CLAY MINERALS IDENTIFIED IN THE RED QUATERNARY DEPOSITS FROM CETATE AREA (DOLJ COUNTY, ROMANIA), USING XRD METHOD

NEGREANU Ştefan, SOARE Barbara

Abstract. The area from which samples were collected is close to the limit between the counties of Dolj and Mehedinţi, about10 km north of the Danube. 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. For a precise understanding of the conditions of the analysis, there are presented the methods used for this purpose in detail.

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

Rezumat. Minerale argiloase identificate prin difracţie de raze X, din depozite roşii cuaternare, zona Cetate (judeţul Dolj, România). Zona din care au fost culese probele pentru analize se găseşte în apropierea limitei dintre judeţele Dolj şi Mehedinţi la aproximativ 10 km nord de Dunăre. 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. Pentru o înţelegere exactă a condiţiilor de analiză sunt prezentate detaliat metodele utilizate în acest scop.

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

INTRODUCTION

On the right side of the road from Cetate to Hinova, at about 8 km northwest of Cetate (Fig.1), there are several 400-500 m long open pits for the exploitation of sands and gravels. Vertically, the walls of the deepest open pit we took samples from are between 15 and 20 meters. The coordinates of this open pit are 44°9'10"N and 22°59 7"E.

At the top, there can be observed the soil horizons, developed on the first 1.5-2 m. Underneath, there appear dusty-sandy reddish deposits based on which soils developed. Their thickness varies between 1 and 2.5 m, sometimes even 3 m. The cause that induced these thickness variations is the erosion surface, which pushed down the soil horizons to the detriment of the silty deposit. The next level consists mainly of very fine and coarse gravels, the last ones having the lowest rate. The matrix of these gravels consists of sands and silts with a very low percentage of clay. Below the gravels with red matrix, on a thickness of 1.5-2 m, there appear thin alternations of sand and coarse gravel, with discontinuous red bands. From this site, there were taken samples from the loess like deposit located immediately below the soil profile as well as from the red gravel matrix. From the neighbouring open pits, there were collected samples only from the loess like deposit and the gravel matrix. Overall, there were analysed 8 samples. On the hydrogeological map 1:100 000, sheet 40d Cujmir (VLAD & ROBU, 1981), this type of deposit is considered to have been formed in the upper part the middle Pleistocene.

MATERIALS AND METHODS

Before starting the granulometric separation by sieving, the samples of gravel, sand and red clay were left in a thin layer to get dry. After drying, the agglomerations, reaching sometimes several centimetres in thickness, of sand, clay and fine and very fine gravel, could be easily

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

disaggregated in particles under 2 mm, due to the partial loss of water absorbed by the clasts, especially by the clay. The next step was sieving using a sieve 2 mm mesh. After this stage, the pelitic fraction was obtained by centrifugation.

Through a series of chemical and physical processes, it is aimed at removingthe minerals, which do not belong to phyllosilicates, as much as possible from the lutitic fraction. This removal allows a clear formation, at maximum intensities, of the characteristic peaks of different phyllosilicates. In the detritic deposits containing clay or lutitic fraction, among the minerals that should be removed, we mention quartz, carbonates, feldspars, iron oxides and hydroxides.
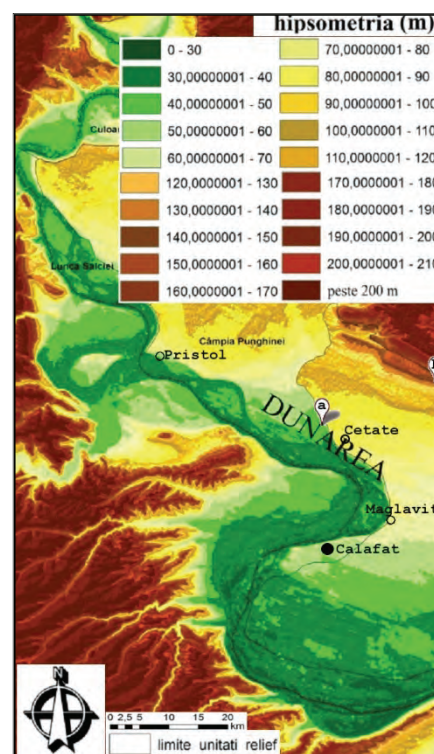
The flocculation of clay minerals that can cause the formation of agglomerates larger than1mm in the natural environment (HILL, 1998) leads to the increase of the background of the diffractograms and produces the reflexes of diffuse diffraction. The phenomenon of aggregation of the fine particles in suspension is strongly influenced by the existence of organic matter.

The removal of the organic matterwas carried out using the method proposed by KUNZE & DIXON (1986), which requires the treatment with 10% hydrogen peroxide by successive additions up to its total removal, followed by 2-3 washings with distilled water.

The removal of the carbonates was made using diluted weak acids, attentively surveying the reaction, in order to avoid, the exposure of the phyllosilicates to an acid environment, together with the removal of carbonates, as this may affect their structure (OSTROM, 1961). In order to remove the carbonates from the analysed samples, we used the method presented by RABENHORST & WILDING (1984).

The extraction of the fraction < 2μ. After eliminating the causes that would prevent the dispersal of the fraction < 2μm, it follows the deflocculation process. This is done by adding a dispersant, a very commonly used one being sodium hexametaphosphate known under the commercial name of Calgon (JIPA, 1987).

For centrifugation, samples have to fill between a quarter and half of the glass tube; then, distilled water is added, leaving a free space at its top to avoid spilling during centrifugation. The sample is centrifuged for 20 seconds and, then, the solution is transferred into clean tubes. The new tubes are centrifuged for 10 minutes. After centrifugation, a part of the solution is removed, so that to keep about 1 cm sample (solid + liquid) in the tube, and then the remaining sample is homogenized. Of the < 2 μm fraction, 5 ml were used for the saturation with $MgCl_2$ and 5 ml for the saturation with KCl.

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. After the treatment, washing with distilled water was performed 3 times to remove all the salts that cause the flocculation of the clay minerals.
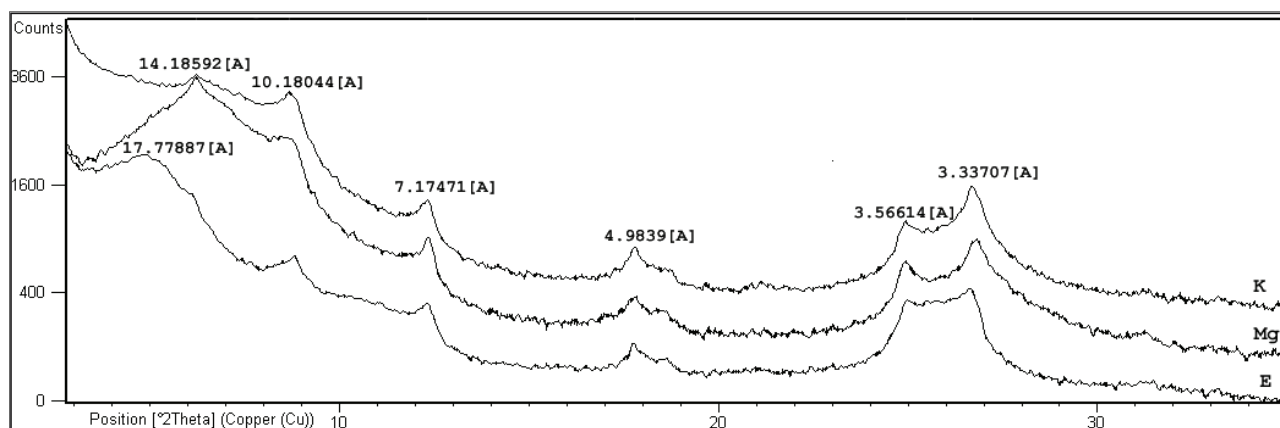

Figure 2. Diffractograms of the samples saturated with K^+(K), Mg^{2+}(Mg) and glycol ethylene (E) from the gravel matrix.

For **ethylene glycol treatment,** it was used a desiccator. There are added 100-200 ml of ethylene glycol in the desiccator and the sample slides are placed on a ceramic plate. They are left in an atmosphere with ethylene glycol vapours overnight or the desiccator is put in the oven at 60°C for at least 8 hours.

The heat treatment. The slides with samples were placed in an oven and heated at 330°C and 500°C for one hour. Immediately after removing them from the oven, they were analysed to prevent the rehydration of the sample.

A set of the samples saturated with Mg^{2+} was left to get dry at 20°C, while the other set was treated with ethylene glycol. Of the samples saturated with K^+ there were made 3 sets of slides, 2 of them for the thermal treatment. 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, scan range 2 ÷ 80° 2θ. Diffraction data were analysed and processed using X'PertQuantify and X'Pert High Scoreprograms. To obtain information about the amount of clay minerals identified based on X-ray diffractograms, it was used the calculation method of MOORE & REYNOLDS (1997).

RESULTS AND DISSCUSIONS

On the diffractograms of the samples saturated with K^+, rendered in Fig. 2, we can observe the presence of certain peaks corresponding to the interplanar distances with values of 14.18Å, 10.18Å, 7.17Å, 4.98Å, 3.56Å and 3.33Å.

The diffractogram of the sample saturated with Mg^{2+} presents the same intensity on most of the aforementioned peaks. The exception is represented by the 14.18 Å peak, where we can observe an increased intensity of the response compared to the sample saturated with K^+.

By applying the treatment with the ethylene glycol, there is noticed the increase of the interplanar distance from 14.18 Å to 17.77 Å, without any significant changes in the other peaks.

After heating the sample to 330°C, there is only a reduction of the intensity corresponding to the distance from 14.18 Å (Fig. 3). After heating the sampleto 500°C, this reflex disappears and the same thing happens with the 7.17 Å and 3.56 Å.

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

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 lack of expansion and retention of the reflex plane (001) after the treatment with ethylene glycol and heating to 500°C .
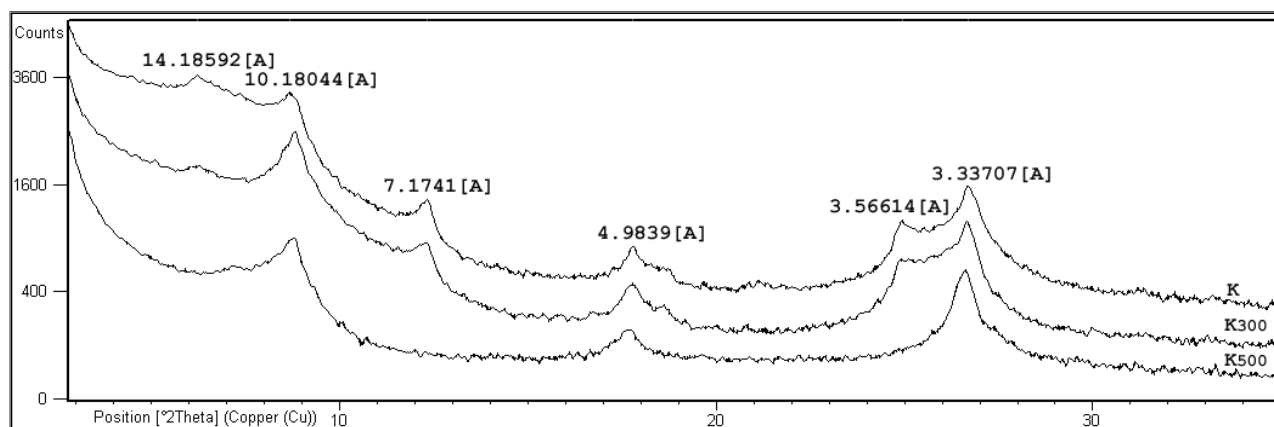

Figure 3. Diffractograms of the clayish fraction from the gravel matrix, saturated with K^+, (K), heated at 330°C (K300) and 500°C (K500).

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

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 by taking into account that the basal distance of smectite is 14-15 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.

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. 3, it can be seen how the reflex from 14 Å of the saturated sample decreases in intensity after heating to 330ºC, while at 500ºC, it does not reach the value of 10 Å, but remains at the value of 12.29 Å.

The presence of a broad peak in the range 14 to 15 Å, which collapsed partly as a result of the heat treatment, it can be interpreted according to BARNHISEL & BERTSCH (1989) as coming from a hydroxy-interlayered smectite. Such interstratification, according to the same authors, is a solid solution with smectite and chlorite as extreme terms. Their formation is primarily due to the penetration of the expandable clay minerals, of the polymers of aluminium hydroxides in the interlamellar space (OLSON et al., 2000).

The percentages of the clay minerals in the pelitic fraction separated from the red loess like deposits from Cetateare 4% kaolinite, 16% smectite, 80% illite. In the matrix of the red gravels, there are present the same minerals with as lightly different quantitative share: 5% kaolinite, 22% smectite, 73% illite. The other samples show percentages close to the afore mentioned values, the average being 76% illite, 19% smectite, 5% kaolinite.

CONCLUSIONS

The clay minerals identified in the study area are illite, smectite and kaolinite. According to the behaviour observed after the treatment with ethylene glycol and heat, smectite seems to be partly chloritized.

The participation of the three minerals in the clay sized fraction is approximately uniform, illite having a share of over 70%, smectite of 15-25% and kaolinite of 4 or 5%.

At Cetate, it is observed the decrease in the smectite content of the fraction < 2μm in higher, loess like deposits compared with the lower ruditic deposits. The illite content varies inversely as compared with that of smectite, increasing in the upper horizons. This quantitative difference is not very large (a few percents), but it was found in all the analysed cases. 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.

REFERENCES

BARNHISEL R. I. & BERTSCH P. M. 1989. Chlorites and hydroxy-interlayered vermiculite and smectite. In J.B. Dixon and S.B. Weed (Eds.) *Minerals in soil environments. 2nd ed*. SSSA, Madison. Wisconsin: 729–788.

HILL P. S. 1998. Controls on floc size in the sea. *Oceanography*. **11**(2):13-18.

JIPA D. 1987. *Analiza granulometrică a sedimentelor. Semnificaţii genetice*. Editura Academiei Republicii Socialiste România. Bucureşti: 128 pp.

KUNZE G. W. & DIXON J. B. 1986. Pretreatment for mineralogical analysis. In: A. Klute (Ed.) *Methods of soil analysis. Part 1. Physical and mineralogical methods*. 2nd ed. Agronomy. Monograph 9. ASA and SSSA. Madison. Wisconsin: 91–100.

MATEI L. 1986. *Minerale şi roci argiloase. Partea a III-a: Metode de analiză a mineralelor şi rocilor argiloase*. Tipografia Universităţii din Bucureşti. 124 pp

MOORE D. & REYNOLDS R. C. 1997. *X-Ray Diffraction and the Identification and Analysis of Clay Minerals, 2nd ed*. Oxford University Press. New York. 378 pp

OLSON C. G., THOMPSON M. L.,WILSON M. A. 2000. Phyllosilicates. In: Sumner M.E. (Ed.). *Handbook of Soil Science*. Boca Raton. CRC Press: F77–F123.

OSTROM M. E. 1961. Separation of clay minerals from carbonate rocks by using acid. *Journal of Sedimentary Petrology*. 31: 123-129.

RABENHORST M. C. & WILDING L. P. 1984. Rapid method to obtain carbonate-free residues from limestones and petrocalcic materials. *Soil Science Society American Journal*. **48**: 216-219.

VLAD V. & ROBU DIDINA. 1981. *România Harta hidrogeologică scara 1:100 000, foaia 40d Cujmir*, Publicată de Institutul de Geologie şi Geofizică. Bucureşti.

Negreanu Ştefan
University of Craiova, Department of Geography
Al. I. Cuza Str., no. 13, 200585, Romania
E-mail: giurgiustefan@yahoo.com

Soare Barbara
University of Bucharest, Faculty of Geology and Geophysics
E-mail: barbara.soare@gg.unibuc.ro