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**THE OCCURENCE OF HALLOYSITE IN DEPOSITE
OF THE POLTÁR FORMATION**

(Plate XVI—XVII, Textfigs. 1—4)

Abstract: The authors in this paper describe the first occurrence of halloysite in the Pliocene deposits of the Poltár Formation. Halloysite is concentrated in the form of the so-called armored mud balls in gravels. X-ray study showed a different degree of dehydration of fully hydrated halloysite. By the selection diffraction in the electron microscope was proved that the tubes of halloysite were unrolled. Further on the basis of differential thermal analysis and morphologic study in the electron microscope we studied degree of structural regularity of kaolinite in the psammitic-psefitic and pelitic sediments. It was proved that kaolinite with comparatively better perfection of lattice forms cement in coarse-grained sands and originated during diagenesis. Kaolinite with weakly ordered structure in clays was according to our opinion transported to the sedimentary basin in the elastic form and we do not suppose more intensive changes during sedimentation and diagenesis under influence of the surrounding environment.

Introduction

D. Andrusov and V. Zorkovský (1950) named deposits of the Ipel valley as the „Poltár Formation“. The latter is formed of gravels, sands, clays and their transitions. Fire resistant, stoneware and brick clays represent the important raw material base of the ceramic industry in Slovakia. However, their ratio in regard to the whole volume of sediments of the Poltár Formation is very small. According to the present knowledge (M. Mišík 1956, F. Tomšů 1957 and E. Kanceliř 1958) the highest quality have the fire resistant clays formed of kaolinite, which J. Konta (1957) marked as kaolinite of the fireclay type. They originated in a fresh water lake of Pliocene age into which was transported by intensive kaolinitic weathering disintegrated material from the north (i. e. Palaeozoic phyllites of Spišsko-gemerské rudohorie).

Our endeavour to know detailly genesis of clays led us to their mineralogical study in all sedimentary types of the Poltár Formation. In this paper, we determine mineralogical composition of the so-called armored mud balls which occur in gravels, clay cement in sands and gravels as well as beds of clays occurring in these psammitic-psefitic sediments. At the beginning we determined the collected samples by imbibimetric method (J. Konta 1956, 1961) with purpose to find simply and quickly relevant anomalies in mineralogical composition. We suppose that in so thick complex has to be greater mineralogical variety opposite to the present state. Our study allowed to find a mineral which by imbibimetry, optical, differential thermal, X-ray and electron microscopic studies was identified as halloysite. Up to the present, this mineral has not been described from deposits of the Poltár Formation. In the presented work, I. Kraus evaluated results of all methods applied and elaborated the final discussion about genesis. H. Gerthofferová made microphotographies in the electron microscope and selection diffraction with calculation. I. Krížani made imbibimetry and curves of gravimetric thermal analysis.

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Geological Position and Macroscopical Description of the Samples Studied

Sample 1. In the middle of 0,5 m thick layer of gravels in the erosion furrow near Kalinovo village, 500 m north-east of the elevation point 236,5 m there occur well reworked, globular to moderately elongated forms of white clay with aleurolitic-sandy admixture (Pl. XVI, Fig. 1). Surface of these forms is covered by sand and gravel. They resemble the so-called armored mud balls described by J. Petránek and M. Dopita (1957) and J. Petránek (1963). They are not washable, they have earthy fracture and a size of a nut to fist. They occur mainly in the lower part of the gravel beds with typical cross bedding. The gravels are almost exclusively formed of angular to subangular quartz. According to M. Mišík (1956) gravels of the Poltár Formation represent disintegrated and to a short distance transported material of lateral — secretory veinlets from the crystalline slates. On the basis of X-ray study we found out that it is fully hydrated form of halloysite $4\text{H}_2\text{O}$.

Sample 2. During erosion of gravels and after their deposition occurred looseness of balls. We have found them even 100 m. from the primary occurrence. Surface layer of sand and gravel protected the clay core against disintegration. These displaced balls are composed of partly dehydrated halloysite (metahalloysite).

Sample 3. Clay cement of gravels in which the balls occur. It is probably formed of dehydrated halloysite and kaolinite.

Sample 4. Grey-white sandy clay. It forms direct underground of gravels with halloysite balls. It is formed of slightly ordered kaolinite.

Sample 5. Chocolate-brown plastic clay occurring in the form of dentritic veinlets in strongly kaolinized Palaeozoic phyllites 50 m. west of the sample 1. It is formed of slightly ordered kaolinite with illitic admixture.

Sample 6. Clay cement of coarse-grained siliceous sands with accessory amount of muscovite from the sand pit 500. m east of Kalinovo. On the contrary to the samples 4, 5 und 7, this kaolinite has higher degree of lattice perfectness.

Sample 7. A layer of grey-white sandy clay in the middle of coarse-grained siliceous sands of the sample 6. It is again slightly ordered kaolinite.

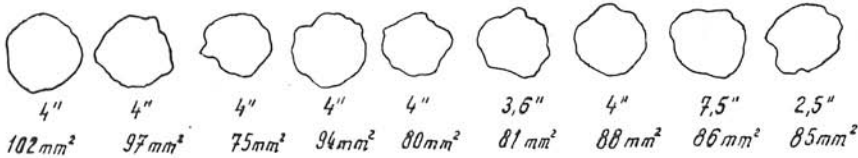
Imbibimetric Study

Method to examine a drop of water and ethylene glycol on the polished section of unconsolidated clay sediments was elaborated by J. K o n t a (1956, 1961). By this method, we have studied the samples 1 and 2 and for comparison purposes a sample of halloysite from Biela Hora locality near Michalovce, all in natural state. The sample 5 was in the form of artificial disc provided by washing. The kaolinic cement of sands and gravels in other samples was not suitable for preparing of the artificial disc due to bad adhesion of kaolinite. Results are on the fig. 1.

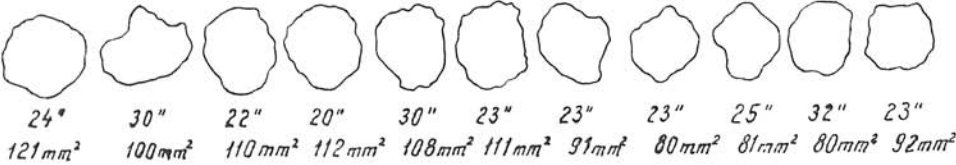
Different mineralogical composition of the samples 1 and 2, halloysite from Michalovce locality and on the other hand of the sample 5 shows to be very distinct in results of imbibimetry. The samples 1 and 2 have wettability, i. e. ratio of planes occupied by drops of ethyleneglycol and water ($P_{\text{egl/aq}}$), 1,1 or in halloysite from Michalovce 1,2, while the sample 5 in which besides weakly ordered kaolinite was illite found by X-ray method value of $P_{\text{agl/aq}}$ was close to 2. In this case, value of $P_{\text{egl/aq}}$ the whole confinement of drops of water and ethylene glycol as well as speed of imbibition are very similar to those of „blue“ clay from Vonšov locality, where J. K o n t a (1964) found besides kaolinite an admixture of „open“ illite. However, J. K o n t a (1957) emphasized the morphological similarity found in the electron

sample 1

WATER

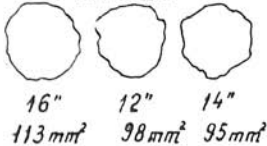


ETHYLENEGLYCOL



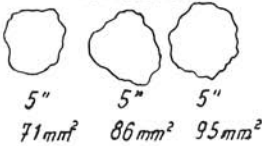
sample 2

WATER



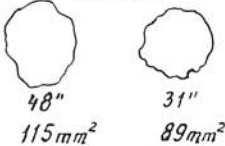
Halloysite MICHALOVCE

WATER

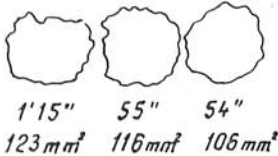


sample 5

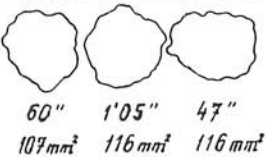
WATER



ETHYLENEGLYCOL



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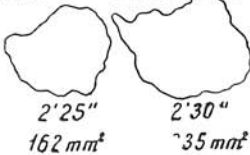


Fig. 1. Imbibimetrical analyses with aid of water and ethylene glycol.

microscope and identical course of DTA curves between the Vonšov „blue“ clay and Poltár clay.

However, it is necessary to mention, that the samples studied are but little convenient for polished blocks in the natural state as they have sandy and aleurolitic admixture which may influence our values of wettability. Therefore we have to regard also these results as orientation and preliminary. In further study we plan in wider scale to make detail imbibimetric study of deposits of the Poltár Formation.

Optical Study

The armored mud balls have the typical aleuro-pelitic structure in the polarisation microscope M. F. Víkulová and A. V. Chabáková (1962). The basal mass is formed of fine-dispersed isotropic aggregate. The aleurolitic admixture is composed of subangular quartz grains of the mean size 0.01 mm. (10—15 %) and scales of muscovite. Zircon occurs but rarely.

Further we have studied the oriented aggregates of the fraction below 2 microns of the sample 2 in immersion liquid. Here the clay mass forms also very fine-dispersed aggregate without anisotropy. Therefore we could measure only the mean value of the index of refraction N_m of aggregates of individual scales, which is 1.54. This value well agrees with that of the Michalovec halloysite (1.539) measured by J. KONTA (1957).

DTA Curves

Fire-clays of the Poltár Formation have typical DTA curves showing kaolinite with weakly ordered structure, by J. KONTA (1957) named as kaolinite of the fire-clay type. So far, we have not deal with the question whether our kaolinite is of the fire-clay type. This question needs detailed X-ray study. Therefore we do not use the term „fire-clay“ for kaolinite with weakly ordered structure.

Our DTA curves were gained with aid of equipment with automatical fluent registration. Speed of rate of heating is 50° per minute, weight 1 g. In all cases we used fractions below 2 microns. To the typical clays of kaolinite type with weakly ordered structure belong the curves of the samples 4, 5 and 7 on the fig. 2. Their first endothermic reaction culminates under 120 °C. Exothermic reaction under 300 °C in the sample 5 belongs probably to organic materials. The presence of illite in this sample reveals by striking low temperature of the dehydroxylated endotherm. In the samples 4 and 7, the dehydroxylated endotherm under 540 °C or 560 °C and blunt cone-like exothermic reaction under 940 °C show clearly the presence of kaolinite with weakly ordered structure. Shift of the dehydroxylated endotherm to the temperature of 590 °C and comparatively sharp and high final exothermic reaction in the sample 6 show better ordered lattice of kaolinitic mineral, which differs by its final exotherm from all curves of the fire-resistant Poltár clays published up to the present (M. MIŠÍK 1956, F. TOMŠŮ 1957, J. KONTA 1957 and E. KANCLÍŘ 1958).

It is practically impossible to identify halloysite only on the basis of DTA curves. J. Vtělenský and F. KUPKA (1962) stated that dehydrated halloysite behaves as kaolinite with well ordered structure during the differential thermal analysis. Some difficulties are also in reliable interpretation of the first endothermic reaction under 120 °C which besides halloysite is present also in kaolinites with weakly ordered structure — it is shown by the curves of the samples 4, 5 and 7. These complications follow from the fact that we cannot distinguish in DTA curves surface and molecular water.

R. W. GRIMSHAW, E. HEATON and A. ROBERTS (1945) quote that dehydration in halloysite occurs much earlier (30—60 °C) than in pure kaolinites. T. SUDO and H. TAKAHASHI (1956) found that a different degree of ordering of halloysite manifests in a position of dehydroxylated endotherm. In this case, halloysite with well ordered structure of lattice has dehydroxylated endotherm under 570 °C. Gradually, in agreement with decreasing degree of ordering of structure of halloysite, the top of the dehydroxy-

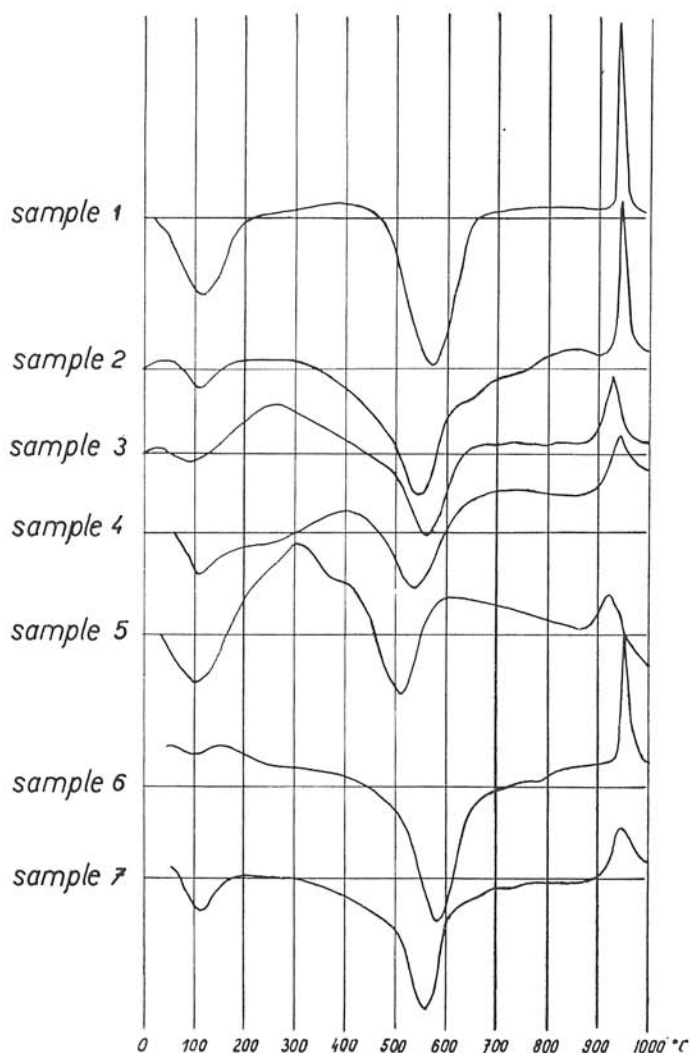


Fig. 2. DTA curves of the samples studied.

lated endotherm shifts down to 518 °C and contemporaneously shallows. Starting from this standpoint very interesting are differences in DTA curves of fully dehydrated and only partly dehydrated form of halloysite (samples 1 and 2). Deeper dehydroxylated endotherm and its shift to 30 °C higher temperature (585 °C) would have to show better perfection of lattice of halloysite on the contrary to partly dehydrated halloysite together with more intensive exothermic top. However, making such conclusions we must be very careful as here took place special conditions under which the curves have been studied. Under special conditions we understand increasing of temperature, granularity and a weight of samples. These factors influence the whole course of curves (R. C.

Mackensie 1957). Due to the reason mentioned also our conclusions have only relative character for our two samples studied on the equipment under identical conditions.

Chemical Analysis

Chemisms of halloysite we have studied by the chemical analysis of the sample 2. For comparison we illustrate chemical analyses of individual technological types of the fire-resistant clays of the Poltár Formation given by F. T o m š ů (1957).

Analysis A sample 2 fraction below 2 micrones analysed inž. P o l a k o v i č o v á.

Analysis B clay SIM fraction below 1 microne F. T o m š ů (1957).

Analysis C clay IM fraction below 1 microne F. T o m š ů (1957).

Analysis D clay IG fraction below 1 microne F. T o m š ů (1957).

Table 1

	A	B	C	D
SiO ₂	42,37	47,75	46,15	48,45
TiO ₂	—	0,32	0,95	1,00
Al ₂ O ₃	37,15	34,58	32,55	32,04
Fe ₂ O ₃	—	1,11	1,40	1,36
FeO	0,41	—	—	—
MnO	0,01	—	—	—
MgO	0,72	0,28	0,32	0,28
CaO	0,21	1,72	0,48	0,70
Na ₂ O	0,03	0,12	0,17	0,12
K ₂ O	0,07	1,13	1,10	1,75
P ₂ O ₅	0,04	—	—	—
Loss by drying 110° C	6,83	—	—	—
Loss by annealing 110—900° C	13,30	13,23	16,98	15,00
Molecular ratio SiO ₂ : Al ₂ O ₃	1,94	2,34	2,40	2,56
Sum	101,14	100,24	100,20	100,72

Table 2

	Molecular ratio		
	SiO ₂ : Al ₂ O ₃	H ₂ O : SiO ₂	H ₂ O : Al ₂ O ₃
Sample 2	1,94	2,31	3,06
Average values from 12 chemical analyses of metahalloysite according to R o s s — K e r r (1934)	1,90	2,33	2,21

For clear view, we compare values of molecular features in the sample 2 with the mean values gained from 12 chemical analyses of metahalloysites by C. S. R o s s and P. F. K e r r (1934). C. S. R o s s and P. F. K e r r (1934) write that transitional

stage of hydration of halloysite with value of $n\text{H}_2\text{O}$ from $2\frac{3}{4}$ up to $3\frac{1}{2}$ with basal spacing 001 7.9 up to 9.6 kX they did not obtain. In our case, there is in the sample 2 discordance between value of $n\text{H}_2\text{O}$ (3.06) gained by chemical analysis and basal spacing which moves between 7.4 and 7.9 Å, typical for metahalloysite found by X-ray study. Therefore determination of H_2O content in the chemical analysis of the sample 2 was controlled by gravimetric thermal analysis. Result of GTA on the fig. 3 and determination of H_2O content in chemical analysis show quite good agreement between determinations of H_2O content by the both methods. Determining H_2O content by GTA we found that leakage of interlayer (molecular) water comes very quickly up to 120 °C and then very slowly up to 400 °C. The amount of the interlayer water found by GTA is 7.50 %. It is clear that in chemical analysis up to 110 °C the whole amount of the interlayer water does not escape. This difference in our case is 0.70 %. The whole difference in the content of the interlayer and lattice waters found by chemical analysis and by GTA is 0.83 %. If in calculation of the whole water content in the sample 2 we insert the water amount gained by GTA — 19.30 %, then $n\text{H}_2\text{O}$ is 2.94. From the mentioned is seen that there is but a little difference between H_2O content gained by chemical analysis and GTA. So excess of water in the sample 2 might be caused by the presence of hydrargillite. Its presence is shown also by the spacing 4.84 Å in diffractometer of the sample 2, fig. 4 and excess of Al_2O_3 shown by chemical analysis. Contemporaneously we emphasize that also P. F. Kerr, P. K. Hamilton and R. J. Pill (1950) and R. E. Grimm (1953) give the analysis of metahalloysite with $n\text{H}_2\text{O}$ value 3.

By the manometrical method, adapted by J. Turan (1965) we found that the main part of CaO content in the sample 2 is connected with calcite, while MgO does not enter into carbonates. Finally, values of the molecular ratio $\text{SiO}_2:\text{Al}_2\text{O}_3$ in the mentioned chemical analyses show relatively high purity of the sample 2 on the contrary to the fire-resistant clays of the Poltár Formation given by F. Tomšů (1957).

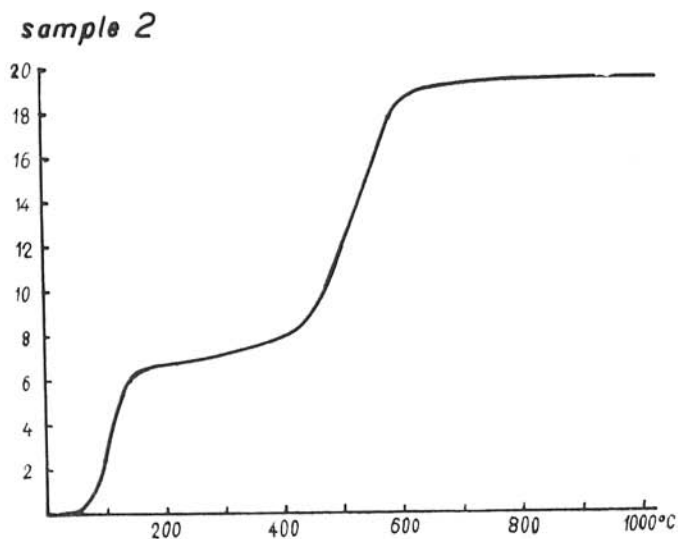


Fig. 3. GTA curve of the sample 2.

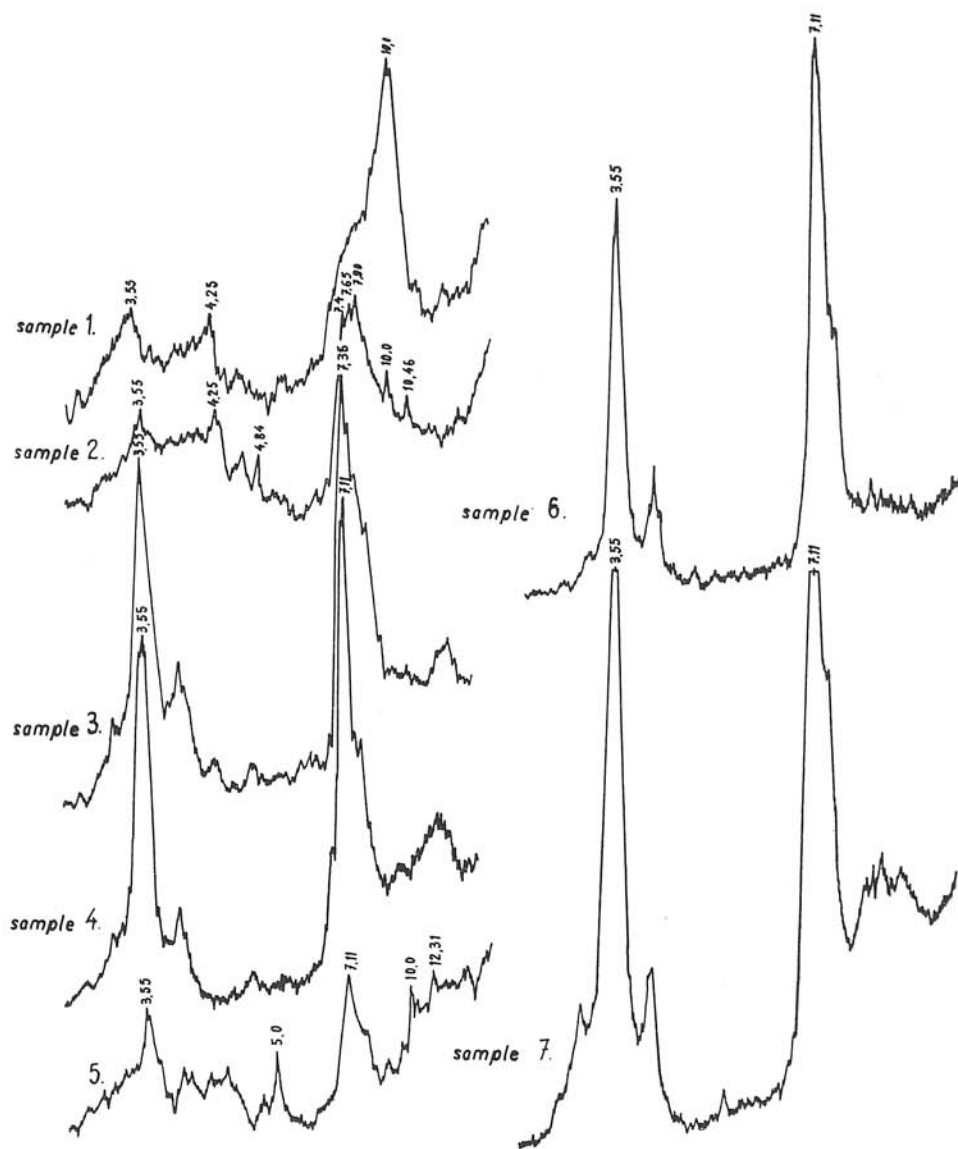


Fig. 4. X-ray graphs of the samples studied.

X-ray Study

X-ray analysis of the samples in question we made with aid of diffractometer GON-3, 40kV, 10 mA. Fe, K radiation, exit diaphragm 10, inlet one 2. The time constant in the samples 1, 2, 3, and 5 was 16 sec., in other samples 8 sec, 2° per minute.

Fraction below 2 microns in all samples was sedimented in the oriented samples.

Photographs were made by R. G a v e n d a from the Dionýz Štúr's Geological Institut in Bratislava.

Clays of the Poltár Formation were studied by X-ray method by J. K o n t a (1957) and mainly by M. M i š í k (1956). The last mentioned author studied mainly the most important technological types of the fire-resistant clays. Besides kaolinite he determined only in two samples the presence of illite.

Our X-ray graphs on the fig. 4 allow to divide the samples studied to several groups. To the first group belong the samples 4, 6 and 7. They are formed of symmetrical spacings 7.11 and 3.55 Å which belong to kaolinite. To the second group belongs the sample 5 in which besides 7.11 and 3.55 Å occur spacings 10.0 and 5.0 Å belonging to illite. The spacing 12.31 Å may show the presence of clay mineral with mixed structure. The third group is formed of the samples 2 and 3. Especially characteristic is the X-ray graph of the sample 2. There occurs besides weak spacing 10.4 Å, which belong to halloysite ($4\text{H}_2\text{O}$) distinctly asymmetrical „oscillating“ spacing ranging between 7.40–7.90 Å which is typical for partially dehydrated halloysite (metahalloysite). Spacing 4.84 Å is very important; it belongs to hydrargillite (van der M a r e l 1961). The sample 3 contains besides dehydrated halloysite, to which belongs asymmetrical sharp spacing 7.35 Å, also a considerable amount of kaolinite. This manifests by intensive spacing 3.55 Å. Higher content of kaolinite in the sample 3 (in comparison with the samples 1 and 2) is shown also by microphotographs made in the electron microscope. The last group forms fully hydrated form of halloysite with spacing 10.0 Å in diffractograph of the sample 1. The basal spacing of kaolinite or metahalloysite did not occur. Interesting was a determination of asymmetrical character of spacings in the samples 1, 2 and 3. In the sample 1 we see in the spacing 10.0 Å the rush descent to smaller and a gradual descent to higher angles. In the samples 2 and 3 with spacings 7.40–7.90 or 7.25 Å we see the opposite phenomenon.

The important result of the X-ray study is that in the samples 1, 2 and 3 we may gradually determine dehydration process of changing of the fully hydrated form of halloysite. The sample 1 belongs to the fully hydrated form of halloysite. X-ray graph of the sample 2 belongs to partially dehydrated halloysite (metahalloysite). The sample 3 probably contains dehydrated halloysite ($2\text{H}_2\text{O}$) with essential admixture of kaolinite.

Study of the Samples by the Electron Microscope

Preparates for the study by the electron microscope were prepared by suspension method. The samples studied were in small concentration dispersed by ultrasonics in the distilled water and put on the collodion membrane. Morphology of particles was studied in the electron microscope Tesla BS 242.

The samples 1 and 2 belonging to halloysite are characterized in the electron microscope mainly by the tubular development (Pl. XVI, Fig. 2, 3, 4 and Pl. XVIII, Fig. 1). Fibrous form of halloysite (T. S u d o and H. T a k a h a s h i 1956) was not found. We did not find also for halloysite typical association with allophane mentioned by T. S u d o and H. T a k a h a s h i (1956), M. H a r m a n (1964) and L. N. N o v o s e l o v a (1962). Besides halloysite on the microphotographs occur superimposed tablettes with irregular form of margin, frequently elongated which can be regarded at first sight as kaolinite (Pl. XIV, Fig. 2 and 3). They are especially frequent on the microphotograph of the sample 1 (Pl. XVI, Fig. 2) and here they were identified by the X-ray analysis as halloysite $4\text{H}_2\text{O}$. In this connection are very

interesting particles of „conical“ form in the typical form visible on the Pl. XVI, Fig. 4 and Pl. XVII, Fig. 1. We determined them as beginning stage of unrolling of halloysite tubes. Then elongated, irregular forms represent more or less unrolled tubes of halloysite. This opinion is supported by the fact that in the sample 1 have not been found the basal spacing of kaolinite. The most important for this result is the selection diffraction which confirmed correctness of our idea. We compared the framed tube of halloysite with elongated, supposed unrolled tube of halloysite from the same sample and framed on the microphotograph Pl. XVI, Fig. 3 (rolled tube of halloysite see on the Pl. XVII, Fig. 2). Values of the selection diffraction an individual spacings in the both cases are absolutely identical. Calculated values of spacings of the selection diffraction from the both cases are following:

Table 3

No. of line	hkl	d	I
1	020	4,39A	VS
2	200	2,56	VS
3	040	2,22	VW
4	240	1,675	S
5	060	1,485	VS
6	400	1,285	M
7	420	1,235	S

Intensity of lines: VS—very strong, S—strong, M—medium and VW—very weak.

The found values „d“ well agree with those described by V. I. Michejev (1957) for halloysite. Finally, morphological differences between unrolled tubes of halloysite (Pl. XVI, Fig. 2 and 3) and kaolinite (Pl. XVII, Fig. 2, 3 and 4) are clear on first sight also on microphotographs.

We could not distinguish dehydrated halloysite from fully hydrated form on the basis of morphological features of the tubes in the electron microscope. T. F. Bates, F. A. Hildebrand and A. Swineford (1950) and T. F. Bates and J. J. Comer (1959) affirm that due to dehydration of halloysite the tubes split on their margins, become flat and very often unrolled. All these features we can see very well in our case in both fully hydrated and partly hydrated forms of halloysite. This fact is surely caused by another fact that in consequence of working conditions existing during the study in the electron microscope (vacuum, high temperature) we cannot practically determine the morphology of the fully hydrated form of halloysite in natural state. In agreement with the opinion of T. F. Bates, F. A. Hildebrand and A. Swineford (1950) the DTA curves of the samples 1 and 2 (Fig. 2) showed that halloysite $4H_2O$ has higher degree of crystallinity and probably also higher degree of ordering of lattice than metahalloysite. We made such conclusion on the basis of shift of the dehydroxylated endotherm in the sample 1 (approximately 30 °C towards higher temperature) as well on the basis of higher peak of the final exotherm under the temperature of 950 °C.

Discussion to the Genesis Question of the Poltár Clays

The most complete and in the present accepted opinion on the genesis of the Poltár and especially fire-resistant clays was expressed by M. Mišík (1956). We should like to call attention to some new observations by the mineralogical study of our samples. It is clear that from the mentioned and up to the present only occurrence of halloysite in the gravels of the Poltár Formation is impossible to make conclusions of wider acceptance and reach, especially if we do not know its distribution and the whole ratio in the sediments of the Poltár Formation. To gain so many facts as possible which could allow to solve the origin of halloysite, we determined the mineralogical character of clay cement in sands and the proper sandy clays in the sand pit near Kalinovo (samples 6 and 7). From this standpoint we compared degree of ordering of structure in kaolinite in the sands and in the proper clays on the other hand.

In the last time J. Vtělnský and F. Kupka (1962) determined degree of crystallinity (ordering) of kaolinites very detailly. Bad crystallinity of kaolinite manifests by disarrangement of individual layers and disarrangement in mutual disposition of layers. The X-ray study allows to find the both disturbances. By differential-thermic study we can determine only disarrangement of layers. The conditions during our X-ray study did not allow to determine and compare degree of arrangement of individual kaolinites. Therefore we concentrated our study to the DTA Curves and morphological study in the electron microscope. According to H. H. Murray (1954) both deep and temperature of dehydroxylated endotherm are in kaolinites with well arranged structure in general higher. Contemporaneously the final exotherm in these kaolinites is sharp and high. In our case we could determine very well a different degree of arrangement of kaolinite in the samples 6 and 7. The sample 6 represents kaolinic cement of the sands in the sand pit near Kalinovo. The sample 7 descends from 0.5 m thick intercalation of sandy clay from the same locality. The DTA curve of the kaolinic cement is characterized in comparison with the curve of kaolinic clay by clearly higher degree of order of lattice. It is shown also by position and deep of the dehydroxylated endotherm as well as the whole course of the final exotherm. This statement well agree with morphological development determined by the electron microscope. On the microphotograph (Pl. XVII, Fig. 3) we see well limited pseudo-hexagonal tablets of kaolinite. On the contrary to this, on the microphotograph Pl. XVII, Fig. 4 kaolinite has not pseudo-hexagonal form, but is visible its fragmentary character with irregular sharp angles.

D. D. Kotelnikov (1958) on the basis of morphological features of clays of the Russian platform made some genetical conclusions. He stated that well developed pseudo-hexagonal crystals of kaolinite form mostly the cement of the aleurolitic-psammitic rocks. Irregular fragments of kaolinite, on the contrary, concentrate mainly in clays. According to the author mentioned, intensity of the diagenetic changes of clay minerals in pelitic and aleurolitic-psammitic deposits is different. In clays during deposition and diagenesis in consequence of weak permeability connection of individual particles with surrounding environment is very aggravated. Diagenetic changes under the influence of the surrounding environment are but weak or absolutely absent. The aleurolitic-psammitic sediments have high porosity. In these sediments, there is an intensive and lasting connection of clay cement with the surrounding environment in the sedimentary basin. In these sediments are more favourable conditions for the origin of authigenic minerals in the stage of diagenesis.

Starting from the facts mentioned we affirm that kaolinite with better degree of

order of structure, forming the cement in sands of the Poltár Formation, originated in the stage of diagenesis and is of authigenic character.

The main mass of clays of the Poltár Formation, represented in our case by the samples 4 and 7, has been transported after kaolinic weathering of phyllites in the primary weathering zone in the elastic state and during sedimentation and diagenesis we do not suppose intensive changes under the influence of the surrounding environment here.

Similarly, J. Březina (1957) has found by sedimentary-petrographical study of kaolinic clay from the Banka deposit near Piešťany well crystallized kaolinite in the cement of sands and conglomerates and weakly krystallized kaolinite of the fire-clay type in the proper clays.

And now let us approach nearer to the problem of the origin of the armored mud balls of halloysite. There are two possible principal ways of interpretation of their genesis. The first is that halloysite concentrated to limited degree under special conditions in the primary weathering zone. During erosion and transport of these primary deposits of halloysite might originated the mentioned armored mud balls. This opinion is supported by the form and the whole character of the balls. The typical signs of concretions we can study neither microscopically nor optically. The balls occur mainly at the base of the gravels with typical cross bedding described. Then, according to preliminary study by aid of the electron microscope it is accessory, but stable occurrence of halloysite in all studied sediments of the Poltár Formation as far known. And finally, this opinion is supported also by unrolled, at the margins splitted and weakly crystallographically limited tubes of halloysite in the proper balls.

The second possible way of interpretation is that halloysite is regarded as authigenic product originated during diagenesis in the sedimentary basin. There are several works dealing with genesis of halloysite, for instance those by C. S. Ross and P. F. Kerr (1934), S. Aomina and K. Wada (1962), F. V. Čuchrov, S. J. Berchin, P. Ermilov, V. A. Moleva and E. S. Rudnickaja (1964), L. N. Novoselova (1962) and many others, which prove a gradual recrystallisation of allophane to halloysite. T. Sudo (1959) quotes the occurrence of halloysite of the sphaerical form in clays of Japan. He supposed that globular particles of allophane gradually pass to the fully hydrated form of halloysite with contemporaneous change of the form. T. F. Bates (1959) and T. F. Bates and J. J. Comer (1959) even affirm that there exists the absolute morphological change in minerals of the kaolinite group. According to these authors, well crystallized hexagonal tablettts of kaolinite change to lath-shaped crystals gradually rolling up to tubes of halloysite $4\text{H}_2\text{O}$.

In our case we did not find in connection with halloysite the presence of allophane. From among free Al-hydrates we determined a weak spacing belonging of hydrargillite in the sample 2. Therefore we have not enough evidences as far to explain the origin of halloysite by recrystallisation of allophane or free Al-hydrates, although we do not exclude also this way of the origin.

In each case, genesis of halloysite and its relationship to other clay minerals in sediments of the Poltár Formation will be necessary to solve in wider scale. As far we express the opinion that halloysite occurs in the form of armored mud balls in J. P. Petránek's (1963) sense. Halloysite balls we regard as being syngenetic in regard to the gravels in which they occur, i. e. they were also transported together with the gravels. That fact is important: the balls occurring directly in the gravels belong to the fully hydrated form of halloysite. The balls loosened during erosion after sedimentation of the whole complex are formed of partly dehydrated halloysite (metahalloysite).

From the mentioned we judge that dehydration of halloysite has been done after sedimentation of the gravels and occurs also in the recent. The most intensive dehydration occurs in the proper clay cement of the gravels studied.

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E x p l i c a t i o n s o f t h e P l a t e s

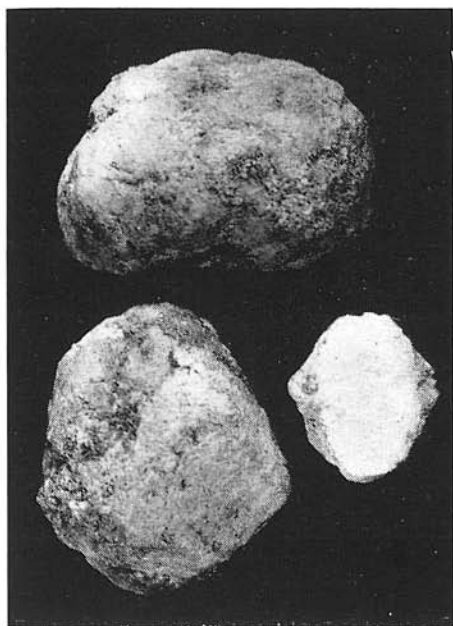
Plate XVI

Fig. 1. Armored mud balls of halloysite. $\frac{1}{2} \times$. — Fig. 2. Selection diffraction of the tube of halloysite. — Fig. 3. Selection diffraction of unrolled form of halloysite. — Fig. 4. Tubes of halloysite (A), transitional forms of the „conical” form (B) and unrolled tubes of halloysite (C).

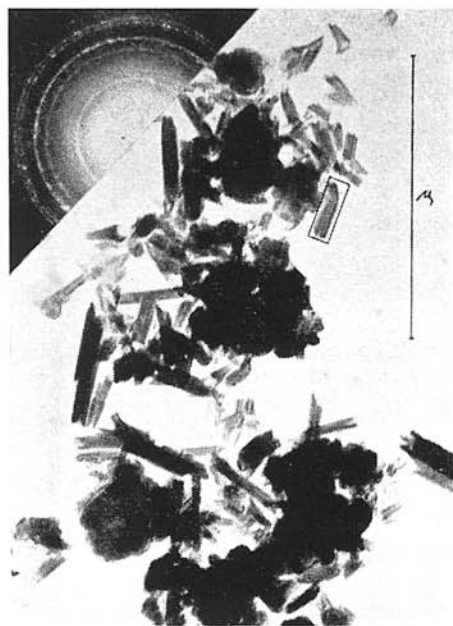
Plate XVII

Fig. 1. Partly unrolled „conical” tubes of halloysite (K). — Fig. 2. Splitted (A) and superimposed (B) tubes of halloysite with kaolinite (C). — Fig. 3. Pseudohexagonal tablettis of kaolinite. — Fig. 4. Fragmentary kaolinite.

Translated by V. S c h e i b n e r o v á.



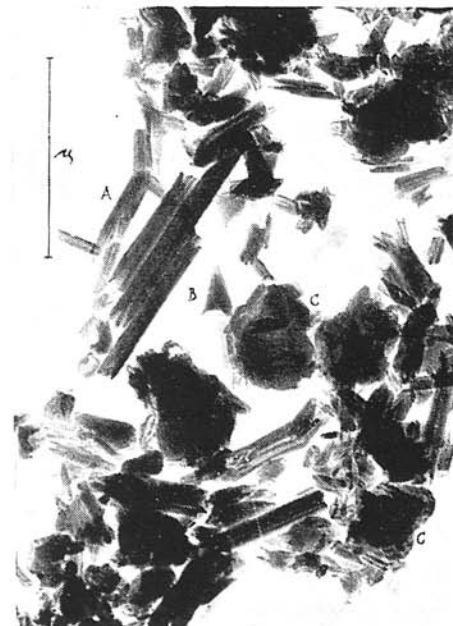
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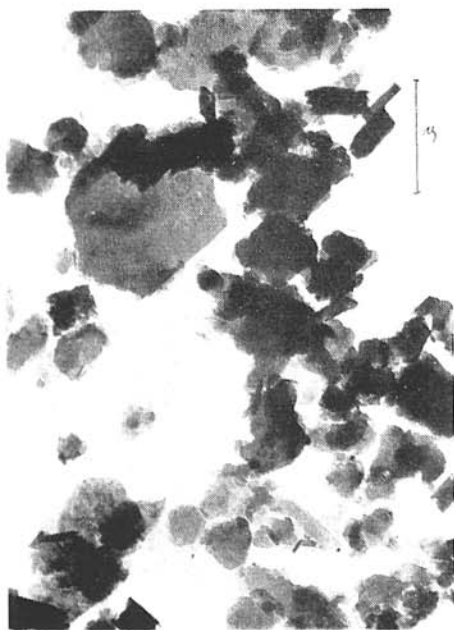
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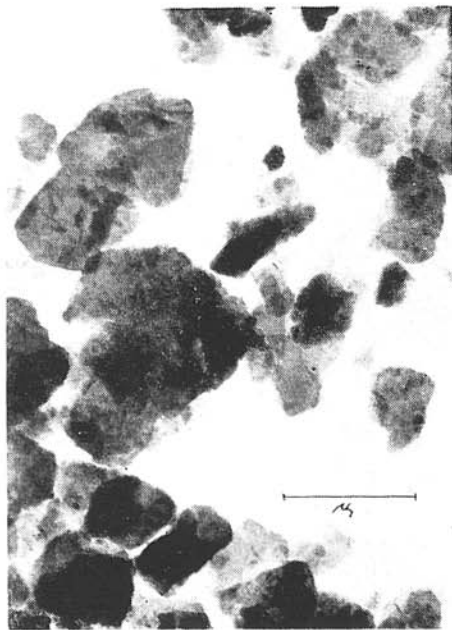
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