Geology of Kaolin Deposits

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KAOLINITE OCCURRENCES IN HUNGARY

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In the framework of a concise but brief paper I am endeavouring to summarize and pass into review our knowledge in connection with kaolin occurrences in Hungary, mentioning there where this appears to be necessary the most important steps of the development and the prospection.

Clay mineral prospection started in Hungary on a broader scale at the beginning of the 50's, when instruments essential for their study became more and more widespread. Since the geological bases, to which I shall refer later on in detail, were more favourable to the formation of three-layer clay minerals rather than to kaolinite, prospecting activity in the country was mainly concentrated on momtmorillonite, illite and clay minerals of a mixed structure. In addition prospection of kaolin represented a constant source of interest for geologists on account of its industrial importance.

With a view to the fact that the Conference is dealing with genetic questions of kaolin mineral, I myself am limiting my paper to the prospection of this mineral in Hungary and to its results being, however, aware that genetics of kaolinite are inseparable from the investigation and study of the formation of other minerals.

This statement is specially valid for mineral associations of kaolinite occurrences in Hungary, since the majority of industrially important depositions is of hydrothermal origin as against those formations which were brought by surface weathering.

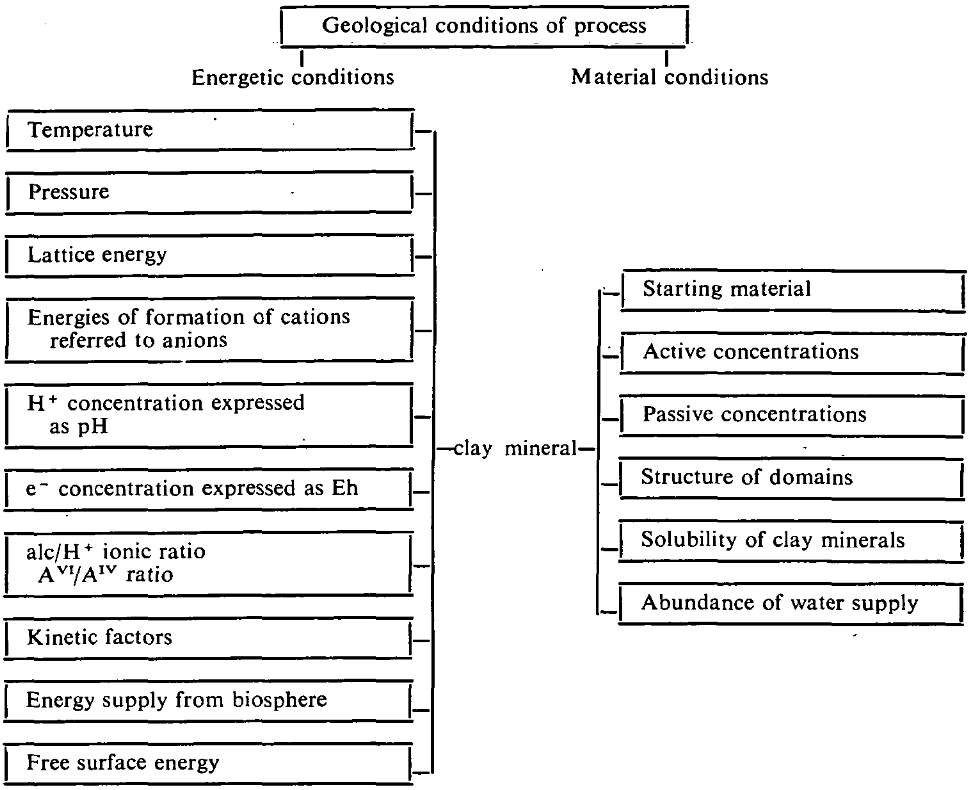
Considering those geological formations in which kaolinite mineral is occurring in whatever a proportion and among some other minerals, we are faced with a rather varied picture. From the point of view of the characteristics of the formation, it appears to cast a light on the material and energy factors of the genetics as well as the geological conditions under which the process took place. All this is shown in Table 1.

Useful information may be obtained to this effect if due consideration is given to the site where the process took place formerly, thus to find out whether it occurred in the 0—5 km zone of the continental crust, on the surface of the continent or in the hydrosphere. In the first case the main process is an epigenetic and hydrothermal alteration, in the second one it is due to weathering, and in the third one it is mainly diagenesis. In the first two cases it is, of course, a primary formation; it is another question again whether the present occurrence of kaolin minerals is as a matter of fact a result of transportation and sedimentation of the primary kaolinite, as well as of process having taken place in the meantime (secondary deposits), which also applies to the third case.

Passing in review the above sequences, hereunder we are explaining kaolinite occurrences and their characteristics in Hungary as follows.

TABLE 1

Physical and chemical factors of clay mineral formation (the author's compilation)



As we have already mentioned, the majority of kaolinite occurrences in Hungary worth consideration are connected with a hydrothermal activity. This circumstance determines the mineral composition of kaolin deposits which is different from kaolinites formed by granite weathering, and the utilization is also markedly different from that.

For the sake of better understanding this peculiarity, let us cast a glimpse on the hydrothermal process itself and let us consider that superheated steam issuing from a zone of great depth, exerts hydrothermal action on a rock. It will dissolve the rock according to its mineral constitution; will saturate with respect to this or that ion, and as a result concentration, Eh and pH parameters determined by temperature and the chemical reactions etc. come to exist. If any crystallization is initiated, its outcome is determined by the actual parameters of the solution. The solution will deposit certain components by crystallization and absorb some others by a dissolving action. Thus, the agency is in a permanent continuous interaction with its material surroundings. The geological process is then very complicated, in this case but as a rule it will not tend to evolve towards any extreme as it has been stated. The overall results is a clay mineral association which belongs to one of several well-defined types, and hence the geological process as a mirror image of the mineral facies will itself be subject general rules overrinding inicidental conditions.

In conclusion it does not appear to be very remarkable that the number of clay mineral species forming in hydrothermal system — a system that must be regarded as completely open — should be rather small, similar to the number of phases forming from melts, a number determined by the phase rule, since the process in question takes place in a closed system. It therefore appears that even in an open geological system parameters cannot vary quite independently from each other, but on the contrary, their range of variation is confined more and more as the process advances.

Here I would briefly refer to the fact that some authors are doubtful about the possibility of the hydrothermal formation of kaolinite deposits and attribute the formation of deposits to the effect of meteoric water along the fissures. In some of the cases it is indeed a hard job to delimit these two kinds of formations, especially in case if the former seams have come to the surface as a result of erosion. In such cases both ascendent and descendent water effect may be proved on the deposit mixed with one another.

However, those deposits I am talking about at present have doubtlessly been formed in consequence of a hydrothermal effect since they are placed in such a zone-like system which can only be explained with the lawfulness of hydrothermal alterations.

All authors agree that hydrothermal argillization, starting out from the lode, exhibits a zonal geometry dimensions of which are related to the dimensions of the lode. This zonality consists in the qualitative and quantitative distribution of original minerals and alteration products in the individual zones of argillization, implying a flow directed from the lode into the country rock. The flowing medium is water or steam under pressure, probably no hoter than 400—450 °C, which in its course decomposes the minerals formed from a dry igneous melt in succession, according to their relative instabilities. The decomposition products are then reconstituted into phases corresponding to the concentration conditions of the prevailing hydrothermal physical and chemical conditions. The fundamental cause of the zonality being the change in the K/H ionic ratio in the course of the spatial evolution of the process.

Fig. 1 shows the stability area of K-mica to lie between those of K-feldspar and

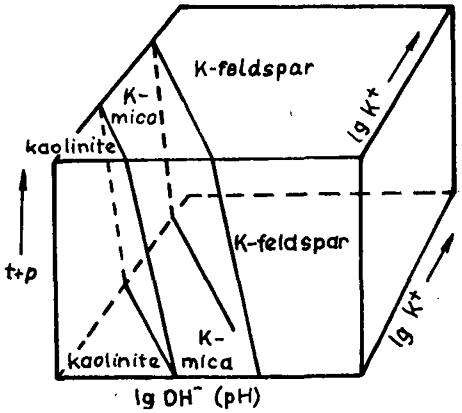
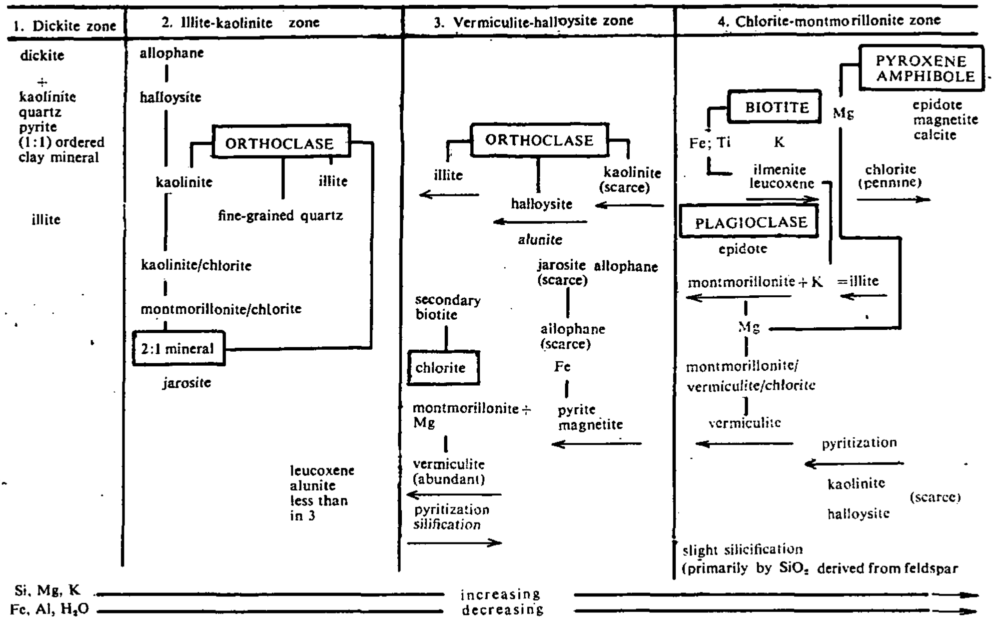


Fig. 1. Equilibria of kaolinite, K-mica and K-feldspar in a coordinate system calibrated in pH (lg OH^-), lg K^+ and temperature+pressure (after GARRELS and HOWARD, 1957)

kaolinite in a strip with a width of about 1.5 pH units and a temperature up to 500 °C. From the above the consequence may be drawn that in the simplest case the spatial distribution of the mineral, when advancing toward the lode the K-feldpsar — sericite — kaolin zone follows one after the other. The actual situation is, however, much more complex than that described above, and generally one may distinguish 4 zones among which in that one being next to the lode there is the most kaolinite presenting a very satisfactory crystallization (Table 2).

TABLE 2

Zones of hydrothermal argillization and the mineral decomposition and clay mineral formation processes taking place io them (the authors original compilation)



In the granite of the Velence Mountains in Hungary one may find some zones accompanying the fluorite lodes and containing kaolinite-illite zones which later on pass over into a montmorillonite-chlorite zone.

In the course of the alterations of the volcanic rocks considerably bigger and more interesting hydrothermal deposits were formed in Hungary as compared to the former ones.

Whereas the post-magmatic alteration of intrusive rocks gives rise to rather monotonous clay mineral associations, the hydrothermal argillization of volcanic rocks may lead to the formation of highly differentiated mineral associations. This is due to the typically lower temperatures and pressures prevailing in the process and which, in addition to the formation of pure clay mineral species, also renders possible the formation of phases of a transitional nature. The temperature limit of intrusive and volcanic hydrotherms may — to our mind — be drawn approximately at the $p-t$ conditions of dickite formation. These represent the lowest $p-t$ parameters of the most instrusive processes and the highest ones of most of the volcanic hydrotherms.

The formation of hydrothermal clay minerals in volcanic rocks in Hungary was studied primarily in the Tokaj and Mátra Mts, and to a lesser extent in the Börzsöny Mts as well as in some other scattered localities. On account of both its dimensions and its peculiar mineral associations, it was studied — in particular — the hydrothermal clay mineral formation of Tokaj Mts. The area was studied from geological and depositological point of view by the authors: GY. VARJÚ, T. ZELENKA, G. PANTÓ, E. MÁTYÁS, E. NEMECZ and others.

Hydrothermal argillization of the rhyolite and andesite rocks of the Tokaj Mountains was of a rather great extent mainly on the south-west part and in the Mád—Szerencs basin. The geological setting of argillization consists of a body of acid pyroclastics 300—400 m thick with interbedded and overlying rhyolite-andesite lavas. Hydrothermal argillization is connected with two swarms of faults: one striking NW—SE is very deep, thus the most intense argillization is connected with them. Another swarm which strikes NE—SW is also characterized by a more moderate argillization and by the formation of mainly quartz veins. The Mád—Királyhegy area is a particularly fine example of hydrothermal argillization. The distribution of clay minerals in the vicinity of the lode traversing the Királyhegy is illustrated in *Fig. 2.* The distribution exhibits a characteristic zonality, and the radius of hydrotherm influence is obviously a function of the lithology. The hydrotherms have surged along a fissure that separates a rhyolite lava from some pyroclastics. While the alteration in rhyolite extends, as usual, to some meters only, in that of the much more permeable pyroclastics it reaches many hundred meters. The zone thickness is thus quite considerable and its succession starting outwards the lode is as follows: the central zone is a quartzite and directly next to it we find a kaolinite-dickite zone. This one is highly crystalline and this explains the fact that the Királyhegy kaolinite is not plastic. The kaolinite zone is accompanied by a broad rectorite zone of 140 m width and after that a montmorillonite-illite zone follows.

These succession of zones deviates to a certain extent from the zonality mentioned above in Table 2, since the geochemical setting of Királyhegy is richer in silica and poorer in Mg than the andesite rocks.

In consequence hydrothermal solutions exiting from the lode decompose at the outset the feldspars and the ferrous minerals, taking away the Fe, Ca, Na and K ions. As a results of the ratio increase of the growing SiO_2/Al_2O_3 concentration, conditions for the formation of 3-layer type minerals are given and take place in the rectorite and montmorillonite zones.

Characteristics of the Királyhegy kaolinite, contrary to the Sedlec and Cornwall kaolinites, lay in the fact that their mineral composition is more complex in consequence of which the kaolinite contents of the raw material is low. Another characteristic feature is that kaolinite occurs always together with a considerable quantity of silica which sometimes forms a coherent hard quartz framework besides the always present high quantity of quartz fraction under 1 μm.

This latter one cannot be removed with economic means and is also present in the sedimentary kaolinite of the basin. This kaolinite always contains a relatively high quantity of quartz and thus the Al_2O_3 content of the best industrial qualities does not even surpass 25%. On the other hand, if in the course of ceramic utilization quartz is artifically introduced in the ceramic mass, certain advantages may result from the fact that quartz content of the natural raw material is much finer and thus more reactive chemically than an artificially ground quartz additive. In consequence of the high SiO_2 content, refractory values also increase which can be raised consid-

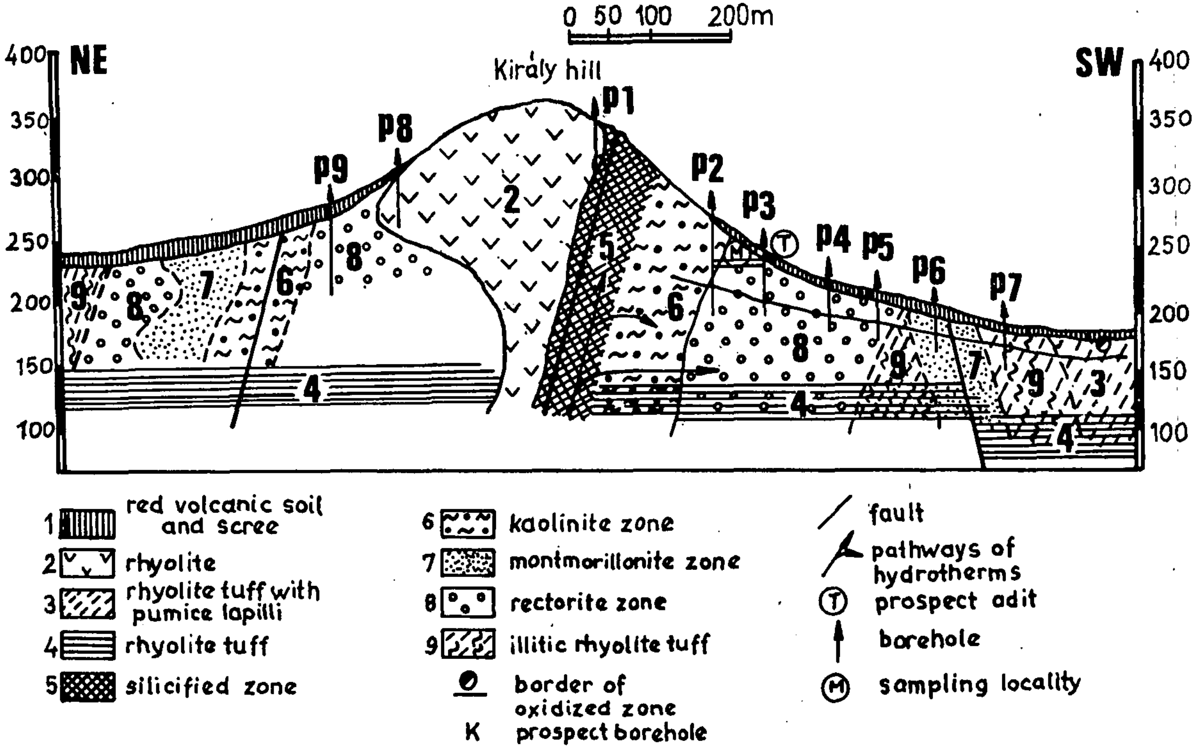


Fig. 2. A northeast-southwest geological profile through Királyhegy, Mád, Hungary (NEMECZ *et al.*, 1963)

erable by special burning of the frequently, encountered alunite mineral present on kaolin deposits, and this increases to a great extent the Al_2O_3 content.

As a final conclusion hydrothermal type kaolin of the Királyhegy deposit may be utilized in manifold ways in the industry, but it appears to be fact that the processing of the raw material requires a very careful preparation.

It is interesting that at Mád and its broader environs, hydrothermal argillization has produced a considerable variety in the kaolinite crystallinity. Next to the foci of hydrothermal activity, kaolinites tend to be highly crystalline with sharp grain outlines, whereas lattice disorder tends to increase away from these foci.

Laboratory evidence has shown that the clay of the Makkosside at Mezőzombor is a remarkably crystalline kaolinite. This same locality has, however, furnished some kaolinite characterized by remarkably weak 001 and 002 reflections, giving X-ray patterns that agree with those of the tubular type kaolinites of Minas Gerais and Les Eyzies. According to axis *b* there is in addition an. expressively irregular mineral, so called kaolinite$_d$ (fireclay) in the kaolinite mines of Szegi which exhibit typically vague reflections in the 4.45—3.76 Å range. Treated with potassium acetat it gives a 14 Å complex that is not destroyed by washing and drying, whereas the highly crystalline Mezőzombor kaolinite is reconverted into a 7 Å mineral almost in consequence of atmospheric humidity. This points to the fact that the Szegi kaolinite$_d$ is a mineral of a highly irregular structure. Likewise such samples are known from the kaolinite mines at Szegi being irregular according to two axes i. e. they contain halloysite minerals. They present that particular feature according to which when ignited on air they are reconverted into kaolinite at a temperature as low as 80—100 °C or when treated hydrothermally at a temperature of 150 °C which goes to prove that they represent structure variations of halloysite being unknown up till now. These variants of regularity at the crystal lattice level may, as shown above, occur within one and the same deposit. Observations at disposal do, however, not permit to give a detailed interpretation of their formation. This complex situation indicates that their irregularity is due to several simultaneous factors.

I should like to point briefly to the fact that hydrothermal kaolinization may occur in andesite rocks too, however, on account of the composition of the mother rock, a more complex clay mineral association is formed in this case. In consequence of the overlapping of the mentioned zones, kaolinite always mixes with illite, expanding clay minerals and chlorite.

Exceptionally, however, kaolin rich deposits may also be formed such as e. .g at Nadap (Velence Mountains), Pilis Mountains but on account of its high pyrite contents, this kaoline is not used for the time being.

According to some of the authors formation of the deposits may exclusively be due to the effect of descending waters. The recognition that most of these kaolinites are of hydrothermal origin too, came much later, but even in the present state so our knowledge we cannot distinguish kaolinites of hydrothermal and supergene origin except by studying the geological conditions. Thus, if the lode wedges out and upwards, the lode fissure peters out in an impermeable formation, the argillization accompanying the lode ceases above the clay mineral; sulphide minerals occurring together with the clay minerals i. e. the clay-mineralized parts are in a close spatial connection with minerals of a hypogene origin such as topaze and pyrite. At Pázmánd (in the Velence Mts) these characteristics together with some others may be considered to be arguments for primary kaolinization. At present prospection of such type of deposits has started in Hungary and may lead to the opening up of new kaolin raw material reserves along with an adequate preparation of same.

No mention will be made of kaolin deposits formed by surface weathering and still existing. They are very well known all over the world. In Hungary, however, such occurrences are not very frequent.

Nevertheless, I should briefly mention some surface weathering products which remained in place and clay minerals of which have been studied in detail.

In conclusion we may state that the Hungarian subaerial clay are dominated by 3-layer type minerals some of which exhibit swelling, and most of which are randomly interlayered. The clay minerals are very poorly ordered. Random stacking is much more pronounced in red than in grey clays. In the red clays iron minerals are in an amorphous state. Typically no crystalline iron mineral can be demonstrated in red clays, and in this respect subaerial clays considerably differ from bauxite iron minerals of which are invariably crystalline and clay minerals of which are mainly kaolinite instead of being of the 3-layer type.

All these conditions of the formation offer explanation for the fact that terrigene clay minerals in Hungary are generally formed in a temperate, whereas bauxites in warm climatic circumstances.

We do know some less important deposits (e. g. Romhány, Petény, Sárisáp) in which redeposited kaolin materials can be found as a result of surface weathering. The original material i. e. its characteristics have changed on account of reworking and transport, their grain size became smaller and of less regular shape. As a result of the above their plasticity increases as well as their raw binding strength; however, their iron content could not decrease to such an extent in order to form a first class raw material.

Now, I intend to give you a short survey on the clay mineral composition of marine sedimentary rocks covering a great part of Hungary. Clastic deposits formed in geosynclines, oceans, inland seas and lagoons, sometimes in considerable thickness, play an important role in Hungary as well as elsewhere.

Some of the authors are in favour of the detritic origin of marine clay minerals ascribing the divergencies in composition to differential settling in sea water. Another group of workers takes sides for the syngenetic transformation of clay mineral and finally the third recent group has proposed the complete and independent synthesis of clay minerals from ions dissolved in sea water.

The endeavour to concert instance of the three above outlined hypotheses of marine clay mineral formation is made difficult by the fact that the authors usually fail to specify any criteria of mineralogical distinction between clay minerals formed in different processes.

Instead of going into the details of these problems, some concrete chaarcteristic examples in Hungary will be quoted.

The Eocene deposits — together with coal-deposits — in the North-Eastern Bakony Mts represent strata formed during strong oscillatory movements, at sites rather close inshore with temporary shoreline displacements. In some profiles in boreholes 500 m deep samples of freshwater and even subareal formations do appear. The approximative ratio of the four groups of clay minerals is given inTable 3. The invariable presence and even dominant amount of kaolinite$_d$ is evident in the vicinity of coal deposits. The abundance of kaolinite$_d$ decreases in the upper layers, but it is important to note that some kaolinite$_d$ remains even above the coal layer and only the layer above it is altogether devoid of kaolinite. This distribution indicates that selective settling has taken place, and also proves that the presence of kaolinite$_d$ in deposits underlying the coal seams ("underclays") is not, as has been assumed, due to a kaolinitizing influence of organic acids. The presence of kaolinite$_d$ indicates a

TABLE 3

Distribution of clay minerals in cores of the Balinka 217 borehole (the number of crosses points to the relative amount of the given miheral)

Depth (m)	Kaolinite	Illite	Montmorillonite	Interlayered illite/montmorillonite
45.0— 47.0	+ +	+	+ +	+
135.6—138.8.	+	+	+ + +	
364.8—372.8	+	+	anom	+
416.2—426.0	+	+	anom	
442.7—442.8	—	+	—	
443.1—444.0	+	+	anom	
444.2—447.5	+	+	anom	
	Coal,	“companion seam”		
445.3—445.9	+	+	anom	
	Coal 1. seam			
448.4—454.0	+ +	+	—	+
462.05—462.6	+ + +	+ +	+ +	
475.2—478.1	+ + + + +	+	+	+
	Coal			
481.3—483.7	+ + + +	+	—	+ +

nearshore settling accompanied then by coal formation, too. The strata above are again of the offshore type, as indicated by a transitory increase in the abundance of montmorillonite being able to travel farther in suspension.

Apart from the mineral distribution the changing X-ray pattern of the minerals are also worth noting. One finds that ordering in the clay mineral lattice is low not only in the mineral kaolinite, but even more in the other clay minerals, as a result of detrital structure damage during transport and of irregular cation adsorption.

An additional change of the layers below the coal deposits, especially the dissolution of the minerals contaning iron and the removal of the iron ions—if not deposited as pyrite — is not only a possible but also a very likely process. Just this process makes these deposits suitable to use as supplies of raw materials too, as they contain a refractory clay with a high kaolinite content, which becomes nearly white in.the process of calcination.

As compared with the three- or four-layer minerals, the amount of kaolinite is small in the several thousands of meters thick Pannonian deposits and other sedimentary rocks found at great depths in most parts of Hungary. There are two reasons for this. On the one hand, there is the selective settling, as preferably the montmorillonite gets to areas farther from the shore; and on the other, in the strong elecrolyte that is in sea water rather the transformation of the kaolinite present, than is formation is favoured by the diagenetic processes taking place there.

It was intended to give you a short review of the occurrences of kaolinites of different origins in Hungary. As a consequence of intensive mining the stocks of kaolinite have been decreased considerably. Kaolinite has many different uses, most of it is used as filler in paper production and as a raw material of various ceramics.

In the field of ceramics the production of white wares and refractories are the main users. Each of these requires a different quality met by kaolinites of different genetic conditions. This underlines the expansion of the prospecting of kaolinite raw materials. One of the promising but still little studied fields is the prospecting of the primary and secondary deposits formed in the hydrothermal transformation of acid volcanics. It is evident that these are not identical with the kaolinites formed as residual weathering products of granites. But in view of their high kaolinite content and the presence of other minerals which — like fine quartz — sometimes even favourably affect their use, they are also important raw materials.

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