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METHODS AND TECHNIQUES USED FOR ESTABLISHING THE AGE AND GENESIS OF PELITIC ROCKS. APPLICATIONS IN GEOGRAPHY

METODE ŞI TEHNICI DE STABILIRE A VÂRSTEI ŞI GENEZEI ROCILOR PELITICE. APLICATII IN RAMURI ALE GEOGRAFIEI

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Abstract: In the sedimentary domain, clays represent about half of the detritic rocks in terms of frequency. Clasts with the diameters smaller than 2 or 4µm, according to the used scale, clays, also called pelitic rocks, have to contain as deposits more than 60% clay minerals of the entire petrographic assembly in order to be categorized as clay rocks. Sediments (the primary material) on the base of which they form after the occurrence of diagenetic processes (porosity reduction, cementation of clasts, dissolving of certain minerals and precipitation of others etc.) are known as muds. The type of clay minerals, their morphology, as well as the morphology of the deposits they belong to, the presence and proportion of different chemical elements characteristic to certain well-established depositing environments, gives us clues about the origin of the primary material and about the transformations, it underwent from the initial depositing stage to the moment the sample is taken.

Key-words: clays, clay minerals, spectroscopy of infrared absorption, X-rays diffraction
Cuvinte cheie: argile, minerale argiloase, spectroscopie de absorbtie in infrarosu, difracţie de raze X

Introduction

Taking into account the extremely reduced dimensions of clay minerals, which makes difficult they analysis by means of usual microscopic methods, numerous experts recommend starting their study with a scanning electronic microscope. This type of microscope (scanning electronic microscope or SEM) offers information regarding the morphology of clay minerals as well as a qualitative and semi-quantitative analysis of their chemism. The obtained results represent a solid starting point in the further determining of clay minerals, at a more accurate precision by means of X-ray diffractometry, IR absorption spectrometry, differential thermal analysis (DTA), thermogravimetric analysis (TG), derived thermogravimetric analysis (DTG).

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The other minerals and lithoclasts, which make up the pelitic deposits together with clay minerals, offer us important information about the source area of the initial material after the performance of the analysis of thin sections in the cathodoluminescent polarizing light that is a chemical analysis used in establishing the proportion of different chemical elements and of the isotopes of different elements (oxygen, carbon). These data correlated with the data offered by clay minerals, which may develop after the weathering of primary materials (feldspath, mica etc.), give us the possibility to reconstruct a paleorelief or a palaeoclimate.

Clay deposits also give us information about the age of different events using diverse methods, such as palaeontological, micro-palaeontological, radiometric, paleomagnetic methods, or thermoluminescence measuring.

The accurate achievement of the enumerated operations allows, among others, the easier location of economically valuable resources these deposits may hold (hydrocarbons etc.), as well as the anticipation and avoidance of negative effects induced by certain clay deposits upon human communities due to the increased potential of gravitational processes.

Methods used in the identification of minerals

X-rays diffraction

X-rays, also known as Roentgen radiation, represent a form of electromagnetic radiation the wavelength of which oscillates between 10 and 0.1 nanometres.

They were observed and described for the first time by Wilhelm Conrad Roentgen in 1895. In 1912, Max Theodor Felix von Laue achieved an experiment, which supposed the projection of X-rays on a copper sulphate crystal and the registering of its effect on a photographic plate. The regulate disposal of light points on the photographic plate led von Laue to three conclusions:

- the atomic particles inside crystals are disposed arranged and repetitively within the three-dimensional space;
- the atomic arrangements displays distances of about the same order as the X-ray wavelength and, consequently, as diffraction occurs, the third conclusion is also valid;
- X-rays are only of ondulatory and not of corpuscular nature, as some researchers considered, or both of corpuscular and ondulatory nature as others considered.

In 1913, William Lawrence Bragg extended von Laue's conclusions formulating the law that holds his name; during the same period, he published the first crystal structures for NaCl, KCl, KBr, KI. This law presently represents the base of X-ray diffraction studies.

In the case of clay minerals, the method consists in applying a fascicle of X-rays on a oriented clay sample or not. The rays that penetrate the crystal determine the excitation of the crystal atoms followed by the emission of radiations with the same frequency as the incident rays. Afterwards, the radiations emitted by the reticular plans, which oscillate in phase, generate a coherent fascicle that may be detected.

The condition for rays to oscillate in phase is given by Bragg's law:

$n\lambda=2d \sin\theta$, where

n-the entire number corresponding to the diffraction order;

d-distance between the reticular plans from the crystalline network;

θ-diffraction angle.

By means of this law, knowing the value for the wavelength of the used radiation and of the measured diffraction angle, we may find out the distance value d, which is proper to each type of crystal, this being in fact the utility of this method.

The apparatus used for such analyses is called X-ray diffractometer. It mainly consists of a radiation source, called X-ray tube, a monochromator for choosing the used wavelength, slits, that allow us control the fascicle shape, a sampler holder, and a detector.

The glass X-ray tube is vacuumed and has inside a metallic anode (made of Co or Cu), which emits X-rays when it is bombarded with electrons. The source of the electrons is an incandescent filament.

Infrared absorption spectroscopy

When crossing through an optical prism, solar light decomposes in the colours of the visible spectre.

In 1800, Frederick William Herschell measured the temperature of each colour resulted after this process. When noticing that the temperature of each colour increases from violet to red, he tried to measure the temperature of the zone following immediately after the red colour, the zone where human eye perceive no colour. The temperature was the highest of all registered temperatures. He called these radiations with high temperature caloric radiations, which are presently known as infrared radiation.

Infrared radiations comprises electromagnetic waves the wavelength of which oscillates between 700nm and 1000µm. These limits, expressed as values of the frequency (cm^{-1} or, in other words, the number of wavelengths included in one centimetre) are of 12,500 cm^{-1}, respectively 10 cm^{-1}.

The interval corresponding to infrared radiation is separated intro three regions:

- near infrared (NIR), which comprises the frequencies between 12,500 and 4,000 cm^{-1};
- mid infrared (MIR), frequencies between 4,000 and 650 cm^{-1};
- far infrared (FIR), frequencies between 650 and 10 cm^{-1}.

This method takes into account the fact that the atoms grouped in molecules in gases, liquids or solids are not in repose, they register a periodical vibration. The frequency of inter-atomic vibrations oscillates between 10^{13} and 10^{14} cycles per second.

If the molecules of a substance are irradiated by a succession of monochromatic IR radiation (a single wavelength), these last ones will be entirely or greatly absorbed if their frequency corresponds with the frequency of inter-molecular vibrations.

This method mainly consists in measuring the power of a fascicle of IR rays before and after its interaction with a sample. By representing the percentage of absorbed radiation and of the frequency of each radiation, we obtain graphs that may be interpreted in terms of intramolecular vibration. Each graph obtained for a known substance is used for the comparison with the graphs obtained for the unidentified substances. These graphs also offer us information about the structure of the molecule and about the type of links inside it.

In identifying the silicates, clay minerals belong to, the strong absorption band centred around 1,000 cm^{-1} is taken into account as it not appears at other minerals.

For the studies regarding the absorption of IR radiation in the case of clay minerals, there are used frequencies ranging between 4,000 and 400 cm^{-1} and wavelengths between 2 and 25μm.

The results of the analyses are more accurate if the dimension of the analysed particles (clay minerals) is lower than the value of the lowest used wavelength, namely below 2μm.

The device used for this method is called IR Spectrophotometer. It contains a source of infrared rays, a compartment where the sample is placed, a lens, a monochromator, a detector, and a processor.

The source is an incandescent lamp with quartz walls that functions at low voltage and the filament of which, usually made of wolfram, heats to 2,200 ^{o}C, and thus emits IR rays. After the interaction of IR rays with the sample, they are more or less scattered, the lens focussing the radiations again. The monochromator separates the infrared radiation in different wavelengths bands.

The scanning electronic microscope

In 1929, Hugo Stintzing from Giessen University, Germany, proposed the utilization of a ray formed by electrons for scanning an object. The first scanning electronic microscope is achieved by INSA Ruska in 1933, but the enlargement of the analysed sample was quite reduced (ten times). The production of high quality scanning electronic microscopes (SEM) starts in Great Britain in 1965 and shortly after in Japan.

Scanning electronic microscopy is based on the interaction between a fascicle of electrons and the analysed sample. When the fascicle hits the sample, there are generated secondary electrons (electrons emitted by the sample due to the impact), X-rays, heat and light. In order to obtain images, there are mainly used secondary electrons. The resolution of the images is of 0.01 microns.

This procedure gives us information about the dimension, morphology, and disposal of particles in the analysed sample. Moreover, we can obtain a qualitative and semi-quantitative estimation of the chemical composition.

A SEM (Fig.1) is made up of an electron gun that generates a fascicle of electrons. Its diameter is further modified under the action of certain electromagnetic lenses, according to the power they are crossed by the values oscillating between 0.4 and 5nm. Further, the fascicle interacts with the scanning coils. When regulating the electric voltage, these generate a magnetic field that determines the deviation of the electrons according to a pattern well established in plan, and thus achieving a scanning of the sample. The secondary electrons resulted after the interaction fascicle-sample are collected and amplified by a secondary detector. The effect of this process is the appearance of a voltage the value of which leads to the formation of light spots of different intensities. All these spots finally give the image of the analysed object. It is worth mentioning that the entire analysis process by means of SEM is made in vacuum conditions.

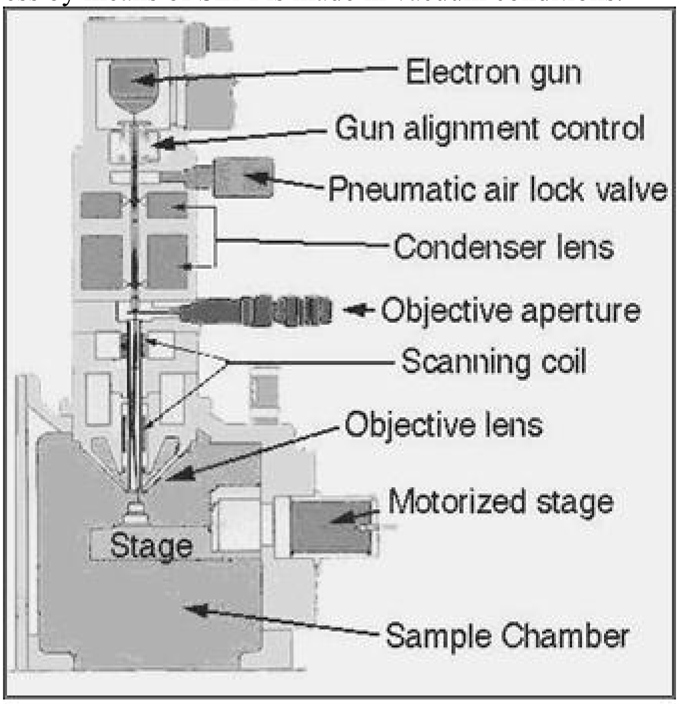

Fig. 1 Schematic diagram showing the basic components of a SEM (Schatten, 2008)

Thermal analyses

Thermal analysis represents the study of the link between the properties of a substance and its temperature, when the substance is heated.*Differentiated thermal analysis (DTA)* is the simplest and the most used method of thermal analysis. It consists in measuring the difference between the temperature of the analysed sample and that of a control sample that do not undergoes thermal reactions at the temperatures used during the experiments (usually Al_2O_3 or SiC).

Clay minerals, as compared to the control sample, undergo a series of physical-chemical transformations depending on their reticular structure and chemism, when temperature increases. All these modifications determine, at precise temperature values, consumption or discharge of thermal energy (endo- or exothermal reactions). Based on these effects, there have been fundamented the criteria for identifying clay minerals through DTA.

At all types of clay minerals there occur three thermal phenomena related to:

-loss of hydration water;

-disorganization of the network due to the loss of the OH group;

-complete decomposition of the crystalline network and the appearance of new mineral phases characteristic to high temperatures.

The devices used for measuring this feature contain the following main components: analysed sample chamber, an oven, a device for regulating temperature, a data registering system. The sample chamber contains two containers made up of chemically inert material (alumina, silica, platinum), one for the analysed sample and the other for the control sample. We also find here the key component of the entire device, the thermocouple. It is made up of conductors built from two different metals. At both ends of a conductor, the junction with the other type of metal is achieved. The two formed junctions are introduced one in the container with the analysed sample and one in the container containing the control sample. The free ends of the thermocouple are linked to a voltmeter that registers the voltage modifications each time a thermal reaction occurs. The result appears as a curve that displays the amplitude of the thermal reactions at different temperature values. The curve is called thermogram.

Thermal gravimetry measures the modification of the weight of the analysed sample as temperature increases. The weight may decrease because of the loss of different substances that transform into gases (water, carbon dioxide) or may increase due to its reaction with the substances of the atmosphere it is located in. Scales that transmit the data to a computer make the measurement of the weight variations.

Cathodoluminescence. When a fascicle of electrons interacts with the surface of a solid, its energy determines the appearance of many physical processes such as the emission of secondary electrons (SE), backscattered electrons (BSE), X-rays, and cathodoluminescence (CL). The light emitted due to cathodoluminescence phenomenon belongs to the visible spectre, the wavelength of which oscillates between 400 and 700 nm. This phenomenon that appear both at organic and inorganic substances is induced by the energy discharge due to the passage of anions, molecules, or crystals from a state of electronic excitement to the equilibrium energy state or even to a lower one. Certain elements present in the analysed sample, such as copper, manganese, rare earths, favour cathodoluminescence, while others inhibits it, as it is the case of iron. For studying the cathodoluminescence of minerals, there are used thin sections of the analysed rocks.

By analysing the colours resulted after cathodoluminescence one may estimate the chemical composition of the minerals, their crystal zoning, twinning, and age succession for different generation and types of minerals.

The simplest and cheapest devices, which use this type of analysis, are the cathodoluminescence petrographic microscopes. Their main components are a small, vacuumed chamber and a support inside that holds the sample. The support may be moved horizontally on the x, y directions. The main component is the source of electrons represented by a cold cathode electron gun. All these components are attached to a petrographic microscope.

Methods used for age

Thermoluminescence

The term of thermoluminescence refers to the phenomenon of light emission by a crystal or a body containing crystals when heated. The first scientific mentioning of this phenomenon is considered to be that of Robert Boyle, in 1663, who noted “a glimmering light” from a diamond by “taking it in bed with me, and holding it a good while upon a warm part of my naked body”. Boyle continued his experiments, supplying heat to the crystal through friction, contact with hot iron or a candle flame. In the next centuries, other scientists emphasize the phenomenon described by Boyle in the case of other minerals (fluorine, sulphur, quartz). The oldest mentioning of the term thermoluminescence dates from 1895, when it seems to have been used by Wiedemann&Schmidt.

The utilization of this feature for establishing the age started in the ‘50s, but the method acquired sufficient precision only in 1960, when it was applied in archeology for dating ceramic artifacts. Thermoluminescence is induced by the presence of network deficiencies inside the crystals (ions that do not usually belong to the network, small cracks induced by stress). These deficiencies (called electrons traps) modify the regularity of the electric field that links together the atoms or the ions of a crystal. When crystals are under the action of an energy form (solar heat, heat of a volcanic eruption, of a fire, radiation emitted through the decomposition of radioactive elements), a part of the electrons pass from the electronic cover of the atoms in the conductivity band, where they can move freely. Most of these electrons will be assimilated by the ions of the network, but part of them will remain in electronic traps.

If crystals are heated or exposed to strong light, these electrons can combine with the ions of the network, process that emits photons. The emitted amount of light (photons) depends on the number of “captive” electrons, while their number depends on the radiation generated by the radioactive elements of the mineral or of the rock where it develops. By establishing how many captive electrons may generate annually a certain amount of the analysed sample, one may easily establish its age. The equipment used for studying TL is rendered in Fig. 2. The sample is placed on a plate positioned above a heat source. At high temperatures, due to the release of the captive electrons, photons are emitted. These are transformed in electric impulses by means of a photomultiplicator. The values registered for light activity are rendered in a graph together with the temperature values at which they were registered, obtaining the brightness curve.

Paleomagnetism

Paleomagnetism method uses the features of certain minerals of directing according to the geomagnetic field as the needle of a compass. Such minerals are called iron magnetic. Their behaviour gives us information about the magnetic inclination and declination at a certain moment.

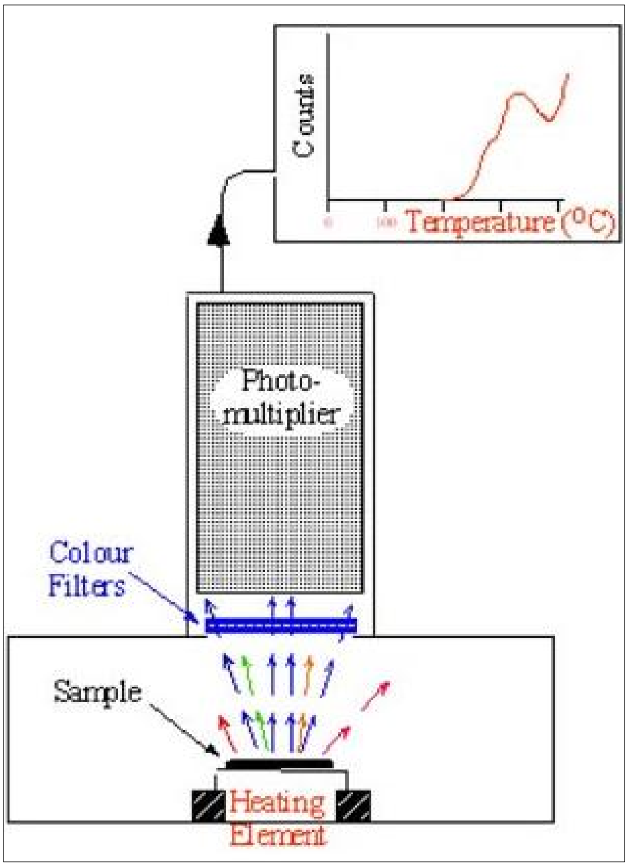

Figure 2. The basic instrumental components for thermoluminescence measurements (after Aitken, 1985.)

Presently, when the magnetic poles are located in the same hemisphere with the geographical poles, but they do not coincide, the polarity of the geomagnetic field is considered to be normal. When geomagnetic poles are inversed, polarity is called inverted polarity.

In the geological eras, there were registered many periods characterized by normal and inverted polarity. The time interval when one or another type of polarity was registered can be established by studying the remanent magnetism of different rocks (magmatic or sedimentary) that contain iron magnetic minerals and which formed at that time.

When for obtaining paleomagnetic data, there are analysed volcanic rocks or artifacts, rocks that are not arranged from the initial position, which were heated above Curie temperature (the temperature at which minerals are no longer iron magnetic, and thus, when temperature decreased below Curie value, they re-become iron magnetic and direct according to the magnetic field of the moment), we call the method thermoremanent magnetism, TRM. When paleomagnetism is analysed by using minerals of sedimentary rocks, we refer to depositional remanent magnetism, DRM.

The results of this method are materialized in a paleomagnetic scale that renders the periods characterized by inverted and normal polarity and the time interval corresponding to each of them.

Radiometric method

It is the main method of absolute dating and it is base don the phenomenon of radioactive disintegration of the isotopes of certain chemical elements (U, Th, Rb, K, C).

Through the disintegration of the radioactive element (RD) contained in a mineral since its crystallization, it progressively passes in a derived or radiogene element (RG). As the duration of the total disintegration of an element is most of the times theoretically infinite, in practice, it is considered the reducing to one half period, the period when half of the radioactive atoms pass into radiogene atoms. Knowing the reducing to one half period of each radioactive element and measuring the amount of RD and RG, one may establish the time passed since the beginning of the disintegration to the moment of analysis, interval that represents the rock age.

Palaeontological, micropalaeontological, and palynological methods

All these methods are relative dating methods, as they cannot supply precise numerical values about the age of different formations as it happens in the case of absolute dating. The principle used by them is that of palaeontological succession, which stipulates that in a continuous succession of fossil layers, the lower ones are closer to the ancestral form of organization, while the upper ones are more evolved.

The difference between methods resides in what each of them studies – palaeontological method studies fossils of macroscopic life forms (mammals, mollusks etc.), the micropalaeontological method uses microscopic forms of life (foraminifera, Radiolaria, Ostracoda), while the palynological method deals with pollen and spores of fossil and present plants.

Applications of the rendered methods in different branches of geography

Soil Geography, Geography of the Quaternary, Geomorphology, Hazards Geography, all are more or less related to the study of clay minerals.

Thus, in Pedology, the proportion and type of clay minerals determine the nomenclature of certain soil types. The most relevant example is that of vertosols, the soils the structure of which is induced by the swelling of smectite clay minerals. The proportion of clay minerals in a soil influences its texture and the way it may be agriculturally used.

In the study of paleosoils, the type of clay minerals may supply information about the climate under the influence of which they developed: kaolinite and halloysite appear in a climate corresponding to equatorial and humid tropical areas, smectites appear in the subtropical zones, palygorskite in the desert and semi-desert areas, while chlorite and illite develop in polar climatic conditions and minerals belonging to the interstratification groups in temperate zones.

In geomorphology, in order to establish the age of different phenomena, it was made reference to the succession of river terraces. Thus, it was establish the age of loess in Romania. The use of thermoluminescence in a study achieved in two locations (Tuzla and Giurgiu Malu-Rosu) led to precise values for these deposits that date between 8,000 and 3,000 years old. The used minerals from loess deposits (feldspath, quartz) are also noticed in pelitic deposits located on terraces, through the analysis of which we may establish their absolute age.

The same method (together with the carbon dating method or the paleomagnetic one) may be applied to obtain an accurate age for different formations generated by Quaternary glaciations.

Landslides may have catastrophic effects when they affect settlements. Together with other factors (slope, structure), the presence of clay deposits, the type and proportion of clay minerals determine the appearance and development of such phenomena.

Establishing the mineralogy of such deposits by means of the above mentioned methods is a necessity if one may want to prevent the occurrence of these kinds of accidents through different works or to avoid casualties through the evacuation of the people in the area if there is not possible to reduce or control the landslide risk.

Benthonic deposits or the ones displaying a great content of montmorillonite (mineral that may increase at least four times its volume after water absorption) represent the most hazardous element in triggering landslides.

The present paper intends to bring to geographers' attention certain methods they are not usually used to work with. Many of them are methods used in geology, but, as it happens in other fields, the limits of certain branches of geography and geology are more or less interrelated, leading thus to the gradual and reciprocal taking over of the methods that were strictly used by one of them in the beginning.

REFERENCES

AITKEN, M.J., (1985), *Thermoluminescence Dating*, Academic Press, London

BALESCU S., LAMOTHE M., MERCIER N., HUOT S., D. BALTEANU, A. BILLARD, J. HUS, (2003), *Luminescence chronology of Pleistocene loess deposits from Romania: testing methods of age correction for anomalous fading in alkali feldsaprs*, Quaternary Science Reviews 22

BROWN M.E., (2001), *Introduction to thermal analysis, techniques and applications,* Kluwer Publishers, Netherlands

BROWN M.E., GALLAGHER P.K., (2008), *Handbook Of Thermal Analysis And Calorimetry: Recent advances, techniques and applications (Volume 5),* Elsevier

BUTLER R. F., (1992), *Magnetic Domains to Geologic Terranes*, Blackwell Scientific Publications

GUCSIK A., (2009), *Cathodoluminescence and its application in the planetary sciences*, Springer-Verlag Berlin

MATEI L., (1986), *Minerale si roci argiloase,partea III-a*, Bucuresti

McKEEVER S. W. S., (1988), *Thermoluminescence of Solids*, Cambridge University Press

McMULLAN D., (1993), *Scanning electron microscopy 1928 – 1965*, Presentation at the 51st Annual Meeting of the Microscopy Society of America, Cincinnati, August

PAGEL M., BARBIN V., BLANC P., OHNENSTETTER D., (2000), *Cathodoluminescence in Geosciences*, Springer Verlag

REEVES G. M., SIMS I. and CRIPPS J. C., (2006), *Clay Materials Used in Construction*, Geological Society, London

YACOBI B.G., HOLT D. B., (1990), *Cathodoluminescence microscopy of inorganic solids*, published by Plenum Press (New York)

*** (2002), Preface-special Issue: *Cathodoluminescence in the Geosciences*, Mineralogy and Petrology