

# DATA ON THE GEOLOGY AND MINERALOGY OF THE MANGANESE ORE DEPOSIT OF URKUT. I.

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Manganese Ore Mines of Urkut

## INTRODUCTION

The manganese ore occurrence of Urkut is one of the most important ones of Central-Europe, hence, it is comprehensible that several workers dealt with it from geological and mineralogical viewpoint. References are referred to only in enumerating the most significant works.

The ever increasing requirements of the production and ore dressing, further the different industrial pretensions necessitated a more detailed and systematic examination of the occurrence. These investigations aim at the furtherance of the production as well as broadening the scientific knowledge concerning the deposit.

The final goal of these investigations carried out by systematic geological, mineralogical and geochemical examinations is to outline the characteristic features of the differently developed ore-fields of the manganese oxide deposit of Urkut as well as to learn in details its genesis.

For this purpose seemed to be the convenient to carry out the initial investigation of the area of the „Lejtakna“ (Slope) as its exploitation is at present under way, thus its characteristics can be traced. These examinations are, however, supported also by the mining points of view as this field offers one of the best quality ores.

The manganese oxide ores of upper Liassic age in Urkut was recognized in the field connected with to-day's „Lejtőszakna“ (Slope) in 1917 by V. MENYHARDT. The mining started in 1935 proceeded at fluctuating rate in the shaft No. I, when considering this field as being exhausted, the present Slope was deepened in 1952–53 to exploit the pillar of the shaft No. I. These works resulted in the prospection of the south-eastern region of the Slope from 1958 on.

The south-eastern area of the Slope is located on the plateau embraced wedgelike by faults of post-Eocene age which limit the Csárda Hill and Köves-tábla. The manganese oxide ore deposit is located in this field complicated by

faults and folds. On the southern edge of the deposit a transitional zone between the carbonate and oxide ore types is stretched. The manganese oxide deposit situated in a basin-like structure is lobedly denudated on higher levels. The autochthonous deposit is bordered by a pisolitic, red clayey, detrital zone as shown in Fig. 1.

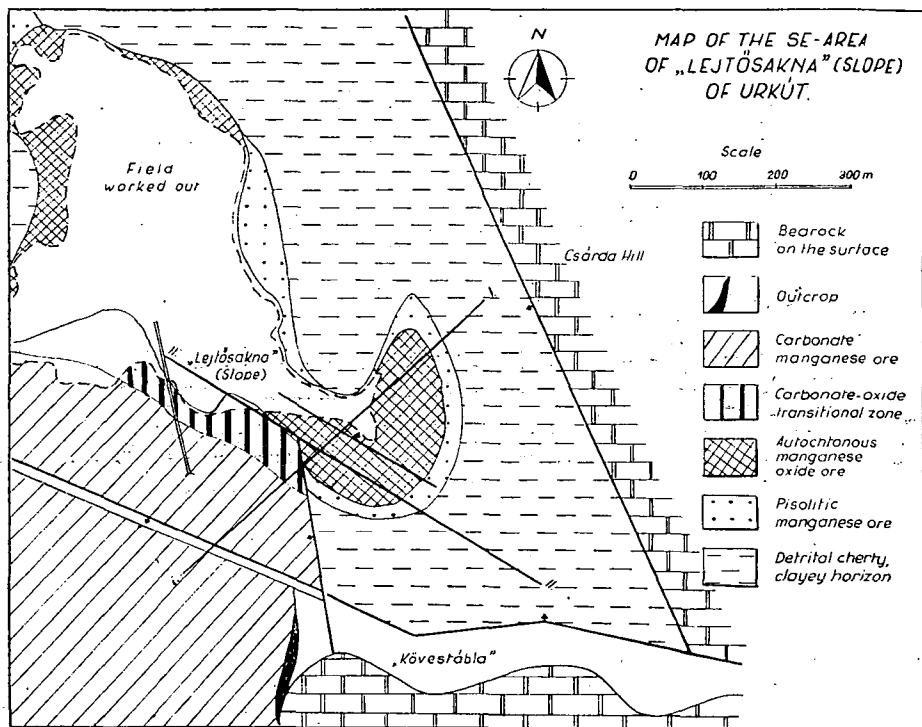


Fig. 1. Map showing the generalized surficial geology of the Slope

The south-eastern part of the Slope is of discontinuous development. On the lower-, middle- and upper-Liassic rocks upper-Cretaceous clay and thereon stretching further lower-, and middle-Eocene layers are deposited.

*Lower Lias:* The lower Lias is represented by rynchonellian cherty limestone. This series is connected with the field of the southern edge where also Liassic rocks are on the surface.

*Middle Lias:* The middle Lias is represented by red-pink cherty limestone, chert-flour, clay with detrital chert and chert-banded clay found in the immediate bedrock. The red-pink limestone reaches 35–40 m thickness, usually is of thick bedded character, whereas in general on the upper part is nodular. On the greater part of the area the more spread rock is the chert-flour which is the altered type of the cherty limestone or the chert rubble. On the eroded areas the middle Lias is represented by red, detrital-cherty clay. This rock consists of the several times re-deposited material of the cherty

limestone of middle Liassic age. Of course, the ore deposit is absent over such areas. In the immediate underlayer bedrock of the autochthonous ore deposit brown, chert-banded clay of 0,1—1 m in thickness is settled.

*Upper Lias:* The upper Lias formation consists of carbonate and oxide manganese ores and the rocks accompanied the ores. In the ore series different rocks can be found. At the south-eastern edge of the Slope a manganese carbonate ore bed trends. The manganese carbonate ore developed here in two

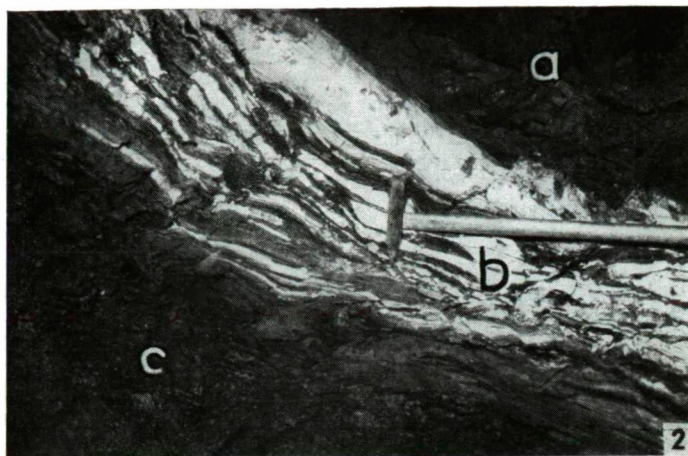


Fig. 2. a) radiolarian clayey marl; b) manganese carbonate layers; c) layered manganese oxide ore

main-types. Beneath brown — light brown, fine-striated, while above green — light green — brown, coarsely-banded manganese carbonate ore is located. At the boundary of the two types a gray, rodochrositic bed of 15—20 cm thick is generally located, containing often 30 per cent or more manganese (Fig. 2).

The ore deposit in general has a thickness of 5—5,5 m. The manganese carbonate ore is overlain by dark gray, radiolarian clayey marl bed. This rock here has turned clayey in some places bearing vestiges of alteration.

The manganese oxide ore is developed in several types like the manganese carbonate ore. Its lower part as a rule is clayey and of layered development (Fig. 3), whereas its upper part is clayey but nodular (Fig. 4).

The thickness of the manganese oxide ore bed is ranging from 4,5 to 5,5 m on the south-eastern part of the Slope. Towards the eroded edges manifolded, re-deposited, detrital ore types appears in the place of the layered, nodular types of the ores. On the eroded parts at first the material of the ores is less contaminated, further on, however, firstly chert rubble, red clay appear and finally the deposit turns barren (Fig. 5).

In the roof of the manganese oxide deposit the yellow, white mottled radiolarian clay, the altered type of the dark gray radiolarian clayey marl is frequent.

*Lower Cretaceous:* It is represented by gray clay, limestone-detrital clay extending tongue-like into the western part of the area.

*Lower Eocene:* The whole area is covered by lower- and middle Eocene rocks. On the basis of the series usually red clay, bauxitic clay, light gray, pyritical clay is located. The characteristic rock of the lower Eocene is the dark gray carbonaceous clay. The middle Eocene is represented by nummulitic limestone. The series is considerably broken due to late tectonical movements and owing to its aquifer character is dangerous for mining.

*Pleistocene:* The whole area is covered with pleistocene clay, yellow, sandy loess ranging in thickness from 5 to 10 m.

The sections I—I and II—II, respectively, of the field of the Slope are shown in *Fig. 6*.



*Fig. 3.* Loose, layered manganese oxide ore.



*Fig. 4.* Nodular manganese oxide ore



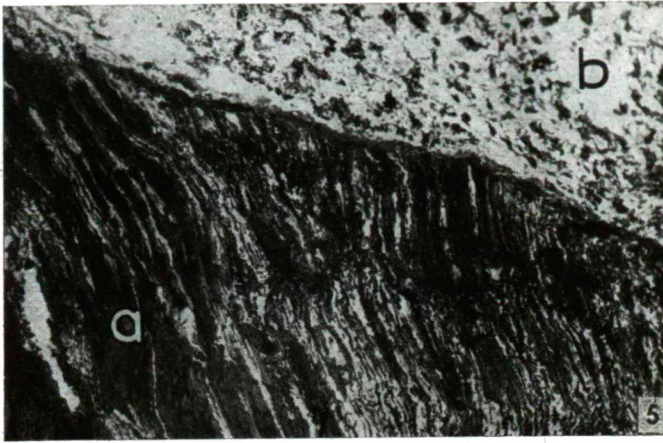


Fig. 5. a) layered manganese oxide ore; b) pisolitic ore

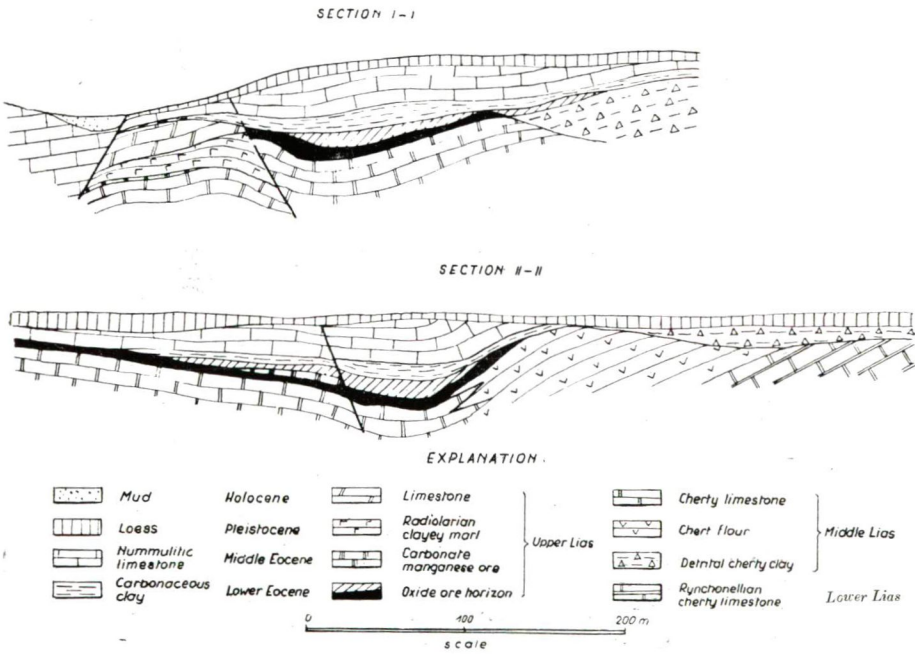


Fig. 6. Section along I—I and II—II.

*The structure and composition of the manganese  
oxide deposit of the Slope*

The real value of the area prospected is the manganese oxide ore deposit of high quality whose thickness ranges from 4,5–5,5 m on the basis of the data obtained. The structure of the deposit in general shows no considerable variations. The best illustration of the sequence of the strata is shown in Fig. 27.

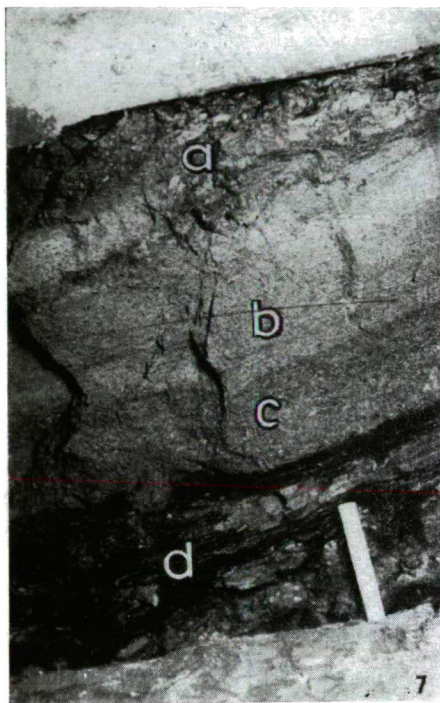


Fig. 7. a) nodular oxide ore; b) yellow ferruginous layer („iron-sand”); c) fine-grained, loose „manganese-sand” layer; d) black, layered, clayey manganese ore

The ore series is immediately underlain by brown, chert striated clay (*m*). At the basis of the ore series a brown clay of 30–60 cm thickness is located often containing also manganese granules (*l*). Thereupon there is superimposed a loose, black manganese oxide ore (*k*) frequently containing ore nodules of 1–5 cm in size. The material of these nodules is mainly cryptomelane. The ore contains then and there 38–40 per cent manganese, however, 30 per cent is ever reached, even sometimes surpassing it. The thickness of this layer is 1,50–2.0 m. On this stratum a bluish gray, fine-grained „manganese-sand” is deposited in a thickness of 10–50 cm (*j*), drawing the attention with its striking bluish-gray color, loose structure and with extremely high — 48–50 per cent — manganese content.

Close on the „manganese-sand” a yellow, ferruginous layer (*i*) of similar structure with a thickness of 5–10 cm follows. The iron content of this layer

is 45–50 per cent, whereas its manganese content is very low, nearly 1–2 per cent. The iron is present in this layer as limonite as it is shown by DTA examination. Over these fine-grained strata a compact bed (*g*) is often located in a thickness of 10–20 cm. The bulk of its material is dense, cryptocrystalline cryptomelane with pyrolusite. In the section studied a thin white-yellow clayey layer (*h*) is discernible, this, however, appears not generally.

On the above-mentioned layers a brown – light brown fine striated clay bed (*e*) of 2–2,5 m thickness is deposited, wherein ore nodules of 5–20 cm in size are embedded. The matrix of the ore nodules largely consists of cryptomelane, wherein pyrolusite veinlets can often be observed. The iron content of the clay is often over 20 per cent; the manganese content of the nodules is 40–45 per cent. In some places between the strata *e* and *g* – as seen also in the section in Fig. 27. – a brown, clayey, layered manganese oxide ore bed is found (*f*).

In the upper part of the deposit another 0,5–1,0 m thick brown, striated, clayey, layered manganese ore bed is located (*d*), whereon often pyritic, manganese carbonate containing, green clayey layers (*b*), followed by dark gray, radiolarian clayey marl (*a*) and as alteration product of the latter, yellow clay (*a*<sub>1</sub>) is deposited. In the upper part of the deposit over or betwixt the green clayey carbonate strata a manganese ore layer (*c*) is located of some cm-s thick as seen in the section.

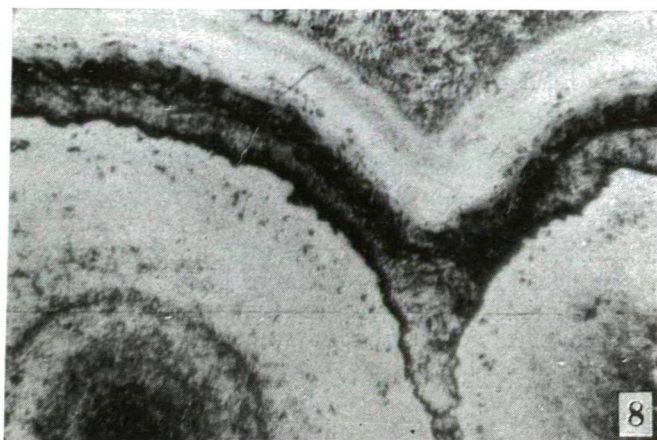
#### MANGANESE OXIDE MINERALS OF THE ORES

On the basis of microscopical examination the presence of the cryptomelane, pyrolusite and manganite among the different manganese oxide minerals can be undoubtedly established in the ores of the Slope.

The cryptomelane is fairly abundant in the ores. The bulk of the ores is often built up from it. The cryptomelane is commonly cryptocrystalline, forms very fine-threaded, feltlike aggregates. The cryptomelane – depending upon the grain-size, the porosity – sometimes can be well polished, sometimes is too porous and it is not or poorly polishable. The botryoidal, concentric globular structure, colloform banding, rhythmical layering characteristic of crystallization from colloidal state can often be seen on polished ore sections as seen in Figs. 8, 9, 10 and 12.

Sometimes icicle-like aggregates of the very fine-threaded cryptomelane are also to be observed as seen in Fig. 10. The aggregates are almost normal to the surface of the botryoidal, globular structure. The cryptomelane is often replaced by pyrolusite. The replacing extends either from the edges of the cryptomelane veinlet towards its center as seen in Fig. 11, or along fine fissures tends from the center outwards. The massive replacement intergrowth of cryptomelane and pyrolusite as well as the symmetrical layering made up alternately by thinner or thicker cryptomelane and pyrolusite layers can also be found.

The pyrolusite is also very abundant in the manganese ores of the Slope. Its appearance is fairly manifold. It appears in fine crystalline form interwoven the similarly fine crystalline matrix made up mainly from cryptomelane. The cryptomelane-replacing pyrolusite is often very fine grained. Occurs, however,



*Fig. 8.* Concentric globular structure of cryptomelane. The center of the globules is too porous to polish. The cavity between the globules and the shell filled out by manganite. Plain light,  $\times 25$ .

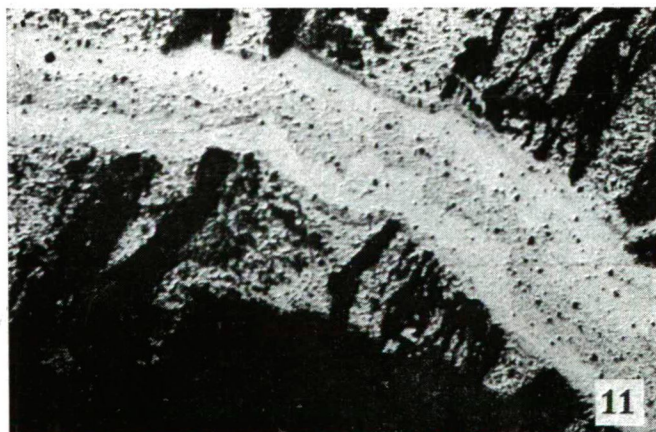


*Fig. 9.* A detail of a concentric, botryoidal structure. At left cryptomelane (gray) followed by a pyrolusite layer (white) the center of which is porous. The pyrolusite layer is limited by a very thin sammetblende (Nadeleisenerz) veinlet from the manganite (right, medium gray). A manganite veinlet cuts across the cryptomelane and pyrolusite in southeast-northwest direction. Plain light,  $\times 100$ .





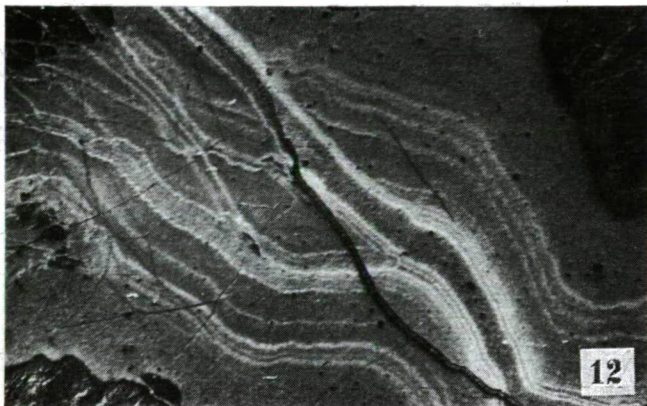
*Fig. 10.* An other field of the same surface as shown in Fig. 9. but photographed with crossed nicols. At left fine-threaded cryptomelane aggregates nearly normal to the surface. At the top a thin manganite veinlet — the same as in Fig. 9. — trends in west—east direction.  
Crossed nicols,  $\times 50$ .



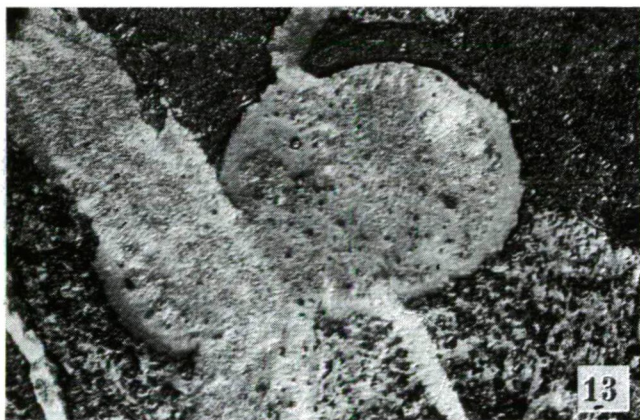
*Fig. 11.* Cryptomelane veinlet (medium gray) replaced by pyrolusite (white) progressing from the edges toward the center. Plain light,  $\times 50$ .

in form of fine-grained aggregates appearing in patches in the matrix. It may occur also in coarse-grained fibrous aggregates even in veins, when presumably replaced the formerly vein-filling manganite. Often can be seen that the pyrolusite entangles in thinner or thicker veinlets the porous matrix as seen in *Fig. 15*.

In the ores of Urkut also the manganite is not a rare mineral. Its well developed crystal aggregates intruding into the cavities filled out by chalcedony, can often be found as shown in *Fig. 16*. The manganite occurs frequently as



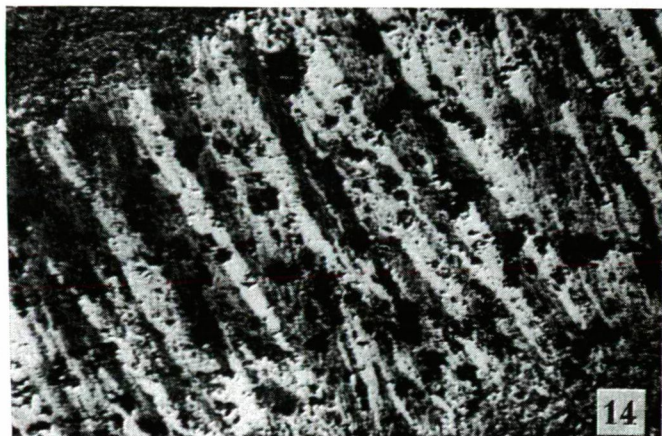
*Fig. 12.* A complex symmetrically layered veinlet made up from cryptomelane (gray) and pyrolusite (white). Crossed nicols,  $\times 50$ .



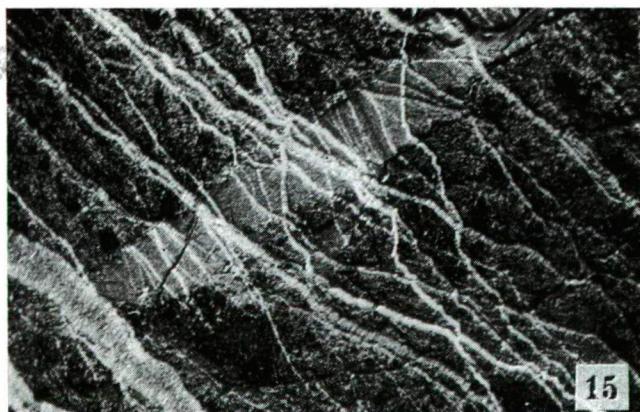
*Fig. 13.* Cryptomelane (medium gray) replaced by pyrolusite (white). Crossed nicols,  $\times 50$ .



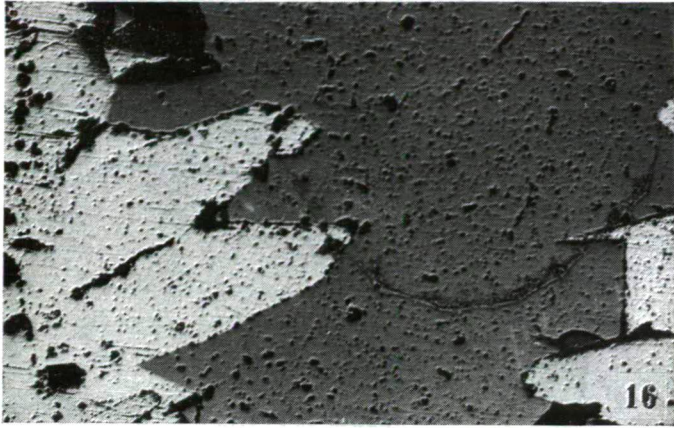
cavity-filling, sometimes in coarse-grained crystal aggregates as seen in *Figs. 17* and *18*, or in veinlets filling out fine fissures as seen in *Figs. 10* and *19*. Manganite crystal aggregates can also be found in some concentric globular structures in cavities between the shells (*Figs. 8–10.*) which cavities are presumably caused by shrinkage due to crystallization from the earlier colloidal state. Where the manganite as cavity filling occurs, it is surrounded by a thin layer of sammetblende (Nadeleisenerz). It is presumable that this layer protected the manganite from a later oxidation. It is to be noticed that the blood-red inner reflex characteristic of manganite can often be observed.



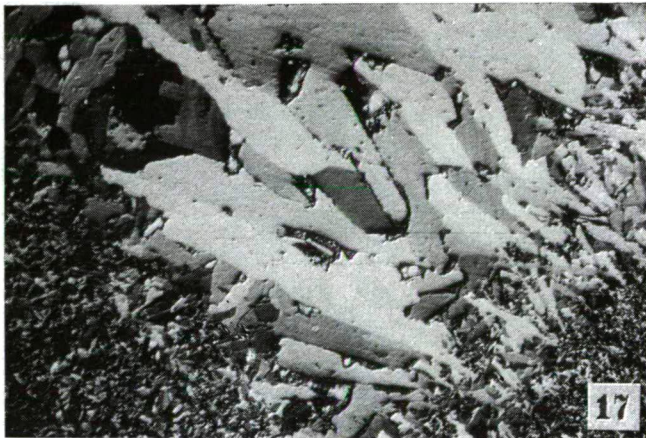
*Fig. 14.* Coarse fibrous crystal aggregate of pyrolusite forming veinlets of 1 mm thick in cryptomelane. Crossed nicols,  $\times 50$ .



*Fig. 15.* Pyrolusite veinlets (white) entangle the porous matrix (dark gray). Crossed nicols,  $\times 50$ .



*Fig. 16.* Manganite crystals intruding in cavity filled out by chalcedony. Plain light,  $\times 100$ .

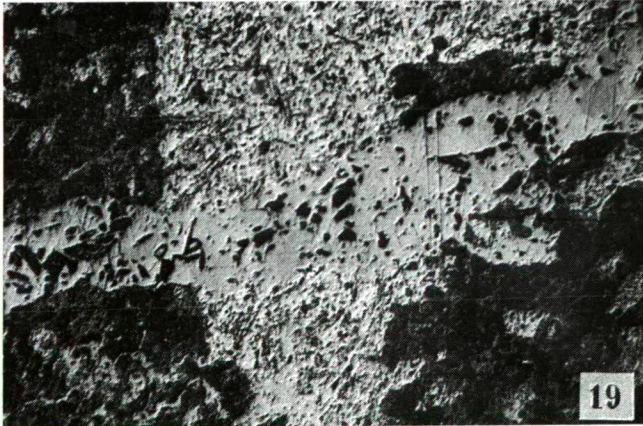


*Fig. 17.* Coarse-grained crystal aggregate of manganite bordered by fine-grained manganite of mosaic structure. Crossed nicols,  $\times 100$ .





*Fig. 18.* Coarse-grained manganite as cavity-filling bordered by a thin layer of sammetblende (Nadeleisenerz). Matrix is cryptomelane. Crossed nicols,  $\times 100$ .



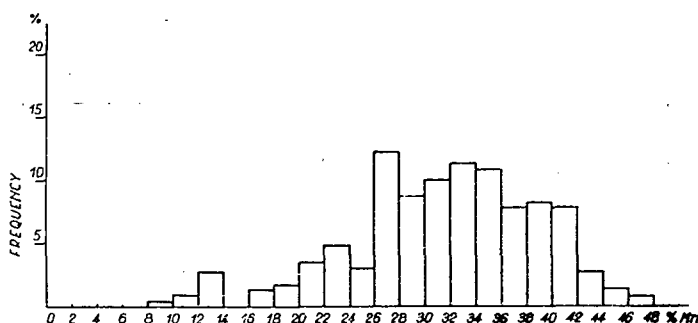
*Fig. 19.* Manganite veinlet (light gray) cuts pyrolusite aggregate (white). The manganite in the veinlet is fairly coarse-grained, the pyrolusite is fine-grained of mosaic structure. Plain light,  $\times 50$ .

## FREQUENCY DISTRIBUTION OF SOME ELEMENTS IN THE ORES OF THE SLOPE

The frequency distribution of some components has also been examined on the basis of analytical data of 230 samples collected systematically from the area of the Slope. The analyses were carried out by the Laboratory of the Manganese Mines of Urkut. The authors are indebted to Dipl. Chem. Ing. J. SZABÓ and his co-workers for the data. The analyses refer to the Mn, Fe, P, SiO<sub>2</sub> content of the samples.

The histograms showing the frequency distribution of manganese also supports the statement that the ore of the Slope is of high quality. In the histogram (*Fig. 20*) a sharp, dominating maximum can not be seen; between 26 per cent and 42 per cent manganese, however, a flattened maximum can be established, wherein the sorting shows no considerable fluctuation. Nearly 77 per cent of the samples ranges between the limits mentioned.

The frequency distribution of the iron content is quite of a different



*Fig. 20.* Frequency distribution of the manganese.

character. The iron content varies from 2 per cent to 30 per cent, that is, between smaller limits than the manganese content. A dominating maximum appears between 10 and 12 per cent followed by a lower second maximum at 18–20 per cent and by a still lower third maximum at 26–28 per cent. The Fe content in most of the samples — that means 70 per cent of the samples — is between 6 and 14 per cent. The second and the third maxima appear presumably due to the relatively high iron content of the clayey matrix wherein nodular oxide ore is embedded. The Fe content of the ferruginous clayey mate-

rial is considerably higher than that of the ore nodules embedded in it. Thus, e. g., an ore nodule separated from the clayey matrix of the stratum c contains 41,30 per cent manganese and 9,07 per cent iron, whereas the manganese content of the clayey material is only 0,82 and its iron content is 25,83 per cent. In an other sample from the same layer the manganese content of an ore nodule is 39,14 per cent and the iron content 9,56, whereas the nodules-embedding clay contains 30,99 per cent iron and 2,88 per cent manganese.

The histogram of the  $\text{SiO}_2$  distribution is bimodal showing two maxima, the first appears at 6–8 per cent, the second one at 10–12 per cent. The  $\text{SiO}_2$

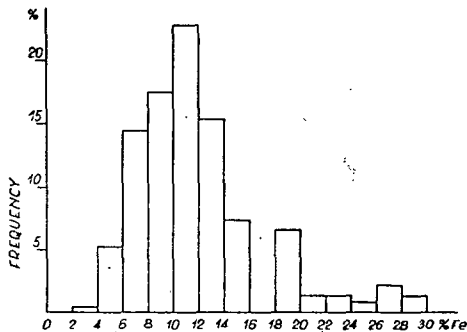


Fig. 21. Frequency distribution of the iron.

content generally changes from 2 to 26 per cent; higher  $\text{SiO}_2$  content than the upper limit mentioned can only be established in 1,6 per cent of the samples.

The frequency distribution of the P content is of interest from practical point of view. The P content varies between 0,00–0,70 per cent; the dominating

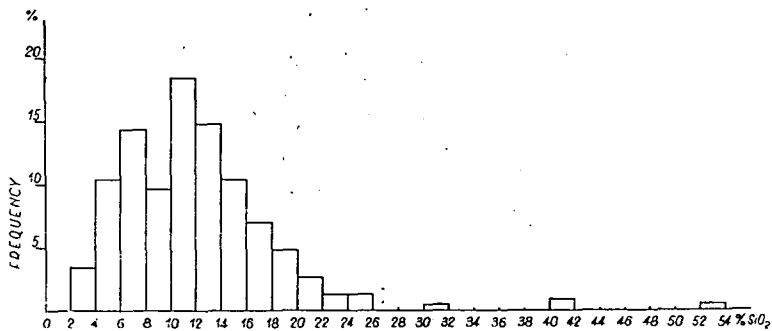


Fig. 22. Frequency distribution of the  $\text{SiO}_2$ .

maximum lies between 0,20–0,25 per cent P content. The phosphorous content of the bulk of the samples is over 0,20 per cent P which fact is to be taken into consideration at the ore dressing and using.

On the basis of these data it was also studied whether or not a relationship between the P–Fe and P– $\text{SiO}_2$  contents of the samples can be found.

ASOKE MOOKHERJEE [1961] dealing with the distribution of minor elements of gonditic manganese ores, states that the P content in the ores mentioned

generally increases by increasing Fe content. This statement is supported by him by plotting % P versus % Fe of 159 samples.

The diagram plotting the % P vs % Fe of 230 samples collected from the area of the Slope, shows a similar relationship as mentioned by MOOKHERJEE. The two diagrams are of the same character. The relationship is interpreted by MOOKHERJEE as chemisorption of  $\text{PO}_4$  anions on the colloidal  $\text{Fe}(\text{OH})_3$ . In his opinion the lower line (denoting also in our diagram) would represent

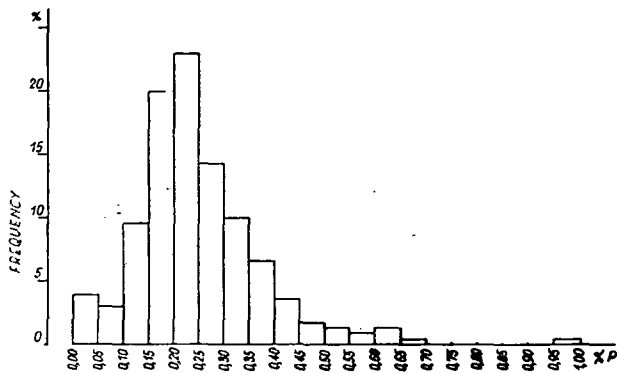


Fig. 23. Frequency distribution of the phosphorous.

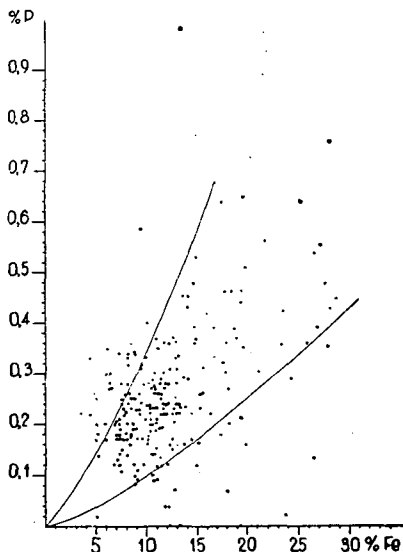


Fig. 24. Relationship between the P and Fe content of 230 samples from the Slope:

the „threshold” concentration of  $\text{PO}_4$  anions needed to flocculate different amounts of colloidal  $\text{Fe}(\text{OH})_3$ . The upper line — very roughly — perhaps may represent the saturation values. This statement, however, according to MOOKHERJEE, is only a „much-too-oversimplified” view as the effect of other electrolytes and similarly or opposite charged colloides as well as their mixing rate is also very essential. We are in full agreement with the view mentioned



above, namely, whereas in the samples of the Slope the relationship mentioned between P and Fe content is quite clearly seen, in a diagram plotted on the basis of P and Fe content of 115 samples from an other region, from the edge-part of shaft No. II, this relationship cannot be pointed out.

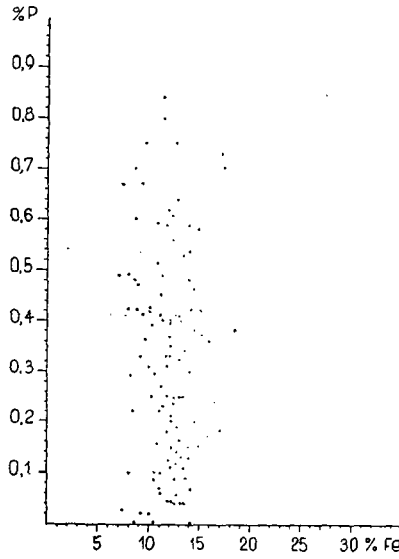


Fig. 25. Relationship between the P and Fe content of 115 samples from the edge-part of the shaft No. II.

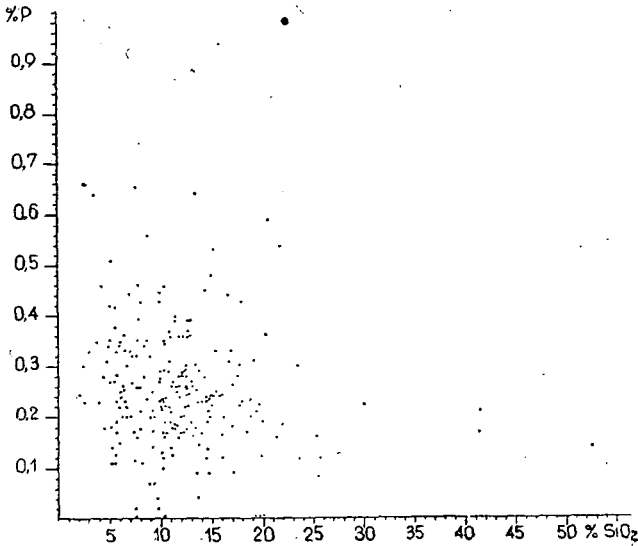


Fig. 26. Relationship between the P and SiO<sub>2</sub> content of 230 samples from the Slope.

Relationship can similarly be established between the P and SiO<sub>2</sub> content, however, for the time being, only in the case of the samples from the Slope. It is to be noted that similar relationship in the samples originating from the area of shaft No. II, again can not be established.

The detailed interpretation of the relationships between P—Fe and P—SiO<sub>2</sub> content — where they are valid — as well as the interpretation why this relationship exists in the area of the Slope but not in other areas, e. g., in that of shaft No. II, we intend to give in the future on the basis of further

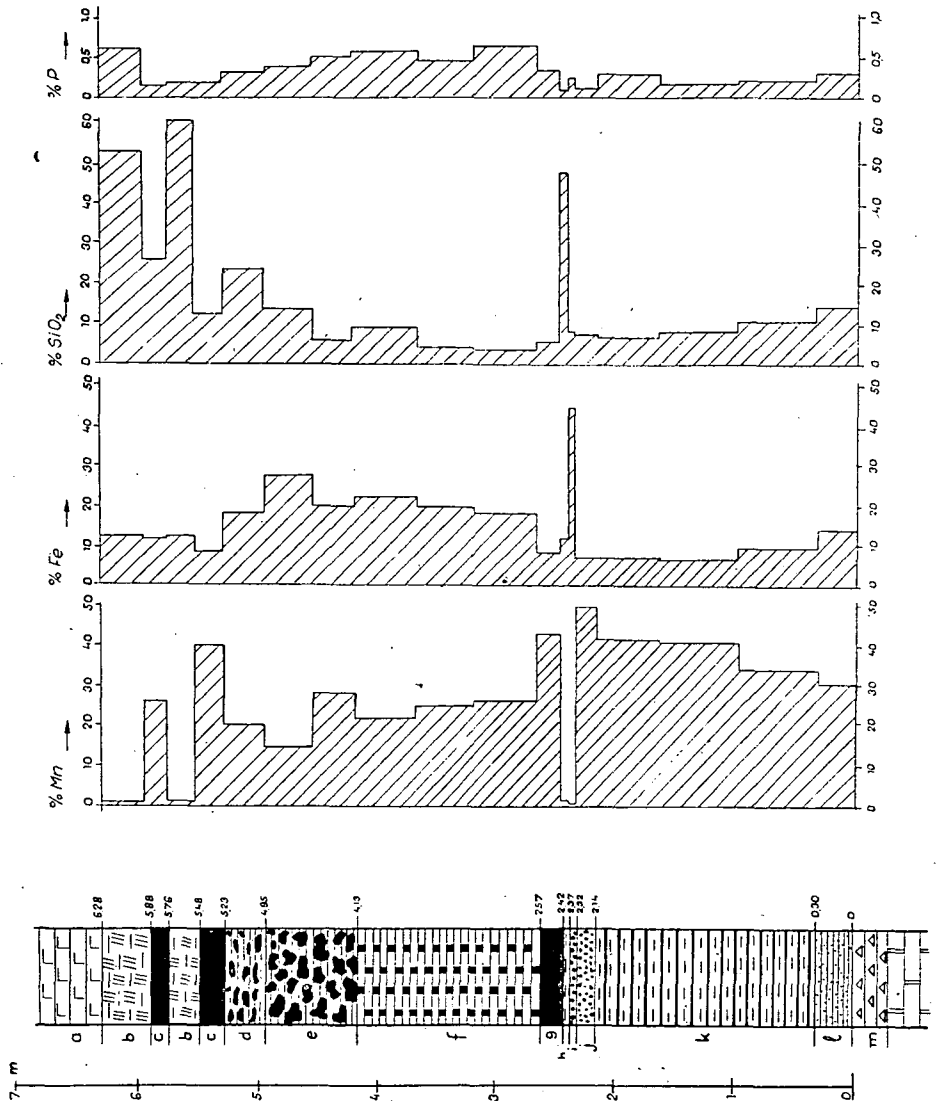


Fig. 27a. The change of the Mn, Fe, SiO<sub>2</sub>, P content in the layers of the section

examinations in the field and model experiments in the laboratory.

It is to be noted that further relationship can be established between the P and Ca content of the samples. The Ca content increases with increasing P content. The clearness of this relationship, however, is blurred by the fact that the Ca content belongs not only to the calciumphosphate which is present in the samples possibly as fluorapatite mainly in very finely distributed. The corresponding examinations under way are not limited to the area of the Slope but they refer to the whole area of Urkut.

The frequency distribution of the Mn, Fe, P and SiO<sub>2</sub> as well as the relationships between P—Fe and P—SiO<sub>2</sub> discussed above are valid for the whole area of the Slope. The question may arise how far the same is seen in the case of the typical section examined in detail.

#### THE CHANGE OF THE AMOUNT OF SOME COMPONENTS IN THE CONSECUTIVE LAYERS OF THE SECTION DISCUSSED

The relationship valid for the whole area of the Slope in the section examined can also be established.

The phosphorus content downwards from the layer *c* gradually increases, then it decreases in general from the layer *g* though with smaller fluctuations. Parallel with this change, through the same layers, an increase of the Fe content can be seen and though not in any details, but generally is still observable the corresponding decrease of the SiO<sub>2</sub> content. Even in some layers this relationship can exactly be stated. Thus, e. g., in the clayey layer *b* the SiO<sub>2</sub> content is very high and the P content considerably decreases related to that of the over- and underlying layers. In the yellow, ferruginous layer *i* the increase of the P content can be stated corresponding to the increase of the Fe content.

The change of the carbonate CO<sub>2</sub>, organic C and H<sub>2</sub>O in the consecutive layers was also investigated. The results are plotted in Fig. 27b. The carbonate CO<sub>2</sub> content gradually increases from the top towards the layer *g*, then in the layer *b* reaches a relatively high value. Apart from this value and from the decrease to be established in the underlying layers *i* and *j*, the carbonate CO<sub>2</sub> content further increases towards the layer *k* and only in the layer close above the bedrock can some decrease be stated, however, the CO<sub>2</sub> content is still higher than in the upper layers. Where it was possible, the CO<sub>2</sub> content of the selected ore and the clayey material was separately determined. In the selected ore samples the CO<sub>2</sub> content was always higher than that of the clayey part which fact is presumably to be interpreted that the carbonate particles, inclusions in the oxide ore were protected from the dissolution and from the occasional oxidation.

The determination of the organic C content in the ores from Urkut up to day were not carried out or at least data referring to their organic C content were not published, although its determination seems to be essential from the point of view of the genesis of the deposit, since an environment, rich in organic material, different circumstances for the deposition of the manganese may mean as an environment poor in organic material. Beside the determination of the organic C content of the single layers, the paleobotanical, pollen-analytical

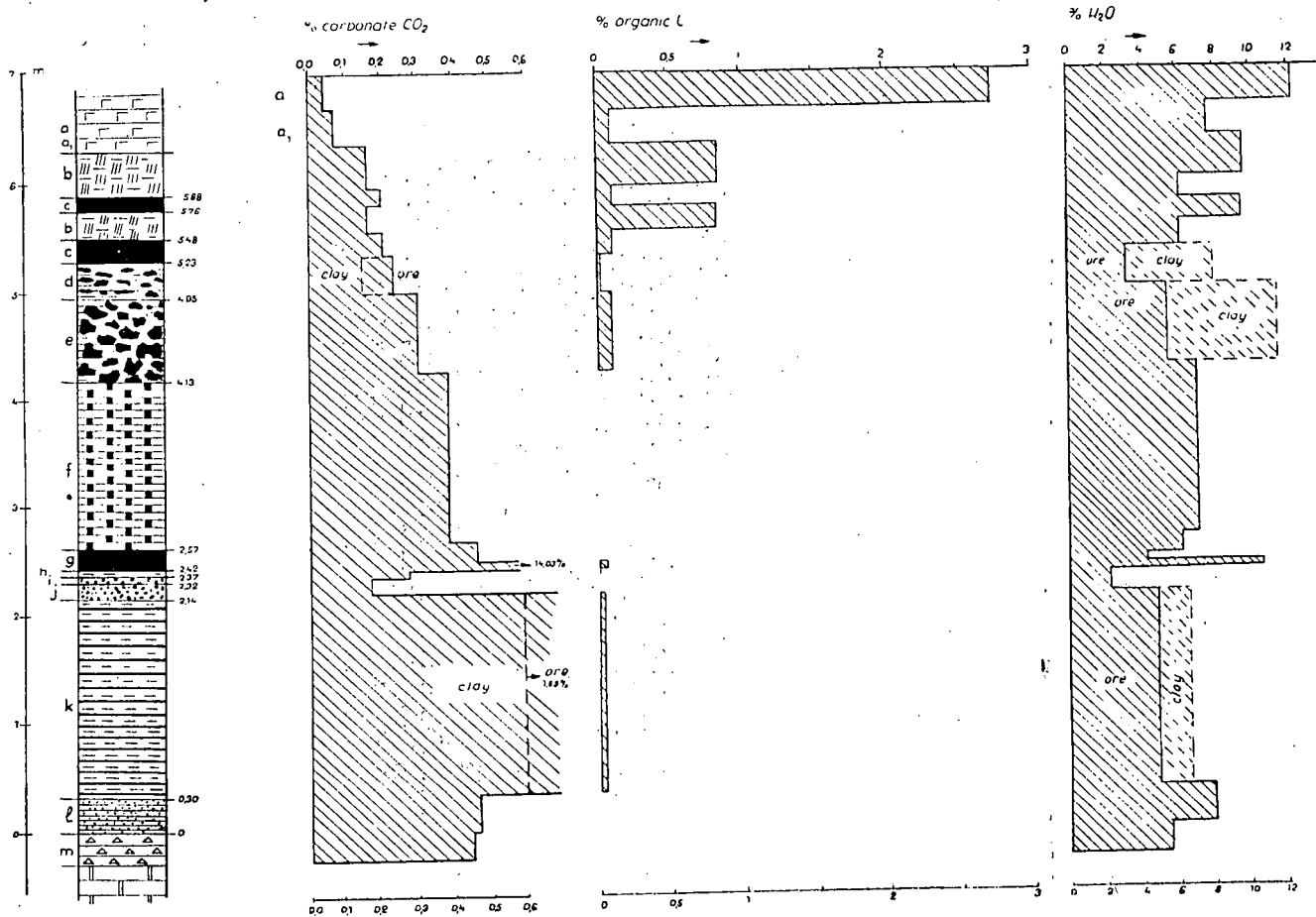


Fig. 27b. The change of the carbonate CO<sub>2</sub>, organic C and H<sub>2</sub>O content in the layers of the section



examination of the section discussed as well as further samples from other areas of the deposit were carried out by P. SIMONCSICS and M. KEDVES [1961].

The organic C content is extremely high in the dark gray, radiolarian clayey marl layer (*a*) and still considerable also in the green clayey *b* layer which fact well agrees with the results of the investigations of P. SIMONCSICS and M. KEDVES referred to as even in these layers were the most pollen and other relicts of plant origin to be detected and determined.

The organic C content after high values of the uppermost layers rapidly decreases, even in some layers was not to be determined. As in the case of the carbonate CO<sub>2</sub>, the organic C content of the selected ore and the clayey part was separately determined. The organic C content within the same layers was higher in the selected ores than in the clayey parts. In some layers the organic C was absent or at least not present in determinable amount. This fact, however, does not mean that the layers in question do not contain traces of organic relicts, only the organic material is fully decomposed and only its silicified remnants can sometimes well be observed in thin sections. Thus, e. g., in the yellow „iron-sand” layer *i* only a minimal organic C content was to be determined, in thin section such a formation can be observed which possibly may be considered as of organic origin.

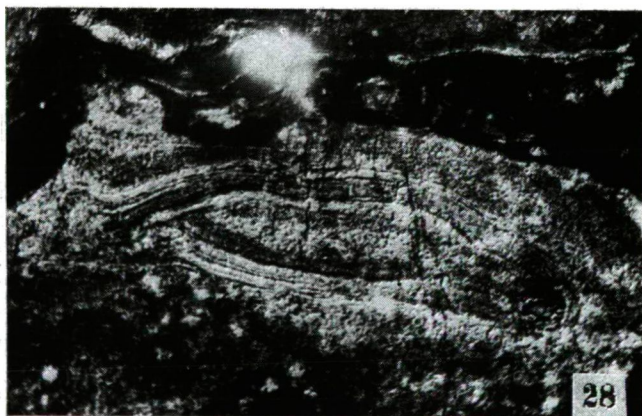
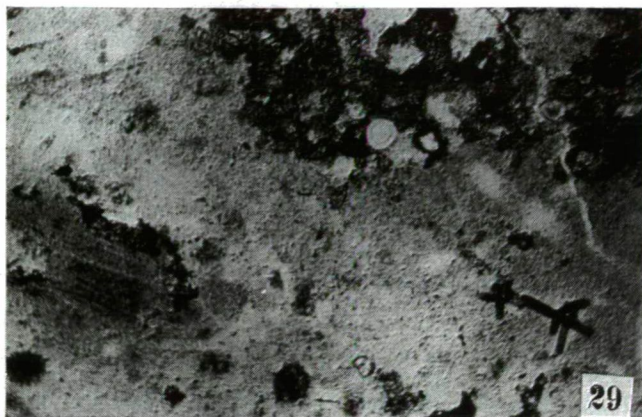


Fig. 28. Organic remnant in thin section from the material of the layer *i*. Plain light,  $\times 100$ .

In thin sections made from the material of the bedrock (layer *m*, brown, cherty-striated clay) formations presumably of organic origin can also often be found: e. g. pollens, tube-like formations surrounded and partly also filled out by chalcedony both in length and cross-sections which may mean the places of former algal threads as well as branching formations which are presumably also of plant origin.

From the change of the H<sub>2</sub>O content is to mention that the water content of the selected ore and clayey samples separately examined, where it was possible, the H<sub>2</sub>O content of the clayey samples was higher.



*Fig. 29.* Thin section from the material of the layer *m*. Organic remnants in opaline matrix; at right a branching formation possibly of plant origin. Plain light,  $\times 50$ .



*Fig. 30.* Thin section from the material of the layer *m*. Branching algal tubes at right. The chalcedony surrounding the tubes mentioned in the text can also be seen. Plain light,  $\times 50$ .

The study of other areas of the manganese deposit of Urkut on the basis of investigating the geological structure, the sequence of the different layers at different points, the composition of the layers, the mineral association as well as the frequency distribution of the major and some minor elements, further the paleobotanical investigation, in the concept of this paper, is under way.

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