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SCANNING ELECTRON MICROSCOPY OF *GLOEOCAPSOMORPHA* AS PRODUCED FROM KEROGEN OXIDATION

Abstract

The microphytofossil-rich part of kukersite kerogen (kukersine) (Plate 1), was concentrated from the kukersineous limestone (seam "B/C", Kohtla, north-eastern Estonia). Samples were subjected to controlled mild oxidation with nitric acid to

(1) study the morphostructural features of disintegrating kerogen particles, and

(2) obtain microphytofossils. The initial kukersine, as well as the nitric acid and potassium hydroxide treated kukersine, particles were examined under the scanning electron microscope (Plates 2, 3).

Oxidized kukersine particles of two morphotypes revealed varying disintegration features depending on the content and preservability of fossil structures. Kukersine morphotype 1, the microfossil-rich component,was more resistant to oxidation in comparison to morphotype 2. The latter bound more nitrogen and oxygen and lost more organic matter (Table 2). Spore-like tetrad units of morphotype 1 were the most oxidation- resistant parts of kukersine particles.

Introduction

1. Objectives

The kerogen component of kukersite (kukersine) is composed of distinct morphostructural varieties. These individual aggregate-like, globular or platy kerogen particles, mostly 100-300 μm in size, can be identified on the basis of microphytofossil content and surficial morphology and classified into separate groups of morphotypes. The origin of morphostructural features and biological affinity of kukersine particles has been previously analysed by both, the chemists and paleontologists (see most of the references). Earlier contradictory results might have partly resulted from the fact that samples and rock types studied by individual researchers were predominantly of one certain structural type, to which they paid particular attention, but other structures went unnoticed. The present study focuses attention on the microfossil-rich kukersine variety, abundant in limestones, and on the results of its controlled oxidation. Already M. Zalessky [1] commented that the best-preserved *Gloeocapsomorpha* fossils can be obtained from limestones that alternate with kukersite seams. However, this fact seems to have been almost forgotten.

Until recently there has not been any convincing proof as to the origin of microphytofossils occurring in kukersine particles:

(1) do they form an original complete organism - a colony of cyanobacteria [1-4], a colony of green alga [5, 6]; or

(2) are they separate fossil units in kukersine particles (possibly a reproductive or resting stage of cyanobacteria, [7, 8])?

The latter interpretation does not mean that the kukersine particle is of synthetic origin (as reported in [9-11]). Still, it is imperative that one obtains the description of the ultrastructural features of microfossils that occur inside those particles before making

an interpretation about their fossil affinity. Stepwise oxidative destruction of aggregate-like kerogen particles (colonies by Zalessky [1], a part of tallomoalginite by Ginsburg [12], kukersine morphotype 1 by Kôrts [8]), was thought to contribute to the solution of the problem. Describing the ultrastructural features of the fossils is not the task of the present article, but would be the topic for a paleontological paper.

The aim of the experiment was to disintegrate the kerogen particles and to isolate individual structural units as well-preserved microphytofossils. Oxidative destruction by nitric acid has not been previously used as a preparation method in order to obtain phytofossils from kukersineous rocks.

An additional aspect in this research concerned the selective chemical destruction that might occur in kukersine particles of different structure: morphotype 1 - those which contain well-preserved microfossil structures, and morphotype 2 - those in which the original fossil structures are nearly destroyed. For this purpose the second component from the same sample, kukersine morphotype 2, was used for comparison. The earlier scanning electron microscope (SEM) studies [8] developed the conclusion that kerogen particles might be composed of various chemical constituents and selective degradation should reveal which parts of fossil structures are the most resistant ones and have favoured the fossilization.

Scanning electron microscopy has provided the general morphology of *Gloeocapsomorpha* [3, 5, 13] and details of the inner structure of kerogen particles [8], but until recently transmission electron microscopy was predominantly used in the study of *Gloeocapsomorpha*-kerogen [6, 14, 15]. Ultrastructural features, enabling the confirmation of the systematic position of microfossils, are still lacking although SEM provides good prospects in future research. SEM was used in Estonia to study the kukersite kerogen already in the 1970s [16], but no photos were published. Some laboratory techniques worked out at that time are applied in this research even now.

2. Oxidation Method in Organic Geochemistry and Paleobotany

Structural investigations of insoluble oil shale kerogen have often included controlled oxidation to obtain soluble derivatives of polymeric components of the kerogen. Alkaline potassium permanganate, nitric acid, chromic acid, ozone and other oxidants have been used to disintegrate the kerogen. Although the method has been widely used in its many modifications, the initial kerogen and its residues (if the kerogen has not been totally dissolved during the experiment), as produced by various oxidants, have rarely been the subject of scanning electron microscopy [17]. There is no need for such studies if the kerogen is homogeneous in its morphology, structure and chemical composition. The kukersite kerogen, however, is comprised of at least three different varieties separable on the basis of fossil structural content and their preservational state. The varieties should reveal differentiated disintegration features.

In Estonia, while studying the chemical composition and structure of the kukersite kerogen, mild stepwise oxidation with several oxidants has been used and the composition of low molecular weight carboxylic acids analyzed [18, 19]. Morphologically heterogeneous kerogen from kukersite seams "A" and "B" (Kukruse Regional Stage) was used in these oxidation experiments. The first works of that kind were started already at the beginning of the 20th century [9, 20], when several oxidants ($KClO_3 + HNO_3$; HNO_3) were put into use to disintegrate the kukersite kerogen.

There are also other oxidation techniques, which are common laboratory procedures in paleobotanical studies, that have not been used in the earlier efforts to extract microfossils from the kukersite kerogen. Examples of these techniques include (1)

cleaning palynomorphs - spores and pollen, and (2) releasing higher land plant fossils from disturbed carbonized organic matter [21-23]. Schulze's solution, which is a mixture of concentrated nitric acid and potassium chlorate (used hot or cold), is the most common strong oxidant which is able to macerate higher land plants and sporomorphs. In this solution the structureless organic matter oxidizes into humic acids to be removed afterwards with weak base. The fossil, suitable for paleontological research, is left intact.

The selection of the oxidant depends on the type and preservability of the organic matter. The oxidant type, its concentration and processing time are important factors in this experimental work. Proper selection of these variables is required in order to avoid damage to fossil specimens or the emergence of secondary structures in the fossils. In the present work, slow oxidation at room temperature with 68% nitric acid was preferred so as to document the stepwise desintegration of kerogen and to avoid fast decomposition of basic morphological structures.

Experiments

1. Rock Sample

The rock sample originated from the kukersineous limestone (seam "B/C",Kiviôli Member, Viivikonna Formation, Kukruse Regional Stage of the middle Ordovician) of Kohtla oil shale quarry in north-eastern Estonia. A sample of kukersineous limestone weighing 4 kilograms was taken from the fresh cut at the quarry and crushed into 2-3 cm pieces. Then, 500 grams of the sample were selected for the oxidation experiment. This limestone is rich in the debris of marine invertebrates: echinoderms, bryozoans, brachiopods, microgastropods, trilobites, ostracodes. The description of the Kohtla section has been published previously [24].

2. Kukersine Decalcification

The kukersine was concentrated from the kukersineous limestone by treatment in 10 % HCl solution. Separation of the specific morphotype from the bulk kerogen rock sample was effected by taking advantage of the differences in the specific gravity of kukersine particles. This density difference depends on the inner kukersine composition, i. e. the presence or absence of fossil structures. This aspect was noticed by one of the authors while preparing kukersineous limestone samples for paleontological studies [8].

During the decomposition of the rock sample in the 10 % HCl solution, the low-density kerogen (morphotype 1, MT1) concentrated on the surface of the solution. This MT1 was pipetted from there to a filter paper, washed with distilled water and left to dry for 48 hours at room temperture. The fact that the extracted 12 grams of "light" kukersine (MT1) formed a nearly homogeneous concentrate was confirmed later by comparative SEM studies. These compared the morphotype 1 and the "heavy" kerogen residue (mostly morphotype 2, MT2). The latter had settled to the bottom of the vessel. A measured amount of MT2, 16 grams, were taken for analysis. It did not contain many microphytofossils.

The extracted *Gloeocapsomorpha*-kerogen MT1 consisted of yellow algal lumps of mostly 100-250 μm in size. It had smooth surface sculpture and an aggregate-like appearance. This suggests the presence of microfossils (Plate 1, figs. *1* and *2*). Single bright yellow particles revealed general surface corrosion, but their amount in the kerogen is small. The inner structure that appeared in cross-sections of these kukersine particles (Plate 1, figs. *3* and *4*) showed well-preserved microphytofossil structures: individual cell-units (capsules) of 2-4 μm in size, grouped in dyads and tetrads forming

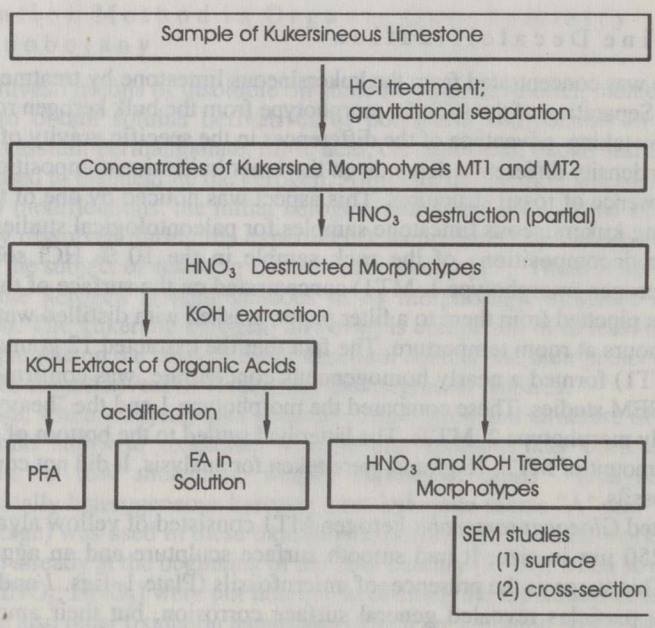
spherical structure, predominantly 8- 20 μm in diameter. The size of these spherical microfossil units varies depending on the number of cell-units inside. The cross-section reveals two basic types of the inner structure for the spherical units: first, dyads of oval cells (Plate 1, fig. *4*), and second, tetrads (maybe 8 to 16 cells) with cells of angular outline (Plate 1, fig. *3*).

Data about the elemental composition of the extracted kukersine, separated into concentrates, are presented in Table 1. The kukersine residue, MT2, contained more inorganic admixture in comparison with kukersine concentrate, MT1. The two concentrates differed as well in oxygen to carbon (O/C) ratios and oxygen concentration. It is known that chemical demineralization does not cause significant changes in kerogen atomic ratios [28]. The slight differences can be partly dependent on the composition of the organic matter.

Table 1. **Elemental Composition (%) and Atomic Ratios of Kukersine Morphotype 1 (MT1) and Morphotype 2 (MT2) Concentrates**

Morpho-type	W^a	A^d	C^{daf}	H^{daf}	N^{daf}	O^{daf}	H/C	O/C
MT1	0.29	20.2	76.0	9.6	0.3	14.1	1.52	0.142
MT2	1.32	36.1	72.3	9.3	0.3	18.1	1.54	0.191

An outline of all procedures used during sample processing is depicted in Figure.



Sample preparation and analyses (see the text for the abbreviations)

3. Kukersine Oxidation

The controlled oxidation of kukersine (MT1 and MT2) was carried out at room temperature using 68 % nitric acid as an oxidant. Potassium hydroxide solution (0.5-1 %) was used to remove polyfunctional acids formed during the destruction process. These polyfunctional acids (PFA) are the derivatives of kukersine macromolecules. The PFAs of kukersite kerogen and the humic acids of oxidized coal are alike in several features (insoluble in acids and soluble in alkaline solution), but have differing chemical natures [25].

Both kukersine concentrates were divided into 4 samples, of 1.4-2.6 grams in weight. These samples were treated with nitric acid for 48, 72, 90 and 96 hours, respectively. The fourth sample of MT1 was treated for additional 96 hours. The chosen reaction times were based on earlier studies of kukersite kerogen oxidation.

According to the elemental composition and the atomic ratios of the nitric acid-treated kerogen, the MT2 bound more nitrogen and oxygen - having ratios of H/C = 1.36-1.38 and (O+N)/C = 0.42-0.49. The values for the MT1 fraction were H/C = 1.31-1.34 and (O+N)/C = 0.36-0.44. These data differ from earlier results [18] where no preferred decomposition of structural elements of heterogeneous kukersite kerogen (seam "B") was observed in the oxidation experiment.

The percentage of organic matter (after nitric acid treatment) reached 104.0 - -110.8 % for MT1, and 102.1-110.4 % for MT2 (Table 2). The polyfunctional acids were extracted into the potassium hydroxide solution and after the KOH treatment 50.5- 84.5 % of the organic matter of MT1 was preserved. In the MT2 fraction 42.8-60.8 % preserved. In addition to polyfunctional acids, the amount of low molecular weight acids, fulvic acids (FA), was determined. In total, the kukersine MT1 lost 26.3-53.5 % and MT2 43.0-59.3 % of organic matter as a result of acid and base treatment (Table 2). After the 192 hour oxidation, kukersine MT1 disintegrated and dissolved in the KOH solution. Other treated samples were collected, washed with distilled water, and prepared for microscopic studies.

Thus it can be noted that kukersine morphotype 2, the sample residue, disintegrated more effectively and lost more organic matter in comparison with MT1, which contained well-preserved fossil structures. This means that these concentrates differ in chemical composition, MT1 being more resistant to acid and base treatment. As with the original kukersine, half or less of the sample was preserved for microscopic studies. It must be kept in mind that only the best-preserved material could be studied.

Scanning Electron Microscopy

1. Preparation of Specimens

The original kerogen, and the specimens obtained from the oxidation experiment, were divided into two parts for microscopic studies. One part was prepared for the study of general morphological features, shape and size, as well as to document surface damage caused by acid and base treatment. The individual kukersine particles were mounted on a thin gelatin cover on SEM stubs and gold-coated. Fifty to one hundred specimens were studied from each fraction and approximately 20 of them were photographed.

Another part of every fraction was prepared for sectioning in order to study the inner structure and its changes. Specimens were mounted in glue (PF-6) and after desiccation in plastic tubes (for 2-3 days at room temperature), these were sectioned using a metal-bladed knife. After being removed from the plastic cover, the sectioned slices

were glued to SEM stubs. Specimens were not treated with alcohol to avoid shrinking effects that would spoil sectioning. The structures of 50-60 kukersine particles were documented from cross-sections of a certain sample and approximately 10 specimens were photographed.

2. Optical Examination and Results

Earlier SEM studies of oxidized heterogeneous kukersine (unpublished results by the authors) allowed one to conclude that the disintegration of the kukersine particle starts with the decomposition of the matrix material, instead of with the spherical morphostructural microfossil units. The latter are more resistant to this degradation. The present study confirmed this observation, and it appeared that the process continued by breaking off spherical morphostructural units and their surface corrosion. Kukersine particles of morphotype 2, which contained more matrix material, disintegrated more completely (Table 2).

Table 2. **Kukersine Organic Matter (OM) after HNO_3 and KOH Treatment**

Sample	Time	OM after HNO_3 (%)	OM after KOH (%)	PFA (%)	FA (%)	PFA + FA (%)
Morphotype 1						
1	48	104.7	70.1	15.1	19.5	34.6
2	72	110.8	84.5	11.2	19.5	26.3
3	90	106.9	62.1	21.3	23.5	44.8
4	96	104.0	50.5	27.1	26.4	53.5
Morphotype 2						
1	48	110.4	60.8	11.9	37.7	49.6
2	72	103.8	60.8	17.2	25.8	43.0
3	90	109.0	51.3	24.2	33.5	57.7
4	96	102.1	42.8	29.1	30.2	59.3

As the amount of organic matter increases slightly during the oxidation process in nitric acid solution, the actual influence of the nitric acid treatment on kukersine particles can be observed once the polyfunctional acids have been extracted. Silurian palynomorphs that have been treated with Clorox in short-term oxidation experiments [26] increased remarkably in size (up to 19 %). It is possible that a slight increase in the amount of organic matter (5-10 %), caused by oxidation with nitric acid in the present experiment favoured cross-sectioning of kukersine particles which would otherwise have been too fragile for successful sectioning for SEM studies.

The first two oxidations (48 and 72 hours) did not show substantial damage in MT1, the microfossil-rich componentof kukersine. Slight, differenciated decomposition of morphostructural elements was seen after the 90 hour test. Remarkable destruction occurred after 96 hours of oxidation, but mostly in particles containing dyads. Spherical morphostructural units (microfossils) became partly detached from the surface of the kukersine particle and possessed thinned coverings in the 96-hour acid treatment residue (Plate 2, figs. *1* and *2*). Cross- sections showed that microfossil structures (walls) inside had become fused with the matrix material (Plate 2, fig. *4*). The disintegration features were observed especially in the KOH treated residue (Plate 3, fig. *1*), where microfossils possessed collapsed surfaces.

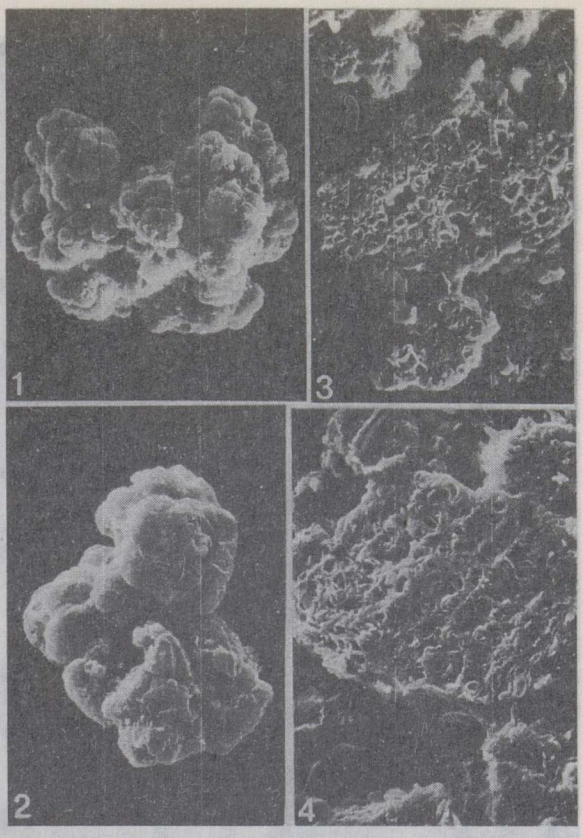


Plate 1. The original kukersine, morphotype 1: figs. *1* and *2* - general outlook of kukersine particles (magnification for fig. *1* - 480, for fig. 2 - 800); figs. *3* and *4* - cross-sections of kukersine particles showing the inner microfossil structures (magn. for figs. *3* and *4* - 1,000)

The cross-sections of 96-hour acid treatment residues of kukersine particles, which contained tetrad microfossils, showed minor destruction effects (Plate 2, fig. *3*), but base treatment had slightly damaged the tetrad walls (Plate 3, figs. *2* and *3*).

Oxidation residue from the 192-hour test (Plate 3, fig. *4*) still contained microfossils, but with thinned walls, partly fused with the matrix.

Results and Discussion

Oxidation with sodium hypochlorite and nitric acid, which are milder oxidants than the Schulze's solution, have seldom worked well in treatment of Paleozoic plants [23]. Nitric acid (68 %) worked well enough with kukersite kerogen and the fossil structures were revealed after disintegration in nitric acid and a base.

Results of the experimental study confirmed that the particles of kukersine morphotype 1 are entirely formed of well-preserved microfossil units. All these units, dispersed from kerogen particles in the oxidation process, are spherical or oval. It may be noted that the microfossil walls are more resistant to degradation than the matrix material in morphotype 2 particles.

After partly dissolving the organic matter of kukersine particles, the coverings of microfossils became thinner and shrank in the SEM vacuum tube, leaving the impression of opened cups of *Botryococcus*. Still, this is a secondary feature caused by acid and base treatment. Exposed cross-sections did not reveal original arrangement of

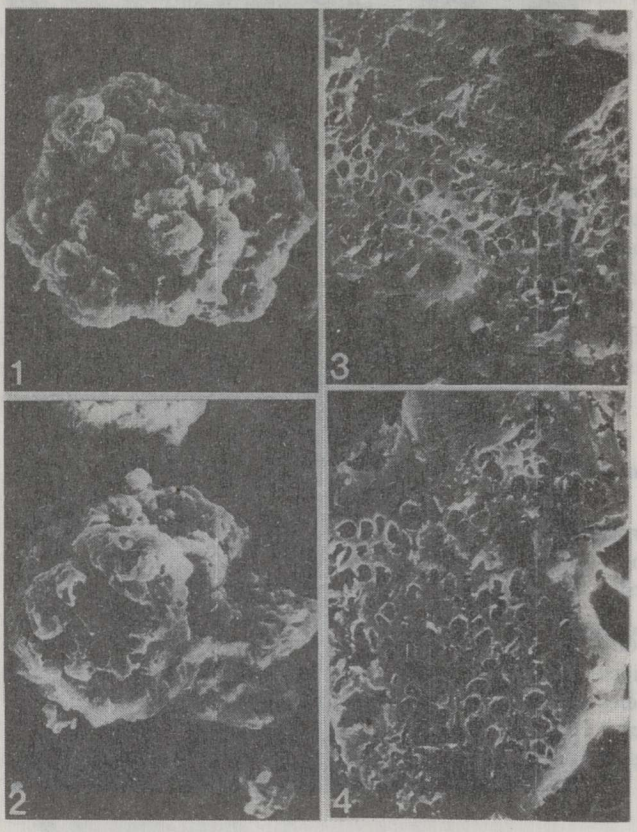


Plate 2. Kukersine MT1 after 96 hour oxidation: figs. *1* and *2* - general outlook (magn. for fig. *1* - 800, for fig. *2* - 1200); figs. *3* and *4* - cross-sections (magn. for fig. *3* - 1,200, for fig. *4* - 1,400)

cell-units of *Botryococcus*-type, i.e. cup-like dyad units forming radial structures. Instead, the parts that detached from kukersine particles were, without exception, spherical or oval.

Since the kukersine disintegration seems to reveal no microfossil structures referable either to cyanobacteria (colonies of *Entophysalidaceae*) or the green alga *Botryococcus* (cup-like cells or autospores of the colony), the microphytofossils of kukersine need to be redescribed on the basis of diagnostic ultrastructural features documented by the present and earlier SEM studies. This means that,at the present time, the biological affinity of *Gloeocapsomorpha prisca* Zalessky remains unclear. Nevertheless, it is certain that morphostructural units of different chemical structure are present in the kukersine particles and the most resistant parts, isolated from kukersine particles in the course of oxidation and base treatment, are not colony structures but probably spore- or sporangium-like (dyads, tetrads, 8-, 16-cell) units. Recently published results by Derenne et al. [27], on the spectroscopic features of *Gloeocapsomorpha* revealed by transmission micro-FT - i. r., demonstrated that phenolic moieties in the kukersite originate from *Gloeocapsomorpha* and not from the organo-mineral material of the kukersite. The present experiment demonstrated that it is even possible that fossil structures might be of different chemical composition. Dyad- and tetrad-containing kukersine particles showed differing resistances to nitric acid and potassium hydroxide treatment.

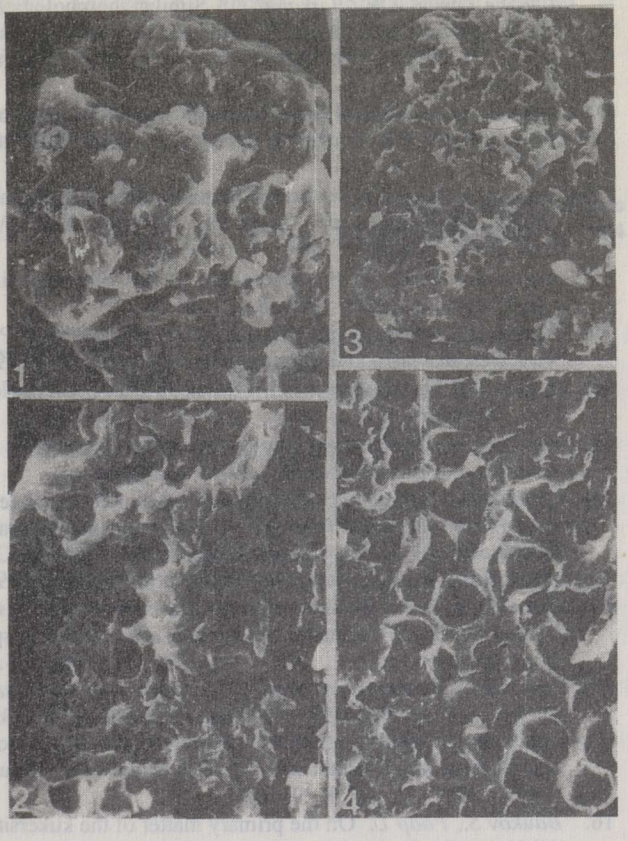


Plate 3. Kukersine MT1 (*1-3*) after 96 hour oxidation and KOH treatment, and (*4*) after 192 hour oxidation (magn. for fig. *1* - 1,600, fig. *2* - 3,200, fig. *3* - 1,200, fig. *4* - 4,000)

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