DATA ON THE GEOLOGY AND MINERALOGY OF THE MANGANESE ORE DEPOSIT OF URKUT II

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Manganese Ore Mines of Urkut

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INTRODUCTION

In their previous work [Gy. Grasselly—J. Cseh Németh, 1961] the authors have dealt with the geology and mineralogy of the most valuable field, i. e. with that of the Slope ("Lejtakna") of the manganese ore deposit of Urkut. In order to continue their investigations they intend to describe on similar basis the further fields of the manganese ore district to be able to give a comprehensive picture of the deposit from geological and mineralogical viewpoint.

The field of the Slope is situated in the E part of the manganese oxide ore district at present known. On the SW part of the district lies the field of the shaft No. II extending to W uninterruptedly but in carbonateous development. The area is structurally strongly disturbed in his S boundary and the prospecting points to strongly denuded area poor in exploitable ores. The exploration of the field of the shaft No. II began in 1941 and since then is continually produced.

On the E boundary of the shaft No. II ranges essentially a denudation-zone but in one part the uninterrupted deposit crops out where the open cut mining of "Bocskorhegy" (Mt. Bocskor) has been opened in 1959 and still in work.

The field of the shaft No. III is situated between the field of the Slope and the area of carbonateous development. Essentially it may be divided into two fields, i. e. into northern and southern, respectively, as these fields are separated owing to the denudation. The northern field remained in the field of a syncline, whereas the southern area is the continuation of the manganese bed of the Slope, dipping uniformly in W direction. The two fields of the shaft No. III on the W are interrupted by a big re-accumulated zone and between this zone and the field of carbonateous development already mentioned follows again a manganese ore field of layered development. This field — named also deep level area — is structurally the continuation of the field of the shaft No. II but the two parts are thrown with about 100 m-s level difference along the Csinger-fault. The area of the shaft No. III has been worked since 1953.

In the southern part of the area, i. e. in the field of the "Kövestábla" smaller autochtonous oxide bed has been explored by recent prospecting whose detailed knowledge is the aim of further examinations.

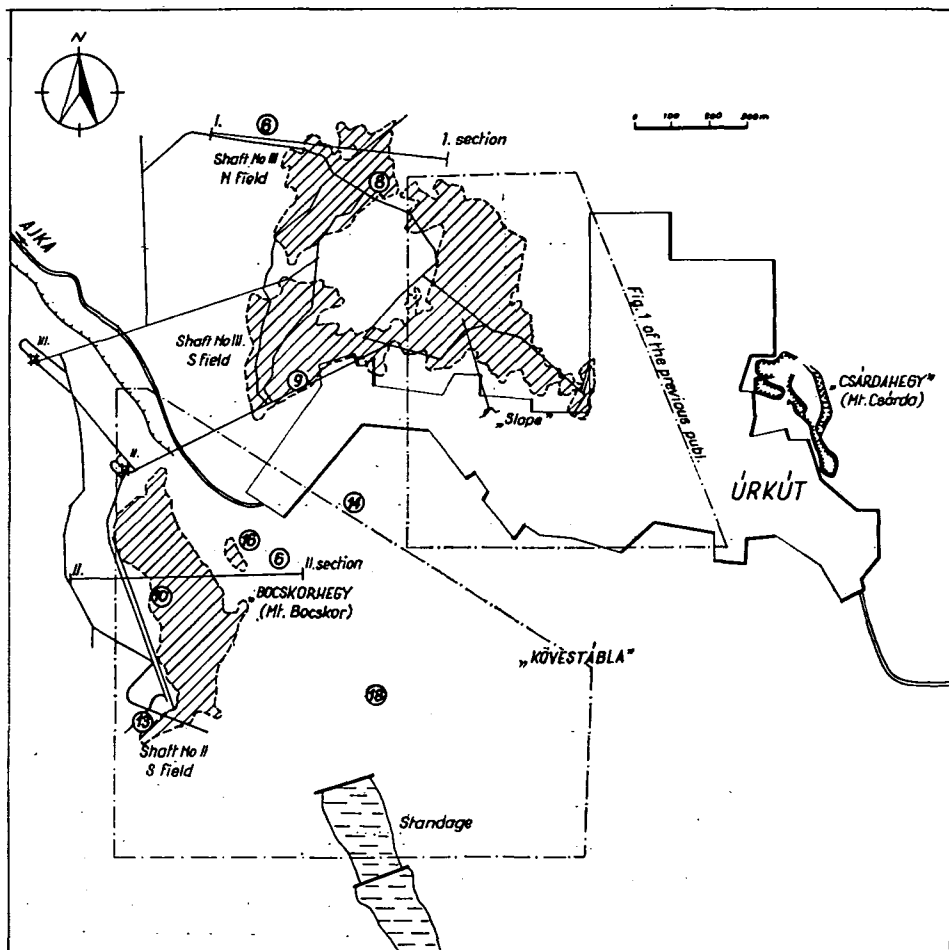The location of the areas mentioned is shown in *Fig. 1.*

Fig. 1. Sketching geological map of the manganese ore district of Urkut showing the locations of the sections discussed in the present and in the previous work. The numbers in circles mark the corresponding *Figs.* in the text.

THE GEOLOGICAL STRUCTURE OF THE AREAS

In the geological structure of the areas investigated is of fundamental characteristic that in the capping of the manganese beds everywhere Cretaceous layers are deposited whereas in the field of the Slope only the Eocene can be found. So, he denudation, oxidation and re-accumulation of the manganese series in the area nvestigated is limited only to the Pre-Cretaceous era.

Lower Liassic: in the Lower Liassic rhynchonellian cherty limestone, in some places crynoideal limestone can be found. These Lower Liassic rocks have been reached merely in some places of the area discussed, first of all in the explored field of the "Bocskorhegy" and of the "Kövestábla". Connecting to these areas on the surface still lower Liassic layers are frequent.

Middle Liassic: it is represented by red, pinkish cherty limestone, red nodular limestone as well as by clay with cherty streaks in the underlying basement. The cherty limestone is leached in the greater part of the area, firstly in the northern and southern territory of shaft No. III and its relict, the chert-flour, is very frequent.
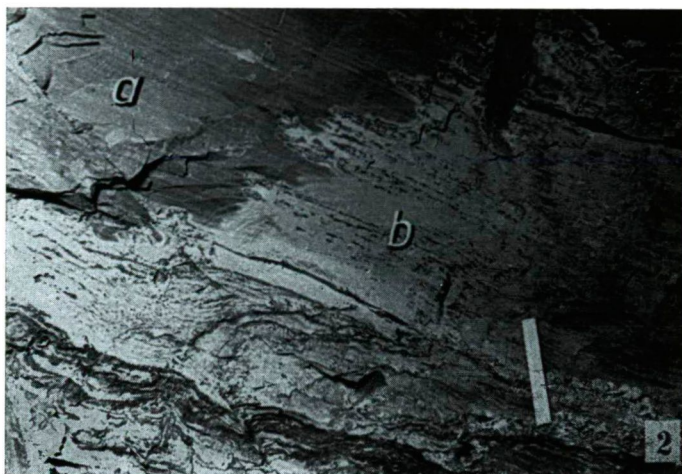

Fig. 2. Alteration and transition, respectively, of dark gray radiolarian clayey marl (*a*) into yellow radiolarian clay (*b*). Shaft No. II.

Fig. 3. Re-accumulated (reworked) manganese series, manganese ore, chert and limestone fragment. N field of the shaft No. III.

In other areas the Middle Liassic rocks are often re-accumulated and in these cases the Middle Liassic is represented by clay series with chert debris of greater thickness.

Upper Liassic: in the area investigated the manganese carbonate ore remained in patches, the oxidized manganese beds as well as the dark gray radiolarian clayey marl in the capping of these and the yellow radiolarian clay formed by the alteration of the latter belong to the Upper Liassic. These rocks may be found in their original places merely in smaller parts of the area, mostly they are re-accumulated, even sometimes traceless denuded.

The thickness of the oxidized ore bed in the areas discussed is generally 2—3 m reaching the 5—6 m thickness only in some places of the "Bocskorhegy". The smaller manganese carbonate ore patches to be found in this field represent transition zones too, inasmuch pure carbonate ore beds are to be seldom established, as the oxidation has already been started in some part of the bed. In the territory of "Kövestábla" the manganese oxide ore is present in two beds separated from each other by yellow radiolarian clay of larger thickness.

Dogger: on the W boundary of the manganese oxide ore field, i. e. on the western border of the shaft No. II and in the deep level field of the shaft No. III, a more completely developed Jurassic sequence can be found. The ore is everywhere of carbonateous development and on the carbonate ore series a chert bank of 0,3—0,5 m in thickness is situated, thereupon a brown, 3,0—5,0 m thick ammonitic marl is deposited turning into thick, green, cherty calcareous marl. The ammonitic marl — on the basis of his fauna — is still Upper Liassic (Toarcian) whereas the green, cherty calcareous marl belongs to the Dogger. The underlying manganese carbonate series was protected by this cover from the devastation as well as from the oxidation. Oxidation of smaller degree can be found merely in some places along tectonical lines.

Cretaceous: at the end of the Jurassic, during the New-Kimmerian orogenetic movements, the structural unity so far of the manganese ore fields is broken down and a considerable devastation is started. The oxide ore territories will be partly reworked, reaccumulated, so in these fields the Cretaceous starts with re-accu-

Fig. 4. Manganese oxide ore (*b*) overfaulted onto manganese carbonate bed (*a*) in the transition zone of the shaft No. II, where the Dogger can already be found in the capping.

Fig. 5. Re-accumulated oblique-layered, detrital capping series in the open cut mining of the „Bocskorhegy".

mulated rocks. These rocks have been built up at first from broken fragments of the manganese ore bed, later different fragments, e. g. chert and limestone debris, respectively, are mixed to them.

In the further part of the Cretaceous, dark gray carbonaceous clay (Aptian), gray nodular limestone is deposited turning gradually into yellowish-white requiaenian limestone (Albian). The latter becomes into western direction thicker and reaches the maximal thickness of 150 meters.

Eocene: the area of the shaft No. III is covered beside the Cretaceous also by Eocene rocks among them in the Lower Eocene by carbonaceous clay and in the Middle Eocene by nummulitic limestone. Eocene formations in the field of "Bocskorhegy" and "Kövestábla" and of the shaft No. II can only in insignificant patches be found.

Pleistocene: the area is covered by sandy loess in patches of 1,0—5,0 m in thickness.

THE DEVELOPMENT OF THE MANGANESE OXIDE ORE BEDS

Sector of shaft No. III: in the northern part of this field the manganese oxide bed generally reaches 2,0—3,0 m. In the lower part of the manganese ore series generally brown clay with manganese patches of 0,5—0,7 m thickness is deposited, whereon fine-bedded manganese oxide ore follows. The layers are mostly very uniform in the bed of shaft No. III, thicker ore banks or nodules can seldom be found. On the other hand, the oxidized ore types of loose structure are very frequent. In the field there can be found in several places carbonate—oxide ore transition zones, wherein compact manganese oxide ore banks — sometimes thicker than 0,5 m — can be found *("Stückerz")*. In the layered manganese oxide ore bed relicts are frequent maintaining the bedded structure but becoming clayey during the oxidation process.
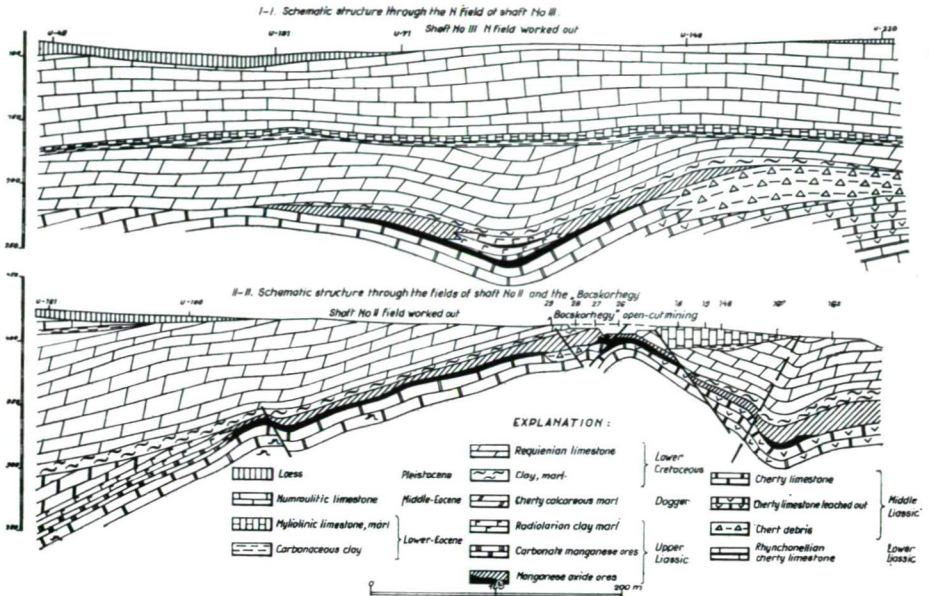
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Fig. 6. Geological sections through the fields of the shaft No. III and of the shaft No. II and of the „Bocskorhegy", respectively.

In the cover of the manganese bed phenomena pointing to oxidation and other alteration, respectively, are frequent, as shown in *Fig. 7*. Where the oxidation had already been started, often can be noted that the upper part of the bed becomes gradually loose and clayey.
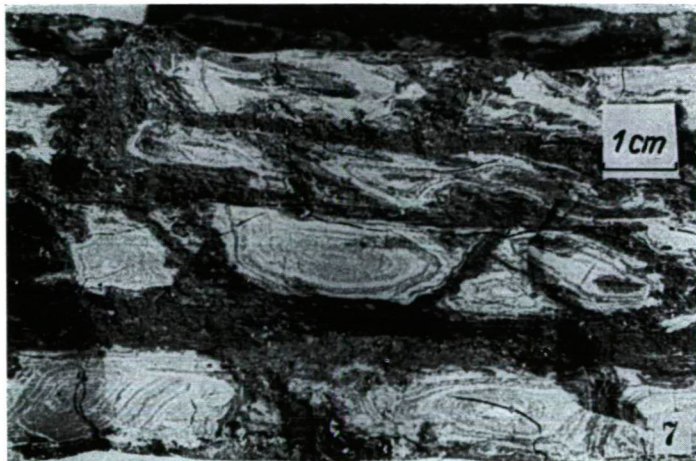

Fig. 7. Yellow radiolarian clay altered due to oxidation of the manganese bed. The fissures are filled with manganese oxide. The sample originates from the „*a*" layer shown in *Fig. 9*. Shaft No. III.

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The section of the north and south field of the shaft No. III — as shown in Fig. 8 and 9 — is such an area wherein in the lower part the carbonateous ore development is still to be found. It can be stated that the almost 2 m thick carbonate bed is impoverished in manganese content more than in average, on the other hand that the manganese content in the overlying loose, layered manganese oxide ore fluctuates at random, even within the same layer. In the yellow radiolarian clay explored 5—10 cm thick manganese oxide streaks can be seen.

In the eastern boundary of the areas of shaft No. III in the bed there can often be found autochtonous parts thinning out replaced by coarse — fine — detrital manganese layers, finally after 10 m or more breadth they too turn into denuded areas. In some places — in the vicinity of chute No. 4 — the "muddy" manganese oxide beds of considerable thickness are frequent representing the average quality of the original manganese bed and they consist of the completely ground material of the original manganese beds.
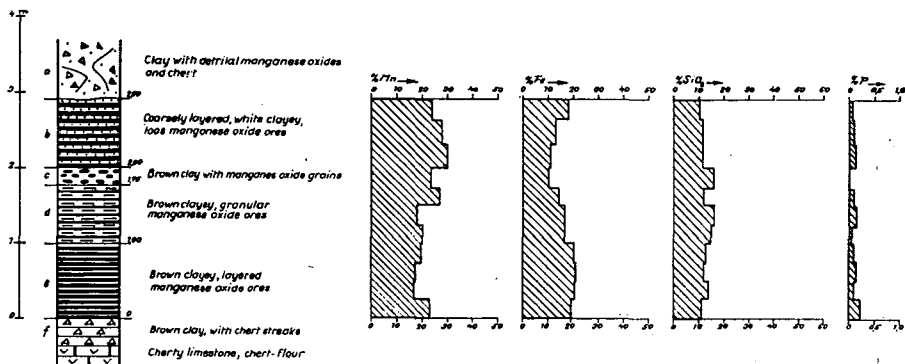

Fig. 8. Section of the ore bed and the distribution of the Mn, Fe, SiO₂ and P content therein· N field of the shaft No. III (+275).
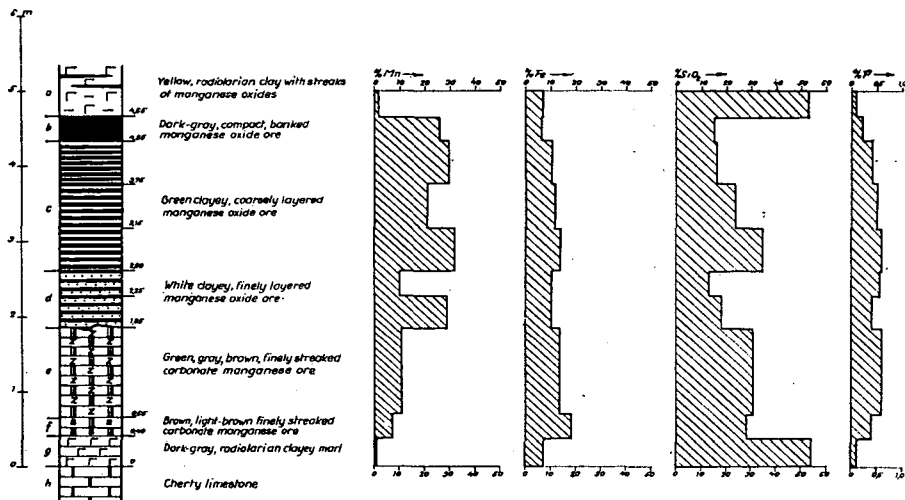

Fig. 9. Section of the ore bed and the distribution of the Mn, Fe, SiO₂ and P content therein. S field of the shaft No. III (+315), transitional zone.

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The development of the manganese oxide ore bed of the deep level area of the shaft No. III on the basis of exploratory boring seems to be similar to the development of the manganese bed of the shaft No. II discussed later.

Sector of shaft No. II: the most uniformly developed area of the manganese ore district was the field of the shaft No. II. In the western border of this field there is a manganese carbonate ore bed of 8,0—10,0 m in thickness. This bed thinned out gradually toward east and in the exploitation border of to-day, through a transition zone, turns into a totally oxidized bed.

The oxidized manganese bed consists of manganese oxide ore types of different structure in accordance with the original carbonate ore types. This recognizable character, however, more and more vanishes moved away from the transition zone presumably owing to surface-effects and a more increased oxidation, respectively. This feature is shown in *Fig. 10* by the section of principle. Therein is seen how the different carbonateous layers pass into adequate oxidized ones among them into manganese oxide layers of different structure.

CARBONATE | OXIDIZED

Dark gray radiolarian clayey marl — Yellow radiolarian clay

Gray rodochrosite bank (0,30—0,40 m) — Compact, banked, oxidized manganese ore

Green, gray, brown, coarsely streaked manganese carbonate ore (1,50—3,00 m) — Green, clayey, coarsely layered manganese oxide ore

Brown, light-brown, coarsely streaked manganese carbonate ore (0,50—1,50 m) — Brown clayey, coarsely layered manganese oxide ore

Gray rodochrositic bank (0,20—0,30 m) — Compact banked manganese oxide ore

Black, light-brown, finely streaked manganese carbonate ore (1,00—4,00 m) — Brown clayey, finely layered manganese oxide ore with nodules of manganese ore in brown clay

Brown, light-brown, finely streaked manganese carbonate ore (1,00—2,00 m) — Brown clayey, finely layered manganese oxide ores; granular manganese oxide ore

Nodules of manganese oxide ore

Green, gray, finely streaked manganese carbonate ore (1,50—2,50 m) — Brown clay, finely layered granular manganese oxide ore

Dark gray radiolarian clayey marl (0,50—0,70 m) — Yellow, brown radiolarian clay

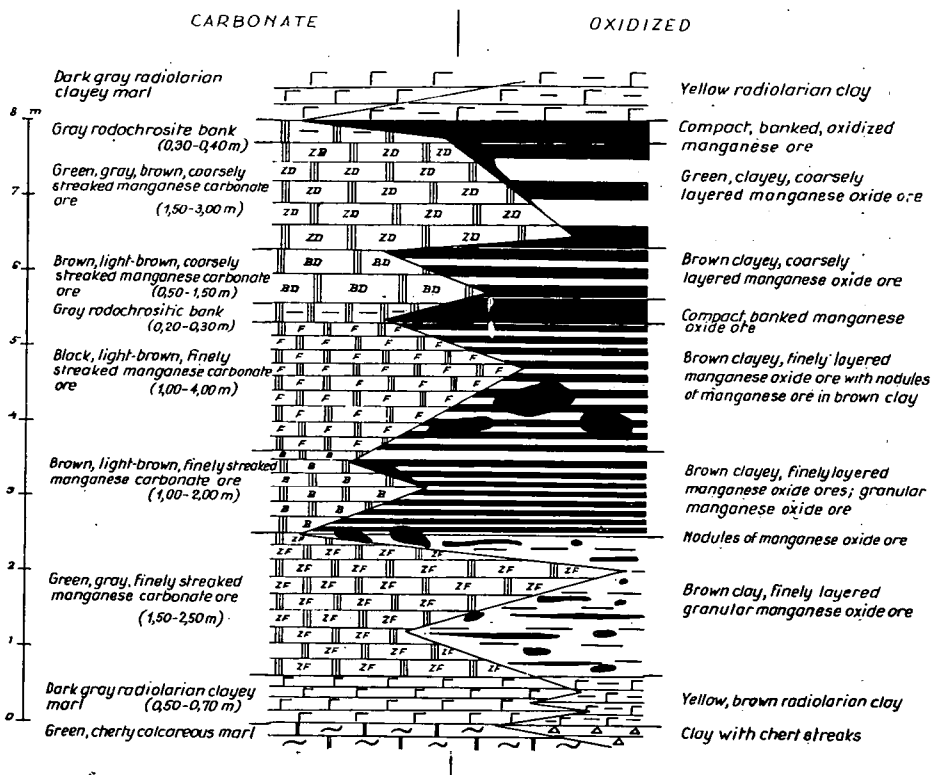Green, cherty calcareous marl — Clay with chert streaks

Fig. 10. Section of principle at the edge of the shaft No. II showing the effect of oxidation.

In the bottom of the bed, dark gray radiolarian clay is settled in a thickness of 0,50—0,70 m turning into yellow — gray clay during the oxidation as visible in *Fig. 2.* Thereupon green-gray fine-banded carbonate ore follows, 1,50—2,0 m in thickness from which brown clay with manganese grains and streaks, respec-

tively, is formed. In the boundary of carbonate — oxide ores, manganese oxide nodules are frequent as seen in *Fig. 11*.

On the fine-banded, green, gray manganese carbonate ore, manganese carbonate layers of similar appeerence but light brown in color are settled in 1,0—2,0 m thickness. During the oxidation from these layers brown argillaceous, fine-banded manganese oxide ore, granular manganese ore, rarely layers with minute manganese oxide nodules are formed. In the middle of the bed black- light brown, fine — banded manganese carbonate ore is deposited 1,0—2,0 m in thickness containing, beside the rodochrosite, manganese oxides too. From these types are formed due to the oxidation the brown, argillaceous fine-banded manganese oxide
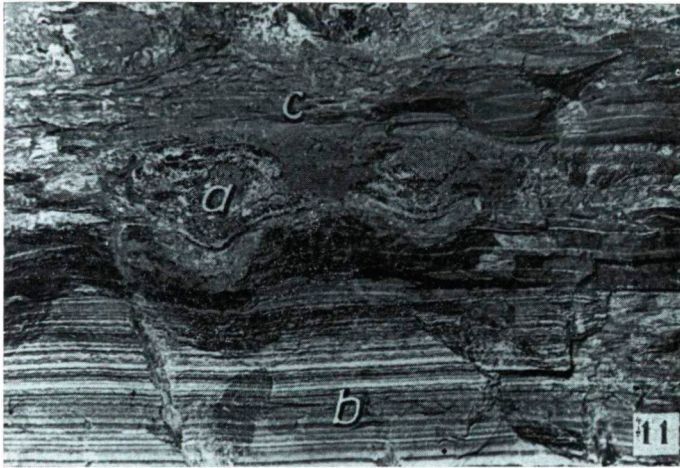
Fig. 11. Manganese oxide nodules (*a*) in the boundary of green, gray fine-layered manganese carbonate ore (*b*) and of manganese oxide ore (*c*). Shaft No. II.

Fig. 12. Manganese oxide bank (*a*) oxidized from black, carbonate ore with remnant of the latter (*b*).

layers wherein manganese nodules, often reaching 1,0 m, are frequent. Within these nodules relicts of the manganese carbonate ore — meanwhile becoming argillaceous — can be found as it is seen in *Fig. 12*. On the black carbonate layers gray rodochrositic layer is settled 0,2—0,3 m in thickness, from which compact, banked manganese oxide ore is formed during the oxidation.

In the upper third of the bed there are coarse-banded manganese carbonate ore types. The thickness of these brown—light brown ores ranges between 0,50—1,50 m. During the oxidation they turned into brown, argillaceous, coarse-banded ore, however, the oxidized manganese ore types of loose structure are also frequent.

In the upper part of the bed green — gray coarse-banded manganese carbonate ore is deposited forming due to later oxidation mainly green argillaceous coarse-bedded manganese oxide ore. Along the boundary of the manganese carbonate and of the oxide ores consequently a compact oxide ore bank — 0,3—0,5 m thick — is situated.

The manganese carbonate bed is covered by gray rodochrositic bank of 0,3—0,4 m in thickness forming during the oxidation also a compact oxide ore bank.

In the capping of the manganese carbonate bed there is a dark-gray, banked, radiolarian clayey marl wherein, however, rarely manganese carbonate streaks can be noted. These resulted in yellow radiolarian clay and oxide streaks, corresponding to the adequate manganese carbonate ones, respectively.

In the transition zones, as a rule, the oxidation has begun in the upper part of the bed and has gradually increased toward east. It is to be mentioned that the continuity of the beds in the southern part of the shaft No. II is limited to smaller areas due to strong tectonical movement, a uniform development can only be established in smaller continuous areas. The capricious disintegration of the bed renders difficult the identification and gives problems in the exploitation. The characteristics of the bed of the shaft No. II is demonstrated by *Fig. 13*.
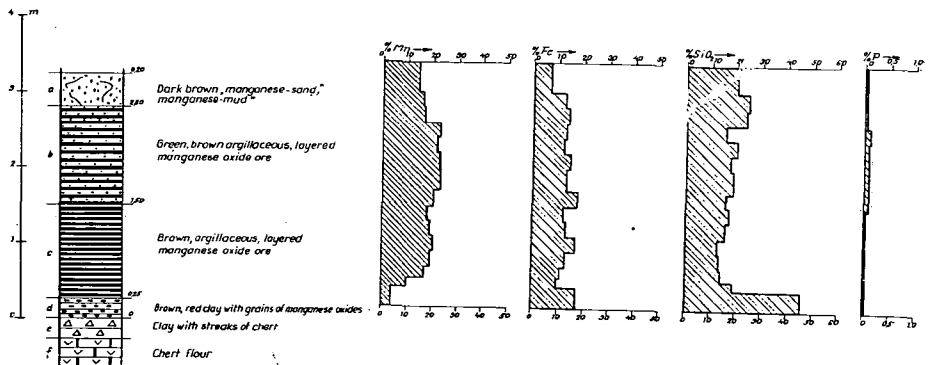

Fig. 13. Section of the bed and the distribution of the Mn, Fe, SiO₂, P content therein. Shaft No. II, borehole U-164.

"*Bocskorhegy*": The manganese bed of shaft No. II gradually rises to the surface and along the Csinger-fault it crops out in the caving where this anticline structure has been opened up in the last years. The manganese bed of this area is learned in details. The development of the bed is shown in *Fig. 14* and the view of the open
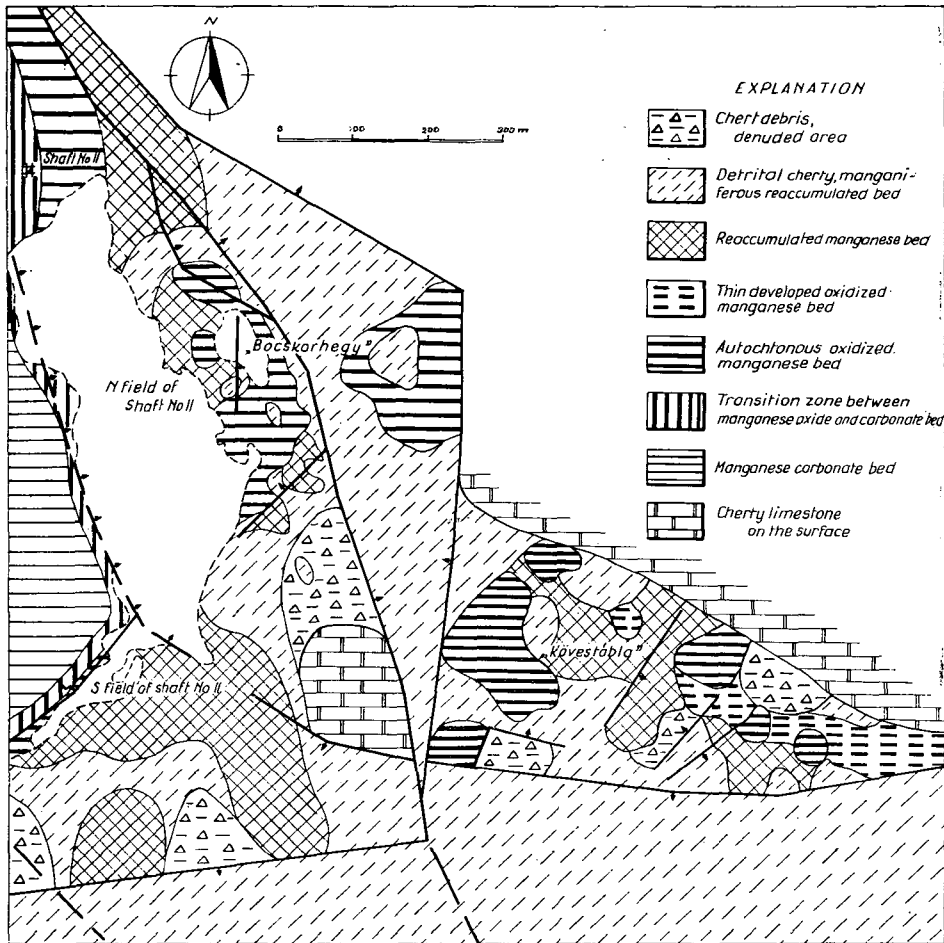
Fig. 14. Sketch of the ore-development on the fields of shaft No. II, „Bocskorhegy" and „Köves-
tábla", respectively.

EXPLANATION

Chert debris, denuded area

Detrital cherty, mangani-ferous reaccumulated bed

Reoccumulated manganese bed

Thin developed oxidized manganese bed

Autochtonous oxidized manganese bed

Transition zone between manganese oxide and carbonate bed

Manganese carbonate bed

Cherty limestone on the surface

cut mining of the "Bocskorhegy" is shown in *Fig. 17*. The development of the bed
is essentially similar to that of the shaft No. II only in the chemical composition,
firstly in the essential decrease of the P content, there reveal minor differences.
The thickness of the beds are nearly the same but in the "Bocskorhegy" re-accumu-
lated interbeddings are frequent *(Fig. 15)*. The pecularities of the bed of "Bocskor-
hegy" are shown by the section in *Fig. 16*.

"*Kövestábla*": in the "Kövestábla", i. e. in the continuation of the open cut
mining of the "Bocskorhegy", along complicated structural lines in smaller area
autochtonous manganese ore can be established, mostly re-accumulated before
the Cretaceous. According to the development of this area also originally there
had existed a thinner manganese carbonate bed here and there with double-bed
development as mentioned above.

Fig. 15. Layered manganese oxide bed interrupted by a re-accumulated part in the open cut mining of the ,,Bocskorhegy".
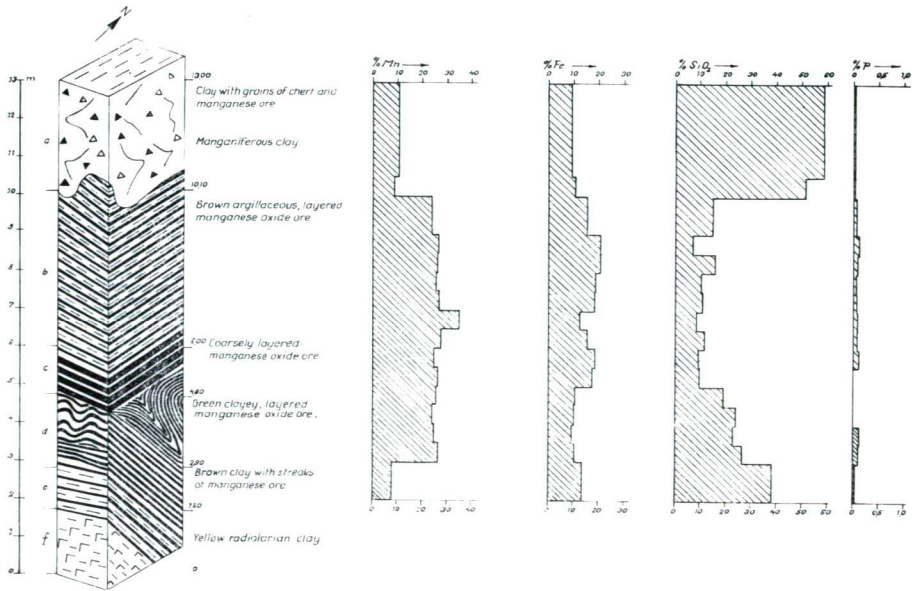
Fig. 16. Section of the exploratory shaft of the ,,Bocskorhegy" and the distribution of the Mn, Fe, SiO₂ and P content therein.

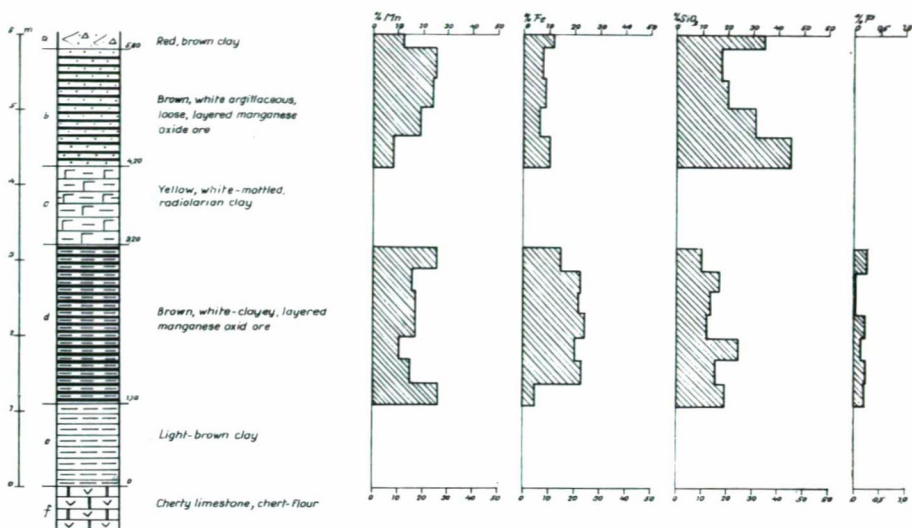*Fig. 17.* View of the open cut mining of the ,,Bocskorhegy".

Fig. 18. Section of the bed and the distribution of the Mn, Fe, SiO₂ and P content therein. ,,Köves-
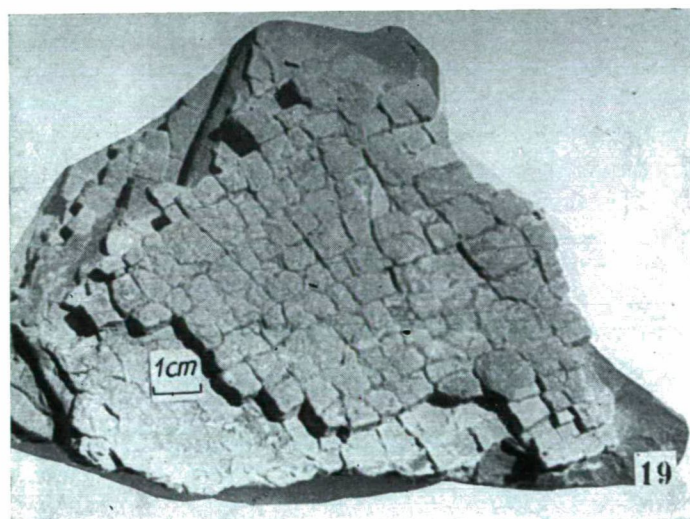tábla", borehole K-72.

Fig. 19. Sample of manganese carbonate ore showing the rhombohedral cleavage, collected
from the Slope.
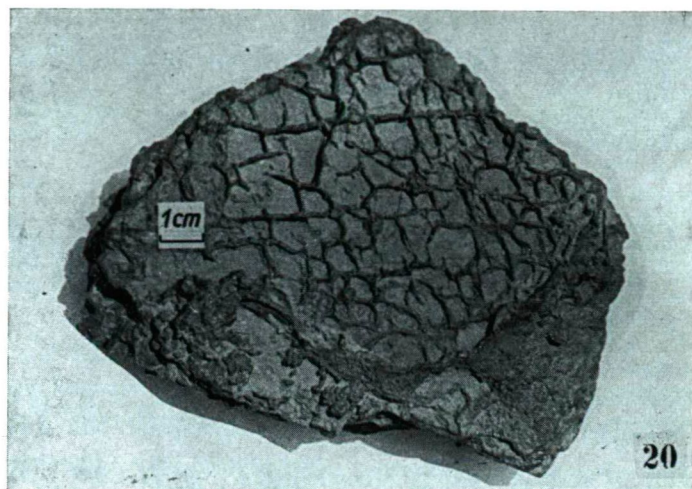
Fig. 20. Fissures according to cleavage direction filled by manganese oxide during oxidation. Collected from the „Kövestábla".
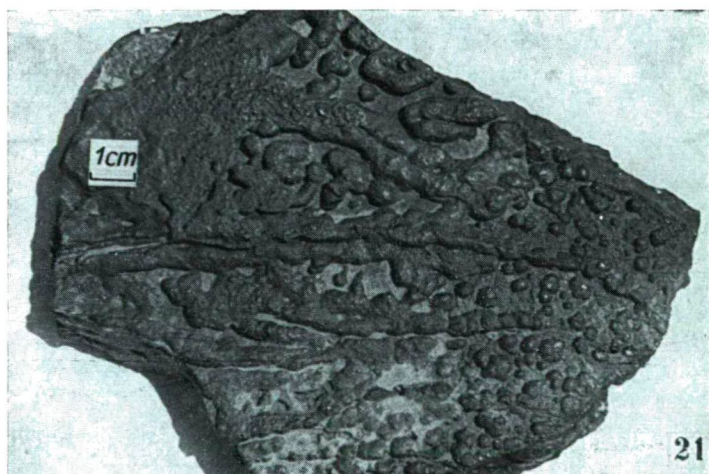
Fig. 21. Surface of an oxidized cleavage plane. Collected from the „Kövestábla".

The carbonate bed croped out in the western part of the anticline of the "Köves-tábla" — as can be seen in *Fig. 1* of the pertinent previous publication of the authors — is oxidized, banked and bedded. The oxidation often proceeds along the rhombo-hedral cleavage planes of the original manganese carbonate ore as seen in *Fig. 20*, The reticulation along the cleavage is well visible in the sample shown in *Fig. 19*. however, without any detectable oxidation. Along the planes of the oxidized layers there can often be found also globular — vesicular surface indicating to colloform formation shown in *Fig. 21*.

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The mineral composition of the ores of the areas investigated is fairly mono-tonous and essentially is like the mineral association of the ores of the Slope. How-ever, a fact and an assumption, respectively, is worth mentioning. As it has been already mentioned in our previous work about the geology and mineralogy of the Slope, the manganite in the ores of Urkut occurs more frequently than the ave-rage, stated in the literature. In the field investigated, especially in the transition zone between carbonate and oxide ores, *the manganite is relatively very frequent.* It occurs as cavity filling in coarse-grained crystal aggregates within the stubby prisms show a rhytmical, zonal arrangement *(Fig. 22)*. Sometimes the manganite forms radiated aggregates built up from larger crystals, which aggregates are sur-rounded by a band of smaller manganite crystals of mosaic structure *(Fig. 24)*. Then and there the cavity is filled by manganite crystals arranged at random *(Fig. 23)*. It forms often veinlets filling fissures in the cryptocrystalline cryptomelane — pyrolusite matrix formed earlier. These fissures are often produced by shrinkage of the earlier colloidal material due to the loss of water.

The crystals within the manganite veinlets form sometimes irregularly arranged aggregates or they are symmetrically grown into the fissures from its both sides and the little open space in the middle of the veinlet is often filled later by chal-cedony.

The replacement of manganite by pyrolusite can well be observed in many polished ore sections as for example in *Fig. 25*, where the replacement of the man-ganite crystals embedded in fine crystalline matrix consisting of cryptomelane and pyrolusite, is already started. Under higher magnification also within the single manganite crystals minute pyrolusite veinlets and patches, respectively, are seen.

For the sake of supporting the ore microscopical observations also the *differen-tial thermal analysis* of some of the samples in question was carried out. The samples for the DTA were taken from the polished ore sections investigated microscopically.

At the identification of the manganite by DTA the problem may arrise that iron oxides as the lepidocrocite and goethite have their characteristic endothermic peak between the same temperature interval as the manganite itself, that is, between 300—400 °C.

Therefore, DTA curves were made for comparison from two "limonite" samples. One of them originates from Urkut and was taken from a limonitic crust of a manganese ore concretion. The other sample (compact, radiated) was admixed to manganite in a ratio of 5—10—20 per cent. In addition, the iron content of some samples investigated by DTA was also been determined and taken as if it were present as FeOOH. The DTA curves of the "limonite" samples and those of the mixtures, respectively, show that partly the characteristic endothermic peak of


Fig. 22. Cavity filling consisting of aggregate of rhythmically, zonal arranged manganite crystals. Crossed nicols, ×68.

Fig. 23. Crystal aggregate of manganite. Crossed nicols, ×68.

Fig. 24. Manganite as cavity filling. On the left greater columnar manganite crystals, right from the middle aggregate of smaller manganite crystals of mosaic structure, right very fine-gra-ined pyrolusite with cryptomelane: the cavity is bordered by a rim of manganite crystals. Crossed nicols, ×68.

Fig. 25. Manganite crystal remnants in fine-grained pyrolusite-cryptomelane groundmass. The manganite crystals are already partly replaced by the pyrolusite. Crossed nicols, ×136.
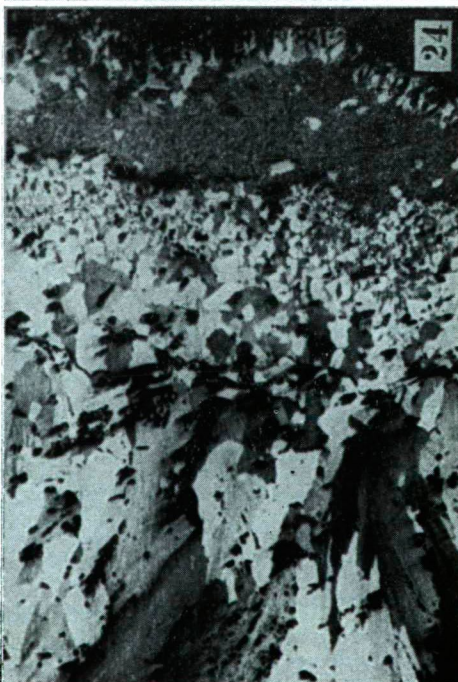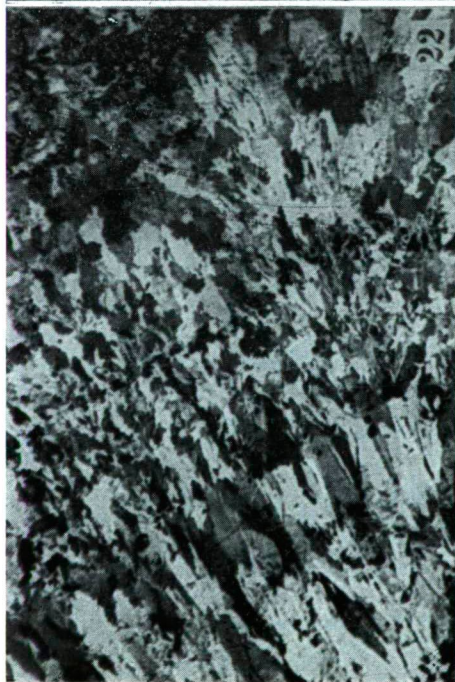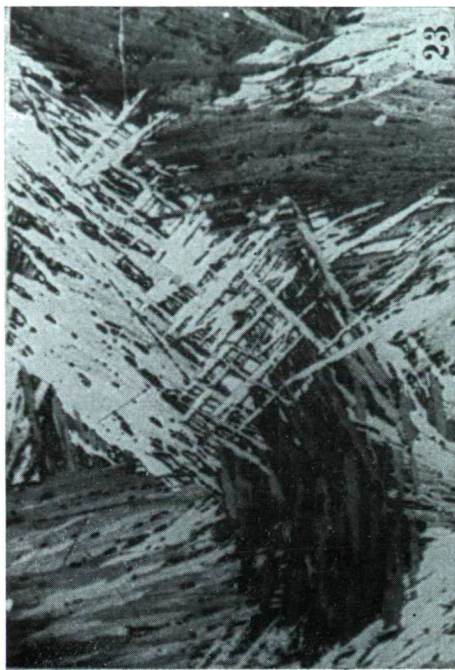
Figs. 22—25.

the "limonite" samples is at somewhat lower temperature than that of the manganite partly by decreasing "limonite" content in the mixtures the corresponding peak becomes considerably smaller *(Fig. 38)*. On the other hand, according to the analyses, the iron content of the samples, calculated as FeOOH, does not exceed 14 per cent. Such amount of goethite or lepidocrocite can not result in such pronounced peaks as seen in our DTA curves. Hence, the endothermic peak between 300—400 °C, in accordance with the microscopical observations, indicates the presence of manganite.

The iron content and the corresponding FeOOH content, respectively, of the samples is as follows:

S a m p l e	Fe ≈ Fe OOH		DTA curve, see in Fig.
	in weight per cent		
Selected material of a small manganite veinlet. Sample No. II/4	4,55	7,23	39/1—b
The same sample but the material is selected from the compact matrix. Sample No. II/4	7,12	11,33	39/1—a
Selected material from a manganite veinlet. Sample No. II/5	0,84 .	1,33	39/1—d
The same sample but the material is selected from the compact matrix. Sample No. II/5	2,84	4,52	39/1—c
Manganese ore sample with cryptomelane and pyrolusite and manganite. Sample No. II/15	4,39	6,98	39/2—h
Compact, radiated, fibrous aggregate of manganite and MnO₂ modification. Sample No. III/4	trace		40/1—c
Black, oxidized manganese ore sample taken from the carbonateous field of the shaft No. III	8,60	13,68	40/2—d

Figs. 26—28. Fine-fibrous, plumose or fan-like aggregates of a MnO₂ modification in a veinlet of silky luster containing considerable amount of manganite too. Crossed nicols, ×68. The DTA curves of the material of this veinlet and that of the surrounding matrix, respectively, see in *Fig. 39/1 a—b.*
Fig. 29. Colloform bands of cryptomelane bordered in some places by sammetblende. Between the bands later manganite. Plain light, ×68.
Fig. 30. Colloform cavity-filling. The wide, multilayered band is composed largely of cryptocrystalline MnO₂ modification alternating with thinner cryptomelane layers. The numerous cracks presumably resulted due to the shrinkage of the gel-like material. Plain light, ×68.
Fig. 31. Fragments of a multi-layered colloform band consisting of MnO₂ modification and cryptomelane cemented by a ferruginous groundmass wherein minute manganite crystals are embedded. Plain light, ×68.
Fig. 32. Multi-layered cavity-filling consisting of alternating layers of cryptocrystalline MnO₂ modification and cryptomelane. Left it is intersected by a manganite veinlet. At bottom, in the middle, there is also manganite. In top, middle, very poorly polished cementing ferruginous matrix. Plain light, ×68.
*Fig. 33.* Colloform, cryptocrystalline cryptomelane in ferruginous matrix. Plain light, ×68.
*Fig. 34.* Coarse-fibrous pyrolusite crystal aggregate. Crossed nicols, ×68.
Fig. 35. Ferruginous fragments bordered in places by thin interlayered rim of sammetblende and pyrolusite, cemented by poorly polished, felt-like fine-crystalline pyrolusite. Right cryptocrystalline cryptomelane. Crossed nicols, ×68.
Fig. 36. Cryptocrystalline cryptomelane (in top, left) bordered by interlayered bands of very fine-fibrous pyrolusite oriented arranged and of cryptomelane. Crossed nicols, ×136.
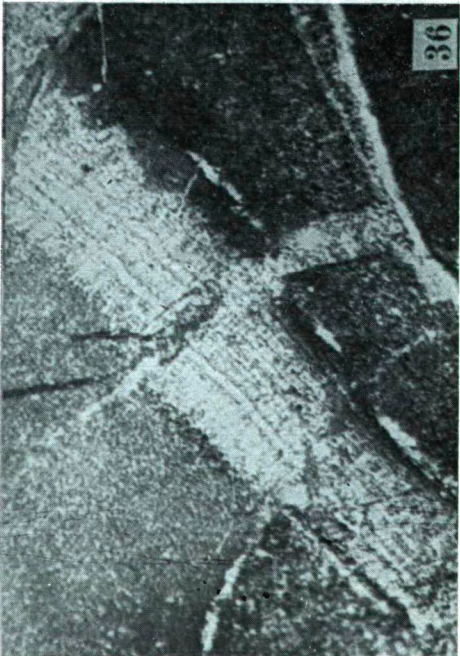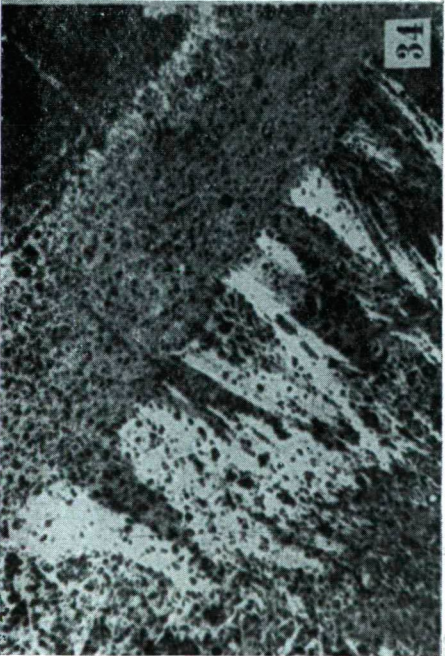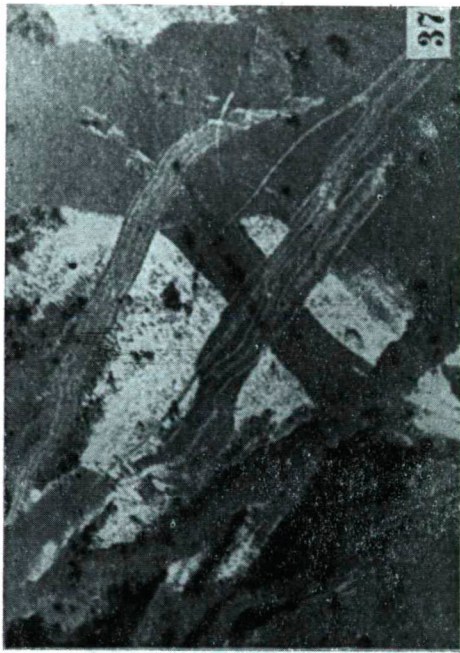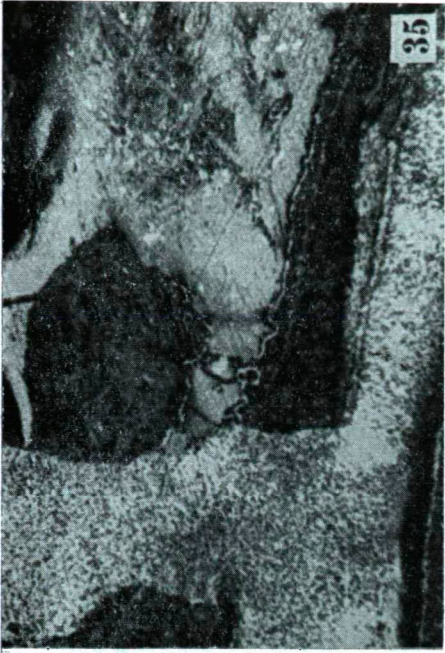*Fig. 37.* Very fine-fibrous pyrolusite aggregate and complex symmetrically layered veinlets of similarly fine-fibrous pyrolusite in the groundmass consisting, of cryptomelane. Crossed nicols, ×136.

Figs. 26—29.

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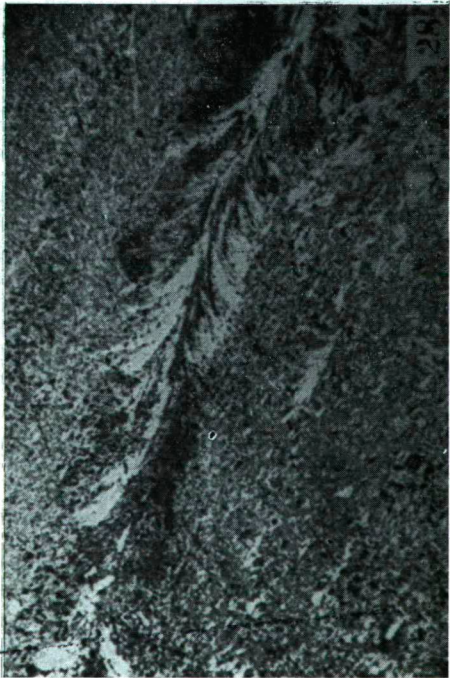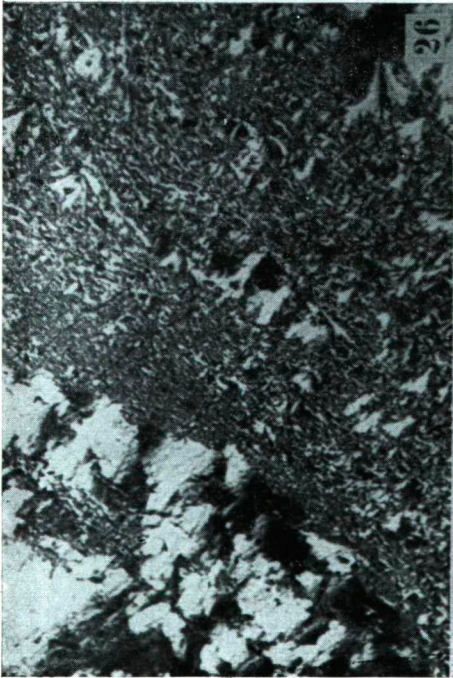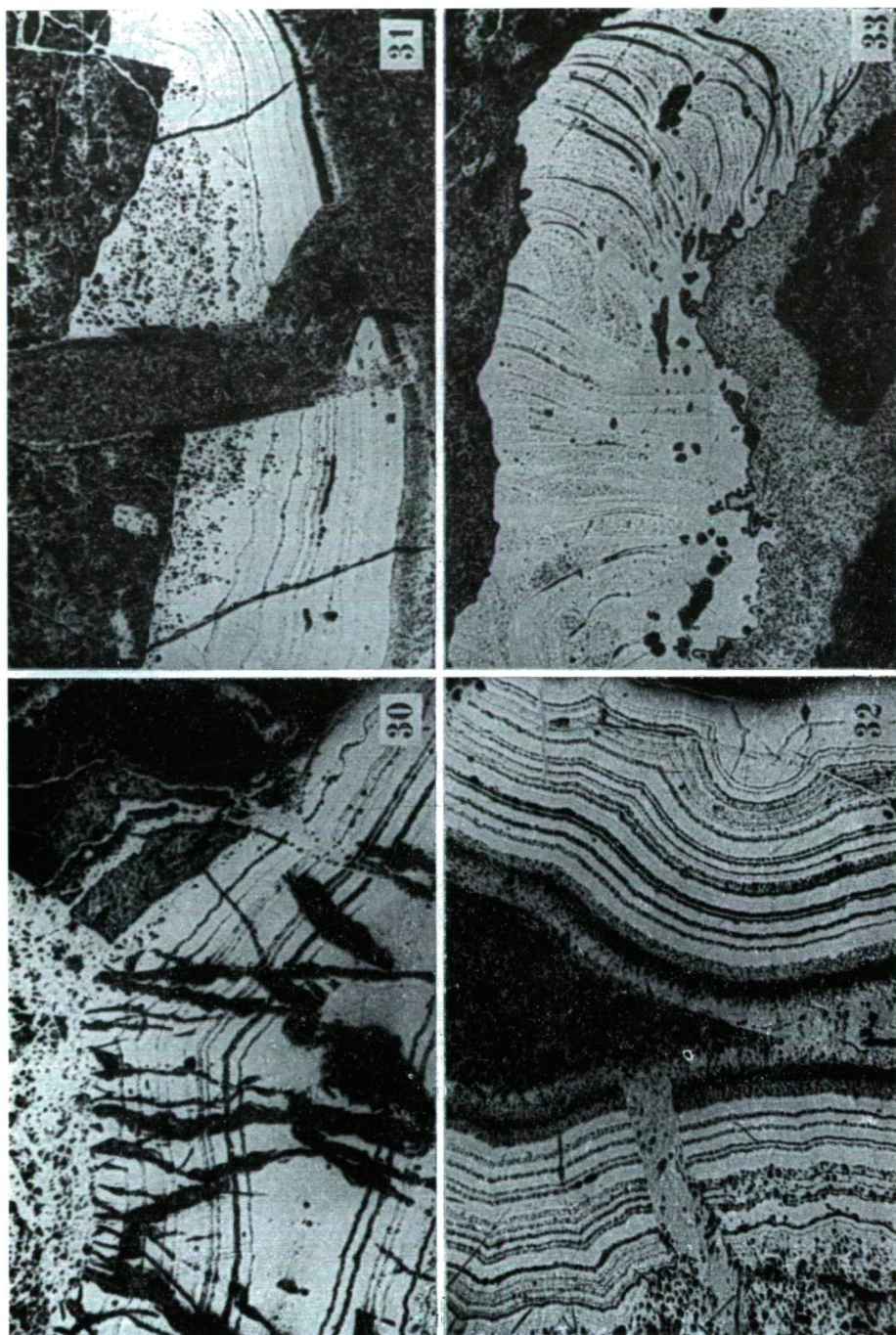
Figs. 30—33.

Figs. 34—37.

The DTA curves show a further peculiarity too. Namely, the endothermic peak corresponding to the β-$MnO_2 \rightarrow \alpha$-Mn_2O_3 transformation is not always at about 620—640 °C as it would be in the presence of the most stable β-MnO_2 modification, i. e. in that of the pyrolusite but this peak is at about 600° even at a lower temperature as shown in *Figs. 39—40*. The peak mentioned appears at lower temperatures mostly in samples containing manganite phase too, although the presence of manganite can not be considered as a preliminary condition of the lower temperature of the $MnO_2 \rightarrow Mn_2O_3$ transformation. In samples containing only pyrolusite, with or without manganite, the peak is always over 600 °C. It may be supposed that the presence of manganite may be associated with the appearance of a MnO_2 modification other than pyrolusite which modification would have a lower temperature of transformation. The pyrolusite and the other modification assumed can occur together, For example the DTA curve of a fine-fibrous pyrolusite sample of silky luster from Urkut shows, beside the small manganite peak at about 300 °C, a small endothermic peak at 580 °C and a greater one at 640 °C. The latter corresponds
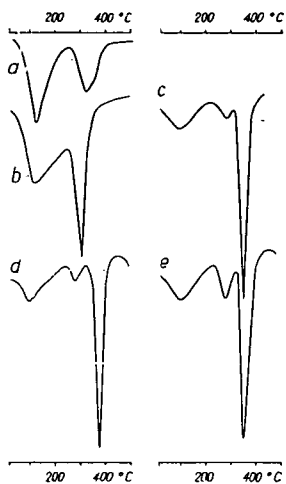

Fig. 38. DTA curves of limonite samples and those of mixtures of limonite + manganite, respectively:
  a) Limonitic crust of a manganese ore concretion from Urkut
  b) Limonite 100 per cent
  c) Limonite 5 per cent — manganite 95 per cent
  d) Limonite 10 per cent — manganite 90 per cent
  e) Limonite 20 per cent — manganite 80 per cent.

to the pyrolusite, whereas the former may origin from an other MnO_2 modification. *(Fig. 41)*.

The question is, the presence of what kind of MnO_2 modification may be supposed. GLEMSER, GATTOW, MEISIEK in their detailed and manysided papers [1960, 1961], concerning the $MnO_2 \rightarrow Mn_2O_3$ transformation, stated that the more disordered was the structure of the MnO_2 modification from which the stable β-modification formed, the lower is the temperature of the transformation. This temperature is — in their opinion — at 620 °C in the case of β-MnO_2 (corresponding to natural pyrolusite), 600 °C in that of the ramsdellite and the transformation of the β-MnO_2 into α-Mn_2O_3 takes place at a still lower temperature (between 500—540 °C) in the case of γ-, η- and δ-MnO_2, respectively.

DTA curves relating to artificial and natural γ-MnO_2 modification can be found in several papers but at present the aim is not to give a comprehensive enumeration of publications dealing with the DTA of the different MnO_2 modifications, merely some of them are mentioned. Thus, for example SOREM and CAMERON as well as ZWICKER et al. dealt with the occurrence of a wide-spread manganese oxid, that of the nsutite and mangano-nsutite, respectively, which may be considered as a natural modification of the γ-MnO_2. The last mentioned authors give the DTA curves of these manganese oxides too. Similarly, SREENIVAS [1957] gives the

DTA curves of an artificial and a natural γ-MnO_2 in his paper. Several DTA curves of different MnO_2 modifications, among them that of the γ-MnO_2 too, are given in the paper of MCMURDIE and GOLOVATO [1948].
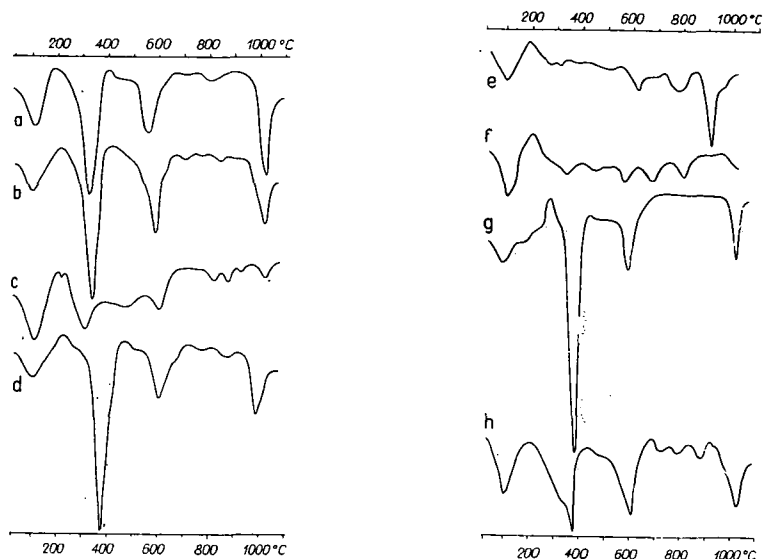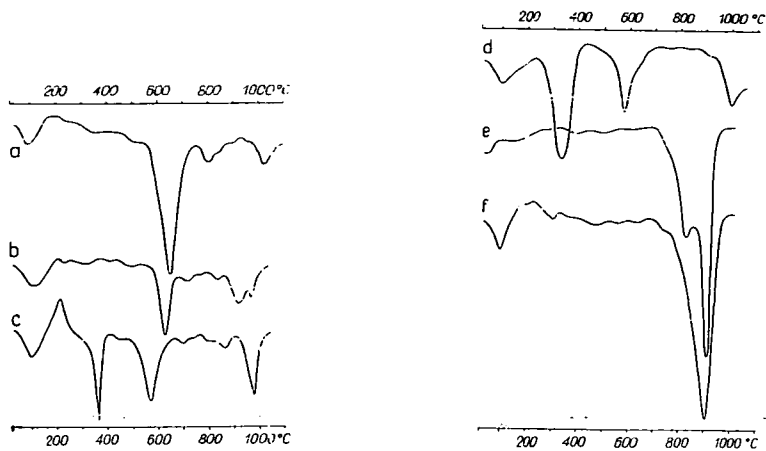

Figs. 39/1 and 39/2. DTA curves of samples taken from the shaft No. II.

a) Sample taken from the compact ground-mass of the polished ore section No. II-4.

b) Sample taken from a fine manganite veinlet from the same polished ore section.

c) Sample taken from the compact ground-mass of the polished ore section No. II-5.

d) Sample taken from the same polished ore section but from a manganite veinlet.

e) Sample from a compact, breccia-like oxide ore No. II-2.

f) Sample taken from a fine-banded, earthy, lustreless ore. Parallel to the banding minute harder veinlets. Polished section No. II/6.

g) Sample taken from a fine-fibrous aggregate of silky luster consisting of manganite and pyrolusite. Polished section No. II/11.

h) Sample taken from a compact, hard, complex ore specimen. Polished section No. II/15

According to the referring works and our own DTA curves it may be supposed that the samples — the DTA curve of which shows an endothermic peak at a lower temperature than 600 °C — beside the pyrolusite or instead of pyrolusite perhaps contain an other MnO_2 modification. These samples contain mostly also manganite and are formed from manganese carbonate due to oxidation. This MnO_2 modification supposed to be other as pyrolusite is in polished ore sections sometimes extremely fine-fibrous, forming fan-like or plumose, frostwork-like aggregates showing a characteristic undulatory extinction.

Naturally, the DTA and the microscopical investigation alone are not sufficient for accurate identification of the MnO_2 modification supposed to be a sub-variety of possible γ-MnO_2. Its presence in the ores of Urkut is to be proved by further X-ray investigations.

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Figs. 40/1 and 40/2. DTA curves of samples taken from the shaft No. III.

a) Sample taken from the compact, crystalline part of the polished section No. III/I.

b) Sample taken from the same polished section but from in other, fine-grained, compact part.

c) Sample taken from polished section No. III-4. Rhytmically arranged, radiated, fibrous aggregate of manganite and MnO_2.

d) Black, oxidized sample from the neighbourhood of carbonate and manganoan calcite, resp., shaft No. III. carbonate field.

e) Pinkish, crystalline manganoan calcite from the carbonate field of the shaft No. III.

f) Black, poorly layered nodule from the shaft No. III. Sample No. III/2.
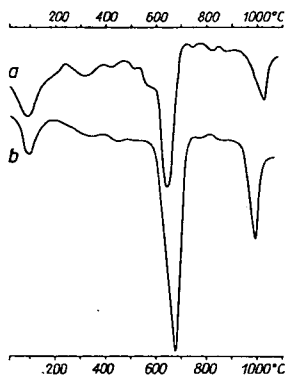

Fig. 41. DTA curves of pyrolusite samples

a) fine-fibrous pyrolusite of silky lustre (Urkut)

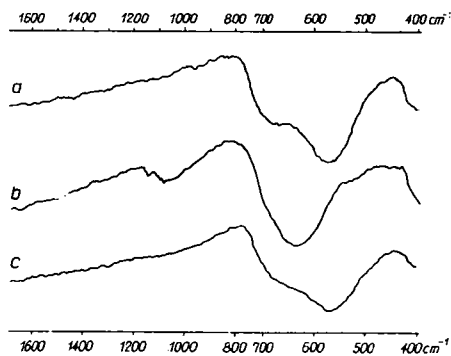*b)* Coarse-grained pyrolusite as fissure-filling (Urkut—Csárdahegy).

Fig. 42. Infrared absorption spectra of pyrolusite samples

a) Pyrolusite from Ilmenau

b) Fine-fibrous pyrolusite having silky lustre (DTA curve of this sample see in Fig. 41/a.)

c) Coarse-grained pyrolusite (DTA curve of this sample see in Fig. 41/b).

Still, to have assumed its presence as a probability, certain circumstances played a role:

a) the microscopical picture of some of our polished ore sections bears undoubtedly resemblance to the microphotos in the papers of Sorem and Cameron [1960] as well as in that of Zwicker et al [1962], respectively.

b) The results of the DTA relating to the artificial and natural γ-MnO$_2$ modification, available in the literature, and our own DTA curves show a close agreement as to the temperature of the characteristic endothermic peak.

c) The infrared absorption spectra of a coarse-grained pyrolusite sample from Urkut (Csárdahegy) and of the fine-fibrous pyrolusite having silky luster, mentioned above (on the DTA curve of which an endothermic peak is at 580° close before the peak of the pyrolusite), considerably differ as shown in *Fig. 42.* For comparison, the infrared absorption spectrum of a pyrolusite sample from Ilmenau considered as a standard is also given.

d) The MnO$_2$ modification supposed to be different from pyrolusite occurs mostly associated with manganite and in ores formed from manganese carbonate due to oxidation.

Zwicker et al. [1962] point to the fact that the proximity to carbonate ores is characteristic of the occurrence of nsutite. They suppose that it is among the first manganese oxides along the birnessite formed due to oxidation from manganese carbonate. In their opinion the nsutite may be formed in slightly alkaline environment and its formation is afforded by contact of manganese carbonate with oxygen-rich water.

The conditions in the manganese district of Urkut, especially in the transition zone between carbonate and oxide, at the rim of the shaft No. II, are particularly suitable.

It is also to mention that E. Nemecz [1962] ascertained by X-ray investigations the presence of manganite in the black manganese carbonate ore of Urkut.

Assumably the further examinations may clarify the identity of the MnO$_2$ modification in question.

The *cryptomelane* is also fairly frequent in the oxide ores. In general it is cryptocrystalline having often colloform structure pointing to the formation from gel. Sometimes it is intimately intergrown and/or interlayered with fine-fibrous or similarly cryptocrystalline pyrolusite or with the MnO$_2$ modification mentioned *(Figs. 30—33, 36, 37).* It occurs often as cavity-filling or impregnating the ferruginous groundmass. The layered, colloform cryptomelane aggregates are sometimes coming apart along the layers at the edges presumably owing to the shrinkage due to the loss of water of the gel-material and the cavity formed between the layers are filled with later manganite *(Fig. 29).* Manganite veinlets intersecting the colloform cryptomelane can also often be observed *(Figs. 30 and 32).* The signs of the later reaccumulation of the original ore beds can sometimes also be observed in the polished ore sections. The fragments of earlier manganese ores are embedded in ferruginous cement *(Fig. 31)* or vice versa, ferruginous fragments are cemented by cryptocrystalline cryptomelane and/or pyrolusite *(Fig. 35).*

The *pyrolusite* forms sometimes coarse-grained aggregates or it is coarse-fibrous or it appears in cryptocrystalline aggregates alone or together with cryptomelane or forms in the latter very fine-fibrous, oriented veinlets interlayered with cryptomelane or forms patches consisting of aggregate of unoriented very fine fibres. *(Figs. 34—37.)*

In most of the polished sections investigated amorphous ferruginous ground-mass impregnated with manganese oxides can be observed, *sammetblende* often is seen as thin border and its appearance point to formation from colloidal state. In carbonate ores as thinner or thicker veinlets of fissure-filling is often seen the whitish—slightly pinkish *manganoan calcite* too, the DTA curve of which is shown in Fig. *40/2*.

REFERENCES

GATTOW, G., GLEMSER, O. [1960]: Über die Umwandlung künstlicher Braunsteine. — Naturwis-senschaften *47*, 59.

GLEMSER, O., GATTOW, G. and MEISIEK, H. [1961]: Darstellung und Eigenschaften von Braun-steinen I. — Z. anorg. allgem. Chem. *309*, 1—19.

GATTOW, G., GLEMSER, O. [1961]: Darstellung und Eigenschaften von Braunsteinen. II und III. — — Z. anorg. allgem. Chem. *309*, 20—36, 121—150.

GRASSELLY, GY., CSEH NÉMETH, J. [1961]: Data on the Geology and Mineralogy of the Manganese Ore Deposit of Urkut I. — Acta Miner. Petr. *14*, 3—25.

McMURDIE, H. F., GOLOVATO, E. [1948]: A Study of the Modification of Manganese Dioxide. — — Journ. Res. Nat. Bur. Stand. *41*, 589—600.

NEMECZ, E. [1962]: Mineralogical investigation of the manganese carbonate ore of Urkut. — Un-published. Paper presented at the Meeting of the Hungarian Geological Society in Urkut, Sept. 1962.

SOREM, R. K., CAMERON, E. N. [1960]: Manganese oxides and associated minerals of the Nsuta manganese deposit, Ghana, West Africa. — Econ. Geol. *55*, 278—310.

SREENIVAS, B. L. [1957]: Gamma-manganese dioxide from Mysore, India. — Mineral. Mag. *31*, 605—606.

ZWICKER, W. K., GROENEVELD MEIJER, W. O. I. and H. W. JAFFE [1962]: Nsutite — a widespread manganese oxide mineral. — Amer. Miner. *47*, 246—266.