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Weathering of smectite and illite-smectite under temperate climatic conditions

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ABSTRACT: Weathering profiles developed on the top surface of a bentonite (containing Al-Mg montmorillonite) and a K-bentonite (containing mixed-layer illite-smectite (I-S)) under Central European temperate conditions were studied by XRD, HRTEM, FTIR, K-Ar and chemical analyses. Weathering of montmorillonite results in the decrease of cation exchange capacity (CEC), total surface area and Mg content. The process is interpreted as montmorillonite dissolution and precipitation of amorphous SiO₂. Weathering of I-S produces an increase in CEC and total surface area. The XRD data suggest dissolution of I-S and appearance of smectite as a separate phase at intermediate depths. The fixation of ammonium is documented in the topmost sample. In both profiles, abundant aeolian contaminants, including mica, were identified and their migration was traced using K-Ar dating.

KEYWORDS: detrital mica, dissolution, illite-smectite, K/Ar dates, smectite, weathering.

The minerals of the I-S group undergo different alteration processes at all stages of the geological cycle from weathering to low-temperature metamorphism. The mechanisms of these processes in high-temperature environments are understood better at present (review in Środoń, 1999a) because simple mineral assemblages, characteristic of altered pyroclastic rocks (bentonites), are available for such studies. The complicated mineral composition of parent rocks often makes study of weathering reactions more difficult.

Since Bray (1937) suggested that illite alters towards smectite in soils, numerous studies of this process have appeared (review in Wilson & Nadeau, 1985). Despite that, the mechanism of alteration of illite and I-S during weathering

remains poorly understood. Transformation vs. neof ormation and the role of an intermediate vermiculite phase are currently being discussed (Środoń, 1999a). The process is of vital interest for soil science since it is one of the major natural sources of soil K.

Smectites of variable chemical composition are common products of weathering of volcanic glass and various minerals under different climatic conditions (review in Wilson, 1987). Most often reported is their alteration in weathering profiles towards kaolinite, directly or through mixed-layer kaolinite-smectite (review in Środoń, 1999a). Rare instances of smectite illitization in soils have been published but the evidence is not convincing (review in Środoń, 1999b). According to Righi *et al.* (1998), the most stable smectite composition in soils is high-charge beidellite, which develops at the expense of montmorillonite in Vertisols during pedogenesis at pH > 8.0. Hydroxy Al interlayering

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is common at low pH (Douglas, 1982; April *et al.*, 1986; Wilson, 1987).

The volcanic region of Kremnica in the Western Inner Carpathians (Slovakia) is a good place to study the processes of smectite and I-S weathering under temperate climatic conditions. The weathering profiles sampled for this study were developed on two clay deposits located 6 km apart, one of which contained montmorillonite and the other I-S as the only clay minerals. Thus the weathering reactions of the two minerals under strictly the same climatic conditions could be studied and compared.

MATERIALS

The subjects of this study are contemporary weathering profiles developed on the top surfaces of the Jelšovský Potok smectite deposit and the Dolná Ves I-S deposit. Both deposits are located in the southwestern part of the Kremnicke Vrchy Mountains, in the Western Carpathians (Fig. 1), and belong to the same geological formation (Jastrabá Formation). The formation consists of discontinuous horizons of volcanic extrusions, lava flows and volcanoclastics of rhyolitic composition. A significant part of the volcanoclastics is of explosive origin, and was deposited in lacustrine and fluvio-lacustrine environments (Konečný *et al.*, 1983). The age of the Jastrabá Formation was estimated from micropalaeontological data as Upper Sarmatian–Lower Pannonian (Konečný *et al.*, 1983). Fission-track ages determined from volcanic

glass and biotite from rhyolites are 12.3 ± 1.0 Ma and 12.1 ± 1.1 Ma, respectively (Repčok, 1979).

The smectite of the Jelšovský Potok deposit was formed by alteration of rhyolitic tuffs in a lacustrine environment (Kraus *et al.*, 1994). The smectite is an Al-Mg montmorillonite and it is the only clay mineral of the deposit. Chemical and mineralogical aspects of the clay were detailed by Čičel *et al.* (1992) and Madejová *et al.* (1992). The crystallochemical formula of the montmorillonite analysed in the Sr form is $(\text{Si}_{3.99}\text{Al}_{0.01})^{\text{IV}}(\text{Al}_{1.58}\text{Mg}_{0.29}\text{Fe}_{0.12}^{3+})^{\text{VI}}\text{Sr}_{0.17}\text{O}_{10}(\text{OH})_2$ (Šucha & Kraus, 1999). The deposit is located at the surface and is covered by a ~1.5 m thick weathering zone. The weathering zone and the underlying fresh bentonite rock were sampled in one profile of an open-mine wall. Based on colour differences, the profile was divided into four horizons and representative samples were collected from each (Table 1). An additional sample of the unaltered rock (JP) was collected from the bottom of the pit.

The K-bentonite of the Dolná Ves deposit was formed by low-sulphidation hydrothermal alteration of a smectitic clay, which originated from a rhyolitic tuff (Kraus *et al.*, 1994). The systematic increase in smectite percent in I-S from near zero in the north to 45% in the south of the deposit, is interpreted to reflect the variations in the temperature of hydrothermal fluids (Šucha *et al.* 1992). This deposit is also located at the surface and covered by a ~1.5 m thick weathering zone, which was sampled at various depths (Table 1) as was the Jelšovský Potok profile, in a prospecting open pit (the deposit is not exploited).

TABLE 1. Depth of sampling from the soil surface, total organic carbon (TOC) contents of the bulk samples, and pH of water suspensions of the bulk samples.

	Depth (cm)	TOC (%)	pH
Samples from Jelšovský Potok			
4555	5–30	2.42	5.14
4556	30–60	0.55	4.93
4557	95–110	1.00	4.35
4558	190–200	0.44	4.32
Samples from Dolná Ves			
4502	5–20	1.20	3.95
4503	40–50	0.47	4.55
4504	90–100	0.38	4.42
4505	140–150	0.80	4.38
4506	180–190	0.17	4.65

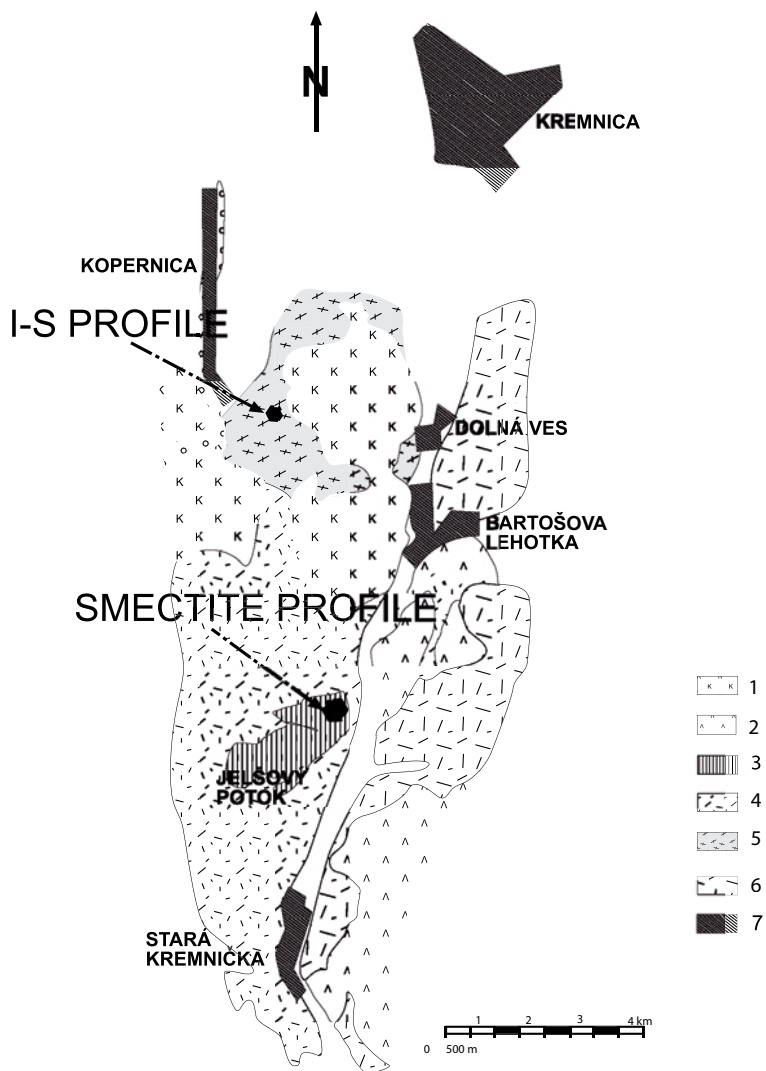


FIG. 1. Geological map of the SW part of the Kremnicke Vrchy Mts with the locations of two clay deposits and the studied weathering profiles. 1 – hydrothermally altered rhyolites and tuffs with dominant kaolinite; 2 – unaltered rhyolites; 3 – Jelšovský Potok smectite deposit; 4 – rhyolites and tuffs altered to smectite, kaolinite, cristoballite and clinoptilolite; 5 – Dolná Ves I-S deposit; 6 – unaltered volcanoclastics; 7 – villages.

METHODS

A few samples (1 kg each) were dried at room temperature and disintegrated gently to pass a 2 mm sieve and then homogenized by hand mixing.

The pH was measured using 10 g of the <2 mm fraction of the bulk samples mixed with 25 ml of distilled water. Chemical composition and total organic carbon content (TOC) were determined for

the bulk samples. The TOC was measured by a standard dichromate technique. For the chemical analyses, the samples were fused with soda plus sodium tetraborate and dissolved in HCl. The SiO_2 was determined gravimetrically; Al_2O_3 , Fe_2O_3 and CaO by EDTA; Mg and Mn by AAS; Ti colorimetrically; and Na, K by flame photometry.

The <2 μm fractions separated from bulk samples by sedimentation in distilled water were used for all

remaining analyses. Prior to fractionation, the samples were dispersed in an ultrasonic bath for 6 min and subsequently treated with Na acetate buffer, H₂O₂ and Na dithionite (Jackson, 1975). Excess soluble salts were removed by centrifugation followed by dialysis.

The XRD analyses of oriented and random specimens were carried out using Siemens D500 (Cu-K α radiation and graphite monochromator) and Philips PW 1710 (Ni filtered Cu-K α radiation) diffractometers. The scan-step for all analyses was 0.02°2 θ and the exposure time varied between 1 and 20 s per step. The 1 s patterns from both random and oriented specimens were used for mineral identification. The XRD patterns with longer exposure times were used for calculations of both fundamental particle and mixed-layer crystal thicknesses using the Bertaut-Warren-Averbach (BWA) technique of Drits *et al.* (1998) implemented in the MudMaster program (Eberl *et al.*, 1996). MudMaster is a program used to calculate crystal thickness from the interference function, which is extracted from intensities of basal XRD reflections by dividing them by the Lorentz-polarization and structure factors. The measurements of the smectite crystal thickness were performed on 001 reflections, recorded for clay samples saturated with ethylene glycol (EG) vapour at 60°C. The measurement of fundamental particle thickness of I-S was performed using 001 reflections of specimens intercalated with polyvinylpyrrolidone (PVP), according to the technique of Eberl *et al.* (1998).

Splits of the <2 μ m fractions of the bulk samples were Sr saturated (4 \times 1 N SrCl₂, followed by washing in distilled water and dialysis) and analysed chemically. Before analysis, the samples were air dried at 105°C. Silicon was determined gravimetrically (after treating the samples with Na₂CO₃ and HF), while Al, Mg, Fe, Ca, K, Na and Sr were analysed by atomic absorption spectrometry and atomic emission spectrometry after digestion in HF + HCl. The CEC was calculated from the Sr content.

The total surface area (TSA) of the <2 μ m fraction was determined by the retention of ethylene glycol monoethyl ether (EGME) using the technique of Novák & Čičel (1972).

The FTIR (Fourier Transform Infrared) spectra were obtained using a Nicolet Magna 750 spectrometer. The KBr pressed disc technique (0.6 mg of sample and 200 mg of KBr) was used for the

transmission measurements. The DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectra were obtained from powdered samples, without any dilution in KBr, using a diffuse reflectance accessory 'Collector' from Spectra-Tech.

The HRTEM measurements were performed using a Philips 420 STEM microscope operated at 120 kV. Small portions of water-saturated <2 μ m fractions in Na form were coated with agar, embedded in Spurr resin and sectioned by ultramicrotome. Under such conditions, the illite layers remain 1 nm thick and the smectite layers intercalated by organic compounds produce inter-layer distances of ~1.35 nm. Details of the preparation and operating conditions are given in Tessier (1984) and Środoń *et al.* (1990). The thicknesses of sets of strictly parallel lattice fringes representing crystals and the numbers of fringes corresponding to the number of layers in a crystal were measured using a binocular with a micrometric screw from negatives taken at the \times 51,000 magnification.

The Ar extractions were made in a glass extraction line following a method similar to that described by Bonhomme *et al.* (1975). The samples were stored under vacuum and pre-heated at 80°C for at least 12 h to remove the atmospheric Ar added to the particles during sample handling. The K was measured by atomic absorption spectrometry after a sample digestion in triacid (HF + HNO₃ + HClO₄), with an accuracy better than 1%. The analytical precision was controlled periodically by measuring the GLO mineral standard. Special attention was paid to the blank of the line and the mass spectrometer before each analysis, by a complete run of the extraction procedure without a sample, providing the 'total' extraction blank. The amounts of ⁴⁰Ar in these blanks were always very small, in the range of 10⁻⁸ cm³/g, and the ⁴⁰Ar/³⁶Ar ratios of the detected Ar were always close to that of the atmosphere. The K-Ar ages were calculated using the usual decay constants (Steiger & Jäger, 1977) with an overall analytical precision better than 2%.

RESULTS

Weathering profile of smectite (Jeřový Potok site)

The bottom sample 4558 of the weathering profile (Table 1) contains only smectite in the

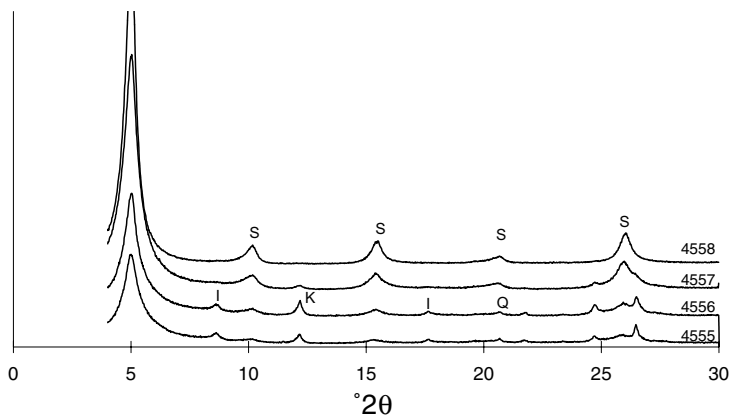


FIG. 2. XRD patterns of oriented specimens of the $<2 \mu\text{m}$ fraction of the Jelšovský Potok weathering profile after saturation with ethylene glycol. Sample 4558 is the bottom sample. S – smectite; I – illite (mica); K – kaolinite; Q – quartz.

$<2 \mu\text{m}$ fraction. Traces of kaolinite, illite and quartz appeared in the next sample (4557), and their amounts increased in the upper two samples (4556, 4555), along with a significant decrease of the intensities and increase of broadening of the smectite peaks (Fig. 2). No mixed-layering effects (peak shifts) were observed (Fig. 2). The mean numbers of layers per crystal (mean thickness divided by 1.7 nm) found using the BWA technique are 6.1 and 5.6 for samples 4558 and 4557, respectively. The number of layers per crystal found in the smectite crystals from the two upper samples (4456, 4455) were 2.0 and 2.1, respectively.

The IR spectrum of original unaffected Jelšovský Potok (JP) sample indicates montmorillonite as a dominant mineral (Fig. 3). The absorption band at 3626 cm^{-1} includes contributions from stretching vibrations of OH groups associated with various octahedral cations. The OH deformation bands at 917 cm^{-1} (AlAlOH), 842 cm^{-1} (AlMgOH), and a shoulder near 880 cm^{-1} (AlFeOH) show partial substitution of octahedral Al by Mg and Fe. Other features in the spectrum, common to all dioctahedral montmorillonites, include a complex Si–O stretching band at 1041 cm^{-1} , an out-of-plane vibration at 624 cm^{-1} due to coupled Al–O and Si–O vibrations, and Si–O–Al and Si–O–Si deformations at 523 cm^{-1} and 468 cm^{-1} , respectively (Farmer, 1974). The band at 799 cm^{-1} indicates the presence of an amorphous silica admixture in the JP sample. The IR spectra of

samples from the top of the weathering profile (4555 and 4556) are similar to the JP sample, though diagnostic bands of kaolinite at 3694 and 695 cm^{-1} and the quartz doublet at 799 and 779 cm^{-1} appear. A significantly lower relative intensity of the AlMgOH band at 844 cm^{-1} clearly indicates lower octahedral Mg content in both upper samples.

The numbers of 2:1 layers per crystal were counted from HRTEM images of samples 4556 and 4558 (Fig. 4). The mean number obtained for the bottom sample (4558) was 5.99, and for the top sample (4556) was 3.03. The observations are consistent with the MudMaster measurements, and document the changes in thickness of the smectite crystals during the weathering process.

The CEC and TSA of the samples decreased significantly as weathering advanced. The CEC reduced from $84 \text{ mEq}/100 \text{ g}$ for the unaltered sample (4558) to $46 \text{ mEq}/100 \text{ g}$ for the top sample (4555). The TSA reached almost $850 \text{ m}^2/\text{g}$ at the bottom of the profile, and decreased towards the top to $\sim 450 \text{ m}^2/\text{g}$ (Fig. 5). Chemical data from the bulk rock (Tables 1, 2) showed an increase in Si, Na, K, Mn, C_{org} and Ti, while the Al, Ca and Mg contents decreased significantly during the weathering process. Analyses of the $<2 \mu\text{m}$ fractions showed a relatively constant amount of Si, an increase in Fe, K, Ca and Na contents, and a decrease in Al, Mg and Sr (exchange cation) contents, from bottom to top of the profile (Table 3, Fig. 5). The chemical composition of the

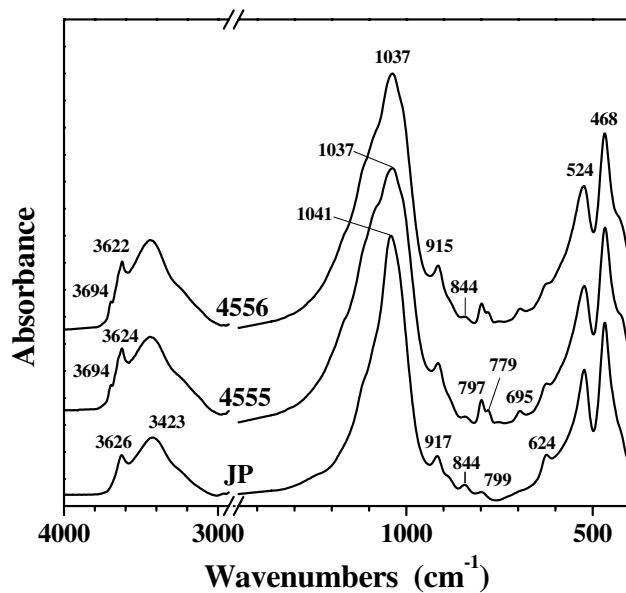


FIG. 3. FTIR spectra of samples from the Jelšovský Potok profile. JP is the additional sample from the bottom of open mine.

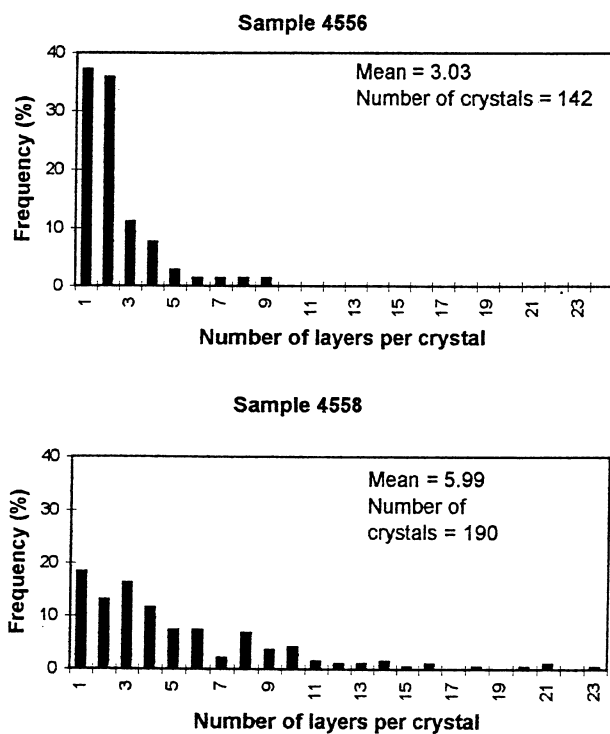


FIG. 4. Distributions of the numbers of layers per crystal at the top (4556) and the bottom (4558) of the Jelšovský Potok weathering profile. The data are counts from HRTEM images.

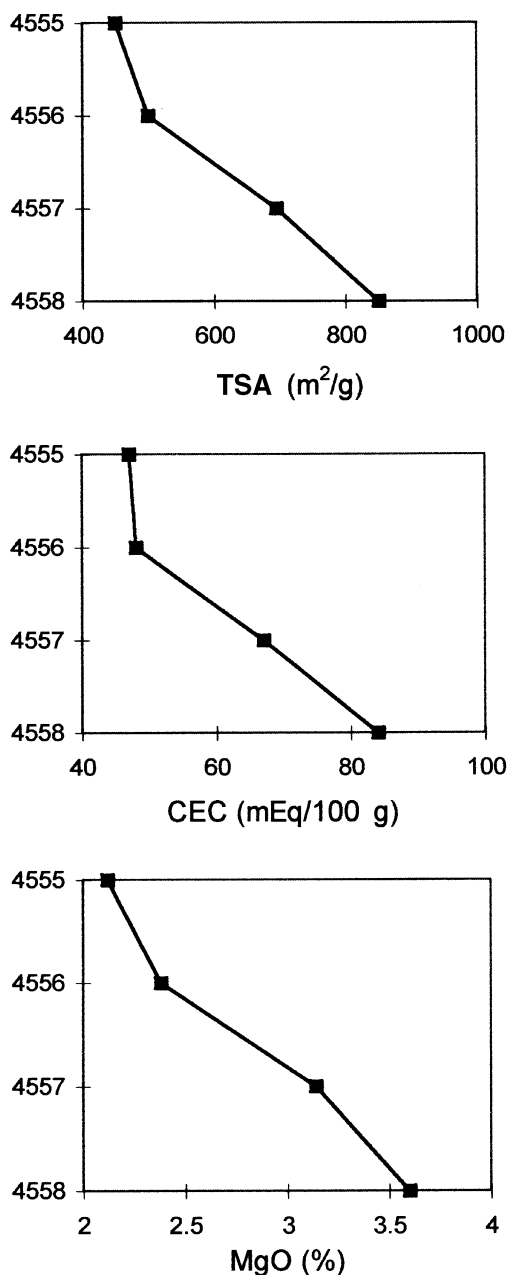


FIG. 5. The TSA, CEC and MgO contents of samples from the Jeřšovský Potok weathering profile.

bottom sample (4558) yielded the following formula: $(\text{Si}_{3.99}\text{Al}_{0.01})^{\text{IV}}(\text{Al}_{1.55}\text{Fe}_{0.13}\text{Mg}_{0.32})^{\text{VI}}\text{Sr}_{0.15}\text{Ca}_{0.01}\text{Na}_{0.02}\text{K}_{0.20}$ and fits well the formula determined for the open mine bentonite (see above).

The K-Ar dates measured for the $<2 \mu\text{m}$ fraction of all the samples collected are presented in Table 4. The sample taken from the bottom of the nearby open mine yielded an age of 0 Ma. The unaltered sample (4558) gave a date which has to be interpreted as close to 0 Ma due to large analytical uncertainty, resulting from very low Ar and K contents. Upwards, the K-Ar dates increased to a value of 282 ± 11 Ma for the top sample. The K-Ar dates were also measured for the <0.02 , 0.05 – 0.1 and 0.1 – $0.2 \mu\text{m}$ size-fractions (Table 4). In the two uppermost samples the ages decrease in accordance with decreasing size-fraction and for the finest fraction are much younger than the corresponding ages for the $<2 \mu\text{m}$ fractions. In the two deeper samples, the 0.05 – $0.1 \mu\text{m}$ fractions yielded the oldest dates. In the bottom sample, this date is older than that of the $<2 \mu\text{m}$ fraction.

Weathering profile of I-S (Dolná Ves site)

The original, unaltered, parent material of this profile is a mixed-layer I-S with 34% expandable layers, as measured using the XRD technique of Środoń (1980). The position of the reflection in the low-angle region indicates R1 ordering (Fig. 6). Towards the top of the profile, kaolinite, illite and quartz appear in all weathered samples (Fig. 6). The I-S peaks become less intense and broader, but their positions are not changed significantly, which indicates stable layer ratio. A weak peak at 1.7 nm (after EG saturation) indicating pure smectite or an R0 I-S, appears in the samples 4505 and 4504, and more clearly in the sample 4503. To test the layer charge of this mineral, sample 4503 was K saturated and subsequently subjected to 20 cycles of wetting and drying, exchanged with 0.1 M SrCl_2 , dialysed, and X-rayed (for details of the technique see Eberl *et al.*, 1986). The position and the relative intensity of the 1.7 nm peak remained unchanged, indicating lack of layer collapse during the treatment, which implies low charge of the smectite layers. The 1.7 nm mineral is a minor component and because of the lack of other peaks cannot be identified more precisely by XRD. The top sample is exceptional. The XRD pattern of this particular sample (4502) indicates less expandable mixed-layer clay. The pattern was modelled (Fig. 7) using the NEWMOD program (Reynolds, 1985), and the best fit between calculated and measured XRD patterns was obtained for I-S (R1, 15% smectite, $N = 4$) with

TABLE 4. K-Ar analyses of grain size-fractions separated from the bulk samples.

Sample	Size-fraction (μm)	K ₂ O (%)	Ar* (%)	⁴⁰ Ar* (10 ⁻⁶ cm ³ /g)	Age (Ma \pm 2 σ)
Jelsovy Potok					
4555	<0.02	0.45	13.84	1.78	119 \pm 18
	0.05–0.1	0.83	12.32	4.15	149 \pm 24
	0.1–0.2	1.06	30.98	5.97	167 \pm 11
	<2	1.25	53.1	12.3	282 \pm 11
4556	<0.02	0.95	21.32	1.69	54 \pm 5
	0.05–0.1	1.27	14.43	4.31	102 \pm 14
	0.1–0.2	2.06	49.65	9.1	132 \pm 6
	<2	1.44	44.6	10.8	218 \pm 11
4557	<0.02	0.33	10.06	1.21	111 \pm 22
	0.05–0.1	0.54	25.01	3.35	183 \pm 15
	0.1–0.2	0.57	22.23	3.49	181 \pm 17
	<2	0.64	32	4.4	202 \pm 11
4558	<0.02	0.09	0.64	0.09	29 \pm 92
	0.05–0.1	0.13	5.29	0.61	139 \pm 53
	0.1–0.2	0.14	3.50	0.4	87 \pm 50
	<2	0.2	2.2	0.23	35 \pm 33
JP	<2	0.2	0	0	0
Dolna Ves					
4502	<2	3.99	40.8	3.42	26.4 \pm 1.3
4503	<2	3.92	18.7	2.3	18.3 \pm 2
4504	<2	3.97	30	4.2	32.2 \pm 2.2
4505	<2	4.06	22.7	3.2	24.4 \pm 2.2
4506	<2	5.16	16.4	1.57	9.4 \pm 1.2

Ar*: radiogenic Ar

⁴⁰Ar*: radiogenic ⁴⁰Ar, expressed in cm³/g in the STP system

crystals that were not found at the bottom of the profile (sample 4506), or in the unaltered Dolná Ves bentonite (compare with Šucha *et al.*, 1996, where HRTEM of the I-S is described in detail). The mean thickness of the mixed-layer crystals in the samples 4503 and 4506, are very close (5.35 and 5.73 nm, respectively, Fig. 9). Measurements of fundamental particle thickness performed using the MudMaster program gave mean values varying between 3.15 and 3.3 nm for all samples. Sample 4502 was not measured.

Both FTIR and DRIFT techniques were used to determine changes in the Dolná Ves weathering profile (Fig. 10). All samples showed strong resemblance over the 4000–1300 cm⁻¹ region with a dominant band near 3635 cm⁻¹ assigned to OH-stretching vibrations. Absorption bands near 3435 and 1637 cm⁻¹ are due to OH-stretching and bending vibrations of water, respectively. Deformation vibrations of ammonium (near

1430 cm⁻¹; Farmer, 1974) can be seen clearly in the spectrum of sample 4502 at 1423 cm⁻¹. The IR patterns of all samples show weak and overlapping absorptions in the 1500–1400 cm⁻¹ region which are assigned to organic matter.

K-Ar dates were measured for five samples of the profile (Table 4). The K-Ar date of sample 4506 from the bottom of the profile (9.4 \pm 1.8 Ma) is younger than the stratigraphic age (12.2 Ma). The weathered samples yielded dates older than the stratigraphic age.

INTERPRETATIONS AND DISCUSSION

Interpretation of the K-Ar data

In the Jelšovský Potok profile, the K-Ar date of the bottom sample as well as of the sample from the open mine is effectively 0 Ma. It is consistent with

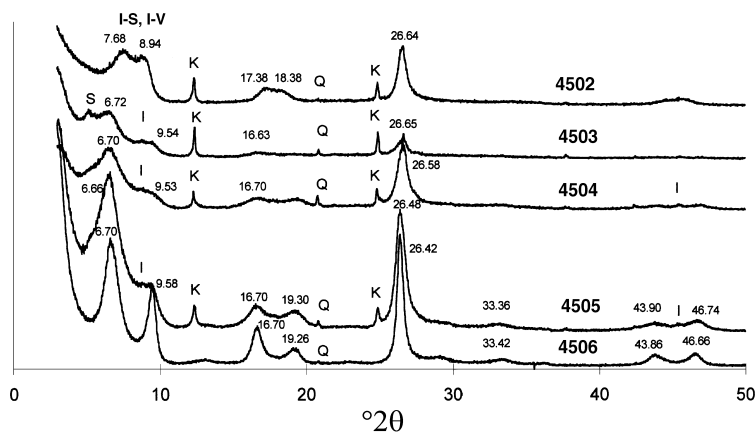


FIG. 6. XRD patterns of the $<2 \mu\text{m}$ fraction of the Dolná Ves weathering profile after saturation with ethylene glycol. Peak positions of I-S reflections are given. The other symbols are as in Fig. 2.

a monomineral, smectitic composition of these samples. Towards to the top of the profile, dates of 202 , 218 and 282 ± 11 Ma were recorded, which are much older than the stratigraphic age of ~ 12 Ma. These results indicate that the small quantity of mica detected by XRD in the samples is of detrital, probably aeolian, origin. The aeolian origin of mica was suspected because the clay deposit is located in the centre of a volcanic field forming a separate group of hills, and thus surface transport of non-volcanic detritus could be excluded. The decrease of dates down the profile probably reflects the selective downward migration

of finer mica particles. This conclusion was based on dates from different size-fractions which showed a positive correlation between particle size and age (Table 4). These data document a large distance (>1 m) over which the mica particles migrated in the rock. The quartz and kaolinite contents are positively correlated with mica, thus their aeolian origin is also suspected.

Using the I-S in the weathering profile at Dolná Ves, the bottom sample yielded a K-Ar date (9.4 Ma) younger than the stratigraphic age of the formation (~ 12 Ma). This date is interpreted as the age of the hydrothermal event which altered the

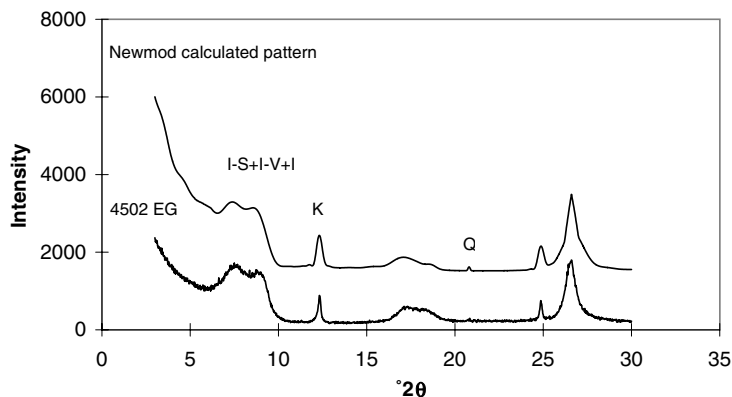


FIG. 7. XRD pattern a of glycolated $<2 \mu\text{m}$ fraction of sample 4502 (top of the Dolná Ves profile) and NEWMOD-calculated pattern representing a mixture of R1 I-S (15% smectite) plus I-V (15% vermiculite) plus kaolinite, mica and quartz (see the text for details).

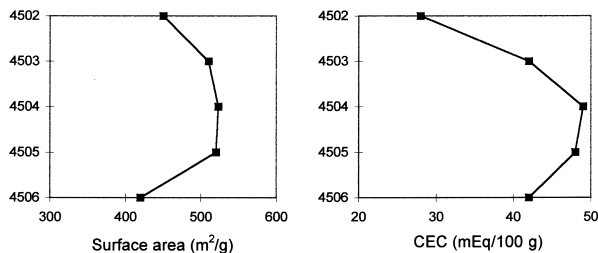


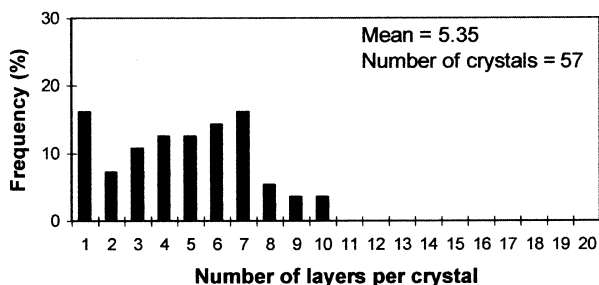
FIG. 8. The TSA and CEC data of samples from the Dolná Ves weathering profile.

Dolná Ves smectite to I-S. The weathered samples have disparate K-Ar dates which are much greater than the stratigraphic age. The fairly constant K contents among the samples 4505 to 4502, combined with the XRD evidence (Fig. 6), suggest that the scatter in the K-Ar data reflects variation in the input of small quantities of old detrital mica which contaminates the hydrothermal I-S of rather stable composition.

Weathering of smectite

The rapid increase in broadening of the 00l smectite reflections towards the top of the weathering profile indicates a decrease in the thickness of the smectite crystals. It may be due to splitting or partial dissolution. MudMaster measurements indicated that the crystal thickness was reduced to 1/3 during the weathering process. It means that either

Sample 4503



Sample 4506

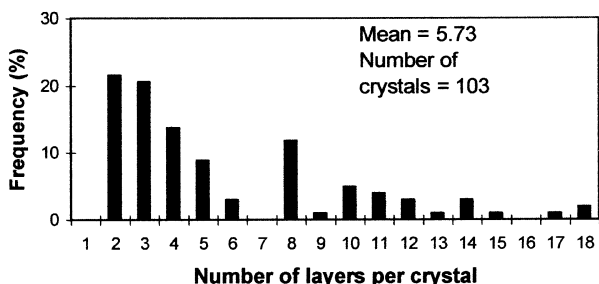


FIG. 9. Distributions of the numbers of layers per crystal at the top (4503) and the bottom (4506) of the Dolná Ves weathering profile. The data are counts from HRTEM images.

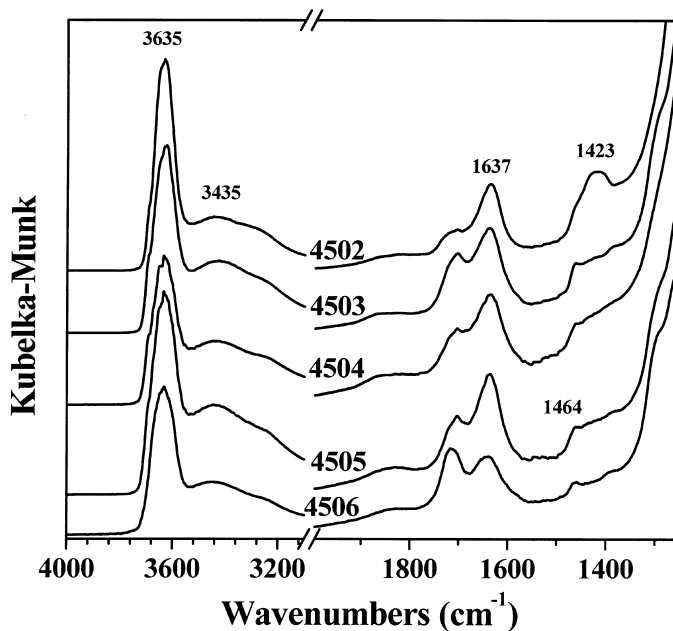


FIG. 10. DRIFT spectra of samples from the Dolná Ves weathering profile.

~66% of the mass of the smectite crystals was dissolved, or an average crystal was split into three, or that both processes occurred simultaneously.

As shown by XRD (Fig. 2) and IR (Fig. 3), sample 4558 is an almost pure smectite. Its chemical composition could therefore be used, together with the theoretical compositions (see Table 5) of kaolinite and muscovite (we expect that the mica of Palaeozoic age in samples 4555, 4556 and 4557 is muscovite), for the calculation of mineral composition of the other samples in the profile. The mica content was calculated from K_2O , and the smectite content was calculated from MgO , assuming no change in the smectite bulk chemistry

during weathering. A similar number for smectite was obtained when SrO was used for calculation, which supports the assumption of constant smectite chemistry (no significant change of the layer charge). All Fe, exclusive of the smectite structure, was assigned to Fe oxyhydroxides. Excess Al_2O_3 was assigned to kaolinite and all excess SiO_2 was assigned to quartz plus amorphous silica. The results of the calculations, summarized in Table 6, show that the smectite content decreased towards the top to 59%, in good agreement with the TSA decrease (Fig. 5). Because of the small amount of quartz (based on XRD) (Fig. 2), the calculation indicated the occurrence of a significant amount of

TABLE 5. Chemical compositions of minerals used for calculation of mineral contents presented in Table 6.

	Smectite	Kaolinite	Muscovite	Fe oxyhydroxide	Quartz
SiO_2	66.3	54	49	0	100
Al_2O_3	22.4	46	40	0	0
Fe_2O_3	2.89	0	0	100	0
MgO	3.6	0	0	0	0
K_2O	0.25	0	11	0	0
SrO	4.32	0	0	0	0

TABLE 6. Mineral composition of the $<2 \mu\text{m}$ fractions of the Jelšovský Potok weathering profile, calculated from data in Tables 3 and 4.

Sample	% Smectite from Mg content	% Muscovite	% Kaolinite	% Fe oxyhydroxide material	% Quartz + amorphous material	Sum	% Smectite from Sr	% Smectite from TSA
4555	59	9	6	3	22	99	57	53
4556	66	11	4	3	16	100	59	58
4557	87	4	3	2	4	100	80	82
4558	100	0	0	0	0	100	100	100

amorphous silica. Muscovite is a detrital component of aeolian origin infiltrated into the soil, as evidenced by the K-Ar study. Thus the decrease of smectite content in the weathering profile resulted from the combination of two processes: dissolution of smectite with removal of most of the dissolved elements except SiO_2 , and simultaneous infiltration of the aeolian dust. These two processes are also clearly reflected in the chemical data of the bulk samples which showed a rapid decrease in Mg content and increase of K towards the top of the profile. The mass balance cannot be calculated from the chemical data because the conservation of any of the elements cannot be assumed due to the detrital input. If the Mg content of pure smectite is used to calculate the amount of smectite in the bulk rocks, then values of 85, 25, 8 and 7% are obtained for samples 4558, 4557, 4556 and 4555, respectively. No traces of hydroxy Al interlayers in smectite were detected, so if any Al was conserved, some kaolinite would have to be authigenic.

Weathering of I-S

Except for the uppermost sample, the XRD basal reflections of I-S (Fig. 6) show stable peak position, a gradual decrease in intensity and increased broadening towards the top of the profile, similar to that observed in the smectite weathering profile. Such XRD characteristics reflect the decreasing percentage of I-S in the sample (intensity), decreasing thickness of the original mixed-layer crystals (broadening) but a stable illite:smectite ratio (peak position). This trend can be explained by partial dissolution of the mixed-layer crystals. If mixed-layer crystals were disintegrated only along the smectite interlayers, or if only some of the I-S crystals were dissolved, clear shifts of the XRD peaks should be observed (I-S becoming less expandable). A decrease in intensity of the peak between 9 and $10^\circ 2\theta$, which is particularly strong (Fig. 6) can be partly assigned to the decrease in the thickness of the expandable complex as was

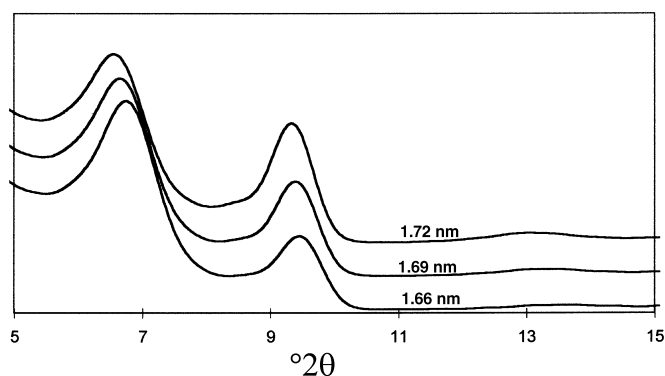


FIG. 11. NEWMOD-calculated XRD patterns of I-S (EG, R1, $N = 5$, 34% S) with different thickness compared to the expandable complex.

modelled using the NEWMOD program (Fig. 11). The smectite component can be detected by XRD as a 1.7 nm peak and by HRTEM. It may have formed by crystallization from solution or by removal of K from the mixed-layer crystals. An aeolian origin is unlikely because smectite is absent from the topmost sample.

The chemical composition cannot be used directly to quantify the mineral composition of the weathered samples as in the case of Jelšovský Potok because the mineralogy is more complex. The approach used utilizes the measured dates under the assumption that the detrital contaminant has the same age, as in the Jelšovský Potok profile. This assumption is justified by the fact that both sites are very close, and the mica is of aeolian origin; thus there is no reason to expect much difference in the ages. The K-Ar ages of Dolná Ves samples were modelled (Table 7) following Šrodoň (1999c) and assuming a mixture of authigenic I-S 9.4 Ma old, and the detrital mica having the extreme ages detected in the Jelšovský Potok profile (282 and 202 Ma). For the I-S, the K₂O content of the unweathered mineral was assumed (5.16%) and for mica the upper and lower limit values (8 and 12%) were tried. From the age and the K₂O content of a given component, its radiogenic Ar content was calculated. The K₂O and radiogenic Ar contents of such 2-component mixtures were calculated as weighted means and then the ages of the mixtures were calculated. By adjusting the fraction of detrital component in such 2-component mixtures, the measured ages were matched by the calculated ages. By comparing the K contents calculated for 2-component mixtures and measured for the real samples, the percentages of K-bearing minerals and the dilutants were calculated. All the models produced quite similar results (Table 7): a few percent of the detrital mica, ~70% of I-S, and ~25% of the remaining components (kaolinite, quartz, smectite and possible amorphous material). This smectite and amorphous material have to be responsible for the increased CEC and TSA (Fig. 9).

Such a calculation is not justified for the topsoil sample because its illite layer percent is different and a significant number of the fixed cation sites are occupied by NH₄. The presence of NH₄ is related to a natural biochemical process since the site is located deep in the forest, far from any agricultural activity. The vermiculite component of the mixed-layer clay in this sample seems

analogous to high-charge smectite in the uppermost part of Vertisols developing from low-charge smectite, as determined by Righi *et al.* (1995, 1998).

The Dolná Ves weathering profile also resembles alteration profiles of the Pennsylvanian underclays because of two important characteristics: two expandable minerals coexist in altered samples and the trend of alteration is reversed in the top sample (K and Mg increase: Elsass *et al.*, 1997).

CONCLUSIONS

(1) The thickness of the zone of measureable chemical and physical alteration in both locations is ~2 m. Above that depth, the alteration is detectable by structural changes of the parent clay mineral, by the changes in the major element chemistry of the <2 μm fraction, and by the appearance of organic matter and mica, both of which infiltrate from the surface down the profile.

(2) The pH profiles of the sites studied are different. In the Jelšovský Potok smectite deposit, the pH increases gradually from 4.3 in unaltered rock to 5.1 in the topsoil. In the Dolná Ves I-S deposit, it remains stable at 4.4–4.6 and only in the topsoil does it decrease to 3.95.

(3) Mica, kaolinite and quartz are present in all weathered samples. The allogenic origin of mica is documented by K-Ar in the Jelšovský Potok profile. Mica is interpreted as an aeolian input. Smaller mica particles migrate faster down the profile. Because of good correlations, quartz and part of the kaolinite are also suspected to be of aeolian origin. The kaolinite-mica ratio, which is much higher in Dolná Ves than in the Jelšovský Potok profile, indicates that some of the kaolinite is probably authigenic.

(4) The calculation, based on K-Ar data (Table 7), indicates a lower aeolian mica content in the Dolná Ves profile than in the Jelšovský Potok profile. This difference probably reflects a lower rate of weathering of I-S with respect to smectite. This conclusion is consistent with the calculated total percentage of primary material in the topsoil: ~60% in the smectite profile vs. 70% in the I-S profile. The documented level of aeolian contamination makes it impossible to perform the mass balance calculations of the weathering profiles based on the assumption that some elements are conserved.

(5) Jelšovský Potok montmorillonite undergoes dissolution in the weathering zone. Neither

TABLE 7. Calculation of the mineral composition of the $\leq 2 \mu\text{m}$ fractions of weathered samples from the Dolna Ves profile based on the measured age (Ma) of the unaltered I-S and the ages of aeolian mica measured in the Jelsovy Potok profile. Four of the models presented represent the complete feasible range of the detrital age and K_2O content of the detrital mica. The measured age is matched by the calculated age by adjusting the fraction of detrital mica in the 2-component mixture. Comparing the calculated K content with the measured value, the fraction of K-bearing clays in the sample is calculated and the calculation of individual components follows.

Sample	Detrital mica		Authigenic I-S		Mixture of pure composition			Measured			Natural mixture		
	Age	K_2O (%)	Age	K_2O (%)	Measured age	Calculated age	Detrital fraction	Calculated K	Measured K	% I-S + Muscovite	% Muscovite	% I-S	% Kaolinite + Quartz + Smectite
4503	282	12	9.4	5.16	18.3	18.1	0.013	4.28	3.25	74.7	1.0	73.7	25.3
4504	282	12	9.4	5.16	32.2	32.1	0.035	4.28	3.30	73.5	2.6	71.0	26.5
4505	282	12	9.4	5.16	24.4	24.6	0.023	4.28	3.37	76.4	1.8	74.6	23.6
4503	202	12	9.4	5.16	18.3	18.6	0.02	4.28	3.25	74.0	1.5	72.5	26.0
4504	202	12	9.4	5.16	32.2	32.2	0.052	4.28	3.30	72.0	3.7	68.2	28.0
4505	202	12	9.4	5.16	24.4	24.3	0.033	4.28	3.37	75.4	2.5	72.9	24.6
4503	282	8	9.4	5.16	18.3	18.4	0.02	4.28	3.25	75.1	1.5	73.6	24.9
4504	282	8	9.4	5.16	32.2	32.3	0.052	4.28	3.30	74.8	3.9	70.9	25.2
4505	282	8	9.4	5.16	24.4	24.6	0.034	4.28	3.37	77.2	2.6	74.6	22.8
4503	202	8	9.4	5.16	18.3	18.7	0.03	4.28	3.25	74.7	2.2	72.5	25.3
4504	202	8	9.4	5.16	32.2	32.5	0.077	4.28	3.30	73.8	5.7	68.1	26.2
4505	202	8	9.4	5.16	24.4	24.7	0.05	4.28	3.37	76.6	3.8	72.7	23.4

structural evolution (mixed layering), detectable by XRD, nor chemical evolution (e.g. towards beidellite), detectable by IR, were registered. However, XRD and HRTEM did document the decrease in thickness of montmorillonite crystals. The lack of chemical evolution of montmorillonite is confirmed by the calculation of mineral composition of the altered samples from the characteristics of the unaltered monomineral sample. The calculation based on CEC, SA and Mg content gives very similar smectite percentages (Table 5). The smectite content in the $<2 \mu\text{m}$ fraction decreases gradually from 100% in the parent rock to ~60% in the topsoil. The decrease in XRD peak intensities is much stronger (Fig. 2) which probably reflects an increasing disorientation of smectite crystals aggregated by amorphous silica.

(6) The calculation of mineral composition of altered Jelšovský Potok samples from the chemical data reveals the presence of a few percent of Fe hydroxides and ~20% of SiO_2 , which is well beyond the few percent of quartz indicated by XRD and IR. Thus, the presence of amorphous silica is inferred. Amorphous silica and Fe hydroxides are interpreted as the products of smectite dissolution.

(7) Dolná Ves I-S undergoes, at the bottom of the weathering profile, a very subtle structural modification, detectable only by XRD (Fig. 7): peaks become broader, their relative intensities and their positions change slightly. Based on the broadening of the peak at $\sim 26^\circ 2\theta$, a decrease of crystal size has to be inferred (cf. Drits *et al.*, 1997). Otherwise the mineral remains unchanged up the profile. A second structural modification takes place in the topsoil, leading to an XRD pattern of much less expandable I-S with the possible presence of 1.4 nm layers according to the NEWMOD model.

(8) A low-charge smectite component (smectite or R0 I-S) appears at the bottom of the Dolná Ves profile, as shown by XRD and the increase in CEC and TSA. It is interpreted as a product of weathering at intermediate depth. It is not present in the topsoil.

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