

Thermal analysis of soils formed on limestone in the Bükk Mountains, North Hungary

¹E. HOFMANN, ^{2,3}T. NÉMETH, ¹A. BIDLÓ

¹Institute of Environmental and Earth Sciences, University of Sopron, Sopron

²Department of Mineralogy, Eötvös Loránd University, Budapest

³Research Centre for Astronomy and Earth Sciences, Institute for Geological and Geochemical Research, Hungarian Academy of Sciences, Budapest

Abstract

The present article discusses the applicability of thermoanalytical methods in the analysis of Hungarian soils formed on carbonate rocks. Up to now only limited mineralogical and soil chemical research has been done on these soils. Soils from the Bükk Mountains, the most varied limestone region in Hungary, were used for the investigations. The aim was to extend our incomplete knowledge on the mineral composition and formation processes of these soils and to demonstrate the possibilities and evaluation potential of thermoanalytical techniques. All the soils investigated were formed on limestone and had different surface soil thickness, influenced by the accumulation of silicate debris and the microterrain. The results of soil mineralogical analysis revealed an extraordinarily high proportion of quartz compared to that of other minerals (especially calcite), indicating that these soils could not have originated solely from the weathering of the limestone bedrock. The results also showed that thermoanalytical methods could complement classical chemical and instrumental (XRPD) methods in research on the genesis of soils formed on limestone.

Keywords: Limestone, soil, Bükk Mountains, thermoanalysis, mineral composition

Introduction

Soil is a complex physical, chemical and biological system, the investigation of which is extremely important from both ecological and economic aspects. Among the many instrumental methods available for soil analysis thermoanalytical methods have been pushed into the background recently. Thermal analysis is suitable for the identification and quantitative assessment of the mineral constituents of rocks, but although minerals were the first compounds to be investigated with thermal analysis, its potential for geology has mostly remained untapped up to now (FÖLDVÁRI, 2008). Since thermoanalytical measurements have only been used as a complementary tool for the assessment of the mineralogical composition of soils if at all. The aim of the present study was to demonstrate of the

potential of thermal methods and how to interpret and utilize thermoanalytical curves.

Thermoanalytical methods were first applied for the investigation of soils in the 1930s. Ross (1931) and Kerr (1934) used thermogravimetric methods to measure soil moisture content and to study soil minerals (halloysite, allophane, kaolinite). Kelley et al. published the thermoanalytical (TG) curves of soil colloids (VAN DER PLAS & VAN REEUWIJK, 1974). As both the grain size of the organic and inorganic constituents and the physical, chemical and biological properties of soils are quite variable, it is necessary to specify whether the analysis was made on fine earth (<2 mm grain) or on soil fractions with a given grain size range. The thermal analysis of original soil samples is only feasible if the clay content is high and the organic content sufficiently low ($\leq 1\%$) (TAN et al., 1986). So most of the research conducted in Hungary has been limited to the thermal analysis of such soil samples. The thermoanalytical studies of FEKETE et al. (2008) and FEKETE (2010) on the mineral composition of Hungarian red soils provided useful data on the composition of the clay content in these samples. In investigations on the poorly weathered/mineralized layers of soils from the Gerecse Mountains (typical basic rock: Dachstein Limestone) the transformed zone was indicated by the weakened bonding structure of calcites, detected as the lower decomposition temperatures of the calcites using thermoanalytical methods (DEÁK et al., 2002).

Thermal analysis is one of the most commonly used methods for the determination of soil moisture content. FÖLDVÁRI & KOVÁCS-PÁLFFY (2002), MARSÍ et al. (2004) and FÖLDVÁRI (2008) used thermogravimetric curves to construct a weathering curve (indirectly a palaeoclimate curve) for a loess section, based on the measurement of the molecular water and hydroxide water content of the samples.

The present work investigated soils found under natural forests and formed on limestone basic rock. Detailed, comprehensive research on soils formed on limestone in Hungary has not yet been reported. The results previously published for these soils focused primarily on leaching effects, the thickness and structure of the surface soil and changes in organic matter content (STEFANOVITS, 1992; SZENDREI, 1998; JÁRÓ, 1999; STEFANOVITS et al., 1999). A recent study on the formation of these soils by NÉMETH et al. (2014) focused on the detailed examination of their mineral composition using thermal analysis and X-ray powder diffraction methods, but only provided preliminary results. Other studies have discussed the classification of these soils using the new soil classification systems (MICHÉLI et al., 2006; BARTA et al., 2009; MICHÉLI 2011; MICHÉLI et al., 2015).

The aim of this study was to assess the applicability of thermal analysis as a technique for the study of soils, focusing especially on the mineralogy of soils formed on limestone basic rock, as knowledge on the mineral composition of these soils is incomplete. Samples were collected from the Bükk Mountains, which have the most varied limestone structure in Hungary and are also the highest karst highland. The results were compared to other chemical and mineralogical soil data, and conclusions were drawn on the genesis of the soils, on their relationship with the basic rock, and on the parameters influencing soil formation processes.

(mostly montane beech forests) not affected by excess water. In order to trace changes between the layers, soil profiles were sampled from diagnostic horizons representative of soil formation processes.

The soil samples were dried at 105 °C and visible organic parts were removed. They were then ground to pass through a 2 mm sieve. The prepared soil fractions (fine earth fractions) served as the basic material for laboratory analysis.

Basic physical and chemical measurements

The basic physical and chemical soil properties analysed included the pH of aqueous and KCl soil extracts (Hungarian standard MSZ-08-0206-2:1978), the calcium carbonate content (Scheibler-type calcimeter, MSZ-08-0205:1978), the grain size distribution (GSD) (MSZ 18094-14:1986) and the total organic matter (humus) content (FAO 1990; BELLÉR 1997).

Thermoanalysis

The thermoanalytical investigation of the mineralogical composition of the samples was carried out using a Mettler Toledo TGA/DSC 1 instrument. The measurements were performed in Al₂O₃ crucibles in a synthetic air atmosphere using a 10 °C/min heating rate. Thermogravimetric (TG), differential thermogravimetric (DTG) and heat flow (HF) curves were recorded. The heat flow represented the flow of heat between sample and control crucibles and indicated the endothermic (valley) or exothermic (peak) processes at given temperatures. The thermal curves were evaluated with TA STARE software. Besides the fine earth fractions (<2mm), various other grain fractions, separated by grain size distribution measurements (MSZ 18094-14:1986), were also analysed. In this case, sample preparation was modified to omit sodium hexametaphosphate in order to keep the carbonate minerals unchanged.

X-ray powder diffraction (XRPD) measurements

The mineral composition of the soil samples was determined with a Philips PW 3710/PW 1050 parafocusing Bragg-Brentano goniometer using Cu-K α radiation ($\lambda = 0.15418$ nm), equipped with a graphite monochromator and a proportional counter. The quantitative evaluation of the digitally recorded XRPD scans was done using a full profile fit method with corrections for preferred orientation and microabsorption.

The mineral composition of the basic rocks was determined with a Siemens D5000 diffractometer equipped with a graphite monochromator using Cu-K α radiation at 40 kV and 40 mA. The step size was 0.05° for 2 sec from 3° to 70° 2 θ . The quantitative mineral composition was determined with the Rietveld full profile fitting method using Siroquant V4 software.

Results and discussion

Analysis of fine earth fractions

The pH values of the soil samples were neutral to slightly alkaline ($\text{pH}_{\text{H}_2\text{O}}$: 6.5 – 8.1; pH_{KCl} : 5.8 – 7.5). The upper soil layers were found to contain lower levels of calcium carbonate compared to the deeper layers, which were closer to the basic rock. The GSD measurements showed that the fine sand and clay-silt fractions were dominant in most of the samples. Although the leaf litter layers and organic parts were removed during sample collection and preparation, samples with extremely high humus contents were also found. These were probably organic layers containing already decomposed leaf litter that could not be detected and separated during sample processing. The results are summarized in *Table 1*.

Table 1

Basic chemical and physical properties of the soil samples. $\text{pH}_{\text{H}_2\text{O}}$: pH of the aqueous soil extract; pH_{KCl} : pH of the KCl soil extract; CaCO_3 : calcium carbonate content; grain size distribution: C% – clay (<0.002 mm), S% – silt (0.002 – 0.02 mm), Fs% – fine sand (0.02 – 0.2 mm) and Cs – coarse sand (0.2-2 mm); H%: humus content; SP%: skeletal part; n.d. = not detected.

Soil profile	Depth cm	pH H ₂ O	pH KCl	CaCO ₃ %	C %	S %	Fs %	Cs %	H %	SP %
1	0-5	6.9	6.6	n.d.	13	30	53	4	27.8	n.d.
	5-20	6.9	6.6	n.d.	23	38	35	4	21.9	7
2	0-10	7.1	6.6	10	7	26	66	1	51.4	37
	10-20	7.3	6.9	9	11	26	62	1	37.0	35
3	0-10	6.5	6.1	7	15	22	62	1	76.3	39
	10-20	7.3	6.7	7	27	18	54	1	33.7	29
4	0-20	7.3	6.8	5	13	6	80	1	49.0	56
	20-50	7.5	7.0	7	9	24	63	4	32.3	67
5	0-10	6.8	6.2	6	17	2	76	5	34.7	11
	10-30	7.4	6.8	7	43	22	32	3	18.7	42
	30-60	7.9	7.1	35	27	42	21	10	7.4	61
6	0-10	6.8	6.1	4	37	30	32	1	20.4	36
	10-20	6.8	5.8	4	49	24	26	1	12.1	4
	20-30	7.6	6.7	7	39	32	28	1	11.3	13
7	0-10	7.2	6.5	5	33	26	40	1	22.9	6
	10-30	7.6	7.0	12	39	32	26	3	10.9	27
	30-50	8.0	7.3	20	19	18	38	25	2.7	34
	50-70	8.1	7.4	23	15	24	31	30	1.6	49

Table 1 cont.

8	0-5	7.7	7.1	10	15	24	52	9	19.1	24
	5-10	7.7	6.9	9	29	26	41	4	6.8	16
	10-20	7.7	7.0	12	27	26	42	5	6.6	23
	20-40	7.9	7.2	23	29	2	59	10	4.0	46
	40-50	8.0	7.5	55	15	4	51	30	1.6	46
9	0-10	7.3	6.8	6	31	6	62	1	22.0	37
	10-30	7.5	7.1	9	33	4	62	1	15.4	56
	30-40	7.7	7.1	13	11	18	68	3	11.0	56
10	0-10	7.6	6.8	5	39	12	29	20	23.2	10
	10-30	7.9	6.9	5	19	10	8	63	2.6	6
	30-70	7.9	6.8	5	19	10	6	65	1.5	9
	70-100	7.7	6.8	5	19	10	9	62	0.6	n.d.
	100-130	7.7	6.8	4	27	2	15	56	0.8	n.d.

Thermal analysis of the fine earth fractions revealed lower peak temperatures than were expected, which was explained by the poor crystallinity of the soil minerals, though the heating rate and sample amount could also have influenced the results. As repeated temperature calibration of the instrument gave the same thermoanalytical curves with different heating rates, it was concluded that poor crystallinity was a characteristic trait of the soil samples investigated, and of the minerals and phases in the soils. The thermal decomposition of smaller particles commences at lower temperatures than that of larger particles, so the onset temperature of the transformation processes is determined by smaller particles (FÖLDVÁRI, 1986). As the grain size distribution of the soil is heterogeneous, decreasing particle size results in the shifting of peak temperatures towards lower values (BUZÁS, 1993). Moreover, the proportion of amorphous and organic phases may have been high in these samples, thus changing the positions of clay minerals, iron minerals and carbonates on the thermoanalytical curves compared to data in the literature. The characteristic endothermic peaks of clay minerals may be shifted to 250–400 °C or even up to 500–600 °C during the thermal analysis of fine earth fractions containing high amounts of organic substances. This was typical of the upper soil layers, which had high humus content (*Figure 2*) and was less pronounced in the deeper layers of the profiles, which had thermoanalytical curves with pronounced endothermic peaks for the minerals (*Figure 3*).

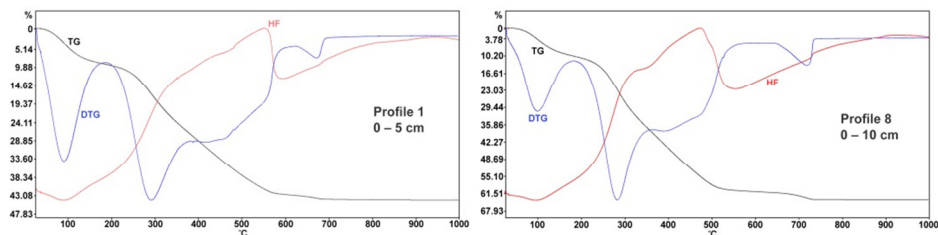


Figure 2

The influence of high organic matter content is apparent even up to 500–600 °C

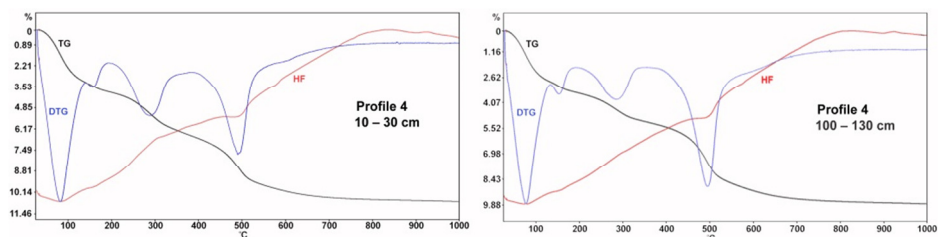


Figure 3

Thermoanalytical curves of deeper soil layers with lower amounts of organic matter, showing characteristic endothermic peaks for minerals

Endothermic dehydration occurs between 50 and 100 °C. Smectite-type minerals were present in almost all the soil samples, except for the topmost layers, giving peaks between 50 and 200 °C on the thermoanalytical curves (characteristic endothermic peak of water loss and adjacent inflexion, corresponding to the loss of the water bound to interlayer cations). Smectites in soils lose their interlayer free water at lower temperatures than typical smectites (FÖLDVÁRI, 2011). Soils usually contain various types of clay minerals, so the dehydroxylation peaks of smectites may overlap with those of other clay minerals (kaolinite, illite), making the precise identification of minerals within the smectite group difficult. Endothermic peaks between 500 °C and 600 °C usually indicate the dehydroxylation reactions of clay minerals, but peaks below 600 °C may also be interpreted as the second peak of chlorites. Quartz appears in the HF curve between 570–580 °C, while calcite has a varying peak temperature between 650–850 °C. The low temperature decomposition of calcite was detected for all the profiles investigated. The weathering of carbonate minerals results in lower onset temperatures for decomposition during thermal analysis, which can be explained by the smaller grain size or crystalline size of calcite or by cation substitution (DEÁK et al., 2002; FÖLDVÁRI, 2011). Ca is most frequently substituted by Mg, but other metals, e.g. Fe or Mn, may also occur (SZAKÁLL, 2007). Mg and Fe were probably the most frequent in the samples investigated, leading to lower decomposition temperatures.

The results of thermal analysis on the fine earth fractions are summarized in Table 2.

Table 2

Results of thermoanalytical measurements: moisture contents and the composition of mineral phases in the soil layers. H₂O% – molecular water content; OH% – structural water content; CM% – total clay mineral content; Sm% – smectite content; Kao% – kaolinite content; Ill% – illite content; Chl% – possible chlorite content; Goe% – goethite content; Fh% – “ferrihydrite” content; Cal% – calcite content; Dolo% – dolomite content; Org% – organic matter content; Q – quartz; +: present based on TG, DTG and HF curves; -: not present based on TG, DTG, HF curves; tr: in traces).

Soil profile	Layer cm	H ₂ O %	OH %	CM %	Sm %	Kao %	Ill %	Chl %	Goe %	Fh %	Cal %	Dolo %	Org %	Q
1	0-5	8.82	-	-	-	-	-	-	-	+	2	-	<34%	-
	5-20	7.37	-	-	-	-	-	-	-	+	2	-	<25%	-
2	0-10	9.21	-	-	-	-	-	+	-	-	6	-	<50%	-
	10-20	7.87	0.58	-	-	-	-	+	-	+	7	-	<36%	-
3	0-10	8.96	-	-	-	-	-	-	-	+	4	-	<65%	-
	10-20	8.37	0.60	-	+	-	-	+	-	+	3	-	<32%	-
4	0-20	9.49	-	-	-	-	-	-	-	+	5	-	<42%	-
	20-50	7.83	-	-	+	-	-	-	-	+	6	-	<30%	-
5	0-10	8.29	-	-	-	-	-	-	-	+	4	-	<34%	-
	10-30	6.45	0.37	-	+	-	-	-	-	+	5	-	<19%	-
	30-60	3.66	1.51	27-36	21-25	0-3	1-15	0-4	+	+	37	-	<7%	-
6	0-10	5.58	-	-	+	-	-	-	-	+	1	-	<21%	+
	10-20	5.17	2.71	46-64	25-34	0-8	4-39	0-11	-	+	1	-	<13%	-
	20-30	5.36	2.77	47-65	26-35	0-8	4-39	0-11	-	+	4	-	<11%	-
7	0-10	5.67	2.90	48-68	28-38	0-9	1-41	0-11	-	+	2	-	<20%	-
	10-30	4.26	2.09	36-49	22-29	0-6	1-28	0-7	-	+	8	-	<11%	(+)
	30-50	2.27	1.60	24-37	7-15	0-6	4-30	0-8	>24	>14	17	-	<2%	+
	50-70	1.85	1.41	20-33	5-12	0-6	1-28	0-7	>14	>8	20	-	<1%	+
8	0-5	6.79	-	-	+	-	-	-	-	+	6	6	<20%	-
	5-10	4.06	3.62	47-84	6-27	0-17	3-78	0-22	+	+	17	25	<9%	-
	10-20	5.32	2.54	44-60	27-36	0-7	1-32	0-9	+	+	3	11	<5%	-
	20-40	3.26	2.70	36-63	7-21	0-12	3-56	0-15	+	+	10	28	<4%	-
	40-50	0.63	11.00	83-90	-	+	+	+	>11	>6	23	57	<1%	-
9	0-10	7.02	0.49	-	+	-	-	-	-	+	2	tr	<21%	+
	10-30	6.12	0.58	-	+	-	-	-	-	+	5	-	<15%	+
	30-40	5.61	0.57	-	+	-	-	-	-	+	9	tr	<12%	-
10	0-10	7.86	0.30	-	+	-	-	-	-	+	2	-	<21%	-
	10-30	3.65	3.47	43-81	4-24	0-17	2-77	-	+	+	-	-	<3%	+
	30-70	3.50	3.72	44-87	0-23	0-19	2-86	-	+	+	-	-	<2%	+
	70-100	3.23	3.40	41-79	1-21	0-17	3-79	-	>13	>8	-	-	<1%	+
	100-130	3.35	3.53	42-82	1-22	0-18	2-82	-	>16	>9	-	-	<2%	+

Analysis of other soil fractions

Other soil fractions were also analysed for all the samples from the soil profiles investigated. The thermoanalytical properties of the different fractions: clay (<0.002 mm), fine sand (0.02–0.2 mm) and coarse sand (0.2–2mm), are summarized below for all the samples, but because of the large number of samples thermoanalytical curves are only presented for selected samples.

The dehydration water loss of *clay fractions* typically occurs between 70 and 100 °C. In the majority of the samples the typical inflexion peaks of the smectite group minerals also appeared around 170 °C. The characteristic exothermic peak at 300 °C could be explained by the presence of organic or other amorphous matter, strongly bound to the clay minerals, and very resistant to decomposition. The endothermic peaks of dehydroxylation reactions are characteristically found at 500 °C and around 600–700 °C. When calcite mineral was also present in a clay fraction, its peak was observed on the DTG curve between 700 and 800 °C. Endothermic and exothermic processes were also characteristic of the clay fractions above 900 °C, indicating the phase transitions of the clay minerals. *Figure 4* depicts the thermoanalytical curves of the clay fraction sedimented from the 20–40 cm layer of soil profile No. 8. Dehydration occurred at 81 °C, while the inflexion peak of the smectite group minerals appeared at 173 °C. The presence of organic and/or amorphous (“ferrihydrite”) phases was evidenced by the weak exothermic process starting at around 300 °C. The dehydroxylation of clay minerals was noted at 503 °C, followed by smaller flat, extenuated peaks at 592 °C and 644 °C (clay minerals/chlorites) on the DTG curve. Finally, the decomposition of calcite took place at 717 °C. The calcite content of the sample was 5% based on the mass loss.

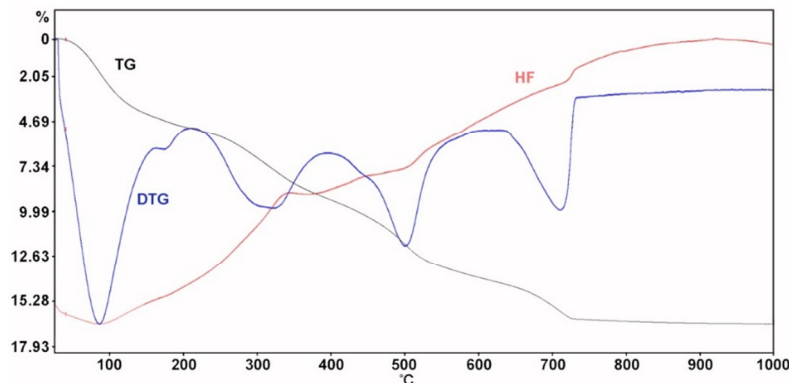


Figure 4

Thermoanalytical curves of the clay fraction sedimented from the 20-40 cm layer of soil profile No. 8.

Dehydration of the *fine sand fraction* takes place at very low temperatures, between 50 and 100 °C. On the HF curve of some of the fractions a larger or smaller exothermic peak could be observed around 300 °C, which may indicate the presence of “ferrihydrite” and/or goethite. Endothermic peaks around 500 °C and 650 °C (characteristic of clay minerals/chlorites) only appeared on the HF curve of a few fractions, but were not typical of the majority of fine sand fractions. The presence of carbonate minerals was detected above 700 °C. The most characteristic mineral in the fine sand fractions was quartz, appearing on the HF curve at 570 °C. *Figure 5* illustrates the thermoanalytical curves of the fine sand fraction sedimented from the 20–50 cm layer of soil profile No. 4. Dehydration took place at 74 °C,

while amorphous “ferrihydrite” and/or goethite phases were indicated by a small exothermic reaction with an onset temperature of 300 °C. Quartz gave a peak at 570 °C. The decomposition of calcite took place at 780 °C, and the calcite content of the sample was 25%.

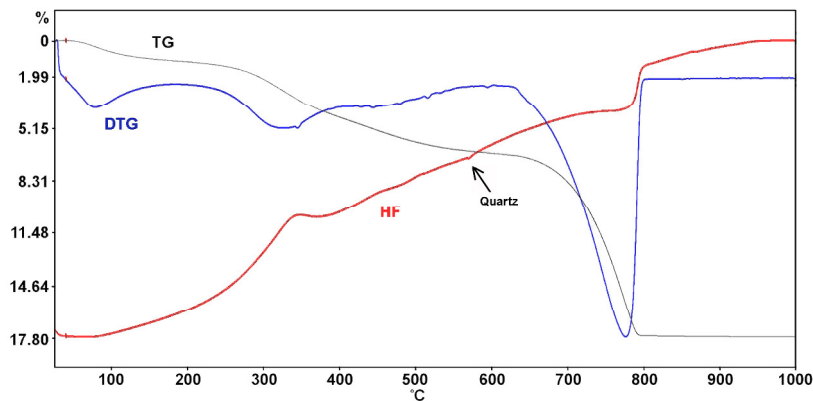


Figure 5

Thermoanalytical curves of the fine sand fraction sedimented from the 20-50 cm layer of soil profile No. 4.

The dehydration of the *coarse sand fraction* also took place at very low temperatures of 50–80 °C. A small exothermic peak at around 300 °C indicated the presence of “ferrihydrite” and/or goethite. The majority of the coarse sand fractions were characterized by small endothermic peaks at 450–500 °C and 600–700 °C (clay minerals/chlorites), but the proportion of these minerals was quite low even in these fractions. Calcite appeared above 700 °C and in some of the samples dolomite was also detected. Quartz was highly characteristic of the coarse sand fractions (570–575 °C).

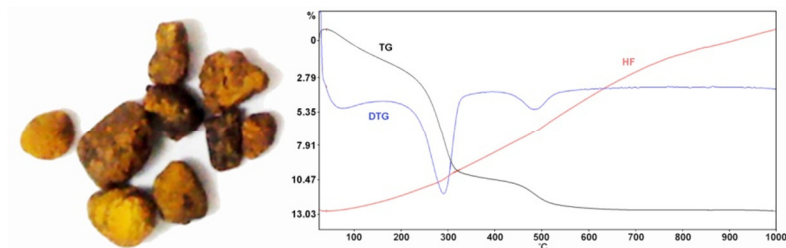


Figure 6

Macroscopic appearance and thermoanalytical curves of coarse sand grains consisting of goethite and a small amount of clay mineral

Figures 6–10 illustrate different types of grains separated macroscopically from the coarse sand fraction of the 30–50 cm layer of profile No. 7. The figures also include the thermoanalytical curves of the respective grain types.

The dark yellow/brown rounded, longish grains shown in Figure 6 had the characteristic appearance of goethite. A certain amount of clay mineral could also be detected on the thermoanalytical curves at 500 °C. Dehydration occurred at 64 °C, and the endothermic peak at 298 °C was characteristic of goethite. The goethite content of the sample was 75% based on the mass loss.

The grains shown in Figure 7 were transparent and were of various sizes, which are characteristic traits of quartz. Quartz was also suggested by the endothermic peak at 570 °C on the HF curve. Calcite was also indicated (825 °C) with a content of 23%. Based on this data the quartz content was estimated as 77%.

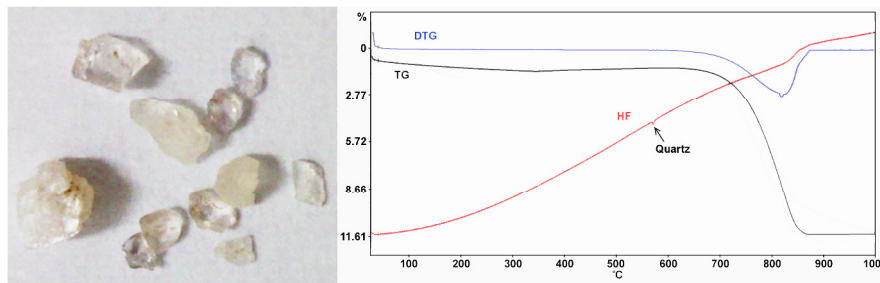


Figure 7

Macroscopic appearance and thermoanalytical curves of coarse sand grains consisting of quartz and calcite

The grains in Figure 8 were whitish-yellow with a roundish shape. Some of the grains were apparently crystalline. Based on their appearance, they were thought to be calcite, which was confirmed by thermal analysis. Calcite decomposition had a peak temperature of 862 °C. The content of calcite was estimated as 84%.

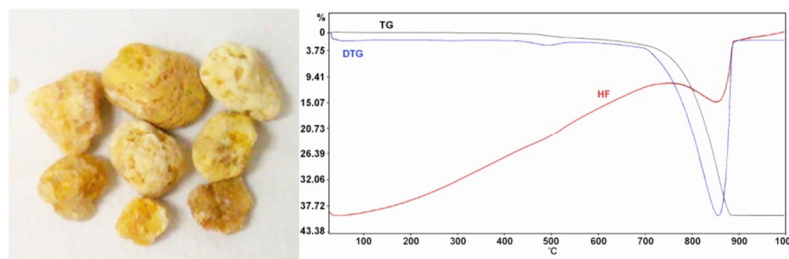


Figure 8

Macroscopic appearance and thermoanalytical curves of coarse sand grains consisting of calcite

The set in *Figure 9* consisted of whitish-yellow grains with cavities containing iron deposits. Based on their appearance they were identified as weathered calcite. Both the slightly widening peak on the DTG curve and the second derivative curve (DDTG) indicated dolomite. Peak temperatures were found at 805 °C and 866 °C for dolomite and calcite respectively. The dolomite content of the sample was 31% and the calcite content 17% based on the mass loss.

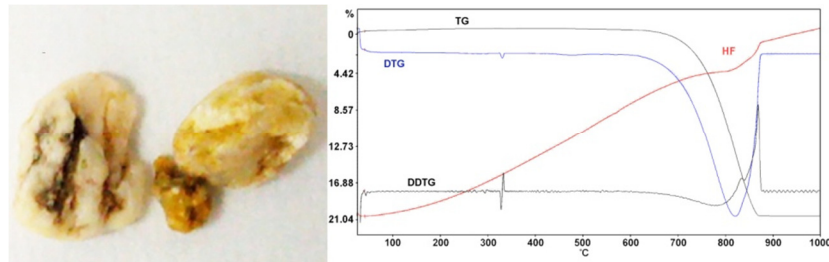


Figure 9

Macroscopic appearance and thermoanalytical curves of coarse sand grains consisting of calcite and dolomite

The white and grey microcrystalline grains in *Figure 10* had the characteristic appearance of calcite. Thermoanalytical curves evidenced the presence of high purity (97–98%) calcite. Peak decomposition temperatures of 876 °C and 857 °C were found for the grey and white calcite, respectively.

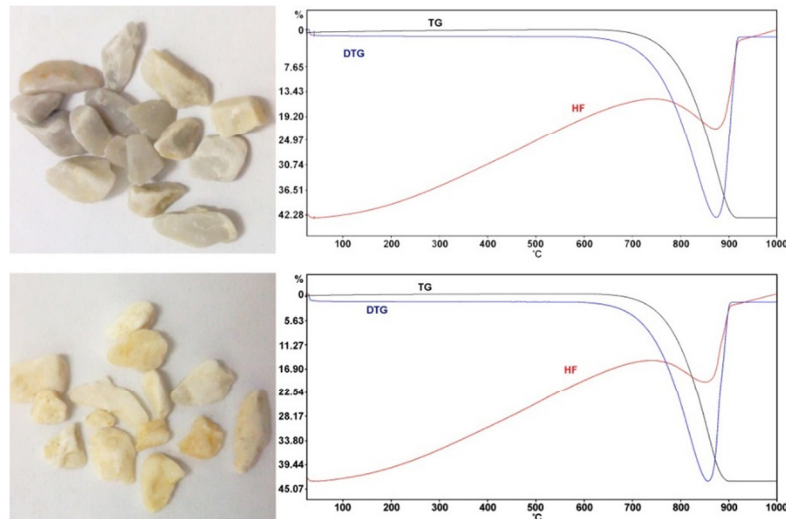


Figure 10

Macroscopic appearance and thermoanalytical curves of coarse sand grains consisting of grey calcite (upper figure) and white calcite (lower figure).

Based on the results of thermal analysis the most characteristic clay mineral in the fine earth fractions was smectite, but they also included kaolinite, (chlorite), illite, calcite, dolomite and quartz. Besides organic substances, amorphous “ferrihydrite” and/or goethite was also present in some samples. The minerals which could be determined best, both qualitatively and quantitatively, were calcite and dolomite. Surprisingly, calcite was not found in all the samples.

The detailed analysis of the other soil fractions showed that clay minerals and “ferrihydrite” were enriched to a greater extent in the small-grained (clay) fractions, while quartz, calcite and dolomite were found predominantly in larger-grained (fine and coarse sand) fractions. It is well known that calcite may be of primary or secondary origin (SZENDREI, 1994). The calcite and dolomite occurring in the sand fractions (primary calcites) originated from the physical weathering of the parent material. Calcite may also be present in low amounts in the fine clay fractions, formed *in situ* by precipitation from soil solutions (secondary calcites) (HORVÁTH, 2005). The presence of goethite in the clay fraction in association with amorphous/organic substances can only be presumed. In the fine and coarse sand fractions, however, goethite often occurs together with amorphous “ferrihydrite”, as was evidenced by the shape of the thermoanalytical curves. The thermal analysis of the grains macroscopically separated from the coarse sand fraction enabled the minerals to be precisely identified both qualitatively and quantitatively.

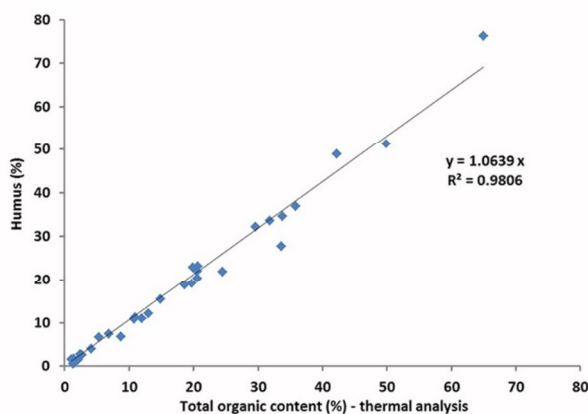


Figure 11

Relationship between the amounts of organic matter content determined by thermal analysis and by the FAO method

The total content of organic substances was also estimated during thermal analysis and compared to the humus contents determined with basic chemical analysis. A strong significant correlation was found between the two methods for all the samples investigated (Figure 11). The values determined using thermal analysis were somewhat higher than the respective humus contents, which was attributed to the presence of amorphous phases bound to organic matter. The application of

thermoanalytical methods allows the organic matter content of the soil to be determined without the use of chemicals.

Table 3

Absolute contents of mineral phases in the fine earth fractions, calculated by correcting the phase percentage values of minerals determined by XRPD with the total organic matter content measured with thermal analysis. *Including illite (illite/montmorillonite interlayer structures); n.d.: not detected; Q: quartz; Ill: illite; Mm: montmorillonite; Kao: kaolinite; Pl: plagioclase; Ort: orthoclase; Goe: goethite; Calc: calcite; Dolo: dolomite; Chl: chlorites.

Soil Profile	Layer cm	Q %	Ill %	Mm %	Kao %	Pl %	Ort %	Goe %	Cal %	Dolo %	Chl %
1	0-5	30	11	n.d.	8	11	2	3	2	n.d.	n.d.
	5-20	36	14	n.d.	11	5	4	4	2	n.d.	n.d.
2	0-10	20	3	3	8	3	3	3	8	n.d.	3
	10-20	29	3	3	3	8	3	2	10	n.d.	3
3	0-10	18	-	9*	n.d.	n.d.	n.d.	n.d.	7	n.d.	n.d.
	10-20	34	-	17*	4	3	3	n.d.	7	n.d.	n.d.
4	0-20	29	-	9*	9	7	2	n.d.	2	n.d.	n.d.
	20-50	35	-	8*	7	11	3	n.d.	5	1	n.d.
5	0-10	26	5	3	10	7	7	n.d.	8	n.d.	n.d.
	10-30	37	7	4	7	8	7	4	8	1	n.d.
	30-60	23	5	5	9	5	5	5	37	n.d.	n.d.
6	0-10	44	4	4	10	8	4	2	n.d.	n.d.	4
	10-20	39	4	9	9	12	7	3	n.d.	n.d.	4
	20-30	34	4	9	11	13	4	3	7	n.d.	4
7	0-10	40	6	4	12	5	5	4	n.d.	n.d.	4
	10-30	37	6	5	11	7	4	4	9	n.d.	4
	30-50	34	10	5	8	8	8	5	15	n.d.	6
	50-70	34	10	5	8	8	6	5	17	n.d.	6
8	0-5	36	-	12*	5	6	2	n.d.	3	16	n.d.
	5-10	14	-	5*	5	7	7	n.d.	7	46	n.d.
	10-20	28	-	11*	5	8	2	8	9	24	n.d.
	20-40	24	-	8*	5	3	2	5	12	38	n.d.
	40-50	3	-	2*	3	2	n.d.	n.d.	10	79	n.d.
9	0-10	44	-	16*	4	8	6	n.d.	n.d.	2	n.d.
	10-30	47	-	10*	4	9	7	n.d.	9	n.d.	n.d.
	30-40	44	5	9*	4	9	5	n.d.	9	3	n.d.
10	0-10	48	10	n.d.	16	n.d.	n.d.	4	2	n.d.	n.d.
	10-30	58	5	10	15	n.d.	n.d.	10	n.d.	n.d.	n.d.
	30-70	49	5	10	24	n.d.	n.d.	10	n.d.	n.d.	n.d.
	70-100	44	12	10	23	n.d.	n.d.	10	n.d.	n.d.	n.d.
	100-130	44	10	10	25	n.d.	n.d.	10	n.d.	n.d.	n.d.

XRPD analysis of the fine earth fractions

In most cases thermal analysis only provides an estimation of the amounts of the mineral phases (except for calcite and dolomite). Thus, the XRPD analysis of the fine earth fractions was also carried out to verify the calculated data. It was

found that the ratios of the individual crystalline phases in the samples did not always add up to 100 %. This was explained by the amorphous matter content of the samples, which could not be determined precisely by XRPD. Thus, the calculated phase percentages are not absolute values, but relative values compared to the sum (100%) of the crystalline phases. The simultaneous application of thermoanalytical and XRPD methods enables soil phases to be studied in more detail. Thermoanalytical methods are suitable for qualitative assessment and for the precise quantitative estimation of organic/amorphous soil phases in the presence of various crystalline phases.

The relative percentage values of the crystalline phases determined with XRPD were corrected using the organic matter content measured with thermal analysis to obtain the absolute concentrations of minerals in the soil samples. The results are detailed in *Table 3*.

Recalculating the results of XRPD measurements using the organic matter contents determined by thermal analysis had the greatest effect on the calcite and quartz contents. Both methods are suitable for the quantitative determination of calcite, but the results of XRPD need to be corrected with the organic matter content, which requires supplementary measurements. With thermal analysis the calcite content can be determined directly in a single measurement. Thermoanalytical methods are thus better suited for the determination of calcite content than the XRPD method. Summarizing the results of the XRPD measurements the following mineral phases were found in the samples: quartz, illite, montmorillonite, illite/montmorillonite interlayer structures, kaolinite, feldspars, goethite, calcite, dolomite and chlorites. Besides the mineral phases the samples also contained significant quantities of organic matter and amorphous material.

XRPD analysis of the basic rock

The results of XRPD analysis on the basic rock (*Table 4*) indicated high purity calcite, proving that the large amounts of silicates in the soil samples could not be the product of the weathering of the basic rock.

Both thermoanalysis and XRPD analysis yielded new results on the relatively unexplored mineral composition of soils formed in limestone on the Bükk Highlands. The silicate and quartz contents in the soil samples were very high, suggesting that these soils could not have originated solely from the weathering of the limestone basic rock. A comparison of different methods for determining calcite content (Scheibler-type calcimeter, thermal analysis, XRPD) revealed that thermoanalysis is probably the most suitable method, as the accurate determination of calcite content with the other two methods is influenced by the presence of organic substances. Thermal analysis is therefore a useful supplementary technique for mineralogical research, especially as regards the carbonate contents of soils formed on limestone, in spite of the fact that this technique has been pushed into the background recently compared to other instrumental analytical techniques.

Table 4

Mineral composition of the basic rock (that of soil profile 1 was not measured). n.d. = not detected

Soil profile	Quartz %	Calcite %	Dolomite %
1	-	-	-
2	n.d.	100	n.d.
3	n.d.	100	n.d.
4	1	99	n.d.
5	1	99	n.d.
6	n.d.	100	n.d.
7	0.5	99.5	n.d.
8	0.5	65	34.5
9	3	83	14
10	0.5	99.5	n.d.

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