

THE USE OF IR SPECTROSCOPY FOR THE STUDY OF RED QUATERNARY DEPOSITS FROM VALEA LUNGULUI AREA (DOLJ COUNTY, ROMANIA)

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Abstract. The investigated samples were taken from the left bank of the Raznic river, about 4 km upstream of its confluence with the Jiu river, from the red loess deposits and from the ruditic matrix of certain deposits of the same colour. Comparatively with the X ray diffraction, IR spectroscopy presents lower possibilities of identification of the minerals in the pelitic fraction, but, it can be successfully used for coarser fraction and easier identification of the quartz or carbonates. Regarding the clay minerals, this method enabled the identification of kaolinite, while the presence of the radiation absorption characterized by frequencies corresponding to Al-Al-OH bonds suggests the presence of dioctaedric minerals such as illite and/or smectite. For a precise understanding of the conditions of analysis, there are presented the methods used for this purpose.

Keywords: clay minerals, loesslike deposits, IR spectroscopy.

Rezumat. Folosirea spectroscopiei IR pentru analiza depozitelor roșii cuaternare, zona Valea Lungului (județul Dolj, România). Probele investigate au fost recoltate de pe malul stâng al râului Raznic, la aproximativ 4 km amonte de confluența acestuia cu Jiul, din depozite loessoide de culoare roșcată și din matricea unor depozite ruditice de aceeași culoare. Comparativ cu difracția de raze X spectroscopia IR are posibilități mai reduse de identificare a mineralelor din fracția pelitică, putând fi utilizată cu succes în cazul fracției mai grosiere unde se identifică cu ușurință cuarțul sau carbonații. În ceea ce privește mineralele argiloase, prin utilizarea acestei metode a fost identificat caolinitul, iar prezența absorbției radiației cu frecvențe corespunzătoare legăturilor Al-Al-OH sugerează prezența unor minerale dioctaedrice de tipul illitului și/sau smectitului. Pentru o înțelegere exactă a condițiilor de analiză sunt prezentate metodele utilizate în acest scop.

Cuvinte cheie: minerale argiloase, depozite loessoide, spectroscopie IR.

INTRODUCTION

10 km W-NW of Craiova, on the left side of the road linking Craiova to Valea Lungului settlement, there are two outcrops with thicknesses of up to 11m. The coordinates of the sampling site are 44°20'58" N and 23°40'15" E (Fig. 1). At the bottom of these outcrops, on a thickness of 2-2.5 m, there can be found yellow-reddish gravels mixed with sands, while towards the top, this layer gets gray. Gravels are generally very fine to medium in the area, the clasts of coarse gravel or small cobbles representing 20%. There can be also found small lenses or layers of gray deposits that appear to be silts or clayish silts. Gravels and sands are heavily pigmented by black compounds present in the outcrop on a thickness of 50 – 75 cm and a length of 20 m, which are disposed in oblique bands. There follows a level composed of coarse and medium gravels dispersed in a mainly reddish-yellowish, medium - coarse sand mass. Above this level, on a thickness of 1.5 m, there appears a loess-like deposit, which has approximately the same colour as the previous one, located just below the soil profile.

The samples were taken from the two outcrops, namely the basis of the last level and the matrix of the reddish yellowish gravel that forms the lowest observed level. There were analysed four samples.

On the geological map 1:200 000, sheet 41 Craiova (MIHĂILĂ et al.), these deposits are indicated as being of lower Pleistocene age.

MATERIALS AND METHODS

The samples of gravels, sands and red clays were left in a thin layer to get dry before starting the granulometric separation by sieving. After this stage, the pelitic fraction was obtained by applying the pipette method. The sample dispersal for taking samples based on the pipette method was made according to the recommendations made by Krumbein in 1933 and presented by JIPA (1988); thus, samples are heated in distilled water up to the boiling point, without allowing the solution to boil. The heated solution was obtained by mixing about 500-750 grams of fraction smaller than 2 mm,

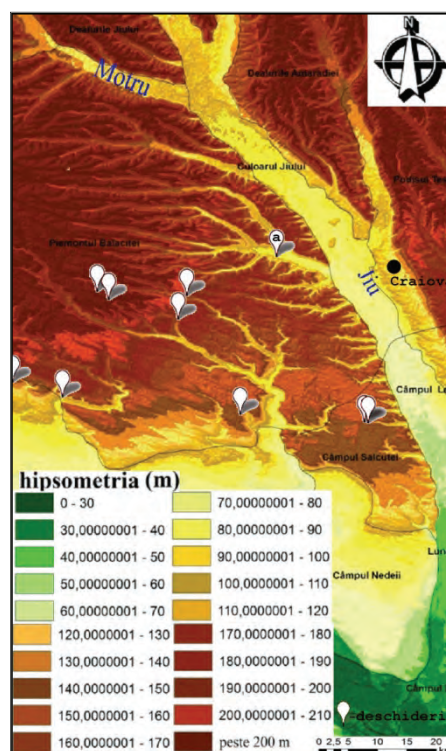


Figure 1. The hypsometric map of the area surrounding the sampling site; a- sampling site. (Original).

obtained by sieving, with about 8-10 liters of distilled water. After heating, from the sedimentation cylinders, it was collected the solution by pipetting, using the data rendered by JIPA (1988) and JACKSON & BARAK (2005).

The layer of about 2-3 cm of suspension obtained in this way was left in an oven at a temperature of 50°C, in covered glasses, until water evaporated. The remaining material was milled in an agate mortar and then analysed as powder.

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, 2001). For a clearer observation, at a second analysis of the absorption spectra in the range of 3000-3800 cm⁻¹, the samples would have to be dried at 150°C over night. As this stage in sample preparation missed, there appeared the spectrum of adsorbed water in the aforementioned region of the spectrum, covering part of the absorption lines useful in the identification of clay minerals. The infrared spectra were obtained with BrukerOptics FTIR spectrophotometer, which, for the range 374-4000cm⁻¹, obtained 2,531 frequency-intensity of absorption couples.

RESULTS AND DISSCUSIONS

The IR spectra performed on the samples taken from the two outcrops indicated the presence of the same absorption bands, minor differences being identified only in terms of their intensity.

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

The absorption around 470 cm⁻¹, also generated by Si-O-Si bonds, can not provide clear information on the mineral responsible for its appearance, because both kaolinite and montmorillonite show strong absorption rates in this area. However, the values, which always maintained above 470 cm⁻¹, may also indicate kaolinite, as montmorillonite displays slightly lower values.

The vibrations corresponding to the frequencies of 535 cm⁻¹originate from 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.

At 696 cm⁻¹, it is indicated the presence of the bond Si-O-Si, a bond which is also non-specific.

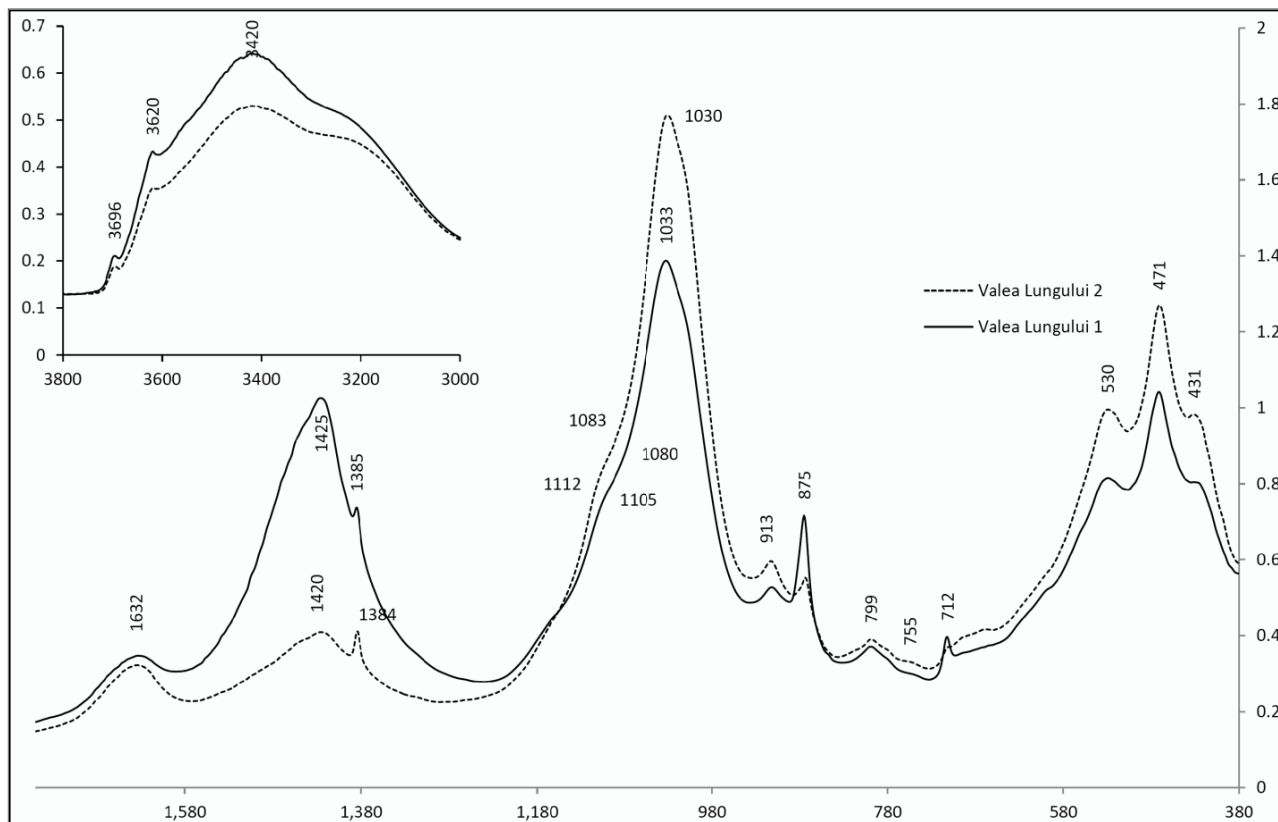


Figure 2. IR absorption spectra for the samples taken from the gravel matrix (Valea Lungului 1) and the loess like deposit (Valea Lungului2); on the horizontal axis, there are rendered the wavenumbers in cm⁻¹.

In Fig. 2, it is rendered the absorption spectrum for the sample taken from the matrix of lower yellow reddish gravel (Valea Lungului 1); the absorption band with an intensity reduced from 712 cm^{-1} is characteristic for the C = O bond from carbonates.

The absorption doublet at 779 cm^{-1} and 798 cm^{-1} is diagnostic for quartz. In the samples taken from Valea Lungului, the absorption intensity is weak and there appear only wide inflections. This indicates the extremely 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.

The vibrations with the frequency of 875 cm^{-1} are deformation vibrations, out of the plane, of $(\text{CO}_3)^{2-}$ (MADEJOVA & KOMADEL, 2001). For the absorption in the range $1382\text{-}1440\text{ cm}^{-1}$, the specialized literature also indicates carbon-oxygen bonds: 1430 cm^{-1} stretching vibration $(\text{CO}_3)^{2-}$ of calcite, MADEJOVA & KOMADEL (2001); $1410\text{-}1490\text{ cm}^{-1}$ frequencies that indicate $(\text{CO}_3)^{2-}$ COATES (2000); $6.90\text{ to }6.97\text{ }\mu\text{m}$ ($1449\text{-}1435\text{ cm}^{-1}$), bands considered to belong to the group $(\text{CO}_3)^{2-}$, HUANG & KERR (1960); 1384 cm^{-1} stretching vibration of the bond C = O of the inorganic carbonyl group, JACKSON (1998); 1365 cm^{-1} , the stretching vibration in the bicarbonate ion COO^- , YRUELA et al. (1998).

The frequencies of 875 cm^{-1} and the $1382\text{-}1440\text{ cm}^{-1}$ range suggest the presence of carbonates, most probably of calcite. The frequencies of $913\text{-}915\text{ cm}^{-1}$ are absorbed by Al-Al-OH vibrations characteristic to the networks of montmorillonite, kaolinite and illite, showing strong absorption (40-80%) in kaolinite and average absorption (20-40%) in montmorillonite and illite, MATEI (1988). In all the analysed samples, the intensity was average, which would suggest the presence of montmorillonite and illite. The absence of a strong intensity at this frequency does not exclude the presence of kaolinite, which was indicated by the absorptions in the range of $430\text{-}538\text{ cm}^{-1}$, but it is present in smaller amounts compared to illite and/or montmorillonite.

The inflection around the value of 1010 cm^{-1} , which follows, occurs in case of illite and montmorillonite. The maximum intensity of absorption registered at $1030\text{-}1034\text{ cm}^{-1}$ was attributed to illite, based on the conclusions drawn by HUNT et al. (1950), who distinguishes it from montmorillonite, indicated by the vibration absorption of 1041.66 cm^{-1} according to the same author.

The range present in all samples in the interval $1080\text{-}1106\text{ cm}^{-1}$ may indicate montmorillonite and/or illite, MATEI (1988). At values above 3000 cm^{-1} , only two frequencies can be used, one at 3620 cm^{-1} , absorbed by all the three aforementioned clay minerals and $3696\text{-}3699\text{ cm}^{-1}$, which is a diagnostic band for the mineral kaolinite (FARMER, 1964). The 1640 cm^{-1} and 3620 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

Mineralogically, based on IR spectra, we can say that the analysed samples contain very small amounts of quartz and carbonates, probably calcite. The significant absorption in the range $1382\text{-}1440\text{ cm}^{-1}$ in the analysed samples from Valea Lungului is due to the frequent presence of rolled calcareous concretions, very poorly cohesive, in these deposits. These concretions led to the increase of the carbonates present in the concretions from which the aforementioned samples were separated. Kaolinite is present, without exception, in all the analysed samples, but it does not display the maximum intensity of the characteristic doublet 1012 cm^{-1} and 1032 cm^{-1} , which indicates the fact that the kaolinite amount is lower than the amount of the other two clay minerals.

Illite seems to be the dominant mineral, while montmorillonite, which shows similar bands of absorption, was not clearly indicated.

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

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Received: March 29, 2014
Accepted: June 30, 2014