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CONTENTS

THE QUANTITATIVE DETERMINATION OF CHRISTOBALITE AND MONTMORILLONITE FROM THE COLLOIDAL FRACTIONS OF BENTONITES BY X-RAY DIFFRACTION[1]

BY

CONSTANTIN CRĂCIUN[2]

Abstract

The Quantitative Determination of Christobalite and Montmorillonite from the Colloidal Fraction of Bentonites by X-ray Diffraction. By using the intensities of diffraction lines (101) for christobalite and (001) for montmorillonite, a quantitative determination method was proposed. For errors under 5 %, the clay fractions must be saturated in a single cation.

The well-known progresses of the X-ray technical equipment and the studies elaborated in this domain, permitted the quantitative interpretation of the results of these analyses.

Our paper represents an attempt to verify through a simple and rapid method, the possibility to obtain of some reproductible data of quantitative analyses of some bentonites with christobalite content.

Materials

In order to avoid as much as possible the influence of the other components as well as the dilution effects which give high errors, we worked on colloidal fraction under 1 μ separated from some bentonites with christobalite content from Gurasada-Tomeşti region.

X-ray diffraction traces were run of the oriented and kalium, calcium and ethylene-glycol saturated samples, after a previous acid treatement. Traces were run by using X-ray spectrometer U.R.S. 50 I.M. with goniometer G.U.R. at 35 kW, 5 mA and scanning at 1° per minute.

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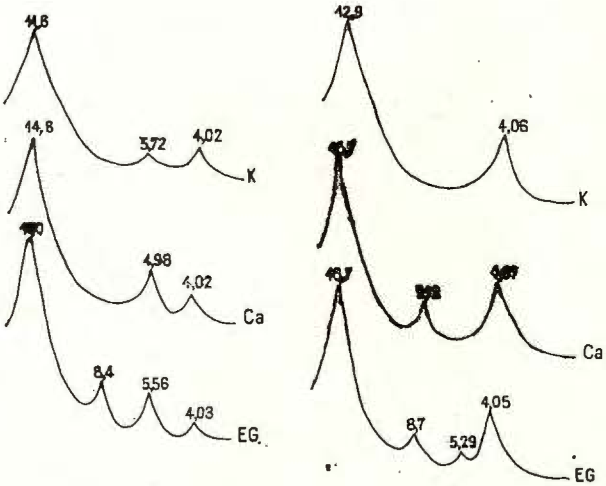
[1] Reported in the session from November 1973.

[2] The Research Institute for Soil Science, Bucharest.

Results and Discussions

The following criteria are used to identify the two minerals: montmorillonite is characterized by its expanding lattice; when K is the exchange ion it frequently has a C-axis spacing of about 11.6—12.9 Å (001).



1 2

Fig. 1. — X-ray diffraction diagrams of the colloidal fractions separated from bentonites.

At the saturation with Ca and ethylene-glycol the basal spacings are 14.8—15.7 Å and 16.7—17.0 Å. On diagrams we can see peaks which indicate the basal spacing 002, 003: 5.72 Å (K), 8.4 Å (ethylene-glycol); 5.12 Å (Ca), 5.29 Å (etylene-glycol). The presence of christobalite is indicated by the peaks at 4.02—4.07 Å.

In the system of these two components the quantitative method consists in the utilization of the numerical values of the diffraction intensities of the basal spacing 001 for montmorillonite and 4.02—0,07 Å diffraction intensities for christobalite.

On account of the differences of the cristal size, cristalization degree, orientation and segregation of the material, suitable to the sample preparation system, we apply to these values the following correction coefficients: 1.5 for montmorillonite and 6 for christobalite.

So, if we consider 1 as the factor for montmorillonite, the christobalite factor is 0.25. These factors were accepted after a verification on admixtures in the laboratory, they corresponding to the given values by **Marel** and **Schultz**.

Table 1 indicates unsignificant fluctuations of the quantitative values for montmorillonite with the saturation cation. It can be observed a rising tendency at the Ca-saturation which is probably due to a higher degree of the material aggregation.

The analytical values show that for sample amounts below 25 mg the variation of results is insignificant, it does not exceed 3%. When the

TABLE 1

The Results Variation According to the Cation which Saturates the Clay Fraction and the Sample Weight

Sample	Weight, mg	Cation	Amount, %	
			Montmorillonite	Christobalite
Vica bentonite	22.7	K	95.0	4.8
	17.2	Ca	94.5	4.5
	17.2	ethylene-glycol	97.6	2.4
Gurasada bentonite	11.1	K	93.6	6.3
	22.1	Ca	93.6	5.4
	22.1	ethylene-glycol	93.8	5.7
Gurasada bentonite	11.0	K	96.9	2.6
	7.6	Ca	97.9	1.0
	7.6	ethylene-glycol	98.2	1.0
Gurasada bentonite	16.6	K	96.7	2.9
	15.7	Ca	96.8	2.8
	15.7	ethylene-glycol	94.5	4.5
Gurasada bentonite	7.2	K	98.0	2.0
	7.4	Ca	99.2	0.5
	7.4	ethylene-glycol	99.0	0.7
Tomeşti bentonite	38.4	K	87.9	11.3
	20.2	Ca	96.8	2.8
	20.2	ethylene-glycol	96.6	3.7
Tomeşti bentonite	40.6	K	86.2	14.0
	10.8	Ca	92.1	7.8
	10.8	ethylene-glycol	87.1	13.0

quantity rises above 25 mg the variations are higher, showing a lowering tendency of montmorillonite, which is probably due to a lower orientation degree, determined by the large amount of samples. For the christobalite it can be observed a quantitative rising tendency in K saturated samples. Generally, the values show variations about 4%, which represent a relative error about 50%.

The causes of the errors for the colloidal fraction saturated with different cations may be the following: the different orientation degree of the specimens, determined by these cations and the sample amount, the small penetration of the X-ray beam or the material segregation determined by the sample preparation method.

Due to the quantitative values variation obtained in the case of saturated samples with different cations, we consider that it is necessary to work on colloidal fractions saturated only in one cation, thus the comparability of the results being ensured.

In order to specify the causes which determine these variations, determinations were done in parallel on some K and Ca saturated samples, varying the material density on the lamella.

Table 2 shows the experimental values and the mean quantitative values for these samples.

TABLE 2

The Results Variation According to the Sample Amount on the Lamella

Sample	Amount, mg	Cation	Montmorillonite		Christobalite	
			experimental values, %	mean value, %	experimental values, %	mean value, %
Gurasada bentonite	8.1	K	98.1	96.1±1.2	1.6	2.6±0.9
	13.0	K	96.8		2.2	
	13.8	K	95.8		3.4	
Gurasada bentonite	15.0	K	96.6	96.7±0.5	2.8	2.9±0.1
	15.6	K	96.5		2.9	
	19.2	K	97.0		3.0	
Tomeşti bentonite	1.7	Ca	97.7	96.8±0.7	2.2	2.8±0.5
	6.5	Ca	96.5		3.1	
	20.2	Ca	96.4		3.2	
	48.6	Ca	91.2		8.8	

As, it can be seen, the variation of results is insignificant when the sample amount does not exceed 20—25 mg, deviations from the mean values being about 1%.

The result for the sample with 48,6 mg is evidently different, and it was omitted at the mean value calculation. It must be point out that in case of such determinations the sample amount must be preserved between certain limits.

Conclusions

By using the X-ray diffraction patterns at the quantitative determination of the colloidal fractions components from bentonites, it is possible to obtain analytical values, which have a practical utility.

In order to obtain minimal errors, with the previously indicated technical equipment, the method presented here specifies the utilization of some samples which have a content as for as 25 mg on the lamella (the area 875 mm^2) and the saturation of these samples in one cation which can be K and Ca.

Even in the most unfavourable cases this method does not present errors higher than 5% in absolute values. Therefore the analytical results must be expressed in percents, the decimal values are recommended as numeric values for statistical calculations.

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DETERMINATION OF THE SPECIFIC SURFACE AREA OF CLAY MINERALS AND CLAY FRACTIONS FROM SEDIMENTS AND SOILS[1]

BY

GHEORGHE GÂŢĂ[2]

Abstract

Determination of the Specific Surface Area of Clay Minerals and Clay Fractions from Sediments and Soils. The results of some methods for the determination of the specific surface area were compared. Taking into account the value obtained by the low-temperature nitrogen method as a measure of the outside specific surface area, and the one of another values as a total surface, specific surface of the interlayer may be calculated.

The release and mobility of the cations, which are very important in the plant nutrition, are processes depending on surface area and nature of mineralogical particles of a sediment or of a soil. For this reason, in the last two decades the researches relating to the estimation of the specific surface area of clay mineral fractions from a sediment and a soil were accentuated.

In the analytical methods for specific surface area a molecular monolayer adsorbed on the particle surface is assumed. Therefore there are distinguished two types of adsorption methods for this determination, namely the adsorption of the non-polar molecules in gaseous phase and the adsorption of polar molecules in liquid phase.

Nelson and Hendricks (1943) used the nitrogen adsorption at his boiling temperature, while Rouxhet and Fripiat (1966) utilized for this purpose argon and crypton. Hul and Lyklema (1968), by a continuous flow technique, carried out the nitrogen adsorption from various nitrogen and helium mixtures by use of a sorptometer Perkin-Elmer/Shell 212 C.

For adsorption in the liquid phase there were employed many reagents as methylene blue (Hul, Lyklema, 1968) ortho-phenantroline (Lawrie,

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[1] Reported in the session from November 1973.

[2] The Research Institute for Soil Science, Bucharest.

1961) and especially ethylene-glycol (Dyal, Hendricks, 1950; Fripiat, Gastuche, 1952; Bower, Gaschwend, 1952; Mortland, 1954; Sor, Kemper, 1959). In addition, the specific surface area was calculated on the basis of anion exclusion measurements (Haan, 1965) and particle size measurements by electron microscopy (Milford, Jackson, 1966).

The required knowledge of the specific surface area of dispersed minerals from sediments and soils in connection with the ion repartition in the heterogeneous systems soil-solution imposed a comparative study of the different methods of the determination of this important quantity.

Materials and Methods

Four clay minerals and eight clay fractions (table 1) were separated as Ca-saturated colloidal fractions under 2 μ, in such a manner that the work includes the principal clay minerals and their interstratifications

TABLE 1

Mineralogic Composition of the Samples

Sample	Mineral	
	predominant	
Kaolinite Zettlitz	kaolinite	
Montmorillonite Wyoming[2]	montomorillonite	
Illite Illinois[2]	illite	chlorite
Halloysite Indiana[3]	halloysite	
Loess Fetești	vermiculite[1] illite interstratifications (vermiculite-illite)	kaolinite quartz sesquioxides
Loess Baziaș	vermiculite illite interstratifications (vermiculite-illite)	kaolinite chlorite quartz
Subhorizon B_s of Iron-humus podzol Jepii Mari Mountain	chlorite illite	kaolinite sesquioxides quartz
Subhorizon A_2/B of grey brown podzolic soil Preajba	chlorite illite	kaolinite sesquioxides quartz
Horizon B of pseudogleyed brown forest soil Lespezi	montmorillonite illite	kaolinite sesquioxides
Horizon C_2 Vertisol Gîrcina	illite chlorite interstratifications (illite-chlorite)	kaolinite quartz sesquioxides
Horizon B of chernosem-like meadow soil Horez	interstratifications (montmorillonite-illite) montmorillonite	illite kaolinite quartz
Subhorizon B/D of iron-humus podzol Tidvele	interstratifications (illite-vermiculite)	kaolinite quartz

[1] All the vermiculites from this work are dioctahedral minerals.

[2] From Prof. M. Mortland's collection (Michigan — U.S.A.).

[3] From Prof. G. Bolt's collection (Wageningen-Holland).

which occur in the soils from our country. The organic materials was decomposed by digestion with 6 % H_2O_2, and the carbonates were dissolved by acidifying with an organic ion —exchanger Merck 4765 × up to pH 5.0.

The techniques for the specific surface area of the minerals with colloidal sizes must solve two problems, namely the outgassing and the water removing and also the adsorption of a certain molecular species on the surface mineral.

In the technique for water removing and outgassing several variants were used: dehydratation at the room temperature in vacuum under 2 mm Hg over P_2O_5, heating overnight at 105°C in a helium flow and dehydratation at the room temperature in a helium flow 24 hours.

The used methods for adsorption determination were: the low-temperature nitrogen adsorption (Hul, Lyklema, 1968), ethylene-glycol retention (method by Fripiat-Gastuche, 1952), the ortho-phenantroline adsorption (Lawrie, 1961) and anion-exclusion measurements with Cl 36 (Haan, 1965).

Results and Discussions

The specific surface area determination by dry methods using nitrogen or vapour ethylene-glycol, after outgassing and water removing, was carried out. A comparison of three proceedings for the water removing indicates some differences of the results (table 2).

For adsorption in gaseous phase, the highest values were obtained by vacuum technique over P_2O_5 which produced a probably complete

TABLE 2

Specific Surface Area Determination by Nitrogen and Ethylene-glycol Adsorption (clay fractions <2μ)

Sample	specific surface area, m^2/g					
	nitrogen adsorption			ethylene-glycol adsorption		
	P_2O_5 in vacuum	He flow at 105°C	He flow at room temperature	P_2O_5 in vacuum	He flow at 105°C	He flow at room temperature
Kaolinite Zettlitz	26.2	25.4	21.5	26.4	24.1	19.8
Halloysite Indiana	46.1	19.8	27.4	49.5	22.1	26.7
Montmorillonite Wyoming	59.2	54.4	53.2	632.0	585	322
Illite Illinois	98.0	97.3	84.4	122.0	116	87
Loess Feteşti	68.7	72.5	68.0	344.0	308	256
Loess Baziaş	74.0	71.6	52.4	320.0	277	241
Subhorizon B_s — Jepii Mari	76.1	74.3	67.2	84.6	72.1	64.5
Subhorizon A_2/B Preajba	68.6	66.4	56.8	74.4	70.8	66.5
Horizon B Lespezi	74.5	71.6	56.3	483.0	466	398
Subhorizon C_2 Gîrcina	77.8	76.4	69.5	95.6	90.8	85.4
Horizon B Horez	94.4	92.1	78.5	411.0	402	367
Subhorizon B/D Tidvele	49.1	51.3	34.9	121.0	119	89.2

removing of hygroscopic water. The use of a helium flow at room temperature presented only a partial water removing accompanied by small values and, for this reason, the same technique was tested but, in addition, the samples were heated at 105°C overnight in a helium flow. The results of the last proceeding were generally as high as the variant with vacuum over P_2O_5. The experiment, however, points out the accentuated errors for halloysite probably due to irreversible water removing, which changes halloysite into metahalloysite by heating at 105°C. Generally, the proceeding of a helium flow at room temperature must not be used because of its partial water removing, which provides the smallest results. For this reason the last technique was not taken into account for specific surface area determinations.

For kaolinite, the differences of the experimental values between the two techniques are only 1—2 m^2/g i.e. about 5—10%, but the two methods have a good agreement.

The montmorillonite presents the same difference between these two techniques but the values for ethylene-glycol are very high in relation to the values of nitrogen adsorption — over 400 m^2/g, due to the interlayer surface. For illite this difference is only about 20 m^2/g.

When the montmorillonite is predominant or present in a high quantity in the clay fractions from sediments and soils, the specific surface area has 300—500 m^2/g in the ethylene-glycol determinations while these values are only 70—75 m^2/g for nitrogen adsorption method. For sediments and soils with illite or chlorite predominance the differences of these avalues are 10—20 m^2/g.

In order to compare the various methods there were utilized just the values obtained by the technique with helium flow over night at 105°C for nitrogen and ethylene-glycol adsorption determination. These results, together with the experimental values of the specific surface area carried out by ortho-phenantroline method and anion exclusion measurements, were presented in table 3. The analytical results of the ortho-phenantro-

TABLE 3

Comparison of Specific Surface Area Values Obtained by Various Adsorption Methods

Sample	nitrogen	ethylene-glycol	ortho-phenantroline	anion repulsion
	specific surface area, m^2/g			
Kaolinite Zettlitz	25.4	24.1	30.1	—
Halloysite Indiana	46.1*	49.5*	37.2	—
Montmorillonite Wyoming	54.4	585	594	489
Illite Illinois	97.3	116	147	112
Loess Fetești	72.5	308	302	237
Subhorizon A_2/B Preajba	66.4	70.8	77.2	55
Horizon B Horez	92.1	402	414	262
Sibhorizon *B/D* Tidvele	51.3	119	127	101

* Values obtained by P_2O_5 in vacuum technique.

line method are in mutual agreement with ethylene-glycol retention method for all the clay minerals and clay fractions. Generally, there is a discrepancy between the anion exclusion method and the ethylene-glycol method since the values obtained with chloride exclusion are always smaller than the results measured according to the retention of ethylene-glycol. This discrepancy is higher for the clay fractions which contain predominantly montmorillonite-like minerals. For example, the Wyoming montmorillonite, the loess from Feteşti and the horizon *B* from Horez show differences about 100 m²/g, 70 m²/g, 150 m²/g respectively between the values carried out by ethylene-glycol retention and chloride exclusion method.

The results of the ortho-phenantroline method are comparable with the values presented by the ethylene-glycol method, but generally the results are with 15—20% higher. These differences are 6 m²/g, 29 m²/g- — 6,4 m²/g — 12 m²/g and 18 m²/g for kaolinite, montmorillonite, illite, Preajba-soil, Horez-soil and Tidvele-soil, respectively. Only at the loess from Feteşti the ethylene-glycol value is higher than the ortho-phenantroline value with 6 m²/g.

The parallelism of the values of methods using polar molecules and the high differences of these results with the values, obtained by nitrogen adsorption method especially for the expandable minerals, suggest an estimation of the external surfaces by nitrogen adsorption and an appreciation of the whole surface of the particles, namely external and internal (interlayer), by one of the other methods. If it supposed, by convention, that the nitrogen adsorption at low temperature determines only the external surface, easily accesible for cations, i.e. the external surface in fact and the broken surface of the layers and its vicinity, and the ethylene-glycol adsorption estimates the whole surface, the accesible surface of the interlayer may be calculated by substraction (table 4).

TABLE 4

External Specific Surface Area and Interlayer Specific Surface Area Calculated by Nitrogen Adsorption and Ethylene-glycol Retention Methods

Sample		specific surface area, m²/g	
		external	interlayer
Kaolinite	Zettlitz	25	—
Halloysite	Indiana	46	3
Montmorillonite	Wyoming	54	531
Illite	Illinois	97	19
Loess	Feteşti	73	235
Loess	Baziaş	72	205
Subhorizon B_s	Jepii Mari	74	2
Subhorizon A_2/B	Preajba	66	5
Horizon *B*	Lespezi	72	394
Subhorizon C_2	Gîrcina	76	15
Hirozon *B*	Horez	92	310
Subhorizon *B/D*	Tidvele	51	68

These calculated values show an external surface of 25—45 m^2/g for the 1 : 1 structure minerals, variation probably due to the nature and particle size of the minerals.

The 2 : 1 structure minerals present a higher external specific surface, and the recorded numbers are comprised between 60 and 100 m^2/g. For analysed clay minerals and clay fractions, the results occur particularly in the interval of 66—76 m^2/g. We must point out the absence of any significant difference in the external surfaces of the expandable minerals, illite or chlorite.

The clay fractions with a predominant content of montmorillonite, dioctahedral vermiculite or interstratifications with these minerals have a high interlayer surface over 200 m^2/g while for illite, chlorite and interstratifications with these clay minerals the internal surface has only 2—19 m^2/g. For subhorizon *B/D* Tidvele soil the value of 68 m^2/g may be assigned to the occurrence of an illite-vermiculite interstratification, where the dioctahedral vermiculite is partially chloritized.

Conclusions

1. The results of various specific surface area methods for the clay minerals and clay fractions on the basis of non-polar and polar molecules are the more different as the interlamellar space has a greater mobility.
2. The specific surface area by low temperature nitrogen adsorption method is dependent on the outgassing and dehydration intensity of the surface: the dehydration techniques by vaccuum over P_2O_5 and by helium flow at 105°C were satisfactory.
3. As the determinations show, the methods, without the low temperature nitrogen adsorption, are in mutual agreement. These results decrease generally in the succesion ortho-phenantroline adsorption, ethylene-glycol retention and anion exclusion.
4. Taking into account the results of the low-temperature nitrogen adsorption method as a measure of the outside specific surface area and the ethylene-glycol adsorption method as a total surface, specific surface of the interlayer may be calculated.

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A METHOD FOR CHARACTERIZATION OF WEATHERING BY USE OF X-RAY DIFFRACTION PATTERNS OF CLAY FRACTIONS FROM SEDIMENTS AND SOILS [1]

BY

GHEORGHE GÂȚĂ[2]

Abstract

A Method for Characterization of Weathering by Use of X-ray Diffraction Patterns of Clay Fractions from Sediments and Soils. A graphical method representing the variations of the basal spacings greater than 10 Å versus the depth in the profile was presented. By this way there may be pointed out the transformation processes of the 2 : 1 clay minerals and the occurrence of polystratifications.

Generally, the weathering of the sediments is proportional with the surface area of component minerals and depends on their chemical reactivity and the aggressivity of the alternation medium. Hence, the 2:1 clay minerals are efficient for researching the direction and the intensity of weathering, because of their highly specific surface area, over 10 m²/g. But these structural types, predominant in the soils and in very many sediments from our country (Gâță, Crăciun, Popescu, 1971), have an accentuated sensibility in weathering processes (Jackson, 1964, de Coninck, Herbillon, 1969). In this way, at colloidal level, the weathering changes the interlayer cation mobility, which may characterize the weathering direction and intensity. Since the comparison of the results as X-ray diffraction patterns is difficult, in this paper is presented a suggestive graphic method, which points out the fluctuation of interlayer cation mobility by using the shift of X-ray diffraction line positions, over 10 Å, as a function of the depth in the profile.

The X-ray diffraction patterns of the clay fractions were prepared by K, Ca and ethylene-glycol saturation. Basal oriented specimens were

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[2] The Research Institute for Soil Science, Bucharest.

subjected to CuK_α radiation on a diffractometer URS—50—IM at 35 kV, 5 mA and scanning at 1° per minute. Ethylene-glycol saturation was accomplished at room temperature in an ethylene-glycol atmosphere by use of a Ca-saturated sample.

The basal parameters (001) were plotted on abscise in term of the depth in the profile on ordinate. The fluctuations of the basal spacings were evaluated by their mean values obtained from three experimental determinations (table 1). These fluctuations did not exceed ± 0.2 Å and decreased when the diffraction line positions decreased too. On each graph basal spacings versus depth, appear three curves corresponding to the potassiun, calcium and ethylene-glycol — saturated clay fractions respectively. The configuration of these curves indicates the transformations which occurred in the interlayers of the 2:1 clay minerals.

TABLE 1

Basal Spacings of some Samples

Sample	Depth, cm	Cation — saturation		
		K	Ca	ethylene-glycol
Loess Socol	300—320	13.7±0.1	14.0±0:2	16.2 ±0.2
Silt loam Cărbunești	270—290	13.7±0.05	13.9 ±0.1	15.35±0.15
A_1A_2 subhorizon Ploștina	0—3	13.5+0	13.75±0,05	14.2 ±0.05
Eluvial-diluvial formation Rînca	140—150	12.7+0	13.45±0.05	14.0 ±0.1
Alterated sandstone Jepii Mari	60—70	13.8±0.05	14.05±0.05	14.25±0.05

When the weathering agents have a small intensity (inceptisols, chernozem, vertisols) on the graph appear the straight lines, if the mineralogical substratum is homogeneous. For example, on the figure 1 are presented the experimental values for a chernozem — like soil (inceptisol) from Socol (Banat) and a vertisol from Valcani (Banat). These two soils have some insignificant variations of the peak positions in term of the depth. In the Socol soil (fig. 1 *a*) only the curve for the ethylene-glycol saturated clay fractions presents a small fluctuation versus the depth, while in the Valcani profile there are some modifications in the *A* horizon, for all three curves (fig. 1 *b*). The last graph points out the changes in the interlayer clay fractions of this horizon where, for K and Ca saturation, the alteration processes generated a slight increase of the basal spacings of the smectite minerals.

When the sediments are not homogeneous and there are polystratifications, obvious shifts may appear at the depth between the two

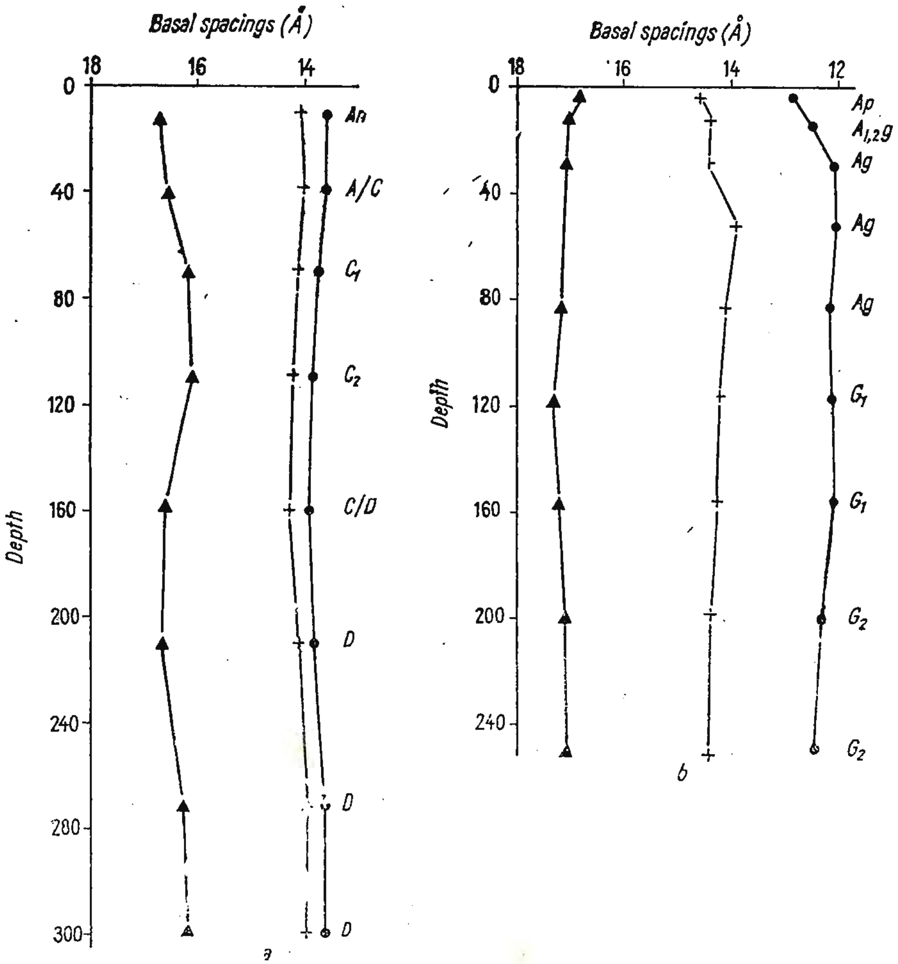

Fig. 1. — Basal spacings of clay fractions as a function of the depth in the profiles chernozem-like soil from Socol (*a*) and vertisol from Valcani (*b*)

● K — saturated clay fractions; +Ca — saturated clay fractions;
▲ ethylene-glycol-saturated clay fractions.

adjacent stratifications as on the diagrams of the figure 2 for the loess profile from Divici (Banat) and the leached brown forest soil from Cărbunești (Gorj). It can be emphasized that these modifications occur on all the curves, i.e. on the K, Ca, ethylene-glycol saturated curves respectively, at the same depth.

In the first profile from Divici appears a discontinuity between 140—180 cm which points out a possible distratification (fig. 2 *a*). The second profile presents two shifts of the (001) parameters, placed at 40—50

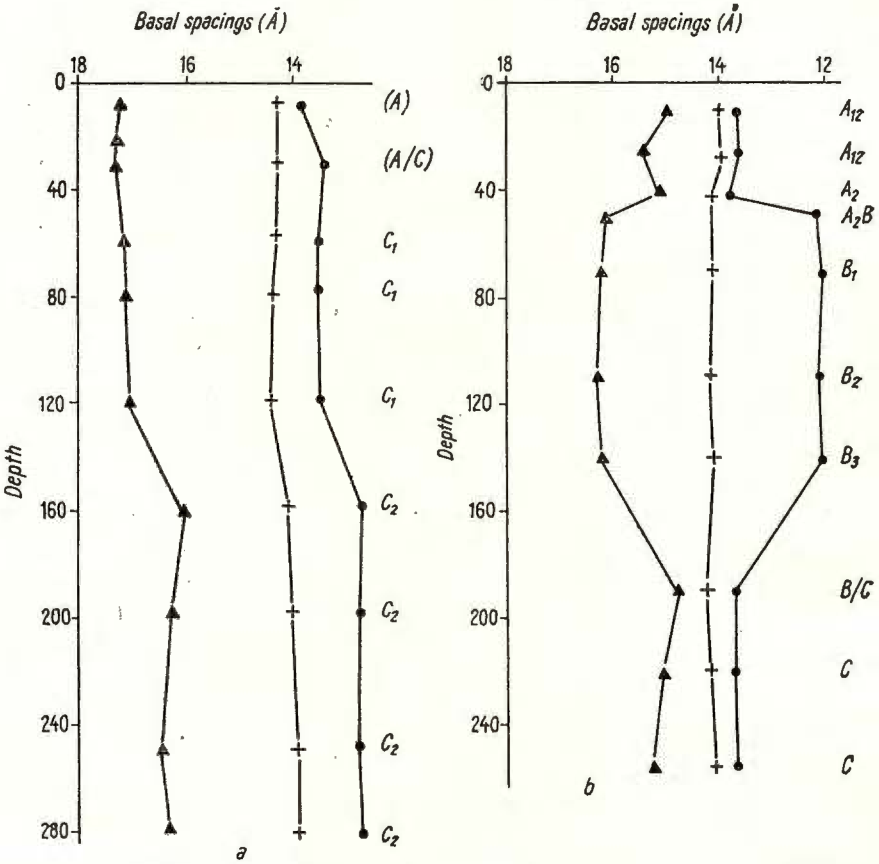

Fig. 2. — Basal spacings of clay fractions in terms of the depth in the loess profiles from Divici (*a*) and leached brown forest soil from Cărbunești (*b*)

● K — saturated clay fractions;
\+ Ca — saturated clay fractions;
▲ ethylene-glycol-saturated clay fractions.

cm and 160—200 cm (fig. 2 *b*). These distinct changes in the interlayer of the smectites indicate three stratifications which were confirmed by their granulometric analyses.

The presented graphic method may also point out the transformation processes of the expandable minerals into chlorite-like minerals by the gradual modification of the interlayer cation species, followed by a selected blocking of a particular cation. For exemple, in the figure 3 there are emphasized the shifts occurred in the horizon *A* of a pseudogleyed grey brown soil from Ploștina (Hunedoara). In both parts of this horizon, A_1 and A_2, occurs as a predominant mineral in the clay fractions, a chlorite-like mineral with (001) parameters 13.5 Å, 13.8 Å and 14.2 Å for K, Ca, ethylene-glycol saturated fractions respectively. Therefore, the weathering produced in the superficial horizon an accentuated increase of the interlayer cation rigidity. The mobility of the cation interlayer increases with the depth in the A_2B and B horizons; at the 110—120 cm depth the smectite minerals are predominant.

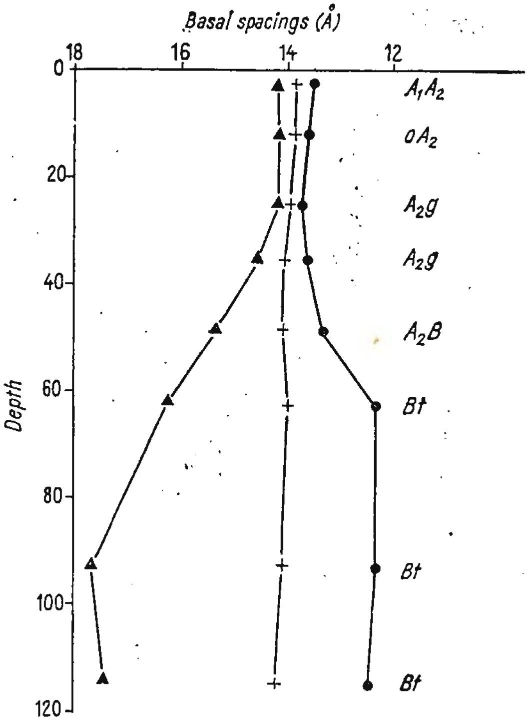

Fig. 3 — Basal spacings vs depth curves for pseudogleyed grey — brown podzolic soil from Ploştina

● K – saturated clay fractions;
+ Ca – saturated clay fractions;
▲ ethylene-glycol-saturated clay fractions.

The graphic method emphasizes at the same time the alteration processes accompanied by gradual shifts of the chlorite-like minerals into smectite minerals in some mountain soils (fig. 4). For a mountain acid brown soil from Rînca (the Parîng Mountains) developed on eluvio-deluvial deposits on gneissic granite, the basal spacing mobility reached its maximum in the superficial A_{12} horizon, then decreased up the A/B one (fig. 4 *a*). In B and D horizons the interlayer rigidity of the chlorite-like minerals is almost the same and the differences between basal spacings of the ethylene-glycol-saturated and K-saturated samples do not exceed 1.4 Å.

An iron humus podzol from the Jepii Mari Mountain developed on Aptian sandstone shows as predominant minerals a chlorite-like mineral in the D and B_s horizons and a smectite-like mineral in the A horizon and B_{hs} subhorizon. There is a gradual modification of the basal spacings with the depth and this vermiculitisation process of the 2:1 minerals reaches in A_1 subhorizon 16.7 Å for the ethylene-glycol saturated 10.8 Å K-saturated clay fraction respectively.

The conclusion from this graphic method is that, in addition to the advantage of the presentation of a suggestive image of the basal spacing fluctuation in a profile, it points out the direction and intensity of the weathering under which the profile developed and may also allow to estimate the polystratification or the homogeneity of the lithological substratum.

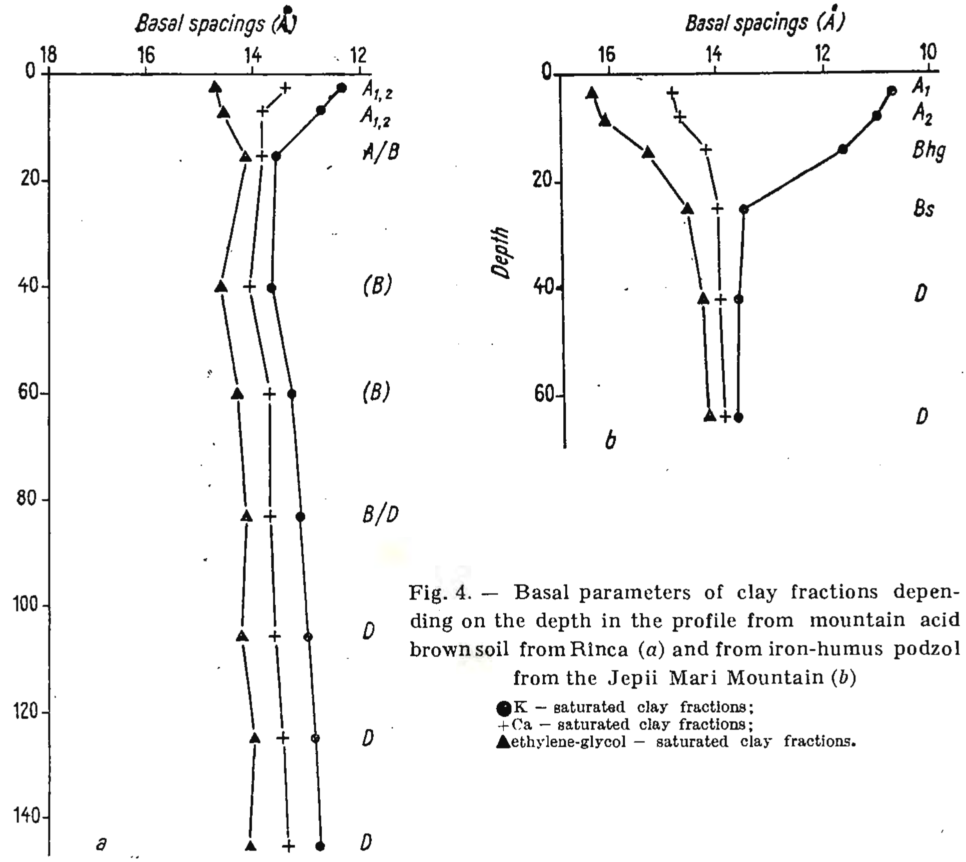

Fig. 4. — Basal parameters of clay fractions depending on the depth in the profile from mountain acid brown soil from Rînca (*a*) and from iron-humus podzol from the Jepii Mari Mountain (*b*)

●K – saturated clay fractions;
+Ca – saturated clay fractions;
▲ethylene-glycol – saturated clay fractions.

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WEATHERING ASPECTS OF SOME GNEISSIC GRANITE FROM THE SOUTHERN PART OF THE PARÎNG MOUNTAINS[1]

BY

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Abstract

Weathering Aspects of Some Gneissic Granite from the Southern Part of the Parîng Mountains. The weathering of the gneissic granite was studied by use of the *p*H, exchangeable cations, colloidal fraction content and X-ray diffraction pattern. Three weathering zones characterized by the sericitisation of feldspars, the alteration of micas and the transformations of the random interstratifications into smectite-like minerals have been identified.

The research of acid rocks weathering in a temperate climate has begun many decades ago; in 1909, by microscope technique, the sericitization of plagioclases and the hydrolisis of alkali feldspars were demonstrated by Lapparent. In the last years, Collier (1961) and Millot (1970) carried out their syntheses about the arenization.

The present paper points out the weathering zones of the gneissic granite from the Parîng Mountains by use of X-ray diffraction patterns.

Materials and Methods

Two series of samples were collected from the Corneşul Mare Mountain (Parîng Mountain); the first series is a gneissic granite which has muscovite, quartz, plagioclases (albite and oligoclase) microcline and some hornblende and biotite in its composition. The second series has about the same composition but in addition also some sericite and chlorite as components.

The *p*H values of the samples were determined electrometrically by using a glass-electrode and the content of the clay fractions <0.002 mm was determined by pipette method.

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[1] Reported in the session from November 1973.

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The samples from two series were dispersed in distillated water and the <2 μ particles were separated by use of Stokes law. Then, these clay fractions were in potassium and calcium saturated.

The X-ray diffraction patterns were carried out with an U.R.S.—50—I.M. difractometer at 7 mA and 35 kV and scanning at 1° per minute.

Results

The analysed samples have the *p*H values between 4.4 and 6.2 and their content of colloidal fractions from 22.3% up to 0.68%. The relationship between the content of these colloidal fractions and the correspondent *p*H values may be given by an expression which has a high curvature radius. Thus, approximately, this clay fraction content — *p*H curve may be considered as a straight line. The statistical estimation of the regression curve gives the ecuation $y = 93.65 - 15.83\,x$ with acorrelation coefficient $c = 0.79$ where y is percentage of the clay fraction and x is the *p*H value (fig. 1). Although the dispersion of the plotted points is high enough, the established correlation points out the increase of weathering by microdivision and hydrolysis which intensifies the disintegration of the minerals at the same time with the intensification of the percolation expressed by *p*H value.

The release of cations from the primary mineral lattices was determined for all the samples of the two series (tab. 1). The preponderent cation in the solution was always hydrogen ion and its content increases with the intensity of the weathering processes. The natrium and potassium ions are practically in about a constant quantity while magnesium and especially calcium ions increase with the alteration.

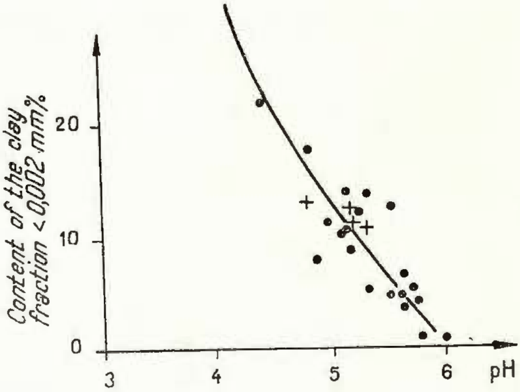

Fig. 1. — The relationship between the content in clay fraction (under 0.002 mm) and *p*H of the solution.

The K/Ca ratio as a measure of hydrolysis of the feldspars and micas decreases while the weathering increases, because of the increasing content of calcium ions remained in the solution after solubilization and removing of alkaline ions.

There were identified three weathering zones characterized by: *a* — the sericitization of the feldspars and incipient alteration of micas; *b* — the increase of the alteration of the mica-like minerals with the appearance of the random interstratifications and of the kaolinite; *c* — transformations of the random interstratifications into the vermiculite-like minerals with the appearance of some smectite-like minerals.

TABLE 1

Exchangeable Cations and K/Ca Ratio of the Gneissic-granite Alterations

Sample	Exchangeable cations meq/100 g					K/Ca ratio
	Ca	Mg	K	Na	H	
a_1	0.28	0.08	0.09	0.11	1.30	0.32
b_1	0.31	0.09	0.07	0.10	1.35	0.23
c_1	0.46	0.12	0.09	0.12	2.67	0.20
a_2	0.41	0.18	0.08	0.14	1.51	0.20
b_2	0.57	0.24	0.09	0.14	1.56	0.16

These three alteration zones of the arenization processes were studied by X-ray diffraction of the samples oriented and saturated in potassium, calcium and ethylene-glycol.

In the first zone *a* on the X-ray diffraction patterns there appear the illite lines at 9.98—9.89 Å, 4.95—4.96 Å and 3.31 Å (fig. 2). The intensity of the last line points out the presence of quartz while the lines at 8.25—8.34 Å and 5.47—5.51 Å may be assigned to zeolite minerals. Feldspars are emphasized by the lines at 4.19—4.07 Å and 3.18—3.27 Å which indicate the oligoclase, albite and microcline as components.

In the second zone b_1 feldspars are not present and there appear besides micas some alterations 2 : 1 minerals characterized by a collapse at 10.4 Å for potassium saturated fraction and a splitting at 11.9—10.9 Å and 12.9—10.9 Å for the fraction saturated in calcium and also in ethylene-glycol. These random interstratifications indicate an accentuated hydrolyse of mica-like minerals with a depletion of potassium from the interlayer as an effect of weathering. This removing of interlamellar potassium partially by hydroxonium ions may be pointed out by the position 10.4 Å for K-saturated fraction and the appearance of the splitting for Ca and ethylene-glycol — saturated fractions. On the diffraction patterns there are also the lines at 7.13—7.14 Å and 3.56 Å assigned to kaolinite.

In conclusion, this stage of weathering is characterized by a hydrolytic alteration of mica-like minerals with a transformation in a random interstratification and by a neoformation of kaolinite.

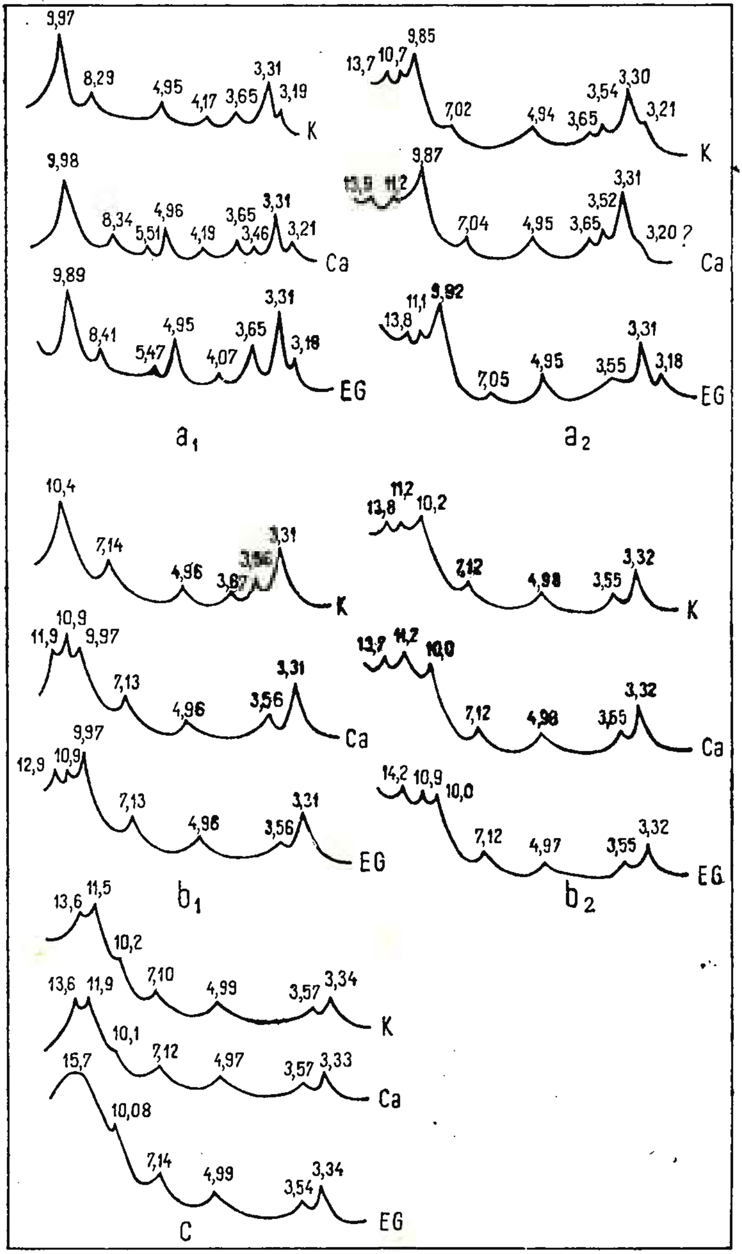

Fig. 2. — X-ray diffraction patterns of clay fractions (under 0.002 mm).

In the third phase of weathering on the diagrams appears a splitting for K and Ca-saturated fractions at 13.6—11.5 Å, and 13.6—11.9 Å respectively ; these lines may be assigned to chlorite-like minerals and a probable chlorite-illite interstratification, predominant in this fraction. The intensity of the line of illite-like minerals at 10—10.2 Å smaller than the lines of the interstratifications and chlorite-like minerals emphasizes the transformation of mica-like minerals into these 2 : 1 minerals during the weathering processes. The genesis of chlorite-like minerals may be ascribed to the mobility of aluminium ions in solutions which are fixed in the interlamellar positions and produce a dioctahedral vermiculite with aluminium and/or iron in interlayer. The broad line on the diagram of the ethylene-glycol-saturated fraction points out the possibility of this genetic phenomenon.

In addition, one must emphasize the position shift of line at 3.33—3.34 Å and the decrease of its intensity as a consequence of the partial transformation of mica-like minerals. Therefore, in this phase of weathering there occur some transformations of layer minerals into vermiculite with interlayer aluminium partially fixed and into smectite-like minerals.

A graphic image of the transformation by weathering of mica-like minerals is presented in the figure 3 which points out the appearance of the interstratifications of chlorite-like and smectite-like minerals.

For the second series, in the first stage a_2 (fig. 2) the occurrence of chlorite minerals appears on the diagrams at 13.7—13.9 Å and 7.02—7.05 Å besides the illite (9.85—9.92 Å, 4.94—4.95 Å and 3.30—3.31 Å) and the

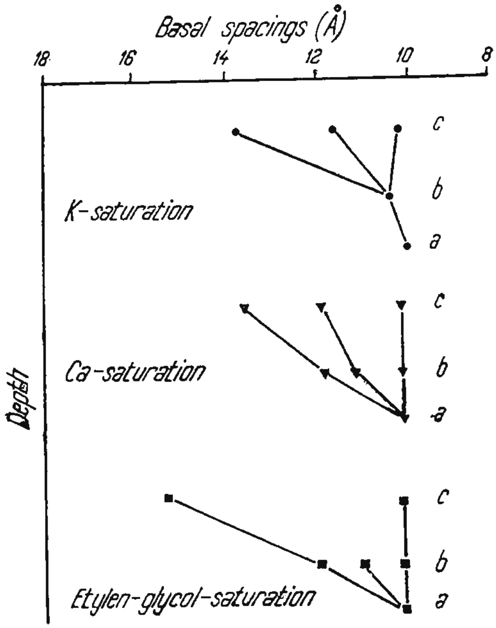

Fig. 3. — The variation of basal spacings of 2 :1 clay minerals with the weathering.

interstratifications (10.7—11.2 Å). The diffraction patterns report also a line at 3.18—3.21 Å assigned to feldspars.

In the second phase of weathering b_2 the quantity of illite minerals decreases (smaller intensity of 10—10.2 line and the shift of 003 line at 3.32 Å), while the content of the interstratifications and chlorite-like minerals increases. The kaolinite appears at 7.21 Å and his line overlies the second basal line of chlorite. The feldspars line at 3.18—3.21 Å disappeared probably because of their hydrolyse and sericitization.

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L'ÉTUDE, PAR LA MÉTHODE À L'ARGON, DE L'ÉVOLUTION DE QUELQUES FAILLES DES CARPATES ROUMAINES[1]

PAR

G. GÂȚĂ[2], M SOROIU[3]

Abstract

The Study of the Evolution of Some Faults from the Romanian Carpathians by the K-Ar Dating. The K—Ar ages of whole rock fault gouge samples collected from a certain region present a pronounced dispersion caused by the heterogeneous mineralogical composition and the different radiogenic argon retentivities of potassium-bearing minerals. By dating the clay fractions, the K—Ar age pattern is quite different, since the minerals containing inherited radiogenic argon or having poor argon retentivities have been eliminated. The K—Ar ages of clay fractions do not depend on their mineralogical composition and indicate the last event of the fault history : the last movement along the fault plane, the last thermal event which affected the fault zone and/or the last periods of mineralizing activity.

La connaissance de l'âge des gisements de minerais est d'une importance particulière pour préciser les critériums de prospection. Dans le cas des gisements hydrothermaux la datation par la méthode à l'argon des produits d'altération hydrothermale peut conduire à établir le moment de la formation de ce type de gisements. Dans ce but, de nombreuses études ont été entreprises en U.R.S.S. et aux U.S.A. en datant des échantillons prélevés des roches qui étaient en exclusivité le résultat de l'activité hydrothermale.

En 1968, Dunham et ses collaborateurs ont déterminé l'âge des minéralisations du Nord de la zone minière Pennine en datant des fractions argileuses au diamètre $<2\ \mu$, séparées des roches argilisées à la suite des processus hydrothermaux. En 1973, Ineson et Mitchell ont daté de la même manière les minéralisations de Derbyshire situées dans le Sud

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° Communiqué à la première Conférence Nationale d'Argile, Bucarest 1973.

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de la même zone minière Pennine. Lyons et Snellenburg (1971) ont démontré qu'il est possible d'établir avec une précision satisfaisante le moment où s'était produit le dernier jeu le long d'une faille lorsque les fractions argileuses du remplissage de la faille sont datées par la méthode à l'argon.

Les auteurs du présent ouvrage se sont proposés de déterminer l'âge de certains gisements produits par l'activité hydrothermale le long des plans de faille. Stimulés par les résultats présentés dans les trois ouvrages cités plus haut, les auteurs ont prélevé 35 échantillons de remplissage de faille provenant de 7 régions, ils ont séparé de ces échantillons les fractions argileuses au diamètre $<2\mu$ ou $<1\mu$, ils ont daté par la méthode à l'argon les fractions argileuses et, en utilisant la diffraction des rayons X, ils ont identifié les minéraux argileux des 20 des fractions argileuses separées.

La séparation des fractions argileuses. La détermination des âges potassium-argon. Les fractions argileuses ont été obtenues par la dispersion du matériel argileux dans de l'eau distillée, par agitation mécanique pendant 2 heures à un agitateur rotatif et par l'addition dans certains cas de l'hydroxyde de sodium comme agent de dispersion. La séparation des fractions argileuses a été faite en siphonnant après 8 ou 24 heures la suspension colloïdale contenue dans une couche superficielle dont l'épaisseur a été déterminée par la loi de Stockes.

L'eau a été evaporée à une température inférieure à 80°C.

La détermination des âges K-Ar a été réalisée en utilisant l'activation aux neutrons rapides pour le dosage du potassium (Soroiu, Popescu, 1971) et aux neutrons thermiques pour le dosage de l'argon radiogénique (Soroiu, Cerei, 1967). La précision des méthodes a été soigneusement vérifiée sur des étalons internationaux tels que P 207, LP 6 Bio etc.

L'analyse par rayons X des fractions argileuses. La composition minéralogique des fractions argileuses a été déterminée au moyen de la diffraction des rayons X, en utilisant des échantillons orientés saturés en potassium, calcium et ethylène-glycol. Dans le calcul ont été employées les intensités des lignes de diffraction pondérées ayant les positions 10 Å pour les minéraux micacés, 7,13 Å pour la kaolinite, 1,38—1,48 Å pour la chlorite et 16,0—17,5 Å, 14,5—15,4 Å et 12,8—11,6 Å pour la montmorillonite saturée en ethylène-glycol, calcium et respectivement potassium. La quantité de zéolithe a été calculée tenant compte des lignes de 7,70—8,25 Å et 5,51—5,08 Å qui indiquent des zéolithes de sodium et de calcium hydratées.

Les analyses de difraction aux rayons X ont mis en évidence que dans les fractions argileuses étudiées les minéraux micacés prépondérents (43—93%) sont accompagnés le plus souvent par la kaolinite (jusqu'à 49 %) et par une zéolithe de sodium et de calcium (jusqu'à 13 %) du type thomsonite — heulandite — chabasite. Certains échantillons contiennent de la montmorillonite (13—38 %) et rarement dans des quantités relativement réduites, de 4—10 %, de la chlorite. Les feldspaths apparaissent sporadiquement et dans des quantités sous 2% (tab. 1).

Une étude analytique des lignes de diffraction montre que le degré de cristallisation des minéraux de type micacé exprimé par le raport des intensités des lignes (001) et (002) présente des variations réduites ayant des valeurs comprises entre 1,35 et 2,64. On prouve ainsi que ces minéraux ont des structures rigoureusement ordonnées et faiblement altérées. Quoiqu'elle varie dans de larges limites, la teneur en potassium confirme cette conclusion et nous indique une gamme entière de minéraux micacés groupés conventionnellement en illites, $K < 5,56$ %, hydromicas, $K = 5,5-6,5$ % et muscovites faiblement hydratées, $K > 6,5$ %. Un diagramme représentant la quantité de minéraux micacés en fonction de l'âge K-Ar (fig. 1) indique une dispersion accentuée des points et montre que l'âge K-Ar des fractions argileuses ne dépend pas de leur composition minéralogiques.

TABLEAU 1

Analyses minéralogiques des fractions colloïdales des roches argileuses étudiées

Échantillon	Composition minéralogique, %					Type de mica	
	Montmorillonite	Chlorite	Illite	Kaolinite	Zéolite	Cristallisation	% K
VA — 25	—	—	91	—	9	1,68	6,75
VA — 31	—	—	80	10	9	1,72	6,72
VA — 32	13	—	66	12	8	1,78	5,56
VA — 33	—	—	84	7	9	2,64	5,87
VA — 34	—	—	80	11	9	1,78	6,54
VA — 35	—	—	82	9	8	2,06	5,70
VA — 36	—	—	61	39	—	2,24	5,34
9365 — T	—	—	76	13	11	2,17	6,74
9367 — T	—	—	84	8	7	2,05	5,15
9373 — T	—	—	83	9	8	1,55	7,07
9375 — T	—	—	85	6	9	1,71	5,96
CP — 76	—	9	54	24	13	1,82	8,10
CP — 78	—	4	76	14	6	1,74	7,93
CP — 79	—	10	64	15	11	1,64	8,31
EB — 10	33	—	50	10	7	1,69	7,45
EB — 14	37	—	51	10	5	1,90	5,35
EZ — 179	28	—	62	4	6	1,74	7,75
EZ — 184	38	—	43	11	8	1,51	6,24
AI — 3	17	—	33	49	—	1,35	5,80
6 C	—	—	93	—	7	2,14	5,07

Interprétation géologique des âges K-Ar des fractions argileuses. Pour l'interprétation géologique des âges K-Ar des fractions argileuses séparées du remplissage des failles le long desquelles ont circulé des solutions hydrothermales, il est nécessaire de tenir compte des processus suivants :

1) Dans le remplissage de la faille ont été inclus des minéraux au potassium arrachés des parois de la faille. Ces minéraux sont évidemment plus vieux que les événements qui se sont déroulés le long de la faille. Les âges obtenus seront donc plus grands que les âges de ces événements.

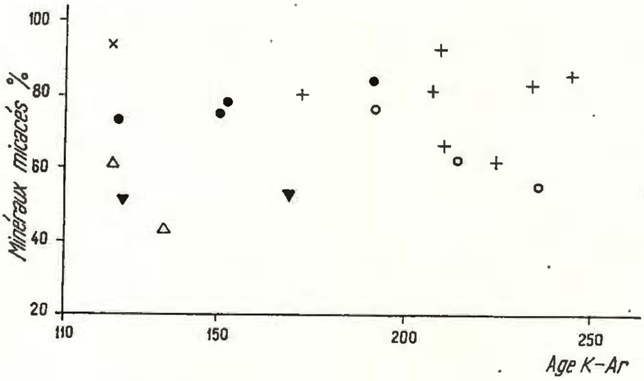

Fig. 1. — Diagramme représentant la quantité de minéraux micacés en fonction de l'âge K — Ar

2) A des moments différents, le long de la faille ont circulé des fluides minéralisateurs ou ont eu lieu des mouvements déterminés par l'évolution tectonique de la région. En dépendant de l'intensité de ces processus, il est possible que les âges K-Ar ne reflètent que les derniers événements dont le théâtre a été le plan de la faille. En d'autres termes, il est bien possible que nous n'obtenions aucune information sur les premiers événements qui y ont eu lieu.

3) Après la fin de l'évolution de la faille, la région où elle est emplacée peut subir un événement thermique régional qui conduise à l'élimination partielle ou totale de l'argon accumulé dans le réseau cristallin des minéraux aux potassium. De même, l'argon radiogénique pourrait diffuser spontanément du réseau cristallin des minéraux au diamètre moins de 2 ou 1μ. Dans ces cas les âges K-Ar seront plus jeunes que le dernier processus géologique déroulé le long de la faille.

En ce qui suit seront analysés ces processus dont on doit tenir compte lorsqu'on tâche de déchiffrer la signification géologique des âges K-Ar des fractions argileuses séparées du remplissage des failles.

Avant d'utiliser la technique de la séparation des fractions argileuses, les auteurs ont daté 13 échantillons globaux prélevés du remplissage des failles situées dans 4 régions. Ultérieurement ils ont daté des échantillons de remplissage de faille prélevés des mêmes régions, mais séparant cette fois les fractions argileuses.

En comparant les valeurs obtenues dans les deux situations, on a pu constater que l'application de la séparation des fractions argileuses a modifié considérablement le tableau des âges K-Ar. Dans une région, deux échantillons globaux de remplissage de faille ont les âges 109±3 et

143 ±4 10^6 années pendant que deux échantillons dont on a séparé les fractions argileuses ont les âges 86,0+2,6 et 76±3 10^6 années. Dans la figure 2 on a représenté sous forme d'histogramme 5 âges obtenus sur des échantillons globaux et 7 âges obtenus sur des échantillons d'où l'on a séparé les fractions argileuses, tous les échantillons étant prélevés evidemment de la même région, dénommée „region *c*''. Les échantillons globaux sont figurés par des rectangles avec des diagonales. Il faut mentionner que dans ce cas deux échantillons ont été datés dans les deux manières. Datés comme échantillons globaux on a obtenu les âges 140±4 et 183±6 10^6 années tandis que les fractions argileuses séparées de ces échantillons ont les âges 100±3 et 123±4 10^6 années. Dans la figure 3 *b* en utilisant la même notation, on a présenté toujours sous forme d'histogramme pour une région dénommée *VA* 4 valeurs d'âges obtenues sur des échantillons globaux et 11 valeurs d'âges obtenues sur des fractions argileuses.

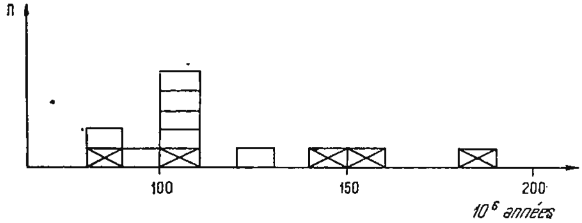

Fig. 2. — Histogramme des âges K—Ar de la région *c*.

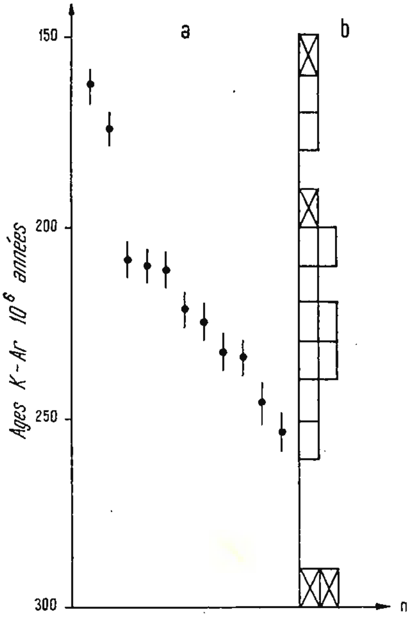

Fig. 3. — a) Diagramme des fréquences et b) Histogramme des âges K—Ar de la région *VA*.

Il est évident que pour obtenir des informations plus exactes sur l'évolution d'une faille, la séparation des fractions argileuses est absolument nécessaire. De cette manière sont éliminés les minéraux au potassium des parois de la faille inclus dans son remplissage. Dans la majorité des cas, ces minéraux „hérités" conduisent à une augmentation de l'âge. Si dans le remplissage de la faille ont été inclus des feldspaths potassiques ayant une capacité de retenir l'argon radiogénique plus faible que celle des minéraux argileux, l'âge de l'échantillon global du remplissage sera plus petit que celui de la fraction argileuse.

Comme on l'a déjà dit, 20 des 35 fractions argileuses datées ont été analysées par la méthode de la diffraction des rayons X. Les résultats de ces analyses semblent montrer que dans les fractions argileuses sont présents seulement des minéraux produits par l'activité hydrothermale ou par le simple jeu des compartiments de la faille.

Dunham et al. (1968) et Ineson et Mitchell (1973) ont indiqué que certaines voies de circulation des solutions hydrothermales peuvent être utilisées par celles-ci à maintes reprises. Ainsi on a établi que les minéralisations uranifères du Sud-Ouest de l'Angleterre se sont formées en trois étapes importantes il y a 290, 225 et 50 10^6 années. C'est à dire, selon l'oppinion de ces auteurs et de beaucoup d'autres encore, la formation d'un gisement n'est pas un événement qui a duré un bref laps de temps, mais par contre il a pu durer plus d'une ère géologique. Si nous revenons aux âges obtenus pour les fractions argileuses provenant de la région *VA*, il ressort clairement du diagramme des fréquence représenté dans la figure 3 *a*, qu'au moins deux événements ont existé dans l'évolution de la faille. Le premier a commencé il y a 253 10^6 années, tandis que le second il y a 170 10^6 années. Tenant compte du nombre réduit de déterminations il est difficile de préciser si les valeurs intermédiaires reflètent des phénomènes géologiques réels ou si elles ne sont que le résultat de la superposition du dernier événement sur le premier. Il est intéressant de noter qu'on a établi par une autre méthode de datation qu'un gisement similaire situé en Pologne a commencé se former il y a 265 10^6 années.

En ce qui concerne la capacité des minéraux argileux à un diamètre inférieur à 2 μ de conserver l'argon radiogénique dans leur réseau cristallin, les travaux de Dunham et al., et Ineson et Mitchell prouvent à coup sûr qu'au moins le long des durées géologique de 300 10^6 années cette condition est pleinement satisfaite à moins qu'un événement thermique ne se produise pas. Si un tel événement thermique a lieu, les minéraux argileux en seront fortement affectés à cause de leur diamètre extrêmement réduit. Les âges de 76 $\pm$ 3 et 86,0 $\pm$ 2,6 10^6 années proviennent d'une faille emplacée dans une zone où sont présentes des roches banatitiques dont l'âge déterminé par Soroiu et Popescu est de 70 10^6 années. Naturellement dans ce cas deux phénomènes : peuvent se supperposer: l'échauffement provoqué par les roches banatitiques et la réactivation de la faille engendrée par la mise en place de ces roches.

Dans le cas des pertes d'argon radiogénique dues à un événement thermique, on peut essayer d'appliquer la méthode graphique de l'isochrone (Harper, 1970; Harper, Sherrer, 1973; Lewis et al., 1973). Nous avons appliqué cette méthode dans le cas des échantillons de la „région *c*". Dans la figure 4 nous avons représenté ces échantillons dans un graphique ayant en abscisse les teneurs en potassium en pour-cent et en ordonnée les teneurs en argon radiogénique en unités 10^{-7} g/g. Nous avons tracé au moyen de la méthode des moindres carrés la meilleure isochrone (York, 1966, 1967). L'isochrone a une interception négative

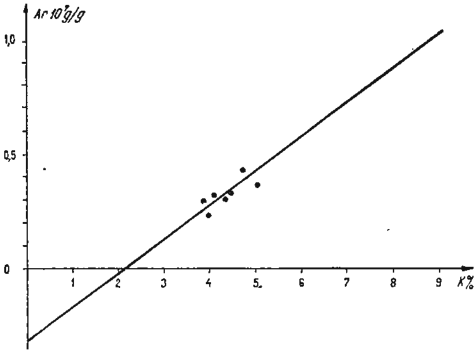

Fig. 4. — Isochrone des échantillons de la région *c*.

qui indique la quantité d'argon radiogénique perdue à la suite d'une événement thermique par tous les échantillons, indifféremment de leur teneur en potassium. Dans ce cas il serait possible que l'existence de la faille ait commencé il y a 198 ± 43 10^6 années, mais la faille a subi un intense événement thermique il y a 70 10^6 années très probablement à cause de la mise en place des banatitites. Donc si la méthode proposée par Harper est correcte (Wilson, 1971), quoique les âges individuels des échantillons soient compris entre 81 ± 3 et 123 ± 4 10^6 années, on peut déduire de la pente de l'isochrone l'âge d'un événement de l'évolution de la faille qui est considérablement plus grand que le plus grand âge individuel des échantillons.

Avant de conclure, nous voudrions mentionner les résultats très encourageants obtenus par Hofmann (1971) dans la datation des argillites de Pensylvanie. Les âges K-Ar ainsi que les âges Rb-Sr des fractions au diamètre inférieur à 2 μ séparées des argillites — 350 10^6 années — indiquent l'âge de la diagenèse tandis que les âges des fractions plus grandes que 2μ — 500 10^6 années — indiquent l'âge des roches qui sont à l'origine des argillites.

Des considérations exposées il ressort l'importance présentée par la datation potassium — argon de certaines fractions argileuses dans la prospection des gisements de minerais et de pétrole.

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CORRELATIONS BETWEEN REFLECTANCE SPECTRA AND THE CHEMICAL COMPOSITION OF APTIAN CLAYS IN SOUTH DOBROGEA[1]

BY

RADU LĂCĂTUŞU[2]

Abstract

Correlations between Reflectance Spectra and the Chemical Composition of Aptian Clays in South Dobrogea. The Aptian clays from South Dobrogea present a lot of hues. For a proper establishment of the colour measurements were carried out in the visible spectrum by defining the main components of the colours. The statistical correlations between these components and the chemical compositions represented by organic matter and the chromophores (Fe^{2+}, Fe^{+3}, Cr, Co, Ni, Mn) were defined.

Colour is one of the most important characteristic of rocks, often helping to solve problems related to their chemical composition, to determine environment conditions in which evolution of rocks took place, and finally to determine their genesis. However, to achieve these objectives the simple macroscopic determination of colour is not enough. Accurate measurments have to be carried out using instrumental methods, one of which is spectrophotometry.

Photometric determinations of colour had been first applied to geology in 1927 by the American researcher Grave. The method had been later developed by several Russian scientists: Grum-Grjimailo (1945, 1959), Slivko (1957), Dancev (1956, 1958).

This paper presents the results obtained by the spectrophotometric study of the colour of Aptian clays in South Dobrogea and the correlations existing between colour and chemical composition.

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[1] Reported in the session from November 1973.

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Materials and Methods of Researches

Researches were based on the Doncev method (1956) by which reflectance capacity of samples is measured by comparison with the reflectance capacity of a white borite plate. Measurements are obtained with the help of a set of filters having different wavelenghts, characteristic of the colours in the visible spectrum. When plotting in a system of rectangular axes, the wavelenght on the abcissa and the reflectance capacity in the ordinate, reflectance spectra of the sample are obtained. The characteristic ordinate of the curve's lower point represents the level of white (w). The difference between maximum and minimum values represents the amount of colour (f), while the difference between 100 and the sum of ($w + f$) represents the amount of black (s). In Dancev's works the amount of colour is labelled with the letter v (from the German adjective voll = total). In the present study it has been labelled with the letter f (from the German word farbe = colour), this labelling being considered more accurate.

In the above working method the interval of the visible spectrum, from 380 to 750 nm has been divided into six zones characteristic of the basic colours as follows: 380—420 nm — violet; 420—490 nm — blue; 490—535 nm — green; 535—595 nm — yellow; 595—630 nm = orange; 630—750 nm — red. The contribution of each of these colours to the total amount of colour has thus been determined.

Measurements were achieved with a spectrophotometre Karl Zeiss Jena VSU—1 to which a special device for reflectance was added. Clay samples were dried at room temperature, a perfectly plane surface was obtained by pressing. Calibration of the spectrophotometre for each wavelenght was made: for 100% T with an immaculate white surface and with a block body for 0% T.

Results and Discussions

In South Dobrogea the Aptian appears to have developed in two facies: continental-lacustrine and marine (Chiriac, 1961). One of the basic lithologic components particularly for the deposits of the continental-lacustrine facies is clay, with a large variety of colours ranging from white to black. Between these extremes of the chromatic scale, other prevailing colours were: rose, yellow, reddish yellow and violaceous.

Their distribution in the ternary diagram of the colour's components as for their percentage repartition in the two facies is illustrated in figure 1. Notice the prevalence of yellow, rose and white in the continental-lacustrine facies and of yellow and reddish yellow in the marine facies.

For groups of colours and for the whole, the three basic components of colours are distributed as shown in table 1.

Two main causes account for the appearance of these colours: presence of organic matters and of certain chromophores: Fe^{2+}, Fe^{3+}, Mn, Cr, Co, Ni.

Influence of Organic Matter. The relationship between the presence of organic matters and dark colours (black, brown) is well known. This is also true for the clays studied in this paper and is supported by the relationship between log (w/s.10) and the organic matter content. Data can be checked by an exponential type curve (fig. 2), with a very high correlation ratio ($\eta = 0.818$) at 34 degrees of freedom. Such a curve may be divided into three parts of which the first corresponds to the ratio values higher than — 1.00 and to an organic matter content lower than 0.5 %, the second represents the interval from 1.00 to 0.08 of the ratio log (w/s.10), corresponding to an organic matter content of 0.5 % to 3.5 %, while the last one corresponds to ratio values lower than 0,00 and an organic matter content higher than 3,5 %.

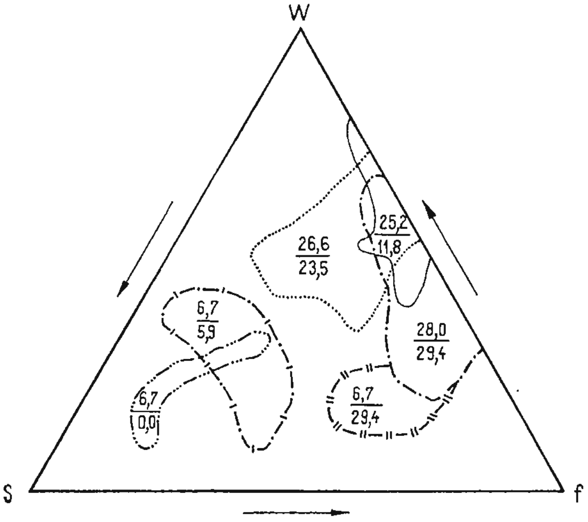

Fig. 1. — Colour distribution of Aptian clays of South Dobrogea and their percentage distribution in continental-lacustrine facies (numerator) and in the marine facies (denominator) ; ——— white; . . . rose ; — . — . — yellow ; —"— raddish yellow ; –/—.—violaceous ; — . . — black.

TABLE 1

Basic Components of Aptian Clays in South Dobrogea

Colour of clays	*w* %	*s* %	*f* %
White	77.5	0.0	22.5
Rose	53.4	0.7	36.9
Yellow	39.5	6.7	53.8
Reddish yellow	17.1	13.0	69.9
Violaceous	41.0	24.0	35.0
Black	22.6	59.5	17.9

Influence of chromophores has been investigated on the base of correlations between reflectance spectra, characteristic of chromophores and their concentration in iron samples. Colour of Fe^{3+} compounds vary from yellow to red, depending on the level of hydration, while Fe^{2+} compounds exhibit, green, violaceous and black. Most of the iron contained in the Aptian clays of South Dobrogea appears in the form of Fe^{+}, thus of the total amount of Fe_2O_3, the percentage of FeO reaches 9.5 % in black clays, 2.9 % in violaceous clays, 1.0 % in rose clays, 6.9 % in the yellow reddish, 0.5 % in the white and 3.6 % in the yellow ones.

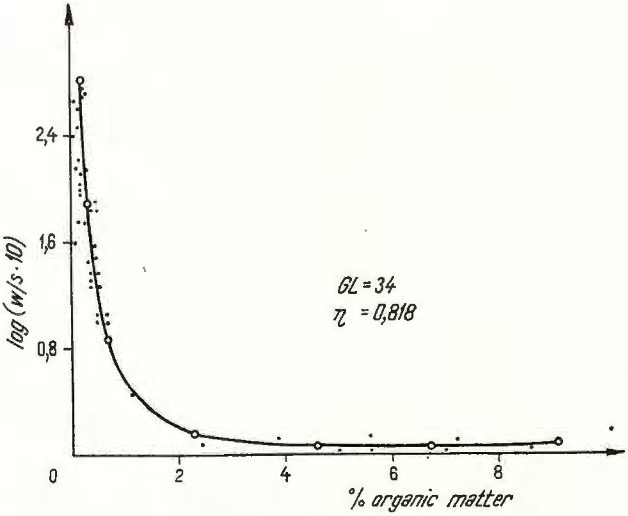

Fig. 2.—Relationship between the ratio log (w/s.10) and % organic matter content of Aptian clays in South Dobrogea.

In the statistical computation of correlations it has been introduced under the total form of Fe_2O_3.

Correlations between reflectance spectra in the 535—750 nm, characteristic of yellow, orange and red — and Fe_2O_3 content, are corroborated by the parabolic equations illustrated in figure 3.

Notice the similarity between white clay and rose clay curves, the latter being shifted to the right with about 1—2 units and exhibiting a correlation ratio with 0.1 higher at the same number of degrees of freedom. Black clay curves are located at about the same interval. Variations of yellow, reddish yellow and violaceous clays are located in the much larger intervals of the x and y parameters. High values correlation ratio, have made possible to estimate the percentage influence exerted by the presence of iron on the colour of rocks.

Chromium is one of the strongest chromophores and may be found either as Cr^{3+}, giving green compounds, or as Cr^{6+} giving yellow compunds. Correlations between reflectance spectra in the green interval (430 — 535 nm) and those in the yellow interval (535—595 nm) and chrome content are direct and linear. They are statistically proved as rose, yellow and violaceous clays in the green interval of the spectrum, and as white, yellow and reddish yellow ones in the yellow interval (table 2).

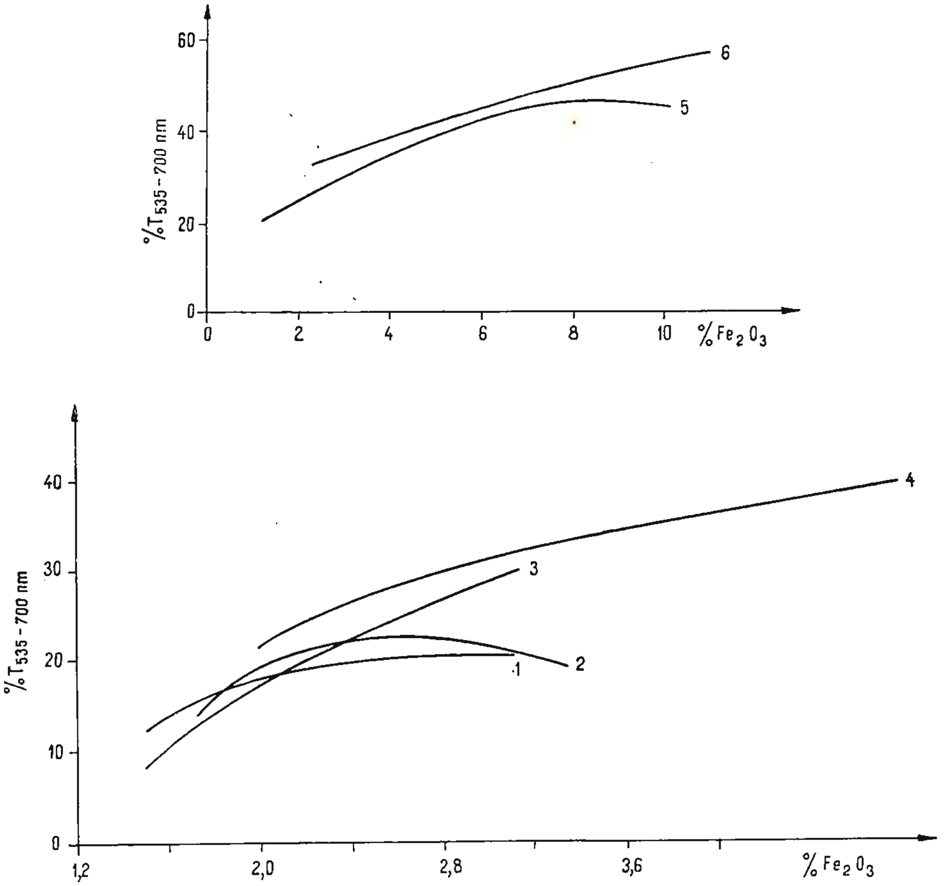

Fig. 3. — Regression of reflectance spectra in the 535—750 nm as related to iron content of Aptian Clays in South Dobrogea.

1, white clays, $y = -12{,}0417 + 22{,}915x - 3{,}889x^2$; GL = 16; $\eta = 0{,}639$; 2, rose clays, $y = -37{,}8624 + 44{,}0956x - 8{,}0359x^2$; GL = 17; $\eta = 0{,}743$; 3, black clays, $y = -26{,}6742 + 28{,}8132x - 3{,}4197x^2$; GL = 6; $\eta = 0.997$; 4, yellow clays, $y = -3{,}8499 + 15{,}3644x - 1{,}3071x^2$; GL = 22; $\eta = 0{,}896$; 5, violaceous clays, $y = 12{,}9346 + 6{,}5490x - 0{,}3069x^2$; GL = 6; $\eta = 0{,}997$; 6, reddish yellow clays, $y = 20{,}0091 + 5{,}2573x - 0{,}2005x^2$, GL = 6; $\eta = 0{,}999$.

Presence of cobalt and of its combinations is generally related to blue. Direct, linear correlations between the blue interval of the spectrum (420—480 nm) and cobalt content have been determined for all groups of clays, except the yellow. Highest percentage of cobalt contribution (9.8) was recorded for the violaceous colour (table 2).

TABLE 2

Influence of Chromophores on the Colour of Aptian Clays in South Dobrogea

Colour of clays	GL	% T 535–750 nm Fe_2O_3		% T 490–535 nm Cr		% T 535–595 nm Cr		% T 420–490 nm Co		% T 490–535 nm Ni	
		η	percentage of the rock's colour	r	percentage of the rock's colour	r	percentage of the rock's colour	r	percentage of the rock's colour	r	percentage of the rock's colour
White	16	0.639	19.0	—	—	0.593*	2.0	0.620**	3.5	—	—
Rose	17	0.743	22.5	0.534*	3.7	—	—	0.480*	4.2	0.510*	1.5
Yellow	22	0.896	42.0	0.549**	1.6	0.651***	8.0	—	—	0.422*	2.2
Reddish yellow	6	0.997	51.0	—	—	0.942**	8.4	0.823*	5.3	0.750*	5.2
Violaceous	6	0.997	26.2	0.776*	2.9	—	—	0.882**	9.8	—	—
Black	6	0.999	14.2	—	—	—	—	0.896**	2.7	—	—

Whereas nichel appears to contribute the least to the colour o rocks (table 2), and only for rose, yellow and reddish yellow clays

No direct correlations between manganese content and reflectance spectra could be determined. However, higher manganese contents of rose clays and the reverse linear correlation between the *w*/*f* ratio and manganese content of rose clays ($r = -0{,}629^{***}$, $GL = 25$), point to manganese contribution to the rose colour of rocks.

Conclusions

1. It is suggested to symbolize the level of colour for a three compounds system (white, black and colour) with the letter *f* (from the German „farbe" — colour).

2. The visible spectrum in the 380—750 nm has been divided into 6 zones characteristic of the basic colours : violet, blue, green, yellow, orange and red. It becomes thus possible to determine the contribution of each colour to the total colour of the rock.

3. Aptian clays of South Dobrogea exhibit the following colours : white, rose, yellow, reddish yellow, violaceous and black. Yellow, rose and white prevail in the continental-lacustrine facies, while yellow and reddish yellow prevail in the marine facies.

4. These differences of colour in clays are due to the presence of organic matters and to the existence of certain chromophores (Fe^{2+}, Fe^{3+}, Cr, Co, Hi, Mn). These findings are supported by the highly significant correlations appearing between log (w/s.10) and organic matter content (fig. 2) and correlations between reflectance spectra of the various zones of the visible spectrum and chromophore content (fig. 3, tab. 2).

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L'ÉTUDE MINERALOGIQUE ET GÉOTECHNIQUE DU GLISSEMENT DE TERRAIN DE MURGEŞTI-MOTOHANI, VALLÉE DE CALNAU[1]

PAR

LUCIAN MATEI, VICTORIA ADELA POJAR[2]

Abstract

Landslide along Calnau River. Mineralogical and Geotechnical Study. The landslide near Murgeşti on the Calnau river took place on the right hillside and affected the Levanthine sediments composed by varveled clay and clayey marl with sand. The chemical and mineralogical studies carried on clay soils related with geotechnical tests pointed out the importance of mineralogical changes in the fraction $<2\mu$ as in the release of the landslide as in the fixing in the vertical profile of landslide surface. In the mean time the analysis pointed out the dependence of the physical-mechanical properties of the clayey soils in conection with their mineralogical composition. Thus, the deposits in which the fraction $<2\mu$ is preponderant illite-montmorillonite the variations in composition between 5–10 % for one of them modify substantially the rate free water-adsorbant water and so the Atterberg limits, the residual strenght and Skempton activity coefficient are changed. So, at Murgeşti the establishment of landslide surface and their differentiations in point of view of their activity is depending on the alteration process of montmorillonitic type, more advanced in this areas of the vertical profile.

L'exécution en parallèle des études minéralogique et géotechniques sur un nombre des échantillons prélevés dans quelques profils qui sectionnent un glissement de terrain, conduit à préciser des relations de dépendence entre la composition minéralogique et les propriétés physico-mécaniques des roches et aussi à préciser les causes intimes qui participent au départ du phénomène.

Dans les cas des glissements du terrain, les changements compositionnels des matériaux argileux sont liés au procesus d'altération qui,

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[1] Communication à la première Conférence du Groupe Roumain d'Étude des Argiles, Bucarest, novembre 1973.

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à sont tour, est dû à la circulation des solutions des eaux dans le massif, cause principale du départ du phénomène.

Le glissement de terrain de Murgeşti-Motohani emplacé dans le versant droit de la Vallée de Calnau s'étend sur une superficie d'environ 100 hectares entre la crête du versant et la berge de la vallée (fig. 1).

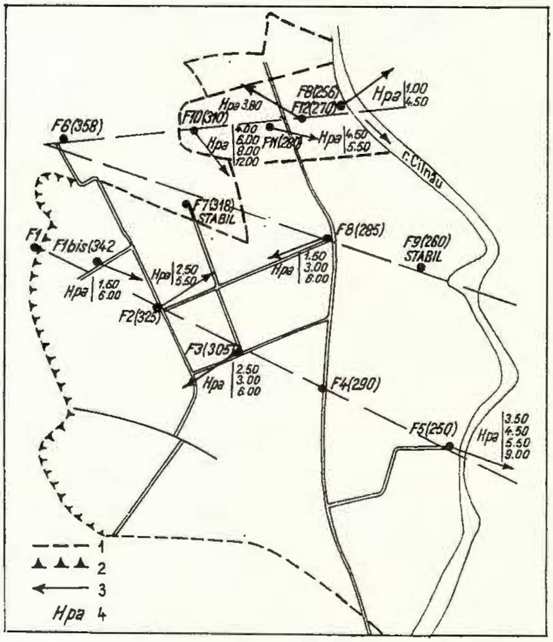

Fig. 1.—La carte avec l'emplacement des forages et les vecteurs des mouvements.
1, la surface affectée du glissement; 2, la crête; 3, les vecteurs des mouvements; 4, les profondeurs des surfaces du glissement.

Le phénomène affecte une série des dépôts de l'âge Levantin qui sont composés d'une alternance des argiles poudreuses — sableuses avec une epaisseur totale de 11—12 m. Elles sont disposées en couches de 20 à 30 cm. Entre celles-ci sont intercallés des horizons minces de sables et de sablespoudreux. Sous ce paquet, délimité en base par une surface de glissement majeure, apparait une série d'argiles marneuses avec un contenu de $CaCO_3$ compris entre 12—21%.

L'étude complexe du glissement de terrain initiée dans le but de dechiffrer des causes du phénomène aussi bien que pour trouver des méthodes pour la stabilisation, a été abordée par l'intermédiaire d'un réseau de forages d'où nous avons prélevé des échantillons de 0 à 14 m de profondeur. Les fonds des forages sont encastrées dans les roches stables au-dessous de toutes les surfaces de glissement.

La poursuite des mouvements horizontaux a été exécutée par des forages équipés avec des tubes „Slope" pendant le printemps de l'année 1971. Les mesurages qui sont effectués avec l'appareil „Enclinomètre", construit par l'Institut d'Études et de Recherches pour les Améliorations Foncières, font découvrir l'existence de quelques surfaces de glissement et leur activité est essayée par des déterminations chimico-minéralogiques et géotechniques.

Ces surfaces de glissement emplacées entre 1,00 et 12,00 m de profondeur (tab. 1) et le nombre maximum des surfaces superposées comptent trois.

TABLEAU 1

Les niveaux des eaux souterraines et les profondeurs des surfaces de glissement mesuréls en forages

No. forage	Niveaux des eaux souterraines (m)		Les profondeurs des surfaces de glissement (m)	Observations
	minimes	maximes		
1	0,10	—		Terrain stable
1bis	0,10	4,00	1,50 ; 6,00	
2	1,60	5,30	2,50 ; 5,50	
3	0,60	1,00	2,50 ; 3,00 ; 6,00	
4	0,20	1,60	—	Forage obstructionné
5	1,50	4,80	3,50 ; 4,50 5,50 ; 9,00	
6	3,70	5,50	—	Terrain stable
7	1,40	3,20	—	Terrain stable
8	0,60	3,00	1,50 ; 3,00 ; 6,00	
9	3,00	4,50	—	Terrain stable
10	0,40	2,00	4,00 ; 6,00 8,00 ; 12,00	
11	1,40	1,60	4,50 ; 5,50	
12	1,20	3,00	3,80	
13	0,00	1,50	1,00 ; 4,50	

Pour la caractérisation de la composition minéralogique de la fraction au-dessous de 2 microns nous avons executé des analyses diffractométriques des rayons X, des analyses thermiques différentielles, des spectres d'absorbtion en infrarouge, des études avec le microscope électronique (fig. 2, 3) et aussi des analyses chimiques pondérales et rationnelles et des dosages des substances de liaison.

Les études cantitatives exécutées sur la fraction $<2\mu$ prouvent une différence en profil vertical des pourcentages de la participation des composants argileux. Marqués par la variation de l'intensité des reflexes des rayons X et par la grandeur des bandes d'absorption en infrarouge, ces changements calitatifs sont :

Les dépôts stables au-dessous de la surface de glissement située à 12,0 m de profondeur ont un fraction $<2\mu$ avec la suivante compositions : illite 76—80%, montmorillonite de 20—23% et kaolinite de 3—5%. Vers la surface du terrain les rapports calculés en pour-cent montrent une croissance quantitative de la montmorillonite jusqu'à

40—43% pour les échantillons qui proviennent de 6,00—8,00 m de profondeur.

Depuis 2,0—4,0 m de profondeur le pourcentage de la montmorillonite est compris entre 62—68% et sa croissance implique une diminution de la quantité de l'illite jusqu'à 36 — 30 %. La kaolinite garde une proportion constante de 2—3%. En même temps l'apparition d'un minéral interstratifié de type illite-montmorillonite est remarquée dans la partie supérieure du profil.

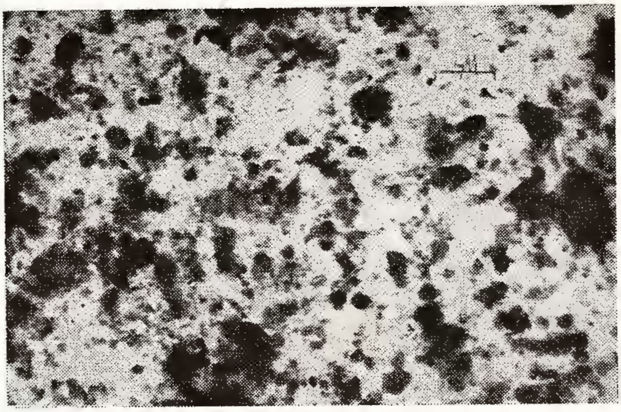

Fig. 2. — L'image enrégistrée avec le microscope électronique ; forage no. 2, profondeur 9,0 m.

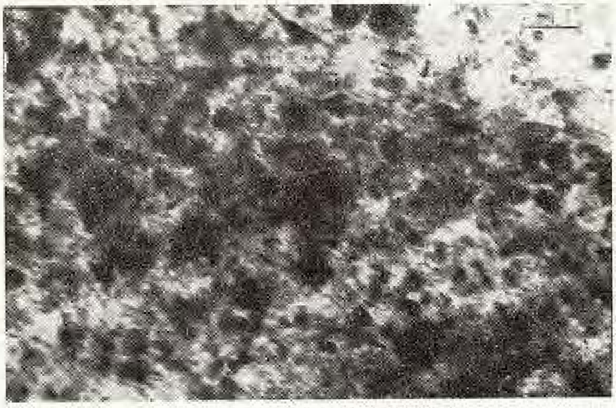

Fig. 3. — L'image enrégistrée avec le microscope électronique ; forage no. 2, profondeur 5,5 m.

Les analyses aux rayons X marquent l'existence de ce minéral interstratifié par une réflexion discrète située à 10,0—11,0 A. D'après les indications de Brindley ce pick atteste que les couches expendables ne deppassent pas une proportion de 5—15% dans la structure interstratifiée.

Sur les spectres infrarouges (fig. 4) l'augmentation de la quantité de la montmorillonite se remarque par l'accentuation des bandes situées à 630, 850, 1 040 et 1 100 cm^{-1}.

D'après le développement des bandes à 800 et 824 cm^{-1} on a apprécié la présence du polymorphe 2M de l'illite (Oinuma, Hayashi). Parfois, la possibilité d'identifier le polymorphe est annulée par l'absorption forte du quartz à 800 cm^{-1}.

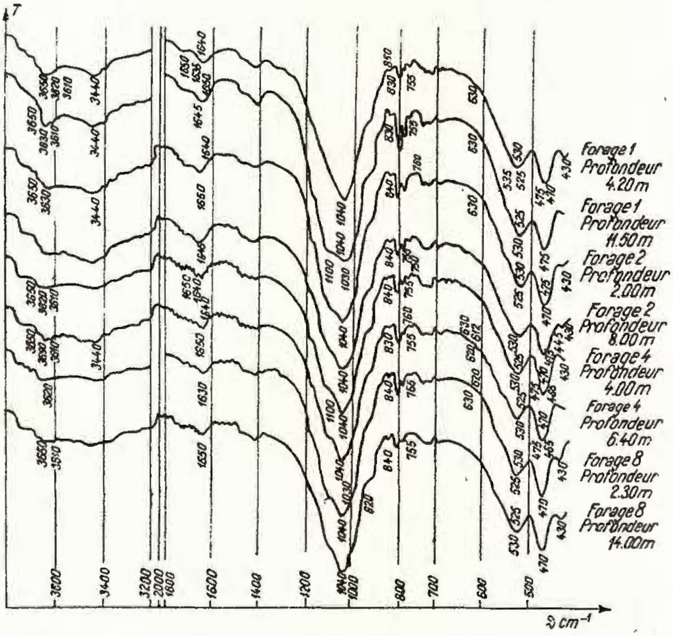

Fig. 4. — Spectres d'absorption en infrarouge.

Les analyses chimiques pondérales et rationnelles prouvent la croissance du degré d'altération des minéraux argileux vers la surface du versant par l'augmentation de la quantité des sesquioxydes et aussi par le changement des rapports interoxydiques entre les cations repartis en positions octaédriques et ceux qui représentent le complexe d'échange.

Ainsi, les échantillons qui sont prélevés d'une profondeur comprise entre 2,0—6,0 m, montrent une teneur en MgO de 2,10—2,40%, dans les analyses pondérales de la fraction $<2\ \mu$.

L'altération du type montmorillonitique des dépôts superficiels, dans lesquels sont localisés la majorité des surfaces de glissement, explique la croissance de la capacité d'échange jusqu'aux valeurs de 31—36 ml/100 g pour les échantillons collectés au-dessous de 8,0 m de profondeur.

En même temps, on constate le changement des rapports quantitatifs entre les cations échangeables : la croissance de la quantité des cations Ca et Mg de 12 ml/100 g à 16 ml/100 g au détriment des cations Na et K.

Le processus d'altération est remarqué aussi par les courbes des analyses thermique-différentielles sur lesquelles on a observé le développement du crochet endothermique compris entre 905—920°C (fig. 5) pour les échantillons qui proviennent d'une profondeur de 2,0—8,0 m. L'allure générale de ces courbes, rappelle celle de la montmorillonite intermédiaire (J. Lucas).

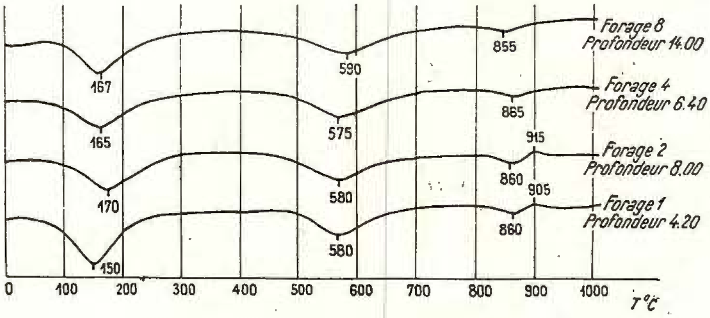

Fig. 5. — Les courbes des analyses thermiques différentielles.

Toutes ces caractéristiques minéralogiques expliquent les propriétés physico-mécaniques des roches argileuses, expression des causes minéralogiques du départ du glissement de terrain ainsi que de la localisation des surfaces du glissement.

L'analyse des paramètres mécaniques (tab. 2). montre des valeurs dépendentes des variations en teneurs mentionnées, quelques dé-

TABLEAU 2

Les parametres physico-mecaniques des roches du glissement du terrain de Murgeşti-Motohani

No. crt.	Forage	Profondeur	N %	P %	A %	% < 2μ	W	W_p	W_1	I_p	Ac	tg $\varphi_{res.}$
1	1	2,00	24	28	48	36	10,8	13,7	53,5	39,8	1,11	—
2	1	6,00	17	26	57	40	11,6	13,8	60,2	46,4	1,104	
3	3	2,00	28	30	42	30	22,4	12,3	48,3	36,0	1,20	0,069
4	3	4,00	10	50	32	22	19,7	13,7	53,0	39,3	1,79	0,087
5	4	6,50	12	36	52	36	26,0	14,1	57,0	42,9	1,19	0,194
6	5	2,00	22	36	42	26	15,0	13,2	52,0	38,8	1,49	0,424
7	5	6,00	14	46	40	28	17,0	13,3	43,0	29,7	1,00	0,324
8	6	6,30	12	41	47	33	32,0	14,8	60,5	45,7	1,28	0,069
9	6	10,00	4	50	46	26	23,1	13,9	50,0	36,1	1,38	0,577
10	6	11,50	6	53	41	25	26,4	16,4	72,0	55,6	2,22	—
11	10	2,00	24	37	39	26	22,4	10,7	44,9	34,2	1,31	0,230
12	1	10,00	40	26	34	22	16,6	—	—	—	—	0,466
13	3	10,00	30	18	52	38	24,0	—	—	—	—	0,176
14	5	8,00	36	27	37	27	20,0	—	—	—	—	
15	6	12,50	6	29	65	38	—	—	—	—	—	0,531
16	8	10,00	9	39	52	34	23,7	—	—	—	—	0,249
17	9	6,00	37	35	28	22	20,1	—	—	—	—	0,176
18	10	8,50	3	72	25	18	—	—	—	—	—	0,249
19	10	14,00	6	66	28	18	—	—	—	—	—	0,212
20	11	4,00	41	43	16	15	21,6	—	—	—	—	0,267
21	13	4,00	47	32	21	9	17,9	—	—	—	—	0,249

tours s'expliquent par la présence des minéraux clastiques et d'autres matériaux de dillution.

Ainsi, le coéfficient d'activité de Skempton (Ac) varie entre 1,11—2,22. La dernière valeur représente un point singulier, mais l'échantillon analysé provient d'une surface de glissement très active. La majorité des matériaux étudiés peuvent être classés dans les groupes d'activité 3 et 4, c'est-à-dire „normal" ou „actif". Grim (1968) renferme dans le groupe „normal" ($Ac = 0{,}75-1{,}25$) les minéraux comme : attapulgite, chlorites et quelques montmorillonites et illites. Dans le groupe „actif" ($Ac = 1{,}25-2{,}00$) un seul minéral : la montmorillonite. Les montmorillonites qui sont saturées de sodium ont un coefficient $Ac = 2{,}00-3{,}00$ représentatif pour le groupe „très actif".

Les résultats de nos essais sont en concordance avec ces indication expliquant la localisation des surface de glissement. En général, la position de ces surfaces suivie les profondeurs où existe une concentration de la montmorillonite.

Nous avons exécuté aussi des essais de la résistance au cisaillement (tg $\varphi_{\text{rés}}$). Les échantillons montrent des valeurs entre 0,06—0,57. Plus ou moins, les valeurs appartiennent aux échantillons riches en montmorillonite, donc provenant des zones superficielles d'altération ou des autres zones qui manifestent un enrichissement de la montmorillonite. Nos données de la résistance au cisaillement sont interprétées d'après les résultats publiés par Kenney (1967) qui a précisé les valeurs suivantes pour les minéraux argileux : kaolinite — 0,27 ; illite — 0,29 —0,49 ; Na — montmorillonite 0,17—0,18 ; attapulgite — 0,57.

En conclusion, on peut noter que la valeur de l'angle $\varphi_{\text{rés}}$ semble plus affectée par la composition minéralogique que par la granulométrie et la plasticité ; finalement la montmorillonite est le constituant qui conduit aux plus mauvaises caractéristiques, importantes pour la stabilité des versants.

La recherche des relations entre les paramètres mécaniques et la composition minéralogique a été effectuée aussi par quelques essais recommendées par Pilot, Amar et Le Roux (1970).

L'examen de la variation de l'indice de plasticité (I_p) suivant la limite de liquidité (W_L) conduit au diagramme (fig. 6) sur lequel on peut définir la composition minéralogique des échantillons ; tous les points indiquent une composition de type illite-montmorillonite. Les échantillons riches en montmorillonite possèdent les plus grandes valeurs des I_p et W_L.

Le diagramme suivant (fig. 7) montre suffisamment la manière dont la minéralogie intervient sur les valeurs des $\varphi_{\text{rés.}}$; en fonction du degré d'altération (dans notre cas), de la quantité de la montmorillonite, ce diagramme démontre que les valeurs de $\varphi_{\text{rés.}}$ sont de plus en plus faibles vers la surface du terrain. Nos résultats confirment la conclusion sur la liste des minéraux argileux, dans le sens des valeurs décroissantes de $\varphi_{\text{rés.}}$ comme l'illite, la kaolinite et la montmorillonite (Kenney, 1967).

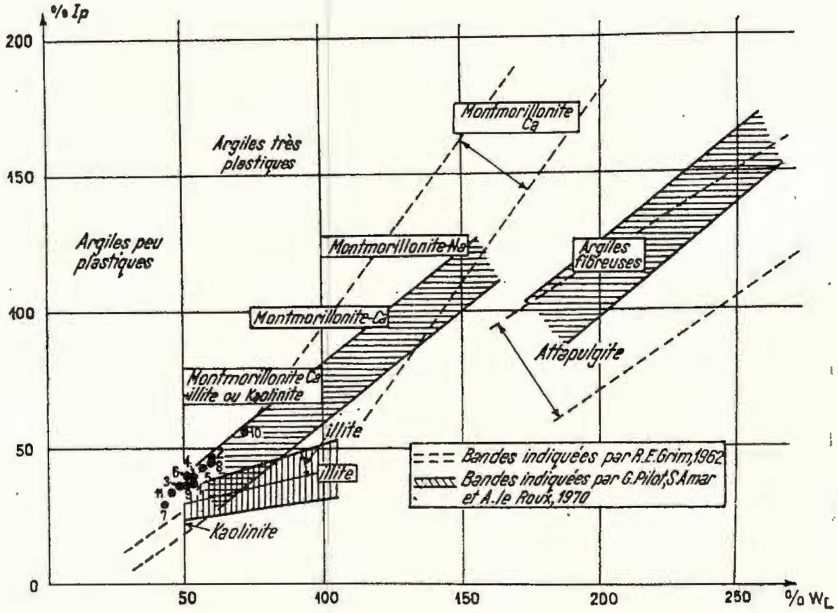

Fig. 6. — Relation entre l'indice de plasticité (I_p) et la limite de liquidité (W_L).

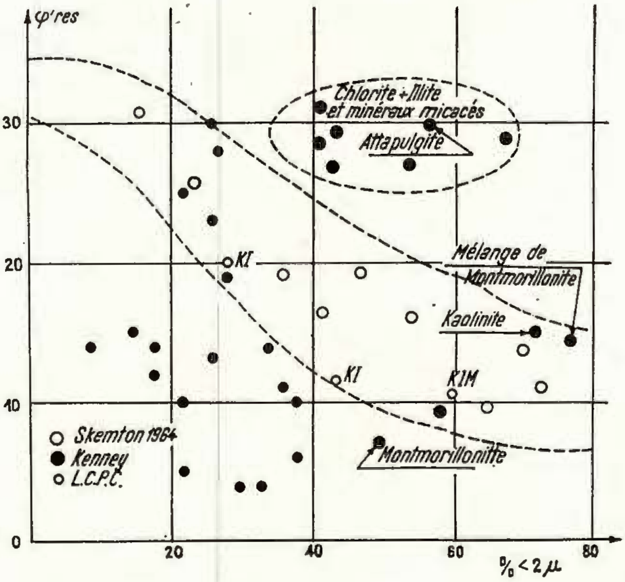

Fig. 7. — Relation entre l'angle de frottement résiduel ($\varphi_{rés.}$) et le pourcentage d'argile (% $<2\mu$).

Une conclusion presque similaire, dans ce point de vue, est obtenue par la poursuite de la relation entre l'indice de liquidité (I_L) et la cohésion non-drainée (C_u), où nos points se groupent dans la zone des minéraux de type 2 : 1 (fig. 8). Mais, dans ce cas un rôle très importants revient à la structure de la roche et à présence des autres minéraux.

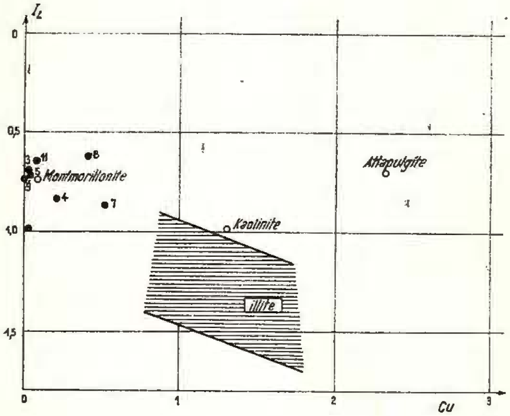

Fig. 8. — Relation entre l'indice de liquidité (I_L) et la cohésion non-drainée (C_u).

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HYDROTHERMAL TRANSFORMATION PHENOMENA IN THE ANDESITE OF PILIŞCA (HARGHITA MOUNTAINS)[1]

BY

GHEORGHE NEACŞU, TIBERIU URCAN[2]

Abstract

Hydrothermal Transformation Phenomena in the Andesite of Pilişca (Harghita Mountains). The mineralogical analysis in diffrerent hydrothermal transformation phases of an andesite containing biotite and hornblende from the Harghita Mountains underlines the close relation between the initial mineralogical composition and the results of the transformation phenomena. Using the Roentgen-structural analysis for the different major mineralogical components, one can draw the conclusion that the transformations followed the next way: hornblende → montmorillonite; biotite → hydrobiotite; feldspar → kaolinite. Independently of the nature of the solutions that have circulated in the country rock, these solutions have destroyed the initial crystalline network and afterwards they have reorganized the new networks in the same space, preserving the initial crystallographical forms.

Introduction

Andesite with biotite and hornblende of Lower Quaternary age spread on a large surface to the south of the Harghita Mountains, west of the town of Tuşnad-Băi. The andesite is generated by a volcanic mechanism that is located in the Pilişca Mare Peak Zone, hence the name — andesite of Pilişca.

The existence of some phenomena of hydrothermal transformation, that have alterated this andesite on large surfaces, determined us to focus our attention on the alteration, and to study their effect both on the principal mineral components and on the entire rock.

The natural openings and some mining works performed in the andesite of Pilişca allowed us to collect the material necessary for the present paper.

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[1] Communication presented at the Meeting November 30th, 1973, Bucharest.

[2] Enterprise for Geological Prospecting, str. Caransebeş 1, Bucharest.

The Transformation Phases

The field observations showed a gradual transformation from the fresh andesite to the entirely transformed andesite, with its structure completely destroyed.

The degree of hydrothermal claying increases gradually to the volcanic furnace, that is in the zone in which the hydrothermal solutions have circulated, and it is accompanied by the change of the colour from dark grey to light white and the change of the rock hardness. The more intensive the hydrothermal transformation phenomena are, the less hard the rock becomes. At the rocks with the same degree of transformation, the higher the hardness is, the higher the content of secondary quartz in the rock is.

In order to follow the progress of the transformation phenomena we performed a mineralogical study with X-rays on individual minerals and on the entire rock, unaltered, and in 2 phases of alteration : moderate and intensive. We noticed :

1. Fresh andesite with biotite and hornblende (unaffected by hydrothermal transformations).
2. Moderately alterated andesite with biotite and hornblende, with relict structure (affected partially by hydrothermal solutions). First phase of alteration.
3. Intensively alterated andesite with biotite and hornblende, with the initial structure destroyed (entirely transformed). Second phase of alteration.

The development of the main component minerals of the rock has permitted the perfect separation with the clip of the feldspar, biotite and hornblende crystals from the unaltered rock and from the hydrothermally transformed rock thus obtaining monomineral samples.

Besides the study of the separated monominerals, general features of the rock were taken into consideration, diffractograms being effectuated on fraction smaller than 10 microns.

The unalterated rock is compound of the following main components : feldspar (major), biotite, amphibole and glass.

The feldspar, amphibole and biotite were selected from the fresh andesites that were analysed by X-ray (fig. $1_{1,3,5}$). The plagioclase feldspar is an andesine-oligoclase, the clyno-amphibole is a green hornblende, that account the position of the reflexions tends to the composition of a grammatite, and the biotite is a variety which contains more iron (lepidomelan-siderophyllite).

The argillaceous fraction smaller than 10 microns in the first phase of alteration is mainly made up of kaolinite and less of argillaceous mica. In the second phase of alteration the oligoclase-andesine transforms into kaolinite blended with little quartz (fig. 1_2), the green hornblende transforms completely into Ca-montmorillonite and a small amount of quartz (fig. 1_4), and the biotite transforms into hydrobiotite blended with small quantities of kaolinite, illite and quartz (fig. 1_6).

In the second phase of intense alteration the argillaceous fraction smaller than 10 microns of the rock hydrothermally transformed contains illite and less kaolinite and quartz. The biotite in the second phase of alteration is completly transformed into some and some kaolinite (fig. 1_7).

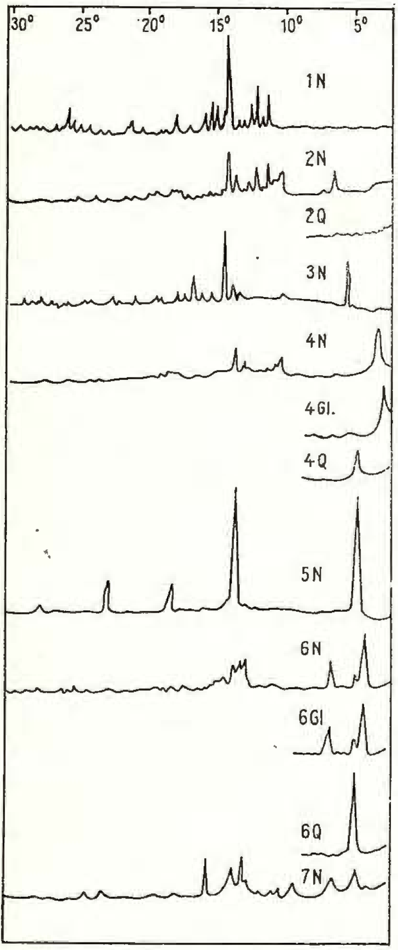

Fig. 1. — The diffractograms of the feldspar, amphibole and biotite, fresh and alterated in the andesite of Pilişca.

It is only the feldspar which remains in small amounts in this phase among the major component minerals of the fresh rock.

The entire diagram of the transformations and the increase per cent of the components is rendered in the figure 2.

The order of alteration, that is the order of increase of the mineral stability in the analysed hydrothermal conditions, is the following :

hornblende → montmorillonite → illite

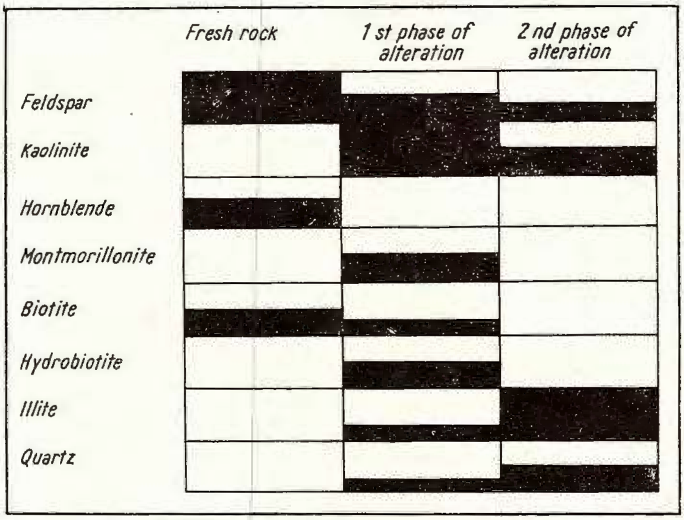

Fig. 2. — The mineralogical composition of the fresh rock and of the andesite of Pilişca in the first and the second phases of alteration.

biotite → hydrobiotite → illite
feldspar → kaolinite → illite

Conclusions

In the first phase of moderate alteration, the plagioclase transforms into kaolinite, the hornblende into montmorillonite, and not into chlorite as it usually transforms, the biotite into hydrobiotite, as Walker (1949, 1950) first mentioned in the soils. This phase is characterized by the keeping of the initial structure of the rock. The pseudomorphoses are present; the building of the new networks preserves the crystallographical directions of the old network. The mineralogical composition of the initial rock gives the new paragenesis. The solutions destroy the initial networks, acting by the hydration of the rock, washing the alkalis and the alkaline-earth.

In the second phase of intensive alteration, the montmorillonite hydrobiotite and kaolinite transform into illite. No more pseudomorphoses. The solutions act upon the rock producing an important quantity of K^+.

The above alteration diagram is available for all hydrothermal alterations in the Harghita Mountains.

The most intensive phase of alteration is characterized by the presence of the illite and the increase of the secondary quartz. The presence of the illite and hydromica is a feature of the intensive phenomena of hydrothermal argillization very numerous in the Harghita Mountains. The so called „kaolin of Harghita" is in fact a hydrothermal clay, with a high content of *il*lite-hydromica, fact that explains the high degree of plasticity of this „kaolin" in comparison with the classic kaolins.

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A METHOD OF PREPARING THE ORIENTED SAMPLES FOR THE DIFFRACTOMETER X-RAY ANALYSIS [1]

BY

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Abstract

A Method of Preparing the Oriented Samples for the Diffractometer X–Ray Analysis. An essential condition in the diffractometrical operations that could eliminate the disturbing effects is to obtain good diagrams. An important fact that counts in obtaining a proper diagram is the way of preparing the samples. The paper presents a method of obtaining the clay oriented samples, homogeneous and with a constant thickness. A fast and efficient method of glycoling, which consists in treating the samples with a mixture of alcohol and glycerol, is also proposed.

Introduction

In the diffractometry works, it is an essential condition to get a good diffractogram in order to have a proper interpretation. The diffractograms must offer the possibility of a real and minute characterization of the crystalline network constants belonging to the analysed samples.

In the practic activity it is often noticed that disturbing phenomena render the obtained diffractograms difficult to be intrepreted. The causes of wrong results are : the X-ray tube, the precision of the focusing and adjustment of the goniometer, the used detector and recorder, as well as the way the sample is prepared and its features.

In the practic analyses of diffractometry the unoriented and oriented samples are used (paste or oriented blades).

The present paper, being far from solving this problem, tries to present a method of preparing oriented clay blades, for TUR M 61 diffractometer.

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[1] Communication presented at the Meeting November 30th, 1973, Bucharest.

[2] Enterprise for Geological Prospecting, str. Caransebeş, 1, Bucharest.

We think that it is useful to present our trials concerning this problem, for the method has several advantages, especially in the domain of the series analyses.

The Amount of Material

The method is based on the obtaining of a suspension of argillaceous minerals in water, in a determined volume, taking into work a known amount of substance, without a pre-separation of the argillaceous fraction.

After grinding and passing the sample through the sieve of 0.06 mm, 2—3 g of sample is put into a marked cylinder of 50 *cc*, and we pour distilated water until the level reaches the mark and shake for 5 minutes. We let it to settle for 1 minute and then from a depth of 1 cm from the surface we collect 4 *cc* of suspension containing fractions smaller than 10 microns according to Stockes law; the suspension is dropped on 2 glass blades with the dimensions of 35/25 mm (2 *cc* on each blade), and then these samples are heated into an oven at 40°C for 1—2 hours.

The amount of the sample was established after several experiments at 2—3 g, taking into account the quality of the diffractograms obtained with this amount.

From a certain quantity of the sample taken into work of 2—3 g, on the glass blade it is obtained 20—30 mg of substance, that represent an average thickness of the sample of 60—100 microns.

The tests made on illite, kaolinite and montmorillonite showed that the best samples are those which have 20—100 mg of material on the blade.

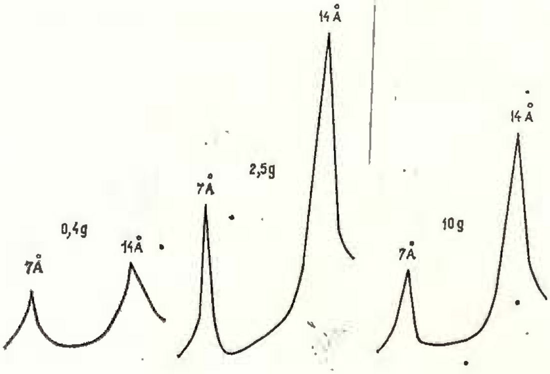

Fig. 1. — Diffractogrames obtained for initial different amounts of material.

For montmorillonite, the samples with more than 30 mg material on the blade crack and the surface becomes unhomogeneous.

For the samples of illite and kaolinite 3 g of samples (30 mg of material on the blade) is not comfortable, the suspension becomes too dense and for quantities larger than 100 mg material on the blade, the orientation of the particles becomes poorer, and the quality of the diffractograms decreases.

It is very important to choose an average and constant thickness, both for the qualitative analysis and for the quantitative one. For example, using amounts smaller than 2 mg on the blade, the reflex of the montmorillonite decreases gradually, until it vanishes, while the reflex of kaolinite and illite decreases in intensity.

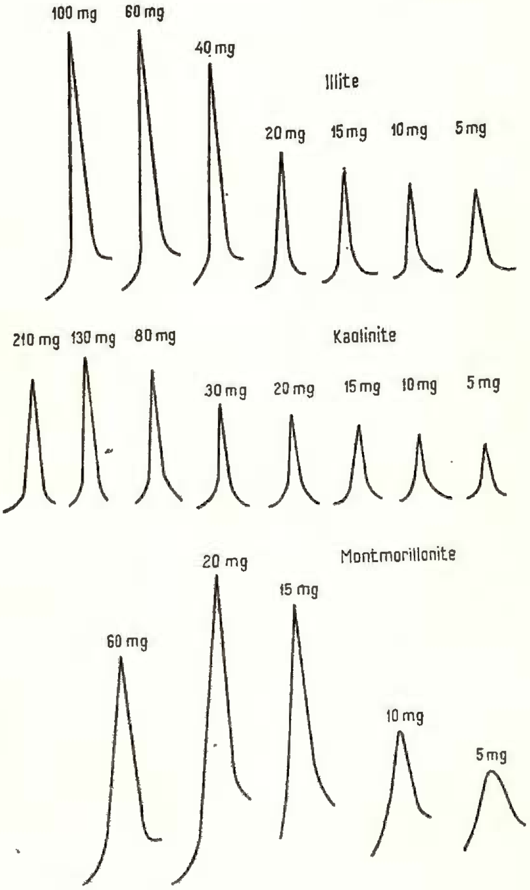

Fig. 2. — Diffractograms obtained for illite, kaolinite and montmorillonite with different amounts of substance on glass blades.

The oriented samples on the blades, prepared according to the technique described above, have the following advantages : they are homogeneous, with a constant thickness, the segregation of the smectites at the sample surface is arrested by the fast heating ; these samples are rapidily prepared, that is very important in case of an urgent analysis. The diagrams obtained for the oriented sample blades, according to the described technique, have a higher quality as compared to the samples obtained by the method of the oriented paste.

The Glycoling

The glycoling is very useful, together with the thermal treatments, for identification of the clay minerals with extensible network, existing in a clay sample (montmorillonite, vermiculite, swelling chlorite).

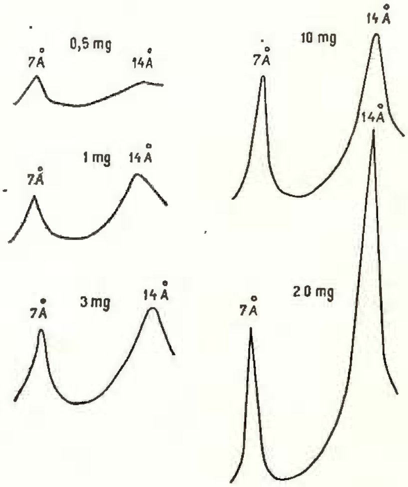

Fig. 3. — Diffractograms obtained for samples of montmorillonite with kaolinite with different amounts of substance on glass blades.

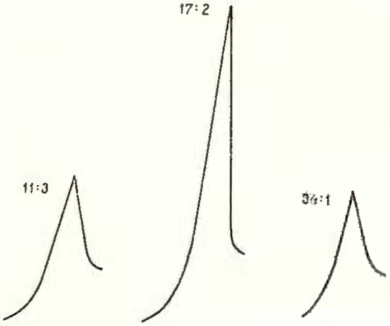

Fig. 4. —Diffractograms of the mixture alcohol : glycerol in different ratios saturating the montmorillonite.

As a general principle, the glycoling aims at the complete saturation of the extensible networks, thus resulting the development of the network along the *c* axis.

In order to get a maximum saturation that would last for a longer time, a mixture of ethylic alcohol and glycerol was used, this mixture being made in different ratios, the best ratio being 17:2.

Due to the alcohol, the glycerol penetrates quickly between the reticular planes, assuring their saturation. After the saturation of the sample, the alcohol is evaporated, and heavier glycerol remains.

Our tests showed that it is not recommended to use a too large quantity of glycerol. Though the network extends, the excess generates absorbtion phenomena that reduce the reflex intensity. The sample is treated with a few drops of mixtured alcohol and glycerol in the ratio 17:2, and after a short time it can be exposed, for the swelling is very rapid.

Conclusions

A fast routine method of preparing the oriented samples and glycoling is presented. We put 2—3 g of substance in a marked cylinder of 50 *cc*, then we discriminate on the blade 20—30 mg clay material smaller than 10 microns. The sample is heated for 1 hour in an oven at 40°C.

In comparison with the oriented pastes, the oriented blades have the advantage of a homogeneous surface and thickness. The rapid drying in the oven arrrests the differentiated segregation of the smectites at the surface of the oriented blade.

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SUR LA COMPOSITION CHIMIQUE ET MINÉRALOGIQUE DE LA FORMATION DES „SCHISTES NOIRS" DE LA VALLÉE DE LA BISTRIȚA ET DE LA VALLÉE DE LA MOLDOVA [1]

PAR

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Abstract

The Chemical-Mineralogical Study of the „Black Shales" Formation of the Carpathian Flysch Zone (Bistrița and Moldova Valleys) allowed to establish the features of the three composing horizons. On the ground of an argillaceous sedimentation, characterised by the presence of illite and chlorite (7 and 14 Å) subordinate vermiculite and interstratifications, during the sedimentation and diagenese phases, some specifical minerals, that impressed particular characters, were superposed. The reducing sedimentation environement is due to the presence of iron carbonates, sulphides and maintaining of the bituminous matter. The iron content is decreasing from the lower to the upper horizons, inverse proportional with silicon.

Le présent ouvrage est une étude chimico-minéralogique de la série des schistes noirs, la plus ancienne formation de l'unité d'Audia du flysch des Carpates Orientales. Vu le térritoire de la Roumanie, dans cette formation on a reconnu et séparé les trois complexes lithologiques suivants (Filipescu et al. (1952) et Băncilă (1955, 1958) etc.) qui correspondent à trois horizons lithostratigraphiques :

a) Le complexe basal, épais d'approximativement 800 m dénommé aussi la „complexe sphérosideritique", est constitué d'une alternance de schistes argileux noir-grisâtre, parfois siliceux, d'arénites quartzifères et de marnocalcaires. Ce qui est caractéristique, c'est la remarquable fréquence des intercalations sphérosidéritiques.

b) Le complexe moyen est dénommé le complexe schisteux avec des silicolites (lydiennes) (épais d'environ 250 m) dans la composition duquel

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dominent les schistes argileux, les silicolites et moins souvent les concrétions sidéritiques, qui sont localement remplacées par des concrétions calcaires ou dolomitiques.

c) Le complexe supérieur „des grès glauconitiques silicifiés" (épais de 100—150 m) est constitué par une alternance de grès glauconitiques silicifiés et de schistes argileux noirs, grisâtres et verdâtres, parfois de silicolites. Les concrétions sont beaucoup plus rares et de nature calcaire.

Le matériel analysé a été prélevé des affleurements des vallées de la Bistriţa et de la Moldova.

Des études chimico-minéralogiques sur les schistes noirs ont été executées jusqu'à présent par Savul et Cornelia Botez (1950), Băncilă et Papiu (1962), Iliescu et al. (1962), Filipescu et al. (1966, 1968), et Grigorescu (1969).

Composition chimico-minéralogique

Les roches analysées ont été classifiées en deux groupes lithologiques : *a*) roches silico-alumineuses à teneur variable en silice libre avec ou sans carbonates ; *b*) roches carbonatées représentées par des calcaires dolomitiques et des roches sidéritiques qui, d'après leur texture appartiennent soit aux sphérosidérites (ellipsoïdales ou lentiformes) soit aux pélosidérites (stratiformes).

La présence de la silice libre en différentes proportions nous a conduit à adopter le terme génétique de roches silico-argileuses, en partant de la prémise que presque l'entière quantité de silice est de nature chimique ou organo-chimique.

Les méthodes d'investigation utilisées ont été l'analyse chimique totale, la diffraction des rayons X et l'analyse thermique différencielle.

On a étudié 43 échantillons des couches argileuses, la majorité (33) provenant de l'horizon moyen (schisteux à lydiennes), 5 échantillons provenant du complexe inférieur et 6 échantillons du complexe supérieur.

Pour les roches carbonatées le principal complexe sur lequel on a insisté a été celui inférieur (sphérosidéritique), duquel on a analysé 22 échantillons et celui supérieur (les grès glauconitiques silicifiés) duquel on a analysé un échantillon. Dans ces deux derniers complexes, les carbonates sont représentés par les calcaires plus ou moins dolomitiques.

a) *Composition chimique* (v. tab. 1 *a*, *b*). En examinant le tableau 1 *a*, il en résultent les conclusions suivantes : pour les schistes argileux et les silicolites les limites de variation de la silice, dans l'horison supérieur, sont assez proches, indiquant des conditions d'accumulation plus ou moins analogues et plus uniformes que dans les horisons moyen et inférieur, où les valeurs oscillent entre des limites très larges.

Du même tableau il résulte que les principaux composants sont la silice et l'alumine, le reste des éléments se trouvent sous 5%. L'excès en silice (en moyenne générale de 63%) détermine un abaissement massif de l'alumine qui peut être sous-unitaire dans les lydiennes, effet plus prononcé dans l'horison moyen. Il en est de même dans les roches carbonatées où la proportion en silice est plus élevée dans le complexe moyen par rapport à celui inférieur.

Nous allons faire toutes les considérations pour la moyenne de ces valeurs.

Puisque la silice chimique domine nettement sur celle clastique, fait constaté par les études microscopiques, nous avons utilisé le nom de „série silico-argileuse". Tenant compte de la quantité totale de silice, le terme de lydienne a été appliqué à tous les silicolites massifs contenant plus de 75% SiO_2. En ce qui concerne les appréciations géochimiques nous avons tenu compte constamment de ces apports supplémentaires de silice. L'alumine résulte de manière prépondérante des minéraux argileux. La silice liée aussi que l'alumine se trouvent dans les feldspath détritiques, dont la participation est subordonnée. Entre l'alumine et la silice on constate donc une corrélation inverse.

Dans les complexes inférieur et supérieur, les valeurs de l'alumine sont plus élevées (au-dessus de 17%) que dans le complexe moyen (environ 9,9%). Remarque la limite supérieure de ce composant qui dans tous les trois horizons est proche (18%, —19%, —19%), fait qui indique une grande similitude constitutionnelle des fractions argileuses (v. tab. 1*a*).

Parmi les composants à participation moyenne, le fer se trouve sous forme oxydée aussi bien que sous forme réduite. Les schistes argileux présentent un contenu plus réduit que les roches carbonatées mais pour tous les deux, l'horizon moyen est le plus pauvre.

Le fer trivalent, qui provient des minéraux argileux (hydromicas et chlorite) et de l'oxydation des carbonates ferreux, a lui aussi comme limites supérieures des valeurs très proches pour tous les trois complexes (4%, —4%, —3%) fait qui indique son origine plus ou moins primaire (v. tab. 1*a*).

En moyenne, la teneur minimum en Fe_2O_3 de l'horizon moyen est dû à la dilution par l'apport de silice. Le fer total est corrélé avec l'alumine, c'est-à-dire avec les apports d'argile du milieu de sedimentation (v. fig.) Les analyses roentgénographiques confirment la présence des septéchlorites ferreuses. Le potassium (K_2O) est lié exclusivement aux hydromicas (illite). On observe une indépendance entre la teneur en K et en silice. Même dans la constitution des illites dégradées, le potassium varie largement selon le degré d'altération.

Ainsi par le calcul on a apprécié la quantité de l'illite tenant compte de la teneur en alumine et non pas de celui en K.

En général, les roches argileuses présentent des teneurs très proches des principaux oxydes (de Fe, Al, Ti et K) fait qui nous conduit à conclure que toute la série des schistes noirs a un fond sédimentologique argileux commun (illitique) sur lequel se superposent différents composants lithologiques, sin-, ou diagénétiques, qui diluent la composante argileuse primaire, imprimant des caractères différents aux roches résultées ; la silice clastique conduit à la formation des grès argileux ; la silice organogène et diagénétique — depuis des argilites siliceuses jusqu'à des lydien-

TABLEAU 1

La constitution chimique (limites de variations et moyennes). Schistes argileux et silicolites

Complexe	éch.		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O
Supérieur	5	Limite de variation	58,80—60,98	15,40—19,96	2,26—4,86	1,00—2,68	1,06—4,14	2,17—3,43	2,69—3,76
		Moyenne	60,20	17,76	3,57	1,96	1,92	2,59	3,18
Moyen	32	Limite de variation	54,82—89,90	0,08—19,90	0,29—4,69	0,27—2,66	0,57—7,99	0,30—2,46	0,32—3,65
		Moyenne	73,38	9,92	2,10	1,00	2,54	1,45	1,59
Inférieur	6	Limite de variation	48,24—63,56	14,78—18.17	3,17—3,93	0,90—1,88	1,02—8,07	1,33—2,06	1,39—2,47
		Moyenne	55,44	16,92	3,86	1,45	4,00	1,70	2,18
a)		Moyenne générale	63,14	14,86	3,16	1,47	2,82	1,91	2,31

Roches carbonatées

Complexe	éch.		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	K_2O
Moyen	9	Limite de variation	11,89—71,68	1,04—6,10	0,73—12,58	0,21—1,03 (3,78—15,30)	7,39—44,32	1,62—4,11	0,30—1,40
		Moyenne	36,10	3,74	3,74	0,84 (9,5)	25,79	2,34	0,61
Inférieur	22	Limite de variation	6,50—40,62	0,15—8,55	0.35—6,24	5,46—38,20	5,23—36,57	2,69—8,79	0,35—1,40
		Moyenne	16,94	4,40	2,39	22,69	13,94	5,74	0,75
b)		Moyenne générale	26,52	4,07	3,06	14,76	19,86	4,04	0,68

nes ; la calcite et la dolomite, — depuis des marnes jusqu'à des calcaires plus ou moins dolomitiques; la sidérose —depuis des ferrolites jusqu'à des calcaires ou marnes sidéritiques.

Dans les roches analysées le matériel argileux est constamment présent sauf dans deux échantillons dont l'un est un sphérosidérite de la Vallée de la Sadova, bassin de la Vallée de la Moldova et l'autre d'Obcina Feredeului.

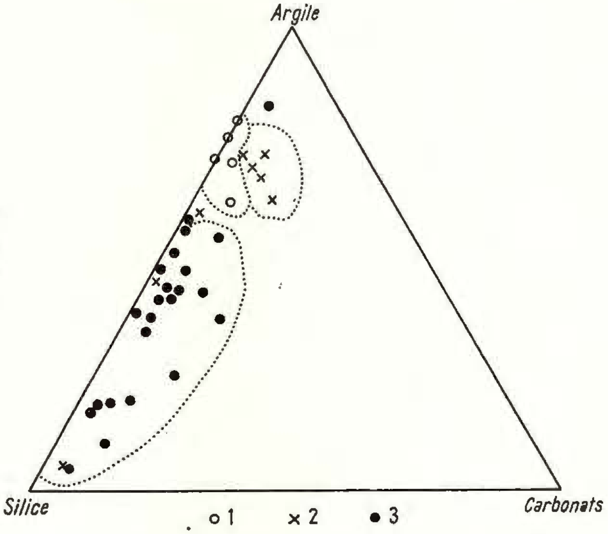

Fig. — La constitution minéralogique des „schistes noirs". 1, complexe supérieur ; 2, complexe moyen ; 3, complexe inférieur.

Les données des analyses indiquent évidemment que le matériel argileux principal est l'illite et que les valeurs du Fe_2O_3 total ne sont guère influencées dans les argilites par l'association avec les sphérosidérites.

En conséquence, on constate que pour la série silico-argileuse le rapport $Al_2O_3 : Fe_2O_3$ se maintient entre 2—4 pour 85% des échantillons de l'horizon moyen, tandis que dans celui supérieur tous les échantillons analysés s'inscrivent dans cet intervalle (100%).

Il s'ensuit que le fond de la sédimentation ferro-argileuse est approximativement constant, indépendamment des apports d'autre nature.

Pour la caractérisation des roches carbonatées, où les apports de silice sont complètement subordonnés, en rapport avec la série silico-argileuse, nous avons utilisé la valeur du rapport $SiO_2 : Al_2O_3$ en obtenant l'image suivante :

— l'horizon inférieur : de 22 échantillons deux sont pratiquement sans argiles, 15 présentent le rapport entre 2 et 4 (dont 13 sont des roches sidéritiques et 2 des roches calcaires) ; pour 5 échantillons le rapport varie entre 4 et 5,5 (4 pélosidérites et 1 marnocalcaire) ;

— l'horizon moyen (plus pauvre en sidérose) présente des apports supplémentaires de silice. Des 9 échantillons, 7 ont le rapport au-dessus de 7, pour deux il varie entre 4 et 5,5 et 1 seul (un marnocalcaire dolomitique-sidéritique) se situe entre 2 et 4.

Il en résulte une corrélation inverse au niveau des trois horisons, entre la teneur en fer et en silice, la sidérose caractérisant l'horizon inférieur plus pauvre en silice.

En conclusion, on admet que les apports de fer diminuent successivement et que la sidérogenèse a été remplacée dans les horizons moyen et supérieur par la calcarogenèse. Les roches calcaires se présentent sous forme d'intercalations stratifiées ou de concrétions.

Les apports de silice ne modifient guère le caractère illitique du fond argileux.

Par la diffractométrie des rayons X on a identifié et on a même dosé sémiquantitativement des minéraux majeurs de la roche.

Les diagrammes ont été obtenus en irradiant les poudres désorientées entre 2—20°θ. Pour les argiles et les calcaires on a utilisé un anticathode de Cu avec filtre de Ni, tandis que pour les échantillons à teneur élevé en fer, un anticathode de Co avec filtre de Fe.

Pour déterminer les minéraux argileux on a préparé les lames orientées qui ont subi les testes classiques : échantillon au naturel, après traitement à l'éthylène-glycol, après chauffage à 350 et à 550°C. Après chaque étape la lame a été irradiée entre 2°—15°θ.

b) *Composition minéralogique* (v. tab. 2 *a*, *b*). Les principaux minéraux argileux de la série silico-argileuse sont les illites, les chlorites de 14 Å et 7Å, les interstratifiés (10—14*c*) et (14*c*—14*v*). Les minéraux subordonés sont la silice libre, les carbonates et les feldspaths chalco-sodiques. Parfois on a mis en évidence la pyrite, l'hématite et la substance organique.

Les analyses chimiques indiquent aussi le soufre élémentaire et le phosphate de calcium, minéraux sans signification génétique.

Les résultats sont insérés dans les tableaux minéralogiques à contenu sémiquantitatif. Ils ont été obtenus en corrélant les données chimiques avec celles de l'ATD et roentgénographiques.

L'illite domine la fraction argileuse, suivie par la chlorite, la vermiculite et les interstratifiés.

Il est bien connu (Millot, 1965) que l'illite et la chlorite sont des minéraux spécifiques du flysch surtout pour le flysch de type alpin, et sont considérés des minéraux remaniés et diagénétiques.

La première hypothèse que nous faisons sur la genèse des illites est qu'elles sont d'origine détritique continentale, après une préalable dégradation pédogénétique. Dans la même phase on peut trouver la vermicullite. Ces minéraux, résultés de la dégradation des illites ou des micas, sont livrés ensuite à la mer du flysch, où commence le processus d'agradation halmirolitique. Simultanément se manifeste aussi l'évolution de la montmorillonite en illite qui se trouve dans les interstratifiées. Sans doute l'épigenèse conduit plus loin le phénomène d'agradation en certains cas jusqu'à la formation des micas authentiques.

TABLEAU 2

La constitution minéralogique (limites de variation et moyennes). Schistes argileux et silicolites

a)

Complexe	éch.		Illite	Chlorite	Quartz Calcédoine	Calcédoine opale	Feldspath	Calcite et dolomite	pyrite
Supérieur	5	Limite de variation	56,5—71,5	2,8—7,6	18,8—24,7	0,6—6,5	1,8—6,5	0—7,4	0—2,1
		Moyenne	64,08	5,56	21,30	2,98	3,86	2,32	1,07
Moyen	32	Limite de variation	21,0—70,3	0,8—7,5	19,0—70,7	0—22,2	0—13,7	0—15,8	0—1,5
		Moyenne	35,24	2,83	41,64	11,57	3,20	4,53	0,37
Inférieur	6	Limite de variation	54,5—68,1	2,5—5,3	18,1—34,3	—	2,4—3,9	1,8—14,4	0—8,6
		Moyenne	61,88	4,1	23,63	—	3,17	7,11	1,53
		Moyenne générale	53,73	4,16	28,85	7,27	3,41	4,65	0,99

Roches carbonatées

b)

Complexe	éch.		Illite	Chlorite	Quartz Calcédoine	Feld-spath	Sidérose + substitutions	Sidérose — substitutions	Calcite et dolomite	Pyrite
Moyen	9	Limite de variation	3,3—21,1	0,6—4,8	3,0—59,6	0—8,0	(4,2—33,7)*	(3,4—24,5)	11,4—84,0	0—2(18,1)
		Moyenne	10,34	2,38	28,13	3,25	(3,1)	(3,1)	43,99	0,65
Inférieur	22	Limite de variation	0—30,1	?	0—23,2	0—8,5	10,9—84,0	8,8—61,6	0—67,0	0—1,3 (6,6)
		Moyenne	14,04	?	7,70	3,51	49,69	36,84	24,16	0,50
		Moyenne générale	12,19		18,95	3,38			34,07	0,57

* Deux échantillons contiennent sidérose.

Dans les roches calcaires l'illite se trouve aussi comme minéral spécifique, primaire, avec les chlorites, surtout dans le cas où la formation a été affectée par des efforts tectoniques. Une semblable association aux schistes noirs a été signalée par Millot (1965) dans les dépôts mésozoïques du Bassin Parisien.

La genèse des chlorites peut être liée à la transformation halmirolitique, quoique nous ne les trouvions pas interstratifiées avec la vermiculite et la montmorillonite. La présence de l'association de l'illite nous indique une transformation partielle diagénétique de la montmorillonite en chlorite ou bien l'accroissement de la chlorite autour des noyeaux d'illite. La chloritisation apparaît dans les processus de diagenèse comme un phénomène général sans intervention métamorphique. Nous admettons que seulement une diagenèse avancée a dirigé la transformation des septéchlorites ferreuses du type berthierine en chlorites ferrifferes de 14Å.

On considère que les septéchlorites ont une origine primaire liée aux apports massifs de fer qui conduisent à la formation des ferrolites.

La glauconie a été déterminée uniquement dans les grès par la voie microscopique.

Considérant que l'apparition et la disparition des minéraux index est le critère fondamental de la zoneographie nous avons interprété l'omniprésence de l'illite.

D'après les indications de Weaver, nous avons utilisé le degré de cristallinité de l'illite pour saisir les différents degré d'évolution antérieure au métamorfhisme. La technique de Kubler que nous avons adoptée est simple et significative, les résultats des déterminations étant directement liés à l'état d'ordre et de désordre structural de l'illite.

Quand les conditions de diagenèse sont très avancées elles provoquent une amélioration de sa structure cristalline et seulement quand les conditions de métamorphisme sont atteintes apparaissent les polymorphes ordonées des micas.

Pour l'horizon supérieur et inférieur les mesurages indiquent une diagenèse modérée qui n'atteint pas le stade du métamorphisme. Seulement dans l'horizon moyen la tendance est plus prononcée et on peut discuter d'un stade anchimétamorphique. De même la paragenèse illite-chlorite indique une évolution épigénétique très avancée. Ces minéraux sont considérés par Dunoyer de Segonzac (1969) comme minéraux index pour la phase du débu du métamorphisme. Les mesurages indiquent dans cette zone une cristallinité uniforme.

Dans le cas d'un métamorphisme prononcé les polimorphes 1Md de l'illite — 2M. La présence des illites sédimentaire trioctaedriques (assez riches en Mg) indique que le niveau d'énergie nécessaire pour obtenir des structures ordonnées a été plus grand.

Puisqu'il ne s'agit pas des illites dioctaedriques (purement alumineuses) qui peuvent donner facilement le polymorphe 2M, on a eu rarement la possibilité de calculer le rapport 2M/2M + 1Md qui peut être un index du degré d'évolution du sédiment. Au point de vue cristallographique l'indice d'Esquevin montre que les illites initiales ont évolué parfois jusqu'à la muscovite, mais de dimensions très fines.

La méthode de Kubler est limitée, nous n'avons pas pu l'appliquer pour les roches carbonatées puisque les diagrammes de diffraction indiquent des quantités subordonnées d'illite ainsi que de K dans les analyses chimiques.

Conclusions lithogénétiques

L'accumulation de la formation des schistes noirs du flysch carpatique a eu lieu dans une mer peu profonde et calme où prédominait la sédimentation argilo-microclastique en conditions euxiniques ou sous-euxiniques. Sur ce fond se superposent parfois des apports détritiques continentaux qui conduisent aux roches détritiques (des brèches et des conglomérats fins jusqu'aux grès et siltites). Les étapes d'aération ont déterminé l'apparition d'une faune benthique, correspondant actuellement aux intercalations calcaires ou marneuses. Les minéraux argileux ont subi des « rajeunissements » par la rétention du K et du Mg des eaux marines, processus qui continue dans les étapes diagénétiques et épigénétiques.

Simultanément, au cours de la sédimentation survenaient de grands apports de fer ainsi que de grandes quantités de substance organique, modifiant le caractère géochimique du milieu en partant des milieux oxydants vers des milieux réducteurs avec CO_2 et H_2S. Si la valeur de l'EH et du SH augmentaient continuellement dans les eaux profondes, avec l'affaissement du bassin d'accumulation, celle du pH aurait atteint la valeur minime dans la partie moyenne de la zone avec CO_2 pour augmenter à nouveau vers la zone du fond avec H_2S. Au niveau de cette dernière zone se produisait ainsi une élévation de l'alcalinité qui déterminait la solubilisation de la silice. Celle-ci provenait surtout des restes d'organismes (radiolaires et spongiaires).

L'évolution des minéraux de fer est éloquante et reproduit parfois dans la masse même des sédiments la succesion zonale de Borchaert (1965).

Le fer est apporté dans le bassin sous forme réactive — d'oxydes organométalliques. En petites quantités, on le trouvait sous forme bivalente, dans les sels solubles.

Dans les périodes d'aération, déterminées parfois par les apports des eaux continentales, prend naissance la glauconie. Par l'enfouissement et le recouvrement du sédiment, apparaissent des conditions de réduction.

Si le fer se trouve en grandes quantités il précipite sous forme de sidérose (pélosidérite) ou migre à l'intérieur du sédiment dans une étape suivante (dénommée par Strahov, 1958, ,, phase de rédistribution") donnant naissance aux sphérosidérites. La formation du carbonate de fer a eu lieu surtout au niveau du complexe inférieur (sphérosidéritique) et a diminué lentement jusqu'à l'apauvrissement total dans l'horizon supérieur (grès glauconitiques silicifiés). Dans un stade plus avancé les eaux des zones plus profondes à pH plus élevé, avec de la silice en solution, peuvent se mêler avec celles superficielles avec du bicarbonate ferreux en produisant les leptochlorites. Enfin, dans les zones plus profondes ou par l'accumulation avancée, on arrive à des conditions typiquement euxiniques avec la séparation de la pyrite, passant éventuellement par les stades de greigite et de mackinawite (Berner, 1971).

Si à un moment donné ce stade dévance celui de la zone avec CO_2, les pyrites se forment avant la sidérose; ensuite apparaissent incluses dans la masse de celle-ci. La, présence de la glauconie dans des roches de couleur foncée — bitumineuse — à côté de la pyrite et éventuellement de la septéchlorite et de la sidérose s'explique d'une manière analogue.

Les transformations épigénétiques liées aux étapes diastrophiques conduisent à des chlorites de 14 Å en partant de l'illite et des septéchlorites ferrifères sédimentaires.

La paragenèse illite-chlorite, spécifique à l'étape la plus avancée de l'épigenèse dénommée anchimétamorphisme, achève l'évolution de la fraction argileuse.

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PHYSICAL-CHEMICAL PROPERTIES OF THE BREAZA CLAY USED IN THE PREPARATION OF THE DRILLING MUDS[1]

BY

ION D. PÂRCĂLĂBESCU[2]

Abstract

Ppysical-Chemical Properties of the Breaza Clay Used in the Preparation of the Drilling Muds. Romanian oil industry employs, on a large scale, the Breaza clay to prepare the drilling muds. For this reason it is necessary to know some of the physical-chemical properties of this clay. By means of diffraction of X-rays through crystals, spectral semiquantitative analysis and scanning electron microscopy, five samples from the quarry and one sample of the Breaza clay of the preparation plant in Câmpina have been analysed. Diffraction of X-rays through untreated and ethylene-glycol treated samples revealed the presence of illite, chlorite, montmorillonite and the important participation of mixed-layer structures illite+montmorillonite, chlorite+montmorillonite, corrensite. Scanning electron microscopy underlined the presence of these minerals by the shapes and dimensions of the particles. The spectral semiquantitative analysis revealed the percentage participation of the main chemical elements. The structures of the crystalline network, the percentage participation of the ions and the shapes and dimensions of the mineral particles may explain the rheological properties of the Breaza clay.

At present, in Romania, the oil industry uses the Breaza clay, on a large scale, at the preparation of the drilling muds. In the quarry where the raw material is being extracted from, there are clearly revealed three layers (see the sketch in fig. 1) : at the top, layer *A*, a little sandy, overlying the *B* layer made up of marls, while at the basis lie the clays of the *C* layer. In the advancing front of the quarry, five strata have been separated in the marl-clayey layers, according to their colour : at the contact with the sandy stratum a green marl 5, under it a reddish marl-packet 4, the stratum 3 is dark green, distinct from the greenish colour of packet 2, the stratum 1, the thickest one, is a red clay, incorporating also a green lens.

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[1] Reported in the session from November 1973.

[2] Institute for Petroleum and Gas in Ploieşti.

There have been analysed roentgenostructurally, chemical-spectrally and by means of a scanning electronic microscope five representative samples of the above mentioned marl and clay layers, as well as the Breaza clay delivered by the Câmpina preparation plant to the drilling enterprises.

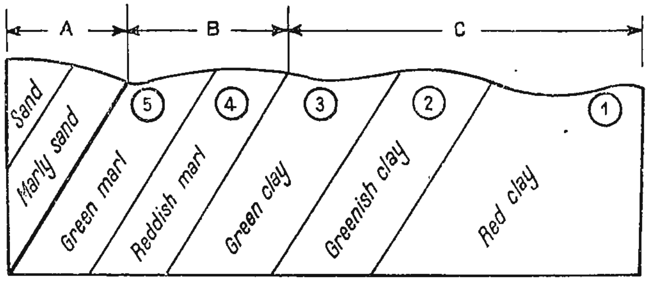


Fig. 1.—The sketch of the Breaza quarry.

The X-ray structural analysis were made by means of an X-ray diffractometer — DRON—1 — under the following working conditions: radiation Cu $K\alpha_1$, Ni filter having a δ thickness of 0.02 mm. Soller filters 1.5, slits 1 : 0.5 : 0.5 : 0.5, speed 1°/min., the time constant 20, the scale of diffracted radiation intensity 100 div. = 50 imp./sec. The voltage upon roentgen tube 28 kV, at an intensity of 30 mA.

In order to be able to accurately determine the mineralogical composition of these samples, there have been also in parallel analysed the diffraction diagrams for the untreated samples and for the samples treated with ethylene-glycol, the latter exerting its influence only upon the crystalline structures by swelling them and leaving intact the ones which cannot incorporate the ethylene-glycol molecule (Grim, 1968).

Sample 1, from the basis of the quarry, contains the following crystalline structures as shown by the diffraction diagrams for the untreated sample (fig. 2) and for the sample treated with ethylene-glycol (fig. 3): -chlorite, particularly revealed by the spectral parameter $d/n = 7$Å, as well as by $d/n = 14$ Å, a structure that is not influenced by ethylene-glycol; -illite, indicated by the spectral parameter $d/n = 9.56$ Å, a parameter that is not influenced by ethylene-glycol (fig. 3); -zeolites, spectral parameters $d/n = 7$ Å, 4.09 Å and 3.16 Å, uninfluenced by ethylene-glycol treatment; -montmorillonites with various degrees of water saturation and different cations, as it results from the comparison between the parameters in figure 2 and those in table 1 (Grim, 1968). The ethylene-glycol treatment of montmorillonites increases the magnitude of the first basal planes by 4—12 Å, 4.25 Å being the critical diameter of the ethylene-glycol molecule (Pârcălăbescu, 1971). For example, there are well disclosed the spectral parameters of 18 Å, 15.4 Å, 12.5 Å; -chlorite+montmorillonite, revealed not only by the diffraction parameters shown in figure 2. but also by the parameters of the ethylene-glicol treated

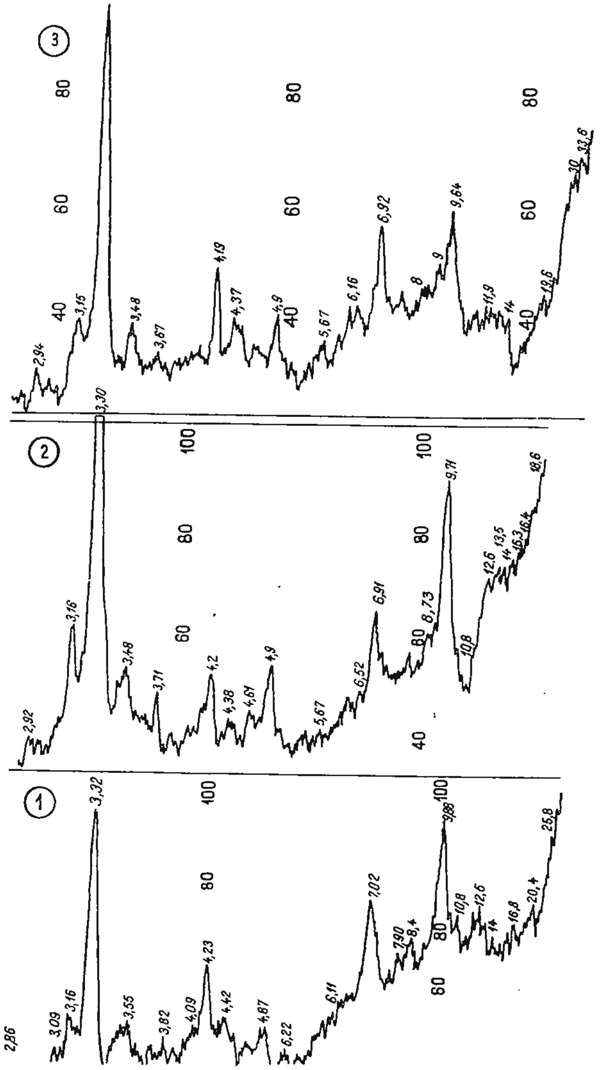


Fig. 2.—X-ray diffractometer patterns of samples 1, 2, 3.

sample, where to the diffraction series of the untreated structures there are added (fig. 3) the diffraction series of the ethylene-glycol treated crystalline nets (tab. 2); -illite+montmorillonite with an important percentage of participation, taking into consideration the magnitude of the intensity of the main spectral parameters of the diffraction series, both for the untreated sample (fig. 2) and also for the ethylene-glycol treated sample (fig. 3 and tab. 2).

TABLE 1

(001) Reflections, in Å, from Montmorillonite with Different Cation Saturation

H^+	Lu^+	Na^+	Ca^{2+}	Mg^{2+}
10.0	9.5	9.5	9.5	9.5
12.4	12.4	12.4	—	—
15.4	15.4	15.4	15.4	15.4
18.4–19.0	19.0	19.0	18.2	19.2
21.4–22.4	22.5	—	—	—

TABLE 2

X-ray Diffraction Series of:

Illite		Chlorite		Corrensite		Illite + montmorillonite + ethylene-glycol		Chlorite + montmorillonite + ethylene-glycol		Corrensite + ethylene-glycol	
d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
9.93	s	14.3	m	28.3	m	33–34	s	32.87	s	32–33	s
4.9	m	7.2	s	14.2	s	16.5	s	16.4	m	16.2	s
4.45	s	4.8	s	10	m	11	m	10.9	s	10	m
4.28	w	4.6	w	7	w	8.4	w	8.2	s	8.1	m
4.1	w	3.6	s	5	w	6.7	w	6.6	s	7	w
3.87	m	2.9	m	4.7	m	5.6	m	5.1	m	3.6	m
3.64	m			3.5	m	4.8	m	4.7	m	4.6	m
3.35	vs			3.34	vs	3.34	vs	3.28	vs	3.34	vs

vs-very strong; s-strong; m-medium; w-weak.

Sample 2, macroscopically differentiated from sample 1 only by colour, contains, as per the diffraction diagrams, the same crystalline structures identified in the red sample taken from the basis. The participation of zeolites is higher, if we take into account the magnitude of the intensity of the spectral parameter d/n = 3.16 Å.

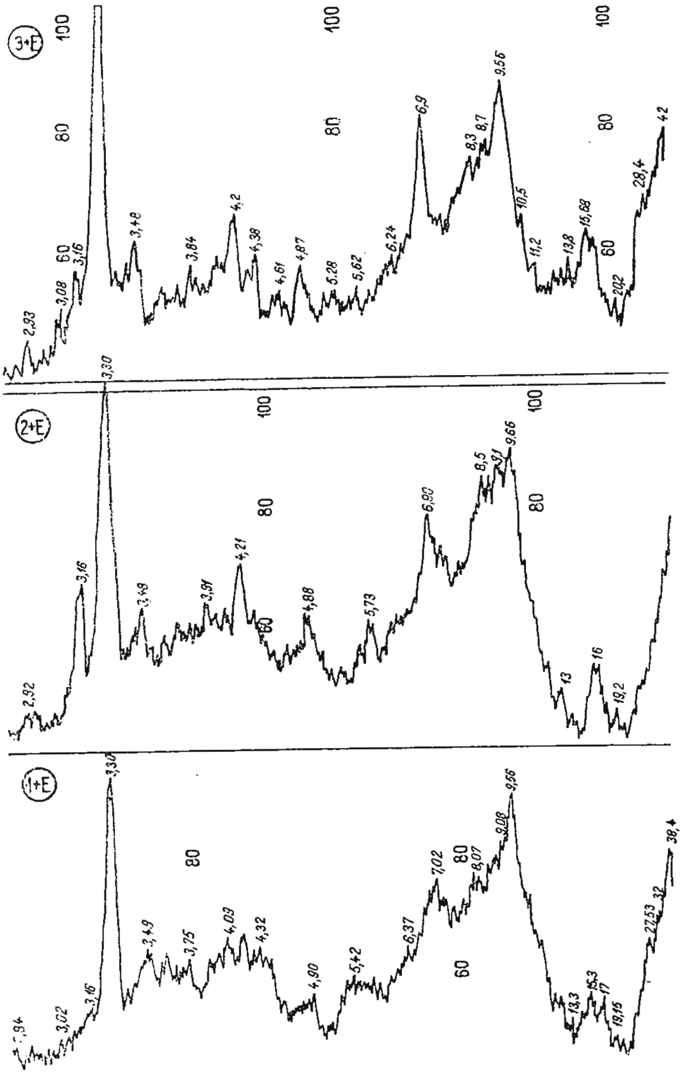


Fig. 3.—X-ray diffractometer patterns of samples 1, 2, 3, treated with ethylene-glycol.

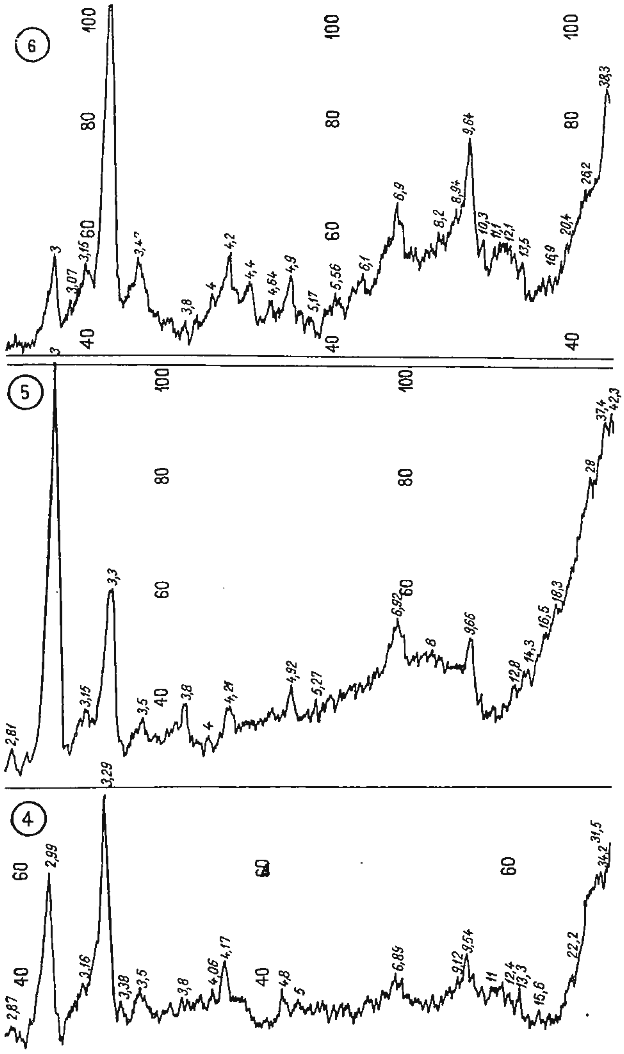


Fig. 4.—X-ray diffractometer patterns o fsamples 4, 5, 6.

Sample 3, separated as per the colour criterium, is not mineralogically different from sample 2, except for a lower participation of zeolites and an increase in the chlorite participation, fact which certainly impresses a darker green colour on this sample. Samples 1—3 form the argillaceous layer of the quarry, the more chloritous packets having a thickness subordinated to the montmorillonitic layer of the basis.

The diffraction diagrams (fig. 4, 5) of sample 4, clearly differentiate the mineralogical composition as against the compositions of the previous

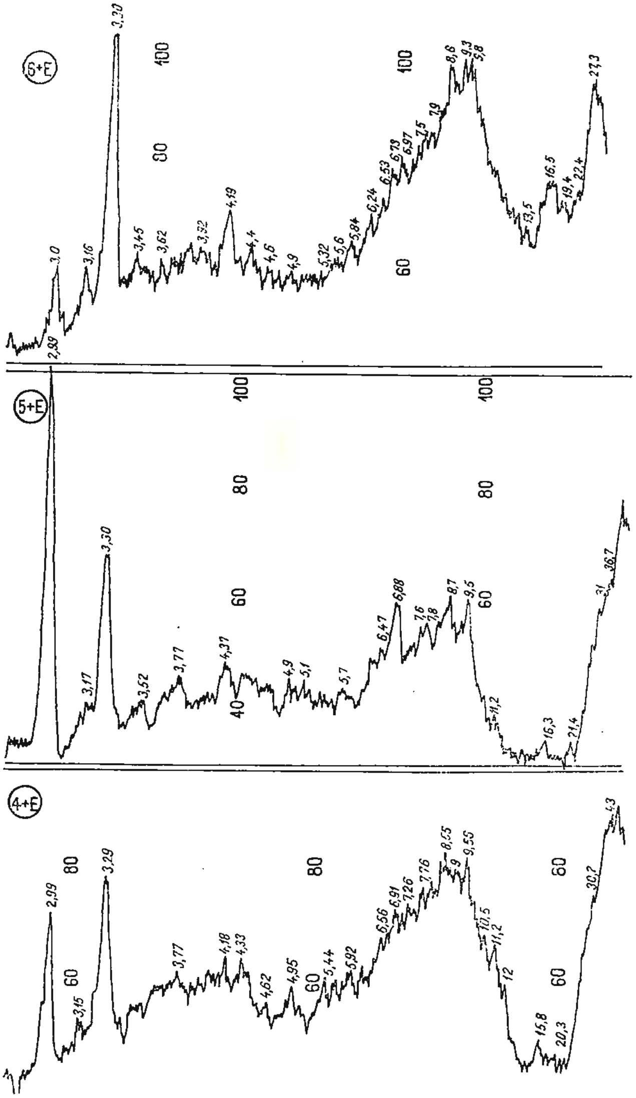
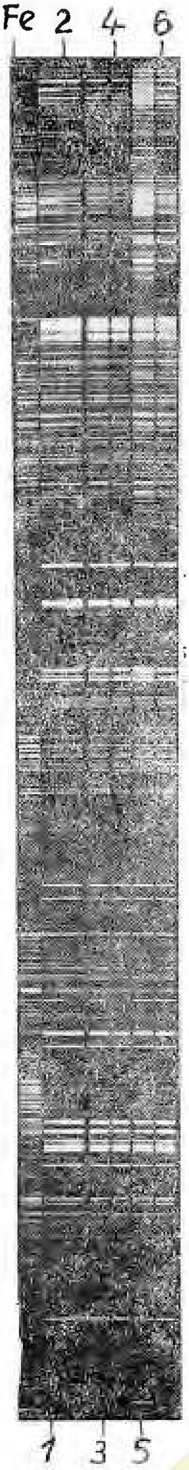


Fig. 5. — X-ray diffractometer patterns of samples 4, 5, 6, treated with ethylene-glycol.

samples. Sample 4 distinguishes itself by a higher participation of montmorillonites, a reduction of illites and particularly of chlorites, a high percentage of manganesian calcite (Pârcălăbescu, 1972), parameter d/n = 2.99 Å, the zeolites being also present. The marl of packet 4, red ni colour, separates layer *B* from layer *C* (fig. 1).

Sample 5 is characterized by a high percentage of the manganian calcite (2.99 Å) and the presence of corrensite + ethylene-glycol (series



28 + 4 Å). The presence of chlorites with a particularly high percentage gives this sample a dark green colour. The diffraction diagrams clearly differentiate the marl layer *B* of this quarry.

It is the material excavated from layers *B* and *C* that is transported to the Cîmpina clay preparation plant. The *C* layer being prevalent in the quarry, the clay delivered by the preparation plant is reddish and preserves the argillaceous character of the basical layer, the presence of calcite — brought about by the marl packets 4 and 5 — included. Indeed, the diffraction diagrams of sample 6, reveal the mineralogical composition of clay supplied by the plant (fig. 4 and 5). The montmorillonitic structures and those of the interlayered minerals chlorite +montmorillonite and illite+montmorillonite are well set of in the ethylene-glycol treated sample (fig. 5 and tab. 2).

The chemical-spectral analyses (Ahrens, 1961; Kler, 1960; Pârcălăbescu, 1967) were made by means of an I.S.P.22 spectrograph. The intensity of spectral lines was determined by means of a Zeiss microphotometer. Spectral coal T_1 was used, with a 6 mm outer diameter, a 4 mm inner diameter, and a 4.5 mm depth of cavity.The ratio between the spectral coal power and rock has been rigorously determined quantitatively as 1 : 1. Burning conditions : 120 V at a current of 10 A, for 4 minutes, with a 6 mm slit opening and an 0.02 mm diaphragm. The chemical-spectral analysis of the samples under study (fig. 6) underlines again the mineralogical composition revealed by the X-ray diffraction diagrams. The prevalence of alluminium silicates brings the participation of the chemical elements within the limits indicated in table 3. The calco-sodic zeolites and the montmorillonites determine an important participation of Na and Ca, the latter having a participation limit of about 30% in the marl of sample 5, at the expense of the presence of calcite, as the X-ray diffraction diagram shows. The presence of chlorites in a significant proportion determines a high participation of Mg, complemented also by the high content of the montmorillonitic structures. The chlorites and montmorillonites also determine a significant participation of the chemical elements Fe and Mn (tab. 3). The crystalline nets of montmorillonites, by their physical-chemical characteristics (Grim, 1968; Pârcălăbescu, 1971), offer space in the interlayered planes, to

Fig. 6. — Spectrochemical analysis of samples.

the chemical elements Cr, Ni, V, Mo which have a participation typical of clays (Katcenkov, 1959; Pârcălăbescu, 1972). The important participation of Al^{3+} in the structure of the analysed medium brings also about the marked presence of Li^{+} and Ga^{3+}, with which it mutually substitutes in the crystalline nets of the argillaceous minerals due to their geochemical characteristics (Keith, 1959; Pârcălăbescu, 1968).

Since the Breaza clay is dried at a low temperature at the preparation plant, in order to get its moisture content from about 30% down to 8% — when it may be considered a dry material — the spectral parameters $I_t - I_f$ for all analysed chemical elements reveal greater magnitude in comparison with the untreated samples. At the spectral analysis of emission in the cavity of the spectral coal the same volume is put for burning, or in the dried sample the concentration of the chemical elements is higher than in the wet untreated samples. Since between the intensity of the spectral parameter $I_t - I_f$ and the concentration C of the chemical elements there is a relation $I = \alpha C^{\beta}$, where the parameters α and β indicate the influence of the burning conditions and of the matrix — whose conditions have been rigorously maintained constant in the spectral analysis of emission (Ahrens, 1961; Pârcălăbescu, 1967) — it is intuited why for the dried sample (tab. 3) there is an increase of the magnitude of the spectral parameter of the intensity as a function of concentration.

Having in view the magnitude of the spectral parameter $I_t - I_f$ for the geochemical indicators Mn, Co, Mo an important participation of these chemical elements in the analysed solid medium is to be noticed (tab. 3). Manganese has a more significant participation in the minerals formed in deep water marine medium, due to the fact that it is stable in ionic solutions and can be transported to long distances away from the shore (Katcenkov, 1959; Keith, 1959; Pârcălăbescu, 1968). Due to their geochemical properties Co and Mo substitute for manganese, fact explaining their presence within the clayey network formed in the abyssal zones.

Typical for the clays formed in those zones are not only the indicated chemical composition and the prevalence of the identified crystalline structures, but also the uniformity and the micronic dimensions of the particles. Studied by means of the electronic scanning microscope Jeol—J.S.M.2, the samples present dimensions and shapes of their particles as represented in figures 7—12. The particles were settled by sedimentation in distilled water on Cu disks. After a prolonged drying, the samples were covered, under vacuum in an evaporator with voltaic arch, with a gold film of 200—500 Å, for lack of the alloy gold (90%)+palladium (10%). By chosing the investigation magnitude and the area of the field under study, it was aimed at revealing the dimensions and shapes of the particles, their mineralogical nature and their prevalence in the mass under study. In figure 1 (plate I) a sector of the investigated field of the sample belonging to the red clay, the elongated shapes of the mixed interstratified chlorite+montomorillonite structure are to be noticed. In figure 2 (plate I)

TABLE 3

Spectro-chemical Analysis

Chemical elements	Wave-length in Å	Clay			Marl		Breaza clay	Estimation of percentage participation, after Kler, 1960
		red	greenish	green	green	reddish		
		Spectral parameter $I_t - I_f$						
Si	2577.13	13	14	11	8	13	10	<30
Al	2669.16	4	5	3	3	5	6	<30
Ca	2721.64	39	—	—	111	33	23	<10
Ca	3269.10	—	—	—	15	—	—	<30
Mg	2915.52	7	11	7	17	13	13	<10
Fe	2636.48	5	5	4	5	4	11	<10
Mn	2914.60	25	—	47	72	—	21	0.3
Cr	2843.25	10	12	11	10	12	18	0.03
Co	3453.50	12	60	21	11	18	43	0.01
Ni	3414.76	36	64	50	28	36	60	0.003
V	3185.39	49	53	67	61	58	75	0.03
Mo	3132.59	9	9	7	8	4	10	0.001
Cu	3273.96	90	101	103	80	100	97	0.003
Pb	2833.06	6	4	16	9	10	15	0.03
Ga	2943.63	29	46	61	34	53	58	0.003
Li	2332.61	24	39	40	26	44	53	0.1
B	2497.77	31	30	45	23	53	51	0.01
Be	3130.41	16	33	27	25	29	44	0.001

the shape of several illites is being reproduced from the clay of sample 2. The quantity of secondary electrons emitted portrays the topography of the particles (Weinbrandt, 1969), since a greater mass of secondary electrons is being emitted by the higher points in comparison with the lowest ones as against the incident beam. Thus, a stereoscopical image of those illites, whose equivalent diameters vary between 3 and 5 microns, has been obtained. The chlorite+montmorillonite structures prevailing in sample 3 — the green clay — are clearly noticed also in figure 1 (plate II). The particle of an elongated shape so graphically revealed in figure 2, (plate II), by its dimensions and shape is typical of a nontronite (Grim, 1968) present with an important percentage in sample 4, as shown by the X-ray diffraction diagram and the chemical-spectral analysis. The mixed-layer structures chlorite+montmorillonite and illite+montmorillonite are revealed in figure 1 (plate III), the former with an irregular shape noticed also in figures 1 (plate I) and 1 (plate II) and the latter with a more regular parallelipipedal shape. A sector has been selected out of the Breaza clay, figure 2 (plate III), in which the more parallelipipedal shapes of the illite+montmorillonite as well as the acicular shape of the nontronite appear in the foreground.

The means of physical-chemical analysis employed are exceptionally complementing each other, a fact for which it is recommended that they should be made use of more widely in researching the physical-chemical properties of the solid medium of fluid hydrocarbon reservoirs.

Conclusions. The raw material out of which the Breaza clay is prepared is made up of crystalline structures : illite+montmorillonite, chlorite+montmorillonite, montmorillonite, chlorite, illite to which zeolites are subordinated and — since the exploitation of the marl layer *B* cannot be avoided — calcite is also incorporated in the clay. In order to obtain better physical-chemical properties for this clay of Breaza, it would be desirable to introduce into the preparation plant only the clays of layer *C*.

Also, in the context of preserving some good colloidal properties of the Breaza clay, care must be taken that moisture should not get down under 8% during the drying operations, otherwise (Pârcălăbescu. 1960; Rogers, 1963) the advanced drying may lead to the destruction of its colloidal characteristics.

By its structural edifice, the Breaza clay may be comparable with the bentonites of Alba Iulia-Ocna Mureş Zone (Neacşu, 1969) and — to a certain extent — with the Wyoming bentonites (Grim, 1968). Prevalent ($>60\%$) are the montmorillonite structures with which chlorite, illite and zeolite structures are also associated.

The physical-chemical properties of a bentonite depend on the mineralogical composition, on the structure of the crystalline nets and on the ions present in those crystalline nets. That is why, in this paper, there was initiated the determination of these two fundamental elements in the physical chemistry of the solid media : the structural edifice of the crystalline nets and the ions present in those minerals.

It is on the physical-chemical properties of this bentonite that plasticity, tixotropy, capacity of forming stable suspensions (Rogers, 1963), capacity of ionic exchange, and swelling, (Grim, 1968; Pârcălăbescu, 1971) depend.

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PLANŞA I

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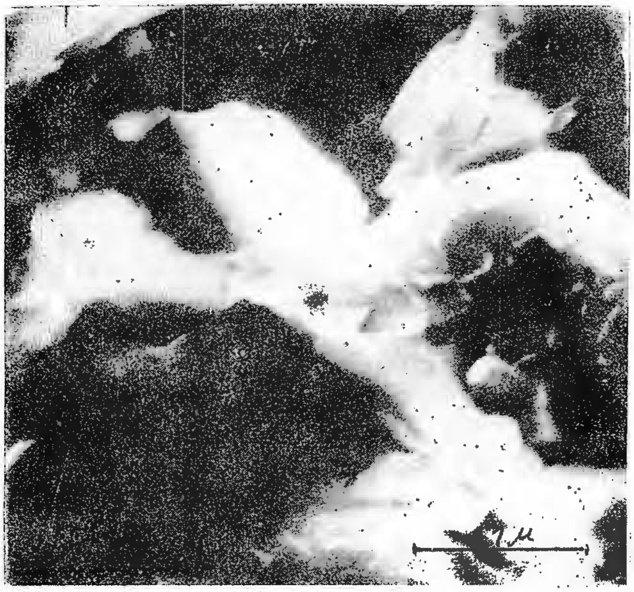
PLANŞA I

Fig. 1. — Scanning electron micrograph of chlorite + montmorillonite from sample 1.
Fig. 2. — Scanning electron micrograph of illite from sample 2.



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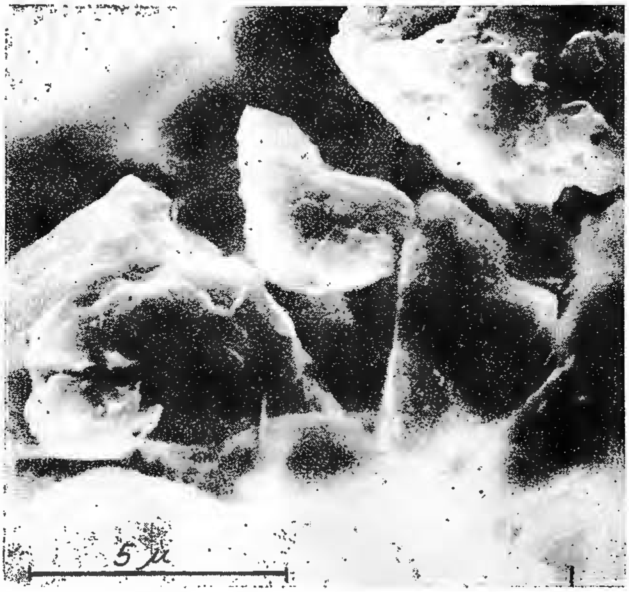

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92-2

PLANŞA II

Fig. 1. — Scanning electron micrograph of chlorite + montmorillonite from sample 3.
Fig. 2. — Scanning electron micrograph of nontronite from sample 4.

1

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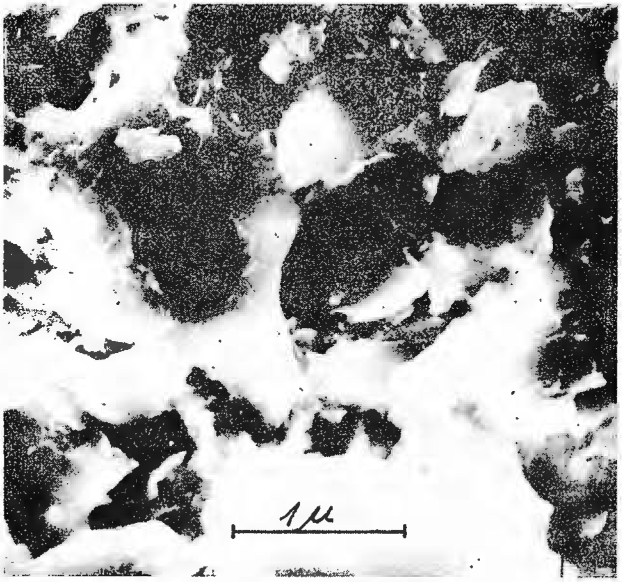
PLANŞA III

Fig. 1. — Scanning electron micrograph of chlorite + montmorillonite and illite + montmorillonite from sample 5.

Fig. 2. — Scanning electron micrograph of illite + montmorillonite and nontronite from Breaza clay.



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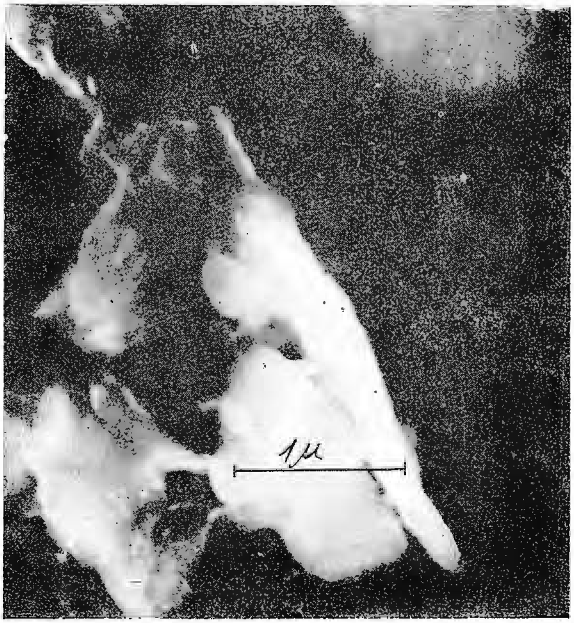

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Pl-4

L'ÉTUDE DE LA RÉSISTANCE AU CISAILLEMENT EXECUTÉ SUR DES ARGILES[1]

PAR

VICTORIA ADELA POJAR, LUCIAN MATEI[2]

Abstract

The Study of the Sheare Strenght on some Romanian Clays. The role of residual strenght measurements is very important in order to predict the long period stability of the hillsides, batters, canals and so on. For this reason the laboratory tests are needed very exactly. The paper points out the influence ofthe mineralogical composition of the $<2\mu$ fraction on the residual strenght. The experiments were carried out by using some Romanian clays. Simultaneously, it is revealed that the influence of the porosity, initial moisture and mineralogical composition of clayey soils on the residual strenght is not important but the residual strenght is dependent on the bindingen materials ($CaCO_3$, Fe_2O_3, FeO, organic compounds) and soil structure.

Dans les études de la stabilité des pantes, avec les problèmes délicats, dans le cas de l'existence des minéraux argileux, qui imposent leurs caractéristiques de faiblesse à la résistence au cisaillement, ont été employées, parallèlement des déterminations sur le terrain et au laboratoire.

Pour ces études, les déterminations in situ se limitent à l'analyse des aspects de la résistence qui est effectuée pendant un temps cours, mais il est déjà connu que les ruptures dans les versants argileux, ou existe une petite perméabilité, ont lieu continuéllement et très lentement.

Les essais de laboratoire permettent un nombre plus large de déterminations comme : la composition minéralogique de la fraction $< 2\ \mu$, la tenneur en $CaCO_3$ et en matières organiques, la limite Atteberg, le poids spécifique etc.

Dans le cas des argiles, il est parfois utile de faire une analyse minéralogique, parce que le comportement mécanique de ces roches est forte-

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[1] Communication à la première Conférence du Groupe Roumain d'Étude des Argiles, Bucarest, novembre 1973.

[2] L'Institut d'Études et de Recherches pour les Améliorations Foncières, Bucarest, Splaiul Independenței, 294.

ment influencé par la nature du minéral dominant. Aussi, cette information minéralogique permet également d'évaluer l'existence et l'importance d'altération du matériel, phénomène dont on ne se rend pas compte dans les essais à long terme sur les échantillons intacts.

Dans tous les points d'un talus naturel ou artificiel, le „squelette" minéral est soumis à un état d'efforts qui est précisé dans le schéma de calcul par les cercles de Mohr.

Quand l'état d'efforts dans tous les points n'atteint pas la courbe intrinsèque, la stabilité est assurée et les déformations sont faibles. Dans certains cas, la courbe intrinsèque peut être atteinte localement et alors, l'argile se plastifie dans ces zones-là et les déformations s'amplifient. A la limite, la zone de plasticité peut s'étendre largement, jusqu'à la rupture totale du talus.

Donc, dans le calcul, apparaissent, à côté du régime hydraulique (pression interstitielle u), les paramètres des matériaux argileux : γ, C et φ.

Les paramètres effectifs — c' et φ' — sont obtenus par des essais avec une vitesse de déformation très lente qui ne fait pas intervenir les pressions interstitielles. Dans le cas des indications pour le calcul de la stabilité sur terme court, les paramètres c' et φ' sont obtenus directement dans l'appareil Casagrande.

Pour le calcul de la stabilité des versants naturels ou des talus qui ont une déformation sur un long terme, il est nécessaire de simuler un déplacement suffisamment grand sur la surface de rupture pour être représentatif à ceux qui se produisent en nature. Le modèle simulé consiste à exécuter quelques cisaillements alternatives avec le même appareil Casagrande, ainsi que le déplacement final d'un point-répère, soit de 10—12 fois plus grand que dans le cas des essais ordinaires (fig. 1).

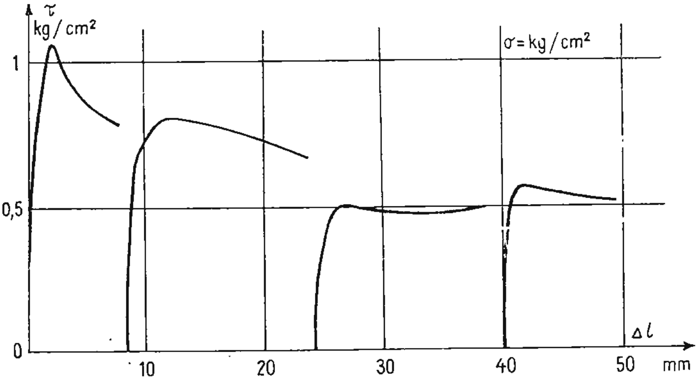

Fig. 1. — Courbe résistance au cisaillement — déplacement.

On constate une réduction des valeurs $\varphi_{rés.}$ par comparaison aux valeurs φ (résistence de bout). Cette réduction est évidente au cours du déplacement parce qu'après avoir opposé un maximum de résistance au cisaillement, les particules d'argile sont orientés dans le sens de la déformation.

Les déterminations effectuées dans notre laboratoire géotechnique sur une variété très large d'échantillons (du point de vue de l'emplacement et de l'âge), montrent des valeurs de la résistance de bout de 20—39° et de la résistance résiduelles de 11—19°30′ (tab. 1).

TABLEAU 1

La résistance au cisaillement de quelques argiles en Roumanie

L'emplacement	L'âge	Résistance au cisaillement	
		φ	$\varphi_{rés}$
Suplac	Pannonien	32°	17°
Mica	Pannonien	39°	19°30′
Murgeşti	Levantin	20°	11°
Tg. Frumos	Sarmatien	31°	15°30′

Les déterminations de la résistance au cisaillement ont été effectuées sur des échantillons intacts avec une forme parallélépipédique de 2 × × 6 × 6 cm.

La surface de glissement formée par cisaillement sur un plan oblique, est généralement irrégulière, fait qui donne une croissance relative de la résistence apparente des échantillons. Nous avons effectuée aussi des essais avec une cisaillement médianne préliminaire qui a conduit à des résultats supérieurs.

Pour les matériaux complets disturbés, avec un certain état de consolidation et qui sont correctement consolidés dans la cassette de cisaillement, on constate qu'indépendamment de l'humidité de la mise en place des matériaux, les résultats des déterminations de la résistence au cisaillement sont similaires pour la même pression normale, humidité sur la surface de glissement. Par exemple, un échantillon d'argile disturbé de Tg. Frumos, étudié par nous sur une large série d'humidité (15, 20, 34 et 40%), montre une humidité résiduelle constante de 26% après les essais à cisaillement.

En même temps, la valeur de la résistance au cisaillement ($\varphi = 30°$) devient $\varphi_{rés} = 15°30'$ pour toutes les humidités initiales.

Conclusions. Toutes les études effectuées pour la détermination de la résistance au cisaillement des argiles conduisent à la conclusion que la valeur de ce paramètre ne dépend pas de la granulométrie et de la plasticité ; la vitesse de cisaillement a un rôle mineur.

Dans tous les cas, la porosité et l'humidité initiales n'influencent pas la valeur de la résistance au cisaillement.

A l'heure actuelle, l'influence de la composition minéralogique de la fraction < 2 μ sur la résistence résiduelle est bien connue quoiqu'il n'existe pas des études executées sur des étalons argileux purs. Enfin, de nombreuses déterminations s'imposent pour préciser l'importance du contenu des substances de liaison ($CaCO_3$, oxydes de fer, matières organiques), de la structure et de l'influence des autres facteurs qui prennent part à la caractérisation d'une roche argileuse.

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MINERALOGICAL COMPOSITION OF SOME TUFACEOUS DEPOSITS RICH IN EXCHANGEABLE POTASSIUM[2]

BY

FLORICA POPESCU[2], VENERA CODARCEA[2] and H. ASVADUROV[3]

Abstract

Mineralogical Composition of some Tufaceous Deposits Rich in Exchangeable Potassium. Some dacitic tufaceous deposits (Tortonian) display an peculiar cation exchange capacity; likewise their saturation with exchangeable potassium is high ($V_K = 18-38\%$). It was stated that this fact is due to the presence of K and Na zeolites — in this case — of clinoptilolite.

In the north-western part of Transylvania, thin strata of tuffs belonging to the clay and sandstone complex, occur. When the compact rocks are found at small depth, the autigenic unconsolidated deposits are frequently rich in tufaceous skeletal material. Among the specific features of these deposits, on which shallow soils occur, is their high content in potassium.

The objective of this work has been the establishment of the cause which determines the high exchange capacity of the potassium in some of the tufaceous deposits. As it will be hereunder shown the study of the clay of these deposits led to the elucidation of this phenomenon.

On this purpose in the area of the Someş Plateau five thin profiles, with the hard rock occurring from 20 to 40 cm depth, have been analysed.

Mineralogical Analysis of Rocks and Coarse Fraction

Rocks of the substratum of tufaceous deposits have the aspect of white, slightly yellowish, porous and friable pelitic sediments.

The mineralogical analysis of rock thin sections (tab. 1) asserts their classification into the group of dacitic tuffs; their lithoclasts are

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[1] Reported in the session from November 1973.

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represented by fragments of dacites and quartzites 0.25—1 mm in diameter. The texture is nonoriented, and the microstructure varies from the lithovitrocrystalloclastic (0.3) to the vitroclastic (P.1) up to the tuffitic (P.5) with strongly argillized paste. The crystal fragments show angular and subangular outlines (quartz, feldspars, garnets, etc.), prismatic ones (hornblende and pyroxenes) or rounded ones (biotite), consolidated by the intermediary of some volcanic ashes with isotropic aspect. The weak effects of anisotropy of the paste are due to the devitrification of glass, phenomenon pointed out also by Mîrza (1970). Most rocks have the aspect of some sediments of primary character; only near Apahida the mineral components oriented, sorted and grouped according to coarse and pelitic zones, evidence the epiclastic character of the rock.

TABLE 1

Mineralogical Analyses of the Rocks from Tufaceous Deposits

Mineralogical compounds	1 Bocşa %	2 Mirşid %	3 Mirşid %	4 Căşeiu %	5 Apahida %
Glassy mass	66.5	67	82	82	76
Lithoclasts	10	—	—	—	2
Feldspars	15.5	17	—	11	6
Quartz	0.5	2	—	2	2
Hornblende	5	—	—	—	—
Hypersthene	2	—	—	1.5	—
Biotite	1	8	9	3.5	4.5
Chlorite	—	—	4	—	7.5
Sericite	—	—	5	—	2
Oxides	—	7	—	—	—

The mineralogical analysis of the coarse fraction (0.06—0.25 mm) of weakly consolidated tufaceous material (fig. 1) shows that they are autochthonous. Besides elements of eruptive nature there are found, to a certain extent, the detrital ones (P. 2 — Mirşid and P.4 — Căşeiu), particularly conspicuous in the case of the sediments formed on tuffites (P. 5 — Apahida). The coarse fraction is mainly composed of paste with isotropic aspect and minerals specific to tuff: feldspars, amphiboles and pyroxenes; as minerals proceeded from late detrital supplies garnet, zoisite, zircon, disthene, etc. also occur. Thus the large percentage incumbent on feldspars, quartz and muscovite in some deposits (P.2, 4 and 5) is due both to detrital supplies and also to those of an eruptive nature (volcanic glass).

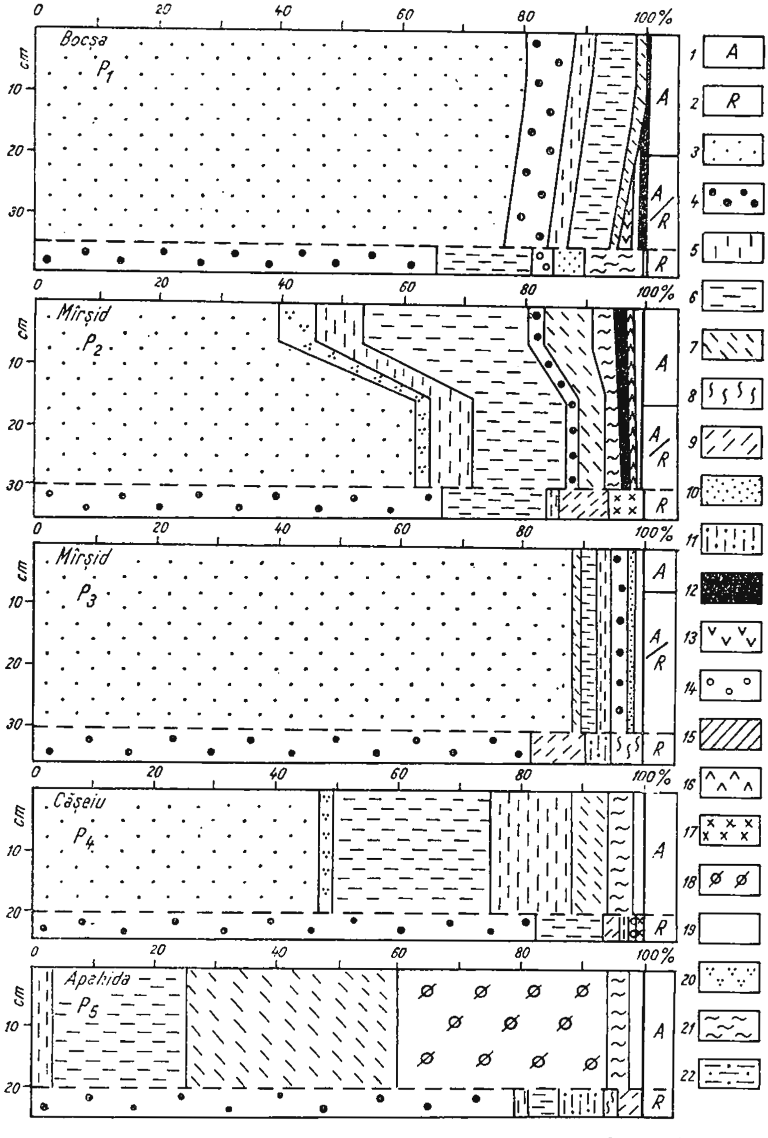

Fig. — Mineralogical composition of the coarse fraction (0.06—0.25 mm) of some tufaceous deposits and subjacent rocks : 1, pedogenetic weathered stratum ; 2, rock ; 3, fragments of amorphous paste ; 4, glass ; 5, quartz ; 6, feldspars ; 7, muscovite ; 8, sericite ; 9, biotite ; 10, hornblende ; 11, chlorite ; 12, zoisite ; 13, disthene ; 14, hypersthene ; 15, garnet ; 16, zircon ; 17, oxides ; 18, grains with oxide films and clay minerals ; 19, other minerals ; 20, dacite fragments ; 21, rock (quartzitic) fragments ; 22, glass and clay.

Some Physical and Chemical Characteristics of Tufaceous Deposits

Clay Mineralogical Analysis[4]

The top layers are dark coloured. Some are nonskeletal and very clayey with properties of swelling and shrinking (P.1—Bocşa). Some skeletal are loamy-skeletal and permeable (P.2,3 — Mirşid, P.4 — Căşeiu);

TABLE 2

*Analytical Data of some Tufaceous Deposits**

Depth cm	Clay < 0.002 mm %	Sand 0.02–2 mm %	Organic matter %	Exchangeable cations							pH (H_2O)
				T me	procents of T					V %	
					Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	H^{+}		
Profile no. 1 — Bocşa											
0–15	70,2	14.1	8.8	61	89.3	6.5	3.3	0.9	—	100	7.4
25–35	73.2	8.1	3.2	60	91.9	4.6	2.4	1.1	—	100	7.6
Profile no. 2 — Mirşid											
0–15	24.4	31.1	5.8	26	55.3	8.3	13.4	1.1	21.9	78.1	5.8
18–30	23.9	30.4	2.6	25	60.9	10.2	16.4	1.8	10.6	89.4	6.8
Profile no. 3 — Mirşid											
0– 7	24.3	43.4	14.8	137	55.6	5.9	32.8	1.0	4.7	95.3	6.5
12–25	22.5	46.9	7.5	125	44.2	9.2	37.8	1.5	7.3	92.7	5.2
Profile no. 4 — Căşeiu											
0–12	45.7	30.9	8.5	64	64,5	14.4	10.4	1.1	9.6	90.4	6.2
Profile no. 5 — Apahida											
0–15	61.0	8.0	8.2	47	67.4	12.9	3.8	1.5	14.4	85.6	6.3

* Chemical and mechanical analyses were executed in the laboratories of the Research Institute of Soil Science (P. Vasilescu mechanical analysis; Adriana Conescu — exchange capacity and pH).

T_{me} — Exchange capacity

V% — Base saturation degree

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[4] The presented data, partially completed (P. 4 Apahida) have been used in a previous work (H. Asvadurov et al., 1974).

the volume weight is small. The deposits lacking on secondary carbonates (P. 1 — Bocşa) are slightly acid (pH = 5.2—6.8). The content of humus ranging from 2.5 to 15% is higher at the surface. In noncalcareous deposits the fulvic acids predominate (fulvic acids : humic acids ratio = 0.2—0.55). Variable cation exchange capacity (T = 25—137 me) is very high, especially in the case of skeletal tufaceous deposits (P.3 — Mirşid with T = 125—137 me). A high exchange capacity of potassium is observed (tab. 2). Thus the tufaceous deposits (rich in coarse fraction of 0.02—2 mm) display a very high saturation with potassium ($V_K = 10-38\%$). No explanation of this feature is known. The high saturation with potassium could be attributed to the presence of salts, to some amorphous hydrated

TABLE 3

A — *Chemical Analysis of the Rocks (g% of the dry mass at 105°C)*

	1 Bocşa	2 Mîrşid	3 Mîrşid	4 Căşeiu	5 Apahida
SiO_2	—	65.56	—	68,47	—
Fe_2O_3	—	1.46	—	1.89	—
Al_2O_3	—	19.68	—	14.44	—
TiO_2	—	traces	—	traces	—
MnO	—	0.016	—	0.050	—
CaO	—	2.25	—	3.90	—
MgO	—	0.81	—	1.09	—
K_2O	1.77	1.52	1.80	1.18	2.31
Na_2O	1.04	0.63	0.13	1.73	0.20
Loss of ignition	6.47	7.72	—	7.30	—
H_2O	6.99	2.14	—	3.67	—
Total	—	99.65	—	100.50	—

B — *Chemical Analysis of some Amorph Compounds in Tufaceous Deposits (0,5 n NaOH extraction)*

	1 Bocşa	2 Mîrşid	3 Mîrşid	4 Căşeiu
SiO_2 %	3.57	5.22	15.19	3.23
Al_2O_3 %	1.13	1.58	2.09	1.60
$\frac{SiO_2}{Al_2O_3}$	5.4	5.6	12.3	3.5
pH in NaF (1:50)	—	7.4	7.6	7.5
V_K %	3.3	13.4	37.8	10.4

gels (allophanes), to weathered primary potassic minerals or to clay minerals with a high content in potassium.

Owing to the carried out studies it was proved that between the various forms of potassium deposits and the saturation with potassium, no satisfactory relationship does exist :

a) Potassium determined in aqueous extract shows low values, between 0.19—0.50 me ;

b) Percentage values of K_2O — total of 1.5—2 >3 g% of clays (tab. 3) are comparable to those of deposits with common V_K;

c) The determined amorphous compounds (tab. 3) with $SiO_2 : Al_2O_3$ between 2.5 and 12.3 and *p*H in FNa (Text Fields and Perrot) under 7.6, as well as the mineralogical analyses do not point out the presence of compounds of allophonic type ;[5]

d) Primary minerals, as biotite (present in the rock, still not encountered — probably weathered — in the fraction of 0.25—0.06 mm) and sodium feldspars are in small amounts.

In order to find an explanation for the high content of exchangeable potassium we paid attention to some potassium clay minerals able to readily release potassium ions.

Clay Mineralogical Analysis

The mineralogical composition of the clay fraction was established by the Rx diffraction. The diffractometer TUR M 61 has been used.[6]

From the aqueous suspension containing the fraction < 1 μ (P.1,2,4) or < 2 μ (P.3 and 5) were prepared oriented slides. The latter underwent the following classical treatments : normal air-drying ; saturation with ethylene-glycol during 24 h after a vacuum ; heating at 350°C and at 550°C.

The clay fraction comprises clay minerals and associated minerals (tab. 4). Two groups may be distinguished :

a) group with the same compounds but in various proportions (P.1 — Bocşa and P.5 — Apahida) and with mixed lattice of (14 c — 14v) type at P.5 Apahida ;

b) group with various compounds but with the same zeolite-clinoptilolite.

The ubiquitous quartz is found solely in proportion of 1—3 %.

The different composition and contents are due to various alteration stages reached by each deposit.

Clinoptilolite is a zeolite not identified as yet in the deposits and soils of Romania ; its formation may be explained by the digenetic alteration of the volcanic glass in a non-marine environment. The cli-

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[5] Compounds of allophonous type have $SiO_2 : Al_2O_3 < 3$ and *p*H values in NaF > 9.4 at 2". (Soil Taxonomy, 1973).

[6] Recording conditions : Cu anticathode ; Ni filter ; 35 kV, 15 mA ; no. of impulses/min. 60.10^3 ; time constant 2 ; goniometric velocity — 1/2°θ/min. ; unfolding velocity of paper : 600 mm/h.

TABLE 4

The X-ray Identification of the Minerals of the Clay Fraction

Localization	Minerals
1. — Bocşa	Montmorillonite Illite Kaolinite-traces Mixed-layers (14N—10) Quartz
2. — Mirşid	Illite Clinoptilolite Vermiculite Chlorite Mixed-layers (14C—14V)+14M(10—14M) Quartz
3. — Mirşid	Montmorillonite Clinoptilolite Illite Mixed-layers (10—14M) Quartz
4. — Căşeiu	Illite Clinoptilolite Montmorillonite Mixed-layers (14M—10) Quartz
5. — Apahida	Illite Montmorillonite Kaolinite Mixed-layers (10—14M)+(14C—14V) Quartz

Note : The minerals are tabulated in the quantitative diminishing order C — chlorite ; M — — montmorillonite ; V — vermiculite.

noptilolite was discovered in Patagonia by Mumpton (1960)[7] in the Sarmiento Formation (Eocene-Oligocene) interbedded with bentonic clays.

Characteristic diffraction maxima are :
$d = 9.00$ Å; 7.94 Å; 3.96 Å and 2.97 Å

---

[7] Chemical analysis indicated by the author:

(K, Na) 4.86 (Ca, Mg)0.31 Al 5.49 Si 30.50 0.72. 19 H_2O

According to Butazova quoted by Travnicova et al. (1973) the sizes of clinoptilolite range from 0.005 to 0.001 mm.

The diffraction maxima are in general resembling those of the heulandite excepting one (004) peak corresponding to $d = 3.96$ Å, which is much more intense for clinoptilolite. The differentiation was also carried out through the treatment of the oriented slide at 350°C. While at this temperature heulandite becomes amorphous, the crystallinity of clinoptilolite does not undergo any alteration. The fact that its structure is not affected even at 550°C proves that we are dealing with a K and Na zeolite.

Likewise with respect to the Ca clinoptilolite which is partially destroyed at 550°C (diagnostic peak from $d = 9.00$ Å being still discert nible), the K and N zeolite maintains its thermic stability up to abou- 700°C.

All these features were observed both in Rx diffraction diagrams and ATD.

The presence of this K and Na zeolite (with a high exchange capacity, especially for K) accounts for the high percentage of K — exchangeable solely at profiles within which it was encountered (P.2, 3 and 4).

The presence of an additional „structural" silica in the lattice of the clinoptilolite as compared to that of heulandite is more responsible for its increased stability than the nature of the exchange cation. This enrichment in silica within the lattice, and the rise of its thermal stability are probably the direct consequence of its volcanic origin.

Conclusions

The deposits of some dacitic tuffs (Tortonian) including tufaceous fractions under 2 mm display a great cation exchange capacity. Correspondingly, the saturation with exchangeable potassium ions is high ($V_K = 10-38\%$). The study of some surface deposits from the Someş Plateau proves that the high saturation with potassium is not due to salinization, to the content of allophanes or some primary potassium-bearing minerals; the content of illite is also in the limits of normal values. The presence of some potassium and sodium zeolites in the predominantly potassic clinoptilolite in the given case, must be considered as the determining factor. Moreover, in the five studied samples, the clinoptilolite was encountered only in deposits with a high exchange capacity for potassium. This is due to the three-dimensional structure with wide channels of the zeolite.

As the potassium occurs under readily assimilable forms[8] the problem of studying the possibility to use such deposits as a source of K supply may be raised.

The presence of montmorillonite in some clayey deposits accounts for their shrinking character, unfavourable for construction and emplacement of pipe-lines.

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[8] The accessible K_2O values (Maslova's method) are, according to Maria Damian very high, of 105—1 680 mg% (Asvadurov et al., 1974).

Likewise the presence of zeolites in some tufaceous deposits requires a geochemical explanation as to the formation of some salinized deposits and soils and of some brackish mineralized waters in the Tortonian facies with tuffs.

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QUELQUES ASPECTS DE L'ALTÉRATION DES MINÉRAUX ARGILEUX DANS LES SOLS SALINS ET À ALCALIS[1]

BY

FLORICA POPESCU[2], LUCIA VLAD[3], N. FLOREA[3], ADRIANA CONESCU[3]

Abstract

Some Aspects of the Clay Mineral Weathering in Saline Alkali Soils. The dominant clay mineral, the montmorillonite, is the most stable in the peculiar conditions of a medium characterised by alkaline — reaction, Na^+ dominant and weak drainage. The most of it derives from illite and chlorite by weathering. The accumulation of $MgCO_3$ in special horizons of the soil is explained by the chlorite alteration too. Simultaneous to the solodisation of the solonetz a weathering of the montmorillonite is produced with eliberation of amorphous silica accumulated in the solodized horizon.

On présente quelques observations sur la composition des minéraux argileux de quelques sols salins et à alcalis de la plaine de Banat.

Matérial et méthods

On a etudié la fraction argileuse ($< 1\ \mu$) séparée de trois sols salins et à alcalis qui se trouvent en differents stades d'évolution : un sol de marécage salinisé solonetzisé (47 Bociar), un solonetz salinisé (57 Diniaș) et un solonetz solodisé (54 Foieni).

Les deux premiers se sont formés sur des dépôts alluviaux et le troisième sur un dépôt loessoïde.

Dans le tableau 1 on donne les principaux caractéristiques chimiques des sols respectifs.

Les sols évoluent sous l'influence des nappes fréatiques bien mineralisées (1—4,1 g/l) et situées à des profondeurs qui varient entre 1,9 et 2,5 m; ils ont comme composant chimique dominant commun le $NaHCO_3$ (la proportion du $NaHCO_3$ dans les nappes fréatiques varie entre 54—

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[1] Communiqué à la première Conférence Nationale d'Argile, Bucarest, 1973.

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82% du total des sels). Dans les sols, sous l'influence de ces nappes fréatiques, se sont accumulés les sels solubles (jusqu'à un contenu maximum de 0,8 g/100 g sol) dont le composant chimique dominant est le Na_2CO_3 et $NaHCO_3$; de sort que tous les sols ont une salinisation de type sodique à l'exception du profil 54 Foieni qui présente dans les horizons solodisés une salinisation bicarbonatosulphatosodique (tableau 1).

En conséquence, dans le complexe d'échange des sols prédomine l'ion sodique et la réaction du sol est très alcaline (*p*H 9—10,3) exceptés les horizons solodisés du profile 54 Foieni.

On a séparé la fraction argileuse saturée en Ca^{2+}.

Les analyses aux rayons X ont été effectuées avec le diffractomètre TUR M—61, prévu d'un anticathode en Cu et un filtre en Ni.

Les lames orientées ont subi les traitements classiques : séchage en atmosphère normale (diagr. N), saturation en vapeurs d'éthylène-glycol pendant 24 heures après un vide préalable (diagr. EG) et chauffage à 300°C et à 550°C (diagr. 300, resp. 550).

Les estimations quantitatives faites pour les minéraux argileux après la methode de Leonard G. Schultz.

Résultats. Suivant les diagrames de diffraction on constate que l'illite, le minéral dominant dans le profil 47 Bociar, diminue depuis la surface (60% à 0—6 cm), vers la base (40% à 130—145 cm) et présente le caractère „ouverte" à la surface et „fermée" en profondeur.

La montmorillonite identifiée à la surface en quantité réduite (10%) augmente vers la base du profil (40%).

De même la chlorite Mg augmente (depuis 10%) en profondeur (à 35%); les interstratifiés formées de feuillets illitiques et montmorillonitiques ou bien formées de chlorite et vermiculite, diminuent depuis 20% à la surface jusqu'à 5% vers la base.

Dans le profil 57 Diniaş le contenu de l'illite (di- et trioctaédrique) de type „ouverte" diminue en profondeur (de 40% à 20%).

La montmorillonite est le minéral dominant dans les horizons *B* et *G* (60%) et se trouve aussi interstratifiée avec l'illite.

La chlorite-Mg présente à la surface (15%) devient très degradée ou interstratifiée avec la vermiculite dans l'horizon *B* et seulement en traces à la base du profile.

Dans le profile 54 Foieni l'illite „ouvert" suit le même cours de diminution le long du profil (depuis 40% à 20%).

Plus particulière est la distribution de la montmorillonite qui dans l'horizon solodisé (0—4 cm) ne se trouve qu'interstratifiée avec l'illite dans un grand pourcentage (50%). Vers le milieu du profil on la trouve comme minéral indépendent (30%) ainsi qu'en réseaux mixtes (avec des feuillets illitiques). A la base (160—180 cm) la quantité augmente vers 60%.

La chlorite est présente soit pure soit interstratifiée avec l'illite mais toujours entre 5—10%.

La discussion des données. A cause de la nature différente du materiel parental et du caractère poligénétique des sols étudiés, on ne peut pas faire des considérations sur la variation quantitative des minéraux argileux sur le profil, comme résultat des processus pédogénétiques

TABLEAU 1

Caractéristiques chimiques générales des sols

Profondeur cm	Horizon	Total sels %	Total sels me 100g sol	Co_3^{--} solubes %	CO_3H^- solubes %	Na^+ solubes %	*T* me 100g sol	Na^+ éch. % *T*	pH	Ca^{++} ($CaCO_3$ + % Ca éch.) me 100 g sol	Mg^{++} ($MgCO_3$ + Mg éch.) me 100 g sol
Sol de marécage salinisé solonetzisé 47 Bociar											
0—6	Asa	0,292	7,74	0	21,7	36,2	19,6	34,5	9,08	5,5	4,2
10—25	—	—	—	—	—	—	—	—	10,04	—	—
47—60	Agsa	0,501	13,37	3,0	29,0	36,5	26,5	58,3	10,12	26,3	12,1
90—105	GC	0,473	11,89	3,9	27,1	40,0	—	—	10,20	—	—
130—145	GC	0,449	10,95	4,1	25,4	42,7	—	—	10,20	—	—
Solonetz salinisé 57 Diniaş											
0—1	A_2	0,229	6,33	0	29,0	39,3	24,8	15,1	8,86	18,8	10,07
1—7	B_1	0,292	7,83	1,7	34,8	36,8	21,3	39,1	9,82	104,5	27,4
7—15	B_1sag	0,527	13,75	4,9	31,5	43,1	21,0	62,9	10,18	155,9	65,3
28—40	B_2sag	0,794	20,76	5,5	29,8	42,8	23,1	70,0	10,36	162,4	52,1
70—85	GC	0,511	14,29	4,1	28,2	41,0	19,0	70,8	10,22	415,5	137
Solonetz solodisé 54 Foieni											
0—4	A_2	0,045	2,56	0	16,5	22,7	14,0	—	6,0	—	—
5—11	B_1	0,158	6,63	0	16,0	37,0	19,4	—	7,90	5,30	2,60
37—50	B_4	0,680	18,25	2,8	26,3	35,0	21,5	66,7	10,10	34,8	24,10
68—100	BC	0,207	13,04	3,0	24,4	34,4	—	—	—	—	—
120—140	Cg	0,193	10,98	3,4	34,8	38,5	14,0	54,1	10,1	250,0	86,2

spécifiques au stade actuel d'évolution de ces sols. On va préciser quelques aspects résultés de l'étude roentgenographique de la fraction $< 1 \mu$ et qui peuvent mettre en évidence le comportement des minéraux argileux dans les conditions de milieu dans lequel évoluent ces sols. Ceux-ci se caractérisent par une réaction très alcaline, par la domination du Na^+ dans la solution du sol et dans le complexe adsorbtif du sol et aussi par un drainage faible qui ne permet pas le lessivage des produits d'altération.

Dans tous les profils de sols l'illite présente la même distribution, de diminution en profondeur ainsi que le contenu en K_2O (tab. 2).

TABLEAU 2

Minéralogie de la fraction $< 1\mu$

Sol de marécage salinisé solonetzisé 47 Bociar	Solonetz salinisé 57 Diniaş	Solonetz solodisé 54 Foieni
Horizon *Asa* 0–6 cm	Horizon B_1 1–7 cm	Horizon A_2 0–4 cm
Illite 60 % Chlorite 10 % Montmorillonite 10 % RM (14 C–14 V)+ + (10–14M) 20 %	Illite 40 % Chlorite 15 % Montmorillonite 30 % RM(10–14M)+ + (10–14C) 15 %	Illite 40 % Chlorite 10 % RM (10–14M) 50 %
Horizon *Agsa* 47–60 cm	Horizon B_2sag 28–40 cm	Horizon *B* 37–50 cm
Illite 55 % Montmorillonite 25 % RM(14C–14V)+ + (10–14M) 25 %	Illite 25 % Montmorillonite 50 % Chlorite 10 % RM(10–14M)+ + (14C–14V) 15 %	Illite 40 % Montmorillonite 30 % Chlorite 5 % RM(10–14M)+ + (10–14C) 25 %
Horizon *G* 130–145 cm	Horizon *GC* 70–85 cm	Horizon *G* 165–180 cm
Illite 40 % Montmorillonite 30 % Chlorite 30 %	Illite 20 % Montmorillonite 60 % Chlorite 5 % RM(10–14M) 15 %	Illite 20 % Montmorillonite 60 % Chrloite 10 % RM (10–14M) 10 %

Note : RM — réseaux mixtes ; C — chlorite ; V — vermiculite ; M — montmorillonite.

Moins évident dans le sol marécageux (47 Bociar) l'illite „ouverte" (surtout dans les horizons natriques des solonetz) indique sa dégradation dans les conditions de milieu spécifiques à ce sol.

Le grand contenu en interstratifiés illite-montmorillonite, l'altération de l'illite ainsi que la distribution quantitative de la montmorillonite et de l'illite sont les éléments qui atestent que la dégradation de l'illite conduit à la néoformation de la montmorillonite. Celle-ci constitue le minéral argileux stable dans les conditions de milieu spécifique.

Ainsi dans le sol marécageux qui évolue surement en conditions d'alcalinité plus récentes en comparaison avec les solonetz, l'illite se trouve en quantité plus élevée, il présente un caractère d'illite „fermée" et le contenu de la montmorillonite est moindre.

Un autre aspect particulier est celui de la dégradation de la montmorillonite dans le profil 54 Foieni (0—4 cm) ou on la trouve seulement interstratifiée.

L'extraction des substances amorphes d'après la méthode de Hashimoto-Jackson (tab. 3) dans le sol marécageux et dans le solonetz salinisé, indique un contenu en silice amorphe très réduit et une distribution uniforme le long du profil tandis que dans l'horizon solodisé du profil 54 Foieni se produit une accumulation (2,3 g/100 g sol) avec un rapport molaire $SiO_2/Al_2O_3 > 10$, probablement comme résultat de la dégradation de la montmorillonite qui n'est plus détectée dans cet horizon.

TABLEAU 3

Analyses de la substance amorphe des sols

Horizon	Profondeur cm	SiO_2 % amorphe	Al_2O_3 amorphe	SiO_2/Al_2O_3	K_2O % de la fraction < 1μ
Sol de marécage salinisé solonetzisé 47 Bociar					
Asa	0—6	0,53	0,17	5,1	4,21
Agsa	47—60	0,95	0,33	4,9	3,71
G	130—145	0,56	0,24	3,9	3,00
Solonetz salinisé 47 Diniaş					
B_1	1—7	0,59	0,20	4,9	3,47
B_2sag	28—40	0,44	0,14	5,1	3,40
GC	70—85	0,50	0,25	3,4	2,20
Solonetz solodisé 54 Foieni					
A_2	0—4	2,30	0,32	12,4	3,80
B_4	37—50	0,76	0,36	3,6	3,10
G	165—180	0,69	0,33	3,6	2,30

Ce comportement de la montmorillonite dans le processus de solodisation constitue l'un des cas caractéristiques (Klages, 1968, 1969; Florea et al., 1974) déterminé par le changement de milieu dans les horizons soumis au processus de solodisation par le changement du chimisme du sol d'une réaction très alcaline à une réaction très faiblement acide (le *p*H déscend de > 10 à 6), par la modification de la nature et du rapport des cations d'échange (Na^+ remplacé par H^+) et surtout par le changement des conditions de drainage à cause de l'apparition et de l'intensification du processus de lessivage.

Dans tous les profils presentés, la chlorite-Mg identifiée en quantités variables peut être liée à la présence des schistes chloriteux des Carpates Meridionales d'où proviennent les sédiments de la plaine.

Dans ces sols la chlorite très dégradée ainsi que ses interstratifications avec la vermiculite suggèrent la néoformation de la montmorillonite comme résultat final de l'altération. Konda (1969) admet la néoformation de la montmorillonite dans les sols salins et à alcalis par la silicification de la chlorite.

La présence et les conditions d'altération intense de la chlorite-Mg explique la teneur élevée en $MgCO_3$ qu'on trouve dans le sol.

Conclusions

Les conditions de milieu chimique et de drainage du sol influencent la formation et l'évolution des minéraux argileux.

La montmorillonite, le minéral argileux dominant dans la fraction argileuse des solonetz, est aussi le plus stable dans les conditions de milieu spécifiques à ce sol (réaction très alcaline, domination du Na^+ et drainage faible).

La néoformation de la montmorillonite se réalise dans la plus grande partie par la dégradation de l'illite.

L'abondance des interstratifiées illite-montmorillonite, le contenu élevé de l'illite „ouverte" ainsi que la distribution quantitative de l'illite et de la montmorillonite sont des arguments pour le mécanisme de la montmorillonite.

L'existence de la chlorite-Mg très dégradée et des réseaux mixtes chlorite-vermiculite suggère aussi la néoformation de la montmorillonite par l'altération de la chlorite-Mg ; comme résultat s'accumulent de grandes quantités de $MgCO_3$ dans le sol.

Le processus de solodisation par les nouvelles conditions de milieu créées réalisent la dégradation de la montmorillonite qu'on ne trouve plus dans l'horizon solodisé. Dans cet horizon comme résultat de cette dégradation s'accumule la silice amorphe qui a un rapport molaire $SiO_2/Al_2O_3 > 10$.

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SOME DATA ON THE CLAY MINERALOGY AND SEDIMENTATION IN THE ABYSSAL ZONE OF THE BLACK SEA [1]

BY

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Abstract

Sur la minéralogie des argiles et les processus sédimentaires dans la zone abyssale de la Mer Noire. L'article présente les résultats des études effectuées sur deux carottes récoltées dans la zone profonde de la Mer Noire. On a obtenu des données sur la distribution en surface des minéraux argileux ainsi que sur la variation en temps de la composition des minéraux argileux. Les auteurs examinent les caractéristiques des régions sources de matériel ainsi que les variations de la vitesse de sédimentation dans la zone étudiée.

Introduction

The investigations of the abyssal recent sediments in the Black Sea pointed out the importance of the clay mineral associations as indicators of the sedimentary processes (Rateyev, 1952, 1964; Butuzova, 1960; Stoffers and Müller, 1972).

According to Stoffers and Müller (1972) the clay minerals distribution in the superficial sediments of the Black Sea is controlled by two source-areas : (1) a northern, illite-rich area and (2) a southern, montmorillonite-rich area. The fluctuation of the montmorillonite and illite contents along cores is regarded as a consequence of the climatic variation during the late Pleistocene (Würm) and Holocene.

The present study is based on the investigation of 42 samples from two cores collected by R/V Pillsbury (Expedition „Odysseus 65", Miami Institute of Marine Science). In one of the cores (P 6507—14) only a sandy intercalation (111 cm—149 cm) was investigated (8 samples; grain-size and clay mineralogy analyses). 34 samples dispersed along

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the whole core P 6507—15 have been analysed for grain-size, clay mineralogy and $CaCO_3$, organic carbon and water contents. All the analyses have been carried out in the laboratories of the Woods Hole Oceanographic Institution.

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Analytical Procedures

Grain-size analysis. Sieving and pipetting have been used conjointly for the grain-size analysis. More details on the working method are presented by Jipa (1974).

For the purpose of this paper only several grain-size parameters are presented : the distribution of clay (< 4 μ), silt (4—62 μ) and sand (62 μ—2 mm) contents and the median values.

Clay mineralogy. X-ray determination of the clay minerals was performed on the < 2 μ fraction. This material was vacuum filtered on silver filters and X-rayed as (1) un-treated, (2) treated with ethylene-glycol, (3) heated at 400°C and (4) heated at 550°C.

The following clay minerals have been identified : illite, montmorillonite, kaolinite, chlorite and vermiculite, as well as irregular mixed-layers.

The discrimination between kaolinite and chlorite was made according to the peaks 3.54 Å (004 for chlorite) and 3.57Å (002 for kaolinite) clearly separated on the diffractograms.

The chlorites having the 14 Å (001) peak-height increased after heating treatement have been considered as Fe-rich chlorites.

Vermiculite was not confidently identified but in several samples devoid of chlorite (failure of the 14 Å peak after heat treatment).

The sharpness index, defined as the width of the 10 Å peak at its half peak-height (Kubler, 1968; Dunoyer, 1969), was calculated as a measure of the illite crystallinity. The ratio of the (002) and (001) peak heights (Esquevin, 1969) is presented as an evaluation of the illite aluminousity.

According to Lucas's (1962) and Thorez and van Leckwijck's (1967) terminology, the mixed-layers belong to the 10—14 M and 14C—14V types.

The method proposed by Biscaye (1965) was used for the semi-quantitative evaluation of the clayey components.

Carbonate, organic carbon and water contents. Leco 72—2 equipment was used for the determination of the organic carbon quantity.

The carbonate content was estimated directly using the volumetric method, as well as through the difference between the total carbon and organic carbon.

The relative calcite content of the fraction $< 2\,\mu$ was estimated by measuring the characteristic 3.04 Å peak.

Statistical treatment. The intensity of the correlation between different parameters was evaluated using the total and partial correlation coefficients as presented by Griffiths (1967).

The 0.05 probability was selected as the significance level for the coefficients.

Lithology of Core P 6507—15

Throughout the deep part of the Black Sea, Ross et al. (1970) separated three lithologic units. All these units occur in core P 6507—15. The observed sequence is presented in table 1.

It is to be remarked the yellow-grey silty mud at 25—40 cm, which appears as a transitional sediment between units I and II.

Results and Discussions

The results of the different types of analyses are presented in tables 2 and 4. Table 3 includes the correlation coefficients.

Grain-size data. As results from plate, except the lowermost 725—1154 cm interval, core P 6507—15 is characterized by important variations in grain-size. However, the statistical analysis (table 3) points out a certain correlation between the grain-size parameters and the sample depth (h) below sea floor. This is substantiated by the values of the correlation coefficients between the silt and clay contents and the sample depth. The sign of correlation is different for the silt content (increasing with h) and clay content (decreasing with h). No correlation appears between the sand content and sample depth.

These data indicate that the Black Sea sediments observed in core P 6507—15 became more and more clayey during their evolution.

The lack of correlation between the sand content and sample depth points out the episodic presence of this material. The sand was probably introduced in the Black Sea Basin during the short moments when the equilibrium in the marginal zones of the sea was broken.

Distribution of clay minerals in surface sediments. The map in figure 1 was made using analytical data of Stoffers and Müller (1972, table II). On this map the variation of the montmorillonite/illite ratio is shown by isopleths. The zones with high content of kaolinite and chlorite are also indicated on the isopleth map, according to published maps of Stoffers and Müller (1972, fig. 2B and D).

The isopleth map (fig. 1) points out the areal prevalence of the illite as compared with the montmorillonite. The influence of the northern tributaries of Black Sea, especially Danube River, is expressed by the strong bend of the isopleths in front of the Danube Delta Area. Supporting recent data of Ross et al. (1970) the 0.3 and 0.5 M/I isopleths (fig. 1) designate a big submarine fan extending up to the abyssal zone of the Black Sea.

TABLE 1

Lithological Description of Core P 6507—15

Unit	Level	Cored interval (depth below the sea floor in cm)	Lithology
I	a	0—25	Carbonate-rich mud, yellow-grey or light coloured. Alternating dark and light laminae.
II	b	25—40	Yellow-grey, silty mud. Apparently similar with the carbonate-rich mud excepting the lack of the light laminae.
	c	40—96	Dark mud rich in organic matter, consisting of dark, yellow-grey and occasional light laminae.
III	d	96—159	Homogeneous grey mud.
	e	159—209	Yellow-grey silty mud, with several sandy laminae
	f	209—270	Blue-grey mud with a 0.4 cm lamina of dark mud at cm 258.
	g	270—302	Darkish-grey silty mud, becoming blue-grey toward the lower part.
	h	302—329	Blue-grey silty mud, with a dark lamina at the upper part.
	i	329—335	Slightly sandy, clayey silt. Sharp bedding boundaries.
	j	335—405	Blue-grey mud with sandy and silty laminae.
	k	405—428	Silty sand, apparently graded bedded. Sharp base; transitional upper boundary.
	l	428—455	Alternating centimetric layers of silty grey mud and (graded) sandy silts.
	m	455—612	Grey-yellow mud with silty laminae (sometime graded) at the upper part.
	n	612—725	Silty sand and sandy silt, apparently symmetrically graded. A 5 cm thick intercalation of yellow-grey mud at the upper part.
	o	725—1154	Yellow-grey silty mud with occasional sandy laminae.

TABLE 2

Distribution of Some Grain-size, Mineralogical and Chemical Parameters in Core P 6507—15

Sample no.	h (cm)	Sd	s	cy	Md	I	M	K	C	M/I	I_a (mm)	Al	$CaCO_3$ %	O.C. %	Water %
		%			(microns)	%									
1	5	1.9	10.4	87.7	<1	51	31	9	9	0.6	6	nd	8.6	4.0	76
2	25	0.3	10.0	89.7	<1	++	+	?	?	nd	nd	nd	11.3	1.5	
3	32	2.8	43.0	54.2	2	57	30	7	6	0.5	7	0.21	0.8	2.2	
4	45	1.0	15.2	83.8	<1	50	35	8	7	0.7	6	0.30	1.8	7.4	
5	95	1.0	12.8	86.2	<1	48	42	5	5	0.9	6	0.26	1.6	8.4	76
6	107	0.2	17.6	82.2	<1	40	47	7	6	1.2	6	0.27	0.6	2.4	
7	157	1.8	9.8	88.4	<1	55	28	7	10	0.5	5	0.30	2.0	2.2	66
8	169	3.3	24.5	72.2	1	61	25	7	7	0.4	5	0.47	2.5	2.1	
9	200	1.2	35.1	63.7	1	49	29	11	11	0.6	6	0.28	3.5	0.7	50
10	212	0.4	24.4	75.2	1	50	32	7	11	0.6	5	0.24	0.6	0.3	
11	263	0.3	14.8	84.9	1	59	31	10	0	0.5	9	0.13	1.2	0.5	48
12	273	0.9	67.4	31.7	10	59	22	11	8	0.4	6	0.25	0.3	0.4	
13	304	0.3	21.4	78.3	<1	41	45	7	7	1.1	8	0.26	0.5	0.2	
14	332	1.6	63.4	35.0	10	40	45	7	8	1.1	5	0.26	1.5	1.5	
15	365	0.1	37.1	62.8	2	38	53	0	9	1.4	9	0.22	3.3	0.8	39
16	407	15.3	62.2	22.5	15	48	37	7	8	0.8	5	0.23	1.7	0.4	
17	417	3.1	59.8	37.1	8	46	41	6	7	0.9	5	0.21	2.1	0.6	
18	427	50.1	32.4	17.5	66	53	29	8	10	0.5	5	0.24	2.1	0.3	
19	484	0.2	30.0	69.8	2	50	30	9	11	0.6	5	0.37	2.1	0.4	
20	553	0.1	13.3	86.6	<1	48	29	11	12	0.6	5	0.25	1.7	0.5	43
21	603	0.2	9.8	90.0	<1	28	60	6	6	2.1	9	0.16	0.8	0.5	
22	614	1.0	61.0	38.0	9	35	50	8	7	1.4	6	0.24	2.0	0.3	
23	616	1.6	76.3	22.1	21	36	48	8	8	1.3	6	0.23	2.2	0.4	
24	617	2.7	81.2	16.1	27	40	44	7	9	1.1	5	0.23	2.4	0.4	
25	624	0.9	75.9	23.2	14	35	53	5	7	1.5	6	0.24	2.7	0.8	
26	645	12.5	61.5	26.0	18	46	30	11	13	0.7	5	0.31	2.4	0.7	
27	663	64.7	27.3	8.0	55	45	36	8	11	0.8	5	0.24	2.0	0.5	20
28	714	28.6	60.7	10.7	44	39	43	9	9	1.1	5	0.28	1.9	0.3	
29	729	1.5	59.6	38.9	5	32	59	4	5	1.8	10	0.17	3.0	0.8	
30	829	3.2	51.7	45.1	5	40	42	8	10	1.1	5	0.31	3.1	0.5	31
31	898	1.6	56.0	42.4	5	26	65	3	6	2.5	10	0.15	3.1	0.7	
32	999	1.0	51.4	47.6	4	32	59	4	5	1.8	9	0.22	3.1	0.6	
33	1050	0.3	52.1	47.6	4	37	52	5	6	1.4	8	0.27	3.2	0.4	28
34	1149	2.0	51.6	46.4	5	36	46	8	10	1.3	5	0.33	3.0	0.9	

h = sample depth below sea floor
Sd = sand content
s = silt content
cy = clay content
Md = median grain-size
I = illite content
M = montmorillonite content

K = kaolinite content
C = chlorite content
I_a = sharpness index
Al = I(002)/(001) (aluminousity index)
O.C. = organic carbon content
nd = non determinable

TABLE 3

Correlation Coefficients between Some Grain-size, Mineralogical and Chemical Parameters of the Sediments in Core P 6507—15

		Sd	s	cy	I	M	K	C	I_c	Al	Ca	O.C.
h	1	+0.14	_+0.54_	_−0.52_	_−0.70_	_+0.60_	−0.18	+0.09	−0.22	−0.08	_+0.53_	_−0.51_
Sd	1		+0.02*	_−0.54*_	+0.11	−0.20	+0.17	_+0.32_	_+0.32_	−0.03	+0.01	−0.17
	2		−0.07*	_−0.55*_	+0.29	_−0.35_	+0.20	+0.31	_+0.36_	−0.02	−0.07	−0.12
s	1			_−0.78*_	_−0.43_	_+0.35_	−0.07	+0.06	+0.05	−0.15	_+0.47_	_−0.43_
	2			_−0.70*_	−0.07	+0.04	+0.03	+0.07	+0.22	−0.13	+0.26	−0.22
cy	1				+0.29	−0.19	−0.02	−0.24	−0.23	+0.16	−0.29	_+0.46_
	2				−0.13	+0.19	−0.14	−0.22	_−0.42_	+0.15	−0.03	+0.26
I	1					_−0.94*_	_+0.52*_	+0.11*	_+0.47_	_+0.36**_	_−0.39_	+0.26
	2					_−0.91*_	_+0.56*_	+0.24*	_+0.45_	_+0.39**_	−0.03	−0.01
M	1						_−0.71*_	_−0.37*_	_−0.63**_	_−0.47**_	_+0.35_	−0.15
	2						_−0.76*_	_−0.40*_	_−0.63**_	_−0.53**_	+0.05	−0.23
K	1							_+0.39*_	_+0.56**_	_+0.37**_	_−0.34_	−0.15
	2							_+0.41*_	_+0.54**_	_+0.36**_	−0.29	−0.28
C	1								_+0.65**_	_+0.51**_	+0.16	−0.23
	2								_+0.69**_	_+0.52**_	+0.14	−0.22
I_c	1									_+0.60_	+0.14	−0.07
	2									_+0.60_	+0.03	+0.04
Al	1										+0.14	+0.17
	2										+0.21	+0.15
Ca	1											−0.12
	2											+0.20

h = sample depth below sea floor
Sd = sand content
s = silt content
cy = clay content
I = illite content
M = montmorillonite content
K = kaolinite content
C = chlorite content

I_c = illite crystallinity index ($I_c = 1/I_a$)
Al = illite aluminousity index
Ca = CaCO$_3$ content
O.C. = organic carbon content
1 = total correlation coefficients
2 = partial correlation coeeficients

The coefficients above the significance level (at 0.05 probability) printed in italics.
* = coefficients corresponding to a closed assemblage of variables
*** = coefficients indicating the correlation of two variables with the third one.

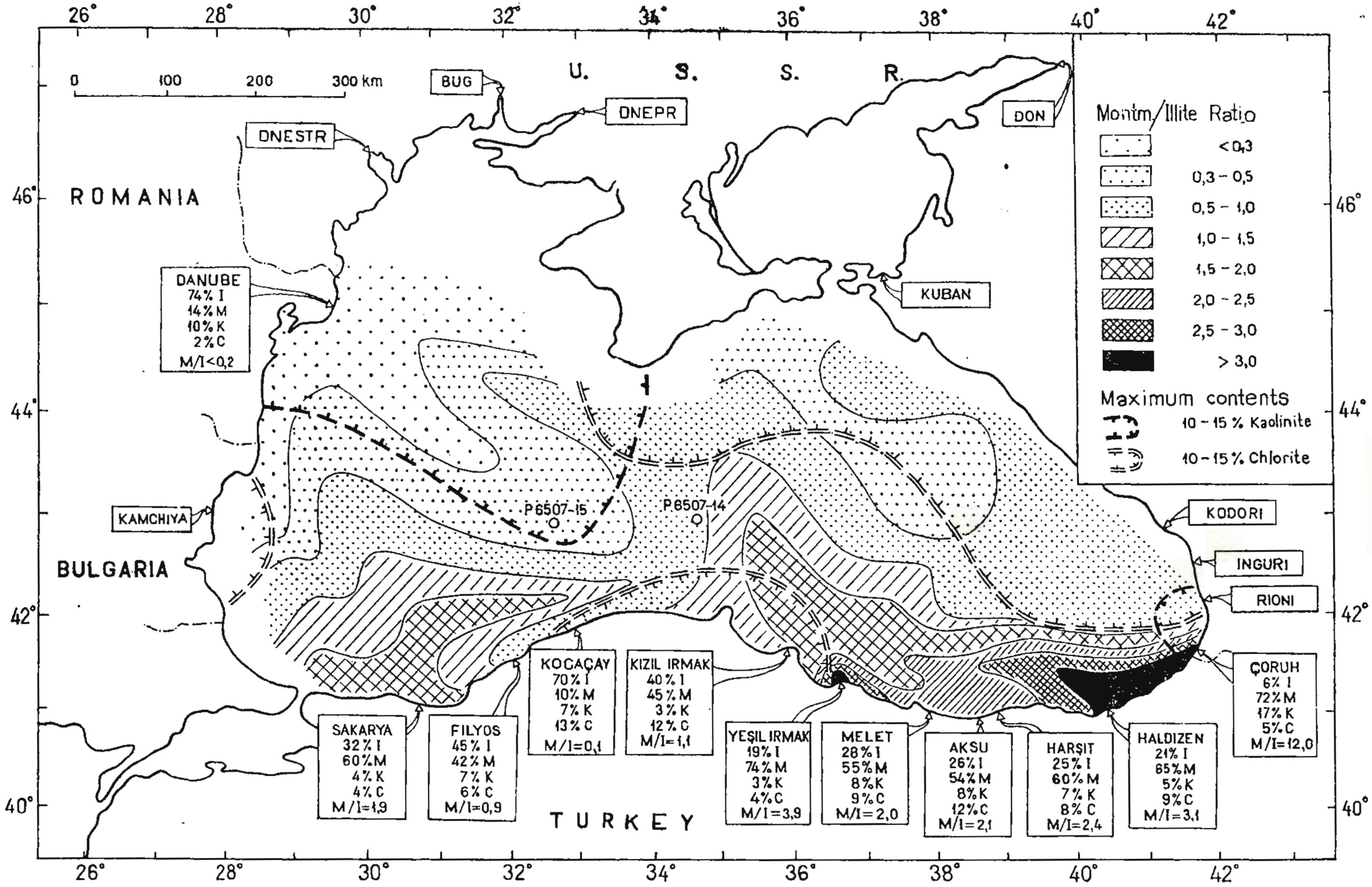

Fig. 1. — Distribution of clay minerals in the Black Sea sediments and in the suspended load of some tributaries (data published by Stoffers and Müller, 1972; reinterpreted by Rădan, 1973).

TABLE 4

Distribution of some Grain-size and Mineralogical Parameters of the Sandy Interbed 111—149 cm in Core P 6507—14

Sample no.	h (cm)	Sd	s	cy	Md	I	M	K	C	M/I	I_a (mm)	AI
		%			(microns)	%						
A	111	0.5	29.5	70.0	1	27	64	4	5	2.3	7	0.23
B	116	2.3	62.9	34.8	10	29	61	5	4	2.1	6	0.24
C	122	37.8	51.6	10.6	52	28	61	5	6	2.1	7	0.20
D	128	58.6	35.3	6.1	72	26	65	5	4	2.5	5	0.20
E	135	65.1	28.8	6.1	68	28	60	6	6	2.1	7	0.22
F	141	65.6	28.3	6.1	90	26	65	4	5	2.5	6	0.20
G	143	67.7	26.2	6.1	96	28	60	5	7	2.1	6	0.20
H	149	63.6	29.6	6.8	100	23	64	6	7	2.8	5	0.25

See explanation table 2.

It is interesting to note that the Mississippi abyssal cone is similarly reflected by the distribution of the montmorillonite content in the Gulf of Mexico (Pinsak and Murray, 1960; reconsidered by Rateyev, 1965).

A less marked inflection of the M/I isopleths appears in the western zone of the Black Sea (fig. 1). This might reflect the partial deposition of the suspended material transported toward the south by the Black Sea circular, surface current.

The third zone with higher illite contents corresponds to the north-eastern zone of the Black Sea. This concentration is probably due to the influxes of sedimentary material supplied by the Sea of Azov.

The montmorillonite, supplied by the Sakarya River and possibly proceeding from the Mediterranean Sea, is transported to the east by the circular, surface current of the Black Sea. The salt water flowing from the Mediterranean Sea could represent another transporting agent, acting in deep waters. As the northern Aegean Sea is a montmorillonite-rich province (Chamley et al., 1962), the suspended sedimentary load of the bottom current entering the Black Sea through the Bosphorous is probably dominated by montmorillonite.

In the south-western Black Sea the isopleths of the M/I ratio are also slightly bended to the north-west. This could reflect another bottom current pointed out by Antipa (1941): a deeper-water replica, with opposite direction, of the littoral circular current.

The M/I isopleths in the eastern zone of the Black Sea (fig. 1) suggest the existence of a deep-sea circular current, moving in the opposite direction to the known surface, cyclonal current. This is rather surprising considering that the Black Sea represents a stagnant basin. However, the absolute age determination of some clastic minerals in the Black Sea

Basin (Krylov et al., 1972, in Shimkus and Trimonis, 1974) supports this pattern of sediment redistribution.

The deep-sea distribution of the montmorillonite in the eastern Black Sea is also reflecting the halmyrolysis of the pyroclastic material (Stoffers and Müller, 1972) brought in deep waters from the narrow shelf existing in this area. The detrital, land-derived montmorillonite, as well as the diagenetical variety were probably redistributed by the above mentioned weak bottom current as suggested in figure 1.

Vertical distribution of clay minerals. The increase of the montmorillonite content toward the lower part of the core P 6507—15 (in accordance with Stoffers and Müller, 1972) is quite evident in plate and table 2. The correlation coefficients make even clearer this feature (table 3): the correlation between illite and sample depth is strongly negative, while the montmorillonite — sample depth correlation is strongly positive. This appears as the mathematical expression of the increasing importance of the northern source-area during the postglacial times.

The negative correlations kaolinite-sample depth and illite crystallinity-sample depth, in spite of being under the significance level are worth mentioning. The negative correlation kaolinite-depth appears as a consequence of the partial coincidence of the illite and kaolinite source-areas. The negative correlation between the illite crystallinity and the sample depth suggests that the illite crystallinity might be less developed at lower levels.

Butuzova (1960) arrived at a similar conclusion, considering that the illite was degraded during the early diagenesis. In our opinion two factors might be responsible for this feature : (1) the southern source, dominant during the glacial times, supplied degraded illite and irregular mixed-layers of the 10—14 M type, and (2) the interstitial water maintained its original lower salinity inhibiting the illite aggradation.

The curves expressing the crystallinity and aluminousity of the illite are in accordance with the evolution of the illite content (plate). This suggests that the northern source-area supplied more aluminous and higher crystalline illite to the Black Sea Basin.

A peculiar feature is shown by the illites from the uppermost part of the core P 6507—15, their crystallinity constantly decreasing upwards. This could be explained by the chemical alteration generated in the northern source-area as a consequence of the warming up of the climate. In this way the 10—14 M mixed-layers would be more frequent in the montmorillonite-rich samples.

The partial correlation between the grain-size and mineralogical parameters provides additional information. Positive, but rather weak correlations exist between the illite, kaolinite, chlorite contents and the sand content. This character could be explained by their common source-area and/or by the larger grain-size range covered by these minerals. The montmorillonite, whose preferential association with the finer-grained fractions of the sediments is well known, is negatively correlated with the sand content.

The illite crystallinity is positively correlated with the sand content, while the correlation with the clay content is negative. Therefore, the sandy sediments are enriched in higher crystalline illite, supplied by the northern source-area.

The Fe-rich chlorite is more frequently associated with the illitic material (influenced by the northern sediment supply), as compared to the montmorillonitic material. A similar association is shown by the distribution of the 14C—14V mixed-layers. This is a consequence of the higher sensibility to the alteration of the Fe-rich chlorite relative to the sensibility of the magnesian variety (Triplehorn, 1970).

Vermiculite was identified with reasonable confidence only in a few samples, all of them rich in montmorillonite. This fact might be an indication for a southern origin of the vermiculite.

Summarizing some above presented observations, it may be concluded that the northern source-area was, and still is, characterized by a sediment supply with fairly high crystalline illite (its crystallinity is decreasing during the postglacial time), kaolinite, Fe-rich chlorite, irregular 14C—14V mixed-layers and, of course, montmorillonite. The clay mineralogy of the southern source-area is marked mostly by the presence of montmorillonite, degraded illite, mixed-layers of 10—14 type (resulting through the advanced weathering of the illite) and occasionally vermiculite.

The turbiditic sequence investigated (core P 6507—14) is characterized by the high montmorillonite contents and low amounts of illite, Fe-rich chlorite and kaolinite. The mean value of the montmorillonite/illite ratio is 2.3 (table 4). Mixed-layers of 10—14M type are frequent. The illite crystallinity and its aluminousity are lower in comparison with that of the illite in the sandy interbeds in core P 6507—15 (table 2 and 4). All these features indicate a southern source-area for the analysed turbiditic sequence.

The high montmorillonite content of the sandy sequence in core P 6507—14 may be explained by the diagenesis of the pyroclastic material existing in the composition of the turbidite material (as pointed out by Stoffers and Müller, 1972).

All graded bedded sequences in core P 6507—15 are marked by the differential deposition of the clay minerals. That is why these beds show higher montmorillonite contents towards the top of the graded sequence, this clay mineral being characterized by a low settling velocity.

Consequently, the montmorillonite appears as a clastic material in case of the core P 6507—15 and as a diagenetic product in core P 6507—14. As the pyroclastic particles generating montmorillonite come from the Anatolian coasts (Stoffers and Müller, 1972), the directions of the transporting currents can be inferred (fig. 2).

Carbonate, organic carbon and water contents in core P 6507—15. The lower part of core P 6507—15 is marked by the uniformity of the carbonate contents and grain-size distribution (plate, table 2). This feature reflects the stability of the sedimentation environment during the glaciation period.

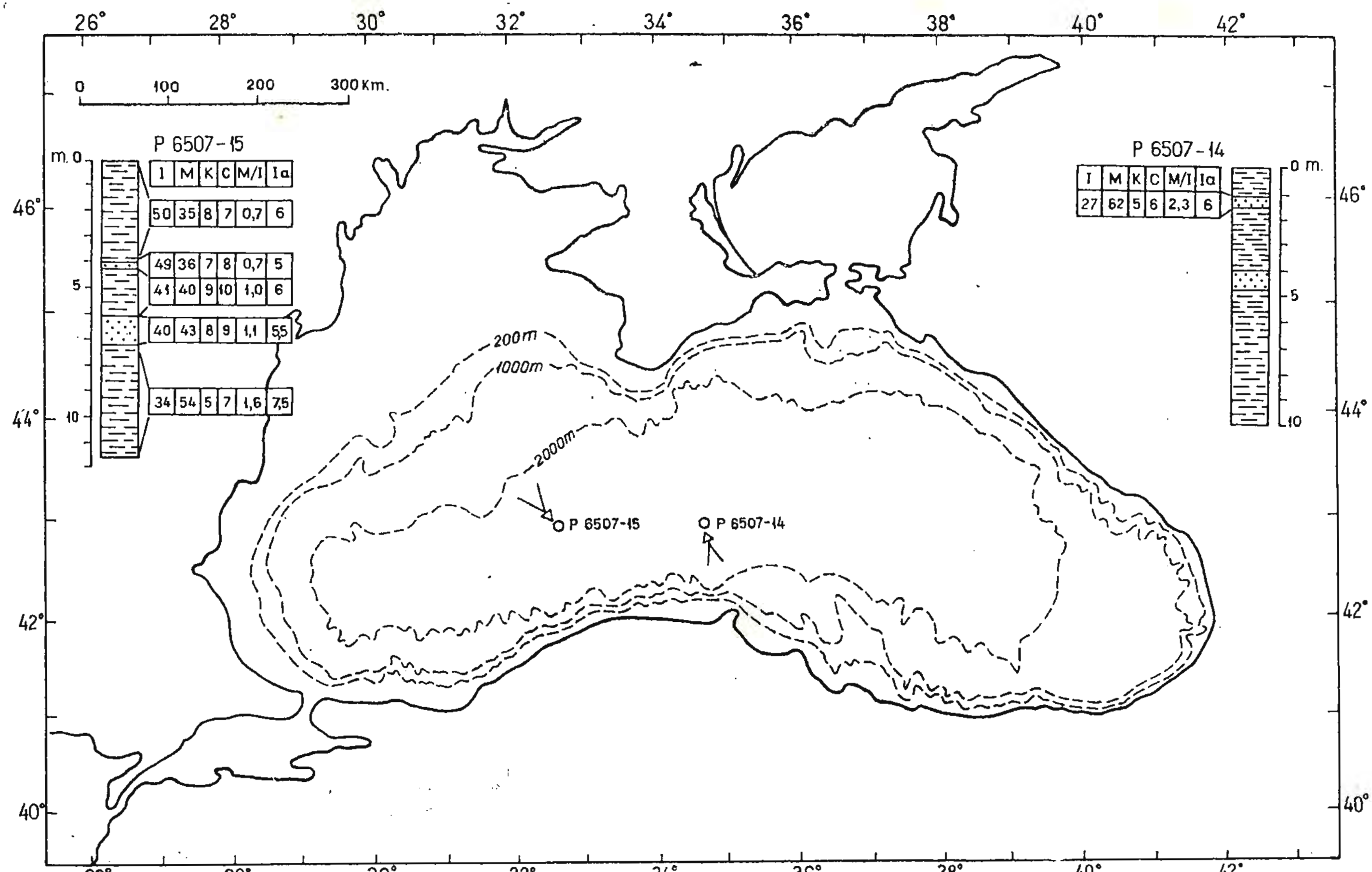

Fig. 2. — Main trends of the transporting currents responsible for the genesis of the sandy interbeds in cores P 6507—14 and P 6507—15. Interpretation based on differences on the mineralogical composition of $<2\mu$ fraction. The clay minerals contents and parameters are indicated on the columns on the left and right sides of the figure: I = illite; **M** = montmorillonite; K = kaolinite; C = chlorite; M/I = montmorillonite/illite ratio; I_a = sharpness index.

Excluding the calcareous mud at the top of the core, the correlation coefficient between carbonate content and sample depth being strongly positive (table 3) indicates the higher importance of the $CaCO_3$ during the glaciation. According to Strakhov (1951) more than 70 % of the $CaCO_3$ is introduced in the Black Sea in solution. At higher concentration of $CaCO_3$ in the sea water (during the lower temperature intervals), the interstitial water of the sediments will also have higher carbonate contents.

The quantity of organic carbon in the sediments varies extensively, from 8.4 % to 0.2 %. The highest content characterizes the sapropelic unit II (table 2, plate). The amount of organic carbon decreases with the depth, a feature also underlined by the statistical data (table 3). The diminishing of the organic carbon appears as the result of the concurrent action of three factors : (1) increasing burial depth, (2) lower phytoplankton productivity during the cold periods and (3) decreasing of the clay content with the depth.

As concern the water contents, these values should be considered as indicative, because the determinations have been made five years after the coring. However, the 76 % value obtained for the top of the core is within the 50 %—80 % limits characterizing the recent muds (Müller, 1967).

The water content decreases with the depth due to the decreasing porosity by compaction (table 2, plate). The fluctuating trend is imposed by the grain-size constitution, the sandy interbeds always containing more water.

Sedimentation rates. Considerring that the two glacial minima (18 000 and 11 000 years in age) could be correlated with the montmorillonitic maxima and some grain-size features of the sediments, several observations on the sedimentation rates can be presented.

On th eabove mentioned presumption, the two glacial events would correspond to the samples 31 and 15 (plate), both of them representing montmorillonitic maxima. Consequently, the lower part of unit III indicates a sedimentation rate of about 80 cm/1 000 years. This is a mean value as some sandy intercalations, characterized by higher sedimentation rates, occur in this section.

The upper part of unit III ranges from the last glacial minimum to the base of unit II (dated as 7 000 years B.P., according to Ross et al., 1970). A sedimentation rate around 60 cm/1000 years seems to characterize this section.

Unit II was deposited in the time interval between 7 000 and 3 000 years B.P. The thickness of this unit in core P 6507—15 indicates a sedimentation rate of about 17 cm/1000 years.

Unit I appears to be distinguished by the lowest sedimentation rate : about 8 cm/1000 years.

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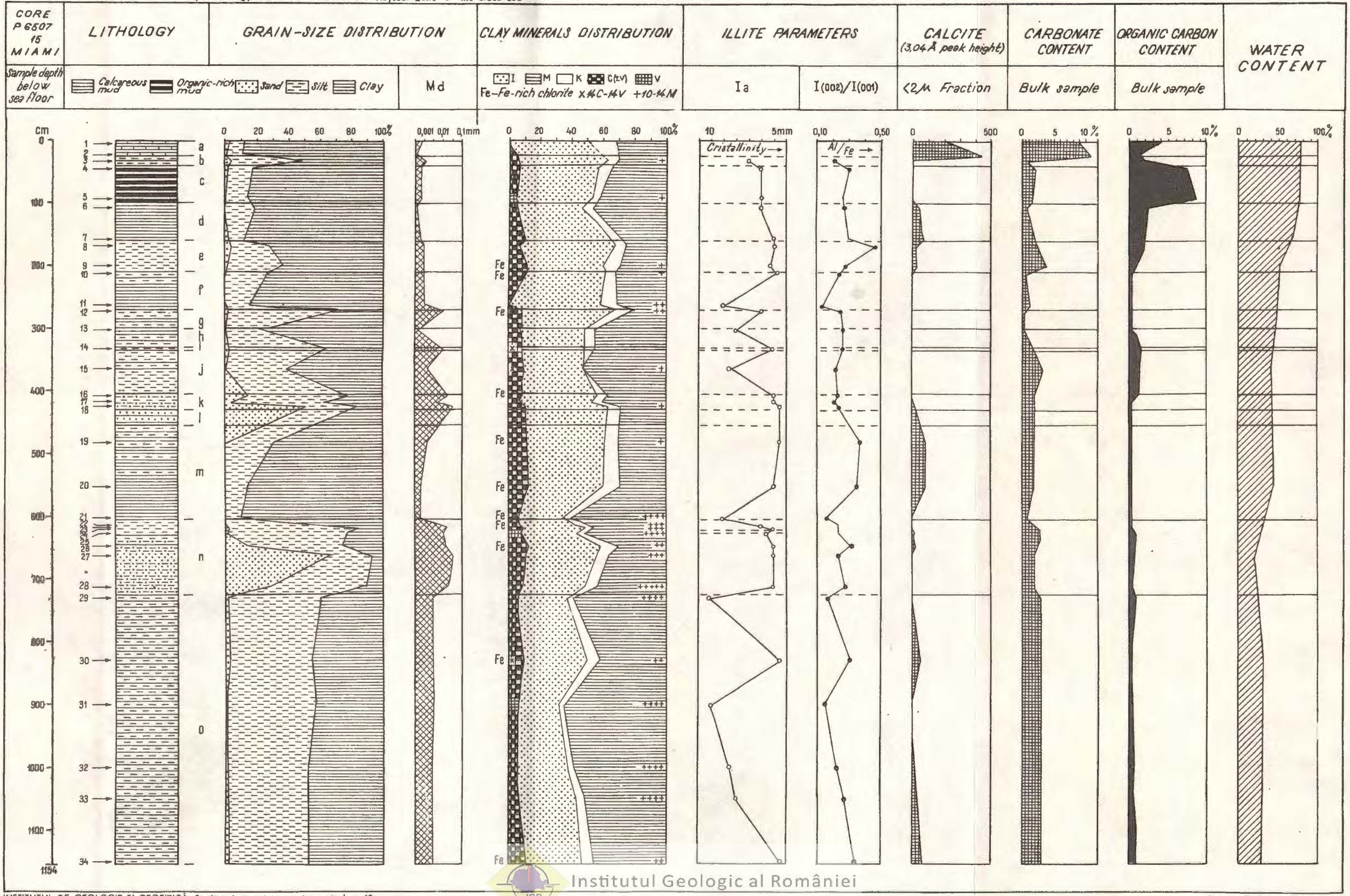
EVOLUTION OF SOME GRAIN - SIZE, MINERALOGICAL AND CHEMICAL PARAMETERS IN CORE P. 6507 - 15.

S. RĂDAN, D. JIPA. Some Data on the Clay mineralogy and Sedimentation in the Abyssal Zone of the Black Sea



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THE INFLUENCE OF THE SULPHIDES ON THE DETERMINATION OF ARGILLACEOUS MINERALS BY THERMAL METHODS[1]

BY

DUMITRU TODOR, GHEORGHE ENACHE[2]

Abstract

The Influence of the Sulphides on the Determination of Argillaceous Minerals by Thermal Methods. It is well known that thermal methods for analyses are succesfully applied to the determination of the clay minerals; this determination is based upon a series of transformations which occur during the heating. The analytical results are altered by the presence of the sulphides in the examined samples, for in their turn they produce transformations that superimpose on those of the clay minerals. The influence can be removed by means of certain methods. The influence concerning the colomorphe sulphides were not sufficiently studied, especially those on the clay minerals. This paper will try to establish in every case the influence determined by these sulphides and the way to remove it.

It is known that the thermal methods of analysis are proper for the determination of the argillaceous minerals; this determinations is based on several transformations that occur when heating. The results of the thermal analyses are strongly influenced by the presence of the sulphides in the samples, which in their turn give a series of transformations that will superimpose on the transformation of the argillaceous minerals, leading to a wrong result.

From the data centralized by Grim (1962), Mackenzie (1957) and Todor (1972) it results that in the last years very many researchers studied the influence of the sulphides on the determination of the argillaceous minerals by thermal methods. These researches were made by means of the differential thermal analyses and they refer only to those sulphides that are well crystallized, which can be separated by sedimentation in a liquid, as a result of the density difference. As regards the influence of the colomorphe sulphides or of those fine dispersed, with the dimensions measured in millimicrons, their study is still difficult, especially by complex

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methods of thermal analyses. The present work aims at the study of the influence of the colomorphe and fine dissipated sulphides on the ATD, TG and TGD curves of the argillaceous minerals of montmorillonite and kaolinite type. For this reason, the study has been started, on the one hand, with the artificial mixtures of argillaceous minerals of montmorillonite and kaolinite type with colomorphe sulphides, precipitated in the laboratory directly into the mass of the argillaceous minerals, and on the other hand, the argillaceous minerals with fine dissipated sulphides of hydrothermal origin.

The analytical record of the thermal phenomena that occur in these cases was made by means of a sophisticated device for thermal analysis, so called „derivatograph'', that for the same samples and in the same time unit recorded automatically the three basic curves of the thermal processes that occur in a sample subjected to a heating program as following: DTA Differential Thermal Analysis, TG Thermogravimetry, and DTG Derivated Thermogravimetry.

The testing experiences were performed maintaining constantly the next parameters: the increasing speed of the temperature in the oven is of 10° C/minute, the system of differential thermo-couple in Pt — Pt-Rh, the atmosphere in the oven was that of the air and the bed for the samples was a metallic one.

Thermoanalytical Data

In order to interpret the thermoanalytical data of the mixtures of argillaceous minerals and sulphides, the analysis of the monocompounds as well as of the natural or articficial blends was made. As it is known, almost every well crystallized sulphide behaves in the same way when heated, first an exothermal effect caused by the decomposition of the sulphides appears on the thermal curves, and at the same time by the oxidation of the metallic cations and sulphur. This effect is followed, at the same time with the increase of temperature, by more or less specific endothermal effects, because their occurence is related to the type of sulphides and, on the other hand, to the experimental conditions and also by the presence of other minerals together with the sulphides in the sample to be analysed.

The occurrence of these effects is based on the chemical reactions that occur as a result of the oxidation of the sulphur to the sulphur oxides by means of the oxygen present in the atmosphere of the oven. These oxides that are very active, in their initial phases, attacking the metallic cations resulted from the decomposition of the sulphides, or the network of the minerals present in the mixture, destroying it partially or entirely. The final result is the formation of the sulphates that gradually decompose with the increase of temperature, releasing sulphur oxides, that this time, due to the high temperature will be released definitively from the analytical system.

Continuing to raise the temperature, some metallic oxides resulted from this decomposition of sulphates will be oxided yielding superior oxides, e.g. $FeO \rightarrow Fe_2O_3$, and others will be reduced, e.g. $CuO \rightarrow Cu_2O$, fact that will lead to the occurrence of other thermal effects. This superimposing of endo- and exotermal effects on the thermal effects specific to the argillaceous minerals, within the temperature range where the argillaceous minerals get new structures, will make the thermal curves unusuable. The temperature range where these effects can occur is large enough and it begins after the exothermal decomposition and of sulphide oxidation effect, and in most cases it doesn't cease at 1,000°C.

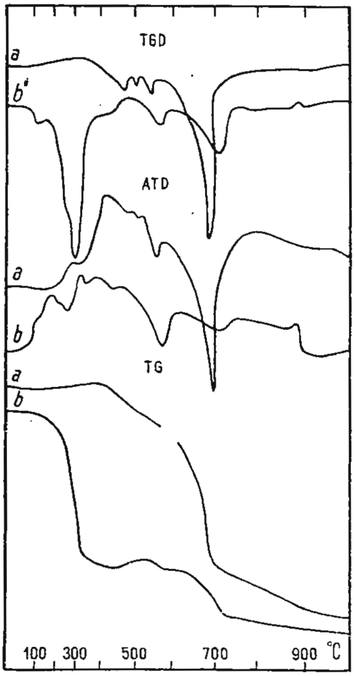

Fig. 1. — The thermal curves of the iron sulphides with different degrees of crystallization. *a* — pyrite, *b* — colomorphe iron sulphide.

Generally speaking about the thermoanalytical behaviour of the well crystallized sulphides, the exothermal effect caused by the decomposition and the oxidation of the sulphides occurs between 400°—500°C. The poorer the crystalline structure is, the colomorphe phase, respectively, the lower is the temperature where the exothermal effect occurs beginning with 200°C. Another noticed analytic fact is that the weaker the crystalline structure is, the simpler the set of endothermal effects is, taking place at a lower temperature. The thermal curves of some iron sulphides with different degree of crystallization are rendered in figure 1, in order to make a comparison with the facts shown above.

Also, when they are present in the argillaceous minerals, the sulphides will behave in a similar way with the facts described above. The influence the sulphides exert on the argillaceous minerals is direct proportional with their percentage content in the sample to be analysed. The influence of the sulphides on the minerals of montmorilonite and kaolinite type is presented in the following text.

The minerals of montmorillonite type present three charcteristical effects on the thermal curves, situated in different ranges of temperature (fig. 2 *a*). The first two endothermal effects are caused by the elimination of the water and OH groups, respectively, and the third effect is caused by a new structural reorganization.

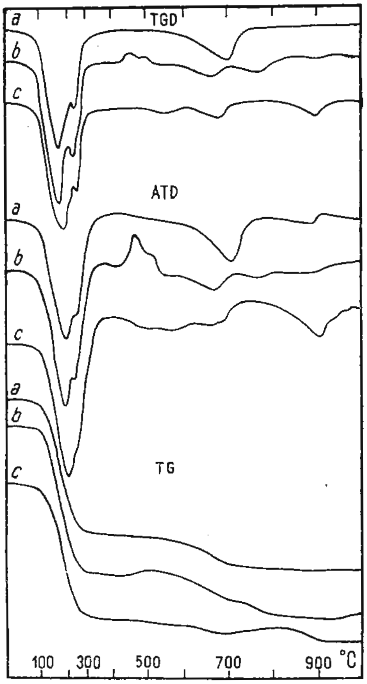

Fig. 2. — The thermal curves of the montmorillonite in mixture with sulphides.
a — monomineral montmorillonite, *b* — montmorillonite with sulphides of hydrothermal origin (Roşia Poieni drill), *c* — montmorillonite with colomorphe iron sulphide.

We notice in figure 2 that in case some fine dissipated sulphides are present in the montmorillonite, which have a high degree of crystallisation, between 450°—530°C, the exothermal effect of the sulphides occurs accompanied by a noticeable increase of the weight. The thermal curves of the montmorillonite are modified, auxiliary thermal effects occur, and thus, the third effect on the new structural reorganization is screened, despite the fact that the content in sulphides of the analysed sample does not exceed 5%. The situation of the thermal curves is changed in comparison with the montmorillonite due to the presence of the iron sulphides in a colomorphe emulsion (fig. 2*c*), because the exothermal effect is absent, this being specific to the sulphides. This absence is explained by its occurrence at a temperature lower than the common temperature for the crystallized sulphides, being located in the temperature range where the adsorbed water contained in the montmorillonite is released, and so this is screened by the above effect. But, at higher temperatures there occur auxiliary effects in comparison with the montmorillonite.

In case that the content of sulphides is high, the thermal curves of the montmorillonite cannot be recognized, except for the endothermal effect for lower temperature where the adsorbed water is released. Such a case is shown in figure 4 *a*.

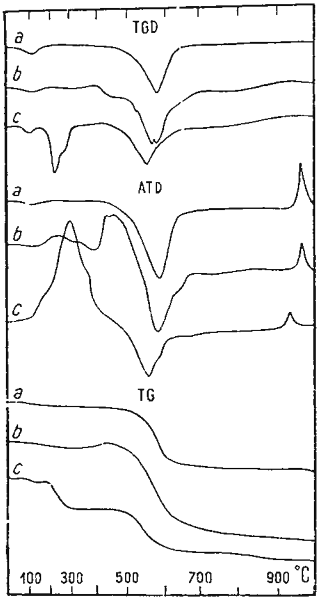

Fig. 3. — The thermal curves of the kaolinite in mixture with sulphides.
a — monomineral kaolinite, *b* — kaolinite with sulphides of hydrothermal origin (the mine of Băiuţ), *c* — kaolinite with colomorphe iron sulphides.

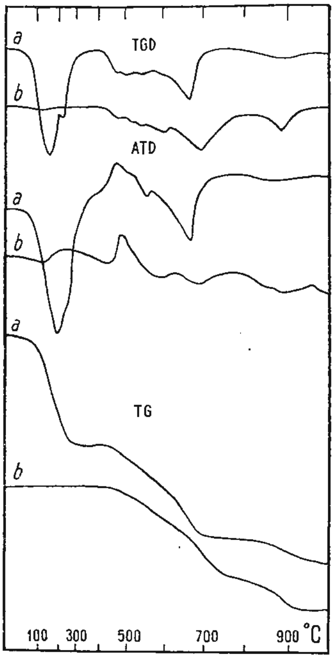

Fig. 4.—The thermal curves of the montmorillonite and kaolinite with over 50% content of fine dissipated sulphides. *a* — montmorillonite (Roşia Poieni), *b* — kaolinite (Băiuţ).

The montmorillonite minerals in comparison with the kaolinite minerals show only two thermal effects on the thermal curves (fig. 3 *a*). The first effect is caused by the releasing of the OH group from the kaolinite network and occurs between 500°–650°C and the other one as a result of the new structural organization, being at 960°C. The influence of the sulphides at a temperature below 500°C is connected to the crystallization degree of the sulphides.

As regards the well crystallized sulphides, their influence upon the kaolinite begins at 400°C as well as on montmorillonite (fig. 3 *b*) with the exothermal decomposition-oxidation effect. At the same time with this effect, the OH group is released from the kaolinite network, as water vapours and the vapours carry with them the sulphur oxides resulted from the oxidation of the sulphide and thus stopping them from carrying into reaction with the metallic cations or kaolinite. This fact weakens the influence of the sulphides upon kaolinite minerals at a temperature higher than 650°C, fact that does not happen in the case of the montmorillonite.

For the colomorphe sulphides, the exotermal decomposing-oxiding effects begin at 150°C, and at 400°C this effect is over (fig. 3 *c*). So the influence of the sulphides upon the thermal effects specific to the kaolinite minerals is poorer.

The above shown thermoanalytical observations are available when the content in sulphides from the mass of the kaolinite minerals is not too high (it does not exceed 30—40%). When the sulphide content, no matter what their crystalline structure is, exceeds the argillaceous mineral content, a set of thermal effects up to 900°C occur on the thermal curves (fig. 4). In this case, the only analytical argument which emphasizes the presence of the kaolinite in the sample to be analysed is the exothermal effect of the new structural organization. This effect will present temperature values lower than the monomineral kaolinite, but these differences do not exceed 30–40°C, and it is caused rather by the blending ratio kaolinite —sulphide than by the influence of the thermal behaviour of the sulphides.

If the content in sulphides is higher than the kaolinite, the exotermal effect of the new structural organization of the kaolinite could disappear entirely.

In conclusion, we can say that the influence of the sulphides, both of those fine dissipated but well crystallized and of the colomorphe ones is pretty strong upon the kaolinite and montmorillonite when heated. Despite this fact, the obtained thermal curves could be used for the identification of the two mineral types, for the montmorillonite taking into consideration the endothermal effect of low temperature, and for the kaolinite the exothermal effect of the new structural organization. In case that the sulphides content is so high that the obtained thermal curves do not give any indication on the nature of the argillaceous minerals, we are obliged to make a separation in liquid, taking into the consideration the difference of density, or to make an acid treatment in order to remove the sulphides. We obtain good results concerning the fine dissipated sulphides, making discrimination in liquids with different densities and in case of the colomorphe sulphides attacking them with a weak acid.

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