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MINERALOGICAL-GENETICAL STUDY OF CLAY SEDIMENTS OF THE POLTÁR FORMATION (SOUTHERN SLOVAKIA)

(Fig. 1—12)

Astract: In sediments of the Poltár Formation the presence of halloysite, gibbsite and diaspore as well as the fact that kaolinite of various degree of structural regularity appears there, was ascertained. On the basis of this information some genetic conclusions are drawn.

Introduction

The complex of the Poltár Formation is formed by sands, clayey sands, partly by gravels and layers of hemixylite. The whole complex lies unconformably on the Paleozoic, more rarely on the Mesozoic and the Miocene. M. Mišík (1956) and later on L. Ivan, B. Leško (1962) considered these fresh-water sediments as Pliocene. V. Hano, I. Horváth (1966) found variously kaolinized porphyroides, overlying Gemeride, probably Carbonaceous phyllites near Poltár. They suggest to use the original term „Poltár Formation" for these sediments only. They designate the plastic clays and sands with the term „Lučenec Formation" as the contrary because of their regional extension.

In my own study of the sediments present in the Poltár Formation I dealt with two fundamental problems. In the first place it was the detailed study of the mineralogical composition. The refractory clays of the Poltár Formation have so far been affirmed to be wholly formed by kaolinite of disordered structure with slight admixture of clay micas. I. Kraus, H. Gerthofferová, I. Križáni (1966) fond halloysite in the form of so called armored clay ball in this area. The assumption of free oxide hydrates of Al-gibbsite and diaspore present in small amount bas been confirmed now. The second problem to which I paid attention was the following of the degree of structural regularity of kaolinite. The degree of structural regularity of kaolinite was found out to be changing in dependence on the way and conditions of its origin.

I. Idenfication of Gibbsite and Diaspore

Gibbsite prevailingly appears in association with halloysite. Besides that it was found together with diaspore in clays of the Poltár Formation at the loam pit near Breznička. Light to dark-grey, slightly sandy clays and white clays are concerned there. They are found in a cut wall 150 m long. They are used for the production of thin-wall bricks and roofing.

Gibbsite and diasphore were found out in the differential-thermic and the roentgenographical way. It was DTA curves compiled under the speed of temperature growth of 50 °C/min and with weighed portion of 0.2 g that for the first time called our attention to the possibility of free oxidehydrates of Al probably present in the sediments of the Poltár Formation.

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Free oxidehydrates of Al and Fe show themselves in DTA curves with endothermic reaction within the interval of 280—400 °C. The position of the peak as well as the amplitude of this reaction at these minerals differ only in small intervals in the individual samples mentioned in literature (V. P. Ivanova 1961, R. C. Mackenzie 1957). As the variation of this deviation itself at the same mineral in dependence on various factors is also evident there, oxihydrates of Al and Fe are difficult to distinguish mutually with certainty by aid of DTA only.

According to R. C. Mackenzie (1957) gibbsite is characterized by endothermic reaction within the range of 320—330 °C. The position of its peak is mainly influenced by the granularity. S. H. Patterson (1964) found out the shift of the granularity towards 300 °C due to the presence of finely dispersed gibbsite. Approximately under this temperature endothermic reaction of gibbsite also culminates in sediments of the Poltár Formation. J. Žemlička (1960) also mentioned the peak of endothermic reaction at free Al hydrate at 300 °C in clays underlying the Most Basin. On the basis of the data of B. Čičel (1958) and J. Konta (1954a, b) on the contrary in bauxites the dehydroxylation of gibbsite is taking place at 320—340 °C.

The endotherm at 300 °C has been so far always considered as the manifestation of the presence of oxidehydrates of Fe in thermical study of the Poltár clays. This reaction was however ascertained in a series of the studied samples (fig. 1) in which the colour has not changed after burning out but always remained greyish-white. This reaction is also manifested by a markedly sharp peak. At samples with Fe oxidehydrates already indicated macroscopically, also by the colour after burning out, to the contrary the peak of the extreme is much more moderate, rounded.

If there are any difficulties in unambiguous identification of gibbsite on the basis of DTA curves, these still increase with possible presence of diaspore or boehmite. Both the minerals, if present in small amount together with kaolinite, are masked in its dehydroxylation endotherm. In the sediments of the Poltár Formation it was just the markedly deep dehydroxylation endotherm (fig. 1, no 3 and 4) that called our attention to the presence of one of these two minerals. Later on this assumption was shown as correct due to roentgenographical identification of diaspore.

Gibbsite was identified roentgenographically on the basis of the reflex of 4.84 Å. The presence of diaspore is mainly indicated by the reflex of 3.96 Å. The roentgenograms were prepared on diffractometer GON-3 from oriented preparations of the fraction less than 2 micrometres under the following conditions: Cu Kα radiation, 30 kV, 6 mA, ascending diaphragm 10, entering diaphragm 2, time constant 8 sec., shift 2 °/min.

By aid of electron microscope I tried to identify allophane in connection with halloysite which appears in the Poltár Formation in the form of so called armored clay balls (J. Kraus, H. Gerthofferová, I. Križáni 1966). The common occurrence of these minerals is current. On an electron micrograph prepared from suspension under Tesla BS 242 microscope small scales without crystallographical delimitation and only rare tube-like forms may be observed (fig. 2). The replica prepared from the same sample indicates the presence of spherical forms and irregularly delimited individuals at first sight resembling allophane (fig. 3). The method of selective dissolution by the mixture of 10 % K_2CO_3 and NaOH employed by M. Harman (1968) on the studied sample, did not confirm the presence of allophane. The roentgenogram (fig. 1, no 2) points to the presence of dehydrated halloysite. Its untypical form should deserve closer attention.

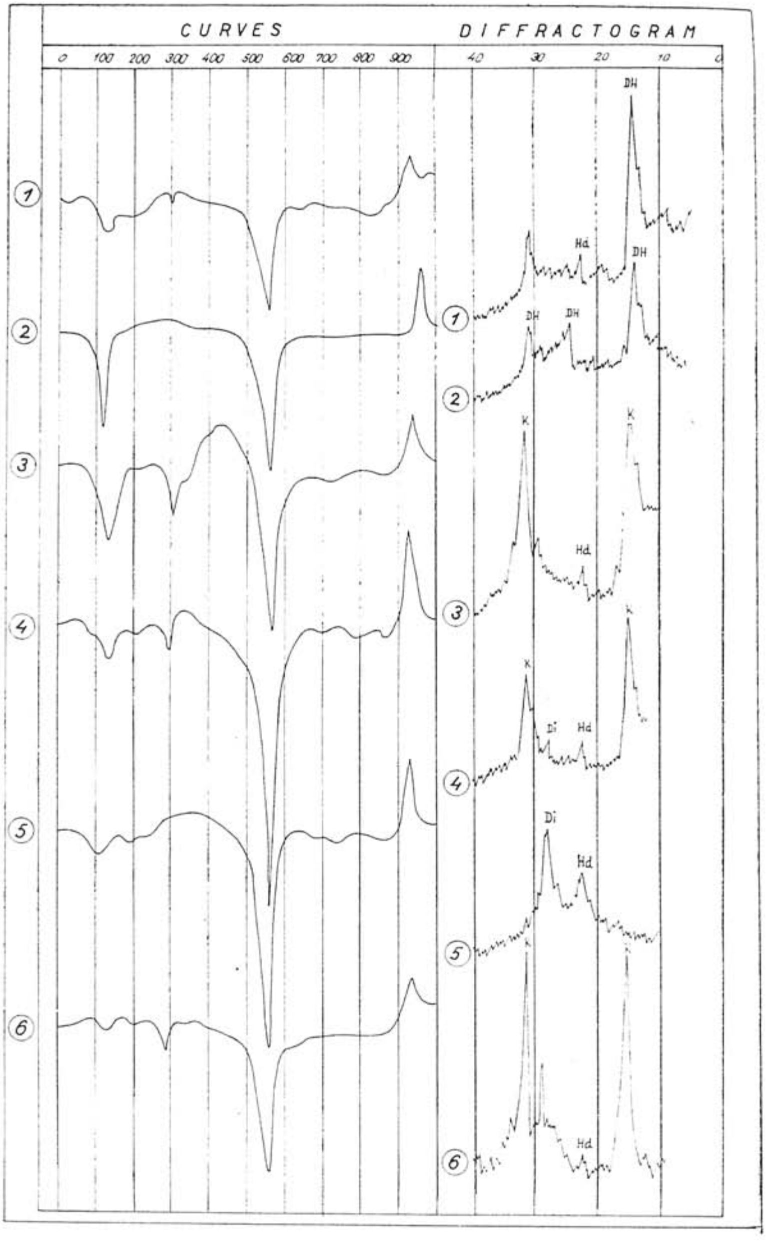

Fig. 1. Gibbsite and diaspore in sediments of the Poltár Formation. 1 — Decomposed andesite agglomerate, boring THV-18, Halič. 2 — Armored clay ball, Kalinovo. 2—6 — Refractory clays from Breznička. K — kaolinite, D — dehydrated halloysite, Hd — gibbsite, Di — diaspore.

Genesis of the Free Oxidehydrates of Al in Sediments of the Poltár Formation

The presence of gibbsite and diaspore is very important from the point of view of knowledge of the whole process of kaolinization of the Poltár Formation. Minerals of the kaolinite group but in the first place kaolinite itself are frequently found associated with Al oxidehydrates. On the other hand it is interesting that in the Bohemian Massif, where in the period between the Permian and the Tertiary the conditions for the origin of extensive weathering crusts were very favourable, the presence of free oxyhydrates of Al has not been so far ascertained in connection with kaolinitic weathering in spite of sufficient investigation of Bohemian kaolin deposits. The only area with free Al oxidehydrates known to be present in connection with clays redeposited by water is the substratum of the Most—Teplice Brown Coal Basin (J. Žemlička 1960).

As to the solution of the relations between kaolinite and free Al oxidehydrates two more or less contradictory opinions have so far been expressed. M. J. Goldman (1949), M. Gordon, J. I. Tracey, M. Ellis (1958) supposed that bauxites in Arkansas had originated directly with decomposition of original alumosilicate minerals. Later on migration of Al took place and at last kaolinite originated by resilicification of bauxite. In this connection the work by C. de Kimpe, M. Gastouche, G. W. Brindley (1964) is surprising, who found out gibbsite to be stable when affected by depolymerized SiO_2 solutions on the basis of experimental study. As they proved at the temperature of 21 °C to 63 °C Al gels in octahedral coordination do not take up more than 1—2 % SiO_2. Only at the temperature of 175 °C perfectly crystallized kaolinite originates.

The second opinion is based on the assumption of kaolinite originating in the first stage of source rock weathering and free Al oxidehydrates originating only with con-

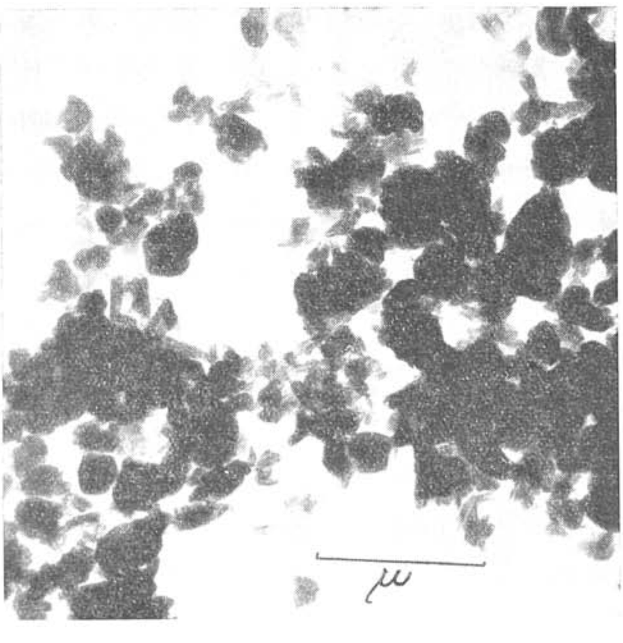

Fig. 2. Halloysite from armored clay ball, Kalinovo. Prepared by M. Harman.

tinuing intense decomposition by desilification of it (W. J. Mead 1915, E. C. Harder 1952, V. A. Eyles 1952, V. T. Allen 1952, 1955, G. Bardossy 1959, T. F. Bates 1962).

W. D. Keller (1958, 1964) tried to answer the question when a certain process manifests. According to him the final product of decomposition of alumosilicate minerals under favourable conditions is mostly influenced by the value of abrasion pH at source minerals and the solubility of Al_2O_3 and SiO_2. The most favourable conditions for direct bauxitization may originate in an environment with the value of abrasion pH within the range of 7—9.5. Under abrasion pH less than 7 usually bauxit originates by passing through the kaolinite stage.

These moments may serve us for getting a correct opinion of the origin of gibbsite and diaspore in the Poltár Formation:

Gibbsite is mainly found in association with halloysite — there are armored clay balls and decomposed andesite agglomerates but simultaneously together with kaolinite it is also present in refractory clays from Breznička, where halloysite is present in accessory amounts only.

We find gibbsite at the primary site of its origin (decomposed andesite agglomerates) or in refractory clay and armored clay balls i. e. in sediments that passed through transportation.

The presence of diaspore was ascertained with certainty in refractory clays from Breznička only, where it is found together with gibbsite in samples which have some macroscopic signs of „flint clay" type. This technological type of clays also shows the highest refractoriness of the whole area. It may be logically supposed a direct connection between the refractoriness and the content of Al oxidehydrates.

Under the present state of investigation of the mineralogical composition of sediments of the Poltár Formation the mutual relation between gibbsite and diaspore cannot be

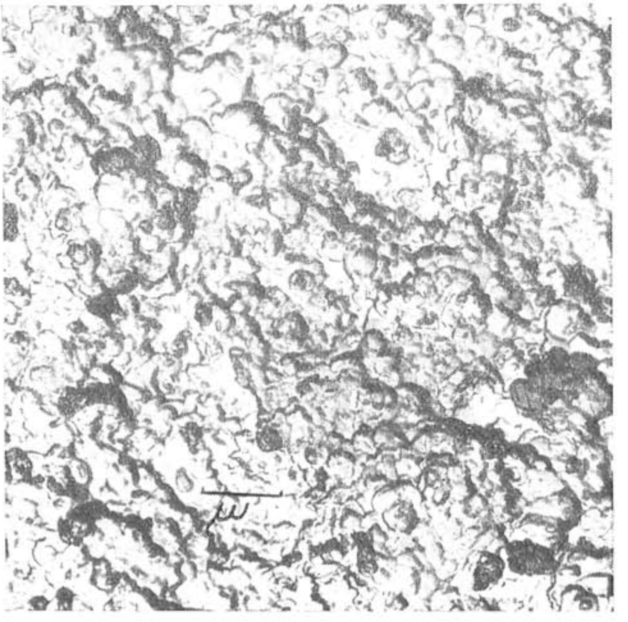

Fig. 3. Halloysite from armored clay ball, Kalinovo — one grade replica of fracture surface, shadowed at 35° — alloy of Pt-Pd, vertically by carbon. Prepared by M. Harman.

so far explained in a reliable way. I only intend to point to the relation of these newly ascertained minerals to the main process that took place in this area — kaolinization.

On the basis of up to present mineralogical study of clay sediments of the Poltár Formation I suppose that the association of halloysite-gibbsite-diaspore originated in the original weathering crust in the final stage of the whole process since no evidence of their authigenic origin in the diagenetic stage has been found. With decomposition of the source rocks in the area under study conditions suitable for their origin formed by d e s i l i c i f i c a t i o n of kaolinite. As I suppose in the final stage of kaolinization the source rocks had relatively high value of abrasion pH. I. K r i ž á n i (oral communication) found out abrasion pH in kaolinized coarse-grained sands at the locality of Ceriny as 7.5. Under approximately such conditions partial carrying away of Si from kaolinite might have taken place. No conditions however arose simultaneously for intense carrying away of Al that would have resulted in breaking up of the structure of kaolinite or source alumosilicates and intense formation of free Al oxidehydrates. This is a reason that no coherent layer of free oxidehydrates of Al has formed in upper parts of original profiles, even primairly kaolini-zed rocks containing gibbsite neither show the general character nor individual signs of laterite. On the other hand halloysite together with gibbsite might have originated in rare cases (andesite agglomerates in boring THV-18) by direct alteration from feldspars or volcanic glass. This is supported by the fact that primarily kaolinized porphyroids, quartzites and mica schists (fig. 4) always contain clay micas besides kaolinite. In a sample of decomposed andesite agglomerate, to the contrary (fig. 1, no 1), only halloysite with gibbsite without clay micas is present. This fact supports the opinion of L. B. S a n d (1956) and T. F. B a t e s (1962) that clay micas do not originate as transitional products with direct origin of halloysite.

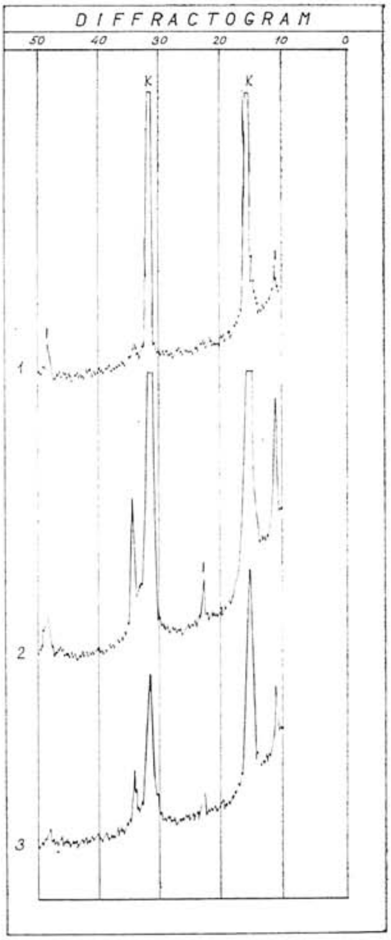

Fig. 4. Kaolinized rocks in situ. 1 — Epizonally metamorphosed quartzite from Zlámanec. 2 — Porphyroid from Horná Prievraná. 3 — Mica schists from Kalinovo.

As to mutual relations between halloysite, gibbsite and diaspor, gibbsite in most cases is found in association with halloysite. Till now no direct proof have been found that could solve their mutual ratio. I suppose that from the standpoint of time halloysite originated after kaolinite and before or simultaneously with free Al oxidehydrates.

II. Relation between the Genesis and the Degree of Structural Regularity of Kaolinite in Sediments of the Poltár Formation

The problems connected with the degree of structural regularity of kaolinite are being very intensely studied in the latest period. Before I am going to, solve this problem in sediments of the Poltár Formation I should call attention to possibilities of interpretation of this knowledge for solving some genetic problems.

H. H. Murray, S. C. Lyons (1960) and P. S. Keeling (1962) pointed to the relation between the degree of regularity of kaolinite and some of its technological qualities (plasticity, quantity of dissolving water, capacity of sorption, solidity, colour of burning out).

For our considerations the information dealing with the relation between the degree of order of kaolinite structure and the way of its origin is more important. J. Slánska (1963, 1964) among others applied this relation in establishing the stratification of sediments in the basins of South Bohemia. The cause of the variability in the degree of structural regularity of kaolinite is seeked in various intensity of weathering processes.

Another factor which may influence the degree of regularity of kaolinite is the character of source minerals and rocks. G. Guiseppetti, B. Pigorini, F. Veniale, G. Peco (1963) ascertained in kaolinization of granites that kaolinite directly originating from feldspars is well ordered vhereas kaolinite originated as final product with weathering of volcanic rocks by resilicification of gibbsite shows a lower degree of order of structure. M. Kužvart (1965), studying kaolin at Moravo-Silesian kaolin deposits, drew the conclusion that kaolinite which originated from sericite of dynamometamorphic origin is pseudomonoclinic, whereas kaolinite that originated with decom-

Fig. 5. Halloysite from armored clay ball, Kalinovo. Prepared by H. Gerthofferová.

position of granite from feldspars is triclinic. Solving the genesis of the Vildštejn Clays in the Cheb Basin P. Šantrůček (1964) proved the so called Pórovina Clays formed by well ordered kaolinite to have originated by weathering of the Smrčiny granite. So called bond clays, to the contrary, with kaolinite of disordered structure sharing in their composition, are genetically bound to crystalline schists.

The most reliable application of the knowledge of the degree of regularity of kaolinite structure may be in mutual distinguishing of primary and secondary kaolinite sediments. It was J. A. Rusko (1965), who called attention to this fact, when he studied a large group of kaolin deposits in the region of the Ukrainian crystalline shield from this standpoint. In all the cases primary kaolinite in residual kaolin differs from kaolinite in secondary, redeposited clays in much higher degree of order of structure.

The fact that primary kaolinite differs from secondary one in the regularity of structure may be influenced by several circumstances but probably the transportation of clay material from primary weathering crusts into basins of sedimentation with following sedimentation and diagenesis is that of greatest importance. H. Takahashi (1959) found out experimentally that mechanical friction of kaolinite results in destruction of its structure and gradually a product of qualities equal to those of kaolinite of fireclay type arises. M. P. Vikulova, V. A. Šitov (1966) also affirm that authigenic kaolinite is of more perfect crystallographical delimitation than kaolinite which passed through transportation in water environment.

On this occasion I intend to call attention to possibility of following of the effect of transportation on the morphological development of halloysite besides that of kaolinite also in sediments of the Poltár Formation. Halloysite which is found in the form of so called armored clay balls passed through transportation from the primary site of

Fig. 6. Halloysite from decomposed andesite agglomerate, bering THV-18, Halič. Prepared by H. Gerthofferová.

origin. The transportation left marked traces also on individual particles of halloysite, which we may study well under electron microscope. They are of short columnar habit, their length never exceeds 1 micrometre, frequently disturbed at the margins and partly stretched (fig. 5). Halloysite from boring THV-18 near Halič, to the contrary, in decomposed andensite agglomerate with preserved structure of the source rock reaches the length of three and also more micrometres, is well delimited and mechanically undisturbed (fig. 6). There is also no doubt that the decomposition of the mentioned rock was taking place at the original site.

A. Oberlin, C. Tchoubar (1958) called attention to the importance of changes in kaolinite structure in the time of sedimentation. T. L. Kesler (1956), D. N. Hinckley (1963) and T. F. Bates (1964) explained the difference in kaolinite structure at large kaolin deposits in Georgia and South Caroline in the way that well ordered kaolinite had deposited in fresh-water environment and disordered one in marine environment.

Another factor affecting the degree of regularity of kaolinite structure is the granulometric composition and porosity of sediments in diagenetic stage. D. D. Kotel'nikov (1958) stated that the intensity of diagenetic changes in clay minerals is different in pelitic and aleuro-psammitic sediments. Well-developed, pseudohexagonal crystals of kaolinite very frequently form the cement in aleuro-psammitic sediments. Irregularly delimited, fragmental kaolinite is mainly concentrated in pelites to the contrary.

Experimental Study

The first results of regularity of structure of kaolinite by aid of roentgenographical analyses were shown by G. W. Brindley, K. Robinson (1964) and later on by H. H. Murray (1954) mainly.

Well ordered kaolinite is mainly characterized by the doublet of the reflexes of 4.18 and 4.13 Å. Further there are reflexes with the index $k \pm 3n$ in the area of 3.5—2.5 Å and the presence of two „triplets" of the reflexes of 2.55; 2.52; 2.49; and 2.37; 2.33; 2.28 Å. At kaolinite with disordered structure the intensity of the reflex of 4.45 Å gradually increases in contrast to the intensity of the basal reflex of 7.15 Å.

In sediments of the Poltár Formation I studied the degree of regularity of kaolinite structure on diffractometre GON-3 by aid of roentgenographic analysis under the following conditions: Cu $K\alpha$ radiation, 30 kV, 6 mA, ascending diaphragm 10, entering diaphragm 2, time constant 8 sec., shift 2 °/min. The samples were shifted through a sieve of 0.04. They were not separated by floating for preferential orientation along 001 to be avoided.

In fig. 7 the record Ia of kaolinite from kaolinized, epizonally metamorphosed quartzites of the Zlámanec Rock is presented. The record 2 represents kaolinite that forms the cement in coarse-grained sands in the sand pit near Hrabovo. Refractory clay of the technological make „IM" from the loam pit in Breznička is on diffractogram 3.

The high content of quartz in the first two samples blocks the doublet of 4.18—4.13 Å as well as some other reflexes. Mutual comparison of all the three kaolinite samples enabled to determine their degree of regularity of structure on the basis of these factors:

1. Intensity and sharpness of basal lines.
2. Intensity of the line of 4.45 Å.
3. Number of the lines.

This comparison led me to the conclusion that kaolinite from the Zlámanec Rock and from the sandstone near Hrabovo is of distinctly higher degree of structural regularity than refractory clay from Breznička. According to the classification of H. H. M u r r a y (1954) the first two samples could be ranged into the limit between the first and second

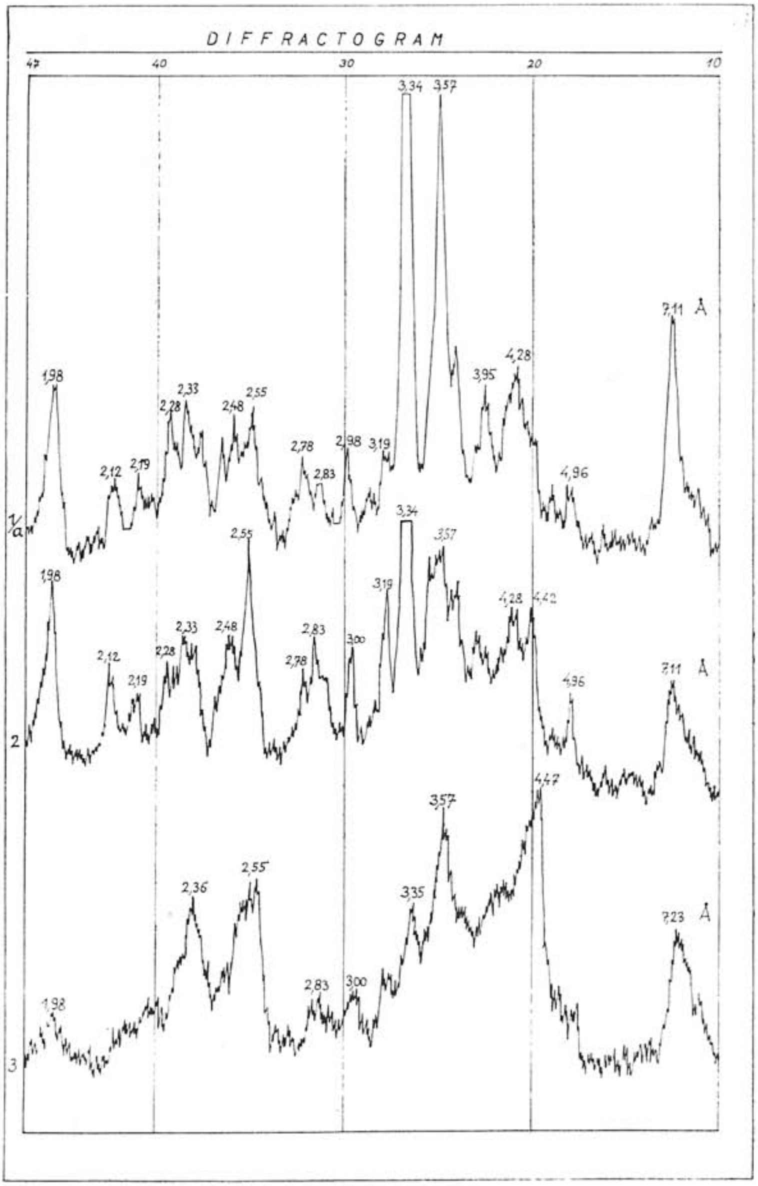

Fig. 7. Following of the structural regularity of kaolinite in sedimens of the Poltár Formation by aid of roentgenographic analysis. 1 — Kaolinite, Zlámanec. 2 — Kaolinite, Hrabovo. 3 — Kaolinite, Breznička.

group whereas the third sample into the last group of very little ordered to disordered kaolinites. Some circumstances also indicate intensity of basal reflexes kaolinite from Zlámanec being of somewhat better degree of structural regularity than that from Hrabov.

The regularity of kaolinite structure was simultaneously studied by aid of DTA on the same samples. The apparatus and conditions of work were equal as in identification of free Al oxidehydrates.

As the works by R. W. Grimshaw, E. Heaton, H. L. Roberts (1945), R. E. Grim (1947), H. H. Murray (1954) showed, the depth and temperature at which the dehydroxylation endotherm culminates is generally greater and higher at kaolinites with well ordered structure than at those with disordered one. Besides that the degree of regularity in kaolinite structure also manifests in different symmetry of the dehydroxylation endotherm. S. B. Hendricks, L. Bramao, J. G. Cady, M. Swerdiow (1952) found out the coefficient of symmetry varying within the interval of 0.78—2.39. The value of the coefficient increases with the decrease in the degree of structural regularity. On the final exotherm the range of temperature is shorter, it is sharp, high and the temperature of the peak is shifted towards higher temperature at well ordered kaolinites.

Studying the regularity of kaolinite structure by aid of DTA we have to take into consideration a series of factors of subjective character in contrast to roentgenographic analysis. It is connected with the fact that with thermical study of clay minerals the course of the resulting curves is greatly influenced by specific conditions under which they were prepared. I have in mind here the increase in temperature, the weighed portion, granularity as well as the content of clastic non-clay constituent. That is the reason that I am going to point to the influence of the individual factors in a concrete way before I start with the interpretation itself.

B. Číčel (1966) dealt with the influence of the first two factors (increase in temperature and weighed portion). He found out their negative influence to be possible to eliminate with mutual suitable ascertaining of the weighed portion and the speed of temperature increase. The optimum conditions of work, he ascertained for an apparatus of the construction equal to our one, agree relatively well with ours.

As it was found out in the study of kaolinite clays of the Poltár Formation, they are the last two factors from the above mentioned — granularity and the content of clastic admixtures (quartz, muscovite, feldspars) — that have the greatest influence on the general course of the dehydroxylation endotherm and the final exothermic peak.

As to the influence of the granularity on the shape of the curves we may say in accordance with many works dealing with these problems that pure clays without or with minimum amount of sandy constituent usually show in the finely dispersed fraction of less than two micrometres a rather deadened course of endo- and exothermic reactions than coarser fractions. We may see it clearly on the sample of kaolinite from Zlámanec. The dehydroxylation endotherm, as well as the final exotherm are much more intense in the fraction up to 40 micrometres (fig. 8, no. 1a) than the same sample, when followed in the fraction of less than two micrometres (fig. 8, no 1b). The peak of the dehydroxylation endotherm is also shifted here by 10 °C related to lower temperature. It is more than probable that well crystallized kaolinite from Zlámanec shows more coarsely dispersed development, greater dimensions of individual particles and therefore it is mainly concentrated in the fraction of coarser granularity.

The last factor — the presence of clastic constituents, mainly of quartz, muscovite

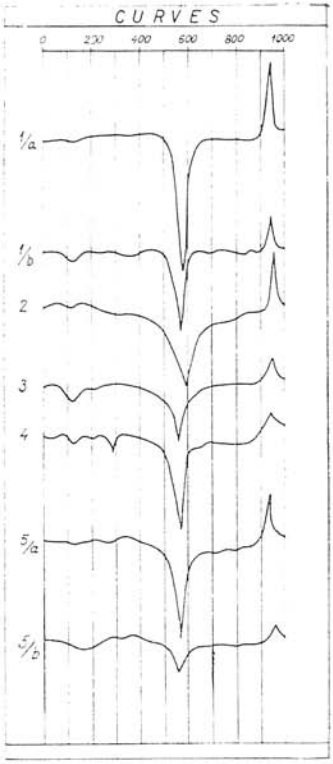

Fig. 8. Following of the structural regularity of kaolinite in sediments of the Poltár Formation by aid of DTA. 1a — Kaolinite of the fraction up to 40 micrometres, Zlámanec. 1b — Kaolinite of the fraction of less than 2 micrometres, Zlámanec. 2 — Kaolinite of clay cement of sands of the fraction of less than 2 micrometres, Hrabovo. 3 — Clayey intercalation in kaolinic sands of the fraction of less than 2 micrometres, Hrabovo. 4 — Refractory clay of the fraction of less than 2 micrometres, Breznička. 5a — Sandy clay of the fraction of less than 2 micrometres, Kalinovo. 5b — Sandy clay of the fraction up to 40 micrometres, Kalinovo.

and feldspars shows an opposite effect. Samples with high content of sandy admixture display lowered intensity of the extremes in natural, unprepared state (fig. 8, no 5 b).

When the fraction of less than two micrometres (fig. 8, no 5a) is obtained by floating, we meet a phenomenon opposite to the foregoing case — the endothermic minimum and the exothermic maximum are getting deeper and sharper. The peak of endothermic reaction also shifts by about 10 °C in relation to higher temperature.

J. Vtělenský, F. Kupka (1962) mention the degree of regularity of kaolinites ascertained on the basis of DTA not to agree with the sequence ascertained roentgenographically in some cases. This is also connected with the fact that by aid of DTA only disturbances inside the individual beds may be found out. Kaolinites having disturbances in the mutual position of beds only, may also show DTA curves not indicating them with perfect degree of regularity.

In this sense the samples studied from the Poltár Formation show the sum of both kinds of disturbances. This is supported by the fact that the sequence of regularity of kaolinite ascertained by roentgenography agrees with the sequence ascertained by DTA. Kaolinites from Zlámanec (fig. 8, no 1a) and Hrabov (fig. 8, no 2) show all signs of better ordered kaolinite, as well as refractory clay from Breznička (fig. 8, no. 4). This statement at last supports very well the morphological development of studied kaolinites, followed under electron microscope on suspensions carried over on collodium support.

The samples from Zlámanec (fig. 9) and Hrabov (fig. 10) with well ordered kaolinite contain well delimited plates of pseudohexagonal development. Opposite to it, in the clay sample from Breznička with little ordered to disordered kaolinite its fragmental development with irregular edges, without pseudohexagonal tabular particles and a distinctly finely dispersed character are evident (fig. 11).

Genetic Aspects of the Studied Problem

On the basis of obtained information of the degree of regularity of kaolinite structure I intend to clarify some genetic problems of kaolinitization in the Poltár Formation.

Primary kaolinite that originated by decomposition of epizonally metamorphosed quartzites of the Zlámanec Rock belongs among kaolinites with the relatively best degree of structural regularity in sediments of the Poltár Formation. Epizonally metamorphosed quartzites found at this locality represent a well preserved weathering crust. This was conditioned by two circumstances. They were the relatively high content of feldspars and micas in the source rock and the fact that these rocks were intensely tectonically disturbed after their formation and before the action of atmospheric agencies, what considerably contributed to their mechanical disintegration. This way the decomposition of original minerals and the formation of authigenic clay minerals were greatly accelerated. Kaolinite from newly discovered kaolinized porphyroids near Horná Prievraná also belongs to this category as the works by I. Horváth (1966, 1967) show.

In both cases the perfect degree of structural regularity is the reflection of the conditions of kaolinite formation. Primary kaolinites are concerned or at kaolinized porphyroids local redeposition to a short distance was possible. According to the degree of structural regularity also kaolinite forming the cement in coarse-grained sands belongs here that beside other localities in the Poltár Formation is also found in the sand pit near Hrabov. In this case however the interpretation of its origin is not so unambiguous.

In porous sediments conditions more favourable for the formation of authigenic minerals in the stage of diagenesis are supposed to arise, as well as in pelitic sediments. If the opinion of V. Hano, I. Horváth (1966) however were accepted, according to which these sediments represent redeposited material of kaolinized porphyroids, the degree of structural regularity would be given more or less primarily then. The first possiblity (authigenic origin) may be substantiated by the fact that a difference in the

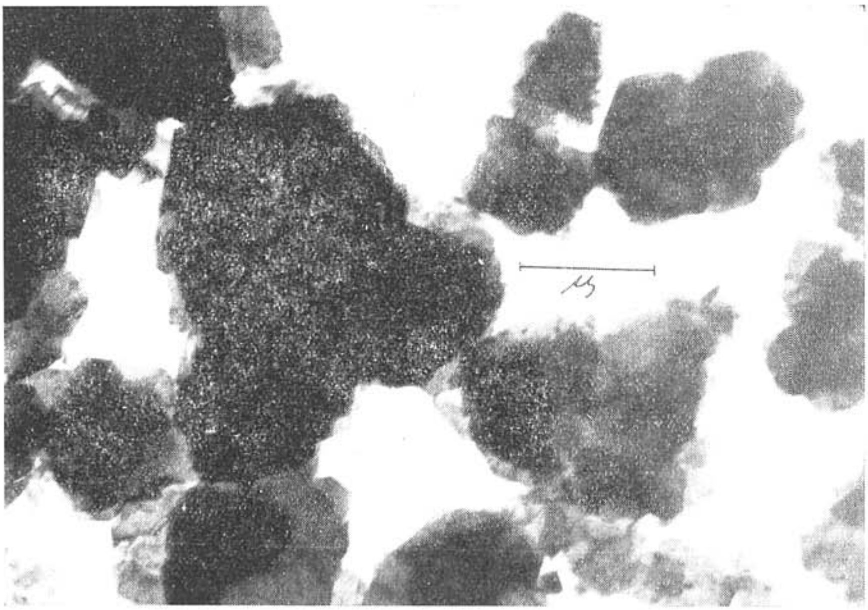

Fig. 9. Well ordered kaolinite, Zlámanec. Prepared by H. Gerthofferová.

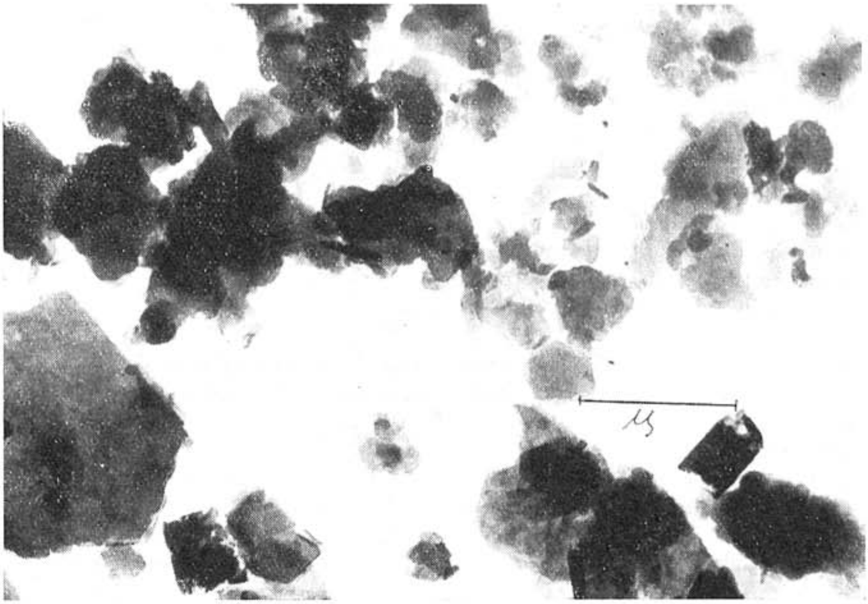

Fig. 10. Well ordered kaolinite, Hrabovo. Prepared by H. G e r t h o f f e r o v á.

degree of structural regularity of kaolinite forming the cement in sands (fig. 8 no 2) and of kaolinite from 0.5 m thick clayey intercalation in the same complex was found (fig. 8, no 3). Kaolinite in clayey intercalation is of lower degree of crystallinity as also its morphological development shows (fig. 12) besides DTA curves. The regularity of its structure approximately agrees with little ordered to disordered kaolinite of refractory clays from Breznička.

The second group includes little ordered to disordered kaolinites of fireclay type that form the principal mass of technologically most important refractory clays. This type represents the refractory clay of the technological mark „IM" from Breznička. This information was however also confirmed at tens of samples from the whole area of the Poltár Formation (I. K r i ž á n i 1966).

Basing on this information I suppose kaolinite with more perfect degree of structural regularity to have originated by weathering of source rocks in primary weathering crusts and we prevailingly find it at the original site. Besides that in places where kaolinite is present in the form of cement in sandy sediments conditions rather suitable for authigenic origin in the stage of diagenesis formed.

The predominating part of clays of the Poltár Formation, to the contrary, was transported in clastic state after kaolinitic weathering of source rocks and I do not suppose more intense changes under the influence of the environment in the course of sedimentation and diagenesis.

On the basis of the study of kaolinized porphyroids in Horná Prievraná and kaolinized quartzites from the Zlámanec Rock another possibility appears to widen our considerations also to the question of the influence of source rocks on the degree of regularity of kaolinite structure. I suppose kaolinization of feldspars in porphyroids

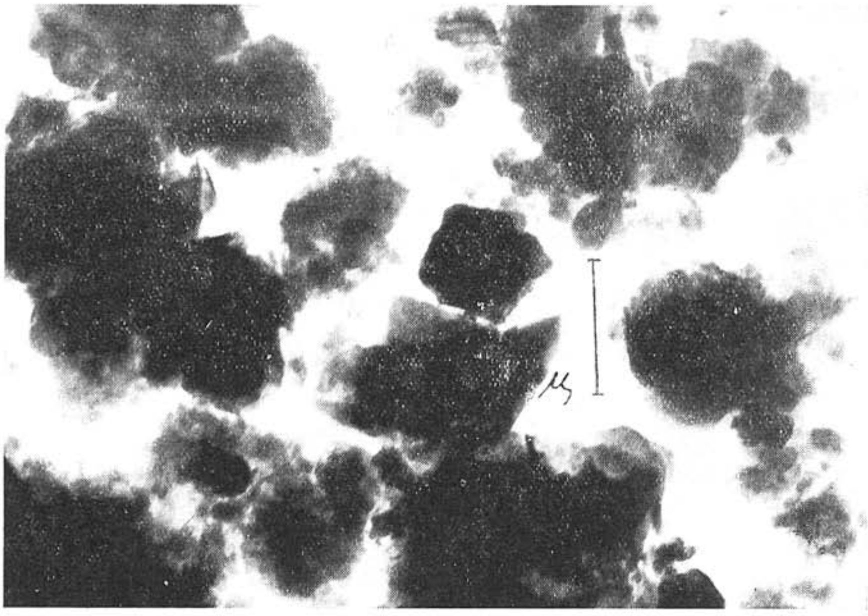

Fig. 11. Little ordered to disordered kaolinite, Breznička. Prepared by H. Gerthofferová.

and quartzites that mostly proceeded in place to have conditioned the formation of kaolinite with relatively better regularity of structure, as it is in the case of Poltár refractory clays themselves. These were transported for a considerable distance into the present basin of sedimentation after kaolinitic weathering of crystalline schists. The petrographic character of source rocks and following transportation are the main causes of the presence of kaolinite with little ordered structure found here.

Time Ranging of Kaolinization in the Area of the Poltár Formation

Closing I should briefly mention the number and time of the stages, in which kaolinitic weathering was taking place in the area under study.

Up to present works enabled to ascertain the age of sediments of the Poltár Formation with relative certainty. It is much more difficult to accept unambiguously an attitude to the question when the kaolinization itself was taking place in original weathering crust. V. Hano, I. Horváth (1966) partly expressed their opinion to this problem, supposing the kaolinization of porhyroids to have taken place in the Pliocene as the consequence, of the presence of a fresh-water lake with high content of humic acids. The mentioned authors did not deal with the relation between kaolinized porphyroids and refractory clays. They also did not deal with the question, when kaolinitic weathering, which produced the principal mass of refractory clays, was taking place. Their work allows to conclude indirectly on the sedimentation of sandy-plastic rocks of the Poltár Formation to the end and after deposition of kaolinized porphyroids.

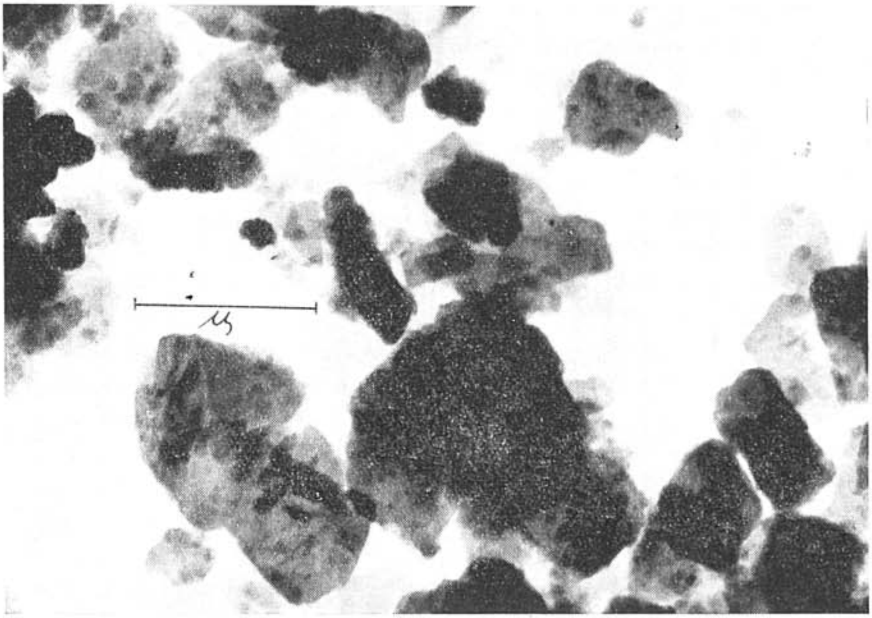

Fig. 12. Little ordered to disordered kaolinite, Hrabovo. Prepared by H. G e o r t h o f f e r o v á.

In this connection it is remarkable that in the whole area of the Poltár Formation besides porphyroids also variously decomposed granites, mica schists, phyllites, quartzites and andesites were found in places, where except andesites the main product of alteration is kaolinite. This makes clear that andesites are the youngest rocks, where we may follow the formation of minerals of the kaolinite group in situ. This knowledge however cannot solve the question, whether kaolinization was taking place in one stage, the earliest in Pliocene, or also earlier.

An important contribution to the solution of this probleme in the Ipeľ Valley was provided by D. V a s s, B. Č í č e l (1964) when they ascertained the terrigenous development of kaolinitic clays near Seľany. They consider them as the local basal member of the Tertiary in the Ipeľ Valley and range them to the Rupelian or the beginning of Aquitanian. The fact that J. S e n e š (1960) ascertained the presence of kaolinitic clays in the Rupelian of the Danube Lowland and G. V á r j u (1959) situates the deposit of kaolinitic clays near Romhány in Hungary in the same period leads D. V a s s, B. Č í- č e l (1964) to the opinion that at the end of the Paleogene regional kaolinitic weathering took place in North Hungary and South Slovakia. In the area of the Poltár Formation itself this stage of kaolinization has not been so far proved. It would be only confirmed if products of kaolinic detritic formation, so far known from near Seľany only, were found directly underlying the Chattian—Aquitanian also in the area of the Poltár Formation.

On the basis of the mentioned facts and the general geological development I suppose the main process of kaolinization in source areas of the Poltár Formation to have taken place in the Pliocene. In this area probably also kaolinic weathering proceeded in the time of Oligocene, even when we so far have no direct proofs for this affirmation.

Conclusion

On the basis of mineralogical study of clay sediments in the Poltár Formation this fundamental knowledge may be presented:

1. The newly ascertained association of minerals — halloysite gibbsite, diaspore originated by desilicification of kaolinite in the original weathering crust. Besides that we know the case when halloysite together with gibbsite originate with direct alteration of andesite agglomerates.

2. In clay sediments of the Poltár Formation besides kaolinite with little ordered structure the presence of relatively better ordered kaolinite was also ascertained. Simultaneously certain relation between the regularity of structure of kaolinite and the way of its formation was also ascertained. Kaolinite with better degree of structural regularity originated by weathering of source rocks in situ. The prevailing part of clays of the Poltár Formation, transported into the basin of sedimentation after kaolinitic weathering shows all signs of little ordered to disordered kaolinite.

3. I hold the opinion that the main process of kaolinization in source areas took place in the Pliocene. Besides that I suppose kaolinic weathering to have proceeded in the time of the Oligocene in this area, even when so far direct proofs of this affirmation are lacking.

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REFERENCES

Allen V. T., 1952: Petrographic relations in some typical bauxite and diaspore deposits. Bull. Geol. Soc. Amer. 63, 7. — Allen V. T., 1955: Relation of porosity and permeability of the origin of diaspore clay. Clays and Clay Min., 3-rd Nat. Conf. Pub. 395, Washington. — Bardossy G., 1959: The geochemistry of Hungarian bauxites. Acta geol. Hung. Acad. 62, 5—6, Budapest. — Bates T. F., 1962: Halloysite and gibbsite formation in Hawaii. Clays and Clay Min., 9-th Nat. Conf., New York. — Bates T. F., 1964: Geology and mineralogy of he sedimentary kaolins of the southeastern United States — a review. Clays and Clay Min., 12-th Na., Conf., Oxford-London—Edinburgh—New York—Paris—Frankfurt — Brindley G. W., Robinson K., 1946: Randomnes in the Structures of Kaolinitic Clay Minerals. Trans. Faraday Soc., 42 B. — C. de Kimpe M. C., Gastouche M. C., Brindley G. W., 1964: Low temperature synthesis of kaolin minerals. Amer. Mineralog. 49, 1—2. — Čičel B., 1958: Príspevok ku mineralógii bauxitov z okolia Mojtína. Geol. práce, Zprávy 14, Bratislava. — Čičel B., 1966: Zmeny charakteristiky krivky DTA zapríčinené zmenami rýchlosti rastu teploty a množstva vzorky. Definícia optimálnych pracovných podmienok pri DTA, spôsob ich vyhľadávania. Sborn. z konf. o DTA a jej využití v silikátoch. Bratislava. — Eyles V. A., 1952: The composition and origin of the antrim laterites and bauxites. Mem. Geol. Surv. No Ireland, Belfast. — Goldman M. I., 1949: Petrology of bauxite surrouding a boulderlike core of kaolinized nepheline syenite in Arkansas. Geol. Soc. Amer. Bull. 60. — Gordon M. J., Tracey J. I. Ellis M. V., 1958: Geology of the Arkansas bauxite region. U. S. Geol. Surv. Prof. Pap. 299. — Grim R. E., 1947: Differential thermal curves of prepared mixtures of clay minerals. Amer. Mineralog. 32. — Grimshaw R. W., Heaton E., Roberts H. L., 1945: Constitution of refractory clays. Part II. Thermal analysis method. Trans. Ceram. Soc. 44 — Guissepetti G., Pigorini B., Veniale F., Peco G., 1963: Weathering materials of igneous rocks and sedimentary deposits from Valsesia, Italy. Internat. Clay Conf., Stockholm. — Hano V., Horváth I., 1966: Niekoľko poznámok o ložisku kaolínu na južnom Slovensku. In press. —

Harder E. C., 1952: Examples of bauxite deposits illustrating variations in origin. Problem of Clay and Laterite Genesis, Symp. AIME, St. Louis-New York. — Harman M., 1968: Identifikácie malých množstiev alofánu metódou selektívneho rozpúšťania pod elektrónovým mikroskopom. In press. — Hendricks S. B., Bramao L., Cady J. G., Swerdiow M., 1952: Characterization of kaolin minerals. Soil. Sci. 73. — Hinckley D. N., 1963: Variability in „crystalinity" values among the kaolin deposits of the Coastal Plain of Georgia and South Caroline. Clays and Clay Min., 14-th Nat. Conf. Oxford-London—New York—Paris. — Horváth I., 1966: Prínos metódy DTA pre prospekciu plastických keramických surovín. Sborn. z konf. o DTA a jej využití v silikátoch. Bratislava. — Horváth I., 1967: Technologické vlastnosti a mineralogická charakteristika surového kaolínu z lokality Horná Prievraná. IV. Konferencia o mineralógii a petrológii ílov, Košice, in press. — Ivan L., Leško B., 1962: Stratigrafická pozícia keramických surovín v neogéne a ich využitie. Geol. práce 63, Bratislava. — Ivanova V. P., 1961: Termogrammy mineralov. Zapisky Vsesoj. Min. Obšč. 1, Leningrad. — Keeling P. S., 1962: The common clay minerals as a continuous series. Science of Ceramics. London. — Keller W. D., 1958: Argillation and direct bauxitization in terms of concentrations of hydrogen and metal cations at surface of hydrolyzing aluminum silicates. Bull. Amer. Assoc. Petrol. Geol. 42, 2. — Keller W. D., 1964: The origin of high-alumina clay minerals a review. Clays and Clay Min., 12-th Nat. Conf., Oxford-London—Edinburg—New York—Paris—Frankfurt. — Kesler K. T., 1956: Environment and origin of the Cretaceous kaolin deposits of Georgia and South Caroline. Econ. Geol. 51. — Konta J., 1954a: Příspěvek k petrografii a genesi Rychnovského bauxitu. Acta Univ. Car. Geol. 9, Praha. — Konta J., 1954b: Petrografické a chemické studium bauxitu od Markušovců. Rozpr. ČAV, řada MPV, 64, 4. Praha. — Koteľnikov D. D., 1958: O morfologičeskoj charakteristike kaolinita osadočnych porod. Doklady AN SSSR 132, 2, Moskva. — Kraus I., Gerthofferová H., Križáni I., 1966: The occurrence of halloysite in deposits of the Poltár Formation. Geol. sborn. Slov. akad. vied 17, 1, Bratislava. — Križáni I., 1966: Geologické a mineralogicko-petrografické pomery ílov Ipeľskej doliny. Diploma work. Prírodovedecká fakulta UK, Bratislava. — Kužvart M., 1965: Geologické poměry moravskoslezských kaolínů. Sborn. geol. věd, řada LG 6, Praha. — Mackenzie R. C., 1957: The differential thermal investigation of clays. London. — Mead J. W., 1915: Occurrence and origin of the bauxite deposits of Arkansas. Econ. Geol. 10. — Mišík M., 1956: Sedimentárno-petrografické štúdium poltárskej formácie. Geol. práce 43. Bratislava. — Murray H. H., 1954: Structural variations of some kaolinites in relation to dehydrated halloysite. Amer. Mineralog. 39. — Murray H. H., Lyons S. C., 1960: Further correlations of kaolinite crystallinity with chemical and physical properties. Clays and Clay Min., 8-th Nat. Conf. London-Oxford—New York—Paris. — Oberlin A., Tchoubar C., 1958: Étude en microscopie et differaction electroniques de l'altération de la kaolinite par l'eau: Influence dessels dissous. Silicates Industriels 24. — Patterson S. H., 1964: Halloysitic underclay and amorphous inorganic matter in Hawaii. Clays and Clay Min., 12-th Nat. Conf., Oxford—London—Edinburg—New York—Paris—Frankfurt. — Rusko J. A., 1965: Kristaličnosť kaolinita ukrajinskych mestoroždenij. Morfologija, svojstva i genezis mineralov. Kijev. — Sand L. B., 1956: On the genesis of rezidual kaolins. Amer. Mineralog. 41, 1—2. — Seneš J., 1960: Základné črty paleogénu Podunajskej nížiny. Geol. práce 59, Bratislava. — Slánska J., 1963: Výsledky petrografického výzkumu klikovského a mydlovarského souvrství. Věstn. ÚUG 38, 6, Praha. — Slánska J., 1964: Příspěvek k petrografii lipnického souvrství v třeboňské pánvi. Věstn. ÚUG 39, 3, Praha. — Šantrůček P., 1964: Kaolinické zvětrávání a genese ložisek vildštejnských jílů v chebské pánvi (záp. Čechy). Sborn. geol. věd, řada G 5, Praha. — Takahashi H., 1959: Effect of dry grinding on kaolin minerals. Clays and Clay Min., 6-th Nat. Conf., London—New York—Paris—Los Angeles. — Várju G., 1959: A Romhány-rögterületén levö (Bánk-Petényi) tüzáloagyag-elöfordulás. Az All. Földt. Int. Évi Jelent. Budapest. — Vass D., Číčel B., 1964: Mineralogicko-chemické a geologické zhodnotenie terigennej formácie na báze tercieru Ipeľskej kotliny. Geol. práce, Zprávy 33, Bratislava. — Vikulova M. F., Šitov V. A., 1966: Novyje dannyje po issledovaniju glinistych porod s pomoščju replik. Sborn. Fiz. metody issled. miner. osadoč. porod, Moskva. — Vtělenský J., Kupka F., 1962: Pokus o využití strukturní variability kaolinitu ke klasifikaci keramických jílů. Sborn. geol. věd, řada TG 2, Praha. — Žemlička J., 1960: O geochemii podložných titaničitých ílů v severočeské hnedouhelné a Sokolovské pánve. Geotechnica 28, Praha.

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