

DATA ON THE DICKITE OCCURRENCE OF MÁD (Hungary)

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ABSTRACT

The rhyolite tuffs of the Sarmatian age in the surroundings of Mád were kaolinized on the action of hydrothermal fluids. The smaller and larger hollows of the porous tuff is filled out with dickite and kaolinite. The dickite could be identified by DTA as well as X-ray pattern. Dickite appears as 15—20 μ long and 3—8 μ wide crystals and the kaolinite always in dense aggregations of micron sized granules. The fact that it is associated with kaolinite shows that special conditions are necessary for it to form, these are, however, still fairly unexplored.

The kaolin occurrences in the surrounding of Mád are already known since some time. Several authors have examined their geological structure, only to mention the papers of Mayer¹¹, Liffa^{9,10}, Rozlozsnik¹³, Koch⁷ and Frits^{2,3,4,5}

Aggregations of rhyolite tuff from the Sarmatian age occur in some places on the surface in fairly thick layers at the north-east of the village in the surrounding of the baring of Bomboly extending north-west of the Kóvágó-hegy (356 m). On the ridge of the mountain a quartzite vein extends in north-eastern — south-western direction and the kaolinization may be brought to a certain extent in connection with it. The occurrence is not homogeneous. The bedrock rhyolite tuff could not be quite altered by hydrothermal fluids. Loose, crumbling parts occur only in subordinate amounts, the greater part is compact, dense, silicified rock. Along the fissures limonite colouration is frequent. Sometimes, however, it is pinkish, lilac which may indicate the presence of manganese. Liffa¹⁰ mentions a smaller limonite enrichment in the mine of Bomboly perpendicularly from the middle of the northern wall of the surface mining as a 0,7—0,8 m wide vein. This vein has stained in a thickness of about 2—2 m both sides of the wall-rocks. Today, of course, nothing of this is any more visible as this part of the mountain has been exploited.

In the present state in the greater part of the area before the wall-face of the surface stripping — over the underside — strongly silicified rhyolite tuffs showing a marked brown ochre colour may occasionally be seen. (Fig. 1.) The silicification of the rock and its kaolinization, as well as its limonitic colouration is not contemporaneous.

The silica is brought by the thermal fluids in considerable amounts to the surface. This is also proved by the surface occurrences. At the silicification and solidification of the loose tuffs these solutions played an important role. In connection with the postvulcanic action starting with siliceous solutions carbonic acid bearing waters penetrated gradually to the surface. The sickering of CO_2 can also up to date be observed in the environment. Koch⁷ also assumes that the spring waters containing only a minimal amount of CO_2 exerted an action at the origin of the iron ores of Mád. At the weathering of the rock the carbonic acid bearing spring waters created a particularly advantageous environment for the kaolinization which could be observed in several places spreading over fairly wide areas.

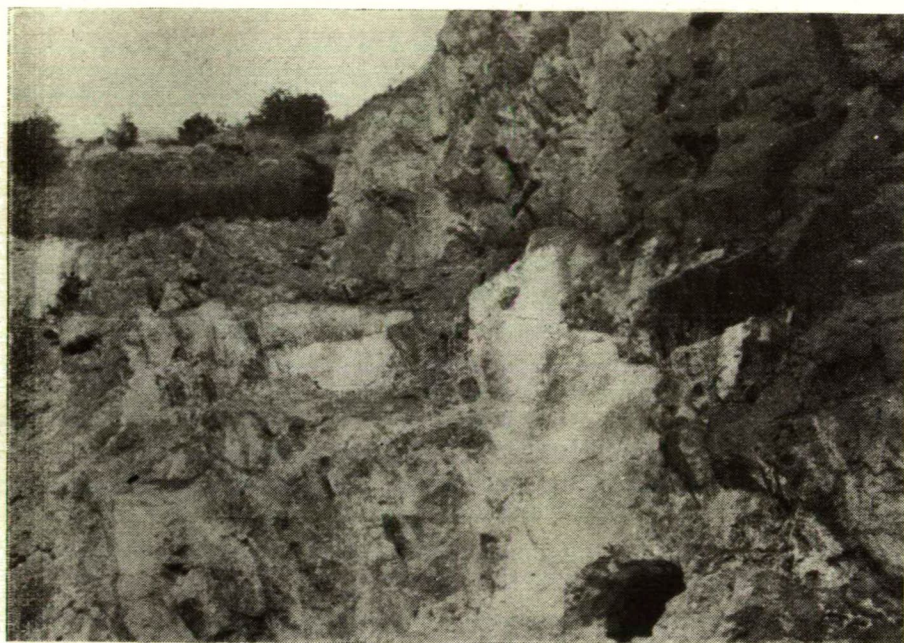


Fig. 1. The opening-up of the kaolin mine of Bomboly

The occurrence of Bomboly is not either homogeneous if the tuff altered in various grades is neglected. Even with the naked eye two kinds of material can be well distinguished. One of them is mentioned by Liffa⁹. He describes a lean almost iron-free material which on igniting becomes snow-white. Its refractoriness is 31—34 Seger cone. The second substance has a little oily feeling seems to be homogenous and is snow-white, loose and crumbles easily. It occur rather in the eastern part of the mine in the form of smaller and larger lentils. Today it can only more be found in small quantities.

Earlier two analyses were made of the clay from Bomboly. The one is described by *Liffa*⁹ the other by *Frits*². The data of the two analyses are as follows:

	Liffa	Frits
SiO ₂	78,0 per cent	66,30 per cent
Al ₂ O ₃	15,0	20,23
Fe ₂ O ₃	—	0,38
CaO	0,4	0,28
MgO	0,8	trace
Na ₂ O + K ₂ O	—	trace
loss on ignition	5,8	12,00
	100,0 per cent	99,19 per cent

Unfortunately, the analyses do not report the exact quality, locality and extent of the silicification of the substance. Thus it cannot be decided whether or not two different substances are involved, or at both occasions the same material was analysed. In any case in both samples the low value of Al₂O₃ is striking, hence a strongly silicified substance may be involved.

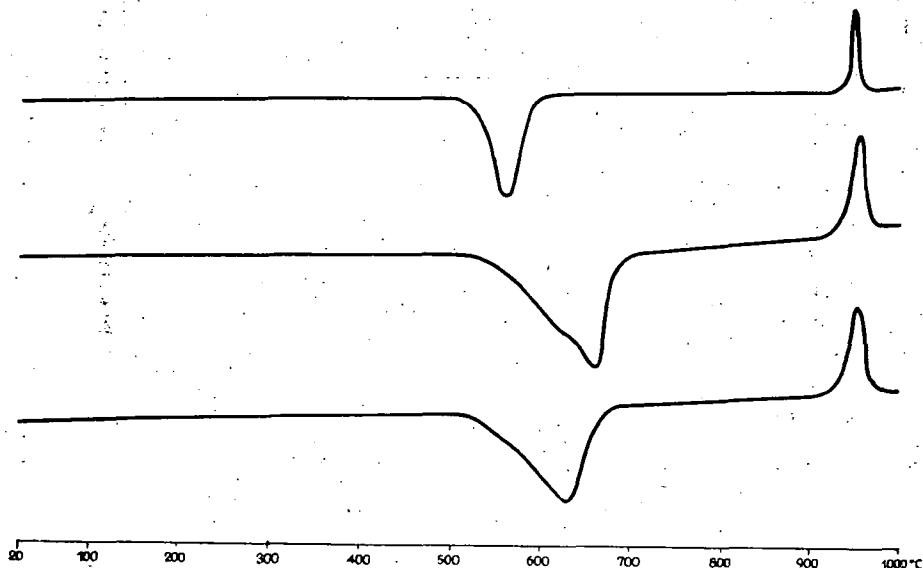


Fig. 2.

Upper: thermal curve of a kaolinite sample

Middle: thermal curve of a dickite sample

Lower: thermal curve of a sample containing kaolinite and dickite.

Locality of the samples: Mád, Bomboly

The author examined both substances and the country rock in detail. According to these examinations these two different sorts of material represent two different minerals belonging to the kaolin group.

The loose substance of earthy appearance having an oily feel and crumbling easily was determined as kaolinite. The DTA curve shows a very characteristic kaolinite peak at about 560°C which is a quite symmetric endotherm peak and finally at about 950°C a very high exotherm peak appears. Apart from these peaks the course of the curve is straight and no disturbing peaks appear on it (Fig. 2.). This substance may also at present be found in the north-eastern part of the mine interlayered in the form of smaller and larger lentils. It should still be mentioned that in this part the country rock, the silicified rhyolite tuff, contains about 1 per cent of SO_4 . Under the microscope the substance is compact and shows a low refraction, it does not contain any inclusions, the size of its particles does not exceed one micron. Crystal forms could not be detected.

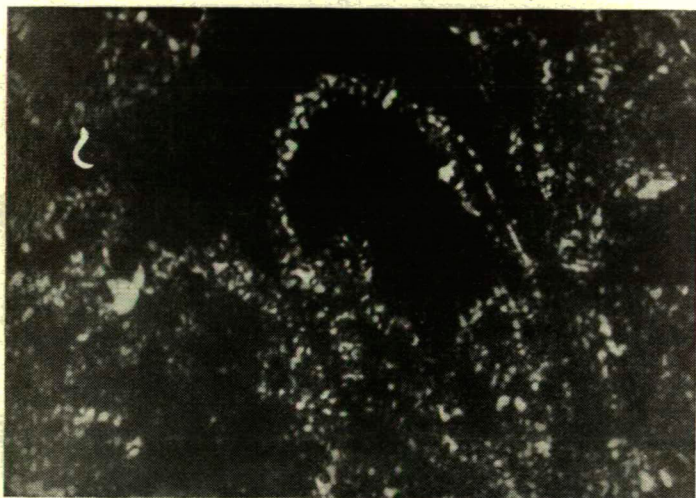


Fig. 3. Kaolinite, as cavity filling. Crossed nicols. 300 ×

It also always shows like the typical kaolinites do the colour reaction with phosphoric acid-benzidine described previously¹². The colour reaction takes place fairly rapidly.

The other material occurs in some places of the area before the wall face in larger amounts. The cavity filling contained in the slightly silicified rhyolite tuff in well visible smaller or larger patches is a loose, white substance. This can be particularly well seen in the case of the pinkish-lilac coloured tuffs. These cavity fillings are particularly interesting under the microscope. In some cases, namely, small distorted scales 6—8 micron wide and 15—20 microns long fill out these cavities of various size. In others a quite homogeneous crystalline substance with a low refraction the size of the particles of which do not exceed one micron fills out the cavities (Fig. 3.). Sometimes also both substances occur side by side, in this case the crystalline scaly substance can be found on the walls of the cavities and is succeeded by the younger formation of the homogeneous

crystalline substance showing a low refraction (Fig. 4.). The limonitic colouration is also well visible in every case, it is limited to the tuff parts and never colours the substance of the cavities (Fig. 5.).

Both substances could be obtained fairly purely from the single cavities. The homogeneous crystalline substance was quite similar to the kaolinite interlayered as lentils. All its properties were identical to those of kaolinite. The DTA curve was also quite the same.

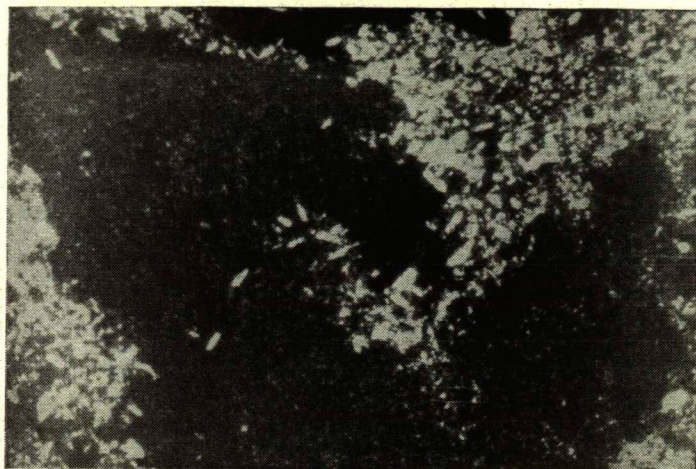


Fig. 4. Kaolinite and dickite as cavity filling. Crossed nicols. 70 ×

The second substance is particularly interesting. The small scales which can frequently be detected scattered on the porous tuff parts (Fig. 6.) are crystals slightly elongated according to the crystallographic axis a . Their refraction is always higher in the environment of kaolinite.

Its DTA curve is quite different to that of kaolinite. Its endotherm peak is assymmetric. From 520°C on it declines gradually. Around 620°C a steeper part follows, and around 650°C a peak appears. It rises suddenly and than from 690°C to 700°C — until the sudden exotherm peak at 950°C appears — the diagram does not show any change. The course of this curve is in good agreement with that of dickite reported in the literature¹⁴, at 590°C and 670°C there are two partially disintegrated peaks and the assymmetric peak gradually approaches the maximum. Whereas, following the maximum the rise is always sudden. If the substance was not pure, i. e. it contained a larger amount of kaolinite, the endotherm peak was somewhat modified which was indicated by the fact that the maximum of the endotherm peak appeared at a somewhat lower temperature, the character of the peak, however, did not change and the exotherm peak always appeared at the same temperature.

It is known that the clay minerals adsorb to a different extent the single dyes and organic substances. This difference can also be seen within the kaolin group itself. It concerns the numerical value of the adsorption, but also the pleochroism which can be induced by various organic com-

pounds. It was, however, the most striking in the case of the colour reaction with phosphoric acid-benzidine. Kaolinite shows a lilac colouration, whereas dickite or substances containing larger amounts of the latter do not or only very faintly exhibit this colour reaction after some time, in which case, however, it is doubtful whether it was due to dickite.

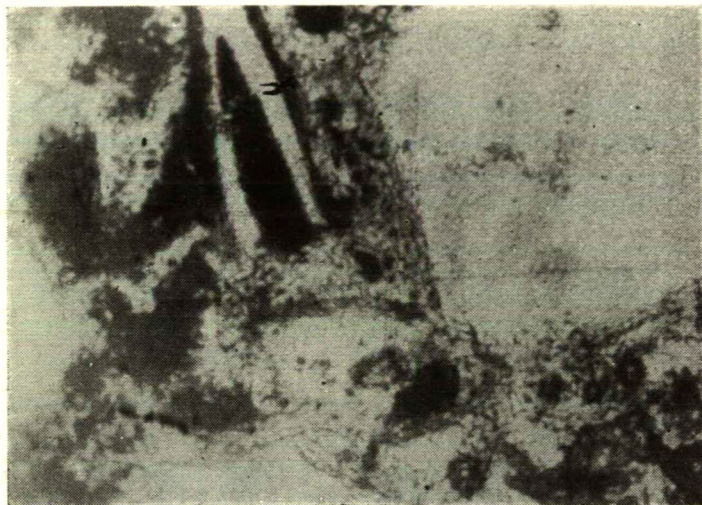


Fig. 5. Kaolinized tuff stained by limonite. 130 \times



Fig. 6. Dickite crystals. Crossed nicols. 300 \times

Since, in the case of the clay minerals the endotherm peak appearing between 500 to 800°C cannot be interpreted unequivocally in every case. X-ray analyses of the substance determined as dickite were also made (CuK, Ni-filter).

The results are as follows:

$d_{(hkl)}$ Å		Smithson & Brown	Brindley
7,16	kaolin (7,15)		
	dickite (7,14)	7,153	7,17
4,30	kaolin (4,43)		
	dickite (4,15)	4,118	4,129
3,81	dickite (3,79)	3,790	3,798
	kaolin (3,84)		
3,585	dickite (3,577)	3,578	3,582
3,347	kaolin (3,347)		
3,108	dickite (3,081)	3,094	3,103
2,810	dickite (2,805)		
	kaolin (2,793)		
2,546	kaolin (2,553)		
	dickite (2,554)	2,558	2,565
2,332	kaolin (2,335)		
2,295	kaolin (2,295)		
2,220	dickite (2,210)?		
2,129	dickite (2,126)		
1,982	kaolin (1,985)		
1,825	kaolin (1,835)		
1,668	dickite (1,668)	1,669	
	kaolin (1,664)		
1,546	dickite (1,546)	1,548	
1,495	kaolin (1,486)?		
1,457	dickite (1,452)	1,457	

The data show that kaolinite and dickite are very closely interwoven, and that it is difficult to separate the two substances. The microscopic examination too shows that dickite occurs in relatively smaller amounts and is mostly deposited on the walls of the cavities, whereas the kaolinite fills up almost completely the cavities and pores not filled up by dickite. The values obtained for dickite are in fairly good agreement with those of *Smithson* and *Brown* and *Brindley*, respectively, although it must be mentioned that the dickite of the sample from Mád exhibited a very poor reflection. This may, of course, also be due to the smaller amount, and to the extensive kaolin impurity.

Concerning the origin of dickite but few data are available. On studying the conditions of the so far known occurrences *Ross* and *Kerr*¹⁴ came to the conclusion that most of the kaolin occurrences of hydrothermal origin contain dickite too. Sometimes the hydrothermal solutions can also be cold solutions, but they do not occur under catathermal conditions, because at this temperature the kaolin minerals, hence also dickite decompose. *Ross* and *Kerr* did not find occurrences which were produced by epigen weathering processes. The occurrences of *Greenwood* and *Williams* though they originate from folded region of sedimentary rocks and although they have not been investigated in detail it is possible that at the origin of these occurrences hydrothermal solutions played a role.

Smithson and *Brown*¹³ have described dickite contained in sandstones from North-England and North-Wales. These occurrences were in no connection with ore veins, what more, there could not either be detected any correlation with the magma. These sandstones of the age of the Middle Jura form the bedrock of carbonaceous layers where reducing environment and a fairly considerable pressure must be taken into account. Anyway, this fact proves that the origin of dickite cannot be exclusively hydrothermal.

On examining the occurrence of Mád it may be seen that the alteration of the rhyolite tuff cannot be the result of a single process, as otherwise it is difficult to imagine that kaolinite and dickite occur side by side. It may also be assumed that the larger amounts of SO₄ occurring in certain parts of the mine could have exerted an influence on its surrounding at the formation of kaolinite. Namely, *Ransome* describes a kaolin occurrence of the Jerome United Verde Extension mine which undoubtedly formed on the action of waters containing sulphates¹⁴. Generally dickite occurs far less frequently than kaolinite. Considering that the stability and variability of the composition of dickite is not so great than that of kaolinite, probably the stability of its structure is greater, thus the fact that it occurs less frequently cannot be explained by its easy decomposition. It may rather be concluded that for the formation of dickite special conditions are needed which are less frequent. Owing to the fact that besides occurrences of hydrothermal origin sedimentary ones are also known it seems very probable that the factors of these special circumstances are very complex. In general, dickite is older in the ore lodes than kaolinite. In Mád too dickite is the older mineral, hence it seems likely that at higher temperatures dickite forms. It seems very likely that at the formation of dickite in sediments the pressure plays an important role. Probably, the range of the pH value is also narrower than in the case of kaolinite.

Finally, it can be said that the genesis of dickite is still very uncertain and further genetical and geochemical knowledge is needed for the solution of the question.

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