CLAY MINERALS IDENTIFIED IN RED QUATERNARY DEPOSITS,
FROM CORLĂŢEL AREA (MEHEDINŢI COUNTY, ROMANIA), USING XRD AND IR

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Abstract. The area from which samples were collected is placed in Mehedinţi County, about 25 km west of the Danube, locality Porţile de Fier 2. The Quaternary loess like red deposits from Oltenia are described in the specialized literature as "red clays" or "red loams". This paper renders data on the type and proportion of the clay minerals identified by X-ray diffraction of the clay fraction separated from both red loess like deposits and older deposits either ruditic with red matrix, mainly silty-sandy or sandy red levels.

Keywords: Quaternary, loess like deposits, clayish minerals, X-ray diffraction.

Rezumat. Minerale argiloase identificate din depozite roşii cuaternare, zona Corlăţel (judeţul Mehedinţi), folosind XRD şi IR. Zona din care au fost culese probele pentru analize se găseşte în apropierea limitei judeţului Mehedinţi, la aproximativ 25 km vest de Dunăre, localitatea Portile de Fier 2. Depozitele loessoide cuaternare de culoare roşie din Oltenia sunt descrise în literatură ca „argile roşii” sau „luturi roşii”. Lucrarea de faţă redă date referitoare la tipul şi proporţia mineralelor argiloase identificate prin difracţia de raze X din fracţia argiloasă, separată atât din depozitele loessoide roşii, cât şi din depozite mai vechi, fie ruditice cu matrice roşie, preponderent silto-nisipoasă, fie nivele nisipoase roşii.

Cuvinte cheie: Cuaternar, depozite loessoide, minerale argiloase, difracţie de raze X.

INTRODUCTION

On the western side of Bungetu Almajel hill, in Corlăţel settlement, it can be observed a 3.5 - 4 m outcrop of loess-like red deposits (Fig. 1). On the left side of the country road linking Corlăţel to Ştircoviţa, alongside Valea lui Radu, approximately 600 m after leaving Corlăţel, there is another outcrop of sands, gravels and loess-like deposits (Fig. 2). The opening is about 7 m high and 15 - 20 m long. The coordinates of this open pit are 44° 23.9' N and 22° 56' E.

In the upper part, beneath the A soil horizon, there appear three layers rich in carbonaceous concretions separated by red loess-like deposits. Beginning with the depth of 4 m, for 0.5 m, a level of mainly fine and very fine pebbles with a red matrix made of silt and sand is present. For the next 2 m, there appears an alternation of gray medium sands and medium gravels. In the lower part of the outcrop, there can be observed very coarse pebbles and boulders with gray sandy matrix. The analysed samples were collected from the loess-like deposits of the first aforementioned outcrop and from the loess-like deposits of Valea lui Radu outcrop. From the last mentioned location, there were collected also fine gravel and matrix samples from the level c, represented in Fig. 2. On the hydrogeological map 1:100 000, sheet 40b Drobeta Turnu Severin, this type of deposit is considered to have been formed in the Upper Pliocene - Lower Pleistocene.

Figure 1. The hypsometric map of the area surrounding the sampling site; H-sampling site. (original)

MATERIALS AND METHODS

After drying, the samples of gravel, sand and red clay were sieved using a 2 mm mesh sieve. The pelitic fraction needed for XRD analysis was obtained by centrifugation and for IR by applying the pipette method.

To prevent the flocculation of clay minerals that can cause the formation of agglomerates larger than 1mm in the natural environment (HILL, 1998), which is strongly influenced by the existence of organic matter, it was carried out its removal by using the method proposed by KUNZE & DIXON (1986), which requires the treatment with 10% hydrogen peroxide.

In order to remove the carbonates from the analysed samples, we applied the method presented by RABENHORST & WILDING (1984) using diluted weak acids.

The deflocculation process was done by adding a dispersant, a very commonly used one being sodium hexametaphosphate or polyphosphate, known under the commercial name of Calgon (JIPA, 1987).

5 ml of the <2 μm fraction, separated by centrifugation were used for the saturation with $MgCl_2$ and 5 ml for the saturation with KCl.
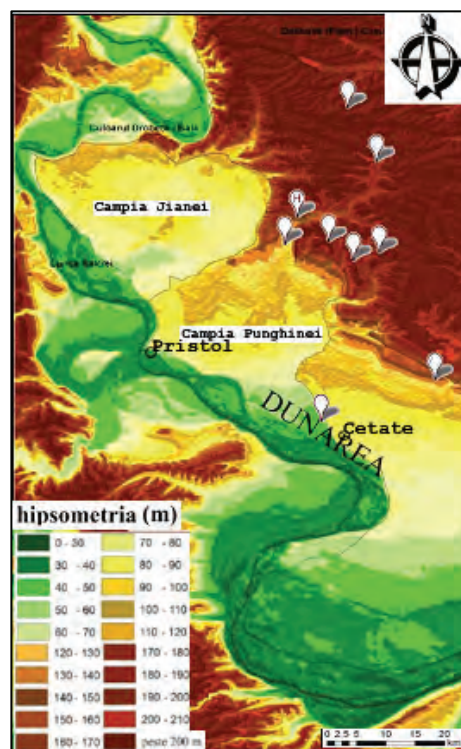
For cation saturation, there were used potassium chloride (KCl) and magnesium chloride ($MgCl_2$), the samples being covered by the solution of a chloride and then centrifuged 3 times. To prevent the flocculation of the clay minerals, after this treatment, washing with distilled water was performed 3 times, to remove the chlorides.

The ethylene glycol treatment was done by adding 100-200 ml of ethylene glycol in a desiccator, the sample slides being placed on a ceramic plate. The desiccator was left in the oven at 60°C for at least 8 hours.

For the heat treatment, the slides with samples were placed in an oven and heated at 330°C and 500°C for one hour. After this period of time, they were analysed right after taking them out of the oven, to prevent the rehydration of the sample.

Diffractograms were obtained from a range of 2θ, 2-40° using a Philips XPert MPD diffractometer, with Cu (40 mA, 40 kV) anticathode, Ni filter, with Kα radiation with a wavelength of 1.5406 Å, scanning step 0.01, step time 1s/step. X'Pert Quantify and X'Pert High Score programs were used to analyse and process diffraction data. Information about the amount of clay minerals identified based on X-ray diffractograms, was obtained using the calculation method of MOORE & REYNOLDS (1997).

The pipette method was performed according to the recommendations made by Krumbein in 1933 and presented by JIPA (1987); mixing about 500-750 grams of fraction smaller than 2 mm, with about 8-10 litres of heated distilled water. The suspension was collected from the sedimentation cylinders according to the data rendered by JIPA (1988) and JACKSON & BARAK (2005). No chemical treatment for the removal of organic matter or carbonates was applied.

For the IR method, the samples were analysed in the form of disks obtained by pressing a mixture of KBr and clay fraction. The mixture used to obtain the disks contained 2 mg sample and 200 mg KBr (MADEJOVA & KOMADEL, 2001).

The infrared spectra were obtained with Bruker Optics FTIR spectrophotometer, which, for the range 374-400 cm^{-1}, obtained 2,531 frequency-intensity of absorption couples.

RESULTS AND DISSCUSIONS

XRD analysis

On the diffractograms of the samples saturated with K^+, rendered in Fig. 3, we can observe the presence of certain peaks corresponding to the interplanar distances with values of 14.01 Å, 9.95 Å, 7.14 Å, 4.97 Å, 3.56 Å and 3.31 Å.

The diffractogram of the sample saturated with Mg^{2+} presents the same characteristics as the previously mentioned sample. A more defined reflex is observed at 14.09 Å due to the absorption of magnesium ions.

Due to the treatment with ethylene glycol, it can be observed an increase of the interplanar distance from 14.01 Å to 17.36 Å, without any significant changes in the other peaks.

After heating the sample to 330°C, it can be observed the complete lack of any reflexes in 14 Å region due to the reduction of the basal distance to the value of 10 Å (Fig. 4). At 500°C, 7.17 Å and 3.56 Å reflexes disappear too.

Based on the information, the clay minerals identified in both the gravel matrix and in the loess-like deposits are kaolinite, smectite and illite.

Figure 2. Lithological succession in Corlăţel area. A-loess-like level with calcareous concretions; B-loess-like material; C-mostly fine and very fine gravels; D-medium sand; E-medium gravels with medium sand pellicles; F-medium gravels; G - coarse gravels and boulders. (original)

Illite was identified according to the characteristic reflexes for the interplanar distances of 10.1 Å, 4.98 - 5.01 Å, 3.33 Å and 2.89 - 2.92 Å. Other characteristics of illite are the lack of expansion and retention of the reflex plane (001) after the treatment with ethylene glycol and heating to 500°C.

The reflexes according to which kaolinite can be identified are those corresponding to the basal distance d (001) ranging from 7.15 to 7.20 Å and, when they are well crystallized, based on the doublets from 4.17 - 4.12 Å and 3.144 - 3097 Å (MATEI, 1986).
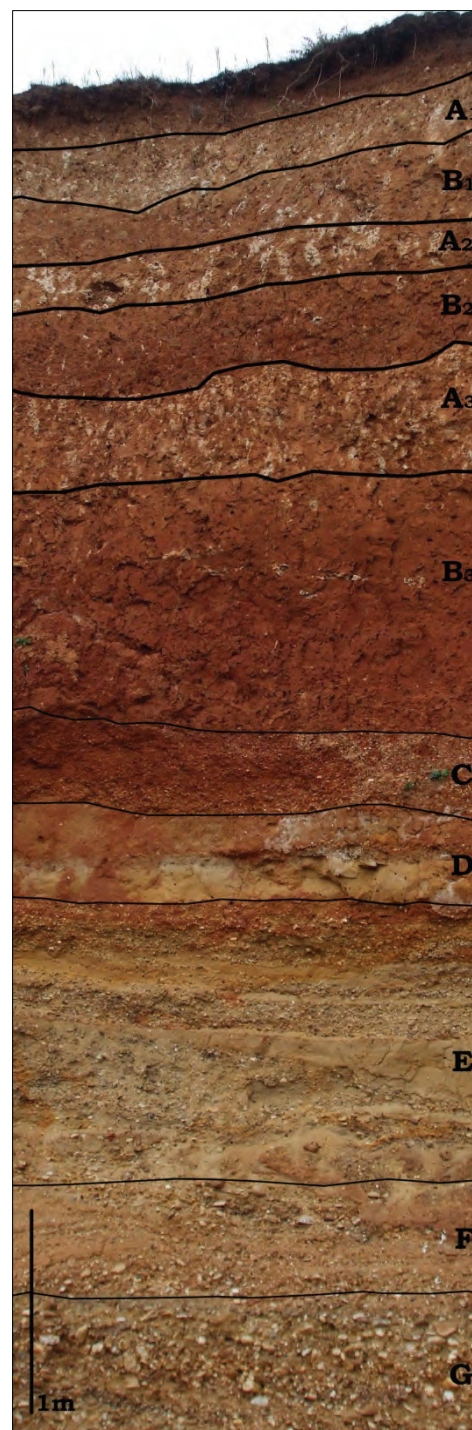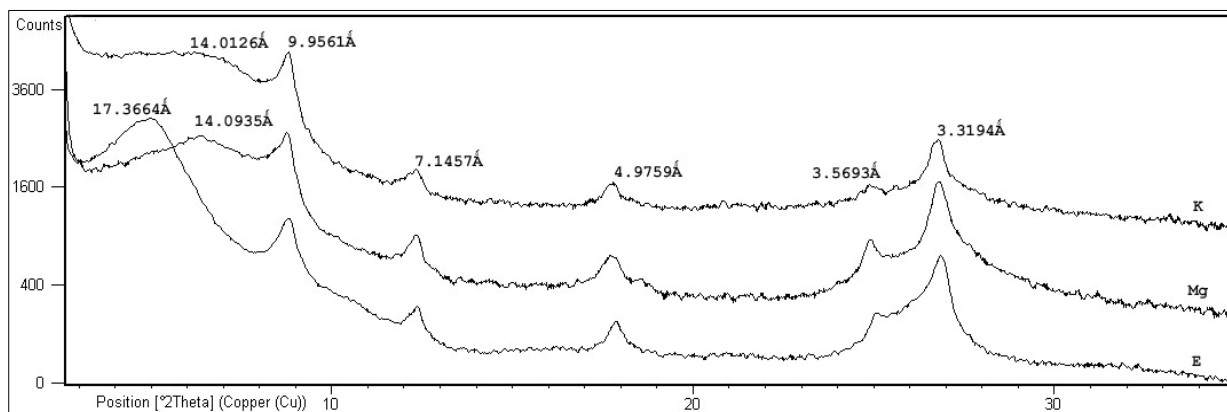
Figure 3. Diffractograms of the samples saturated with K*(K), Mg^{2*}(Mg) and glycol ethylene (E) from the red matrix of the gravel from Corlăţel area.

The lack of swelling, as well as in case of illite, when it is treated with ethylene glycol and also, structural collapse by heating to 500°C, which determine the total disappearance of kaolinite reflexes, are other features of the kaolinite.

The term of smectite used in this paper refers to a clay phase with a structure of the type 2:1, dioctaedric and expandable. This was identified considering the basal distance of smectite as14-15 Å. Another feature used for the identification was swelling induced by the treatment with organic molecules, resulting in the corresponding reflexes d (001) with values of 17 - 17.7 Å.

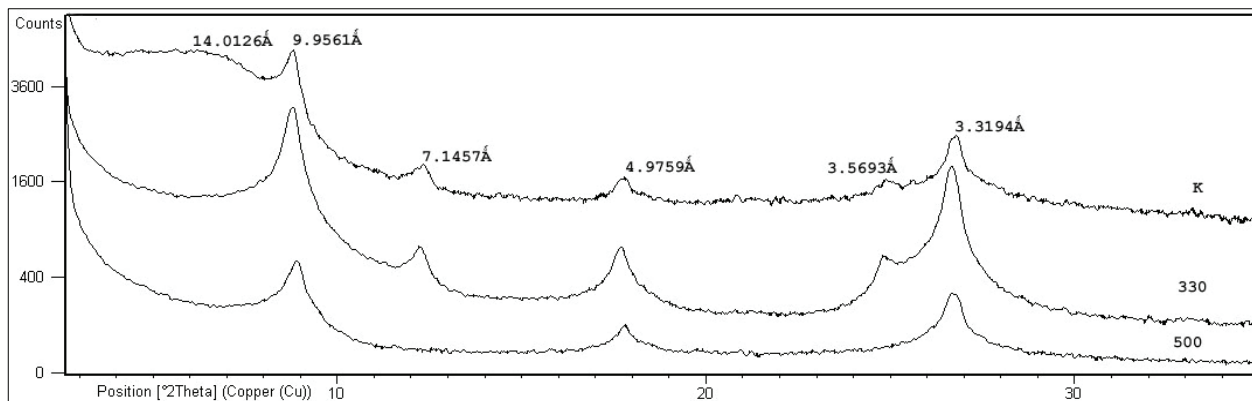Figure 4. Diffractograms of the clay fraction from the gravel matrix, saturated with K*, (K), heated at 330°C (330) and 500°C (500).

The value of 14 Å can also indicate the presence of chlorite or vermiculite minerals, but in their case, the swelling is not observed after the treatment with ethylene glycol. In addition, chlorite keeps the same basal distance after the 300 and 500°C heat treatments.

In case of typical smectites, after heating at 500°C, the basal distance decreases to 9.4-10 Å (the same as in case of illite), depending on the nature of the interfoliar cations.

In Fig. 4, it can be seen how the reflex from 14 Å of the saturated sample disappears after heating to 330ºC, due to the reduction of the basal distance to the value of 10 Å.

The percentages of the clay minerals in the pelitic fraction separated from the red loess-like deposits from Corlăţel are 3% kaolinite, 29% smectite, 68% illite. In the matrix of the red gravels, there are present the same minerals but with a different quantitative share: 1% kaolinite, 56% smectite, 43% illite. The other samples show percentages close to the aforementioned values, the average being 55% illite, 42% smectite, 2% kaolinite.

IR analysis
The IR spectra performed on the samples taken from the two outcrops indicates the presence of the same absorption bands, minor differences being identified only in terms of their intensity (Fig. 5).

The frequencies of 430 cm^{-1} and 470 cm^{-1}, corresponding to the Si-O-Si bond, with high and medium absorption intensity, were identified in all the analysed samples. The first frequency is absorbed by both montmorillonit and illite, but the intensity is significant only in case of kaolinite. Consequently, this band was attributed to the presence of kaolinite.

The second frequency mentioned above, cannot provide clear information on the mineral responsible for its appearance, because both kaolinite and montmorillonit show strong absorption rates in this area. However, the values, which always maintained above 470 cm^{-1}, may indicate kaolinite, as montmorillonit displays slightly lower values.

The frequencies of 535 cm^{-1} correspond to the bonds of the type Al-O-Si (STUBICAN & ROY, 1961) from the network of several clay minerals and, in this case, they cannot provide clear information on a specific mineral.
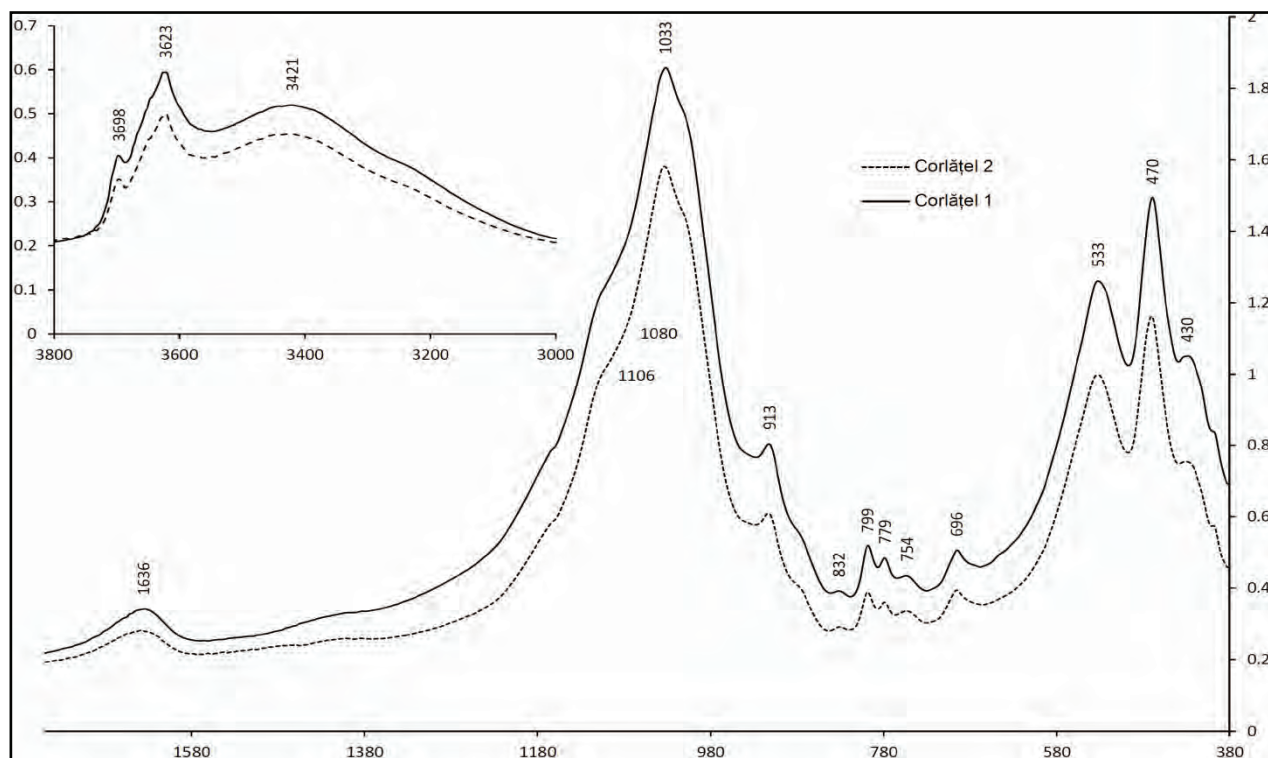
Figure 5. IR absorption spectra for the samples taken from the gravel matrix (Corlăţel 1) and the loess-like deposit (Corlăţel 2); on the horizontal axis, there are rendered the wavenumbers in cm^{-1}.

Another non-specific bond is found at 696 cm^{-1}, indicating the presence of the bond Si-O-Si.

The diagnostic absorption doublet from 779 cm^{-1} and 799 cm^{-1} indicates quartz. In the samples taken from Corlăţel, the absorption intensity is among the lowest compared to the other absorption intensities identified. This indicates a reduced presence of quartz.

The weak and very weak absorption at 755 cm^{-1} was present in all the samples, but it cannot be used to identify the minerals that generated it. 832 cm^{-1} frequency indicates the presence of anion $(CO_3)^{2-}$ (FROST et al., 2004).

The slight shoulder between frequencies 832 cm^{-1} and 915 cm^{-1} corresponds to the deformation vibrations, out of the plane, of $(CO_3)^{2-}$, located at of 875 cm^{-1} (MADEJOVA & KOMADEL, 2001). In the range 1,382-1,440 cm^{-1}, it can be observed a very fine rise, which also indicates carbon-oxygen bonds: 1,430 cm^{-1} stretching vibration $(CO3)^{2-}$ of calcite, MADEJOVA & KOMADEL (2001); 1,410-1,490 cm^{-1} frequencies that indicate $(CO3)^{2-}$ COATES (2000); 6.90 to 6.97 μm (1,449-1,435 cm^{-1}), bands considered to belong to the group $(CO3)^{2-}$, HUANG & KERR (1960); 1,384 cm^{-1} stretching vibration of the bond C = O of the inorganic carbonyl group, JACKSON (1998); 1,365 cm^{-1}, the stretching vibration in the bicarbonate ion COO$^-$, YRUELA et al. (1998).

The frequencies of 913-915 cm^{-1} are absorbed by Al-Al-OH vibrations characteristic to the networks of montmorillonit, kaolinite and illite, showing strong absorption (40-80%) in kaolinite and average absorption (20-40%) in montmorillonit and illite, MATEI (1988). In all the analysed samples, the intensity was average, which would suggest the presence of montmorillonit and illite.

The inflection present at approximately 1,010 cm^{-1}, occurs in case of illite and montmorillonit. Considering the conclusions drawn by HUNT et al. (1950), the maximum intensity of absorption registered at 1,030-1,034 cm^{-1} was attributed to illite distinguished from montmorillonit, which is indicated by the vibration absorption of 1,041.66 cm^{-1} according to the same author.

The "ramp" present in all samples in the interval 1,080-1,106 cm^{-1} may indicate montmorillonit and / or illite, MATEI (1988). At values above 3,000 cm^{-1}, only two frequencies can be used, one at 3,620 cm^{-1}, absorbed by all the three aforementioned clay minerals and 3,696-3,699 cm^{-1}, which is a diagnostic band for the mineral kaolinite (FARMER, 1964). The 1,640 cm^{-1} and 3,620 cm^{-1} bands are assigned to the deformation vibrations, respectively the stretching vibrations of OH groups, belonging to the molecules of water (FARMER, 1974).

CONCLUSIONS

The clay minerals identified in the study area are illite, smectite and kaolinite.

The participation of the three minerals in the clay fraction is approximately uniform, illite having a share of over 40%, smectite of 30 - 60% and kaolinite around 2%.

At Corlăţel, it is observed the increase in the smectite content of the fraction <2 μm in lower, ruditic deposits compared with the higher loess-like deposits. The illite content varies inversely as compared with that of smectite, decreasing in the lower horizons. This quantitative difference it was found in all the analysed cases and might amount over 25%. The abundance of smectite in the ruditic layers can be explained by the petrographic diversity of the clasts, which can provide the cations necessary to the formation of the network of these minerals, or by the size of the smectite crystals, which are smaller than those of illite, and, thus can be easily moved to lower levels.

Based on IR spectra, we can say that the analysed samples contain very small amounts of quartz and even smaller quantities of carbonates, probably calcite. Kaolinite is the clay mineral that is identified very clear using this method by the presence of 3698 cm^{-1} absorption band. The reduced intensities for this frequency correlate well with the small amounts of this mineral, indicated by XRD data. Illite and montmorillonit, showing similar bands of absorption, cannot be separated, as clearly as kaolinite.

The presence of the bands characteristic to the vibration of the bond Al-Al-OH shows that the identified clay minerals are dioctaedric, such positions being occupied mostly by Al^{3+}.

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