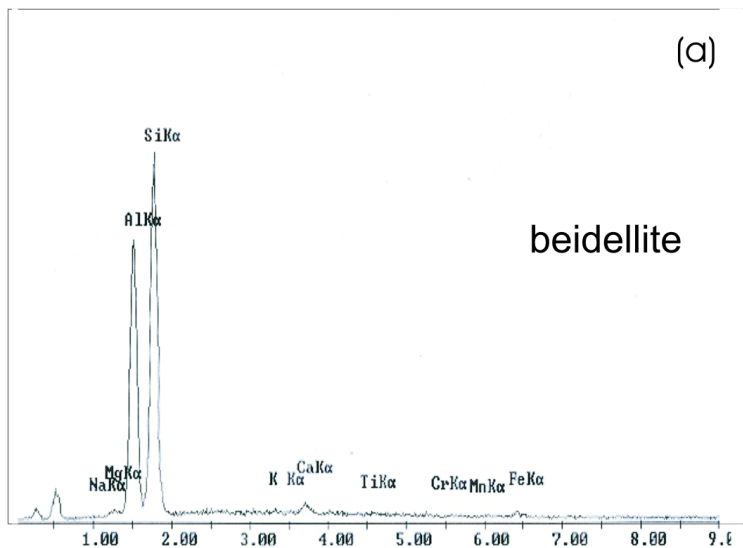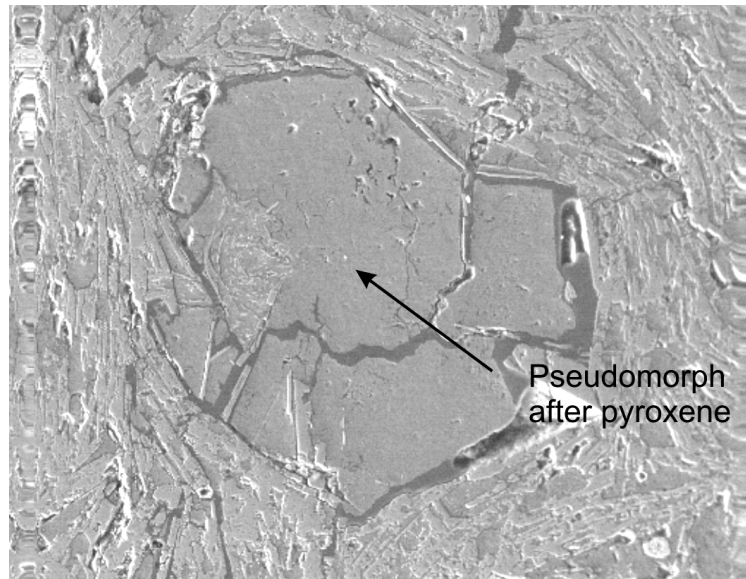
Fig. 2 Energy-dispersive patterns from the microprobe analyzer of minerals occurring in phonolite weathering profiles at Mariánská hora Hill and at Ryzelský vrch Hill.

Sm = smectite, K = kaolinite, A = analcime, An = anorthoclase, Sa = sanidine, Ca = calcite

Fig. 3   A comparison of X-ray powder diffraction patterns of the representative samples from a) U-II/1, b) U-II/2, c) U-II/3 and d) U-II/4 horizons of the phonolite weathering profile at Mariánská hora Hill.

Fig. 4 Electron micrograph of smectite pseudomorph after clinopyroxene phenocryst in green-coloured saprolite (U-II/3) with the energy-dispersive patterns for beidellite (a) and montmorillonite (b), originated from the zoned pyroxene.
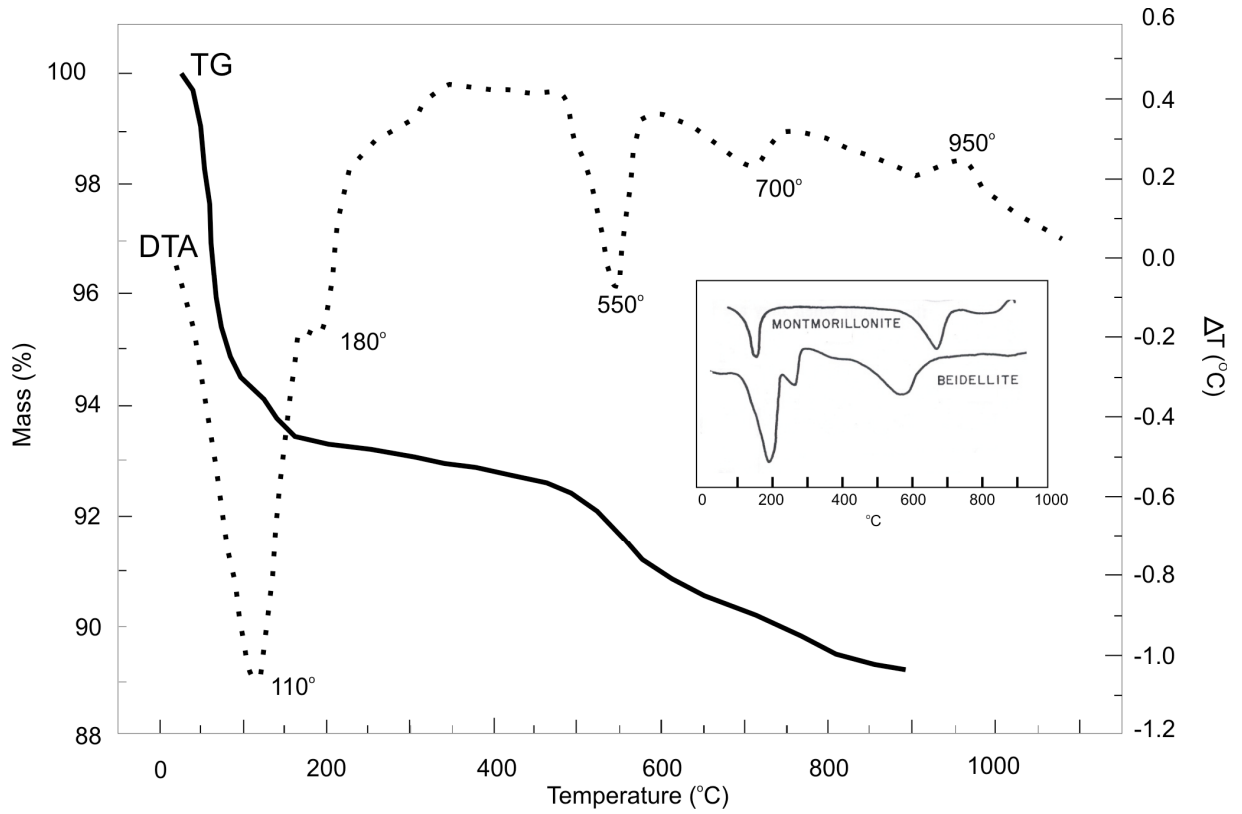
Fig. 5 DTA and TG curves of green saprolite from horizon U-II/3 (sample separated below 25 μm) with smectite as the main component. DTA confirms two kinds of smectite. Minima of endothermic reactions at 550 °C and at 700 °C correspond to beidellite and montmorillonite, respectively. Standard curves for both smectite varieties are included in the figure for comparison.
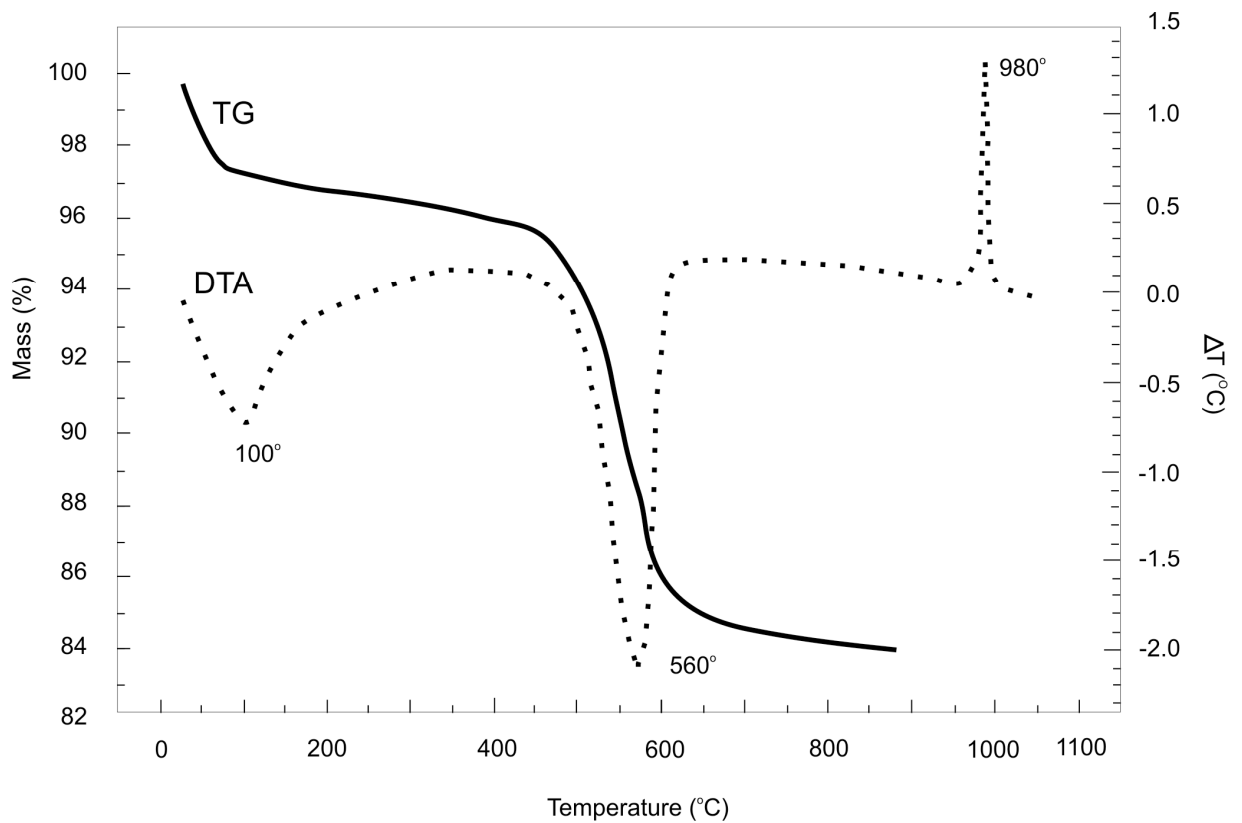
Fig. 6 DTA and TG curves of white saprolite from horizon U-II/4 (sample separated below 25 μm), identifying kaolinite. Endothermic reaction with its minimum at 100 °C indicates some amount of smectite.

Table 1 Chemical microprobe analyses of green saprolite constituents

Sample U-II/3	Clinopyroxene	Na-sanidine*	Anorthoclase*	Beidellite	Montmorillonite
SiO_2	48.75	64.40	66.20	46.16	49.95
TiO_2	0.84	0.24	0.17	0.09	0.08
Al_2O_3	2.39	18.24	18.23	31.11	21.14
Cr_2O_3	0.22	-	-	-	-
Fe_2O_3	-	-	-	1.33	2.00
FeO	15.72	0.53	0.36	-	-
MnO	1.76	0.23	0.08	0.24	0.12
MgO	7.02	0.04	0.06	0.82	3.03
CaO	19.01	0.37	0.48	1.12	1.81
Na_2O	3.12	1.56	5.00	-	0.51
K_2O	0.17	13.82	8.79	0.15	0.47
Total	99.00	99.43	99.37	81.02	79.11

Comment: * Feldspar laths, slightly weathered .

Table 2 Chemical microprobe analyses of white saprolite constituents

Sample U-II/4	Anorthoclase	Kaolinite I	Beidellite	Kaolinite II
SiO_2	64.09	47.51	43.53	48.57
TiO_2	0.88	0.12	0.22	0.62
Al_2O_3	19.46	35.16	33.08	34.09
Cr_2O_3	-	-	0.19	0.19
Fe_2O_3	-	-	1.38	-
FeO	0.37	0.78	-	0.59
MnO	0.23	0.18	0.10	0.22
MgO	0.07	0.08	0.76	0.83
CaO	0.95	0.56	0.63	0.62
Na_2O	5.00	0.45	0.41	0.39
K_2O	8.32	0.22	0.14	0.21
Total	99.37	85.06	80.44	86.33

Comments: Kaolinite I originated from feldspar. Kaolinite II originated by smectite transformation.

Table 3 Cation-exchange capacities of saprolites after parental phonolite

Sample No.	U-II/3	U-II/3a	U-II/4	U-III/1
(in mmol/100g)	Green saprolite		White saprolite	
Potential cation exchange capacity, CEC	29.70	33.50	7.20	5.90
Effective exchange capacity, CEC	27.70	33.00	6.70	5.40
Exchangeable Na^+	0.20	0.53	0.11	0.15
Exchangeable K^+	0.11	0.36	0.09	0.10
Exchangeable Mg^{2+}	5.80	5.90	0.97	0.98
Exchangeable Ca^{2+}	26.80	27.25	5.79	4.60
Exchangeable Al^{3+}	0.18	0.09	0.06	0.08
Exchangeable pH	6.30	6.83	6.77	6.85

U-II/3: natural sample of green saprolite; U-II/3a: fraction below 25 μm of green saprolite;
U-II/4: fraction below 25 μm of white saprolite; U-III/1: additional sample from the overburden.

Table 4 Cation-exchange capacities of pure clay minerals after Grim (1953)

Clay mineral	meq/100 g	Clay mineral	meq/100 g
Kaolinite	3 – 15	Halloysite (2 H_2O)	5 – 10
Montmorillonite	80 –150	Halloysite (4 H_2O)	40 – 50
Illite	10 – 40		
Vermiculite	100–150	Chlorite	10 – 40
Sepiolite-palygorskite	20 – 30		

Values are taken at pH 7.

Table 5 Chemical analyses of phonolite and saprolite samples

	Phonolite	Saprolite samples				Trace elements			
wt%	PH-43	U-II/1	U-II/3	U-II/4	µg g^{-1}	PH-43	U-II/1	U-II/3	U-II/4
SiO_2	56.30	55.89	56.60	57.36	Rb	149	201	195	163
TiO_2	0.54	0.54	0.62	0.73	Cs	4.01	6.89	1.08	2.36
Al_2O_3	19.51	19.28	20.76	23.38	Sr	715	441	490	548
Fe_2O_3	1.62	2.58	2.42	0.91	Ba	1186	1393	1293	1969
FeO	1.13	0.12	0.18	0.05	Th	18.6	20.1	21.1	23.3
MnO	0.15	0.191	0.055	0.03	U	10.2	8.62	2.53	5.76
MgO	0.23	0.50	0.54	0.08	Zr	697	770	702	755
BaO	n.d.	0.126	0.120	0.142	Hf	9.74	10.37	10.63	13.3
SrO	n.d.	0.049	0.056	0.064	Ta	3.07	2.65	2.55	2.81
CaO	2.99	3.66	0.96	0.65	Nb	117	n.d	n.d.	n.d.
Li_2O	n.d.	0.007	0.004	0.006	La	96.4	92.7	107.0	92.2
Na_2O	7.53	3.07	1.86	2.77	Ce	111.2	110.0	122.9	170.0
K_2O	5.68	3.68	6.23	6.49	Nd	25.7	18.0	21.4	37.1
P_2O_5	0.60	0.049	0.058	0.07	Sm	3.13	2.20	2.78	5.07
H_2O+	3.51	4.51	4.70	4.20	Eu	0.86	0.65	0.80	1.48
CO_2	0.11	2.17	0.01	0.13	Gd	2.2	<1	1.2	n.d.
C	-	0.040	1.04	-	Tb	0.32	0.23	0.30	0.50
SO_3	-	0.05	0.03	-	Dy	2.48	2.83	2.04	n.d.
S	0.01	0.014	0.007	0.05	Ho	<0.9	<1.1	<1.1	n.d.
F	0.09	0.126	0.133	-	Tm	0.18	0.25	0.24	n.d.
H_2O-	0.27	2.48	3.72	2.45	Yb	1.65	1.39	1.50	2.10
-O=2F	-0.038	-0.053	-0.056	-	Lu	0.26	0.22	0.23	0.33
Total	100.23	99.08	100.05	99.56	Y	35	n.d.	n.d.	n.d.
CIA	44.87	74.23	64.25	64.69	Sc	0.62	0.47	0.49	1.32
CIW	52.25	71.30	81.20	80.29	V	56.8	62.6	63.6	n.d.
ΣREE	244.4	228.5	260.4	308.8	Cr	1.20	2.1	<0.7	9.0
La_N/Yb_N	41.93	47.84	51.88	31.50	Co	7.5	1.32	0.68	1.85
Gd/Gd*	0.06	0.03	0.03	-	Ni	<28	<9	<9	<9
Ce/Ce*	0.87	0.99	0.95	1.21	Zn	89.8	88.2	75.7	56.6
La/Th	5.18	4.61	5.07	3.95					
Th/Sc	30.00	42.76	43.06	17.65					
Th/U	1.82	2.33	8.34	4.04					
Ti/Zr	4.64	4.82	5.29	5.80					

n.d. – not determined, CIA= [Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)] x 100;
CIW=[Al_2O_3/(Al_2O_3 + CaO +Na_2O)] x 100 in molecular proportions. CaO in both CIA and CIW is CaO in silicate fraction only.
Ce/Ce*= Ce_N/[La_N x (La_N x Nd^2_N)$^{0.33}$]$^{0.5}$
U-II/1: saprock horizon; U-II/3: green saprolite (below 25 µm); U-II/4: white saprolite (below 25 µm).

MINERAL CHEMISTRY

Using microprobe analysis, a continuous series between dominant beidellite and minor montmorillonite was found to be inherited from zoned clinopyroxene in greenish-grey saprolite. Position signs of some analyzed smectites are marked in the diagram according to Borchardt (1989) – Fig. 7. Besides exchangeable Ca, Mg, Na, and K cations, these smectite types adsorb trace elements, such as LREE and Cr. Substitutions in the inter-layer positions of smectites have a great influence on sorption properties, the cation exchange capacity (CEC) being greater for Ca- than Na-varieties. Results of chemical microprobe analyses of the green saprolite constituents are presented in Table 1.

For the white saprolite (U-II/4), microprobe chemical compositions illustrate smectite-to-kaolinite tranformation as a consequence of the progressive replacement of clinopyroxene. The impurities of Fe, Cr and Mn in kaolinite are inherited from the smectite precursor. Chemical microprobe analyses of the white saprolite constituents are tabulated (Table 2).

SORPTION TESTING

Absorption analyses on the raw material fraction were proved at VÚMOP at Praha 5-Zbraslav (analyst H. Macůrová). The cation exchange capacity (CEC) was determined by the Methylene blue method. One of the major results of this study is a demonstration that the green-coloured saprolite and semi-hard saprock with smectite may gain elevated absorption capacities (Table 3). CEC of pure clay minerals after Grim (1953) are compared in Table 4.

5. GEOCHEMISTRY

Because of recent evidence that the REEs, Th, and P may be also mobilized and re-distributed under supergene alteration processes, the samples of phonolite and saprolite were studied using REE and other trace element distributions in the profiles. New major-element chemical analyses were obtained by wet chemical method from the laboratories of the Geological Survey, Prague (analysts Janovská and Šikl) and Faculty of Science, Charles University, Prague (analysts Rýdlová and Vonásková) for phonolite and saprolite samples. The determined concentrations are listed in Table 5.

MAJOR ELEMENT COMPOSITION

The most noteworthy effect of paleoweathering process is the decrease in Na_2O and CaO contents in an earlier stage, reflecting the selective destruction of clinopyroxene crystals and their transformation into smectite. A local enrichment in CaO and CO_2 leads to calcite precipitation over a distance of 1 m near the phonolite contact. In the green-coloured saprolite CaO, Na_2O and CO_2 contents are more reduced, and the enrichment in K_2O results from resistant potassium feldspars. A slight increase in Al_2O_3, MgO and minor Cr_2O_3 contents is probably controlled by smectite neoformation.

The decrease in Na_2O, CaO, $FeO+Fe_2O_3$ and MgO as well as the enrichment in Al_2O_3 are observed in the kaolinitic white horizon. The CIA and CIW indices reflect gradual increase in clay contents (see Table 5).

TRACE ELEMENT DISTRIBUTION

The REE and other trace elements were determined by INAA method in the Nuclear Physics Institute in Řež near Prague (analyst J. Frána). Compared with parental phonolite data, variations in Ba (1186–1393 $\mu g\ g^{-1}$, Rb (149–201 $\mu g\ g^{-1}$) and Cs (4.01–6.89 $\mu g\ g^{-1}$) from the lower smectite-bearing saprolite horizon show a nearly similar contents. Their distribution is controlled by the relative stability of Na-sanidine and anorthoclase feldspars during weathering, after pyroxene breakdown. The initial drop in Sr from 715 $\mu g\ g^{-1}$ (parent rock) to 441 $\mu g\ g^{-1}$ in the saprock reflects partial anorthoclase weathering and apatite dissolution, whereas Sr concentration stabilizes between 441–490 $\mu g\ g^{-1}$ for the remainder part of the green saprolite. In the uppermost white horizon an increase in the concentrations of Ba and Sr was documented.

Zr, Hf, Ta, Y and Nb are thought to be practically immobile upon weathering, and relative enrichment is due to accessory mineral resistance. Transition elements, such as Sc, V, Cr, Co, Ni and Zn, show low concentrations and slight variations only. The effect of the Cr residual enrichment from a clinopyroxene precursor is to be suggested. Contents of the least mobile element–Th– in the saprolite samples (20.1–21.1 $\mu g\ g^{-1}$ Th) are close to those of phonolite. U content displays an extreme variation (10.2 – 2. 53 $\mu g\ g^{-1}$).

CHONDRITE-NORMALIZED REE DISTRIBUTION

The REE concentrations of saprolite samples are given in Table 5 with relatively fresh phonolite used as a geochemical reference. Chondrite-normalized patterns are presented in Fig. 8. The REE are commonly incompatible in the igneous process, but previous studies of REE behaviour during weathering (Nesbitt, 1979; Duddy, 1980; Braun et al., 1993) show that REE can be fractionated and redistributed, especially during the early stages of weathering process.

Parental phonolite from Mariánská hora Hill is characterized by: (i) typical U-shaped REE pattern with strong LREE-enriched slope (Fig. 8), (ii) moderate ΣREE content (around 245 $\mu g\ g^{-1}$), (iii) enrichment of LREE ($La_N/Yb_N=41.9$), and (iv) a depletion in MREE (Ulrych et al. 2000).

The REE pattern for green saprolite (U-II/3) shows inherited trend after phonolite, but the negative anomaly in MREE becomes prominent (Gd/Gd*=0.05–0.03). The most enriched LREE are Ce and La, but a Ce/Ce* ratio is close to one (0.95–0.99).
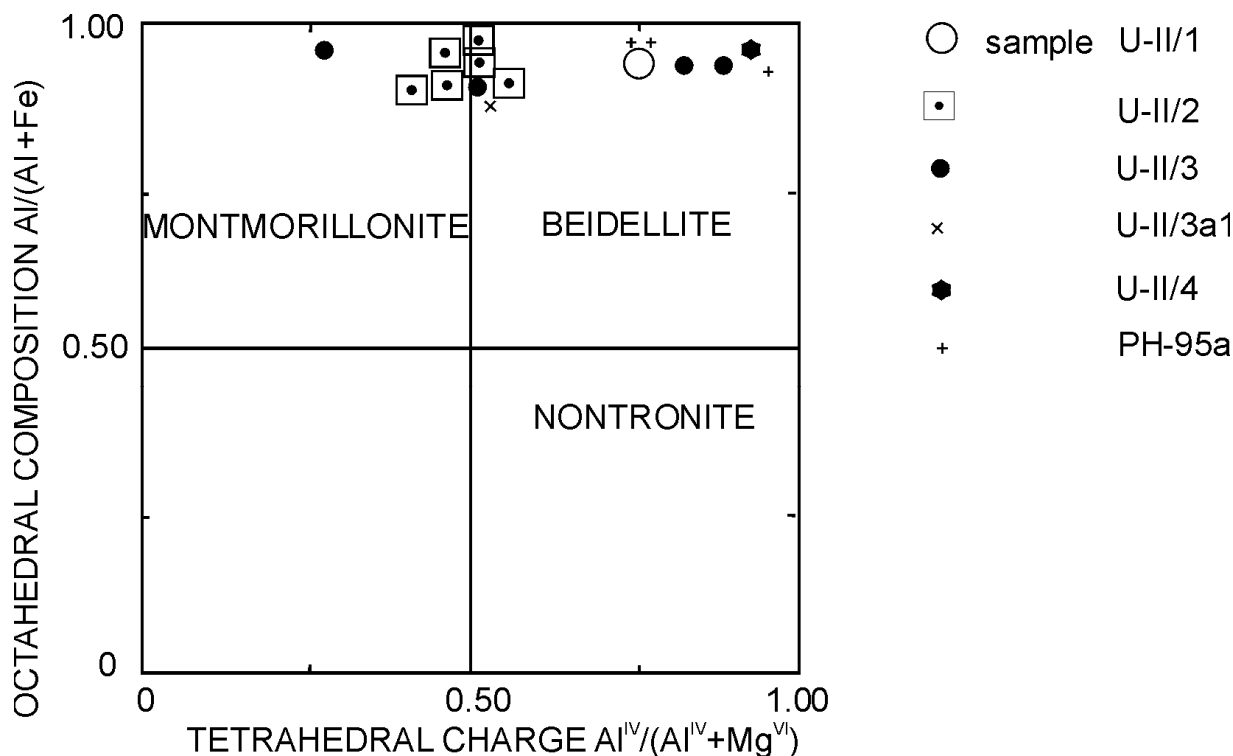
Fig. 7   Compositional range for dioctahedral smectites from phonolite-derived weathering profiles incorporated into the diagram according to Borchardt (1989). PH-95a: Ryzelský vrch Hill, near Most.

White kaolinitic saprolite (U-II/4), immediately above the ferruginous accumulation layer, exhibits LREE enrichment relative to HREE (La_N/Yb_N=31.5) at higher ΣREE content (308.8 µg g^{-1}). An anomaly in MREE is inherited from parental phonolite, but negative Gd-anomaly is lacking here. Ce in amounts of max. 170 µg g^{-1} and the positive Ce anomaly (Ce/Ce*=1.21) were found. Syenitic lateritic profiles of Cameroon (Braun et al., 1990) and of Brazil (Boulangé and Colin, 1994) show higher positive Ce anomalies (Ce/Ce*=7.01); Ce is probably adsorbed on clay fraction (Aagard, 1974).

6.   SOME TECHNICAL APPLICATIONS

There is no doubt that green saprolite and especially its clay component can be a non-traditional raw material for some technical and environmental applications if an improved processing is employed. The decolouring effect on aniline paints, confirmed empirically in the laboratory (Cornu and Schuster, 1907), is due to beidellite-montmorillonite presence.

The type of adsorbed-cation population in smectite reflects the technical pore-water chemistry in concrete. Therefore, this saprolite can be in equilibrium with cement powder, without zeolite neoformation. Slightly weathered and regularly shaped feldspars forming ballast material had negligible impact on concrete homogeneity, and no change in pore size distribution was recognized. It is therefore possible that the dressed saprolite was

employed as a substitute for cement powder (so-called "cemolite") during World War II. Practical use of similar materials in low–pH cement/smectitic clay mixtures was discussed by Push et al. (2003) as a candidate material for backfilling of repositories.

Smectite-bearing saprolite raw material, a promising target for mineral exploration, can be tested (i) as additive bentonite/crushed rock mixture into engineered barrier system to limit water flow and waste dissolution (Engelhardt and Finsterle, 2003), (ii) as adsorbent of undesirable components from contamined surface waters and groundwaters, and (iii) for traditional technology, e.g. pet waste adsorbents. Further profitable applications are dependent on the purity in smectite clay separate as a starting material. Beidellite adsorbs natural organic compounds, pesticides and herbicides as well as trace elements such as REEs and Cr, and may be useful in environmental technology.

7.   CONCLUSIONS

The paleoweathering profiles at Mariánská hora Hill in Ústí nad Labem and Ryzelský vrch Hill near Most display broadly similar compositional characteristics, comprising i) both greenish-grey saprock and saprolite originated under restricted water/rock interaction, and (ii) uppermost white kaolinite saprolite as a product of acid weathering at better drainage. Bulk composition of superimposed saprolites as well as their trace-element contents
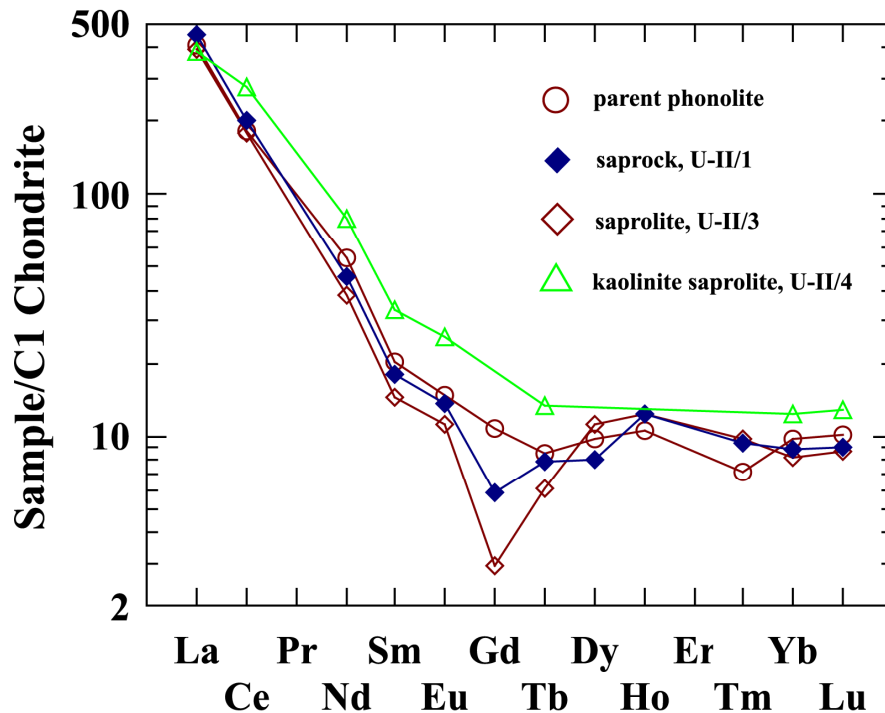
Fig. 8 Chondrite-normalized REE patterns for phonolite and different saprolites; weathering profile U-II (Mariánská hora Hill).

reflect the parental phonolite chemistry and the chemical weathering conditions *in situ.*

The non-negligible values of CEC for green saprolite (33.5 mmol/100g), due to the smectite presence, confirm the early decolouring experiments and binding ability of such materials. The cation exchange capacities for selected elements in mmol/100 g are as follows: Ca^{2+}=26.8, Mg^{2+}=5.8, Na^+=0.20, and K^+=0.11 for smectite-bearing saprolite (U-II/3) and Ca^{2+}=5.79, Mg^{2+}=0.97, K^+=0.09, and Na^+=0.11 for kaolinite-bearing saprolite (U-II/4).

In contrast, argillized phonolite bodies buried beneath lignite seams can be mentioned as an example of "lost" deposits. Although they were re-exposed during lignite mining in the Most Basin/northwestern Bohemia, their usefulness and qualitative properties were recognized too late. Clay residues, composed of dominant kaolinite, minor gibbsite, siderite, and/or goethite, were affected by burial diagenesis.

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Fig. 1 An outcrop of the weathering profile U-II (Mariánská hora Hill) and three superimposed weathering (saprolite) horizons (1–8 m above the phonolite bedrock).