

## CLAY MINERALS IN PALEOSOLS AT VISONTA, HUNGARY

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### ABSTRACT

Clay mineral associations of a paleosol sequence in the roof strata of the lignite mine at Visonta were studied by means of XRD, TEM, FTIR, DTA. Investigations show that several clay mineral phases (smectite, kaolinite, illite, vermiculite) are present together in all the strata. High charge montmorillonite occurs in the present day soil, high charge beidellite is characteristic of the red paleosol and montmorillonite and beidellite are present together in the grey clays. This various clay mineralogy indicate complex genesis of the strata.

Key words: XRD, TEM, layer charge, smectite, beidellite, paleosol, Visonta

### INTRODUCTION

Mineralogical composition, clay mineral association and the characteristics of the clay mineral species were studied in a paleosol sequence in order to reconstruct the environment in which the paleosols were formed. The studied paleosol sequence is situated in the wall of the opencast lignite mine at Visonta (pediment of the Mátra mountains, Hungary). The Mátra mountains consist of Miocene neutral volcanic rocks. On the pediment, Pannonian sediments overly the volcanic rocks on which loess and colluvial sediments were deposited in the Pleistocene. These sediments contain the paleosols.

The area of the opencast mine at Visonta has already been studied by some authors. The geologic and hydrogeologic conditions were studied by MIKLÓS (1967). Complex investigation including geomorphology, paleontology and paleomagnetic measurements was carried out by a working group of KRETZOI, MÁRTON, PÉCSI, SCHWEITZER, VÖRÖS and HAHN (1985). They studied the Eastern II. pit of the „Thorez Mine” where alluvial sediments with paleontological evidence of Pleistocene age were observed. Below the Pleistocene strata, a red clay layer considered to be formed in the Pliocene was found.

Investigations on mineralogy has not been carried out yet. This study on mineralogy is connected to a new research project focusing on soil development, paleopedology and paleoenvironmental reconstruction that was started in 1996. The work was so far concentrated on the Small South pit of the mine. Our results differ from the published data (MICHÉLI et al, 1999, HORVÁTH, 1999).

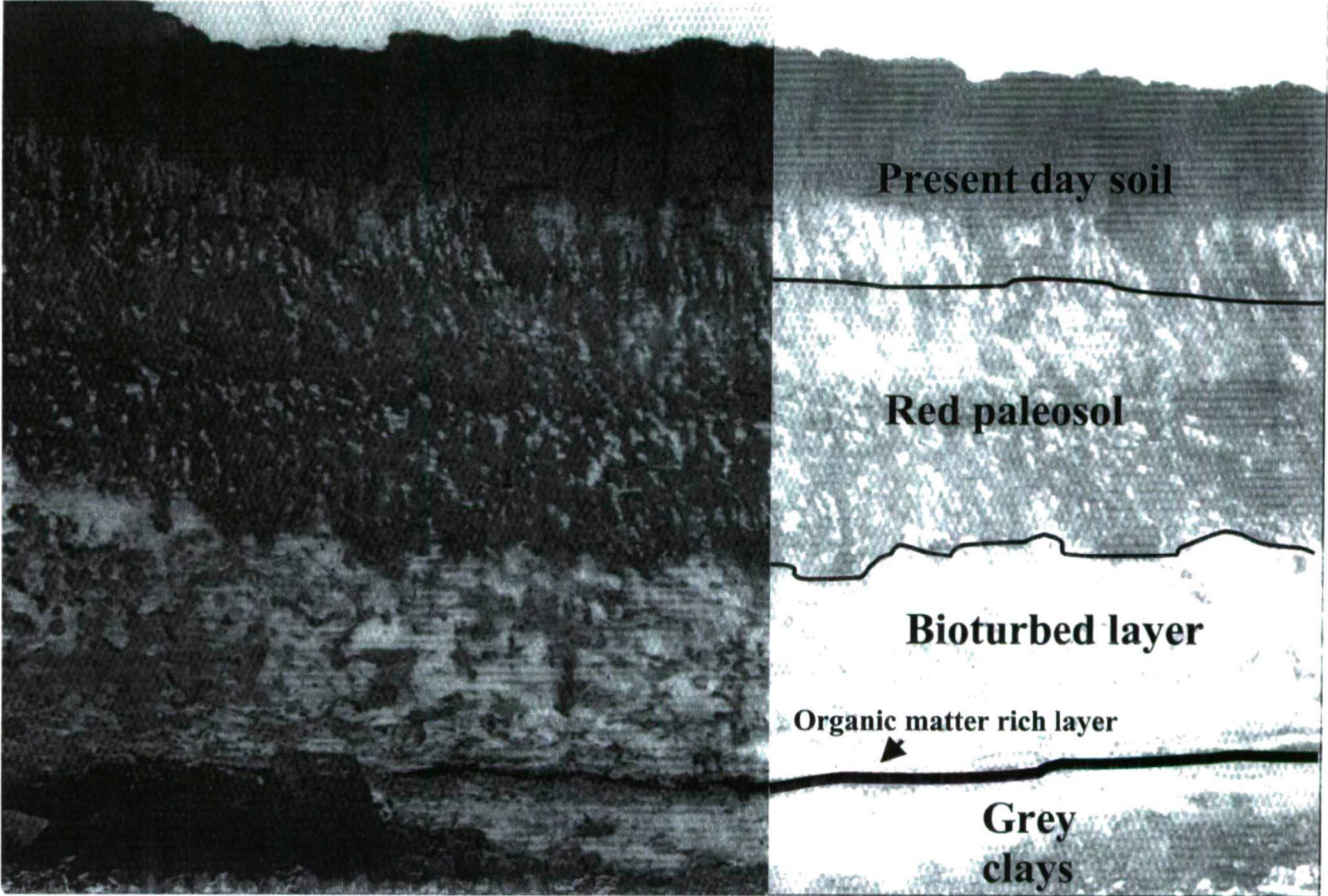
### THE STUDIED SITE

General soil profile description and sampling of the selected layers were carried out using Munsell colour notations. The studied profile (*Fig. 1.*) consists of a Chernozem

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*Fig. 1.* The studied sequence in the lignite mine at Visontia

brown forest soil (Argic Chernozem) on the top with a black „A” (10YR 3/2) horizon and a brown „B” (10YR 6/3) horizon that has prismatic structure, and clay films on ped surfaces. The border between the two horizons is gradual. Below it a  $\text{CaCO}_3$  accumulation horizon (5YR 4/6) was identified that has a sharp boundary to the „B” horizon.

Under it a red paleosol (5YR 5/8) was found that has prismatic structure with slickensides, stress surfaces and black and yellowish mottles basically on ped surfaces. The red paleosol has sharp boundary to the underlying layer. Based on colour and texture this layer consist of different materials. In the upper part a pink silt (5YR 7/4), in the lower part a yellowish fine sand (2.5Y 7/8) is the predominant material. In the matrix greenish grey clay clasts (5Y 5/6) which gradually decreasing in size and abundance towards the top of the layer, large  $\text{CaCO}_3$  accumulations in the bottom part, biogalleries filled with the red material from the overlying layer were found.

In the bottom part of the profile two greyish layers are located. The darker grey (5Y 5/2) one has a black organic matter accumulation horizon that gradually transits into the dark grey clay. The part rich in organic matter was identified as a thin lignite layer (2.5Y 2/0). The lower one has a clay texture and greenish grey colour (5Y 6/4) and is separated by a sharp boundary from the other layer.

## METHODS

The mineral composition of the studied layers and horizons was determined by semi-quantitative X-ray diffraction, differential thermal analysis, Fourier Transform Infrared Spectroscopy and Transmission Electronmicroscopy. Random powder samples were analysed by a Philips PW-1730 diffractometer equipped with a graphite monochromator using  $\text{Cu-K}\alpha$  radiation at 45 kV and 35 mA with  $1^\circ$  divergence slit and  $1^\circ$  receiving slit. Scanning rate was  $0,05^\circ 2\theta$  per minute from  $3^\circ$  to  $70^\circ$ . The total mineral composition was determined by semi-quantitative phase analysis on the random powder samples (NÁRAY-SZABÓ and PÉTERNÉ, 1964). Clay minerals were identified on the Mg-, Ca- K- and Li-saturated, ethylene-glycol and glycerol solvated and heated samples from the clay fraction (less than  $2\ \mu\text{m}$ ) which was obtained by sedimentation.

FTIR spectra were obtained from the clay fraction of the samples with the self-supporting clay film technique. Measurements were made by a BIO-RAD FTS 165 FTIR spectrometer. The clay fraction was also analyzed with DTA (MOM derivatograph). The clay fractions of the red and grey clays were investigated by Transmission Electron Microscopy (Phillips CM 20, acceleration voltage: 200kV)

## MINERAL COMPOSITION OF THE STRATA

In all samples quartz is the predominating mineral, its amount vary between 50 and 80%. The clay mineral content varies between 4 and 40%. The K-feldspar content is negligible (less than 5%). The amount of plagioclase generally decreases from the top to the bottom of the profile: 10-15% in the topsoil horizons, 4-8% in the red paleosol layers, about 2-3% in the bioturbed layer and 3-7% in the greyish clay layers except the lignite bearing layer (13%). The decreasing tendency of feldspar content is related to the higher weathering state of the red paleosol.

From the group of carbonate minerals calcite and dolomite were identified. The amount of calcite ranges between 0 and 60% and it increases from the top to the bottom of the profile. It reaches maximum in the bioturbed layer. Dolomite was identified in some samples, it has the highest value in the greenish grey clay layer (7%). It is detrital in the topsoil and in the red paleosol. Based on  $^{13}\text{C}$  stable isotope data, the calcite is of pedogenic origin, and the dolomite was precipitated in lacustrine environment in the grey clay layer (DEMÉNY and EMBEY-ISZTIN, 1997). Hematite was identified in trace amount in the „B” horizon of the present day soil and in the red paleosol.

### CLAY MINERALS IN THE LAYERS

All the XRD diagrams exhibited 14-, 10-, 7 Å basal reflections on the untreated samples. An example of the changes due to different treatments is shown in Fig. 2. The 14 Å peak on the Ca- and Mg-saturated, ethylene glycol treated samples is shifted to 17 Å. It indicates the presence of smectites or vermiculite. After glycerol solvation this peak

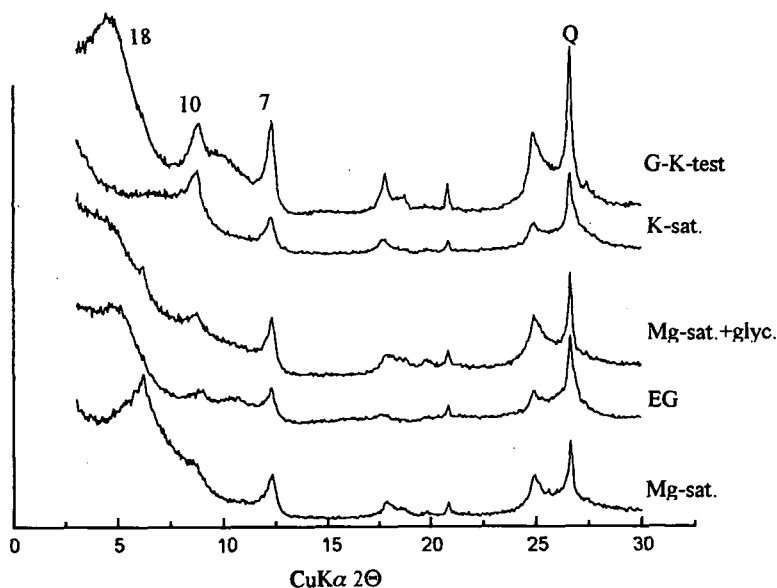


Fig. 2. The XRD patterns of the red paleosol after the different treatments

splits up: the smaller part remains at 14 Å, the major part has shifted to 18 Å. The former represents vermiculite, the later stands for smectite. The peak at 4.72 Å supports the presence of vermiculite. The position of (060) reflection at 1.5 Å shows that the smectite is dioctahedral. The peak at 10 Å belongs to illite and illite/smectite and the 7 Å peak with the 3.58 Å peak is kaolinite. After heat treatment (550°C) the 7 Å peak disappeared, this also indicates the presence of kaolinite (BRINDLEY and BROWN, 1980). Due to potassium saturation, the 14 Å peak of the samples from the topsoil and from the red paleosol collapsed to 10 Å. In case of grey clays a broad peak at around 12 Å appears

besides the 10 Å reflection. After this treatment high layer charge swelling structures collapse to 10.4 Å, low layer charge swelling structures collapses to 12.4 Å. (Fig. 3.) The Green-Kelly test was used to differentiate between montmorillonite and beidellite (THOREZ, 1976). Beidellite is an aluminous smectite having a layer charge mainly due to substitution in the tetrahedral sheet while montmorillonite is mainly substituted in the octahedral sheet. Montmorillonite was identified in the topsoil and in the grey clays and beidellite is present in the red paleosol and in the grey clays (Fig. 4.).

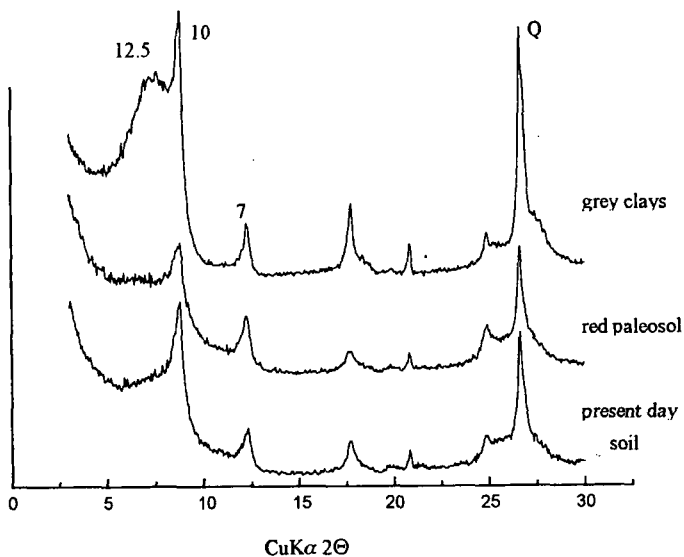


Fig. 3. The XRD patterns of the K-saturated samples of the different layers.

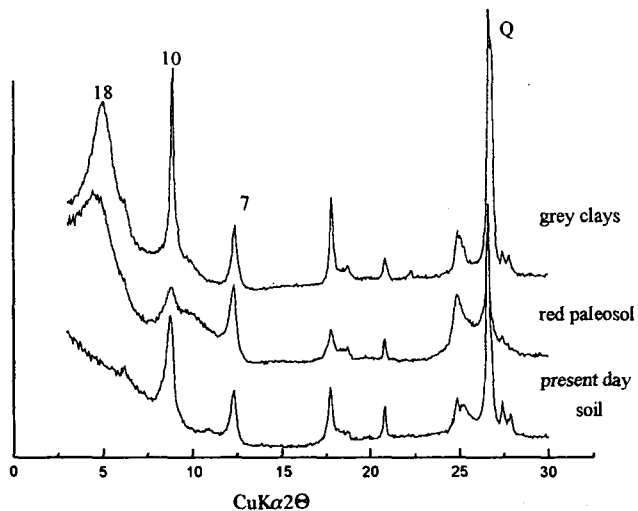


Fig. 4. The XRD patterns of samples after the Green-Kelly test

The determination of smectite crystallinity is calculated from the peak and valley intensity ratio of the (001) and the from presence of (002) reflection of EG solvated samples (THOREZ, 1976). The crystallinity of the smectite increases downward. In the topsoil it is poorly crystalline, in the red paleosol it is moderately crystalline, in the grey clay layers it is well crystalline. This also indicates the different origin of the clay minerals in the grey clays, in red paleosol and in the topsoil.

The FTIR spectra of the clay fraction of all layers are very similar. The aluminous character of the smectites is indicated by a peak at  $916\text{ cm}^{-1}$  that is characteristic of ALOHAI band (RIGHI et al., 1995).

Data obtained by differential thermal analysis present an endothermal peak at  $100^{\circ}\text{C}$  that indicates the loss of adsorbed water, and an endothermal dehydroxylation peak around  $500^{\circ}\text{C}$ , with an endothermal-exothermal peak system at  $830\text{-}900^{\circ}\text{C}$  that shows the phase transformation. The dehydroxylation peak at  $500^{\circ}\text{C}$  is characteristic of soil smectites. The dehydroxylation peak of other smectites occurs at  $700^{\circ}\text{C}$  (MACKENZIE, 1970).

The purpose of TEM investigation was to gain information on the morphology, structure and stacking order. This feature is characteristic of the species within the smectite group. Nontronite and montmorillonite are characterised by turbostratic structure (MERING, 1975) which is indicated by ring-like diffraction pattern. Saponite and beidellite has high stacking order that is indicated by the spot-like diffraction pattern (ZVYAGIN, 1967). The unusually small size of the smectite particles can be observed both in the red paleosol and in the grey clay. The size of the irregular shaped or platy pseudohedral smectite crystallites is only  $0.0x\ \mu\text{m}$  in the clay aggregates of  $0.x\ \mu\text{m}$  size. A somewhat larger ( $0.05\text{-}0.1\ \mu\text{m}$ ) elongated fibrous lath-shaped smectite crystallites also occur (Fig. 5.). The pseudohedral  $0.5\text{-}1\ \mu\text{m}$  sized crystallites of kaolinite are the most characteristic in the grey clay.

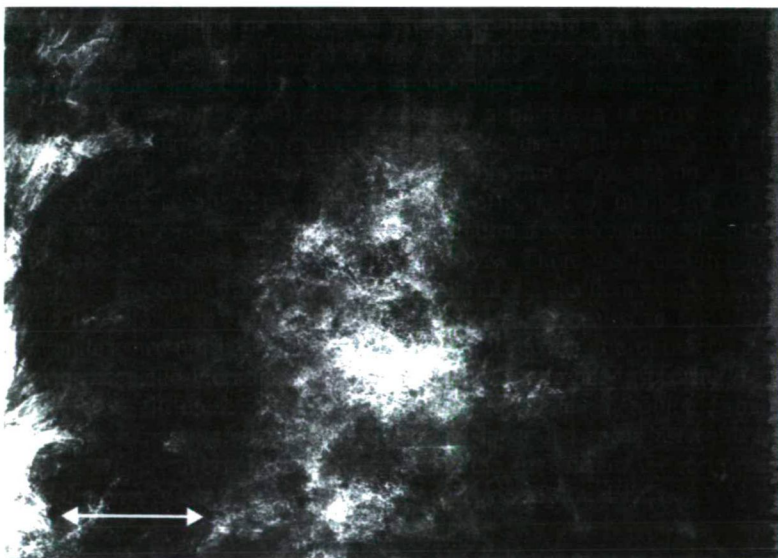


Fig. 5. Electron micrograph of the smectite from the red paleosol showing very fine irregular shaped and elongated lath shaped crystals. Scale bar:  $0.25\ \mu\text{m}$



The ring like diffraction pattern indicates turbostratic structure. This kind of pattern may also be the result of polycrystalline diffraction due to small crystal size. In this case the turbostratic structure is more probable because the single crystal diffraction of relatively larger crystals also shows ring like pattern. The heterogeneity of the material in the grey clay can be observed in *Fig 6*. in which both ring-like and spot-like patterns are present. Ring-like pattern is caused by the presence of smectite and the spot-like pattern is characteristic of a well ordered clay mineral (mica, illite, vermiculite or well ordered beidellite). Based on intensity ratio this ordered phase consists of two polytypes. Preliminary EDS investigation shows the ferrous beidellitic nature of smectite. When comparing to data in literature, the beidellitic smectite in the red paleosol is not as ordered as it can be expected (SUQUET and PEZERAT, 1987).



*Fig. 6.* SAED pattern of a clay particle from the grey clay layer

High layer charge smectites are abundant in soils (ARAGONESES and GARCIA-GONZALEZ, 1991). The low layer charge smectites have authigenic or hydrothermal origin or are formed by weathering of volcanic glass, pyroxenes, amphiboles and feldspars. Low layer charge smectites transformed into high layer charge ones in vertisols having high pH and low organic matter content (RIGHI et al., 1998). We think that high layer charge smectites were transformed from low layer charge ones and also formed by the weathering of intermixed micas and illite in the red paleosol during pedogenesis. Smectites formed from 2:1 phyllosilicates have their charges mostly in the tetrahedral sheet (DIXON and WEED, 1986). The identified high layer charge smectites belong to this type.

The origin of kaolinite cannot be identified with the method used. It can be a weathering product indicating warm humid climate with high leaching rate (SINGER, 1980). According to the fact that it is not the predominant mineral and its quantity is the same in all layers, it is more probably that kaolinite here is not the result of in situ weathering, but it was rather transported within the sediment providing parent material of the topsoil and paleosols. Illite

is originated from the dust mixed to the material at the time of transportation. Illite is a common 2:1 layer silicate in loess (PÉCSI-DONÁTH, 1987).

## CONCLUSIONS

Considering complexity and heterogeneity, the clay mineralogy of the layers in the studied sequence is similar. The small differences between the mineral species and their relative amount supported by other results can answer the questions raised in the introduction. The source of the difference is the amount of the layer charge and from where (i. e. the tetrahedral or octahedral sheet) it derives. Kaolinite can be considered the only stable phase in all the layers though it is not predominating and it is probably detrital in this case. Illite in discrete and in illite/smectite interstratified form is also common. The swelling clays predominate and vary from each other according to layers and genesis. The presence of different types of smectites (beidellite, montmorillonite and vermiculite) indicates heterogeneous origin. The high-charge beidellite in the red paleosol was formed due to pedogenesis probably from a red clay having smectite as a predominating mineral. The layer stacking of this beidellite is poorly ordered and the crystallinity is also poor that suggests pedogenic origin. The high charge montmorillonite and vermiculite are also the result of pedogenesis but in different environment.

## ACKNOWLEDGEMENTS

The authors are grateful to KOVÁCS ISTVÁN and RADNÓCZI GYÖRGY (Research Institute for Technical Physics and Materials Science) for their help in TEM analysis and to Dódony István for discussion during TEM data evaluation and HORVÁTH ZOLTÁN for the contribution during the field work, RUDNYÁNSZKY LIVIA for the photos. The authors thank the Soros Foundation and the OMFb for the financial support.

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*Manuscript received: 30. Sep. 1999.*