University of Sopron

Faculty of Forestry

Theses of doctoral (PhD) dissertation

Mineralogical investigations of soils formed on limestone in the Bükk Mountains

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1. Introduction and aims of the research

The most important aspect of the choice of the topic of the present PhD dissertation was to carry out investigations in a relatively unexplored part of the Bükk Mountains, which will result new scientific data for pedology as well as for soil site survey and soil mineralogy.

In the present work 13 soil profiles were studied in detail, all of which were formed on limestone bedrock in the Bükk Highland. One of the objectives was the investigation of the physical and chemical properties as well as the comprehensive mineralogical assessment of the soils, the detailed characterisation of soil types involving the description of surface soil thickness and soil morphology.

According to the classification system of Pál Stefanovits rendzinas form an individual type in the main class of litomorphic soils with three sub-types: black-, red clay- and brown rendzinas. Since the classification of Stefanovits only a few researchers in Hungary have contributed to the knowledge on rendzina soils. One reason for that could be that these soils are insuitable for agriculture and as such are interesting only to forestry. The investigation of the mineralogy of these soils could provide new and hitherto unpublished results. The research of the mineralogical composition would result new data on the soils formed on limestone. The weathering processes and the origin of the minerals can be tracked also by the qualitative and quantitative assessment of the soil minerals. As the comprehensive research on the mineral composition could provide detailed results, the second objective was the investigation of the applicability of different methods for the assessment of the mineral composition in order to track the origin and transformation of the soils. Thermoanalytical methods were used in the first place to prove their suitability and potential for the investigation of the mineral composition of soils formed on limestone. Results of thermal analyses were justified by X-ray powder diffraction measurements. Besides of that micromorphology was also studied and selected samples were subjected to scanning electron microscopy measurements, too. Evaluation of heavy metal contents was also done in order to study the amounts of metals released into the soil during weathering processes.

Respecting mineral composition, the study of the soil minerals in their original state was aimed. For that no chemicals were applied to maintain original mineral structures in the soil samples (>2mm). If soil fractions were studied, organic matter was removed by the use of H_2O_2.

The number of international publications on the soils formed on limestone is very scarce. The results on these soils, found at locations with different climatic conditions, reported on polygenetic origin and great morphologic, chemical and mineralogical diversity. In this regard the differences in the composition of limestone bedrock as well as in the mineral composition of these soils were also mentioned.

The present dissertation not only aims the acquisition of new data on the mineral composition of soils formed on limestone, but also investigates the origin of these soils and the applicability of different analytical techniques for their research.

Specific aims:

- Investigation of main physical and chemical features as well as mineral composition of soil profiles in order to assess information on soil type, parent material and conditions of soil formation.
- Interpretation of weathering and mineral transformation processes basing on the measured physical, chemical and mineralogical data.

- Investigation of the relationship between bedrock and soil in order to answer the question if these soils could be formed from the weathering of limestone solely.
- Interpretation of thermoanalytical results. Utilization possibilities of thermal analysis in the investigation of soils, formed on limestone.
- Investigation of the applicability and efficiency of the methods for the determination of mineral composition in the case of soils formed on limestone.
- Publication of novel data on the properties, characteristics and mineral composition of the soils formed on the limestone of the Bükk Mountains. Appending of insufficient knowledge, explanation and clarification of contradicting results.

2. Samples and methods

2.1 Sample collection and processing

Samples were investigated from 13 soil profiles, taken from typical plots (in terms of terrain and vegetation) of the Bükk Highland. Plots were characterized by various soil depths, slope angles, and exposures. Hence, both deep and shallow soil profiles were investigated in the research. Samples were collected from the profiles using both disturbed and undisturbed (Kubiena box) sample collection.

2.2 Measured parameters and analytical methods

Basic soil physical and chemical parameters:

Acidity. The pH was measured from solutions extracted with water and KCl solutions according to the standard MSZ-08-0206-2:1978.

Carbonic chalk content. Measurements were carried out using a Scheibler-type calcimeter according to the standard MSZ-08-0205:1978.

Grain size distribution. Determinations were carried out according to the standard MSZ 18094-14:1986.

Organic matter content. The total content of organic matter in the soil samples was measured using the FAO (1990) method.

Mineralogical investigations:

Thermoanalysis. Thermal analyses (TG, DTG, HF) of the samples were run using a Mettler Toledo TGA/DSC 1 type instrument with constant heating rate (5-10 °C/min) in synthetic air atmosphere between 25-1000 ^{o}C temperature range in a 150 μl Al_2O_3 crucible. Measurements were mostly done from whole soil samples, yet a limited number of soil fractions were also investigated.

X-ray powder diffraction: Measurements were done on a Philips PW 3710 / PW 1050 type parafocusing Bragg-Brentano goniometer using Cu Kα radiation (λ= 0.15418 nm), equipped with a graphite monochromator and a proportional counter. The digitally recorded XRD scans were evaluated for quantitative phase composition using a full profile fit method with corrections for preferred orientation and microabsorption.

Micromorphology. From the samples collected with undisturbed sample collection (Kubiena box) thin sections were prepared. The thin sections were investigated using a Nikon Eclipse LV100POL and a Nikon Eclipse 80i type polarization microscopes. Digital images were acquired by the Nikon Intensilight C-HGFI and by the Q Imaging Micropublisher 5.0 RTV cameras. Images were recorded and evaluated using the NIS – Elements AR 4.00.00. and the Image-Pro Plus 7.0 softwares.

Scanning electron microscopy and energy dispersive X-ray analysis (EDX). Electron microscopy and EDX analyses were carried out using a Hitachi S-3400N type scanning electron microscope and a Bruker XFlash Detector 5010 type EDX equipment. EDX spectra were evaluated using the Quantax 200 Esprit 1.9 software.

Heavy metal content. After sample preparation (digestion with HNO_3 + H_2O_2 according to standard MSZ 21470-50:2006) heavy metal contents were measured using a Thermo Scientific ICP-OES (ICAP 6000 series) type plasma emission spectrometer. Data was acquired and evaluated using the iTEVA software.

3. Statistical evaluations

Data evaluation was done using Microsoft Office Excel 2010 (Microsoft Corp., Redmond, USA) and STATISTICA 11 (StatSoft, Tulsa, USA) softwares.

4. New scientific results – theses

New results of the Ph.D dissertation are summarised in the following theses:

1. Mineralogical composition of the investigated soils from the Bükk Highland were dominated by quartz, followed by clay minerals, feldspars, chlorites, goethite, calcite and dolomite. Soil samples contained significant amounts of organic and amorphous material. Basing on the composition of the bedrock (pure calcite, *Figure 1.*) and on the high quartz and silicate contents (*Figure 2.*) I have justified that these soils

cannot originate from the weathering of the limestone bedrock solely.

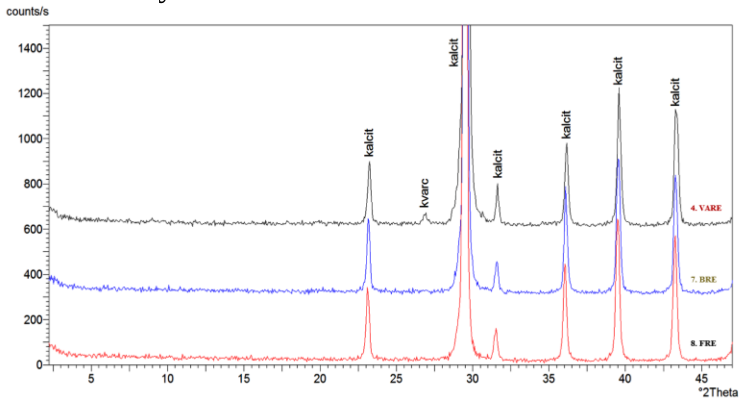

Figure 1. X-ray powder diffraction measurement of the limestone bedrock. Bedrock samples originated from red clay rendzina (4.VARE), brown rendzina (7.BRE) and from black rendzina (8.FRE) soil profiles.

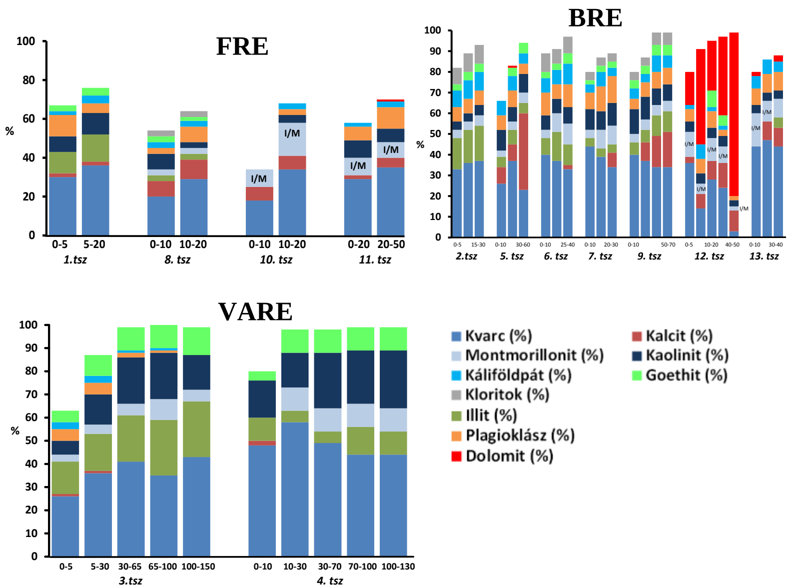

Figure 2. Mineral composition of black (FRE), brown (BRE) and red clay (VARE) rendzina samples in different layers determined by X-ray powder diffraction. (I/M: illite/montmorillonite mixed structures)

2. I have established that according to the results of mineral composition, profile morphology, soil physical and soil chemical measurements, the classification of the investigated soils as different types of rendzinas is not unequivocal, especially in the case of the soils specified as brown- and red clay rendzinas. The classification of investigated soils needs further clarification with both Hungarian and international soil classification systems. The differentiation between brown and red clay rendzinas as well as brown forest soils needs further refinements in the future.

3. According to the mineral compositions I have established that soil formation could have commenced on silicate sediments originating partly from eolian dust material (regional and local), partly from redeposition. The soil material of red clay rendzinas originates from various sources, from partly eolian, partly redeposited earlier sediments.

4. Results have justified that thermal analysis techniques are better suitable for the determination of calcium-carbonate content in untreated soil samples originating from limestone bedrock, compared to X-ray powder diffraction and to Scheibler method, as with thermal analysis the organic matter content does not interfere with the determination of calcite (*Figure 3.*).

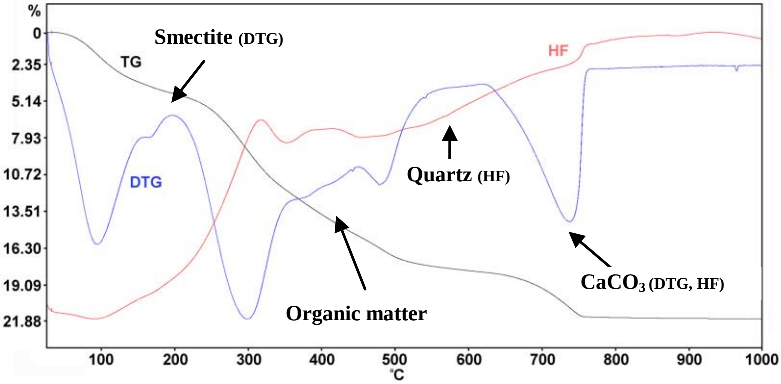

Figure 3. Thermoanalytical curves of soil profile 9. (brown rendzina) 10-30 cm-layer. **TG** (thermogravimetric curve); **DTG (differential thermogravimetric curve)**; **HF** (heatflow).

5. New data were presented for the micromorphological characterisation of soils formed on limestone at the Bükk Highland. The most specific marks of weathering processes are represented by the intrusion of organic soil matter into the cracks of the skeletal material. The description and characterisation of the moder and the „mull-like" rendzina moder humus types were presented. Moreover the characteristic changes in the soil texture were described (spaces between skeletal grains filled by basic material aggregates, then coated or basic material bridges between skeletal grains). I have established that the presence of iron-containing coatings around the inorganic skeletal grains is characteristic to all investigated soil samples (*Figure 4.*). I have investigated and identified the presence of microstructures (nut-like, wedge-like, coating and bridge, crumby, grainy) for the first time ever in the soils formed on the limestone in the Bükk Highlands (*Figure 5.*).

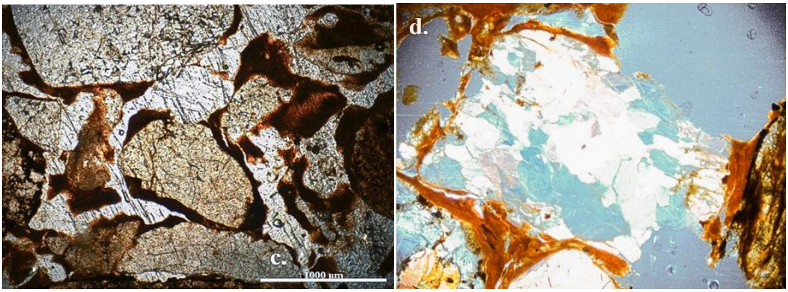

Figure 4. Red clay rendzina soil profile, 10-30 cm layer, iron-containing coating around the skeletal grains (left); 30-70 cm quartz grain with iron-containing coating (right).

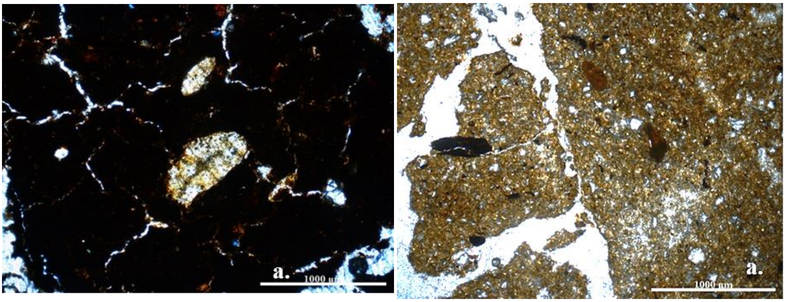

Figure 5. Rounded oviform skeletal grains surrounded by organic soil matter (left); Soil basic material with porphyritic texture and with small cavities in a brown rendzina sample (right).

6. According to the heavy metal content analyses I have established that there were no values indicating a significant contamination in the case of the investigated metals (Al, Ca, Fe, K, Mg, Mn, Na, Co, Cr, Cu, Ni, Pb, Zn), although some slightly elevated levels of Ni and Zn could be detected in some samples (*Table 1.*). These elements are of geogenic origin in the investigated samples and are released during the weathering of the rocks.

		g/kg							mg/kg							
Talajszelvény	**cm**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**pH H_2O**	**H%**
8	**0-10**	10.28	40.89	10.86	1.15	2.21	1.27	0.24	4.11	19.07	34.05	16.39	53.66	187.13	7.1	51.37
FRE	10-20	14.08	43.62	14.80	1.36	2.80	1.81	0.24	6.51	24.53	42.26	23.05	65.60	237.30	7.3	36.98
10	**0-10**	5.82	28.92	6.05	0.75	1.51	0.54	0.34	1.35	10.61	24.53	7.91	38.01	159.09	6.5	76.29
FRE	10-20	18.74	27.09	18.00	1.40	2.57	1.83	0.25	7.11	28.60	31.99	27.07	74.71	164.99	7.3	33.68
11	**0-20**	10.12	33.62	9.97	0.75	1.87	1.04	0.40	1.85	22.82	25.32	11.17	83.98	126.84	7.3	48.96
FRE	20-50	16.59	28.61	16.43	1.00	2.57	1.55	0.25	7.01	32.44	21.58	17.57	57.74	91.05	7.5	32.29
5	**0-10**	15.33	25.10	18.23	1.63	2.40	1.38	0.30	8.87	25.25	34.82	50.50	50.11	178.50	6.8	34.69
BRE	10-30	21.18	15.99	25.59	2.01	3.09	1.98	0.17	13.56	31.31	38.66	70.35	41.13	192.07	7.4	18.74
	30-60	21.66	49.42	25.00	1.92	3.16	1.83	0.20	13.84	37.89	40.69	73.98	25.80	183.15	7.9	7.43
6	**0-10**	16.57	7.59	19.77	1.18	2.92	1.21	0.31	12.14	26.42	22.30	32.33	40.17	125.44	5.9	9.68
BRE	10-25	17.86	5.32	21.58	1.17	3.15	1.17	0.19	14.31	29.55	19.83	37.83	22.95	112.11	6.3	6.51
	25-40	22.90	13.73	27.17	1.68	3.80	1.11	0.19	13.86	36.63	26.26	48.24	20.61	131.35	7.3	4.74
7	**0-10**	24.00	12.38	23.24	1.11	2.83	0.58	0.21	10.35	35.34	17.54	20.83	39.87	91.43	6.8	20.4
BRE	10-20	28.62	10.19	28.28	1.27	3.20	0.65	0.26	11.70	45.05	22.18	26.91	31.03	99.53	6.8	12.14
	20-30	34.14	15.20	32.29	1.49	3.24	0.60	0.25	11.41	51.45	22.83	30.76	26.41	101.28	7.6	11.26
9	**0-10**	17.57	16.75	19.05	1.22	2.95	0.90	0.35	8.93	27.31	19.24	21.73	45.80	108.97	7.2	22.89
BRE	10-30	21.67	19.10	24.30	1.37	3.41	0.96	0.18	12.29	34.24	14.75	29.63	24.75	88.42	7.6	10.85
	30-50	15.36	58.36	19.66	1.01	3.29	0.65	0.16	10.85	28.32	14.13	25.89	13.40	63.29	8.0	2.65
	50-70	13.41	64.34	18.63	0.91	3.13	0.54	0.16	9.64	22.41	15.33	24.83	11.51	55.67	8.1	1.62
12	**0-5**	16.70	38.13	17.25	1.13	11.39	1.22	0.25	8.75	27.94	15.72	19.68	42.03	82.40	7.7	19.08
BRE	5-10	20.10	36.18	20.12	1.02	16.67	1.26	0.16	9.97	31.47	12.95	22.30	26.98	60.38	7.7	6.83
	10-20	21.71	38.35	22.08	1.14	13.97	1.22	0.15	10.44	33.78	15.48	25.01	19.34	65.05	7.7	6.63
	20-40	15.79	73.56	16.61	0.90	22.30	0.98	0.18	8.00	26.83	14.95	19.63	11.95	51.41	7.9	3.96
	40-50	4.60	113.54	4.79	0.29	36.50	0.46	0.20	1.69	6.95	7.41	6.27	3.45	16.81	8.0	1.61
13	**0-10**	14.91	19.78	18.04	1.35	3.25	1.06	0.20	8.77	26.12	14.66	19.70	56.49	129.24	7.3	21.99
BRE	10-30	15.60	23.71	18.22	1.10	2.94	1.02	0.25	9.03	23.77	13.02	21.02	45.91	101.92	7.5	15.38
	30-40	17.29	32.86	20.34	1.27	4.40	1.03	0.18	10.16	25.64	11.07	22.71	32.54	162.54	7.7	11.01
4	**0-10**	17.25	14.35	27.30	1.17	1.82	3.05	0.21	18.63	27.78	47.47	105.12	56.72	271.92	7.6	23.15
VARE	10-30	15.76	5.45	35.82	0.83	1.01	2.22	0.16	24.72	27.66	69.55	110.81	16.59	334.65	7.9	2.63
	30-70	15.86	4.85	38.77	0.82	0.77	2.33	0.14	24.45	29.55	60.52	86.85	12.53	363.76	7.9	1.46
	70-100	12.39	4.23	37.16	0.70	0.50	2.33	0.14	22.30	25.40	49.55	59.77	10.95	340.60	7.7	0.60
	100-130	13.29	4.89	35.83	0.73	0.51	3.74	0.16	20.62	26.83	58.99	88.87	17.01	383.27	7.7	0.81

Table 1. Heavy metal contents, pH value of aqueous soil extracts (pH_{H2O}) and humus content (H%) in the samples (**VARE** – red clay rendzina, **BRE** – brown rendzina, **FRE** – black rendzina). Orange color indicates concentrations higher than respective contamination (B) levels.

5. Bibliograpy of the author's publications considering the dissertation

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