DATA ON THE GEOLOGY AND MINERALOGY OF THE EPLÉNY MANGANESE ORE DEPOSIT

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INTRODUCTION

True, the sedimentary manganese ore deposit of Eplény (Bakony Mts.) in its practical importance lags behind the Úrkút manganese ore deposit, however, in view of the complexity and great interest of genetical problems it deserves a more thorough, detailed study. As it appears from the number of references, there has been no lack of interest in this respect up to the present time.

The Eplény manganese ore became known in 1928 as a surface outcrop, somewhat later than the Úrkút one and at the very beginning there was merely surface mining, then gradually the subsurface mining was begun. A remarkable development in the manganese ore mining in Eplény set on after the second world war when between the years 1945 and 1966 deep-reaching borings and subsurface exposures
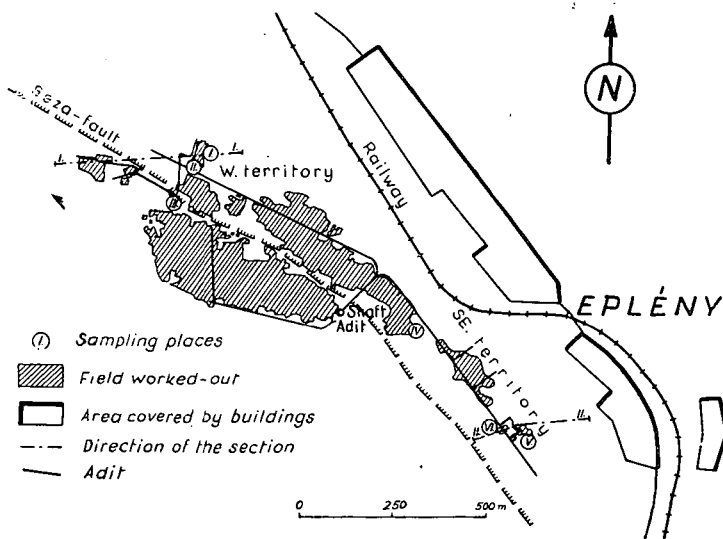

Fig. 1. Map scheme of the Eplény manganese ore deposit showing sampling places and direction of geologic sections

made possible the delimitation of the productive manganese ore beds and a consi-
derable increase of production here.

Sampling places of the Eplény area, place and direction of sections shown in
Figs. 2, 5 and *6* are illustrated in the map to *Fig. 1.*

GEOLOGY OF THE AREA

The Eplény manganese ore occurrence is found in a trench-like structure sur-
rounded by Triassic rocks. Within the area of the occurrence a varied Jurassic se-
quence of strata had developed. The development of Jurassic in Eplény, as compared
with the area of the Úrkút manganese ore field, shows unconformity, what is obvious
from the fact that proceeding from the Triassic borders towards the inner parts of
the basin more and more complete layers can be found.

Jurassic

Lower Liassic. "Dachstein" limestone (white, light-grey, yellow, dense, fine-
crystalline) representing the uppermost series of Triassic turns with conformity
into Liassic limestone of the Dachstein type with similar characteristics. The upper
banks of the limestone formation are of oölitic texture, with Foraminifera, very
small Brachiopoda fossile remains. In higher series of Lower Liassic according to
facies changes, red, pink, brachipodal cherty limestone, red, pink massive crinoidal
limestone and its crinoidal varieties of the "Hierlatz" type could be found.

Middle Liassic. It is known in the area of occurrence in two more important
developments. A more frequent variety is the red, pink nodular or massive crinoidal
limestone, the other the red, green-spotted cherty limestone. Sometimes small man-
ganese grains appear in the crinoidal limestone, in several places manganese ore
embeddings wedging out lenticularly are found.

Besides fully developed Lower and Middle Liassic, unconformity can also be
experienced here. On the NE side of the "primary" oxide area karstic holes and
fissures of Dachstein Liassic limestone are filled with Lower or Middle Liassic
limestone and the Upper Liassic manganese ore series are deposited upon these
unconformable border areas, too.

Upper Liassic. This series of the Jurassic is partly filled with manganese ore
seams, deposited in haphazardly changing thickness upon the uneven surface of
Lower and Middle Liassic formations. The overall thickness of the manganese ore
series is 6—8 m, sometimes it even reaches 20 meters. Below in the ore series is found
the manganese ore, deposited originally in oxide form from seawater accompanied
by clay and clay marl as well, which is usually yellow, brownish below and dark-
grey in the upper parts. The word "primary" which we have used and will use later
indicates that manganese ore separated and sedimented originally in oxide form is
in question, to be distinguished from the secondary manganese oxide ore, having
been formed through oxidation of substances containing manganese carbonate.
Upon the mentioned manganese series the dark grey radiolarian clay marl contain-
ing manganese carbonate bands, lenses, is sedimented. In the W and NE borders
the ore series turns into manganiferous limestone and later barren limestone facies.
Upon the manganese series already within Upper Liassic grey, red laminated limes-
tone is settled.

Dogger-Malm. Lower Dogger is represented by red, nodular limestone with
cherty lens with rich Ammonites fauna. Upper members of Dogger are represented

by grey, greenish-grey and pink posidonian, laminated cherty limestone series. Upon this pink, white, grey cherty marl (radiolarite) representing Upper Dogger and Lower Malm (Bath-Callovian) is sedimented. The varied Eplény Jurassic sequence of series is closed by red, nodular ammonitic limestone.
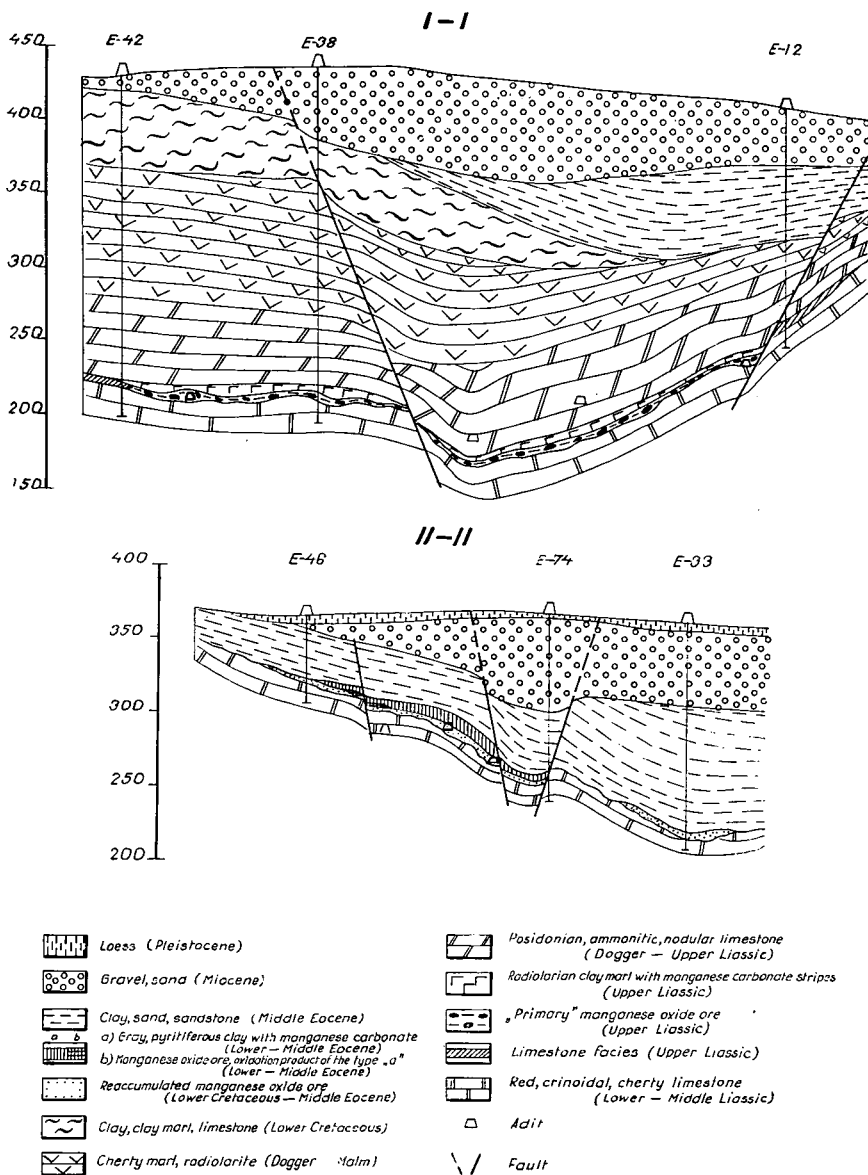

Fig. 2. Geologic sections of the investigated regions. *Fig. 1.*, I—I and II—II.

Cretaceous

In the area of occurrence Cretaceous is present as well in an insignificant thickness. The New-Kimmerian movements taking place upon the border Jurassic and Cretaceous had been quite decisive in forming the structure of the area although this period had played not such an important part in the history of development of the ore series in Eplény as in Úrkút. Cretaceous is represented by multicoloured clay, grey clay marl and limestone.

Eocene

Lower and *Middle Eocene* starts with transported and redeposited (reaccumulated) manganese series in the SE territory. Here one can find the mixed material of the manganese oxide deposit mentioned already in connection with Upper Liassic, together with the material of the overlying and the underlying rocks. Bauxitic clay
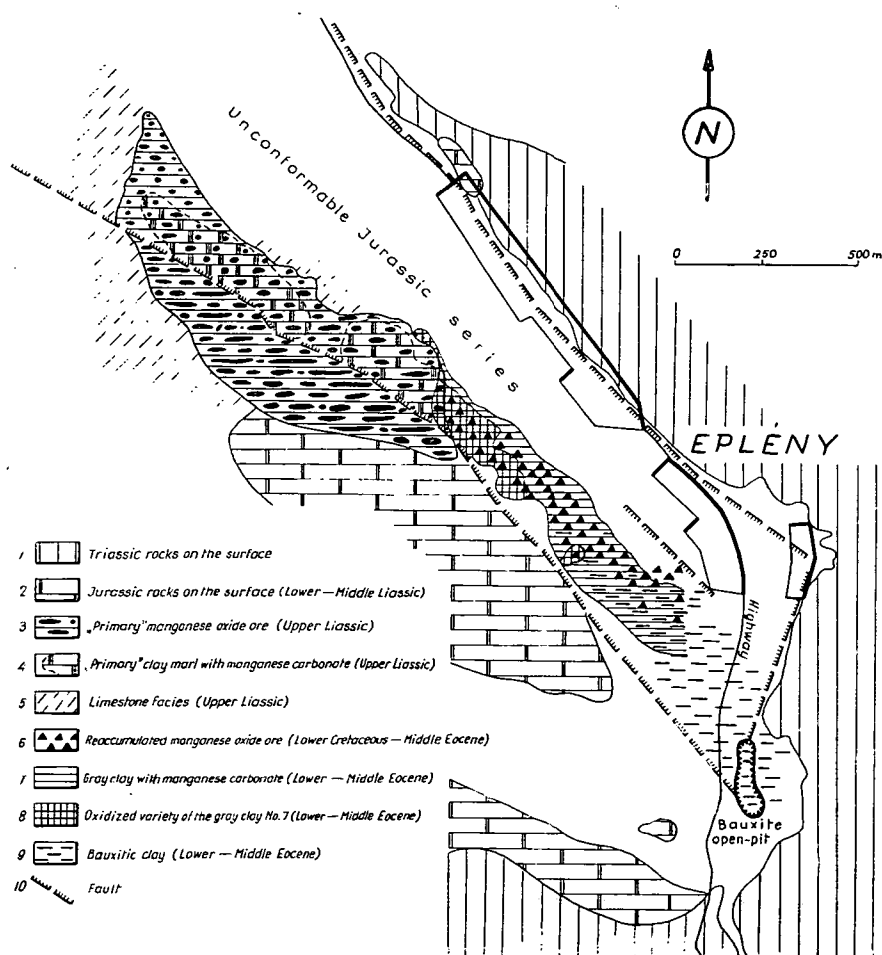

1 Triassic rocks on the surface

2 Jurassic rocks on the surface (Lower — Middle Liassic)

3 "Primary" manganese oxide ore (Upper Liassic)

4 "Primary" clay marl with manganese carbonate (Upper Liassic)

5 Limestone facies (Upper Liassic)

6 Reaccumulated manganese oxide ore (Lower Cretaceous — Middle Eocene)

7 Gray clay with manganese carbonate (Lower — Middle Eocene)

8 Oxidized variety of the gray clay No. 7 (Lower — Middle Eocene)

9 Bauxitic clay (Lower — Middle Eocene)

10 Fault

Fig. 3. A scheme of territorial distribution of Eplény manganese ore types

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is settled upon this reaccumulated manganese series what formation is considerably thickened towards the abandoned surface bauxite mine. As a rule, grey, pyritiferous clay sometimes having considerable manganese carbonate content as well, is settled upon the bauxitic clay. On this substance carbonaceous clay, miliolinic sandstone and in slight thickness nummulitic limestone is settled and this ends the Eocene series.

Miocene

The Eplény manganese ore area is covered from the N by *Middle Miocene* gravel, sand and its maximum thickness reaches 70 m.

STRUCTURE OF THE AREA

The Eplény deposit is an organic part of the structural unit of the Bakony Mountains. The area is remarkably broken, considerably vertical and horizontal replacements could be observed. The structure of the area is characterized by two important, nearly parallel faults, of which the more decisive is the Géza-fault, cutting the area in the middle and the reaccumulated manganese series developed in the footwall of the fault. The other fault closes the Jurassic area from the NE and further on Triassic rocks can be found on the surface. The main direction of the faults is NW—SE. Perpendicular to this direction smaller breaks cut off the area.

NE from the manganese ore area the literature mentions an overlapped structure, namely in several borings Lower and Middle Liassic repeatedly is found. According to newer investigations in the unconformable areas holes, fissures, formed in Lower Liassic "Dachstein" limestone were filled up with Middle Liassic formations as indicated already.

The sequence of different series along I—I and II—II sections as given in *Fig. 1* is represented in *Fig. 2* and the areal distribution of manganese ore types is represented in *Fig. 3*.

DEVELOPMENT OF MANGANESE ORE BEDS

The area of the Eplény manganese ore deposit can be distributed into two groups according to their development.

1. Upper Liassic manganese ore beds of the western territory

a) "primary" manganese oxide ore
b) "primary" clay marl with manganese carbonate content

2. Lower Cretaceous — Middle Eocene and Lower Eocene — Middle Eocene manganese ore beds of the southeastern territory

a) reaccumulated (allochtonous) manganese oxide ore
b) grey, pyritiferous manganese carbonate-containing clay ("secondary")
c) manganese oxide ore ("secondary") formed by oxidation of grey, pyritiferous, manganese carbonate-containing clay.

1. Upper Liassic manganese ore beds of the western territory

a) *Manganese oxide ore*

In the area manganese had been settled already in oxide form from seawater upon the dissolved, corroded, uneven relief of the surface of the underlying rock (from this the name "primary"). The thickness of the manganese oxide series follows the unevenness of the underlying rock, reaching a maximum thickness of 5 m. Manganese ore is embedded in yellow, brown, black clays and dark—grey radiolarian clay marl. As to its structure two main types can be distinguished: there are known globular, reniform ore nodules while the other type is represented by layered, banked, loose manganese ores. The diameter of the ore nodules ranges from a few centimeters to 2,0 m, from outside they are covered with thin or thick ferruginous crust and in the inner parts we can find cherty — chalcedony parts. As a rule the manganese ore of loose structure is elongated and lenticular. Some transition forms between the two types could also be observed with a loose inner structure but showing globular structure from the outside and are delimited from the barren rock by a limonitic layer.

In the area of the south side of Géza-fault the loose, layered ore was more important while on the north side the globular, nodular ore type could be found more frequently. Passing from W towards NW within the oxide bed the ratio of the barren rock increases on behalf of the ore itself. The overall thickness of the series reducing it to the oxide ore is 1,6 m. Considering the total thickness of the oxide ore series the average quality of the manganese ore is the following:

$$Mn: 24,37\% \qquad Fe: \quad 10,65\%$$
$$P: \quad 0,25\% \qquad SiO_2: \quad 20,36\%$$

Taking into consideration manganese ore quality without barren interbeddings, the manganese content of the ore as a rule changes between 30—36 per cent. Histograms constructed relying upon Fe, Mn, P, SiO_2 content determined from samples of the deposit *(Fig. 14—17)* very well show the frequency distribution of the mentioned components.

In connection with this deposit it is an interesting problem — to be clarified later on — that while oxide ore nodules are embedded into dark grey radiolarian clay at the same time differences in the conditions under which pyrite and the manganese oxides of higher valence were formed contradict the simultaneous formation. It can be supposed that formation of pyrite is the result of processes taking place in the clay after the separation of oxide ore nodules.

b) *Clay marl with manganese carbonate content*

Upwards in the "primary" oxide manganese ore series, oxide manganese ore nodules gradually disappear and dark grey radiolarian clay marl is found in the overlying, in the upper layer of which the grey, greenish-grey, yellowish-grey, finely layered manganese carbonate-containing clay marl usually appears lenticularly wedging-out. The manganiferous mineral is the extremely fine-grained rhodochrosite. In its development the manganese carbonate-containing clay marl is very similar to the Úrkút upper carbonate deposit, with a somewhat higher manganese content and a lower iron and phosphorus content. Its average quality:

$$Mn: 14,28\% \qquad Fe: \quad 4,03\%$$
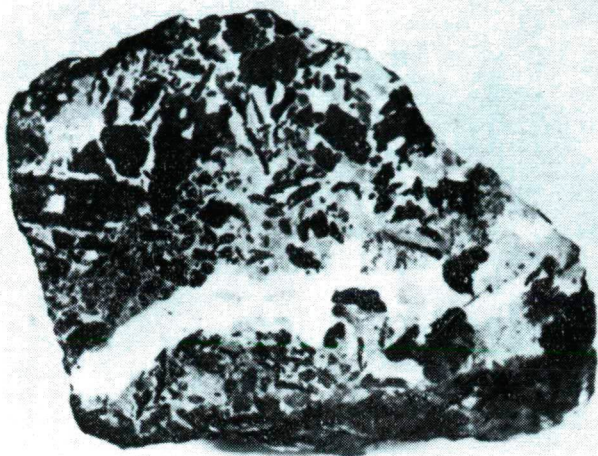$$P: \quad 0,15\% \qquad SiO_2: \quad 22,80\%$$

Fig. 4. Limestone showing brecciated structure with calcite and manganese ore as fissure and cavity fillings. About 1/3 natural size.

In the area between the W and SE mine fields the Upper Liassic formations and also a part of the manganese series became denuded. The manganese carbonate-containing clay marl which had got upon the surface likely had been oxidized, thus a band of layered oxide manganese ore of relatively low grade was formed. While in Úrkút it is just this ore type having great importance for the industry, in Eplény this type of ore has no significance from the point of view of practice. *Fig. 3* shows that manganese carbonate-containing clay marl is restricted to an insignificant area in Eplény, while in Úrkút the upper bed, corresponding to it, stretches over the main carbonate series. Manganese series is wedged-out towards the borders and as a rule turns into limestone facies. Towards the brims very often lonely mangani-ferous limestones appear under the oxide deposits with brecciated structure as can be seen in the photo reproduced in *Fig. 4.*

Geological sections of the Upper Liassic manganese series called "primary", at sampling places I and II in *Fig. 1,* are shown in *Fig. 5.*

2. Manganese ore beds of the southeastern territory

a) *Lower Cretaceous — Middle Eocene reaccumulated allochtonous oxide manganese ore.*

In the SE part of the Eplény area transported and redeposited manganese series is settled upon Lower and Upper Liassic karstic, eroded surface. Its material first of all had been given by the ore material of the previously already settled "primary" beds. In areas near the denuded Upper Liassic beds the ore debris is rather rough,
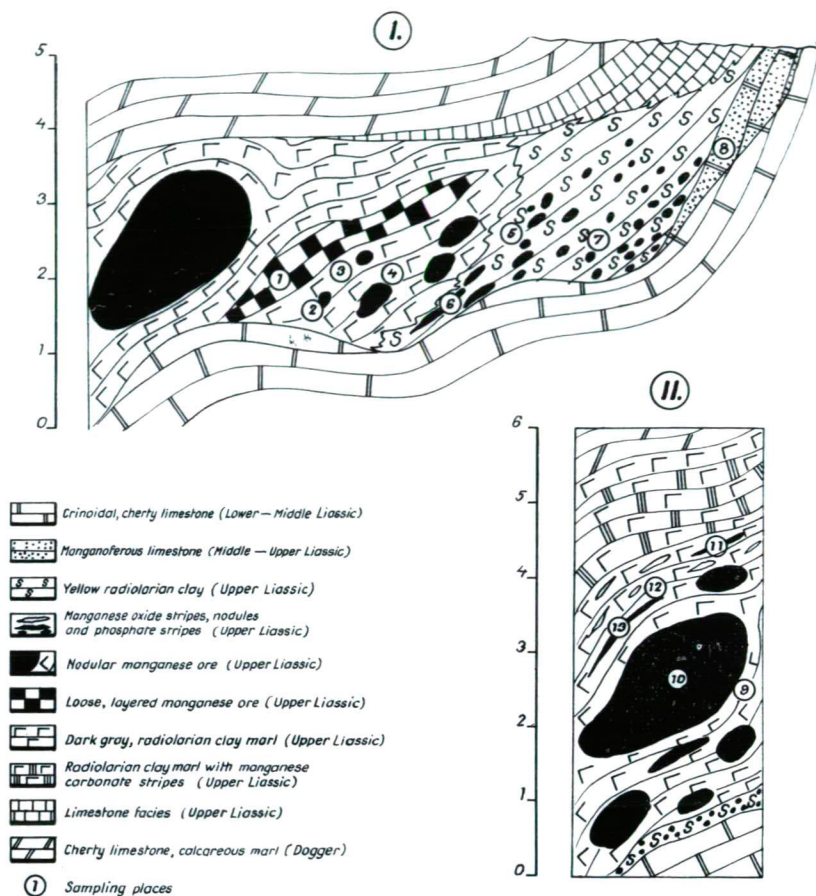
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Fig. 5. Geologic sections of Upper Liassic manganese ore beds at sampling
places I and II of *Fig. 1.*

with a diameter of 1—20 cm, moving on the grain size of the debris gets finer and
other rock debris is mixed to it, mainly chert and limestone.

Generally the upper part of the bed consists of "muddy", very fine ore debris.
The thickness of the reaccumulated ores waywardly changes — filling the karstic
fissures of the bedrock it may even reach 5 meters thickness. The ore quality shows
also a very strong change: for instance manganese content ranges from 17 to 31
per cent, while the phosphorus content is rather low (P: 0,02—0,07%).

In the upper part of the bed bauxitic material is settled upon the undulating
surface.

b) *Lower and Middle Eocene grey, pyritiferous manganese carbonate-containing clay*

By the denuding of the first deposited Upper Liassic beds and later, through
the aforementioned reaccumulation the Eocene transgression made possible to
dissolve certain amount of manganese from the reaccumulated beds later again

manganese carbonate-containing clay ("secondary") was accumulated by chemical processes. This material is first of all connected with the reaccumulated areas, but stretches over the "primary" beds as well and a variety of it with chert debris is known towards the brims. In part of the samples the manganese content ranges from 18 to 24 per cent what approximately corresponds to the quality of the Úrkút carbonate manganese ore, however, the Eplény manganese carbonate material has a considerably lower P and higher S content. Its average quality:

Mn: 15,05% Fe: 9,30%
SiO$_2$: 15,57% P: 0,08%
 S: 4,53%

c) Lower—Middle Eocene oxide manganese ore formed by oxidation of the grey, pyritiferous, manganese carbonate-containing clay

The grey, pyritiferous clay — containing manganese carbonate — is situated relatively near the surface on the Géza-fault side. Thus it became possible already after the sedimentation of the grey, pyritiferous clay, or somewhat later, manganese
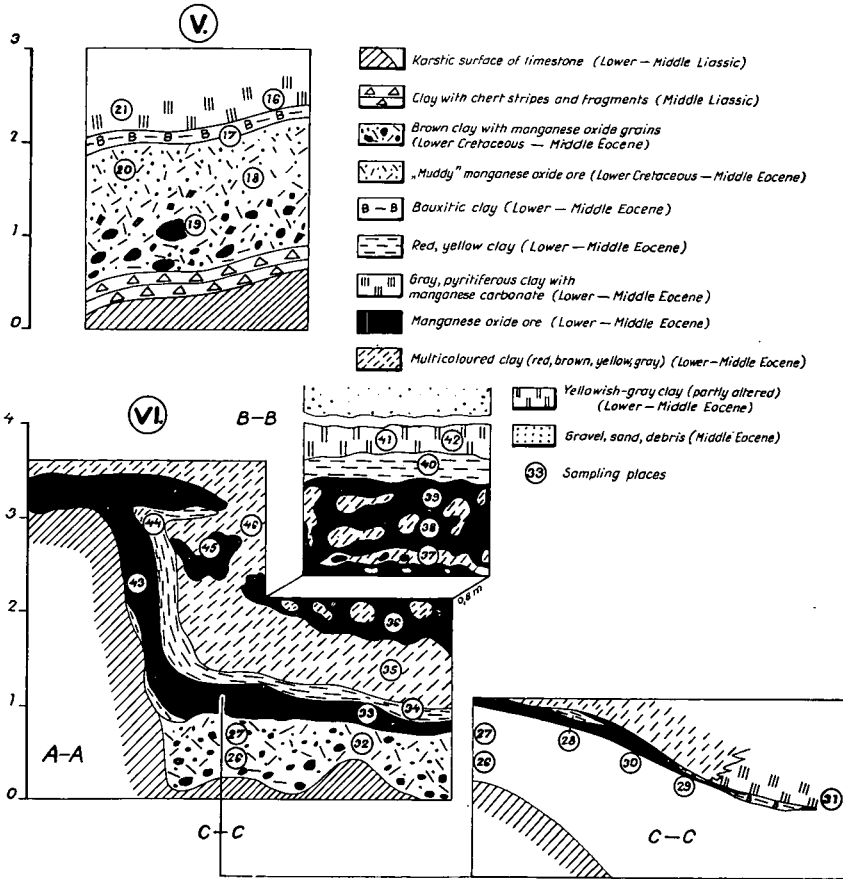

Fig. 6. Geologic sections of the SE territory at sampling places V and VI of Fig. 1.

carbonate being oxidized. At present near the shaft we know oxide ore ("secondary") formed due to the oxidation of pyritiferous manganese carbonate-containing clay, settled upon the reaccumulated oxide ore. This type of ore very frequently has a layered structure, its continuity is interrupted by irregular clayey interbeddings. The transformation of yellow, brown, red clays surrounding the oxide ore, into grey, pyritiferous clay can be followed everywhere. Similar changes are involved here as in the case of the Úrkút layered oxide ores and yellow radiolarian clay. The quality of the ore as a rule can be characterized as follows:

$$Mn: \quad 25{-}28\% \qquad Fe: \quad 8{-}10\%$$
$$P: \quad 0,1{-}0,2\% \qquad SiO_2: \ 18{-}20\%$$

Geological section of the beds of the SE mine field at V and VI sampling places in *Fig. 1* is shown in *Fig. 6*.

POLLEN GRAINS OF THE CLAYS

Similar to investigations carried out with the Úrkút formations it appeared purposeful to orientate first of all as to organic remains, pollen grains, enclosed into the clayey members of the series. On our request, P. SIMONCSICS carried out pollen analytical study of several samples. Relying upon his information the following can be stated:

Dark grey radiolarian clay marl (No 3)* from the "primary" beds contains a number of organic fragments without structure. The number of spores—pollens, is rather few, their state is bad, they are creased, corroded, broken. The presence of the following types could be stated: *Leiotriletes sp., ? Cingulatisporites sp.* The determination of the following is uncertain: *Monosultices sp., Spheripollenites sp., Eucommiidites sp.,* while the presence of a "reticulate cista or alga" could be stated with certainty. All the above mentioned types could be found in Liassic, the type called "reticulate cista or alga" had already been detected by SIMONCSICS and KEDVES from the Úrkút deposit. The lack of the *Classopollis* genus is striking what may indicate that we are having sediments far from the shores.

In a grey, fine-layered material with considerable phosphorus content (No 11) also from the Upper Liassic, less organic remains were observed and the determination of the following genus (with very low occurrence) was also uncertain: *Monosulcites sp., Spheripollenites sp., Eucommiidites sp.* On the contrary, the determination of *Tittodiscus sp.* and *Classopollis torosus* is certain. The latter is mostly characteristic for the Liassic, later it hardly can be found. A single creased example — although the determination is uncertain — of *Multiporopollenites sp.,* was found. If the determination is correct, *Juglandaceae* pollen is possible, this, however, is impossible in Upper Liassic, it may perhaps occur only from Upper Cretaceous.

At the same time not only yellow Upper Liassic clay marl (No 5) from the "primary" series proved to be free of pollens, but the bauxitic clay settled upon the Lower — Middle Eocene "secondary" formation (No 17) and grey pyritiferous manganese carbonate — containing clay from the Middle Eocene "secondary" series as well (No 16 and 21), together with the grey pyritiferous clay (No 22) and yellow clay (No 23).

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* Number in parenthesis here and in the following means sample numbers. Corresponding sampling places see in *Figs. 5, 6,* and short denotation of samples in Table 1.

TABLE 1

Short denotation of the samples investigated

Serial number of the samples	Denotation of the samples	Sampling places	
		age and territory	shown by Fig.
1.	Loose, layered oxide ore		
2.	Oxide ore nodule with ferruginous crust		
3.	Dark grey, radiolarian clay marl		
4.	Oxide ore nodule with limonitic crust		
5.	Yellow, radiolarian clay marl		
6.	Layered oxide ore band from yellow radiolarian clay marl		
7a	Ore grains from yellow radiolarian clay marl		5. I.
7b	Oxide ore nodule from yellow radiolarian clay marl	Upper Liassic, "primary" beds of the western mine territory	
7c	Yellow radiolarian clay marl crust of the ore nodules		
8a	Manganese oxy-hydrate aggregate in white calcite		
8b	Brown, yellowish-brown, sandy, brecciated limestone with manganese ore grains and calcite veinlets		
9a	Compact, grey, crystalline manganese ore lens		
9b	Black, loose, earthy crust of the former		
10.	Loose, earthy oxide ore		5. II.
11.	Grey, layered phosphorus-bearing lens		
12.	Ferruginous lens with manganese ore bands		
13.	Sandy, grey, greenish-yellow stripped phosphorus-bearing lens		
18.	Rounded off manganese ore granules embedded in yellow, brown clay		6. V.
19.	Dense, massive, black ore lens	Lower Cretaceous—Middle Eocene transported and redeposited, allochtonous beds of the southeastern mine territory	
20.	Loose, earthy, "muddy" manganese oxide ore with yellow, brown clay		
26.	Rounded off manganese ore granules and dense, greyish ore fragments embedded in brown clay		6. VI.
27.	Brown manganiferous clay similar to the sample Nr. 26.		
32.	Manganese ore granules in brown clay		
17.	Red, bauxitic clay	Lower—Middle Eocene "secondary" beds of thesoutheastern mine territory	6. V.
16.	Grey, pyritiferous, manganese carbonate-containing clay		
21.	The same as sample Nr. 16.		
23.	Yellow clay from the transitional field		

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TABLE 1—(continued)

Serial number of the samples	Denotation of the samples	Sampling places	
		age and territory	shown by Fig.
24.	Loose, oxidized, partly crystalline manganese ore from the transitional field		—
25.	Loose, oxidized manganese ore from the transitional field		—
28.	Red clay with manganese ore grains		
29.	The same as sample Nr 28		
30.	Clayey, oxidized, hard manganese ore		
31.	Grey, pyritiferous clay		
33.	The same as the sample Nr 30	Lower—Middle Eocene "secondary" beds of the southeastern mine territory	
34.	Red clay with manganese ore grains, similar to the samples Nr 28 , 29		
36.	Clayey, earthy, in some places hard, black oxide ore		
38.	Hard, compact oxide ore pieces in red — white clay (a: red clay; b: white clay; c: ore)		6. VI.
39.	Similar to the sample Nr 38		
40.	Pinkish clay with manganese ore grains		
41.	Light brown — greyish clay with manganese ore veinlets		
42.	Similar to the sample Nr 41		
43.	Black, clayey, layered oxide ore		
44.	Red-yellow clay		
45.	Clayey, oxide manganese ore		
46.	Manganese ore grains in yellowish-pinkish clay		

MINERAL COMPOSITION OF MANGANESE ORE SERIES

The study of mineral composition of manganese ores has been made difficult by the fact that most of the samples — with but a few exception — were earthy, porous, difficult to grind and polish and so it was impossible to prepare polished ore sections of corresponding quality. Thus in the study of mineral composition ore microscopy played by far not too important role and we could rely first of all upon results of differential thermal analysis and X-ray powder diffraction data, supplemented with chemical analysis of a number of samples as well.

D. T. A. curves taken with an ERDEY—PAULIK "Derivatograph" are shown in *Figs. 7, 8, 9* and *10.* Some of the X-ray powder diffraction patterns taken with CuKα radiation are given in *Figs. 11, 12* and *13.* Semiquantitative mineral composition of several samples and ore types, resp., is to be seen on the basis of X-ray powder diffraction data in Table 2.

Data of chemical analysis are summarized in Table 3., while the frequency distribution of some of the main components can be found in *Figs. 14—17.*

Places of sampling *(Nos 1—13)* from Upper Liassic "primary" beds in the W area are shown in sections I and II of *Fig. 5.* Places of sampling from allochtonous reaccumulated Lower Cretaceous—Middle Eocene beds in SE *(Nos 18—20, 26, 27,*
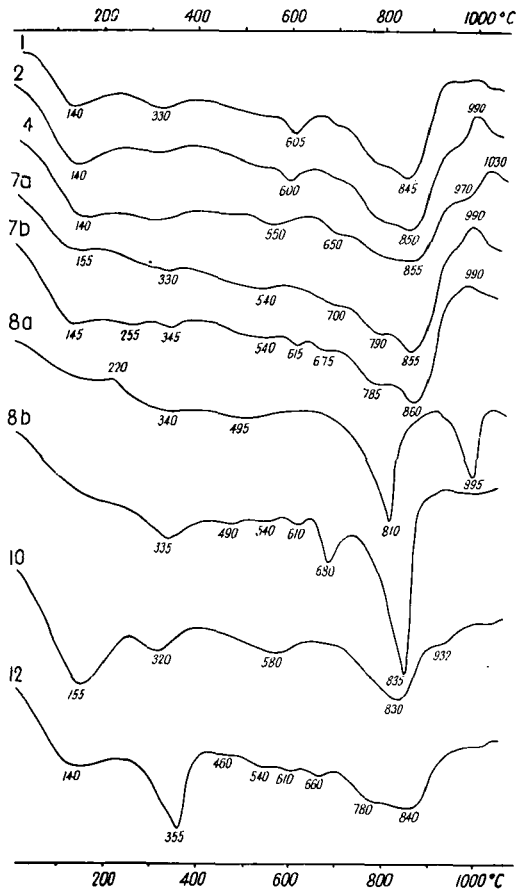
Fig. 7. D. T. A. curves of samples containing dominantly cryptomelane, collected from the Upper Liassic „primary" manganese beds (denotation of samples see in Table 1, their sampling places in *Fig. 5).*
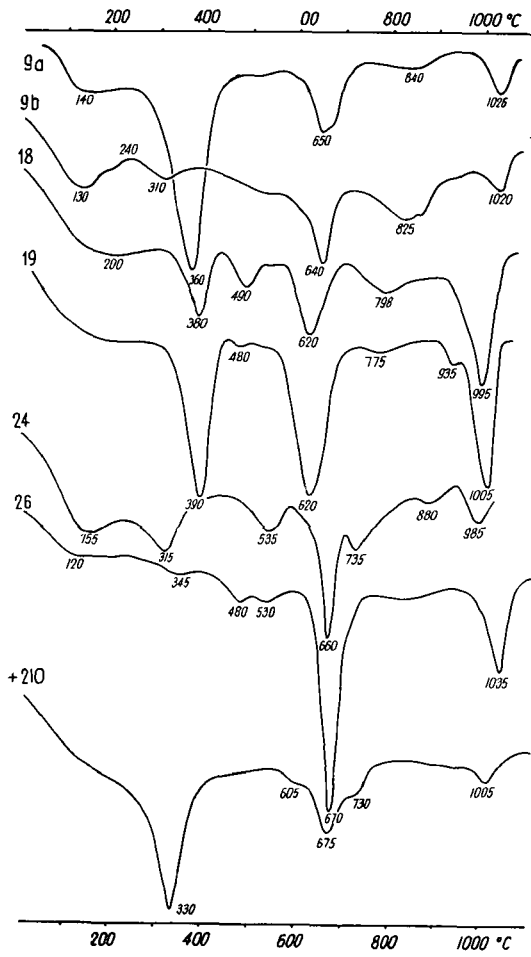
Fig. 8. D. T. A. curves of samples containing dominantly pyrolusite and manganite. Of the samples No *9a* originates from the "primary" bed, Nos *18, 19* and *26* from the redeposited bed and No *24* from the "secondary" bed (denotation of samples see in Table 1, their sampling places in *Figs. 5, 6).*
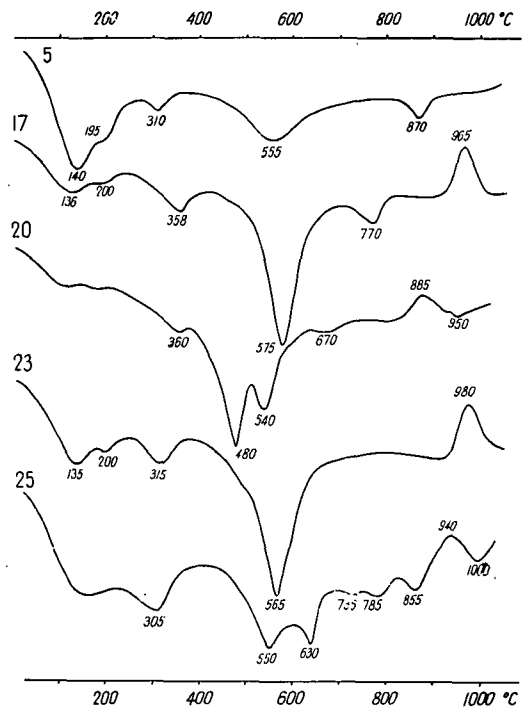
Fig. 9. D. T. A. curves of clayey samples. Of the samples No *5* taken from the "primary", Nos *17* and *20* from the redeposited and Nos *23* and *25* from the "secondary" beds. (Denotation of samples see in Table 1, sampling places in *Fig. 6.*)
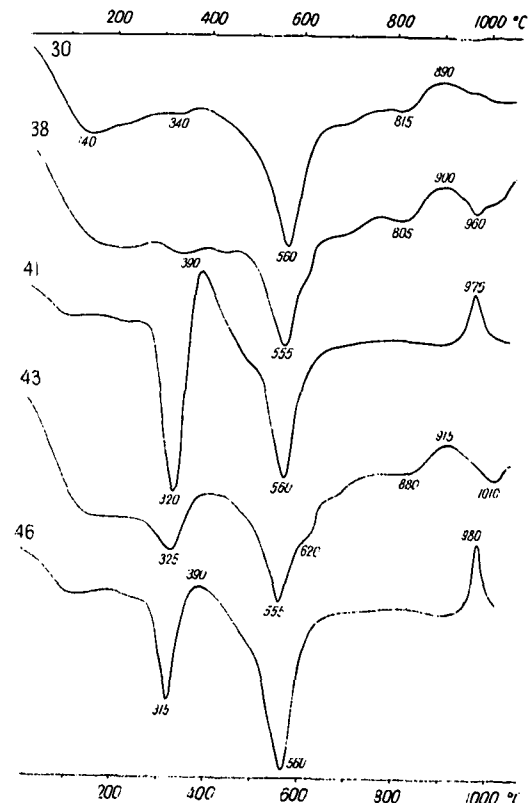

Fig. 10. D. T. A. curves of clàyey samples from "secondary" beds. (Denotation see in Table 1, sampling places in *Fig. 6.*)

32) and from Lower—Middle Eocene "secondary" beds *(Nos 16, 21, 28—31, 33—46)* are shown in sections V and VI of *Fig. 6.*

On the basis of the D. T. A. investigations and X-ray powder diffraction data the composition of the ore can be outlined as follows.

Manganese minerals. In the western, Upper Liassic manganese ore series manganese had been deposited by all probability originally in the form of colloidal manganese oxy-hydrates. As it was already mentioned the manganese ore in this area is present on the one hand in layered, loose earthy form (e. g. samples *1, 6* and *10*) or sometimes in the form of lenses (samples *9* and *12*). However, smaller or larger globular, vesicular ore nodules usually with a ferruginous crust also occur (as samples *2, 4* and *7*). But independent of appearance, in the "primary manganese ore series cryptomelane appears to be the dominating manganese ore mineral as shown on the D. T. A. curves by the expressed endothermic peak between 780—860 °C, as shown in *Fig. 7.*

It could be observed even in polished ore sections of low quality that the matrix of both the loose, earthy, layered type and of the globular, vesicular harder ore nodules is cryptocrystalline cryptomelane containing more or less limonite. The colloform structure suggests a separation from the colloidal state. Alongside the layers or throughout the ore nodule veinlets harder than the matrix are found. The material of these veinlets sometimes is pyrolusite, cryptomelane and sometimes manganite. Sometimes manganite needles or fine fibrous radiated aggregates of pyrolusite and of other MnO_2 modifications, respectively, can be observed.

Besides cryptomelane, pyrolusite, psilomelane and manganite the presence of todorokite and lithioforite is also obvious what has not been detected up to this time either in the Úrkút or the Eplény manganese ores. GY. BÁRDOSSY [1968] examining manganese ore spots in bauxite found near Eplény first pointed out in them the presence of lithioforite and starting from it the identification of lithioforite was successful in ores of the presently studied area, first of all by X-ray powder diffraction patterns, as shown in *Fig. 11.*

X-ray investigations of the manganese minerals of the seams pointed out also the presence — if sometimes in a rather slight amount — of nsutite, groutite, manganoan calcite and rhodochrosite as well.

The comparison of the Upper Liassic manganese seams in the W and manganese ores found in the redeposited and "secondary" beds of the SE territory suggests that there are certain interdependences between mineral composition and areal distribution. Namely while in the Upper Liassic so called "primary", series, relying upon the results of investigations, cryptomelane appeared to be the most frequent and besides it other manganese oxide minerals play only secondary role, among manganese ore minerals of the redeposited Lower Cretaceous — Middle Eocene series the amount of manganite and pyrolusite appears to grow, then in the "secondary" Lower—Middle Eocene beds again cryptomelane and psilomelane are dominating, pyrolusite and manganite being only subordinate. Lithioforite, todorokite, nsutite can also be found in seams of the southeastern field and in sample *No 24* the X-ray examinations detected the presence of much lithioforite as well, or for example in sample *No 25* the amount of nsutite is also considerable as it can be seen in the X-ray diffraction pattern shown in *Fig. 11.* Manganoan calcite, rhodochrosite are also present naturally in a greater quantity in manganese carbonate-containing clays.

Clay and bauxitic minerals. Examination of clay minerals showed that here as well certain areal distribution can be established. As it could be unequivocally stated from the D. T. A. curves of the corresponding samples and from data summarized

in Table 2., among clay minerals of the Upper Liassic "primary" territory montmorillonite and illite are the characteristic ones, kaolinite plays only a subordinate role. On the contrary, in the southeastern Lower Cretaceous—Middle Eocene redeposited and Lower—Middle Eocene "secondary" beds the dominating clay minerals are kaolinite + sudoite (the amount of the two has not been determined separately) and alongside the *b* axis disordered kaolinite "*b*" (fireclay).

To distinguish between kaolinite + sudoite and kaolinite "*b*" (fireclay) was possible not only on the basis of X-ray powder diffraction data but also from the D. T. A. curves. In samples in which kaolinite and sudoite were involved, the exothermic peak between 965—980 °C indicating the formation of mullite, is sharp, while in D. T. A. curves of samples containing kaolinite "*b*", this peak temperature is lower (880—940 °C) and is not so expressed as in the case of kaolinite. All this can very well be seen when comparing D. T. A. curves of samples *No 30, 38* and *43* with those of *Nos 41* and *46*.

This distribution likely can be connected with differences between the conditions of separation and sedimentation. According to the suppositions manganese ore from the Upper Liassic was separated from seawater in colloidal state in form of oxide-hydrates. Thus this condition — first of all the pH — promoted the formation of montmorillonite while the conditions of sedimentation and later of alteration in the SE "secondary" Lower and Middle Eocene favoured the formation of kaolinite.

As it has already been mentioned previously between the transported and redeposited seams from the Lower Cretaceous—Middle Eocene and the "secondary" series of the Lower—Middle Eocene there is bauxitic clay which markedly thickens towards the abandoned bauxite open-pit. *(Fig. 3.)* In connection with this it can also be stated that in samples where the dominating clay mineral is kaolinite + sudoite and "fireclay" the X-ray examinations showed also the presence of gibbsite, boehmite, diaspore, the amount of which sometimes may be quite remarkable (samples *38 a-b; 41; 46*).

Other minerals. Besides clay and bauxite minerals the presence of goethite, pyrite, hematite, calcite, quartz and anatase in various amount can be detected. What about the limonite incrustation of the nodular ores, from the temperature values of endothermic peaks between 300 and 400 °C in the D. T. A. curves it can be supposed that besides crystalline goethite, pointed out by X-ray investigations and observed under ore microscope, also the presence of lepidocrocite or even more of amorphous limonite can be considered. This is even more suggested by the lower peak temperature (305—330 °C) than in the case of goethite meaning dehydration of FeOOH in some of the samples and then after this peak by the appearing of an exothermic peak, what can be interpreted by recrystallisation.

Mention also must be made of the phosphorus-bearing grey, greenish — yellow bands in the Upper Liassic series (samples *No 11* and *12*) between the radiolarian clay marl with manganese carbonate content and the dark-grey radiolarian clay marl enclosing the ore seams. Examining the phosphorus-bearing mineral of these bands earlier the presence of fluorapatite had been supposed. It was unequivocally stated by Gy. GRASSELLY [1968] by detailed chemical, X-ray powder diffraction data and infra-

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Abbreviations used in the X-ray powder diffraction patterns of *Figs. 11, 12* and *13* are as follows: An: anatase; Boe: boehmite; Cal: calcite; Cr: cryptomelane; Gi: gibbsite; Goe: goethite; Gr: groutite; Gy: gypsum; Ill: illite; Ka: kaolinite; Ka „b": kaolinite "b" (fireclay); Li: lithiophorite; Mn: manganite; Mn—Cal: manganoan calcite; Ns: nsutite; Py: pyrite; Pyrol: pyrolusite; Q: quartz; Rhod: rhodochrosite; Su: sudoite; Tod: todorokite.
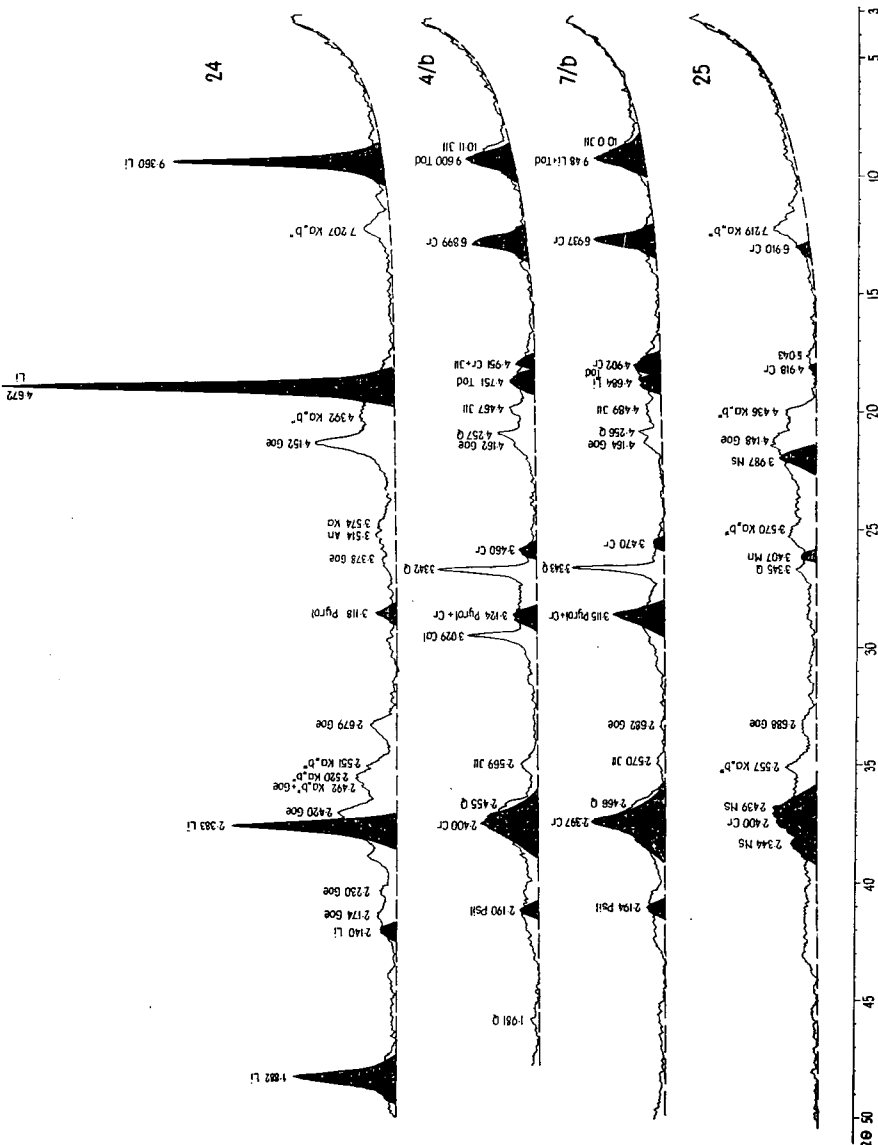
Fig. 11. X-ray powder diffraction patterns of samples containing cryptomelane, lithioforite, todorokite, nsutite.
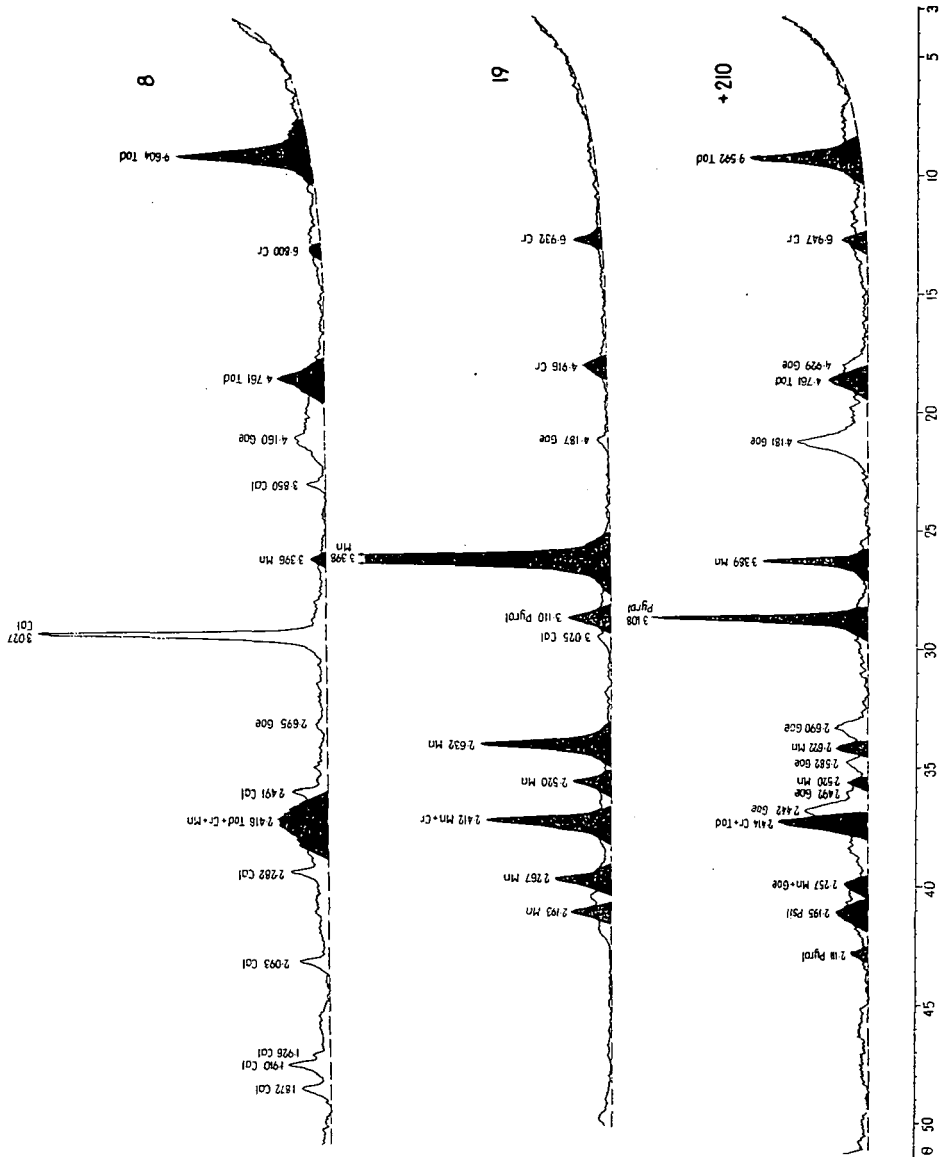
Fig. 12. X-ray powder diffraction patterns of samples containing pyrolusite, manganite, cryptomelane and todorokite.

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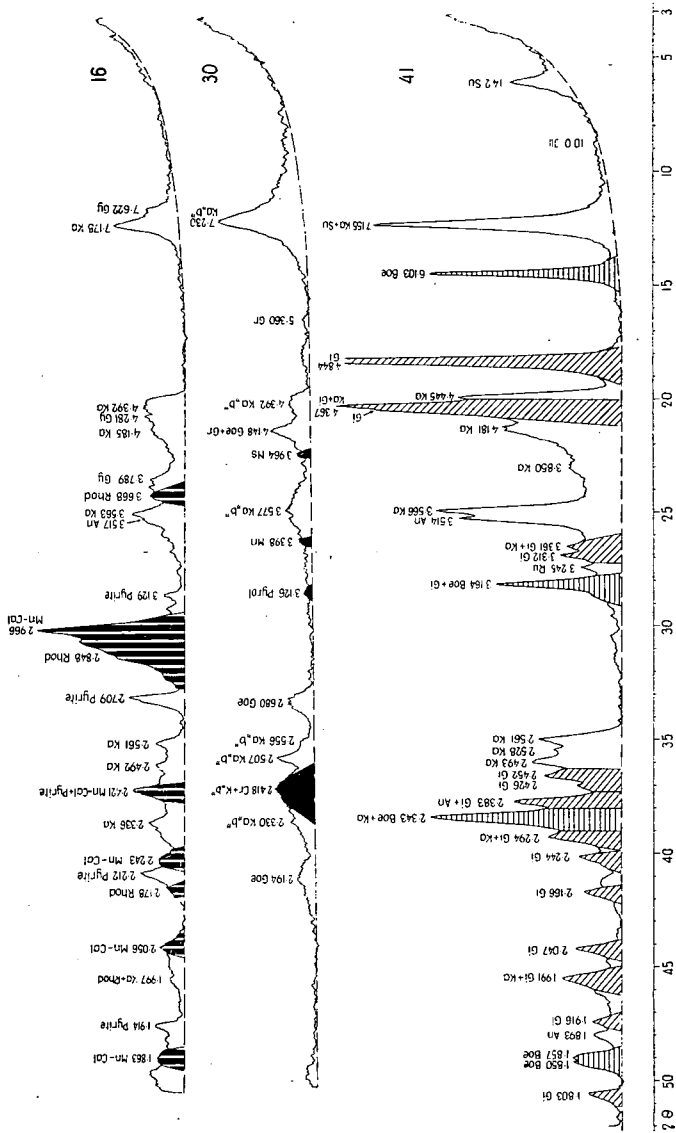
Fig. 13. X-ray powder diffraction patterns of samples containing kaolinite + sudoite, kaolinite "*b*" (fireclay), gibbsite, boehmite, manganoan calcite.

TABLE 2

Semiquantitative estimation of the mineral composition of some samples on the basis of X-ray powder diffraction patterns

Serial number of the samples	Estimated amount of the components						
	>80%	80—60%	60—40%	40—20%	20—8%	8—2%	<2%
I. Upper Liassic "primary" beds of the W ore field							
3.			montmorillo-nite	illite	quartz, pyrite	manganoan cal-cite, feldspar	
4b[1]			cryptomelane	todorokite	illite	psilomelane, pyrolusite, goethite, quartz, calcite	
5.				montmorillo-nite, illite	quartz, goethite	kaolinite	manganoan calcite, rhodochro-site, feldspar
6.				cryptomelane, pyrolusite, lithioforite + todorokite (together)	illite	quartz	
7b[1]			cryptomelane	lithioforite + todorokite (together)	pyrolusite	psilomelane, goethite, quartz	
7c			montmorillo-nite	quartz	illite goethite	manganoan calcite, feldspar	
8b[2]				todorokite, calcite		cryptomelane, goethite	manganite

9a				pyrolusite	goethite	cryptomelane	psilomelane, groutite, lithioforite	quartz
10.				cryptomelane		psilomelane, illite, manganite	pyrolusite, lithioforite, goethite, quartz, calcite	
II. Lower Cretaceous- Middle Eocene reaccumulated allochtonous beds of the SE ore field								
19.[2]			manganite			cryptomelane, pyrolusite	goethite, calcite	
20.				pyrolusite	psilomelane	kaolinite, illite	goethite, quartz	
III. Lower Cretaceous- Middle Eocene „secondary" beds of the SE ore field								
17.	a		kaolinite			hematite, goethite	illite, anatase, calcite	
	b	kaolinite+ sudoite					calcite, goethite, anatase	
16.[3]					kaolinite, manganoan calcite	rhodochrosite	pyrite, gypsum	anatase
24.[1]				lithioforite		kaolinite "b" (fireclay) goethite, pyrolusite		

[1] X-ray diffraction pattern of these samples see in *Fig. 11*.
[2] X-ray diffraction pattern of these samples see in *Fig. 12*.
[3] X-ray diffraction pattern of these samples see in *Fig. 13*.

TABLE 2 — (continued)

Serial number of the samples		> 80%	80—60%	60—40%	40—20%	20—8%	8—2%	< 2%
				Estimated amount of the components				
				III. Lower -Middle Eocene "secondary" beds of the SE ore field				
25[1]					cryptomelane, nsutite, kaolinite "b" (fireclay)	goethite	manganite, quartz	
30[3]				kaolinite "b" (fireclay)	cryptomelane		nsutite, pyrolusite, goethite, groutite, manganite	
38.	a		kaolinite + sudoite			goethite, hematite	gibbsite, boehmite, anatase	diaspore
	b		kaolinite + sudoite			gibbsite	goethite, anatase	
	c				kaolinite "b" (fireclay) cryptomelane	todorokite	pyrolusite, gibbsite	
41[3]			kaolinite + sudoite		gibbsite	boehmite	illite, anatase	
43.					kaolinite "b" (fireclay) cryptomelane, psilomelane	goethite	pyrolusite, manganite, gibbsite	boehmite
46.			kaolinite + sudoite			gibbsite	goethite, anatase	

[1] X-ray diffraction pattern of these samples see in *Fig. 11*.
[2] X-ray diffraction pattern of these samples see in *Fig. 12*.
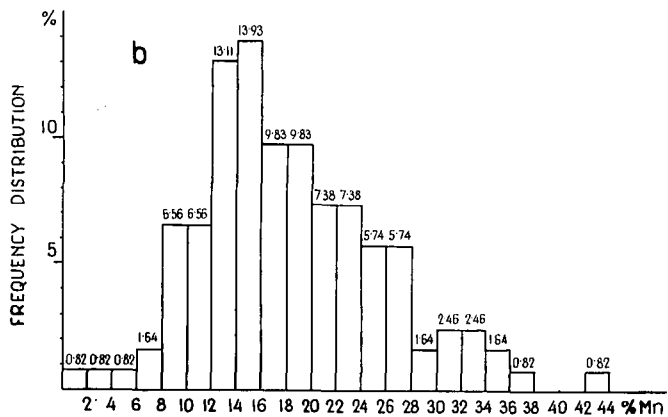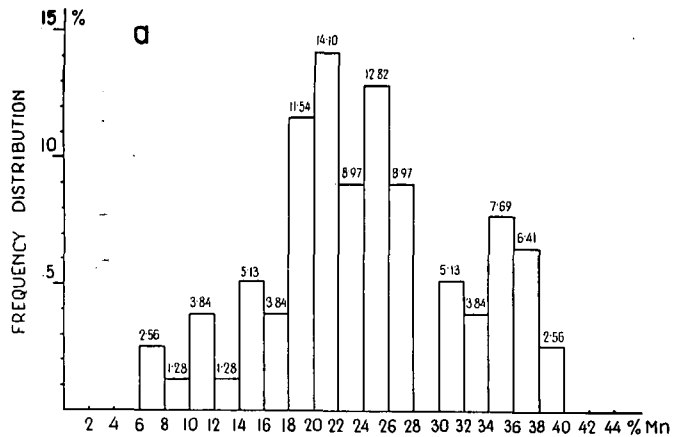[3] X-ray diffraction pattern of these samples see in *Fig. 13*.

Fig. 14. Mn frequency distribution in the "primary"
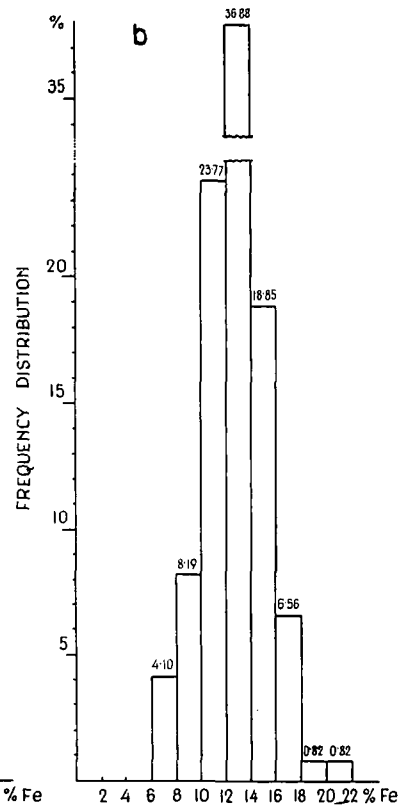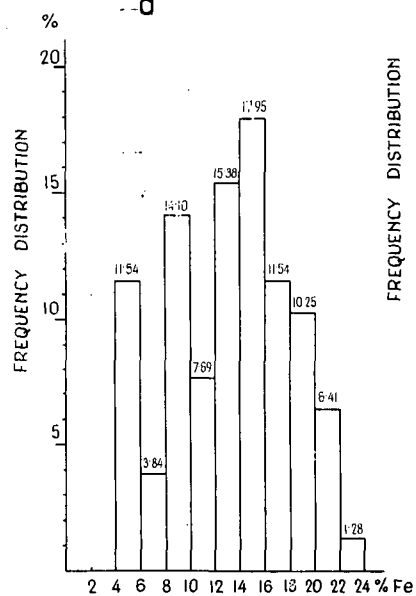*(a)* and in the redeposited *(b)* region.

Fig. 15. Fe frequency distribution in the "primary"
(a) and in the redeposited *(b)* region.

TABLE 3

Fe$_2$O$_3$, MnO, active O and alkali content of some samples

Serial number of samples	Fe$_2$O$_3$%	MnO%	O%	Na$_2$O%	K$_2$O%	MnO$_x$ x=
1.	3,99	58,42	10,66	0,35	3,5	1,808
5.+	10,25	not determ.		0,19	3,47	—
6.	5,58	53,58	9,83	0,3	2,87	1,812
7a	3,79	59,84	11,17	0,35	2,85	1,827
7b	3,82	63,06	11,45	0,35	3,52	1,804
8a	—	58,61	11,69	0,31	0,67	1,884
8b	6,91	41,96	8,44	0,36	0,94	1,891
9a	50,75	22,40	4,15	not determ.		1,821
9b	9,97	42,15	8,61	not determ.		1,905
10.	12,17	33,89	7,12	0,32	3,30	1,931
12.	27,60	41,43	6,52	0,15	2,10	1,920
15.+	38,05	8,07	1,46	—	1,67	1,801
18.	2,59	66,16	10,99	0,1	2,04	1,736
19.	2,47	71,65	10,22	0,1	0,85	1,632
20.	17,14	24,14	3,96	0,2	0,3	1,727
24.	19,59	49,70	10,23	0,12	0,4	1,912
25.	16,20	33,24	6,84	0,18	0,8	1,912
30.+	9,54	28,79	5,55	0,25	0,54	1,854
38.	10,05	29,43	6,07.-	0,69	0,3	1,914
41.+	2,67	—	—	0,05	0,2	—
43.	24,61	21,75	4,68	0,5	0,75	1,954

Remarks: Data of samples denoted with+ refer to average samples, the other data to selected material.
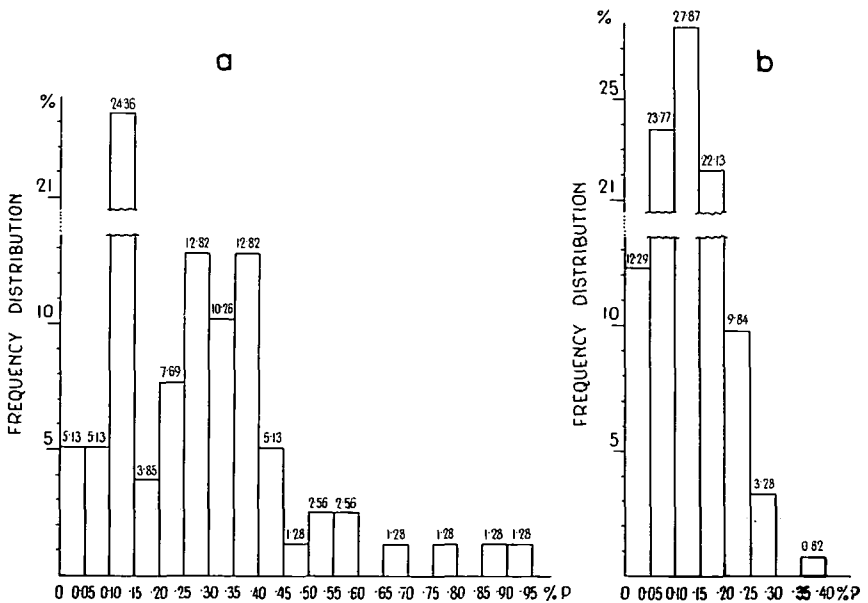

Fig. 16. P frequency distribution in the "primary" (a) and in the redeposited (b) region.
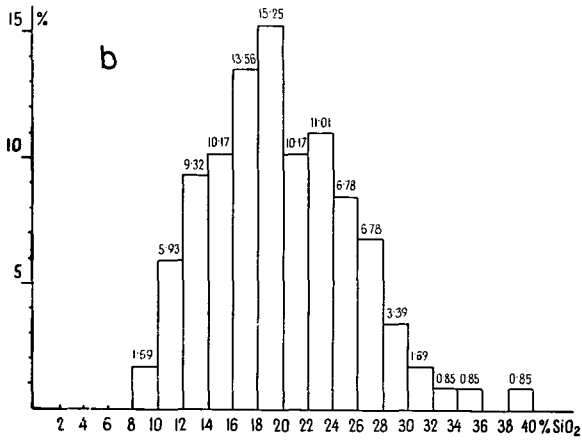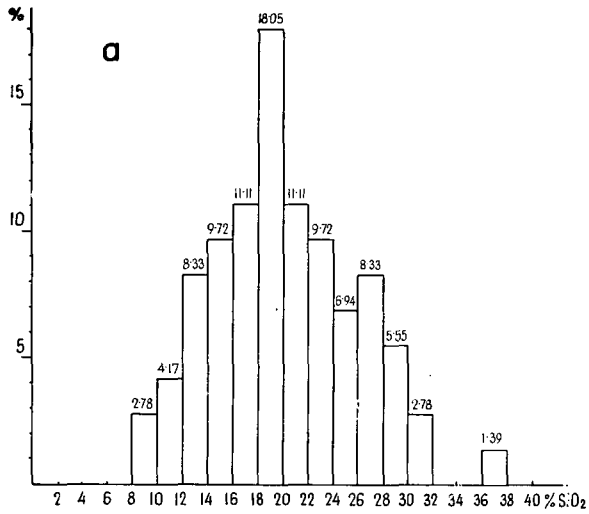
Fig. 17. SiO$_2$ frequency distribution in the "primary"
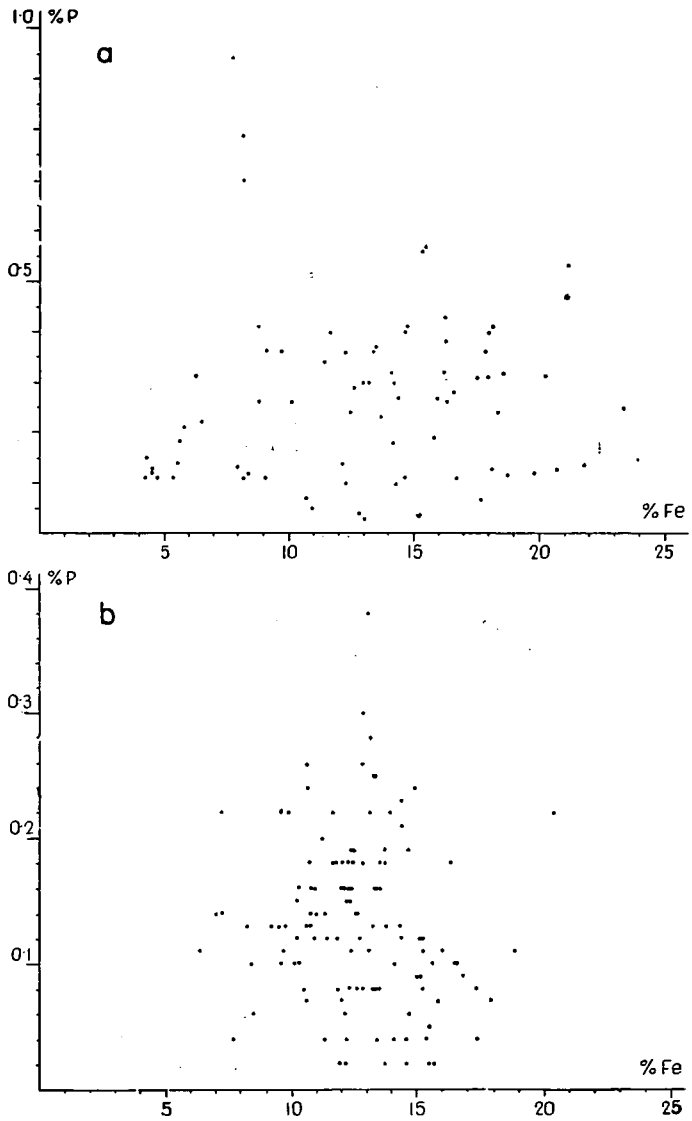*(a)* and in the redeposited *(b)* region.

Fig. 18. Correlation between Fe and P content in the "primary"
(*a*) and in the redeposited (*b*) region.

red spectroscopy that in the Úrkút and Eplény fields the phosphate-mineral is hydroxy-carbonate-apatite, with a low F-content, which is very near dahllite.
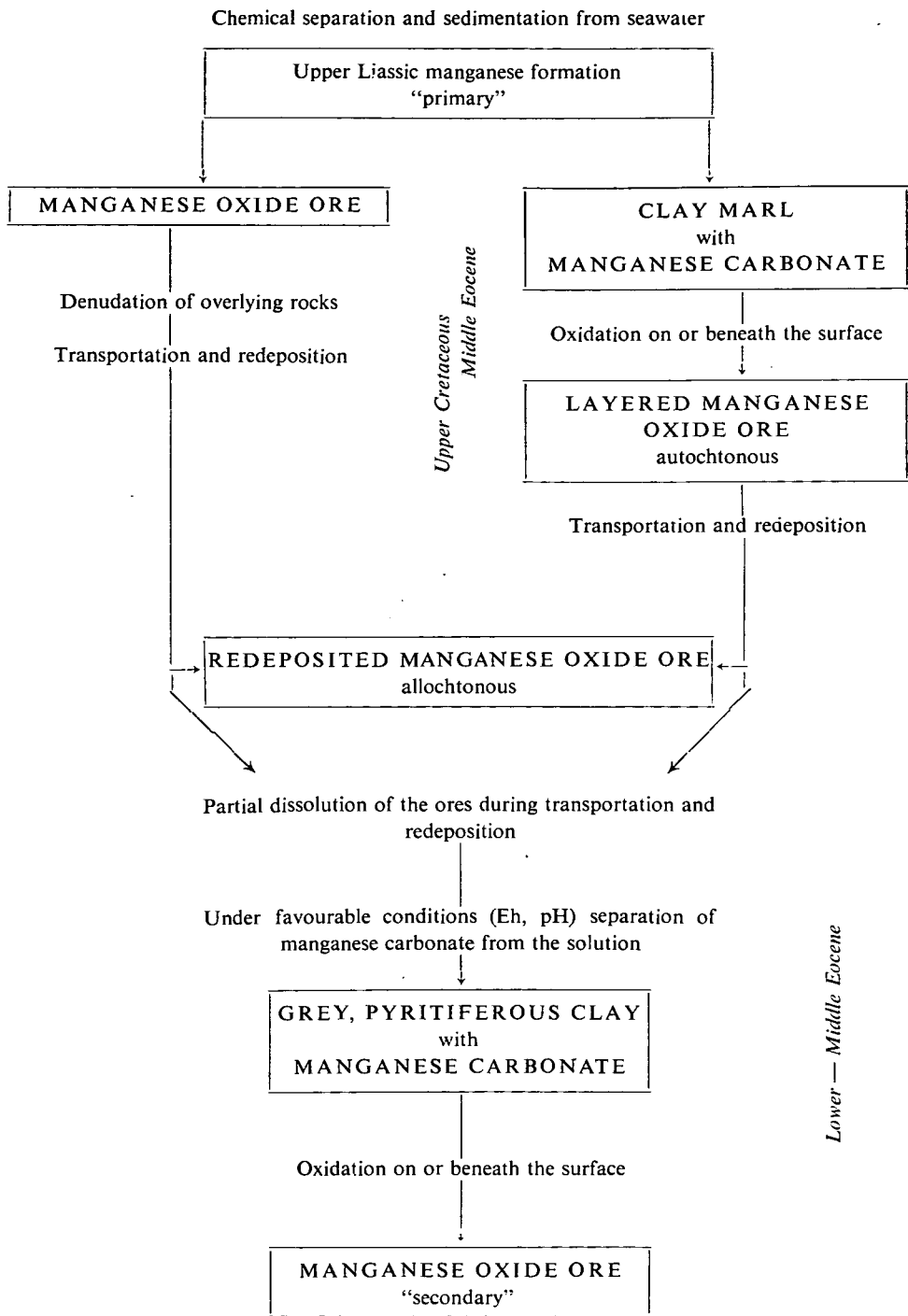
Chemical analysis first of all aimed to establish whether there is any difference in the distribution of Fe, Mn, P, SiO_2 between the "primary" area and the redeposited beds. On determining the above mentioned components in 78 samples taken from the "primary" beds and in 122 samples of the redeposited area, the frequency distribution is shown by the histograms represented in *Figs. 14—17.*

On comparing histograms of these two areas it can be stated that those of the primary area, either in the case of Mn, Fe or P have several maxima, while, on the contrary, in the redeposited area on the one hand the chief maximum appears at a lower percentage and the histogram will be more balanced, near unimodal on the other. In the course of the transportation and reaccumulation of the material of the „primary" beds — as it has already been mentioned above — partly manganese could be dissolved: the overall manganese content of the reaccumulated manganese beds is somewhat lower than that of the "primary" beds. At the same time the process of transportation, redeposition, dissolution and precipitation connected with these, may result in a more even distribution of the components. The only exception is SiO_2, in the distribution of which no marked difference could be established relying upon the histograms.

A very interesting picture can be obtained concerning the correlation between Fe and P content in the two areas *(Fig. 18).* On the basis of 78 samples collected from the "primary" territory certain positive correlation seems to exist and although the points are rather scattered, as a rule the P content increases with the Fe content. Similar interdependence was pointed out by GY. GRASSELLY and J. CSEH NÉMETH [1961] in the manganese ore beds of the Úrkút slope, as was also stated by ASOKA MOOKHERJEE in the Indian gondites [1961]. This latter author pointed out that this connection can be interpreted by the chemisorption of the PO_4 anion by colloidal, positively charged $Fe(OH)_3$. In contrary to this Fe per cent *versus* P per cent does not show such a connection in the reaccumulated area. It seems probable that a correlation between iron and phosphorus content can be experienced only in territories where iron precipitated mostly in colloidal from and PO_4 also reached in the solution the required concentration and so through chemisorption there was a possibility for PO_4 being sorbed. In areas, however, as e.g. the redeposited beds of the SE field in Eplény, where rough or fine debris of the "primary" manganese ore seams and that of the overlying and underlying rocks were already in solid form and redeposited again and where colloidal iron hydroxide did not play such a part as in the "primary" seams, the adsorption of PO_4 did not take place, even more when both in the transporting and depositing medium PO_4 concentration decreased below the value necessary for the flocculation of colloidal $Fe(OH)_3$.

Detailed analysis has been made from several samples first of all to determine the total amount of manganese oxides, the manganese — iron ratio and the overall grade of oxidation of manganese ores coming from different series. Data are summarized in Table 3. The grade of oxidation at least suggests that in oxide ores mostly manganese oxides — oxy-hydrates of higher valence — are found and the Mn:O ratio is under the value $MnO_{1,8}$ only in the case of a few samples, first of all where considerable manganite content is involved.

Summarizing, the formation of the Eplény manganese ores can be outlined as follows:

Chemical separation and sedimentation from seawater

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┌────────────────────────────────────────────┐
│        Upper Liassic manganese formation     │
│                   "primary"                  │
└────────────────────────────────────────────┘
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┌──────────────────────────────┐   ┌──────────────────────────────────────┐
│ MANGANESE OXIDE ORE   │   │   CLAY MARL   │
└──────────────────────────────┘   │   with   │
                                                     │   MANGANESE CARBONATE   │
Denudation of overlying rocks   └──────────────────────────────────────┘

Transportation and redeposition   *Upper Cretaceous*   *Middle Eocene*   Oxidation on or beneath the surface

                                                     ┌──────────────────────────────────────┐
                                                     │   LAYERED MANGANESE   │
                                                     │   OXIDE ORE   │
                                                     │   autochtonous   │
                                                     └──────────────────────────────────────┘

                                                     Transportation and redeposition

┌──┐
│ REDEPOSITED MANGANESE OXIDE ORE   │
│   allochtonous   │
└──┘

Partial dissolution of the ores during transportation and
redeposition

Under favourable conditions (Eh, pH) separation of
manganese carbonate from the solution

┌──────────────────────────────────────┐
│ GREY, PYRITIFEROUS CLAY   │
│   with   │
│ MANGANESE CARBONATE   │
└──────────────────────────────────────┘   *Lower — Middle Eocene*

Oxidation on or beneath the surface

┌──────────────────────────────────────┐
│ MANGANESE OXIDE ORE   │
│   "secondary"   │
└──────────────────────────────────────┘

ACKNOWLEDGMENTS

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