

## CLAY MINERALS IDENTIFIED IN RED QUATERNARY DEPOSITS, FROM VALEA ANILOR AREA (MEHEDIŢI COUNTY, ROMANIA), USING XRD AND IR ABSORPTION ANALYSIS

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**Abstract.** On the territory of Oltenia (region located in the SW part of the Romanian Plain) are encountered on large surfaces red loess or loess like deposits of Quaternary Age. This kind of deposit is described in the literature as “red clay” or “red loams”. Similar deposits of different ages can be found in Northern Bulgaria or Hungary. This article presents data on the type and proportion of clay fraction (<2 $\mu$ ) minerals identified using X-ray diffraction and IR absorption analysis. The clay fraction was separated from both the loess like deposits and older deposits below them. All older deposits of gravel-sand matrix are coloured red due to iron oxides. The sample collection area location is the village of Valea Anilor in Mehedinţi County, about 30 km east-northeast from the Danube, Porţile de Fier. Two different methods were used to separate the clay fraction, both being presented for clear understanding of the analytical conditions. The identified clay minerals are of three types: illite, smectite and kaolinite. The most abundant kind of clay mineral it is illite, representing over 50% of clay sized fraction and the least present it is kaolinite with a presence of maximum 5%.

**Keywords:** Quaternary, loesslike deposits, illite, kaolinite, smectite, X-ray diffraction, IR absorption.

### 1. INTRODUCTION

From geomorphologic point of view the area is located at the intersection point of Bălăciţa Piedmont (part of the Getic Plateau) and Pungina Plain (part of the Romanian Plain).

About half a kilometer from the center of the Valea Anilor, where the DC 121 turns its E-W to N-S direction, there is a sand and gravel quarry. The coordinates of this point are 44°21'44.41"N; 22°55'36.23"E (Fig. 1), and the maximum height of this opening is around 11 meters. At the top, for a thickness of 1-1.5 m, there is the soil layer. Under the soil layer, seven levels are separated and denoted in letters from A to G as follows:

- level “G” with a thickness of 4 meters, consists of dark brown silty sand (according to Shepard, 1954 classification);

- level “F”, consisting of medium gravel with a red sandy matrix and a thickness of 20-30 cm. A detail of this level is shown in Figure 2, Image 2;

- level “E”, also red, is composed mainly of sand that brings together elements of medium and coarse gravel;

- level “D” is homogeneous, consisting of medium and coarse gravel dazled with gray or greyish yellow sand;

- level “C”, red color with black areas due to magnesium compounds or organic matter covering the clusters. It consists of fine, medium and coarse gravel in a sandy matrix with medium grain predominance. In figure 2, Picture 3, one can see a detail of this level;

- level “B” is discontinuous, consisting of medium yellow or gray sand;

- level “A” is usually continued with the level

"C". Granulometric is composed of medium sands at the top and grows to the lower part, where blocks with lengths of 20-50 cm can be encountered. This level is gray with mainly abundant black and red stripes (Image 4 of Fig. 2). Samples for identifying the type of clay minerals were collected from the level "C", "F" and "G".

Lower levels from "A" to "E" belong to the upper horizon of the Căndești Pebbles, age of the lower Pleistocene.

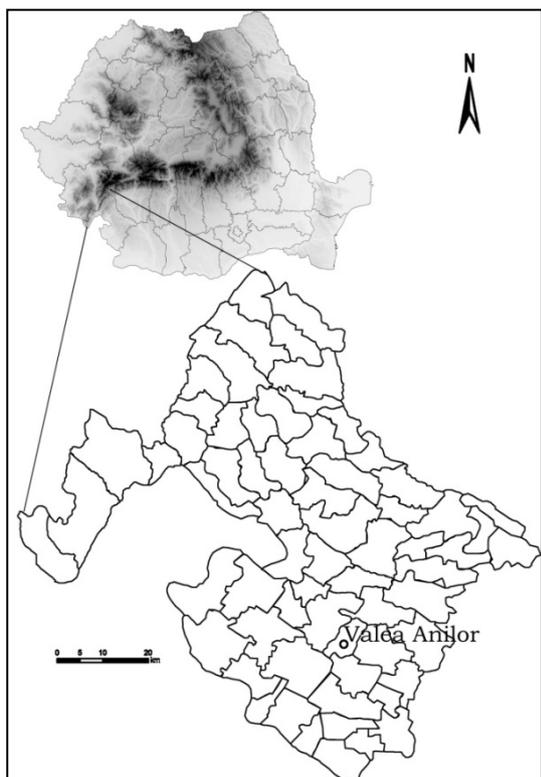


Figure 1. Position of Valea Anilor settlement, within Mehedinți county, Romania.

Levels "F" and "G" are part of the deposits named in the older literature "red clay", actually loessoid deposits. Their color in Bălăciței Piedmont varies from yellowish gray to yellowish red or brownish red, and at the bottom there are intercalations of reddish clayey sands, sometimes with small gravel elements (Schoverth et al., 1963). The particle size distribution of these deposits is described as a sandy clayey silt (Liteanu et al., 1967), while other authors gives a sample of the deposit, percentages of 52% clay, 34.2% silt and 13.8% sand (Schoverth et al., 1963), showing increased variability in granulometry.

The origin of these two levels is considered as deluvial proluvial, due to the presence of small gravel elements. The age was determined to be medium Pleistocene, by taking into consideration the stratigraphic position of loessoid deposits with respect

to the deposits of the lower Pleistocene age they cover (Schoverth et al., 1963; Liteanu et al., 1967).

## 2. MATERIALS AND METHODS

The gravel, sand and loessoid material samples were sieved through a 2mm mesh sieve. Prior to being sieved, the material was allowed to dry.

Two methods have been used to collect the material  $< 2 \mu\text{m}$ : the centrifugation method for X-ray diffraction analysis and respectively the pipette method for IR absorption analysis.

The organic matter can cause flocculation of clay minerals, generating agglomerations greater than 1 mm in the natural environment (Hill, 1998). The removal of organic matter has been done using 10% hydrogen peroxide (Kunze & Dixon, 1986).

To separate the fraction  $< 2 \mu\text{m}$  by centrifugation method, carbonates have been removed using weakly diluted acids (Rabenhorst & Wilding, 1984). After this operation, the clay minerals have been treated with  $\text{MgCl}_2$ , KCl, ethylene glycol and heated to  $330^\circ\text{C}$  and  $500^\circ\text{C}$ .

A Philips XPert MPD type diffractometer has been used, equipped with Cu anticathode (40 mA, 40 kV), Ni filter,  $1.5406 \text{ \AA}$  wavelength of  $\text{K}\alpha$  radiation, 0.01 scanning step and 1s/step time. A  $2-40^\circ$   $2\theta$  interval has been used. For the analysis and processing of diffraction data, the X'Pert Quantify and X'Pert High Score programs have been used.

A computation method (Moore & Reynolds, 1997) has been employed to determine the percentages of different types of clay minerals in the fraction  $< 2 \mu\text{m}$ .

The pipette method has been applied on a mix of about 500-700 grams fraction less than 2mm and 8-10 liters of distilled water (Jipa, 1987).

Gathering the suspension from the sedimentation cylinders has been performed by using the data from Jipa, 1987 and Jackson & Barack, 2005. No treatment has been applied to remove the carbonates or organic matter.

Further, for the IR absorption analysis a mixture of 2mg sample and 200mg KBr has been prepared (Madejova & Komadel, 2001). This mixture has been pressed in discs' format.

A Bruker Optics FTIR spectrophotometer has been used to obtain IR spectra, which can obtain 2531 frequency-absorption intensity couples for the range of  $374-4000 \text{ cm}^{-1}$ .

## 3. RESULTS AND DISCUSSIONS

The closest region to our area with a thorough investigation concerning granulometry, mineralogy,

weathering and paleoclimate of red deposits of similar age, Pliocene to Lower Pleistocene, is in Hungary (Fekete & Stefanovits, 2002; Kovács, 2007; Kovács, 2008; Kovács et al., 2011; Kovács et al., 2013).

Similar deposits to those found in Valea Anilor are described south of Danube, in Bulgaria (Angelova, 2008).

In Romania, study of the mineralogy of clay fraction from red loess-like deposits has not received much attention, our study being first of this kind in this region.

Most of the samples analyzed from Bălăcița Piedmont, either loessoid or the matrix of red gravel, display black particles of medium to fine sand size. These particles have been observed during the separation of the clay fraction by the pipette method. In all the cases, a black concentrate has resulted on the bottom of the vessel in which the suspension was heated. In some locations, this black concentrate has been attracted to the magnet, which may justify the assumption of the presence of magnetite mineral. The same thing did not happen in Valea Anilor case, the samples from this location owing their color to the organic matter or to the manganese hydroxides and oxides that covers the sand grains.

The black particles are uniformly disseminated and approximately in equal amount present in both the red gravel matrix and the upper red loessoid deposits.

The reshuffling of the type "A" black stripes in figure 2, Images 1 and 4, is the process that probably led to the dissemination of the black particles mentioned in red loessoid deposits and fine to medium gravel from their base.

### 3.1. XRD analysis

The peaks corresponding to the interplanar distances of 13.2Å, 10.01Å, 7.16Å, 4.98Å, 3.56Å and 3.32Å can be observed on the diffractograms of the samples saturated with K<sup>+</sup> (Fig. 3). The diffractogram of the Mg<sup>2+</sup> saturated sample presents similar characteristics to the previously mentioned sample. The only difference consists in the presence of a better-defined reflex at 13.65 Å, due to the absorption of magnesium ions.

The treatment with ethylene glycol has led to increasing the interplanar distances from 13.2Å to 17.31Å, without any significant changes of the other peaks.

Because of the heating process the sample at 330°C, the total lack of any reflex in the range of 13-14 Å is observed, due to the reduction of the basal spacing to 10 Å (Fig. 4), and by heating the sample at

500°C it can be observed also that the reflections corresponding to the distances 7.16 Å and 3.56 Å disappear.

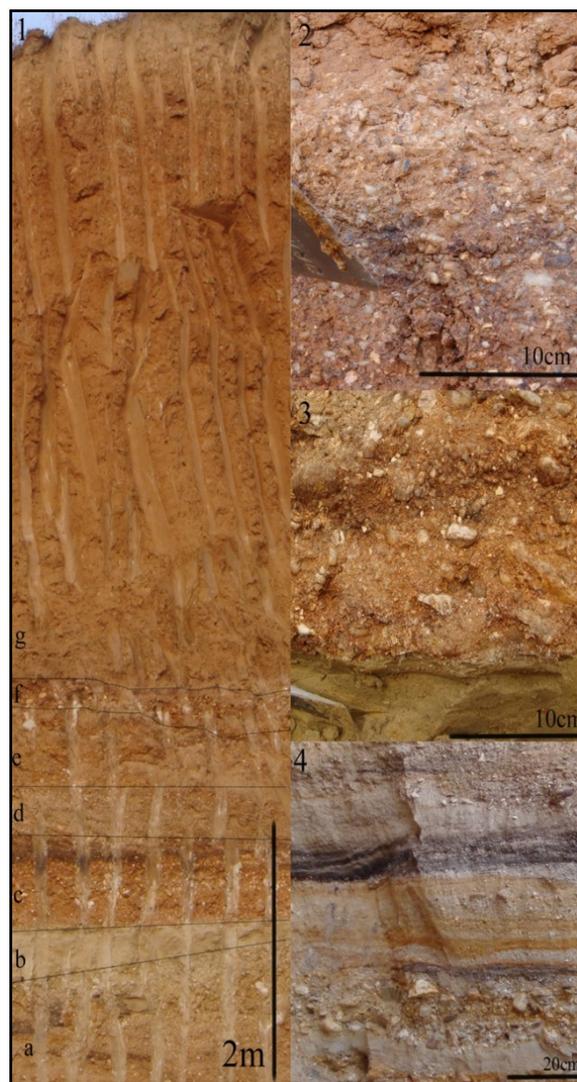


Figure 2. Valea Anilor layers succession (image1). Details of levels „f”, „c” and „a” (images 2, 3 and 4)

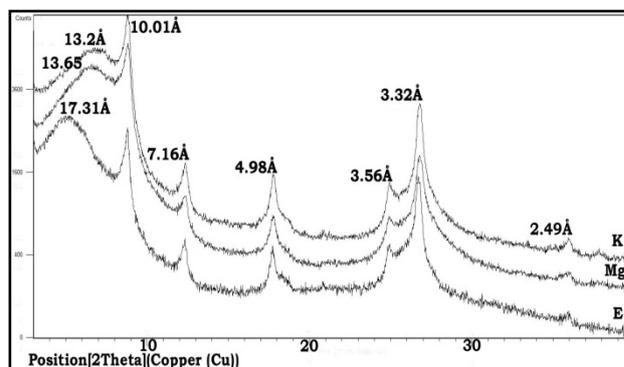


Figure 3. Diffractograms of the clay fraction from the gravel matrix, saturated with K<sup>+</sup> (K), Mg<sup>2+</sup> (Mg) and ethylene glycol (E)

The analysis of diffractograms indicates the possibility that clay minerals from the gravel matrix

and loessoid deposits are kaolinite, smectite and illite.

Interplanar distances of 10.01 Å, 4.98-5.01 Å, and 3.32 Å have been used to identify the illite. The presence of the reflections corresponding to the plane (001) because of treatment with ethylene glycol and heating at 500°C have been also considered to be characteristic to illite.

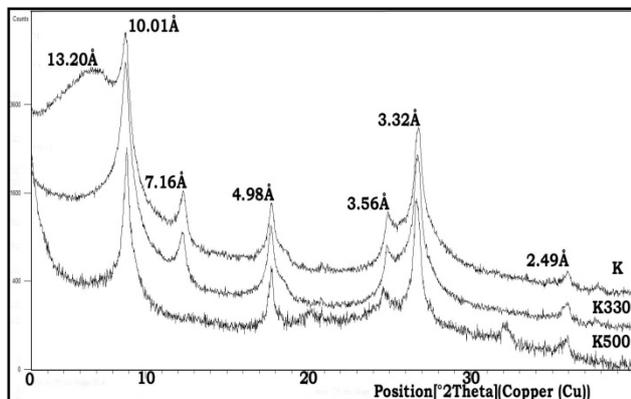


Figure 4. Diffractograms of the clay fraction from the gravel matrix, saturated with K<sup>+</sup>, (K), heated at 330°C (K330) and 500°C (500).

Kaolinite can be identified by the reflections corresponding to the basal distance  $d(001)$ , with values from 7.15 to 7.20 Å (Matei, 1986). Other characteristics of kaolinite are: lack of swelling after ethylene glycol treatment and complete disappearance of any reflection as a result of heating at 500°C.

The term smectite used in this paper refers to 2:1 type, dioctahedral and expandable clay minerals. This type of mineral has been identified as corresponding to the basal distance of 14-15 Å. Another indication of the presence of this mineral is the swelling occurring after treatment with organic molecules and which can increase the interplanar distance  $d(001)$  to values of 17-17.7 Å.

The broad peak between values 6 and 8,2θ was arbitrarily assigned the value of the basal spacing of 13.2 Å, this being the value in the middle of this peak, the actual basal distance being greater than this.

Values in the range of about 14 Å can also indicate the presence of chlorite and vermiculite minerals because swelling after ethylene glycol treatment does not occur. Chlorite also retains the same basal distance after heat treatment while typical smectites after being heated to 500°C, the dictation is reduced to 9.4-10Å.

In figure 4 we can see how the reflex around 14Å disappears after the sample is heated to 330°C due to the reduction of the basal distance to 10Å.

The percentage of clay minerals in the separate clay fraction from red loessoid deposits in the Valea

Anilor are 5% kaolinite, 32% smectite, 63% illite.

In the matrix of gravel levels "C", "F" the same types of clay minerals are present but with a slightly different percentage: 7% kaolinite, 25% smectite, 68% illite.

In approximately 80% of the analyzed sites in Bălăcița piedmont, the smectite content in the fraction of <2µm of the upper, sandy deposits was lower by 15% -45% than in the ruditic inferior deposits. In the Valea Anilor the situation was reversed, the smectite content rising in the finer horizon, but with a small difference of 13%. In the illite the rule seems to be inversely compared to the case of smectite, the content rising in the higher horizons compared to the lower ones.

### 3.2. IR analysis

The IR spectra of the samples taken from two openings indicate the presence of the same absorption bands, with small differences only regarding the intensity of these bands (Fig. 5).

The frequencies of 430 cm<sup>-1</sup> and 470 cm<sup>-1</sup>, corresponding to the Si-O-Si bond, with medium and high absorption intensities, have been identified in all analyzed samples. The first frequency is absorbed by both montmorillonite and illite, but high values of intensity are encountered only in case of kaolinite. This frequency was assigned to the kaolinite considering the absorption band intensities.

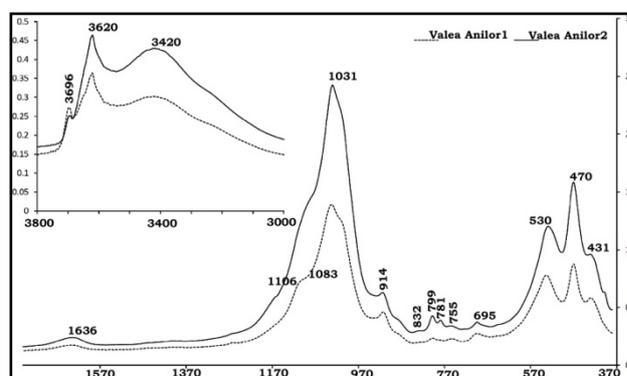


Figure 5. IR absorption spectra for the samples taken from the gravel matrix (upper line-Valea Anilor 2) and the loess like deposit (lower line-Valea Anilor 1); on the horizontal axis, are rendered the wavenumbers in cm<sup>-1</sup>.

The second frequency mentioned cannot provide clear information regarding the mineral whose network has been absorbed, because both kaolinite and montmorillonite display strong absorption in this area. The fact that all the frequency values are above 470 cm<sup>-1</sup> could indicate the presence of kaolinite, as montmorillonite absorbs frequencies with slightly lower values.

The 535 cm<sup>-1</sup> frequency level corresponds to Al-O-Si bonds (Stubican & Roy, 1961) of the network of several clay minerals and therefore it cannot indicate a particular mineral. The 695 cm<sup>-1</sup> frequency level corresponds to another type Si-O-Si non-specific bond.

The quartz can be identified by using the characteristic absorption doublet of 781 cm<sup>-1</sup> and 799 cm<sup>-1</sup>. Compared with other absorption intensities that are illustrated in figure 5, the doublet behaves low intensities, thus indicating a presence of quartz in very low quantities. The presence of (CO<sub>3</sub>)<sup>2-</sup> anion is indicated by the frequency of 832 cm<sup>-1</sup> (Frost et al., 2004).

Another element that suggests the presence of carbonates is the frequency range between 832 cm<sup>-1</sup> and 914 cm<sup>-1</sup>. It corresponds to deformation vibrations out of the plane of (CO<sub>3</sub>)<sup>2-</sup>, located at 875 cm<sup>-1</sup> (Madejova & Komadel, 2001).

The very fine inflection in the range of 1,382-1,440 cm<sup>-1</sup> indicates also carbon-oxygen bonds: 1,430 cm<sup>-1</sup> stretching vibrations of (CO<sub>3</sub>)<sup>2-</sup> from calcite (Madejova & Komadel, 2001).

The frequencies in the range of 1,410-1,49 cm<sup>-1</sup> indicate (CO<sub>3</sub>)<sup>2-</sup> (Coates, 2000); the bands of 6.90 to 6.97 μm (1,449-1,435 cm<sup>-1</sup>) are considered to belong to the group (CO<sub>3</sub>)<sup>2-</sup> (Huang & Kerr, 1960); the frequency 1,384 cm<sup>-1</sup> is due to stretching vibrations of C = O inorganic carbonyl group (Jackson, 1998) and that of 1,365 cm<sup>-1</sup> corresponds to the vibrational stretches of COO<sup>-</sup> bicarbonate ion (Yruela et al., 1998).

The frequencies in the range of 913-915 cm<sup>-1</sup> indicate the Al-Al-OH bonds from the montmorillonite, kaolinite and illite networks. The strongest absorption (40-80%) is associated to the kaolinite network, whereas montmorillonite and illite determine an average absorption of 20-40% (Matei, 1988). The intensities recorded on the IR spectra of all analyzed samples display average values, suggesting the presence of montmorillonite and illite.

The inflexion corresponding to 1,010 cm<sup>-1</sup> level is generated by both illite and montmorillonite. Hunt et al., (1950), considers that the maximum absorption intensity recorded at 1,030-1,034 cm<sup>-1</sup> is determined by the presence of illite, as montmorillonite is identifiable at the frequencies over the threshold 1,041.66 cm<sup>-1</sup>. The interval 1,080-1,106 cm<sup>-1</sup> may also indicate montmorillonite and/or illite (Matei, 1988).

The values in the range of 3,696-3,699 cm<sup>-1</sup> correspond to frequencies associated to the kaolinite mineral (Farmer, 1964). All these three clay minerals have absorption bands at 3,620 cm<sup>-1</sup>. The 1,640 cm<sup>-1</sup> and 3,620 cm<sup>-1</sup> bands indicates the deformation

vibrations and stretching vibrations of the OH group, belonging to H<sub>2</sub>O (Farmer, 1974).

#### 4. CONCLUSIONS

The clay minerals identified in the studied area are illite, smectite and kaolinites. The percentages of the three clay minerals in the clay fraction are on average 62% illite, about 30% smectite and about 5% kaolinite. The analyzed samples have content close to clay minerals irrespective of sampling level, loess-like deposits or the red matrix of the two gravel levels. Unlike other areas investigated by us, from Bălăcița Piedmont to Valea Anilor, the percentage of smectite is higher in loessoid deposits than in the matrix of red gravels.

IR absorption analyses indicate the presence of very small amounts of quartz and carbonates (probably calcite). The 3698 cm<sup>-1</sup> absorption band indicates the presence of kaolinite. The reduced intensities of this frequency correlate well with the small amounts of this mineral indicated by the XRD data. Absorbing similar frequencies, the illite and the smectite could not be identified as precisely as the kaolinite by IR spectrometry.

The presence of Al-Al-OH deformation vibration bands alone, without any absorption that could indicate the presence of Mg<sup>2+</sup> or Fe<sup>2+</sup>, demonstrates that the identified clay minerals are dioctahedral, such positions being occupied by Al<sup>3+</sup>.

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