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DATA ON THE GEOLOGY AND MINERALOGY OF THE OIL SHALE OCCURRENCE AT PULA, HUNGARY

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SUMMARY

The gravelly sand of basaltic and basalt tuff substance forming the basement of the oil shale and the overlying alginite was taken stratigraphically one rhythm. So the sequence overlies directly the erosion surface of the Upper Triassic dolomite. In its roof carbonate mud, humic clay and aleurite are found.

The oil shale is of rhythmic structure locally with thick (several metres) "massive" oil shale intercalations.

The lower ten metres of the bore Put—7 is alginitic carbonate mud of massive type with a few coalified plant remnants. The ostracod half-shells and Diatoma-skelets are frequent. This is overlain in about 10 m thickness by carbonate-muddy alginite of inhomogeneous structure with the remnants of Botryococcus colonies and diatoma-skelets. Above it thin aleurite intercalation is found which is followed by alginite of massive type down to 15 m and this is replaced by clay marl and sandy aleurite of 1 to 1.5 m thickness. Between 8 and 13 metres alginitic aleurite, aleuritic alginite and carbonate mud alternate, then carbonate mud and clay marl, finally clayey aleurite follow.

The formations are for the most part built up by minerals of predominantly micron size, thus these were determined by means of X-ray diffractometer. The percentual determination of the individual phases was impossible just because of the locally widespread amorphous material.

The frequent minerals of the bore's formation are as follows: aragonite, calcite, dolomite, quartz and locally feldspar, and clay mineral also frequently occurs. In the lower section of 20 metres aragonite plays a predominant role. Small quantities of calcite, dolomite are characteristic, the quartz is sometimes absent, the feldspar is subordinated. Between 20 and 5 m three smaller sections can be separated where aragonite is absent and is replaced by calcite and dolomite.

It has been determined that in spite of its instable structure aragonite may remain when the enclosing rock is clayey, less permeable, or oil shale. In our case both criteria exist.

The possibility of formation of aragonite is explained by the fact that the lagoon enclosed by the ring-shaped tuff barriers of the volcanic crater had been heated by the subsequent hot springs so there was a possibility to $CaCO_3$ to precipitate in form of aragonite.

In the bore the periodical occurrence of aragonite and the change in the mineral composition are explained by the fact that this lake of warmer water was periodically inundated by colder water of higher salt concentration from outside. During these phases the precipitation of aragonite ceased, the grain size of the sediment changed and quartz becomes predominant, in general.

INTRODUCTION

The area of Hungary is covered by Neogene and Quaternary basin formations in about 85 per cent. Their average thickness is 1500 metres, in extreme cases these may amount to 5,000 metres, too. Their formation characterizes the evolution of the Paratethys region, *i. e.* the older Miocene formations are of normal haline shallow water origin. The Upper Miocene is of brackish sequence, the Pannonian formation is brackish-fresh and makes evident the deposition in shallow water. The Quaternary formations are mostly of freshwater and eolian terrestrial origin. The oil shale formation investigated in the strata sequence of the bore Put—7 in Pula is assigned to the middle sequence of the upper part of the Pannonian sequence which can be assigned to the Pliocene after the international stratigraphic scale. Its appearance is connected with small-sized basalt crater formed within the intramountain lagoon (Tapolca — Nagyvázsony Basin) of the Bakony Mountains, *i. e.* of the southwestern members of the Transdanubian Central Mountains, and this is the filling material of this crater [Á. JÁMBOR, G. SOLTI, 1975].

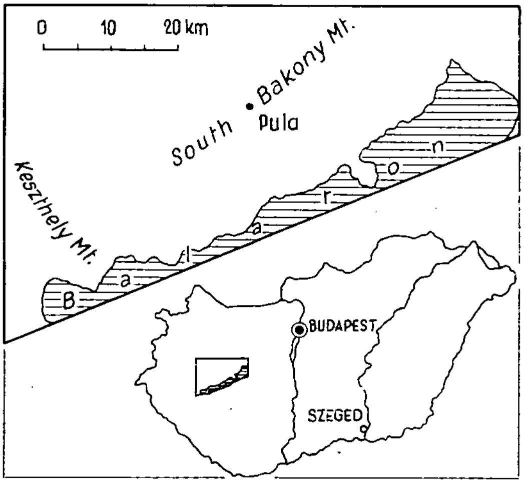

Fig. 1. Plan of the bore

To carry out the laboratory investigations on the samples of the prospecting bore Put—7 settled in 1975 for the survey of the oil shale instructions were given by the Hungarian State Geological Institute to the Department for Mineralogy, Geochemistry and Petrology of the Attila József University. From the cores sampling was carried by every half metres. To evaluate our investigations the strata sequence of the bore was obtained by researchers of the Hungarian Geological Institute (Budapest).

According to this, the oil shale series (alginitic sequence) together with its sedimentary cover and gravelly-sandy floor of basalt tuff substance can be imagined as a rhythm of medium size, its total thickness hardly surpasses 50 metres. The sequence directly overlies the erosion surface of the Upper Triassic dolomite.

The oil shale series is of rhythmic built-up. On the basis of the investigated strata sequence of the bore Put—7 it can be divided into subrhythms, in certain sections into series, moreover into layer pairs of annual formation. The size and order of magnitude of the subrhythms may be rather different. In the upper boundary and final stage of the subrhythms sections and intercalations of oil shale substance can be repeatedly observed which are thin and of several, max. 10 cm thick in general, and which consist of mostly brown-coloured, parallel, macroscopically homogeneous lamellae of hundredth or tenth mm thickness. The series built up by these layer pairs remains unchanged just after drying the sample occasionally foliation or separation can be observed in the sample's margin. These parts accumulated during a relatively long time under undisturbed conditions and contain rather small quantities of non-combustible material. High C_{org} values can be expected in them, much higher than determined in the average samples. Their porosity, permeability, bulk density and carbonate content are low. Their total thickness within the sequence is insignificant.

In case of another textural type the colour and material quality is the same the only difference is that the thin-lamellated structure cannot be observed by eyes and separation can be hardly observed. This subtype is characterized by relatively higher porosity and permeability, the bulk density and carbonate content is low.

When describing the core samples massive, lamellar and "shoe sole" texture types were distinguished, after G. SOLTI.

"Massive" oil shale or alginite. The term "massive" is suggested by Á. JÁMBOR. Macroscopically this oil shale type is unstratified, along the distinctive boundaries are separation traces, at least. Within the sequence it can be stated as a general tendency that the unstratified oil shale is relatively of coarser grain size composition (the aleurite and fine-sand fractions are characteristic). As to our opinion, on the basis of the textural and structural similarities the term "massive" can be used also in the case of alginitic marl, alginitic carbonate mud. It is to be emphasized that within the oil shale sequence the unstratified parts are thinner than 10 m in every cases.

Thin-stratified oil shale type. It is characterized by the frequent alteration of 0.1 to 5.0 mm thick lamellae of different colours of green, white and pale-grey. The "shoe sole" type occurs rarely and only in the upper part of the sequence. The dark-brown colour and the transparent paper-likely flexible lamellae are characteristic.

Carbonate mud. It was found in the upper part of the sequence resp. above the alginite, as well as in the bottom of the sequence. The upper "marl" and the completing "alginitic" marl are of low diagenetic degree, thus the term carbonate mud refers better to the consistency of the rock, to the conditions of formation as well as to the mixed-carbonate mineral composition (see later). In the bore Put—7 the role of Algae changes in well observable manner and replaced gradually by chemical processes during sedimentation. The term carbonate mud was used in case of several samples from which no material had been analyzed, in these cases the local macroscopic description was re-evaluated.

It is considered to be important to determine the quality of stratification since among others conclusions can be drawn to the state of movement of sedimentation medium, *i. e.* to the environment of accumulation. The sediments of undisturbed waters into which the alginites can be assigned, resp. its layers are parallel with one another and often but not always with the layer surfaces determining the form of accumulation.

The layers of the investigated sequence have two members in general, thus pair-lamellation can be spoken of. In their macroscopic description the terms "thin-stratified" or "of lamellar formation" were used. The paired lamellar formation is characteristic of the rock where one of the members — almost without exception the upper member — is of subordinate thickness. Since their material quality is different, the observable parting is found here.

Regarding the relation of the thin lamellae, the type of parallel formation, within this the simple, lamina-structure predominate; the gradated and homogeneous formation of the layers is less frequent *(Fig. 2)*.

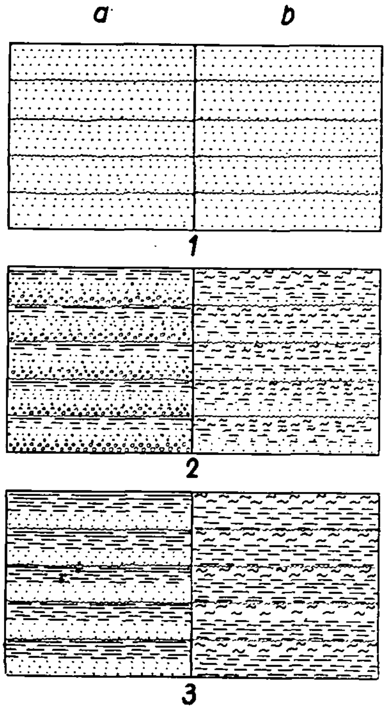

Fig. 2. Structure of the laminae and lamina pairs (Applying the data of Botvinkina, Allen and others).

Legend: the marks used do not relate by all means to material quality.

a) theoretical types, *b)* formation characteristic of the material investigated.

1. Homogeneous lamina. Along the separating line the material quality may be different as thin intercalation, at the same place parting can be occasionally observed.
2. Gradated lamina-paired structure. Oriented and gradual change in material quality and grain size within the lamina paisr, at the boundary of the lamina pairs parting can be observed.
3. Banded "paired lamina pair" of double structure. No gradualness can be observed at the boundary of pairs, the laminae are separated, parting is frequent at the boundaries. Lamina pairs are repeated several times, occasionally in sections of greater thickness these are constant; in this sense the lamina pairs are homogeneous resp. the rate and course of sedimentation are rhythmic.

To classify the stratified sediments the thickness of them is often used. Referring to literature data, below 3 mm thickness very thin lamellae, between 3 and 10 mm thin lamellae, between 10 and 30 mm moderately thick layers are mentioned [*e. g.* L. N. Botvinkina, 1965].

According to the classification the thin-stratified sections of the alginitic sequence the very thin lamellation is characteristic. In our descriptions, since the annual periodicity is probable in numerous cases, further distinctions are used: the thinnest lamination is of hundredth mm size, within the oil shale sequence the lamina of tenth mm size are most frequent.

No distinction was made between the thin-lamellated (3 to 10 mm) and medium thin-lamellated (10 to 30 mm) formations since these types were observed in negligible quantity within the investigated sequence. Above the thickness values listed above (i. e. above 3 mm) uniformly the term lamellar in cm size (or thin-stratified) was used.

The oriented grain size change which could be observed occasionally in the lamina and stratum members is called gradation.

STRATA SEQUENCE AND TEXTURAL PECULIARITIES IN THE BORE PUT—7

The bottom of the bore: 55 m. The outlined strata sequence and stratification (certain textural features) of the bore Put—7 is shown in *Fig. 3.*

53.2—(55.0) m. The oldest layer reached in the bore is of Upper Triassic age and is grey dolomite with calcite veins.

39.3—53.2 m. The dolomite is overlain by basalt tuff lapilli, basalt tuffite and basalt-sand with basalt pebbles (39.3 to 41.8 m). The dip of the members decreases from down, at 39.3 m the contact with the alginitic sequence lies in a sharp boundary.

30.0—39.3 m. Alginitic carbonate mud. It is of "massive" type. It is of light greenish-grey colour, locally darker-coloured section can be observed, the change of colour is continuous and can be assigned to relatively finer grain size and to intercalations of higher clay content.

The formation is uniform, parting is rather infrequent and in these cases no special change in the material quality can be observed (Plate I., photos 1—4.). On the basis of parting the dip of the upper part of greater thickness is only several degrees, the lower is of 5 to 15° dip.

In the case of some greater samples parting can be observed along steep-dipping or vertical planes, the dark-green coloured, bright, clayey coat of the parting surfaces between 38.0 and 38.5 resp. 33.5 and 34.0 m relates to displacement.

The rock contains small number of coalified plant fragments, rarely the impression of a leaf of deciduous trees and monocotyledonous stems occur, the latter ones bound to parting surfaces. The ostracod half-shells are frequent (Plate I, photo 1). Only the fragments of mollusc shells were observed.

Disturbed bedding (*e. g.* micro-folding, clay pebbles, etc.) was not observed. In the slides prepared perpendicularly of the parting surface slight orientation was found (Plate I, photo 3), but annual or other rhythmicity which could be connected with precipitation of sediment transport could not be observed. In the textural pictures, especially under higher magnification, the spot-like appearance of the organic matter can be fixed, but regarding the section of about 10 metres its distribution is uniform. Within this section the uniform distribution of carbonate content relates to the regularity of material supply. The porosity of the rock is high (about 40 per cent), its bulk density is of medium measure. Diatom shells are frequent.

26.0—30.0 m. Strongly carbonate-muddy alginite. It is of "lamellar" formation. According to the change of stratification and material quality the colour of the rock is green, light-green, off-white, white. Change of colour could be occasionally observed also within the lamina pairs. The well-defined green colour occurred in the parting surfaces.

The rock is inhomogeneous. The thickness of the lamina pairs extends from tenth to several millimetres, the latter ones are of similar quality than the former

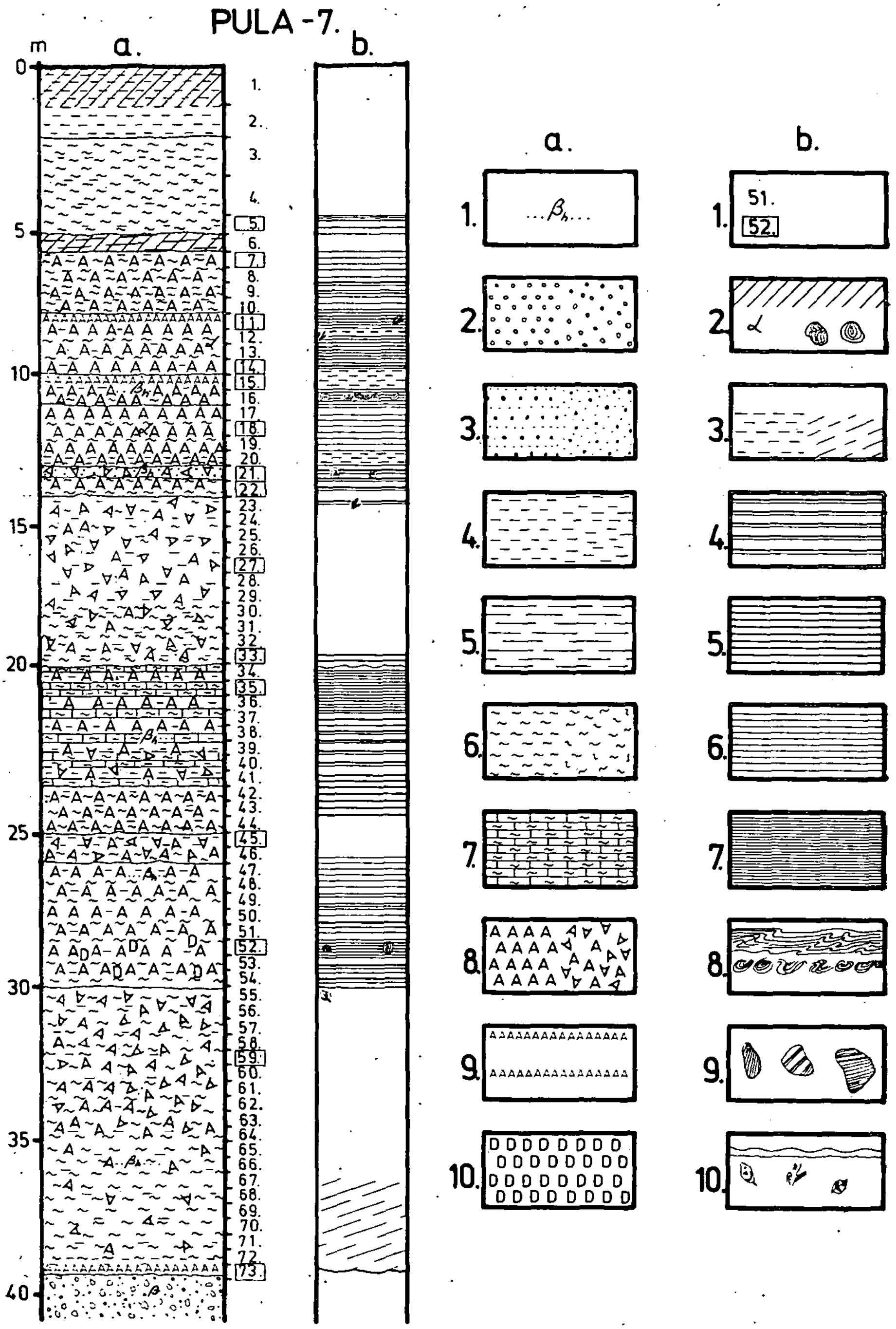
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Fig. 3.

member (30.0—39.3 m) but are not predominant. At the boundaries of the lamina pairs the rock favours the parting, these boundaries may be gradual, resp. sharp. All the three lamellar types occur *(Fig. 2.)*. The laminae of carbonate mud are predominating, their quantity gradually decreases upwards though the diatom-bearing and clayey laminae are rather frequent. The formation is nearly horizontal, parallel; between 28.5 and 29.0 m it is convolute within a smaller section. In the lower part of the section the lamina pairs formed series, the thickness of which amounts to several cm.

Sporadically it contains basalt fragments, coalified plant fragments and a few ostracode shells. In the parting surfaces the plant fragments are more frequent. The remnants of the Botryococcus colonies are frequent according to stratification, resp. less frequent indicating the fact that lived only in certain period of the year.

The carbonate content increases resp. decreases according to the lamina members, this may relate to the rhythm of material supply. The porosity of the rock is changing, its bulk density proves to be low.

24.5—26.0 m. Carbonate-muddy oil shale (alginite). It is of "massive" type. It is of light greenish-grey colour, horizontal parting can be rarely observed; rather angular-granular parting is characteristic. In the greater pieces desoriented microfissuredness was observed. Both the upper and the lower boundaries are gradual. The rock is homogeneous, the distribution of carbonate content is uniform. On the basis of the textural pictures the organic matter occurs in spots but without orientation and in uniform distribution within the interval (Plate II., photos 1 and 2.).

19.6—24.5 m. Alginite with changing carbonate mud content. It is built up by the alteration of thin "stratified" and somewhat thicker "massive" sections. Lamina members of light greenish-grey, yellowish-grey, green-overshadowed brownish-yellow, greenish-grey and off-white colour were found. The whitish colour indicates the diatom-shells, the yellowish ones the carbonate mud, the darker ones either the accumulation of the organic matter, or the increase of quantity of clay minerals.

The section is inhomogeneous, the lower boundary is gradual and up to about 21.5 m it contains alginite of "massive" type as thin intercalation (which is homogeneous itself). The upper part is of thin-lamellar formation. The thickness of the

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Fig. 3. Sequence *(a)* and stratification *(b)* of the bore Put—7.

Legend:

a) Sequence: 1. rocks containing basalt sand intercalations. 2. conglomerate resp. gravel-bearing rocks. The ordered signs (left side) concern the stratified, the randomly shown marks denote the unstratified formations (in the following it is to be understood in the same sense). 3. sands and sandstones of different grain size (mostly between 0.06 and 0.2 mm). 4. aleurite and aleuritic rocks (mostly between 0.002 and 0.06 mm). 5. rocks containing clay and clay intercalations. 6. rocks of marl and considerable carbonate quantity. 7. carbonate mud; where the dolomite quantity proved to be high, the base-mark of dolomite was used. 8. oil shale (=alginite and alginitic rocks), the randomly placed signs "A" relate to the "massive" type resp. to kindred formation. 9. sections containing alginite of thin-stratified type. 10. diatomite intercalation.

b) stratification and other signs: 1. number of samples, those investigated in detail are in frame. 2. humic ricks with limonite spots and lime concretions. 3. the clear sections are untsratified ("massive" type). The sections of broken line are stratified along the indistinct boundaries. Horizontal lines denote the horizontal and nearly horizontal, oblique lines denote the oblique bedding. 4. series-forming lamina-paired formation. 5. lamina-pairs of cm thickness of order of magnitude. 6. laminapairs of mm thickness of order of magnitude. 7. lamina pairs thinner than mm. 8. lamina-pairs of folded or otherwise dieturbed bedding. 10. hiatus or discordance. 11. coalified plant fragments, stem resp. leaf impressions.

lamina pairs, resp. of the intercalations of "massive" type ranges from tenth mm up to several centimetres. These form occasionally series. In the lower section the boundaries are indistinct, often separation cannot be observed, while in the upper part the boundaries are rather sharp. In the upper part the changes in colour are more expressed. Separation independent of direction and of vertical type occur, clayey or other phenomena relating to displacement could not be observed at these surfaces. The structure of the lamina pairs is homogeneous and may be both gradated or paired.

Between 21.5 and 22.0 m basalt tuff grains of rounded shape and 3 mm diameter were found in the parting surfaces (Plate II., photo 3).

The grain size of the rock is changing, regarding the whole section from down to upwards decrease of grain size can be tendentiously observed.

Bedding is nearly horizontal, on the basis of the core samples neither wedging nor thickening can be determined, the lamina pairs are parallel with one another. Sporadically small coalified plant fragments, occasionally a few ostracod half-shell are found, between 21.5 and 22.0 m shell fragments also occur.

The upper part is characterized by the annual periodicity, the lower one produces rhythmic sedimentation based on different reasons. The change in carbonate content may also be related to this fact. The porosity is high, the bulk density is low, but both of them obviously changes depending on the material quality.

13.4—19.6 m. Alginite (oil shale). It is of "massive" type. Its colour is greenish-shaded light yellowish brown. Certain gradualness can be observed both towards the bottom and the overlying strata. The sample between 16.0 and 16.5 m is most characteristic of the "massive" type, this section contains Botryococcus spots in great numbers. By 1 to 5 cm the air-dried samples become of horizontal parting by hits though no change in material quality can be osberved at the parting surfaces.

The lower sample of the section (19.0—19.6 m) is of transitional type, from the series of lamina pairs of several cm thickness it contains intercalations, while the "massive" part contains smaller clastic sedimentary grains, in addition to the small quantity of carbonates. The upper samples develop gradually from those underlying them (13.4—15.0 m), after slides (Plate IV., photos 1—2) slight orientation can be fixed. Most dissimilar is the sample between 13.4 and 14.0 m which consists of the alternation of the "massive" type and of the lamellar thin-stratified type. The material of the thin-stratified intercalations is mostly carbonate mud, but the quantities of aleurite and clay fractions are also significant.

In general, it can be stated that the "massive" type is of coarser, while the thin-stratified one of finer grain size. This is not valid of the carbonates, these are nearly without exception of very fine, sub-micron grain size. From the middle part of the section the quantity of carbonates shows considerable increase (14.5—17.5 m) both up and downwards.

Bedding is nearly horizontal. The whole part contains only a few coalified plant fragments but it is to be noted that at the parting surfaces of the stratified intercalations of the upper part greater impressions also occur.

13.0—13.4 m. Aleuritic clay marl and sandy aleurite. It is loose and easily friable. Its colour is light yellowish-green. It contacts the overlying strata with a clay-layer of 2 mm, and the underlying one with a layer consisting of coarse grained sand containing rounded basalt grains of 0.5 to 2.0 mm diameter. In the middle of the sample there is also a fine sand layer of 4 mm thickness and of basalt-detritus.

Part of the material to be investigated is indistinctly, the other part well stratified. The thickness of the laminae changes between mm and cm order of magnitude. Within the thicker ones gradation can be observed. In several cases the well thin-stratified laminae are dark-brown and of clayey material. At the parting surfaces corresponding to stratification the coalified plant fragments are frequent (Plate IV., photo 4). Bedding is nearly horizontal.

According to the varied laminae the carbonate is rather different, the rhythmicity in material supply can be imagined.

Porosity changes within wide limits, the bulk density is obviously higher than in case of the previous samples.

Similar mineral composition and textural picture were observed in the section of 11.1—11.6 m of the bore Put—3 (Plate V., photos 1—2).

8.0—13.0 m. Alginitic aleurite, aleuritic alginite and carbonate mud alternate. This is a "thin-stratified type". Light greyish-green, greenish-grey, yellowish-brown, yellowish-greenish-brown, "russet" rusty brown, light creamy-yellow, white-off and white coloured laminae occur.

No petrologically uniform term can be applied which would be valid of a longer section within the given interval. It is built up by lamina pairs of changing material, and the ratios within samples are also different. Studying separately the laminae if it is possible as a function of thickness, their homogeneity can be fixed. The laminae containing Botryococcus colonies, consisting of carbonate mud and being of lamellar type can be distinguished and these occasionally consist mostly of clay minerals. It is to be noted, however, absolutely pure material can be found, neither. Regarding the stage of filling up this is evident. The varied shades of colour indicate also the fact that among the lamina types which seem to be determined, numerous transitions may exist.

In the lower sample and in the samples between 9.0 and 10.5 m there is relatively more clay, while in the samples between 10 and 11, resp. 8.0 and 8.5 m the intercalations of alginite laminae of "shoe sole" type predominate. In the lower two metres between the parting surfaces "russet" rusty-brown spots are found. In several parting surfaces basalt tuff detritus, basalt sand lenses can be observed. The thickness of the lamina pairs is mostly of tenth millimetres, the "thin-stratified" intercalations are of "paper" thickness. The carbonate laminae are somewhat thicker, and can be characterized by a thickness of millimetre order of magnitude. Each lamina pairs are of constant thickness, wedging is infrequent.

Bedding is nearly horizontal, in 10.7 m laminae of folded position can be observed. The whole section contains coalified plant fragments, in the strata surfaces greater monocotyledonous plants of desoriented position are rather frequent (Plate V., photo 3).

The quantity of carbonates is changing and rhythmicity of material supply can be rendered possible. The carbonate material is microcrystalline at most (Plate V., photo 4). Porosity is low, the bulk density is changing.

6.0—8.0 m. Carbonate mud. It is of "thin-stratified" type, and of light, slightly greenish shaded creamy yellow and white-off colour; between 6.5 and 7.0 m sections of darker colour also occur. In several places strips more abundant in algal skelets and of darker greenish-yellow colour can be found. In certain parting surfaces dark-brown, occasionally blackish spots can be observed, this is probably limonite coat.

The rock is characterized by the paired laminated structure. The thicker lamina is carbonate mud, the thinner is pelite. The thickness of the lamina pairs is tenth of mm, resp., mm at most. The boundaries of the pairs is sharp in general, and parting is also frequent. Between 7.0 and 8.0 m series and bundles were also observed.

Bedding is nearly horizontal, the thickness of the laminae is constant, except that of series and bundles. In the sample of the upper part a few drying fissure seem to be probable. The rock contains sporadically a few small coalified plant fragments. The carbonate content increases resp. decreases according to the lamina members. The rock is of medium porosity, its bulk density is changing.

4.8—6.0 m. Clay marl, clayey aleurite. It is of "stratified" type. Light brownish-yellow or white-off strips alternate with brownish-grey ones, some of the parting surfaces are of distinct greenish shade.

The rock is built up by lamina pairs of changing thickness of 0.1 to 10.0mm, most of them are of about 0.5 mm thickness. Lamina pairs form series, the relatively thicker laminae are found though in small number always at the bottom of the series.

2.3—4.8 m. Carbonate mud. It is of pale yellowish-green colour. At the top of the layer 3 cm thick, grey, hard, compact, macrofauna-free limestone of total core diameter and of conchoidal fracture can be found.

1.2—2.3 m. Slope loess? It is of brownish-yellow colour and strongly calcareous.

0.0—1:2 m. Aleurite. Unclassified, and of brown clolour, humic and clayey.

From the surficial outcrop of the geysirite cone of the oil shale occurrence several samples were also investigated. The rock is built up nearly solely of carbonates. It is built up by loose, porous banks of about half metre thickness resp. by the random network of these banks. Plant impressions and fragments infrequently occur though sometimes certain porous parts remind to moss colonies. In one side of the hardly approachable cone the freshwater limestone contains great number of freshwater snails in a thin strip:

Valvata piscinalis O. F. MÜLLER (rare)
Valvata sp. (rare)
Stagnicola palustris O. F. MÜLLER (rare)
Planorbis planorbis L. (frequent)
Planorbis spirorbis L. (less frequent)
Planorbis sp. (in great number)
Gyraulus sp. (rare)
Succinea sp. (less frequent)

PREPARATION OF THE SAMPLES FOR MINERALOGICAL-PETROLOGICAL AND X-RAY DIFFRACTOMETRIC INVESTIGATIONS

Because of the considerable quantity of the soluble and insoluble organic matter content the usual slides could not be prepared from this material. If this phenomenon would not exist as a restraining factor, the colloidal grain size would cause troubles and only a few mineral grains were found which could be assigned to the sandy or aleuritic fractions.

Because of these difficulties we tried to determine the mineral composition of each core samples by means of X-ray diffractometric investigations. In the first step the clayey fraction taken in suspension tried to be deposited, but the solution proved to be turbid also during a longer time and finally only a material of very small quantity deposited in the X-ry diffractogram of which no evaluable peaks were found. Having extracted the soluble organic matter and then having suspended in solution the remaining material with $CaCl_2$, then after staying having centrifuged the sample, in the diffractograms of the sample of accumulated inorganic matter evaluable peaks could be hardly found. It proved to be the most applicable method to pulverize the material vithout any preliminary treatment and this was recorded by X-ray diffractometer. Thus, under the conditions of 500/40 imp/sec peaks suitable for evaluation and relative intensity of measurable size were obtained.

In the course of evaluation of the diffractograms the base line displacement was observed in several cases. This has been in connection with the organic matter content, in general. In case of 5 per cent organic matter (C_{org}) between 15 and 25 Θ angles the base line was of normal run, in case of higher organic matter content it was considerably displaced. The displacement was especially obvious in the bore's samples of 16 to 17 m, as well as in those deriving from the depth of 23 m. Between the two extreme values and depending on the organic matter content all the transitions could be observed *(Fig. 4).*

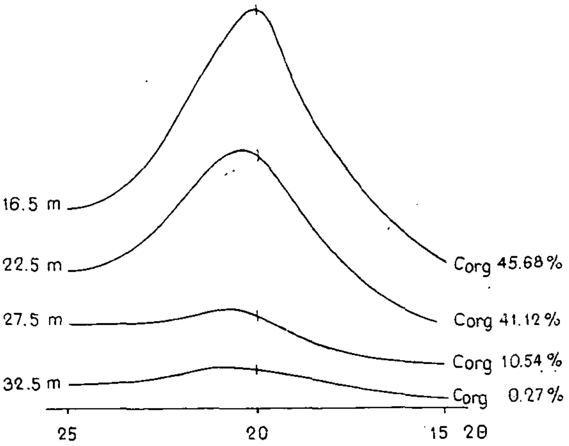

Fig. 4. Base-line displacement depending on the organic matter content.

Another feature of these diffractograms should be mentioned. On the basis of the relative intensities when trying to calculate quantitative relations applying the constants applied and tested till now, no results were obtained. In all cases considerable displacement was observed in case of carbonates in positive direction, which could be controlled on the basis of CO_2 content determined gasometrically. Sometimes in case of slight quantity of CO_2 carbonate mineral of considerable quantity could be computed. In these cases the conclusion has been drawn that the usually X-ray amorphous colloidal material does not contain carbonate but it is rather hydrosilicagel and on this basis it was possible to conclude to the fact that on the one hand clay minerals (montmorillonite, less illite) were also present in most of the investigated samples, and the amorphous material (Table 1) represented considerable quantities, on the other. It is to be assumed that these played a considerable role in the displacement of quantitative relations.

In case of some samples the quantity of the amorphous material has been analyzed by I. Varsányi–Tóth. Applying the method of J. Hashimoto. and M. L. Jackson, [1960] the quantitative relations of the amorphous SiO_2 and $Al(OH)_3$ of these samples showed the following picture (Table 1):

TABLE 1

Data concerning the quantity of the amorphous material

Depth in metres	C_{org}	CO_2	Amorphous material
	in per cent		
6.5	1.69	17.3	6.00
10.5	11.68	8.2	9.44
16.5	45.68	4.3	5.55
19.0	8.89	21.4	6.88
22.5	41.12	6.9	5.55
25.0	30.09	11.8	7.66
28.5	8.52	17.0	17.44
32.0	10.59	21.5	10.33

According to these data in the change of the amorphous material no relation can be found either with the quantitative changes of CO_2, or of C_{org}, or with that of silicate minerals occurring in higher amounts.

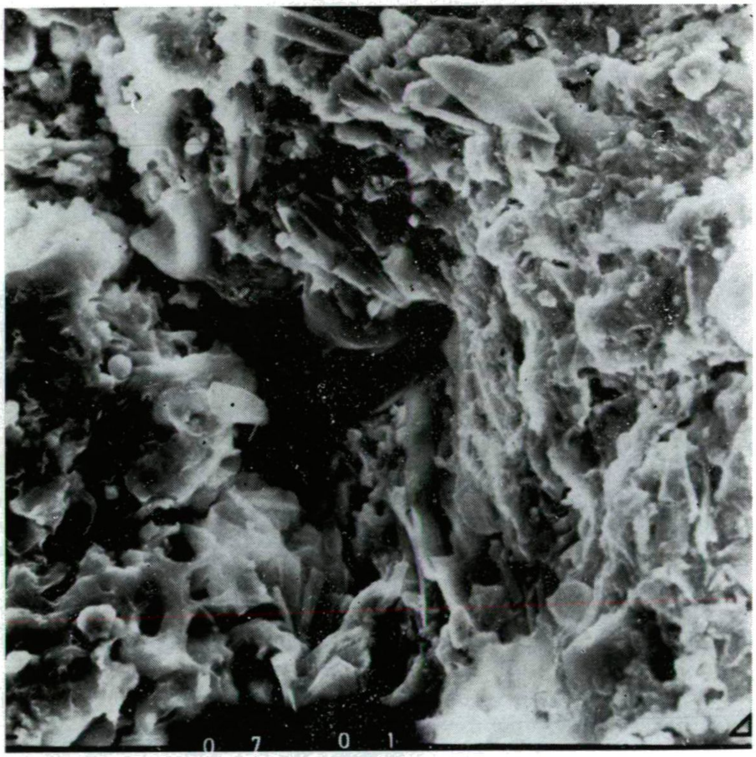

Fig. 5. Oil shale. Surface picture. SEM 1000 X. Record by K. PINTYE—HÓDI. Bore Put—7: 16.0—16.5 m.

The electronmicroscopic picture relates also to the presence of amorphous material of higher amount. In scanning records parts relating to crystalline form could not be identified, only forms characteristic of absolutely irregular, amorphous material could be observe (*Fig. 5)*. In cases where dissimilar textural picture was obtained, the diatom skelet and the coating material of amorphous form could be well distingusihed *(Fig. 6)*.

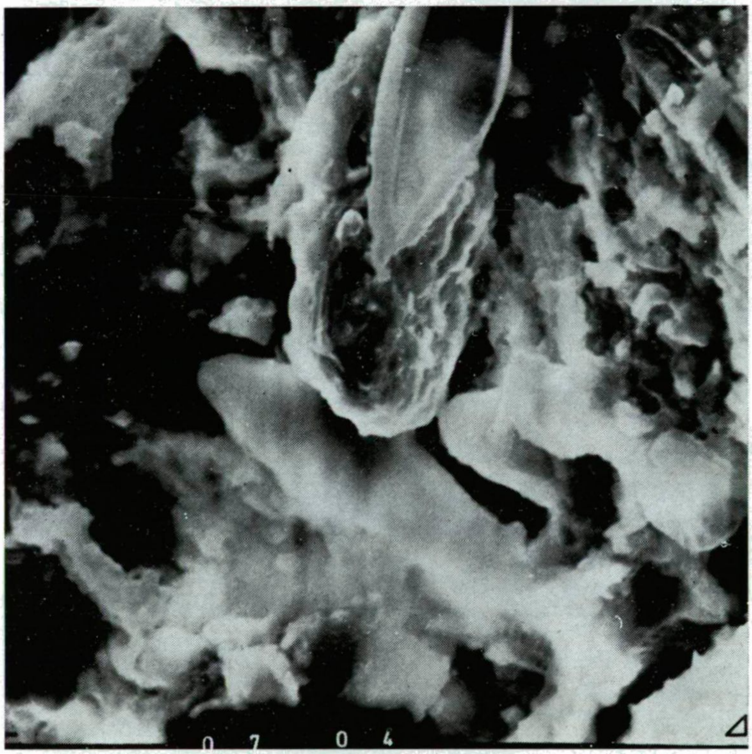

Fig. 6. Oil shale. Surface picture with diatome skelets. SEM 3000 X. Record by K. Pintye—Hódi. Bore Put—7: 16.0—16.5 m.

RESULTS OF THE X-RAY DIFFRACTOMETRIC INVESTIGATIONS

As against to the investigations performed till now it was stated that in the strata sequence of the bore Put—7 the presence of aragonite is common. Investigating its quantitative changes the fact was observed that from the investigated depth of 20 metres down to 40 metres aragonite is of predominant role among the carbonate minerals. Though calcite and dolomite nearly always occur in these samples, the intensity ratios of their most intense peaks are fifth-tenth of those of aragonite. The formation is alginitic marl, but within the interval of 30 to 40 metres it can be considered marl since the carbonate quantity computed from the CO_2 data amounts to about 50 per cent. Between 21.5 and 22 m in the parting surface rounded basalt tuff and basalt grains of 3 mm size can be found which indicate the boundary of the subrhythm.

At about 20 m, i. e. at the bottom of the subsequent subrhythm sandy marl intercalation occurs. Here aragonite gradually disappears and is replaced mostly by calcite, resp. dolomite. From this level towards the higher horizons "massive" alginite occurs, the carbonate content considerably decreases which is also indicated by the lower value of CO_2. In addition to the high porosity, conspicuously small bulk density developed. The change in the mineral spectrum can be followed also in the X-ray diffractogram (Table 2).

TABLE 2

X-ray diffractometric data of the samples deriving from aragonitic and aragonite-free sections

28.5 m			17.5 m		
d_{hkl}	I_{rel}	Phase	d_{hkl}	I_{rel}	Phase
14.022	10	Mont	14.022	9	Mont
9.821	9	I			
6.531	6	Fp			
4.527	7	I			
4.404	10	Mont	4.504	5	Mont
4.228	12	Q	4.290	5	Q
3.840	7	Cal	3.848	6	Cal
			3.736	6	S
3.720	6	Fp			
			3.393	61	A
3.344	47	Q, I	3.344	10	Q
			3.217	27	A
3.241	11	Fp			
3.201	11	Fp			
3.026	35	Cal	3.026	21	Cal
2.883	25	Dol	2.889	10	Dol
			2.701	30	A, Py
2.491	5	Cal	2.487	28	A, Cal
2.435	6	Q			
			2.401	10	A
			2.373	20	A
			2.341	18	A
2.270	11	Q, Cal	2.278	7	Cal
2.190	7	Dol	2.188	8	A, Dol
2.130	5	Q			
			2.107	13	A
2.088	6	Cal			
2.022	4	Dol			
1.980	4	Q			
			1.978	47	A
1.913	12	Cal			
			1.880	31	A
1.871	10	Cal			
1.817	6	Q			
			1.815	18	A

Abbraviations: A — aragonite; Cal — calcite; Dol — dolomite; Mont — montmorillonite; I — illite; Q — quartz; Fp — feldspar; Py — pyrite.

From about 14.5 m the carbonate content rapidly increases and change follow also in the quality of the carbonate minerals, *i. e.* calcite and dolomite become subordinate and aragonite plays the predominant role. In the directly overlying stratum, however, aleurite occurs with decreasing carbonate content and carbonate minerals will be represented by calcite and dolomite again. At the boundary a sandy intercalation consisting of basalt grains occurs which modifies also the mineral spectrum (see Table 3).

TABLE 3

X-ray diffractometric data of the samples deriving from the middle aragonitic and aragonite-free sections

13.5 m			13.0 m		
d_{hkl}	I_{rel}	Phase	d_{hkl}	I_{rel}	Phase
14.484	9	Mont	14.365	12	Chl
			10.377	10	I
			9.931	30	Mu
			8.226	8	Amph
			7.077	20	Chl
5.094	10	Mont			
			4.980	12	Mu
			4.404	6	I
4.426	8	Mont			
			4.247	16	Q
			4.038	8	Fp
			3.744	8	Fp, Mu
			3.532	6	Chl
			3.484	8	Mu
3.384	40	A			
3.344	10	Q	3.344	165	Q, Mu, I
3.265	20	A			
3.196	10	Fp	3.207	50	Fp
3.026	17	Cal	3.026	42	Cal
			2.939	17	Fp
2.883	19	Dol	2.883	37	Dol
			2.784	22	Oliv
2.701	20	A	2.654	11	Dol
			2.566	15	Mu, Chl
			2.541	21	Chl, Dol, Ilm
2.484	23	A, Cal	2.487	20	Cal
			2.454	10	Q
2.401	11	A, Dol			
2.367	13	A			
			2.355	7	Oliv
2.337	17	A			
			2.286	14	Q, Cal
			2.231	10	Q, Oliv
2.190	10	Dol			
			2.121	20	Q
2.102	9	A			
			2.093	11	Cal
			1.990	18	Chl, Mu

Abbreviations: A — aragonite; Cal — calcite; Dol — dolomite; Q — quartz; Mont — montmorillonite; I — illite; Mu — muscovite; Fp — feldspar; Amph — amphibole; Chl — chlorite; Oliv — olivine; Ilm — ilmenite.

In the strata sequence built up by lamina pairs the carbonate minerals are represented only by calcite and dolomite in the interval between about 12 and 8 m, aragonite is absolutely absent. In the overlying carbonate mud calcite and aragonite occur again, here the dolomite is absent (Table 4).

The role of quartz and feldspar is subordinate especially in the carbonate-rich strata, moreover, it can be stated that the decrease of carbonate content is accompanied by the increase of the quartz and frequently of the feldspar quantity. Accordingly, these play a rather subordinate role between the lower 20 to 40 m interval.

TABLE 4

X-ray diffractometric data of the samples deriving from the upper aragonitic and aragonite-free sections

11.5 m			9.5 m		
d_{hkl}	I_{rel}	Phase	d_{hkl}	I_{rel}	Phase
14.721	10	Mont	14.135	12	Mont
5.770	5	Fp			
5.022	5	Mont			
4.470	6	Mont	4.459	10	Mont
4.279	9	Q	4.228	8	Q
4.038	5	Fp	4.020	7	Fp
3.840	5	Cal			
			3.720	10	Fp
			3.624	10	Fp
3.393	45	A			
			3.344	65	Q
3.265	18	A			
3.201	15	Fp	3.162	13	Fp
3.026	37	Cal	3.016	26	Cal
2.889	27	Dol	2.883	18	Dol
2.728	12	A			
2.697	23	A, Py	2.697	12	Py
2.650	3	Dol			
			2.576	6	Mont
2.480	29	A, Cal			
			2.445	7	Q
2.401	12	A, Dol	2.407	5	Dol
2.367	14	A			
2.337	10	A			
2.275	7	Cal			
2.220	8				
2.190	10	A, Dol			
2.107	10	A			
2.097	8	Cal	2.087	6	Cal
1.976	38	A	1.974	12	Q
1.936	4	Cal			
1.902	5	Cal			
1.876	21	A, Cal			
1.815	17	A	1.812	9	Q
1.802	5	Dol	1.804	7	Dol

Abbreviations: A — aragonite; Cal — calcite; Dol — dolomite; Mont — montmorillonite; Q — quartz; Fp — feldspar; Py — pyrite.

The occurrence of clay minerals is common. First of all montmorillonite with or without illite should be taken into account. The lack of montmorillonite was restricted only to a few samples, first of all the material of the lower horizons (downwards from 36 m) contained only illite.

Minerals characteristic of the basalt were found only in few samples. These occurred mainly in the formation which contained coarser-grained material. Olivine, augite and serpentine could be determined. The presence of ilmenite and that of pyrite in the lower horizons proved to be nearly common.

The predominant minerals of the samples of the investigated bore which are characteristic of the formation are as follows: calcite, dolomite, aragonite, quartz, feldspar. The intensity ratios of them were computed so that the reflexion of the diffractogram showing the highest intensity was taken to be 100 and the other intensities were compared to this *(Fig. 7)*. It could be stated that in the formation of the lower horizon aragonite bears predominating role, quartz is sometimes absent and

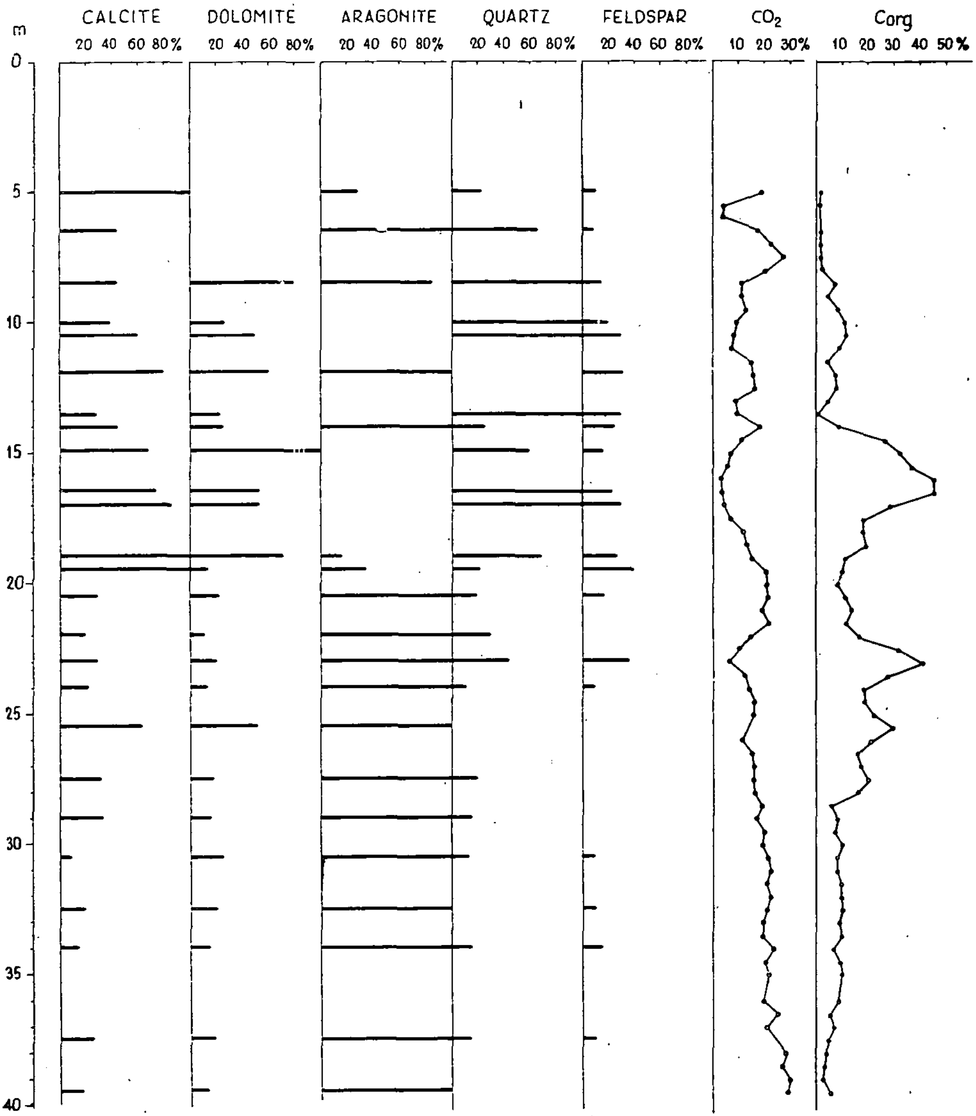

Fig. 7. Change of characteristic minerals as a function of depth.

feldspar is also subordinate. From the point of view of the mineral composition this sequence can be accepted as a uniform series (between 40 and 20 m) during sedimentation no significant displacement or change can be observed.

Between about 20 and 5 m three smaller sections can be distinguished where aragonite is absent and among the carbonates calcite and/or dolomite is of primary importance. In such cases the total carbonate content is lower, in general. At the same time, the quartz content increases, sometimes together with the feldspar content and these form the main minerals of the sequence.

When comparing the quantity of the total organic carbon (C_{org}) and CO_2 content with the mineral spectrum above as a function of depth, the fact can only be stated that in case of decreasing carbonate content the quantity of the organic matter increases, but no correlation was found between the carbonate species, or occasionally with the quartz and feldspar content.

STABILITY POSSIBILITIES AND FORMATION CONDITIONS OF ARAGONITE

It is the first case in the course of investigating the Pannonian sediments that aragonite was found, thus it is worthy to deal with its formation and stability conditions in detail.

F. G. Stehli and J. Hower [1961] demonstrated that in shallow hot water the precipitated carbonates show well-defined composition by means of biochemical and physicochemical processes, and aragonite predominates. In addition to it calcite of high Mg-content may also play an important role. In the abyssal carbonate sediments aragonite plays insignificant role beside the calcite of high Mg-content, i. e. the carbonates formed in abyssal waters are more stable. The range of stability of the $CaCO_3$ minerals was determined under normal conditions, and this is as follows: calcite of low Mg-content < aragonite < calcite of high Mg-content. Consequently, only the calcite of low Mg-content is stable as a function of time.

It has been also demonstrated that in recent carbonates aragonite frequently develops in greater amounts, but it is also known that in Pleistocene carbonates aragonite does not occur. Consequently, aragonite is instable in the sedimentary range and remain during longer times in metastable state when it does not contact aqueous solutions.

It is obvious from the facts mentioned above that in the surface and near-surface regions aragonite is instable under normal pressure and temperature conditions. Transformation takes place by means of solutions. Aragonite may remain, however, during geological times where it was bedded into clayey rocks, oil shale or asphalt of low permeability [in: H. Füchtbauer, G. Müller, 1970; A. Halam, M. J. O'Hara, 1962]. Except the conditions above, aragonite is metastable in the sedimentary and diagenetic ranges.

Taking the presence of aragonite in the bore of Pula (Put—7) it is obvious that in spite of its instable structure aragonite may be preserved if the enclosing rock is clayey and less permeable or if it is an oil shale. No explanation is given, however, on the formation of aragonite since in this case the shallow sea cannot be taken into account, but only smaller or greater lake system being sometimes independent of one another may be in question.

In the environs of the Pula bores Á. Jámbor and G. Solti [1975] determined a lagoon enclosed by the ring-shaped tuff barriers of the volcanic crater which was mostly separated from the sediment-transporting flows of the surrounding oligohaline lake. As a result of the relative depth of the lake, of the independence of wind and of the covering of the water table by algal colonies the fine-lamellar structure resulted in by slow sedimentation might be preserved. Though microflora and pollen analyses evidence a warm climate, the temperature of the lake would not be high enough to make possible the precipitation of $CaCO_3$ as aragonite.

It is to be assumed, therefore, that after the completion of the volcanic activity the hot-spring activity began within a relatively short time which is proved also by the presence of geysirs and in the chemical composition of hot-springs $Ca(HCO_3)_2$ played an important role. This would be an explanation to the higher carbonate content and predominating character of aragonite in the lower part of the sequence in the Pula bore.

The hot-spring remnants occurring in the recent surface are of different consistency. Part of them is compact with minimal porosity, the other part is loose and strongly porous. The occasionally intercalated banks are of abundant snail fauna. On the basis of X-ray diffractometric investigations the part of the sequence containing snail fauna consist nearly solely of calcite in addition to the minimal quartz content, the other types, on the other hand, consist of dolomite independently of the porosity and contains only rarely small amount of calcite or feldspar. The quartz and feldspar derive probably from the Pannonian sediments (Table 5).

TABLE 5

X-ray diffractometric data of the geysirite samples

Material of geysirites (surficial outcrop)								
loose			compact			„snail-bank"		
d_{hkl}	I_{rel}	Phase	d_{hkl}	I_{rel}	Phase	d_{hkl}	I_{rel}	Phase
4.030	10	Dol	4.038	8	Dol			
						3.848	23	Cal
3.706	20	Dol	3.698	20	Dol			
			3.344	6	Q	3.344	4	Q
3.207	4	Fp						
3.026	4	Cal				3.026	260	Cal
2.883	275	Dol	2.883	275	Dol			
						2.839	7	Cal
2.678	12	Dol	2.673	12	Dol			
2.541	10	Dol	2.541	12	Dol			
						2.460	27	Cal
2.403	40	Dol	2.407	32	Dol			
						2.280	40	Cal
2.194	90	Dol	2.192	78	Dol			
						2.093	40	Cal
2.068	13	Dol	2.066	7	Dol			
						1.910	40	Cal
						1.872	40	Cal
1.850	14	Dol	1.850	10	Dol			
1.807	30	Dol	1.807	35	Dol			
1.790	50	Dol	1.788	48	Dol			
						1.624	7	Cal
						1.602	17	Cal
1.568	8	Dol	1.568	8	Dol			
1.545	20	Dol	1.545	17	Dol			
						1.522	9	Cal

Abbreviations: Dol — dolomite; Fp — feldspar; Cal — calcite; Q — quartz

The periodical appearance of aragonite and the change of the mineral composition within the bore can be explained by the fact that this lake of relatively warm water heated by the waters of hot-springs was inundated from outside by a colder water of higher salt concentration from time to time, thus the decrease of temperature and the change of salinity were enough to stop the precipitation of aragonite. Simultaneously, the grain size of the sediment is changing, quartz becomes usually predominating and feldspar plays also more important role. In these cases the quantity of the total carbonate decreases since the lake's water was diluted and its temperature also decreased. The original equilibrium, however, returns within a short time and this allows the conclusion that the incoming colder water quantity of other salt concentration was less significant. In the bore three inundation periods can be distinguished which can be followed also in the change of textural features of the core material. By means of this the sudden change in the mineral composition can be explained.

In relation with the organic matter's quantity slight connection with the mineral composition can be demonstrated, since in the sections where aragonite is absent and the mineral composition changes the percentual quantity of C_{org} will be usually high, which can be caused by the large-scale growth and death of the algal colonies just because of the changed biotope. The greater abundance of the organic matter in certain horizons and in greater depths cannot be sufficiently explained yet.

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EXPLANATION OF PLATES

PLATE I, Bore Put—7.

1. 39.0—39.3 m. Textural picture of alginitic carbonate mud. In the lighter strips the slight accumulation of carbonates can be observed. Ostracods. // N, M = 35 x.

2. 36.0—36.5 m. Alginitic carbonate mud, unstratified ("massive") type. The traces of Botryococcus colonies and spots of organic matter show random occurrence. // N, M = 140 x.

3. 32.0—32.5 m. Alginitic marl, unstratified, though the arrangement of Botryococcus colonies suggests some kind of orientation, the spot-like accumulation of the carbonate content, however, interrupts these "series". Slide is perpendicular of bedding. // N, M = 35 x.

4. 32.0—32.5 m. Section of the previous slide. // N. M = 140 x.

PLATE II, Bore Put—7.

1. 25.0—25.5 m. Oil shale (alginite), unstratified type. The record is a part of a carbonate mud spot in which indistinct Botryococcus colonies and spots consisting of organic matter are shown. // N, M = 35 x.

2. 25.0—255. m. Oil shale (alginite). Section consisting mostly of Botryococcus colonies. // N, M = = 140 x.

3. 21.5—22.0 m. Basalt sand grain from the thinstratified alginite — carbonate mud section of lamina-paired structure. Slide is parallel with bedding. // N, M = 140 x.

PLATE III, Bore Put—7.

1. 20.0—20.5 m. Coalified plant tissue fragment on the surface of lamina of carbonate mud material. Slide is parallel with stratification. // N, M = 140 x.

2. 16.0—16.5 m Alginite. Textural picture of unstratified ("massive") type with a lot of Botryococcus colonies. // N, M = 10 x.

3. 16.0—16.5 m. Section from the previous slide. // N, M = 35 x.

PLATE IV, Bore Put—7 .

1. 14.5—15.0 m. Alginite. Slightly oriented texture, transition between the "massive" and "startified" types, it is inclined to part by shocks, no change in material quality can be observed at the surfaces. Slide is perpendiof the parting surface. // N, M = 10 x.

2. 14.5—15.0 m. Section of the previous slide. // N, M = 140 x.

3. 13.4—14.0 m. Coalified plant fragments on the surface of carbonate mud lamina. N, M = 140 x.

4. 13.0—13.4 m. Textural picture of the lamina of basalt tuff matter. The same section is abundant in clay minerals, as well. // N, M = 10 x.

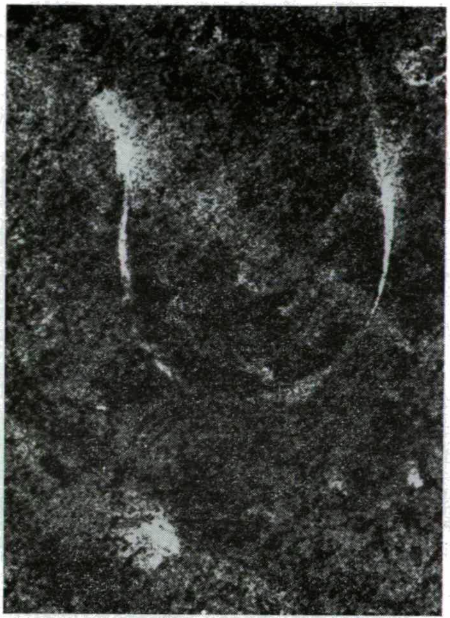
PLATE V

1. Bore Put—3. 11.1—11.6 m. Grain fragments cemented by carbonate mud and of mixed origin From lamina of basalt tuff matter. // N, M = 140 x.

2. Bore Put—3. 11.1—11.6 m. The same but crossed. // N, M = 140 x.

3. Bore Put—7. 9.0—9.5 m. Plant fragment on the surface of a lamina of mostly carbonate mud material. // N, M = 140 x.

4. Bore Put—7. 8.0—8.5 m. Textural picture of carbonate mud. // N, M = 140 x.



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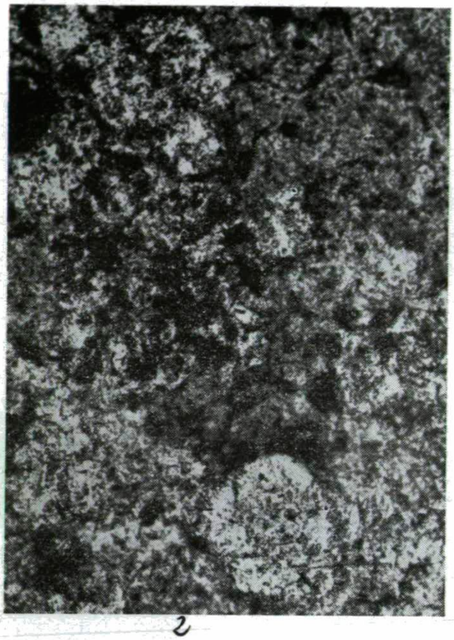

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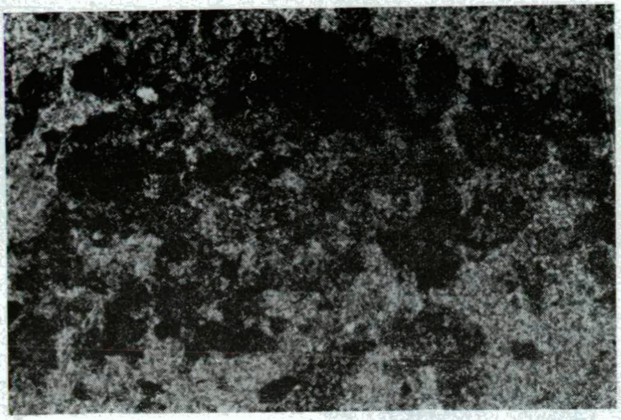

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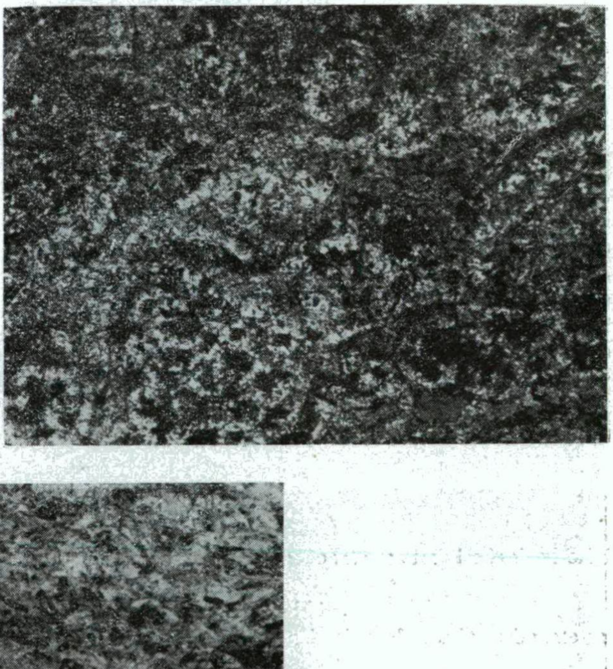

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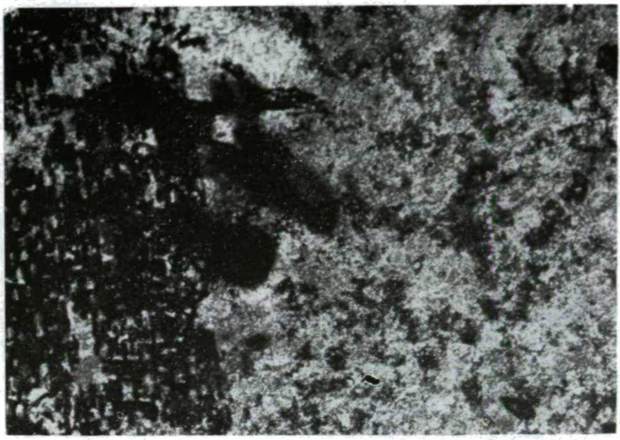

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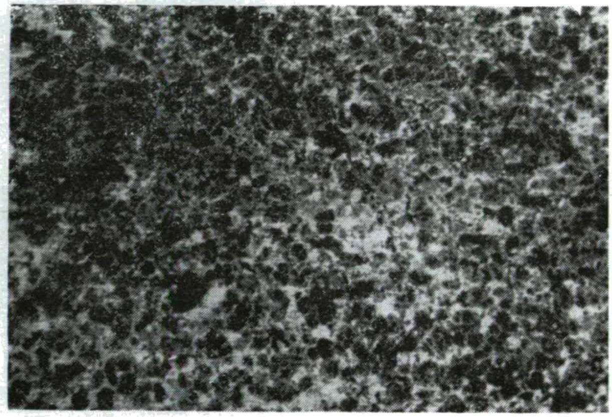

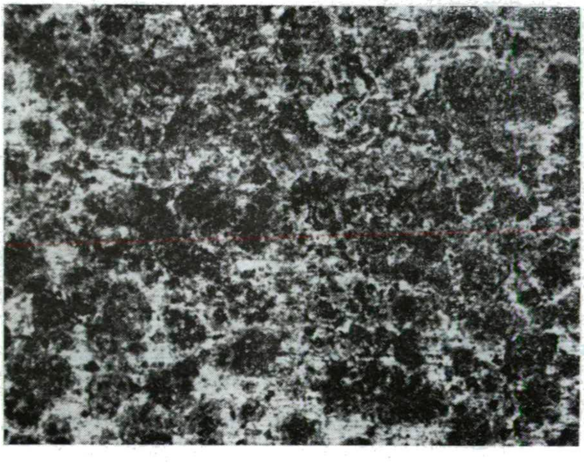

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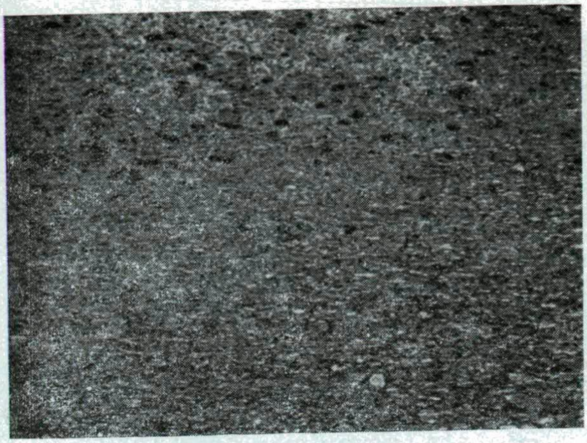

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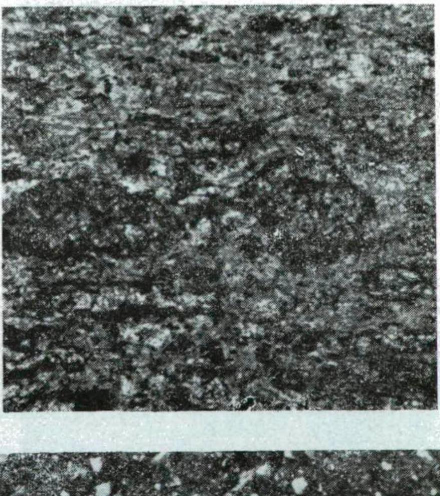

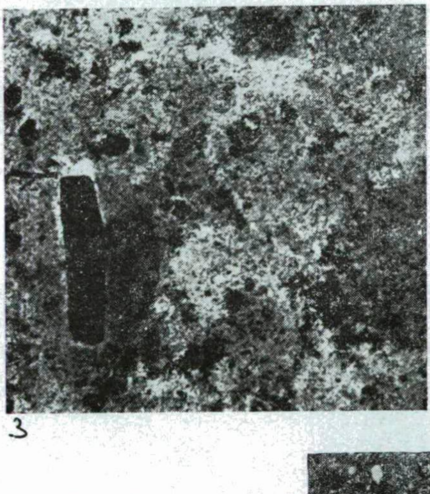

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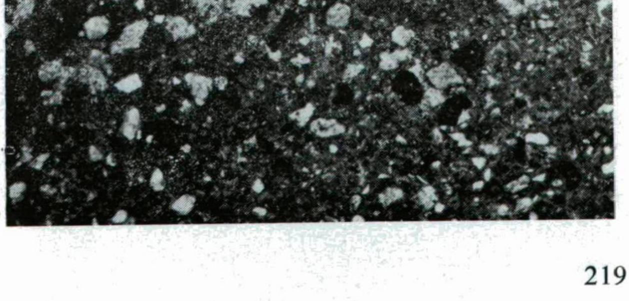

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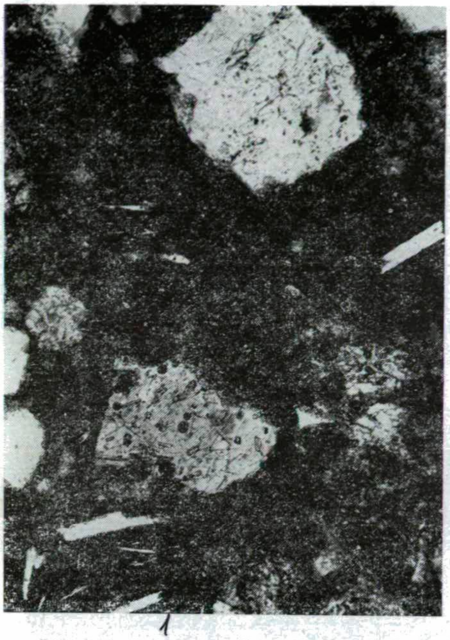
PLATE V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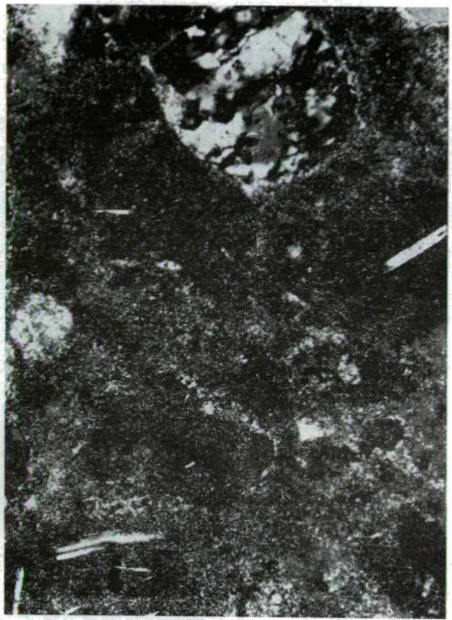
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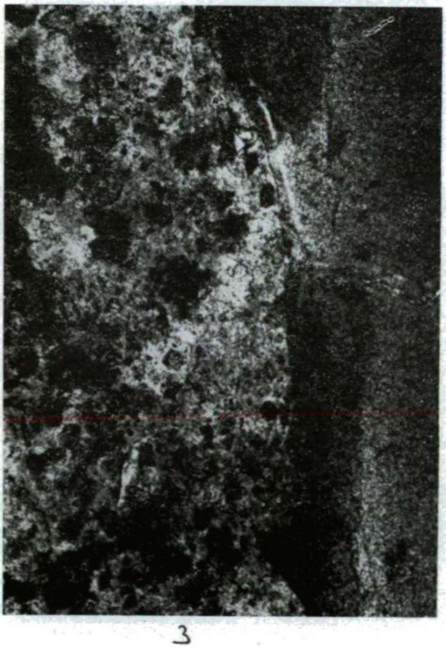
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