

## MANGANESE MINERALS CONTAINED IN THE CLAY-MINERALS OF TOKAJ-HEGYALJA

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### ABSTRACT

In Tokaj-Hegyalja in the vicinity of *Bodrogszegi* and *Füzérradvány* manganese oxide minerals occur as brown spots and patches in the rhyolite-tuffs and rhyolite in the snow white clay minerals — as well as along the cleavage fillings. The substance of these manganese minerals is pyrolusite and psilomelane only in one case, in that of the manganese mineral separating first, it is a mineral association with a low oxidation grade containing  $MnO$ ,  $Mn_3O_4$  and  $MnO_2$ . The substance of the clay minerals associated with the manganese occurrences consists of kaolinite, halloysite, fireclay in *Bodrogszegi* and in *Füzérradvány* of illite, montmorillonite with a mixed structure. The brown spot contained in the substance with a mixed structure of *Füzérradvány* only contained  $Fe_2O_3$  without any trace of Mn.

It may be assumed that the manganese minerals contained in the clay minerals — such occurrences were so far unknown — i. e. their examination will bring us nearer to the recognition of the circumstances under which the occurrence formed.

Some of the clay mineral occurrences of Tokaj-Hegyalja contain in certain places manganese and iron impurities. Particularly two occurrences are interesting in which the manganese minerals concentrate into layers, coats and spots, respectively. One of these is that of the recently fairly thoroughly investigated occurrence of *Bodrogszegi*, the other is the illite occurrence of the *Koromhegy* of *Füzérradvány*. In both places the impurities are different, which may also shed some light on the circumstances of the formation. The more precise examination of these impurities is not only of interest from a theoretical point of view, but the noxious effect exerted by the manganese impurities in the course of the industrial refinement of the minerals might — if these would be better known — also be eliminated.

The kaolin occurrence of *Bodrogszegi* — discovered in 1931 by *Nemcsik* — is in the *Hosszúmajor* (263 m) lane in the vicinity of the *Poklos* (261.8 m), *Cserjés* and *Cigányhegy* (474.4). *Liffa* [13, 14] reports in 1934 and 1935 about the exploitation of those years partly contained in »dense kaolin« and partly in kaolinized rhyolite tuff. He also mentions

manganese coverings occurring in some places in the vicinity of the pit.

According to *Földvári* [2] kaolin is the filling of a basin 750—250 m in size which runs in north-south direction. The kaolin and the stone-powderlike rhyolite tuff proceed into each other without any transition. In 1937 the mining went on already on 4 levels. On the contact surface of kaolin and andesite a few meters of thick red clay may be found.

*Vitalis* [22] in 1939 describes the situation of that time in detail. The kaolin exploited there was owing to the oozing water in the upper layers yellowish lower down it was pure white. The mine did not produce for finer ceramic industry as the iron content of the raw kaolin is rather high. According to the data of the plant the percentage of  $\text{Fe}_2\text{O}_3$  ranges between 2.5—3.5 and the kaolin has burned out into a weak yellow.

*Frits* [6] believes that the basis is formed by Sarmatian rhyolite tuff. It extends to a runway about 200 m long, 30—50 m broad and 25—50 m deep. The borings (90,6 m and 124,5 m) at its north end proved to be barren and proceeded till the end in stone powderlike rhyolite tuffs. The boring situated at the deepest point of the occurrence crossed after 20.2 m to 68,34 m a kaolin layer, below this rhyolite tuff appeared again in the same development as can be found in the northern part of the area.

Mrs. *Földvári* mentions that in Bodrogszegi series of kaolinite-fireclay-halloysite appear. The differentiation was carried out by means of DTA examinations. Namely according to *Grimshaw*, *Keates* and *Hoberts* in the case of the members of the kaolinite-halloysite-fireclay series there is a demonstrable difference in the appearance of the endotherm and exotherm peaks which is detectable on the DTA diagrams.

According to a personal communication of *Frits* in 1958 the material was identified on the basis of X-ray examinations as fireclay.

#### EXPERIMENTAL RESULTS

After the fifties the exploitation of the occurrence of Bodrogszegi following the creation of the subadit made quick progress. The latter starts from the mill along the banks of the Bodrog and runs in the stone powderlike rhyolite tuff beside the kaolin. This rhyolite tuff underwent various alterations. Dark rock-making minerals can altogether not be found in it only in some places quartz and feldspar fragments occur. These rocks containing pumice-stone and lapilis are generally fine-grained. The substance emerging from the subadit, as well as that which can be found on the IV. and V. level under exploitation is fairly uniform. Everywhere it is snow-white the only exceptions are of course, the places coloured by manganese and iron. The substance is relatively loose and crumbles easily. Under the microscope with a magnification of 600—700 also only very few mineral fragments can be detected. Both the quartz and the feldspar split easily and are lobate and crumbled showing that they derive from tuff. In many cases in the feldspar the cleavage can be

well observed, however, twin and zone formation can not be found. In these mineral fragments no changes may be detected, at the most. resorption phenomena appear, in some places the quartz crystals contain corrosion, cavities, but it cannot be definitely established if these developed before, or during the kaolinization. Probably they are not far older than the kaolinization. Under the microscope it is striking that small angular, rectangle square formations appear, sometimes they are vermiform appendixlike. They are characterised by the fact that the cleavage direction is always well visible and very often occur perpendicular to the longitudinal axis of the vermiform appendixlike formations (Fig. 1.). The statement that a very good cleavage direction is involved is also shown by the fact that these formations separate easily into



Fig. 1. Appendixlike kaolinit. Crossed nicols  $\times 300$

small square or rectangle parts along the cleavage planes. Considering that these formations which may be identified with kaolinite crumble very easily their formation can only be anticipated as occurring locally and that they are autochtons during or possibly after the diagenesis of the rhyolite tuff. Namely it can be difficultly conceived that they would have survived any transport as under the microscope it may also be observed that a suspension of this substance crumbles if the cover glass is pressed weakly. Ross and Kerr [19] have described similar formations from sandstones. They consider their origin to be autochton.

The DTA examinations show that the substance of the layers under exploitation are almost identical. In the case of each sample at temperatures between  $100\text{--}200^\circ$  smaller or larger endotherm peaks appear. Mostly at  $140^\circ\text{C}$  the second one around  $365^\circ\text{C}$ , whereas the exotherm one can be found at  $940^\circ\text{C}$ . These data are rather in good agreement with the values concerning fireclay contained in the literature. Of the DTA diagrams of these samples only one of the subadit from the fifth layer is shown (Fig. 2).

G. Bidló was so kind as to examine the same substance with X-rays we also express here our gratitude to him for his kind help. The data of the X-ray grams are as follows: 30 kW, 12 mA FeK $\alpha$  without filter Exposed for seven hours. The following values were obtained:

d	I	Minerals
7,3	w	halloysite, fireclay, kaolinite
4,9	vw	illite
4,46	w	halloysite, fireclay, kaolinite, illite
4,18	vw	kaolinite
3,59	w	halloysite, fireclay, kaolinite
3,38	vw	illite, quartz
2,76	vw	?
2,64	w	illite
2,35	w	fireclay, kaolinite
2,01	vw	?
1,693	w	halloysite
1,496	w	halloysite, fireclay, kaolinite, illite
1,293	w	illite
1,242	w	illite

All the lines are fairly broad and blurred showing that the substance has a dominant colloid character. At the evaluation it is generally striking that the very intensive lines are missing.

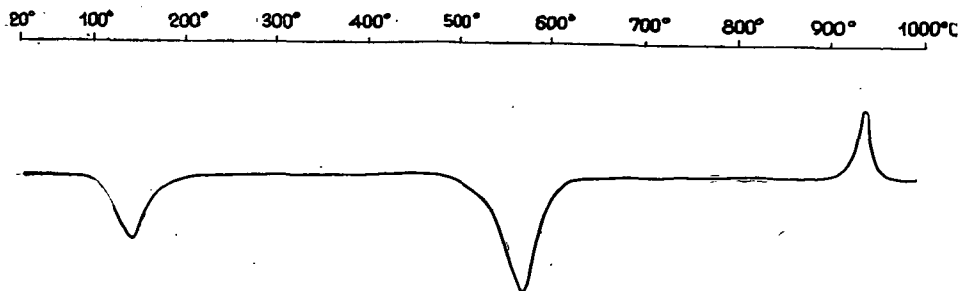


Fig. 2. Thermogram of fireclay (Bodrogszegi)

Hence actually a mineral mixture is involved the thermal changes of which are found at closely the same temperature, therefore, their exact separation and determination cannot be carried out with DTA. Hence, of the kaolin minerals all those which are formed at higher temperature, nakrite and dickite, is lacking. This draws the attention to the fact too that at the formation of this occurrence the influence of hydrothermal solutions — at least of those at higher temperature — did not play an important role, the epigen effect in the course of the diagenesis of the tuff is far more essential. The more significant part of the colloidal substance also supports this.

The reaction of phosphoric acid benzidine of the not contaminated substance [17] proved to be positive and showed a characteristic violet

colour indicating the presence of kaolinite. Kaolinite could also be noted under the microscope.

A recalculation of the chemical analyses which elaborated the material of the I boring of Szegi (the boring localised at the deepest point of the occurrence) shows that the material uniformly contains a very small amount of rock forming mineral). *J. Frits* kindly furnished the analytical data. The amount of orthoclase in the samples taken from various depths of 63—66 is rose suddenly to 15,01 per cent. The albite content is usually 1,05 per cent, exceptionally in the former depth it is 3,67 per cent, the anorthite content amounts to 0,83—1,11 per cent whilst in the depth mentioned above it is 2,50 per cent. Similarly the quartz content also ranges between 4,68—9,84 per cent but for the already known depth where it is 19,56 per cent. Obviously the depth of 63—66 m is a slightly altered rhyolite tuff.

It seems therefore, probable that the altered tuff was already originally finely granular and that the change was fairly uniform in the whole occurrence situated among the andezites. The alkalis must have quickly been washed out and removed, because else owing to the alkaline environment and the high pH value montmorillonite ought to have been formed, as well which cannot even be found in traces. Whereas in other kaolinized and bentonitised areas the liberated silicic acid can everywhere be demonstrated, in the place of this occurrence and in its direct vicinity it cannot be found in large amounts in the north and north-western areas, however, where considerable quartzit covers have been formed, it may be observed.

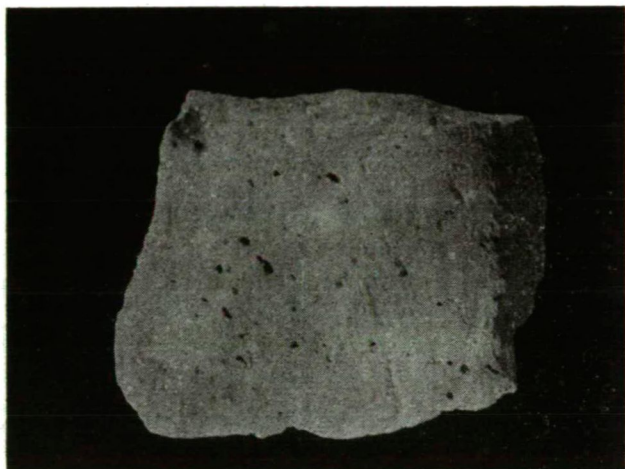
The associated iron must not have played a significant role at the kaolinization considering that both the alkalis and the alkali earth metals appear only in quite insignificant amounts and the aluminum does not either show an important value [1, 18].

Chemically analysed the FeO content of the averages does not exceed 0,3 per cent, and usually fluctuates only around 0,17 per cent. The Fe<sub>2</sub>O<sub>3</sub> content is usually the tenfold.

The MnO content is at the most 0,05 per cent. In some places the amount of manganese is more abundant. This phenomenon can be found in three different appearances. One of these types is in the area of the former office on the IV. level. The manganese appears in small dots. The distribution is completely irregular (Fig. 3). Sometimes an irregular brownish spot begins to develop around the dots. In the case of the other type big brown patches appear which are sometimes 8—10 cm in size (Fig. 4). The spots are entirely irregular as concerns their appearance no system whatever can be detected. Such an occurrence is frequent on the V. level. Occasionally in the middle of these patches small black dots can be observed. The whole spot is a clearly visible stain derived from both the iron and manganese. On the IV. level a third type occurs too which is wadlike and appears in the narrow cleavages of the siderocks. In view of the fact that according to the chemical analyses in the average substance manganese does not play a very dominating role and is usually only present in small amounts this local

abundancy may render possible the drawing of conclusions relating to the circumstances of the formation.

The DTA curves of these samples can be interpreted as follows. The diagram of the sample taken from the dotted part does not show an essential change as regards the pure substance. This is due to the fact that even if the dots are separately prepared the percentage ratio of the



*Fig. 3.* Manganese minerals in small dots



*Fig. 4.* Manganese minerals in brown patches

manganese oxide components is very low and this small amount cannot be evaluated with DTA. Between the spotted part and the not contaminated one direct adjacent already an essential difference could be seen which is illustrated by the position of the exotherm peak. Whereas, in the case of the pure part a properly developed exotherm peak appeared

at 950° C, in the diagram of the patched part the exotherm peak appeared, at a far lower temperature at about 900° C and was far flatter too. This may be attributed to the fact that the iron and manganese contained in the substance shifts the exotherm peak towards a lower temperature, at the same time the manganese oxides in this area show an endotherm peak which can compensate the height of the exotherm peak. This is still more striking if we look at the DTA diagram of the wadlike part where only traces of the exotherm peak are visible (Fig. 5).

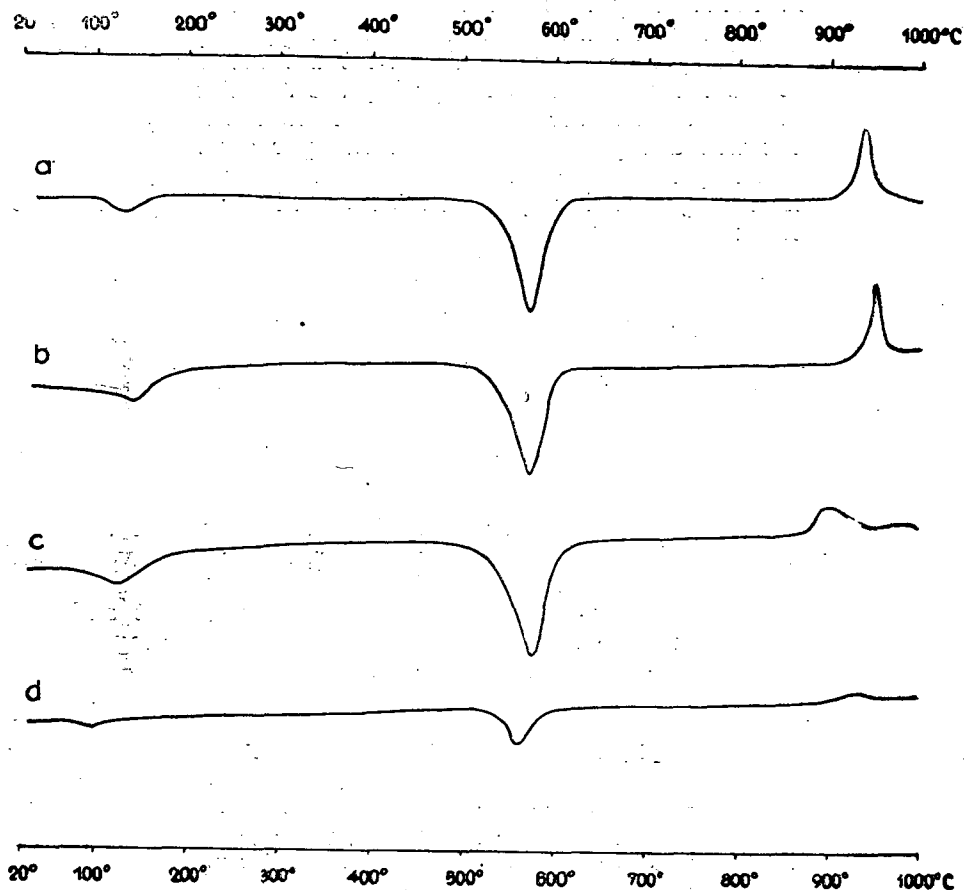


Fig. 5. Thermograms of substance containing manganese minerals (Bodrogszegi) A. manganese in small dots B. clayminerals of the material contains manganese minerals in brown patches C. manganese minerals in brown patches D. wadlike manganese minerals

In the above minerals the endotherm peak ranging between 500—600° C does not change essentially as pyrolusite has in this temperature range an endotherm peak coinciding with the endotherm peak of the kaolin minerals,

(It was not always possible to demonstrate with DTA the mineral association corresponding to the analytically obtained composition of the manganese minerals (MnO<sub>2</sub>-psilomelane). This is due to the fact that the substance prepared by us contained mostly 10—15 per cent of ore and in such cases the DTA method was no more sensitive enough.)

All three types of manganese mineral occurrences of Bodrogszegi were examined in detail; the dotted type (1) from the IV. level the spotted one (2) from the V. level and the wadlike substance (3) from the IV. level. Considering that these occurrences were found in thin layers and small amounts we did not succeed in preparing substance containing exclusively manganese minerals. At the recalculation of the analyses therefore the components composing the silicates derived from the kaolinized part were never taken into account, the manganese and oxygen content was always recalculated to 100 per cent. The analyses of the part relatively abundant in manganese — without recalculation — furnished concerning the MnO, active »O« and Fe<sub>2</sub>O<sub>3</sub> content the following results:

Samples	MnO %	»O« %	Fe <sub>2</sub> O <sub>3</sub> %
1.	4,29	0,46	6,00
2.	8,87	1,95	3,50
3.	59,38	12,46	5,88

Other components were not calculated as from the boring material of this region a complete chemical analysis was available, and we only proposed to examine the manganese enrichments. Among the values of these examinations the MnO and O content as the components of the manganese oxide minerals were recalculated to 100 per cent and the mineral composition of the samples was determined according to the method of *Grasselly—Klivényi*. Accordingly:

Samples	Pyrolusite	Psilomelane
Bodrogszegi IV. level	Manganese mineral association of a low oxidation degree, containing 24 per cent Mn <sub>3</sub> O <sub>4</sub> . The remaining part consists of MnO <sub>2</sub> and MnO. The quantitative distribution could as yet not be established.	
V. level	57 per cent	47 per cent
IV. level, the area of the former mine office	64 per cent	36 per cent

(Among the cations which may occur in the psilomelane the amount of barium corresponding to the mean Ba content of the psilomelane could be demonstrated in the samples.)



All three types are situated very near to one another, not influentially they can be found at distances of 40—50 m. Hence the question arises to what in such a relatively small area the quite varying forms of appearance of manganese is due to.

Whereas the wadlike substance occurs exclusively in cleavages the other two types can always be found in kaolin. Hence, the difference between the substance of type I. and II. is still more striking. Presumably the dots formed at the accumulation of the tuff, i. e. earlier, whilst the spotted appearance would represent a later state owing to the oxidation of these dots. The larger water content of the kaolin may have the greater extension of the patches possible, furthermore, the fact that this whole occurrence is relatively near the surface, where owing to the water of the rainfall a larger amount of underground water is contained in the surface layers, must be taken into account too. The fact that around the dots smaller or larger brown patches may sometimes be observed, i. e. that in the spotted type in some places in the middle of the spots small dots may be found also seems to support this assumption.

The observation that there is an essential difference between the oxidation grade of type 1 and 2 seems also to support this. Of the three types sample 1 represents the lowest grade of oxidation. Considering that the circumstances only render oxidation possible and reductive circumstances should not be taken into account type 1 as it is a substance with a lower grade of oxidation must in any case be considered to represent an earlier state.

This enrichment of manganese minerals is not a general phenomenon but only a local one. These forms of appearances seem to point to the fact that these dots — a manganese mineral association — of lower grade of oxidation got mixed up with the tuff fragments when the tuffs formed. The enrichment of manganese was rendered possible by the separation of the manganese released from the dark rock forming minerals owing to the crumbling of the andezite rocks in the vicinity. According to the analyses the dotted type contains the largest amount of iron and the least the natural was type. A rational interpretation for the difference between the iron content of the dotted and spotted type cannot be given, in fact the latter contains far less iron. Neither its solutions nor the pH conditions afford as yet an explanation for this fact. In the vicinity of Füzéradvány under the ridge of the Emberkő running from north to south was initiated the exploitation of the mine at the beginning of the XIX. century. According to *Földvári* both the eastern and western side represent an area disturbed by faultages. The kaolin lenses are situated in the loose layer group of rhyolite tuff between the top and bedrock quartzit.

According to *Liffa* [15] the adit opened up on the western side of the Emberkő proceeded to the end in dead rock. On the Koromhegy the kaolin is nearer to the surface.

*Frits* [5] describes in detail the formations of the Koromhegy. Concerning the bedrock the opinions are different. Some authors *Liffa*,

*Schréter* [20] and *Frits* assume that under the hydroquartzit of the bedrock rhyolite can be found, others *Földvári* [3], and *Szebenyi* [21] believe that rhyolite tuffs are involved. *Maegdefrau* and *Hofmann* (16) examined some substance of these lenses and termed them »micalike clay minerals«. The occurrence above mentioned represents the purest one of this type. Accordingly this substance was put into the market as illite. The lenses extend almost in a north west, south-south east direction.

The recent exploitations contain already far less of this pure hydro-mica the mixed structure occurs more frequently. Hence the DTA curve of the substance from the mines of the Koromhegy demonstrated this structure well, i. e. in this case the frequent phenomenon that montmorillonite layers were deposited between the illite layers is involved too. On the basis of the DTA it seems as if a mechanical mixture of

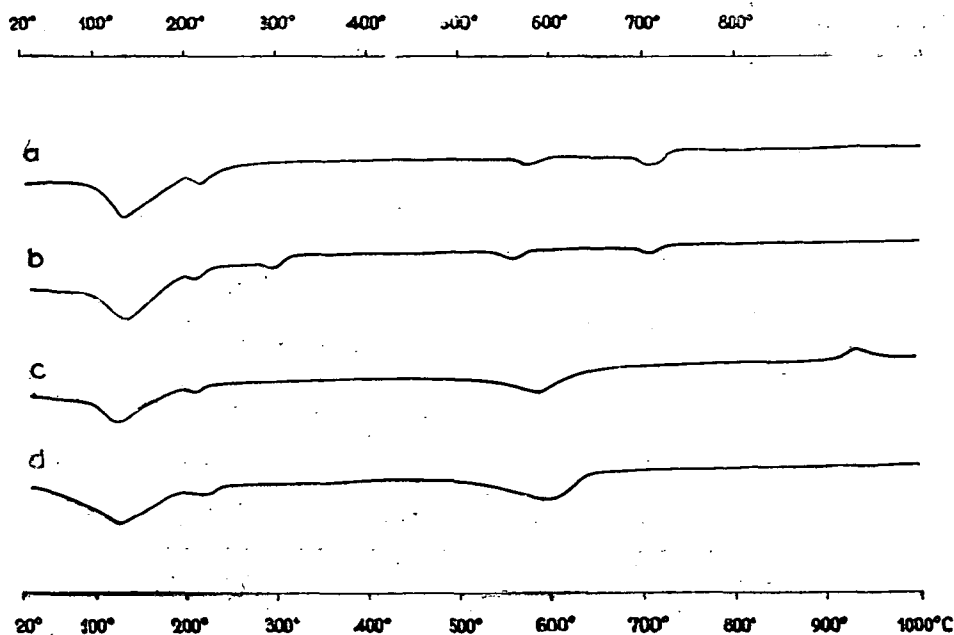


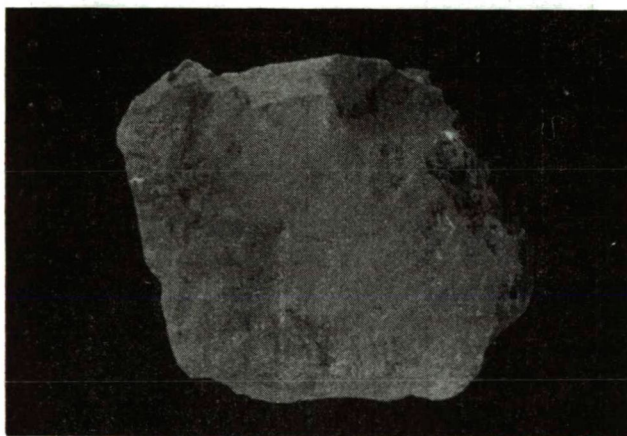
Fig. 6. Thermograms of substances contains manganese minerals (Füzérradvány) A. clay minerals (Koromhegy) B. crystallized manganese minerals (Koromhegy) C. clay minerals (mine Bora) D. substance with brown patches caused by ferric oxide

illite and montmorillonite is represented (Fig. 6). Actually, however, a mixed structure is involved, which is also proved by the X-ray examinations. Namelly, according to the examinations carried out at the Mineralogical-Petrographical and Geochemical Institute of the Charles Uni-

iversity of Prague the substance of the mines of Koromhegy have a mixed structure. As the X-ray examinations also only demonstrate this structure if at least 10 per cent of montmorillonite is contained in the substance a larger amount of montmorillonite content must be taken into account. The DTA examinations also illustrate that beside the illite fairly large amounts of montmorillonite layers are interdeposited. The DTA curve of the more recently exploited mine of Bora is completely identical.

In the last 10 years entirely the same substance was found in the lenses, the only difference being that the interdeposited amount of montmorillonite sometimes varied. This is also supported by the fact that according to the chemical analysis the content of  $K_2O$  of I class substance from the 19/b adit is only 2,35 per cent) and  $CaO$  (2,93 per cent) content is fairly high which on the other hand points to the presence of montmorillonite. This may be the reason that on the basis of the values of the chemical analyses exact conclusions relating to the amount of illite could not be drawn.

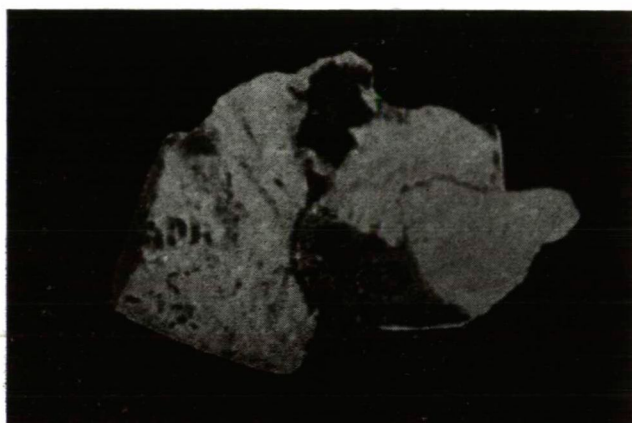
The DTA curve also illustrate well the double initial endotherm peak of montmorillonite, which is a characteristic property of calcium montmorillonite. The endotherm peak appearing between  $500-600^{\circ}C$  is due to the illite, whereas around  $700^{\circ}C$  the peak characterising montmorillonite appears. The exotherm peak appearing between  $900-1000^{\circ}C$  is usually missing.



*Fig. 7.* Brown patches caused by ferric oxide

In these substances with a mixed structure, that originating from the mine of Bora shows in some places a yellowish-brown- and reddish-brown colour (Fig. 7). This colour appears quite capriciously. In the part of the mine earlier exploited along the thin fissures crystallized manganese minerals separate in the snow white substance (1) (Fig. 8), sometimes this mineral association consisting of manganese minerals appears in the snow white substance (1) (Fig. 9).

To compare them with the substance of Bodrogszegi they were also examined in detail. At the chemical analyses also in this case the



*Fig. 8.* Crystallized manganese minerals as thin coatings



*Fig. 9.* Dendritlike manganese minerals

silicate part was disregarded. The results of the selected manganese part were as follows:

Samples	MnO	»O«	Fe <sub>2</sub> O <sub>3</sub>
1. Füzérradvány Koromhegy	15,61	3,10	3,18
2.        "        "	5,08	1,04	11,40
3. Füzérradvány and Bora mine	—	—	2,17

Calculated according to these data the composition of the manganese minerals was the following:

Samples	Pyrolusite	Psilomelane
1. Füzérradvány, Koromhegy	23,5 per cent	76,5 per cent
2. " " "	30,0 per cent	70,0 per cent
3. " " Bora mine	—	—

Whereas on the occurrence of Bodrogszegi the brown spots always contained a significant amount of manganese or manganese minerals, respectively, the brown spotted substance from the mine of Bora is free of manganese minerals and the colour is exclusively due to the ferric ion.

The question arises why manganese is entirely missing in this substance. It may be interpreted by the fact that the exploitation of the mine of Bora is relatively near the surface and the iron solutions oozing may easily dye the pure white substance. It may also be possible that at the crumbling when the iron and manganese separate from each other the impurity brought about by the oozed ferrous solution produces the manganese free spots occurring in the clay minerals.

The presence or absence of manganese oxides in the clay minerals as well as the difference in their composition is in close correlation with the origin of the clay minerals. However, the exact and detailed exploration of this correlation can only be given after the local examination of numerous samples. So far only few samples were available, but we hope that in the future we shall be able to supplement this lack.

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