Bull. Inst. r. Sci. nat. Belg. Bull. K. Belg. Inst. Nat. Wet.	47	41	Brux. 31.8.1971

BIOCHEMICAL COMPOSITION AND SUBMICROSCOPIC STRUCTURE OF MATRICES OF NACREOUS CONCHIOLIN IN FOSSIL CEPHALOPODS (NAUTILOIDS AND AMMONOIDS)

BY

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(avec 11 planches hors texte)

INTRODUCTION

Remnants of nacreous conchiolin matrices variously altered in their ultrastructure have been detected with the transmission electron microscope in more than 250 species (including 203 Cephalopods) of fossil molluscs of different ages (Pliocene to Ordovician) : GRÉGOIRE, 1958, 1959 ab, 1966 ab and unpublished results; GRANDJEAN, GRÉGOIRE and LUTTS, 1964; GRÉGOIRE and TEICHERT, 1965). All these remnants were biuret-positive, which indicates the presence of peptide bounds in these structures.

Using biochemical procedures, ABELSON (1954, 1957) was the first to record persistance of amino acids in fossil mollusc shells. Examples of preservation of polypeptidic portions of the original protidic components have been since reported in shells of fossil molluscs and brachiopods of various ages (*Mercenaria,* Pleistocene : JONES and VALLENTYNE, 1960; Oligocene and Eocene nautiloids : FLORKIN et al., 1961; Pliocene and Pleistocene scallop shells : AKIYAMA, 1964; *Gyraulus trochiformis,* Gastropod, Tertiary of Steinheim : DEGENS and LOVE, 1965; Pliocene to recent non-marine molluscs : HO, 1966; Miocene, Pliocene and Pleistocene *Mercenaria* and *Oliva* : MITTERER 1966; Lower Eocene (*Pinna affinis),* Cretaceous *(Inoceramus)* prism conchiolin : BRICTEUX-GRÉGOIRE et al., 1968; Jurassic to Silurian brachiopods : FOUCART, unpublished observation, 1965; JOPE, 1967, 1969.

The present paper is a biochemical analysis of thirty samples of nacreous substance from Devonian, Pennsylvanian, Permian, Jurassic, Cretaceous, Eocene and Miocene nautiloids and ammonoids, in which the electron microscope had revealed the presence of relics of the original conchiolin matrices.

Abstracts of the results have been given in Archives de Physiologie et de Biochimie (1970) and in Biomineralisation Forschungsberichte (1971). The figures which illustrate the present paper were recorded on new preparations of the material.

MATERIALS AND METHODS

The nautiloids and ammonoids selected for the present study are listed in tables 1 and 2 (file numbers in brackets).

The samples used for the biochemical analyses consisted of the inner nacreous layer of the shell wall from 27 species, of septal mother-of-pearl from 3 species, and of fragments of sedimentary rock surrounding three Jurassic and one Devonian specimens (see table 3).

The shell samples were removed from the surrounding rock immediately before use and the superficial, weathered shell layers were discarded. The rock samples were collected in the proximity (2 mm and 1 cm away) of the outermost portions of the shell wall.

Biochemical analysis.

After several washings and desiccation under vacuum, the samples were weighed, avoiding handling with the fingers.

0.5 N hydrochloric acid was used for decalcification, performed in closed containers placed in an ice-box. E D T A was discarded for the biochemical analyses. Demineralisation is very slow in this decalcifier, which increases the risk of contamination during laboratory handling. Besides, incomplete elimination of E D T A leaves amino groups which could interfere with the subsequent chromatographic analyses (see HARE, 1962).

The organic remnants of decalcification and the solvent were dialyzed against distilled water in closed containers in the cold room. This water was repeatedly changed in order to discard the hydrochloric acid and the free amino acids of the samples. The content of the dialysis bag was evaporated under vacuum in a rotatory desiccator. The residue was hydrolyzed in sealed tubes with 4 ml of 6 N hydrochloric acid for 24 hours at 110 °C.

The amino acids were separated and quantitatively determined with a Beckman Spinco amino acid analyser (method of SPACKMAN *et al.*, 1958).

The acidic and neutral amino acids were eluated from a 50 cm column with citrate buffers of pH 3.25 and pH 4.25. The basic amino acids were eluated from a 5 cm column with a buffer of pH 5.28.

Identification of glucosamine and galactosamine, carried out with a 50 cm column, was performed by elution with two citrate buffers, respectively of pH 4.26 and 5.28, at the temperature of 50 °C (FOUCART, 1966).

X-Ray diffraction

The nature of the minerals composing the samples has been determined by X-ray-powder diffraction analysis (see GRANDJEAN, GRÉGOIRE and LUTTS, 1964). As already pointed out, with the diffractometer available, lesser amounts than 3 per cent of the mineral could not be recorded. Under these conditions, the data reported in table 2 indicate only the predominant mineral found in the samples. On the other hand, substances undetected in the samples selected for electron microscopy (e.g. $FeS2$, $SiO2$, $BaSO4$: see table 1), were recorded in the insoluble, frequently fine-grained mineral residues of decalcification of the material used for the biochemical analyses, which involved much greater amounts of substance (about five to twenty grams) than those used for electron microscopy (a few milligrams and less).

Electron microscopy

The procedures used in preparation of the conchiolin matrices for examination in the transmission electron microscope have been described and discussed elsewhere (GRÉGOIRE, 1958, 1959 ab, 1966 a, p. 13, 1968, p. 16; GRÉGOIRE and LORENT, 1971) namely as regards the artifacts caused by the brittleness which characterizes the fossil organic remnants. The fragments of mother-of-pearl were decalcified with E D T A disodium salt (saturated aqueous solutions of titriplex III, Merck), at pH 4.0 and 7.5.

Fragments of interlamellar matrices collapsed and agglutinated in several superimposed layers after disappearance of the mineral components and too opaque to the electron beam were separated into individual sheets by a short exposure (e.g. a few seconds) in distilled water to ultrasonic waves, using a Headland Ultrasonic equipment.

In other preparations, the interlamellar conchiolin matrices were revealed in their original location in the form of pseudoreplicas remaining attached to the replicas on surfaces of mother-of-pearl polished in tangential orientation and moderately etched, and on etched and unetched surfaces of cleavage along the interlamellar spaces (see GRÉGOIRE, 1966, p. 28 and Fig. 9; GRÉGOIRE and LORENT, 1971).

The different methods used gave concordant results.

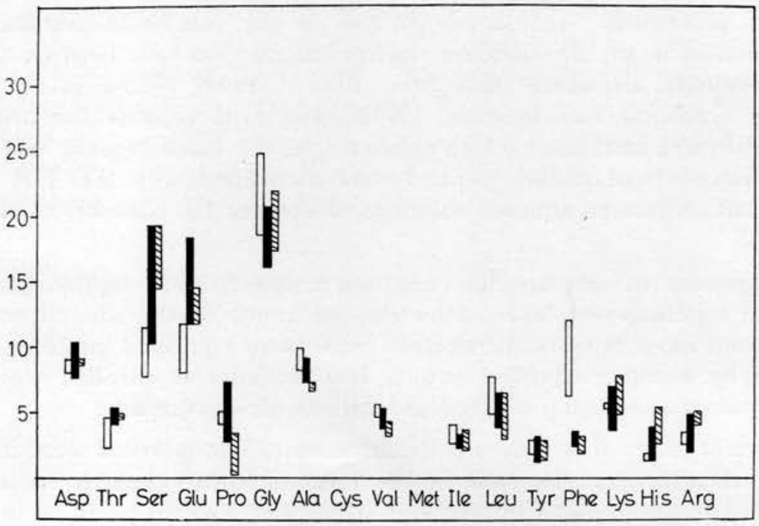
All the observations were carried out with a Siemens Elmiskop I, using a double condenser, a 200 μ condenser aperture, a 30 μ objective aperture and a cold stage.

RESULTS

1. Biochemical analyses

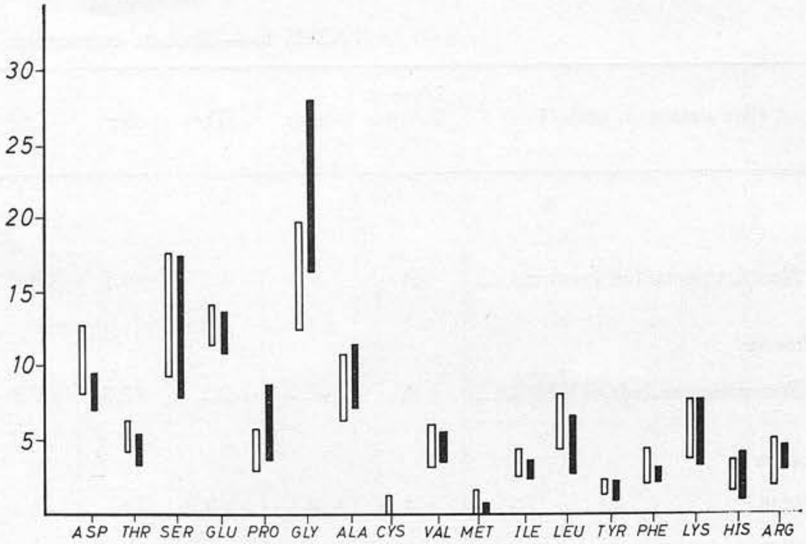
The results of the analyses of the polypeptidic remains of twelve samples of nautiloid shell material (Miocene to Devonian) and of twenty-two samples of Cretaceous and of Jurassic ammonoid shells are reported in tables 1 and 2. The biochemical composition of the sediment surrounding three specimens is given in table 3. In these tables, the amino-acid composition of the fossil proteins are stated as amino-acid residues per 100 total amino-acid residues. This method permits a direct comparison of the results without taking into account the differences in the protidic content of the various samples and the variations in the volume of the aliquots analyzed.

1) In the nacreous substance of all the samples, nautiloids and ammonoids, from geologic periods extending from Miocene to Devonian, and collected in the most various localities, non dialysable assortments of amino acids (polypeptides) have been recorded. The specimens



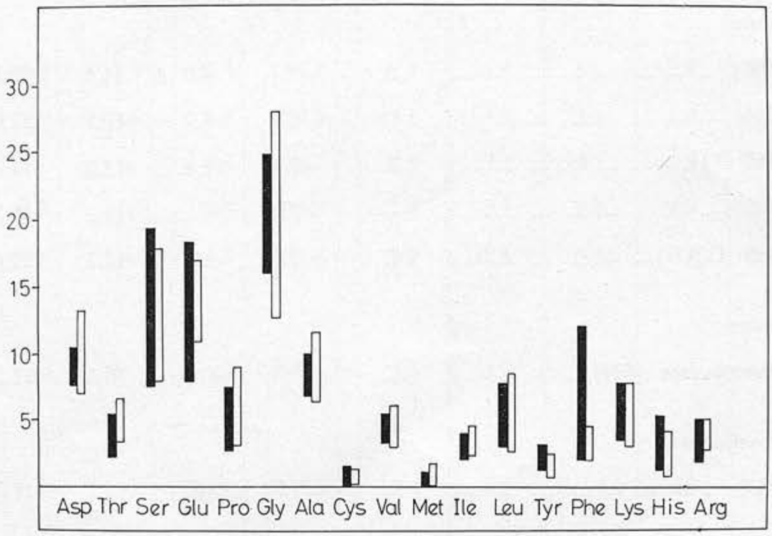
Textfig. 1.

Amino acid composition of shell proteins in fossil Nautiloids
/// Cenozoic Nautiloids.
■ Mesozoic Nautiloids.
□ Paleozoic Nautiloids.



Textfig. 2.

Amino acid composition of shell proteins in fossil Ammonoids.
□ Jurassic.
■ Cretaceous.



Textfig. 3.

Amino acid composition of shell proteins in fossil Ammonoids and Nautiloids.
■ Nautiloids.
□ Ammonoids.

TABLE 1. — Protidic components of the conchiolin matrices. Amino acid residues per cent total amino acid residues.

(See details in table 4)	Mineral Compo-sition	Asp	Thr	Ser	Glu	Pro	Gly	Ala	Cys	Val	Met	Ile	Leu	Tyr	Phe	Lys	His	Arg
NAUTILOIDS																		
Nautilus pompilius (modern)	A	7.1	1.2	9.6	4.4	0.7	31.6	26.6	tr	1.5	0.5	1.4	2.1	1.8	5.1	0.6	0.5	5.3
Miocene																		
Eutrephoceras balc. (1076)	A	7.9	2.3	7.6	7.9	4.0	24.8	8.9	tr	4.6	tr	2.6	4.8	2.8	12.1	5.5	1.6	2.5
Eocene																		
1048	A	9.1	4.4	9.1	11.1	5.0	18.5	9.8	tr	5.4	0	3.4	6.0	1.7	6.1	5.4	1.7	3.4
1022	A	8.0	4.5	11.4	10.8	+	20.0	8.2	tr	5.5	tr	4.0	7.8	2.1	7.9	5.3	1.2	3.4
Cretaceous																		
Cymatoceras (478)	A	7.6	4.8	12.6	18.4	7.4	15.9	7.2	0	4.7	tr	3.4	6.3	+	+	4.7	2.2	4.9
Eutrephoceras (398-999)	A	9.4	5.1	15.8	12.4	+	18.1	8.8	tr	5.3	tr	2.7	4.8	2.3	2.4	5.9	2.4	3.5
(963.2)	C	10.4	+	15.5	15.2	3.8	17.7	9.3	0	4.7	0.3	2.9	4.9	1.9	2.2	6.0	2.2	2.8
Jurassic																		
(990)	A	9.2	4.0	11.4	16.7	4.3	18.4	8.3	tr	4.4	1.3	2.4	4.7	1.1	3.5	5.6	2.8	1.9
(948)	C	8.6	4.9	10.1	11.6	4.1	20.4	7.8	1.5	4.8	0.6	3.4	6.5	3.1	3.3	3.5	1.3	4.5
(949 N)	A	9.1	5.4	13.0	12.1	4.8	18.6	7.4	tr	4.5	tr	3.2	6.0	2.5	3.4	4.1	1.6	4.2
(949)		7.9	+	19.2	15.7	3.5	16.9	7.8	0	3.8	tr	2.4	3.9	1.8	2.5	7.0	4.0	3.6
(949 G2)	C	9.6	4.9	15.7	13.7	2.7	20.7	7.8	0	4.3	tr	2.2	4.6	1.9	2.6	6.3	2.9	tr
Permian																		
Domatoceras (894)	C	8.8	+	15.1	14.5	+	21.8	6.6	0	3.8	0	3.6	6.6	2.8	3.0	6.9	2.7	3.8
Carboniferous																		
(607)	A	9.0	4.6	14.4	11.3	3.3	19.0	7.3	tr	4.3	0.6	2.9	5.5	2.1	3.1	4.8	3.0	5.0
Devonian																		
(713)	C	8.7	4.5	19.4	13.3	+	17.2	7.6	0	3.2	0	2.0	3.1	1.3	1.8	7.8	5.3	4.6

TABLE 2. — Protidic components of the conchiolin matrices. Amino acid residues per cent total amino acid residues.

(See details in table 4)	Mineral Composition	Asp	Thr	Ser	Glu	Pro	Gly	Ala	Cys	Val	Met	Ile	Leu	Tyr	Phe	Lys	His	Arg
MODERN NAUTILOID																		
Nautilus pompilius LINNÉ	A	7.1	1.2	9.6	4.4	0.7	31.6	21.6	tr	1.5	0.5	1.4	2.1	1.8	5.1	0.6	0.5	5.3
JURASSIC AMMONOIDS																		
A. Ammonitina																		
Eoderocerataceae																		
Amaltheidae																		
Amaltheus (987)	C, Fe S_2	12.1	6.0	9.4	14.4	3.5	12.5	6.4	1.4	4.6	+	4.5	8.2	2.4	4.5	3.7	1.8	4.7
Pseudoamatheus (962) ...	A	9.1	4.9	13.9	11.7	4.4	17.8	8.1	0	4.3	1.0	3.0	5.5	2.3	3.0	5.3	1.9	3.6
Pleuroceras (501)	A	9.1	4.9	12.6	13.3	3.0	19.0	7.9	tr	4.5	0	3.4	5.9	1.9	2.5	6.2	2.4	3.3
Psilocerataceae																		
Psiloceras (988)	A	12.2	5.7	9.6	11.4	5.6	13.2	10.9	0	6.1	1.8	3.2	5.8	2.2	3.9	3.6	1.4	3.3
Oxynoticeras (942)	C	8.5	4.3	17.8	13.0	+	19.8	6.9	0	3.0	+	3.0	4.8	2.2	1.8	7.8	3.6	3.7
(941)	C	8.3	4.7	15.5	14.0	3.5	14.7	8.4	0	4.3	1.0	2.4	4.3	2.1	2.4	7.5	3.6	3.1
Asteroceras (946)	C	9.7	6.0	11.9	12.3	4.5	13.4	9.1	+	5.1	tr	2.9	5.3	2.1	3.1	6.4	2.9	5.1
Hildocerataceae																		
Leioceras (405)	A, C, Ba SO_4	9.3	4.6	10.8	12.2	5.9	19.9	7.8	tr	4.3	0.7	3.3	6.2	2.3	3.2	4.1	1.5	4.0
B. Lytoceratina																		
Ammonites lineatus penicillatus (785)	A, C	13.2	6.5	11.5	13.1	5.3	17.4	9.4	tr	5.8	tr	3.1	4.9	1.2	2.8	3.8	+	1.7
CRETACEOUS AMMONOIDS																		
A. Ammonitina																		
Hoplitaceae																		
Hoplites (456, 479)	A	8.0	4.6	12.9	12.4	6.7	19.2	7.2	tr	4.7	tr	3.2	6.5	2.3	3.2	3.4	2.1	3.6
Hoplites (911)	A	8.7	4.5	12.3	12.6	+	21.4	8.0	tr	4.8	tr	3.4	6.7	2.0	2.7	6.0	1.9	4.7
Hoplites (655, 659)	A	8.6	5.1	11.1	16.9	+	17.6	9.0	0	5.0	tr	3.4	8.6	1.5	2.4	5.1	2.6	3.1
Hoplites (648)	A	9.5	5.5	10.8	12.3	4.8	15.0	10.1	tr	5.6	tr	3.8	6.4	1.5	2.5	6.0	2.2	3.8
Hoplites (1023)	A	8.3	4.0	16.6	15.3	+	20.3	7.0	0	3.9	0	3.4	5.6	1.7	2.5	6.7	1.3	3.2
Acanthohoplites (495)	A	9.9	4.9	10.7	12.4	4.2	18.7	8.7	0	5.4	tr	3.7	6.7	1.5	3.2	4.8	1.7	3.2
Placenticeras (386)	A	8.9	5.6	10.8	10.8	4.7	16.3	11.6	+	5.6	0.7	3.3	6.0	1.7	2.8	4.7	2.1	4.4
Leymeriella (517)	A	8.1	3.6	7.9	11.5	8.9	28.1	9.9	+	3.5	0.6	2.2	4.5	0.7	2.4	3.1	0.8	4.0
B. Lytoceratina																		
Turrilitaceae																		
Baculites (393)	A, α quartz	7.1	3.4	17.7	13.6	3.6	19.9	7.9	tr	3.6	+	2.5	2.7	1.1	2.0	7.9	4.1	2.7
(998)	A	9.0	5.3	15.5	13.1	+	18.7	8.5	tr	5.5	+	2.4	4.8	1.9	3.2	6.3	2.7	2.7
(553-4)	A	8.3	4.5	12.9	13.2	5.7	21.0	8.8	tr	4.1	tr	2.5	4.6	1.9	2.3	4.7	1.8	3.7

TABLE 3. — Comparison between the polypeptidic components of the nacreous substances from the shell wall and those of the surrounding sediment.

(See details in table 4)	μg amino acid per gram of undecalcified material	Asp	Thr	Ser	Glu	Pro	Gly	Ala	Cys	Val	Met	Ile	Leu	Tyr	Phe	Lys	His	Arg
Ammonoids																		
(988) shell	46.48	12.2	5.7	9.6	11.4	5.6	13.2	10.9	0	6.1	1.8	3.2	5.8	2.2	3.9	3.6	1.4	3.3
rock	19.11	10.4	+	13.8	11.9	2.9	18.8	9.5	0	5.4	1.3	3.7	6.3	2.4	3.1	5.9	4.5	+
(942) shell	11.65	8.5	4.3	17.8	13.0	+	19.8	6.9	0	3.0	+	3.0	4.8	2.2	1.8	7.8	3.6	3.7
rock	6.64	11.4	6.1	15.1	14.0		24.3	7.9				3.6	6.9	2.1	3.0	+	+	5.6
(941) shell	21.24	8.3	4.7	15.5	14.0	3.5	14.7	8.4	0	4.3	1.0	2.4	4.3	2.1	2.4	7.5	3.6	3.1
rock	10.45	8.5	+	17.1	11.6	+	15.5	6.5	tr	2.8	tr	1.2	1.9	+	1.8	15.7	12.6	4.8
Nautiloids																		
(713) shell		9.6	22.1		11.13	tr	25.3	9.7	0	tr	0	3.9	5.5	tr	tr	8.7	3.9	+
rock		14.5	+	27.4	15.3	tr	20.7	8.6	0	+	+	+	+	+	+	9.6	3.7	+

tested for the presence of this substance contained small amounts of glucosamine.

2) In all the fossil shells analysed, the polypeptides of the nacreous conchiolin are characterized by predominant amounts (in decreasing order) of Glycine, Serine, Glutamic acid, Aspartic acid and Alanine. Comparison of the amino-acid patterns of the nacreous conchiolin matrix in the samples (nautiloids : Text fig. 1; Ammonoids : Text fig. 2) from the different geological ages investigated, did not reveal significant age-bound difference.
Similarly (Text fig. 3) the amino-acid patterns of the nautiloids (Miocene to Devonian) do not sensibly differ from those of the ammonoids (Cretaceous and Jurassic).

3) The amino-acid patterns of the fossil samples differ from that of the modern *Nautilus* mother-of-pearl conchiolin, namely by the considerably lower relative values of Glycine and of Alanine and by relatively higher values of eight to ten amino acids, especially of Glutamic acid, Valine, Leucine, Lysine and Histidine (see tables 1 and 2).

4) The polypeptides recorded in the fossil nacreous conchiolin were also found, however in smaller amounts, in the adjacent sedimentary rock.

2. X-ray powder diffraction analysis of the mineral components of fossil mother-of-pearl (table 4)

1) The nacreous samples of three Tertiary nautiloids and of thirteen Cretaceous nautiloids and ammonoids consisted of aragonite. Calcite was detected in an unidentified Cretaceous (?) nautiloid of unprecise origin (see table 4 : 963-2).

2) The samples of four Jurassic nautiloids and ammonoids were aragonitic and those of seven shells were calcitic. Aragonite and calcite coexisted in the nacreous layers of three specimens.

3) The samples from the Permian and Devonian specimens consisted of calcite, those from the Pennsylvanian orthocerid of aragonite and the principal ray of calcite.

3. Structure of the conchiolin matrices in mother-of-pearl of fossil nautiloids and ammonoids (table 4)

The interlamellar matrices left by decalcification of mother-of-pearl of the modern *Nautilus* shell appear as continuous, soft, highly iridescent and transparent membranes. In the transmission electron microscope, these membranes consist of lacelike reticulated sheets. The trabeculae of these meshworks appear in the form of irregularly cylindrical knobby cords, resembling rhizomes of the garden iris or beech tree roots. The fenestration delimited by these trabeculae is irregularly rounded or elongate (nautiloid pattern : see e.g. Fig. 39, GRÉGOIRE, 1962; Figs 1, 2 and 3 : GRÉGOIRE, 1966a).

In fossil molluscs of different ages and from different stratigraphic levels, the remnants of these matrices consist generally of discontinuous shreds or flakes, differing in colour (generally brown) and in consistency (soft, semi-rigid or rigid). Under the phase contrast microscope (Fig. 15; see also GRÉGOIRE, 1966 b, p. 5 and Fig. 10) these shreds appear in the form of transparent, polygonal-rounded, scattered or clustered flakes, still partly assembled into portions of flaggings. Each flake represents a portion of interlamellar matrix which covers polygonal crystal faces in the original nacreous architecture. The straight ridges that delimit the polygonal areas are remnants of intercrystalline conchiolin bridges that before decalcification wrapped the side faces of crystals (crystal imprints : GRÉGOIRE, 1959b, 1966a; GRÉGOIRE and TEICHERT, 1965; « crystal scars » : MUTVEI, 1969). In all the samples the biuret reaction was positive : the polygonal flakes appeared stained in purple, lilac or violet, with various grades of intensity. In a few samples, dark violet or purple speckles marbled the uniformly lilac background of the flakes.

In the transmission electron microscope, the alterations in the ultrastructure of the fossil nacreous conchiolin, described in details elsewhere (see GRÉGOIRE, 1958, 1959ab, 1966ab, 1968; GRANDJEAN and al., 1964; GRÉGOIRE and TEICHERT, 1965) were also found in the present material.

Preservation or moderate alteration of the nautiloid pattern characterizes the interlamellar conchiolin matrices from several nautiloid samples buried in the Buckhorn asphalitic limestones of Oklahoma (Fig. 13).

In many fossil samples, the nautiloid pattern has been considerably disorganized. A predominant type of alteration found in fossils of all ages, consists of flattening and widening of the trabeculae into ribbon-like structures with smooth surfaces (Figs. 1, 2, 3, 4, 14, 21, 23, 26). These structures form loose networks in which the fenestration is irregularly enlarged.

Coalescence of these flattened trabeculae produces continuous or fenestrate membranes, which can involve extensive portions of the interlamellar conchiolin. In this type of alteration, the polygonal outlines of the original crystals are traced by dense contorted cords, which represent the intercrystalline conchiolin (Figs. 1, 3, 4, 6, 16, 19, 20, 22).

After dislocation (during diagenesis and in part during preparation of the samples) the remnants of the loose networks and of the membranes appear in the form of twisted rods with bud-like expansions, thong-shaped, angulate, and wedge-shaped strands, blades, cords, discs and nodules (Figs. 2, 4, 6, 8, 11, 12, 16, 21, 23).

In a more advanced stage of disintegration, the trabeculae appear fragmented into lenticular or rounded corpuscles of various sizes (20 to 200 mμ in diameter), resembling pebbles in shadowed preparations (Figs. 5, 7, 9, 10, 11, 12, 17, 24, 25). As long as the debris remain agglutinated in their original position, e.g. in pseudoreplicas (Figs. 16, 18, 27) the outlines of the reticulated architecture of the matrices (nautiloid pattern) are still recognizable. More frequently, dispersion and clustering at random of the corpuscles conceals the reticulated pattern (Figs. 5, 7, 9, 10, 11, 12, 24, 25). In some specimens, the corpuscles appear to be pitted with tiny holes (see, e.g. GRÉGOIRE, 1959, Fig. 16) or to contain micronetworks of a dense unidentified material consisting of granules and filaments. Other spheroidal bodies, composed of a relatively transparent centre encircled by a denser envelop in the form of a turban-shaped ring (Figs. 3, 4, 6, 7) (« Papillae » GRÉGOIRE, 1959b; « knobs » : 1966a) characterize the structure of the conchiolin remains in several fossil cephalopods, including the Devonian material (Fig. 17) analyzed in this paper (see also GRÉGOIRE, 1966a, Figs. 13, 26, 33, 34, 36, 40).

Except in the Buckhorn asphalt material (see GRÉGOIRE, 1966a, p. 17 and 18), the alterations in the structure of the conchiolin matrices did not distinctly differ in nautiloids and ammonoids.

DISCUSSION.

1. Reliability of the composition of the samplings

In the modern *Nautilus* shell, the limits of the inner nacreous and outer spherulitic-prismatic (porcelaneous) layers are sharp, which permits an easy separation of the layers and collection of pure nacreous material. In fossil nautiloids, the data of the literature (BØGGILD, 1930; TEICHERT, 1964) report preservation of the outer porcelaneous layer in several specimens. In recrystallized material, the limits are no longer recognizable. In several ammonites, the shell wall is too thin to permit separation of mother-of-pearl from the outer layer. Under these conditions, the whole shell wall has been used for the analyses. In this material, amino acids of the organic components of the outer layer could then be included in the reported amino-acid values.

However, the danger of introducing into the biochemical analyses of the nacreous layers organic material from other structures such as the

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
Nautilus pompilius L. (modern). Nacre from the shell wall in the living chamber. Very hard. Iridescent with yellow-bluish hues.	Aragonite
1. NAUTILOIDEA	
MIOCENE.	
Eutrephoceras balcombensis (CHAPMAN, 1915) (1076). Fyansford Formation. Balcombian. Middle Miocene. Heatherton, (Melbourne) Victoria, Australia. Specimen supplied by Dr. Th. A. Darragh. Hard, 4-7 mm thick, white substance. Inner shell surface iridescent, with pink, violet and green metallic hues. Smell of petroleum during decalcification.	Aragonite
EOCENE.	
Nautiloid sp. (1048). Wemmelian, Baeleghem, East Flanders, Belgium. 3-7 mm thick, very brittle, snow-white, chalky, faintly iridescent substance. Strong smell of petroleum during decalcification.	Aragonite
Nautiloid sp. (1022). Wemmelian, Baeleghem, Belgium. Insoluble fraction only. 3-7 mm thick, very hard, snow-white, faintly iridescent (green hues) material. Strong smell of petroleum during decalcification.	Aragonite
CRETACEOUS.	
Cymatoceras sp. (478). Gault, Vöhrum, Hannover, Germany. 2 mm thick, lustreless, pink, white and chalky, faintly iridescent material.	Aragonite

4

Alterations in ultrastructure of the conchiolin matrices.
Transparent, soft, highly iridescent membranes (interlamellar and intercrystalline conchiolin matrices). Nautiloid pattern : sturdy, irregularly cylindrical trabeculae, studded with hemispheric protuberances, mostly elongate fenestration (see GRÉGOIRE, 1962, Fig. 39; 1966a : Figs. 1, 2 and 3; 1968, Fig. 1).
Grey-brown shreds. Biuret : violet flakes. Widening, flattening and coalescence of the trabeculae into substantial loose networks and membranes. Fragmentation of the trabeculae into rounded corpuscles with or without dispersion. Same alterations in pseudoreplicas (Figs 1 and 2). See also GRÉGOIRE and VOSS-FOUCART, 1970, Plate 13.
Scarce mahogany-brown particles. Biuret : violet flakes. Trabeculae flattened into ribbons, fused into membranes (with traces of fenestration) or fragmented into corpuscles of different sizes, including vesicle-like structures (« knobs », see GRÉGOIRE, 1966).
White, yellowish, rigid shreds. Biuret : violet flakes. Substantial networks of membraneous or varicose trabeculae, fused into membranes. Fragmentation into rounded corpuscles, including vesicle-like structures (« knobs ») (Figs. 3 and 4.) Same alterations recorded in pseudoreplicas. See also VOSS-FOUCART and GRÉGOIRE, 1971, Pl. 1B and 3B.
Dark-brown spongy shreds. Biuret : pink-violet flakes. Trabeculae fragmented into rounded corpuscles, about 30-35 mμ in diameter, still arranged in loose networks (Fig. 5).

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
Eutrephoceras sp. (398). Locality unknown. Specimen supplied by Dr. G. A. Cooper. Pale pink, iridescent and chalky nacreous substance.	Aragonite
Eutrephoceras sp. (999). Menabites, Eutaw Formation, Alabama, U. S. A. Specimen supplied by Dr. N. F. Sohl (U. S. G. S. 27 0 65). 5 mm thick, hard, chalky-white material, iridescent with pink-violet and green metallic hues. Strong smell of petroleum during sample decalcification.	Aragonite
Nautiloid sp. (963-2). Cretaceous ?, probably from Westfalen, Germany. 0.7 mm thick septal material. Very hard, rust-coloured, recrystallized substance. Slight smell of petroleum during decalcification.	Calcite Undissolved mineral : pyrite
JURASSIC.	
Nautiloid sp. (*Eutrephoceras* ?) (990-1). Lower Lias, Whitby, Yorkshire, England. Hard, pink, chalky substance, highly iridescent with purple, violet and green metallic hues, sandwiched between pyritized layers. Smell of petroleum and of H_2S during decalcification.	Aragonite
Cenoceras sp. (948-1). Lower Lias, Region of Lyme Regis and Charmouth, Dorset, England. Specimen supplied by Mr. S. Barney-Hansford. Light brown, recrystallized substance. Smell of tar during decalcification.	Calcite
Cenoceras sp. Lower Lias, Region of Lyme Regis, Charmouth, Dorset, England. Specimen supplied by Mr. S. Barney-Hansford. Very hard, pink-white, chalky substance, iridescent with purple and green hues (949-1). Intense smell of lighting gas and of petroleum during decalcification.	Aragonite

4 (*contd.*)

Alterations in ultrastructure of the conchiolin matrices.
Grey-brown fragments of membranes. Biuret : pale, pink-violet flakes. Substantial loose networks of altered trabeculae (flattening, inflation into vesicles, fragmentation into rounded corpuscles).
Mahogany-brown shreds. Biuret : pink-violet flakes. Networks of widened, flattened trabeculae, fused into membranes or fragmented into rounded corpuscles. Many of these corpuscles contain dense fibrillar and granular material. Spheroidal, vesicle-like structures, some of large size (« knobs »). (Figs. 6 and 7.)
Rust-coloured shreds. Biuret : pink-violet flakes. Substantial, loose networks of contorted membraneous or flattened trabeculae. Fragments of membranes with polygonal outlines. Clusters of rounded corpuscles, some containing micronetworks of dense material.
Rust-brown particles. Biuret : many pink and intensely violet flakes. Networks of cylindrical trabeculae with protruding, hemispheric, bud-like structures. Nautiloid pattern recognizable (Fig. 8). In other areas of the interlamellar conchiolin, flattening, widening and coalescence of the trabeculae into networks of membranes, containing dense filamental and granular substance. Fragmentation into rounded corpuscles.
Mahogany-brown shreds. Biuret : pink-violet flakes and purple spots in a transparent jelly. Networks of trabeculae, inflated, flattened or broken into rounded corpuscles with or without dispersion. Coalescence of the structures (Figs. 9 and 10). Same alterations recorded in pseudoreplicas.
Dark, mahogany-brown shreds. Biuret : pink and pale-violet flakes. Trabeculae inflated, flattened or broken into rounded corpuscles, undispersed or agglutinated in clusters (Fig. 11). In certain areas, polygonal portions of the conchiolin matrices surrounded by intercrystalline cords (imprints of crystal faces) consist of membranes broken into angulate, wedge-shaped fragments.

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
Honey-brown, coarsely recrystallized substance alternating with the pink substance (949-2). Smell of lighting gas and of petroleum during sample decalcification.	Calcite
PERMIAN.	
Domatoceras or *Stearoceras* sp. (422-894). San Andres Limestone, Rio Penasco River, 50 miles east of Alamogordo, New Mexico, U. S. A. Specimen supplied by Dr. Rousseau H. Flower. 1 to 6 mm thick slabs from the recrystallized inner portion of the shell wall, composed of a mosaic of honey-brown and of white transparent crystals. Samples : golden-iridescent, powdery material from the innermost portion.	Calcite
PENNSYLVANIAN.	
Orthocerid sp. (607). Lower Middle Pennsylvanian, Buckhorn asphalt, Sulfur, Oklahoma. Specimens supplied by Prof. C. C. Branson. Segments of orthoconic brevicones, flattened and distorted by compression. Samples consist of brittle, iridescent, blue-violet flakes of cleavage of the nacreous layer.	Aragonite and ray 3,03Å of calcite
Inner mould : grey-white material adjacent to the inner surface of the shell wall (607-6).	

4 (*contd.*)

Alterations in ultrastructure of the conchiolin matrices.
Dark mahogany-brown shreds. Biuret : pink-violet flakes. Alterations as in (949-1); cylindrical or flattened trabeculae, fragmentation into corpuscles, angulate remnants of ribbons and membranes. See also GRÉGOIRE and VOSS-FOUCART, 1970, Plate 11.
Rust-brown soft shreds and brown mud. Biuret : pink and violet flakes. Networks of smooth, cylindrical or varicose, partly flattened fragments of trabeculae, delimiting an irregularly polygonal fenestration. Many spheroidal, discoidal and lenticular corpuscles of different sizes, including vesicle-like structures (« knobs ») (Fig. 12). Similar structures in pseudoreplicas. See also GRÉGOIRE, in C. TEICHERT, 1964 : Fig. 8, K 19; GRÉGOIRE, 1966a, Fig. 37, 38 and 39.
Substantial brown particles and shreds. Biuret : pink, violet and purple-violet flakes and particles. Red grains in a transparent jelly. Nautiloid pattern diffusely altered : flattening, widening, some degree of coalescence of the trabeculae, scarcer protuberances, electron transparent rounded areas in the trabeculae (Fig. 13), different from fenestration. See also GRANDJEAN *et al.*, 1964, Fig. 1; GRÉGOIRE and VOSS-FOUCART, 1970, Plate 4. Alterations in weathered portions consisting of loosening of the nautiloid pattern, varicose inflation and fragmentation of the trabeculae into smooth-edged rods and agglomerated corpuscles of different sizes, coalescence into membranes. Flattening of the trabeculae in other portions of the matrices. See GRÉGOIRE and VOSS-FOUCART, 1970, Plate 5.
Brown particles and mud. Biuret : pink-violet flakes and violet particles. Abundant conchiolin matrix with a typical mural nautiloid pattern (Fig. 14).

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
DEVONIAN.	
Gyroconic nautiloid (Rutoceratidae ?) (713). Lower Middle Devonian, Couvinian, Dinant area, Belgium. Specimen of large size (diameter of the outer whorl : 24 cm), supplied by Dr. J. Bouckaert (Service géologique de Belgique : R 144). Samples consist of hard, dark-brown and coal-black, recrystallized, 1-2 mm thick substance. Strong smell of petroleum during samples decalcification.	Calcite SiO_2 in the residues of decalcification of large amounts of nacreous substance
Grey-brown sedimentary rock (outer mould) in the vicinity (2-10 mm) of the shell wall (713-26).	
2. AMMONOIDEA.	
CRETACEOUS.	
A. Ammonitina.	
Hoplitaceae.	
Hoplites auritus Sow. (456-479). Albian, St. Pô, Wissant, Pas-de-Calais, France. Specimens supplied by Professeur A. DE LAPPARENT.	Aragonite and pyrite
Hoplites auritus Sow. (479). Hauterivian, Albian, Folkestone, England. Samples consist of very brittle, chalky, pink iridescent substance. Strong smell of petroleum during decalcification.	

TABLE 4 (*contd.*)

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples	Alterations in ultrastructure of the conchiolin matrices.
DEVONIAN.		
Gyroconic nautiloid (Rutoceratidae ?) (713). Lower Middle Devonian, Couvinian, Dinant area, Belgium. Specimen of large size (diameter of the outer whorl : 24 cm), supplied by Dr. J. Bouckaert (Service géologique de Belgique : R 144). Samples consist of hard, dark-brown and coal-black, recrystallized, 1-2 mm thick substance. Strong smell of petroleum during samples decalcification.	Calcite SiO_2 in the residues of decalcification of large amounts of nacreous substance	Yellow-brown and black-brown rigid shreds and fragments of membranes, appearing under the phase contrast microscope to be composed of networks and mosaics (see Voss-Foucart and Grégoire, 1971, Fig. 1 A). Biuret : pink and violet polygonal flakes, purple and violet grains, rods, dots, embedded in lumps of a pink jelly or scattered in unstained polygonal flakes (Fig. 15). Predominant alteration of the trabeculae consisting of fragmentation into rounded vesicle-like corpuscles, differing greatly in size and diameter, and encircled by ring-shaped membranes (« knobs ») (Fig. 17). Similar alterations in pseudoreplicas. Portions of loose networks composed of flattened trabeculae with widened fenestration (Fig. 18). Membranes and their fragments (Fig. 16). See also Grégoire, 1966a, Figs 11 and 13; Grégoire and Voss-Foucart, 1970, Plate 2.
Grey-brown sedimentary rock (outer mould) in the vicinity (2-10 mm) of the shell wall (713-26).		Biuret : pink and violet polygonal flakes. Purple and violet dots and rods, embedded in a pink jelly. Fragments of conchiolin networks mixed with flat crystals resisting decalcification with E. D. T. A.
2. AMMONOIDEA.		
CRETACEOUS.		
A. Ammonitina.		
Hoplitaceae.		
Hoplites auritus Sow. (456-479). Albian, St. Pô, Wissant, Pas-de-Calais, France. Specimens supplied by Professeur A. de Lapparent.	Aragonite and pyrite	Light-brown rigid shreds. Loose networks of flattened and membraneous, contorted trabeculae, some with bud-like expansions. Fragmentation into rounded corpuscles which countain extremely thin micronetworks of dense filaments and granules.
Hoplites auritus Sow. (479). Hauterivian, Albian, Folkestone, England. Samples consist of very brittle, chalky, pink iridescent substance. Strong smell of petroleum during decalcification.		Light-brown, semi-rigid fragments of membranes. Biuret : violet flakes. Alterations as in (456).

TABLE 4 (*contd.*)

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
B. Lytoceratina.	
Turrilitaceae.	
Baculites claviformis STEPHENSON (393-13-14). Senonian, Ripley formation, Coon Creek Member, Coon Creek, between Enville and Adamsville, MacNairy Co., Tennessee, U. S. A. Specimen supplied by Dr. N. F. SOHL (U. S. G. S. 25406). Nacre cleaved into slabs, reddish-brown, iridescent with intense purple, green, violet and blue metallic hues. Inner surface of the shell wall golden coloured. Strong smell of petroleum during decalcification of the samples.	Aragonite α-quartz among the residues of decalcification of large amounts of material
Baculites claviformis STEPHENSON. Another sample (998) supplied 9 years later (U. S. G. S. : 25406) by Dr. N. F. SOHL. Brittle, chalky, white-creamy slabs with intense purple and green metallic hues. Strong smell of petroleum during decalcification.	Aragonite
Baculites sp. (553-4) (553-70). Upper Cretaceous, Senonian, Ripley formation, Coon Creek, Mc Nairy Co., Western Tennessee, U. S. A. Supplied by Prof. A. G. UNKLESBAY. Salmon-pink, 4 mm thick, brittle, nacreous layer, iridescent with intense purple and violet metallic hues. Intense smell of petroleum during decalcification.	Aragonite
JURASSIC.	
A. Ammonitina.	
Amaltheus sp. (987-1-2). Oxford clay, Weymouth, Dorset, England. Honey-brown and dark-brown, recrystallized nacre.	Calcite. Mineral undissolved by decalcification : green rods and tablets, grey spongy particles, transparent dark brown blocks : FeS_2

Alterations in ultrastructure of the conchiolin matrices.
Yellow-brown and black-brown rigid shreds and fragments of membranes, appearing under the phase contrast microscope to be composed of networks and mosaics (see VOSS-FOUCART and GRÉGOIRE, 1971, Fig. 1 A). Biuret : pink and violet polygonal flakes, purple and violet grains, rods, dots, embedded in lumps of a pink jelly or scattered in unstained polygonal flakes (Fig. 15). Predominant alteration of the trabeculae consisting of fragmentation into rounded vesicle-like corpuscles, differing greatly in size and diameter, and encircled by ring-shaped membranes (« knobs ») (Fig. 17). Similar alterations in pseudoreplicas. Portions of loose networks composed of flattened trabeculae with widened fenestration (Fig. 18). Membranes and their fragments (Fig. 16). See also GRÉGOIRE, 1966a, Figs 11 and 13; GRÉGOIRE and VOSS-FOUCART, 1970, Plate 2.
Biuret : pink and violet polygonal flakes. Purple and violet dots and rods, embedded in a pink jelly. Fragments of conchiolin networks mixed with flat crystals resisting decalcification with E. D. T. A.
Light-brown rigid shreds. Loose networks of flattened and membraneous, contorted trabeculae, some with bud-like expansions. Fragmentation into rounded corpuscles which countain extremely thin micronetworks of dense filaments and granules.
Light-brown, semi-rigid fragments of membranes. Biuret : violet flakes. Alterations as in (456).

TABLE 4 (*contd.*)

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples	Alterations in ultrastructure of the conchiolin matrices.
Ammonites (Hoplitaceae ?) (911). Gault, Golden Cap, Seaton, Dorset, England. Very brittle, pink, chalky substance. Smell of petroleum during decalcification.	Aragonite and an unidentified ray	Rigid, brown fragments of membranes. Biuret : pale violet flakes. Loose networks of flattened and widened trabeculae fused into membranes and nodules. Debris of cylindrical trabeculae, composed of still agglutinated rounded corpuscles (Fig. 19).
Ammonites (Hoplitaceae ?) (655 to 659). Wealden, Gault, Smalldole, Sussex, England. Shell wall and septa. Brittle, strongly iridescent substance, with pink-violet metallic hues.	Aragonite	Mahogany-brown particles. Biuret : violet flakes. Trabeculae flattened or fragmented into corpuscles.
Ammonites (Hoplitaceae ?) (648-5-1; 649-2; 1023). Wealden, Gault, quarry of the British Portland Cement Manufacturers, in Smalldole, Steyning, Sussex, England. Mural and septal nacreous substances. Brittle, pink-violet, strongly iridescent material.	Aragonite	Dark brown residues. Biuret : pale pink and violet flakes. Networks of trabeculae in the form of contorted cords and ribbons. Other trabeculae disintegrated into corpuscles of small size.
Acanthohoplites hannoverensis Jak. (495). Lower Albian, Vöhrum, Hannover, Germany. Very brittle, pink, chalky material. Iridescence with intense metallic (purple, green, violet) hues. Smell of petroleum during decalcification.	Aragonite	Mahogany-brown shreds. Biuret : pale pink flakes. Trabeculae flattened into ribbons, fused into membranes and disintegrated into small rounded corpuscles.
Placenticeras sp. (386-20-21-22). Coffee Sand, Ratliff, Lee Co., Mississippi, U. S. A. Supplied by Dr. N. F. Sohl (U. S. G. S. 17809). Nacre cleaved into very brittle slabs, iridescent with intense metallic hues (purple, green, violet and blue on the surfaces freshly cleaved; golden on the inner surface of the shell wall). Strong smell of petroleum during decalcification.	Aragonite Pyrite among the residues of decalcification	Mahogany-brown and rust-coloured shreds. Biuret : pink-violet flakes. Flattening, widening and fusion of the trabeculae into a mosaic of polygonal membranes delimited by the remnants of intercrystalline conchiolin (crystal imprints). The central portions of these polygonal areas, corresponding to the central elevations (Mutvei, 1969), are generally empty. Dislocation of the material into pebble- and vesicle-like structures, containing micro-networks of dense granular material (Fig. 21).
Leymeriella sp. (?) (517). Gault, Folkestone, England. Slate-coloured and pink-violet, iridescent, chalky material.	Aragonite	Brown shreds. Biuret : pink-violet flakes. Networks of ribbons fragmented into rounded corpuscles without dispersion. Fenestrate membranes.

4 (*contd.*)

Alterations in ultrastructure of the conchiolin matrices.
Brown-yellowish shreds. Biuret pink-violet flakes. The remnants of interlamellar matrices consist of substantial loose networks of inflated cylindrical, varicose or flattened trabeculae, of membranes and of rounded corpuscles, including vesicle-like structures (« knobs »). (Fig. 20.) Similar alterations recorded in pseudoreplicas. See GRÉGOIRE and VOSS-FOUCART, 1970, Plate 15.
Dark mahogany-brown, semi-rigid particles and mud. Biuret : pink violet flakes. Substantial networks of flattened or membraneous trabeculae. Fragmentation into rounded corpuscles. Coalescence into continuous and fenestrate membranes. Micronetworks of filamental material in these structures.
Substantial fragments of brown, iridescent membranes. Biuret : pink and violet flakes. Alterations as in (393) : loose networks of cylindrical, ribbon- shaped and membraneous trabeculae, fragmented into corpuscles and nodules. Fusion of these networks into membranes. Dense microfilaments in these structures (Figs. 22 and 23).
Dark grey-brown and brown-yellowish particles and shreds. Biuret : pink-violet flakes. Substantial loose networks of flattened trabeculae, fused into fenestrate membranes with crystal imprints. Dislocation into corpuscles. Other trabeculae cylindrical with protuberances (loosened nautiloid pattern recognizable). Identical alterations in pseudoreplicas. See VOSS-FOUCART and GRÉGOIRE, 1971, Plate 2 A.

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
Pseudoamaltheus engelhardti (d'ORBIGNY) (?) (962). Lower Jurassic, Middle Lias, Domerian, Dörnten bei Goslar, Harz, Germany. Very brittle, pink, chalky, iridescent substance with metallic hues. Intense smell of petroleum during decalcification.	Aragonite Undissolved residues : FeS_2
Pleuroceras spinatum BRUG. (*Amaltheus spinatus* BRUGUIÈRE 501-2). Middle Lias, Schloss Banz, Franconia, Germany (see GRÉGOIRE, 1968, Fig. 27). Brittle, pink-creamy and blue iridescent, chalky substance. Intense smell of petroleum during sample decalcification.	Aragonite
Psiloceras planorbis (J. DE C. SOWERBY) (988). Lower Lias, Planorbis zone Range, Hettangian, probably Watchet, Somerset coast, England. Brittle, iridescent brown and blue-violet substance from flattened specimens. Smell of petroleum and of H_2S during decalcification.	Aragonite
Sedimentary rock, 2 to 6 mm away from the specimen. Smell of petroleum during decalcification.	Calcite, traces of aragonite
Oxynoticeras sp. (?) (942). Lower Lias. Region of Lyme Regis Charmouth, Dorset, England. Specimen supplied by Mr. S. Barney HANSFORD. Hard, 2-3 mm thick nacre, recrystallized into white and honey-brown, large crystals. Inner layer cocoa-brown.	Calcite [Among the mineral substance undissolved by decalcification : FeS_2 and $BaSO_4$
Asteroceras sp. (?) (941). Lower Lias. Region of Lyme Regis Charmouth, Dorset, England. Specimens supplied by Mr. S. Barney HANSFORD. (941-35-1). Sample consists of brittle, pink-creamy material, iridescent with violet hues, sandwiched between honey-brown layers in the median portion of the shell. Slight smell of petroleum during sample decalcification.	Calcite

4 (*contd.*)

Alterations in ultrastructure of the conchiolin matrices.
Dark mahogany-brown and pale-brown, semi-rigid shreds with black spots (pyrite). Biuret : pale, pink-violet flakes. Loose networks of cylindrical or flattened, contorted trabeculae, fused into membranes or fragmented into corpuscles. Networks of rounded nodules composed of agglutinated or of fused smaller corpuscles (Figs. 24 and 25). See also GRÉGOIRE and VOSS-FOUCART, 1970, Plate 8.
Mahogany-brown shreds. Biuret : violet flakes. Loose networks of flattened trabeculae. Fenestrate membranes. Fragmentation of cylindical trabeculae into rounded corpuscles (Fig. 26).
Dark-brown and yellowish shreds. Biuret : pink-violet, blue-violet and violet flakes. Networks of flattened trabeculae. Coalescence of the matrix into fenestrate membranes extending over wide interlamellar areas. Clusters of rounded corpuscles. Identical alterations in pseudoreplicas (Fig. 27). Scattered debris of matrix in the form of networks of ribbons, of membranes and of rounded corpuscles.
Grey-brown and brown spongy shreds. Biuret : pink-violet flakes. Enclosed in polygonal areas delimited by the remnants of intercrystalline matrix, networks of cylindrical or flattened trabeculae, fused in part into membranes or fragmented into rounded corpuscles. Micronetworks of filaments are visible in these structures.
Dark-brown shreds (941-35-1); dark-brown particles (941-1). Biuret : (941-35-1) pale, pink and violet flakes, some with scattered black dots (941-1) : pink and violet flakes.

TABLE

Material Mother-of-pearl (shell wall) Description of the samples	Mineral composition of the samples
(941-1) Very hard, honey-brown, recrystallized substance in the inner and outer portions of the former nacreous layer. Slight smell of petroleum during samples decalcification.	Calcite
Sedimentary rock in the vicinity (2 to 6 mm) of the outer limit of the shell wall. Strong smell of petroleum during decalcification.	Calcite
Asteroceras sp. (?) (946). Lower Lias, Region of Lyme Regis Charmouth, Dorset, England. Specimens supplied by Mr. S. Barney HANSFORD. Hard, honey-brown recrystallized substance.	Calcite
HILDOCERATACEAE.	
Leioceras (Harpoceras) opalinum REINECKE (405-8). Middle Jurassic. Upper Aalenian. Lower Dogger, (Opalinus-Ton) Boll, Württemberg, Germany. Specimens supplied by Prof. O. H. SCHINDEWOLF. Brittle, white or pink-white, chalky, powdery substance.	Aragonite and one ray of calcite Mineral residues of decalcification : $BaSO_4$
B. Lytoceratina.	
Ammonites lineatus penicillatus (785). Brauner Jura α, Gammelhausen bei Boll, Württemberg, Germany. Specimen supplied by Prof O. H. SCHINDEWOLF, Prof. Ad. SEILACHER and Dr. Fr. WESTPHAL. 3-6 mm thick shell wall. Hard. In weathered surfaces : dull grey-brown iridescent with greenish hues on the cleavage surfaces (tangential). In polished transverse section : dark-brown stripes on a light-brown background.	Aragonite

4 (*contd. and end*)

Alterations in ultrastructure of the conchiolin matrices.
Networks of cylindrical, flattened and fused trabeculae, some fragmented into rounded corpuscles. Coalescence of this material into fenestrate membranes. Scattered or clustered, rounded, rod-shaped and vesicle-like corpuscles (« knobs »). Grey-black mud. Biuret : many violet flakes. Substantial debris of conchiolin matrix exhibiting the same alterations as the conchiolin remnants from the nacreous layers of the shell wall.
Dark, grey-brown and yellow shreds. Biuret : pink-violet flakes, with variegated spots. Loose networks of inflated or flattened trabeculae, fused into membranes or fragmented into rounded corpuscles. These networks form polygonal areas surrounded by the remnants of intercrystalline cords (crystal imprints). Micro networks of dense filaments are visible in these structures.
Abundant brown shreds. Biuret : faintly pink and violet flakes. Substantial networks of varicose or flattened trabeculae, fragmented into corpuscles or fused into membranes. Similar alterations in pseudoreplicas. See GRANDJEAN *et al.*, 1964, Pl. II, Fig. 3; GRÉGOIRE, 1968, Fig. 26.
Brown, spongy shreds. Biuret : pale pink flakes. Substantial, loose networks of flattened and widened trabeculae, fused into continuous or fenestrate membranes. Fragmentation into rounded corpuscles containing micronetworks of dense filaments and granules. Unidentified rod-shaped or rounded, small, dense corpuscles clustered in polygonal areas limited by dense cords and ribbons (not shown).

spherulitic prismatic (porcelaneous) layer must not be overevaluated. In many nautiloids, as shown in control replication peels examined under the phase contrast microscope, the outer layer, probably weathered before burial of the specimen, has been mechanically eliminated. Besides, the samples of the whole shell wall of modern *Nautilus*, analyzed by DEGENS and SPENCER (1966) do not greatly differ in their amino-acid patterns from our own results on samples from the mural nacreous layer of the same species, cleaned from remnants of the outer porcelaneous layer. As regards the ammonites, the most recent data of the literature (BIRKELUND, 1967; ERBEN, FLAJS and SIEHL, 1968) confirm the predominance, recognized by older authors (see MILLER, FURNISH and SCHINDEWOLF, 1957, ARKELL, KUMMEL and WRIGHT, 1957) of the nacreous layer in the architecture of these shells. An outer layer could not be found in several specimens (MUTVEI, 1967; GRÉGOIRE, unpublished observations 1959-1970).

From all these data, it appears that in the present study the amount of the nacreous substance was probably highly predominant in our fossil samples.

2. Origin of the polypeptides recorded in the samples

Three chief results emerge from examination of the biochemical data collected in this study :

A. In all the samples of fossil shells used, hydrolysis of the dialyzed residues of decalcification freed amino acids. This finding suggests, in agreement with previous consistent records of biuret-positive organic shreds and particles (FLORKIN, GRÉGOIRE, BRICTEUX-GRÉGOIRE and SCHOFFENIELS, 1961; GRÉGOIRE, 1966a) that polypeptides have been preserved for geologic periods extending in the present material from Miocene to Devonian.

B. The amino-acid composition of all the samples collected from fossil mother-of-pearl differs from that of *Nautilus*, the only adequate modern control for fossil nautiloids and ammonoids.

C. In all the fossil samples investigated, there is a striking uniformity of the amino-acid patterns, in spite of considerable differences in age (Miocene to Devonian), localities (scattered on three continents) and taxonomy (nautiloids and ammonoids).

As regards the origin of these polypeptides, contamination of the samples by foreign organic substances must be considered. The contaminants could be : a) Contemporaneous organisms having invaded the shells before the diagenetic changes; b) Organic substances from the surrounding sedimentary rock having diffused into the shell; c) modern contaminants during analysis of the samples.

A. Contamination of the shells of fossil molluscs during life or after death by commensal or parasitic organisms (epizoans, algae, fungi, sponges, corals and especially boring predators) has long been observed (see discussion and literature in GRÉGOIRE, 1966a, p. 12).

As pointed out previously, occurrence of contaminants in samples suggests a cautious interpretation of results of microbiochemical analysis of protidic structures in random samples in which the possibility of invasion by organisms has not been ruled out by thorough control by means of the electron microscope.

In the present material, this control has been routinely performed on samplings of different portions of the shell fragments used.

Very few fossil shells, from wide geographic dispersion, and including the Devonian nautiloid used in this study (713 : see the table), contained unidentified microstructures (see description in GRÉGOIRE, 1966) mixed with the conchiolin remnants of decalcification of mother-of-pearl. The presence of these unusual structures in this Devonian specimen suggested a contamination by contemporaneous foreign organisms. However, compared with the substantial remnants of conchiolin matrices found in this Devonian nautiloid, the foreign material seems to be negligible in amount.

B. The presence of amino acids in the dialyzed residues of demineralisation of the rock surrounding the specimens (in concentration which reaches fifty per cent of the amount of amino acids of the shell samples), raises the question of the origin of the amino acids contained in the shell themselves, either as remains of the original conchiolin or as foreign organic substances diffused into the shell.

As the architecture of mother-of-pearl is relatively impermeable, the possibility of migration into the shells of foreign substances from the sediment seems improbable. On the other hand the following data rather suggest a diffusion of soluble substances from the shell or a migration of shell fragments into the outer mould.

Decalcification of the inner mould of *Pseudorthoceras knoxense* (BUCKHORN asphalt) left substantial biuret-positive shreds characteristic of the mural conchiolin of this species (Fig. 14) (GRÉGOIRE and TEICHERT, 1965). In the immediate vicinity of the living chamber of ammonite shells from Posidonian shales, HELLER (1965) recorded concentrations in organic substances five to eight percent greater than the average organic content of the sedimentary rock. Higher concentrations in amino acids have been also detected near ichtyosaur bones by ARMSTRONG and TARLO (1966). Recent observations by infra-red spectroscopy have revealed the presence of pyritized remnants of soft parts of ammonites around the living chamber (STÜRMER, 1969; ZEISS, 1969).

In the present material, portions of the sedimentary rock collected in the vicinity of the limits of the shells and demineralized in EDTA left biuret-positive fragments of typical nacreous interlamellar conchiolin sheets which still showed the imprints of the original tabular crystals between which these organic sheets were sandwiched. These observations indicate that the shell wall of these specimens had been reduced to the nacreous layers possibly after mechanical destruction of the outer layers and that a process of exfoliation of mother-of-pearl had occurred. In former (unpublished) observations, splinters of fracture scattered in the outer and inner moulds around the shell have been found in a number of fossil molluscs.

The data reported above suggest that if a portion of the amino acids detected in the sedimentary rocks could have their origin in the remains of the body of the animal, diffused into the mould, the major part of these amino acids probably results from the migration of organic material of the shell, either by exfoliation of splinters of fracture from the outermost region of the nacreous layers or by diffusion of conchiolin substances from the same weathered outer portions.

C. The importance of contamination during the laboratory procedures, especially when relatively small amounts of fossil materials are used for biochemical analyses, has been emphasized in an increasing number of papers (HAMILTON, 1965; HARE, 1965; ORÓ and SKEWES, 1966; KORTING and LITZOW, 1952 : PANKOV, 1953). Finger-prints, skin, glassware, chemicals, dust are the main sources of this kind of contamination.

In the present material, concordance of the amino-acid patterns in all the samples which were repeatedly washed in order to discard the substances of the superficial finger-prints, seems to exclude a gross accidental contamination. Such a contamination would result in distinct random differences in the amino-acid patterns. This concordance does not eliminate a systematic contamination, produced for example during the routine procedures of preparation and analysis of the material. However, this last possibility seems also to be ruled out : routine analysis, under the same conditions as those used for the fossil material, of all the reagents and glasswares used, revealed the presence of protidic or polypeptidic components in such small amounts that these components could not be appreciated quantitatively.

From the above data, it appears that the polypeptides detected in the samples of fossil shells analysed in this study do not result from contamination but represent true remnants of the original conchiolin matrices.

3. Paleontological implications

The differences recorded in the structure and in the amino-acid patterns of the polypeptidic conchiolin remnants in fossil cephalopods and in the modern *Nautilus*, may indicate either a composition of conchiolin originally different in species now extinct, or diagenetic alterations of original patterns similar to those of the modern *Nautilus*.

The close resemblance noted between the polypeptidic composition of the fossil shells from suborders such as Ammonitina and Lytoceratina in Ammonoids and especially between ammonoids and nautiloids suggests that these differences between modern *Nautilus* and fossil cephalopods are not taxonomic in nature, but rather result from the influence of diagenetic factors, such as temperature and pressure. Experimental reproduction on modern nacreous substance of the morphological alterations observed in nacreous conchiolin matrices of fossil shells (GRÉGOIRE, 1964, 1966a, 1968) is in favour of this suggestion.

As already pointed out (GRÉGOIRE and VOSS-FOUCART, 1970; VOSS-FOUCART and GRÉGOIRE, 1971) this conclusion does not exclude the fact that some original differences in these patterns might have existed in the extinct groups when the animals were alive but these differences could have disappeared or have been concealed by the more spectacular diagenetic changes.

The similarities in biochemical composition and in ultrastructure, in spite of subsidiary differences (see table 4) (*), of fossil nacreous conchiolin in the samples selected between the Miocene and the Devonian suggest that once the conchiolin matrices had undergone diagenetic alterations — a process which probably developed relatively rapidly after burial — these alterations were stabilized without further important modification during a burial of several hundred millions of years.

This suggestion seems to be supported by results of experimental diagenesis of the conchiolin matrices of the modern *Nautilus* shell, as has been shown in the electron microscope (GRÉGOIRE, 1968) and which will be confirmed in biochemical analyses in a further paper. Recent data obtained by Matter III, DAVIDSON and WYCKOFF (1969) on fossil oyster shells proteins also confirm this suggestion. In the oyster material, the early transformation that reduces the relative amounts of aspartic acid and glycine results in a protidic residue of remarkable stability since it changes little in the long interval between the Oligocene and the Cretaceous.

4. Mineral composition of the fossil samples and ultrastructure of the remnants of conchiolin matrices

The shell of the modern *Nautilus* is aragonitic (BØGGILD, 1930).

The information on the mineral composition of fossil shells is disseminated in a considerable literature (e.g. WADE, 1926; BØGGILD, 1930; SWITZER and BOUCOT, 1955; STEHLI, 1956; REYMENT and ECKSTRAND, 1957; GRÉGOIRE, 1959; REYMENT, 1959; TUREKIAN and ARMSTRONG, 1961; HALLAM and O'HARA, 1962; LOWENSTAM, 1963; GRANDJEAN & al., 1964; YOCHELSON, WHITE and GORDON, 1967; HALL and KENNEDY, 1967; ERBEN, FLAJS and SIEHL, 1969).

Disappearance of the organic components in the recrystallized fossil shells has generally been reported in the past (BØGGILD, 1930; ABELSON, 1957; MITTERER, 1966).

(*) Note the remarkable resemblance between the conchiolin alterations in the Miocene nautiloid *Eutrephoceras* (Fig. 2) and the Cretaceous ammonoid *Placenticeras* (Fig. 21).

In previous (GRANDJEAN & al., 1964) and in the present studies, the crystallographic composition of the nacreous layers has been determined in samples from 212 species of cephalopods : 3 Miocene, 3 Oligocene, 11 Eocene (all aragonitic), 40 Cretaceous (predominantly aragonitic), 74 Jurassic (predominantly calcitic), 5 Permian (predominantly calcitic), 5 Triassic, 37 Pennsylvanian and Carboniferous (aragonitic, aragonitic-calcitic, calcitic), 21 Devonian (all calcitic) and 13 Ordovician (predominantly calcitic).

In our calcitic material, replacement of aragonite by calcite had occurred by recrystallization in situ, which is characterized, as shown by FLOWER (1961), HUDSON (1962), BATHURST (1964), DODD (1966), GRÉGOIRE (1966a, figs. 52 and 53) by the persistance among the coarse calcite crystals of scattered relics of the original aragonitic shell layers, namely fragments of typical nacreous brickwork.

In this and former materials (GRANDJEAN et al., 1964; GRÉGOIRE, 1966a) conchiolin matrices were consistently found in shells in which aragonite had been recrystallized into calcite or replaced by other minerals. These observations are in agreement with the results of petrological (HUDSON, 1962) and of biochemical studies (HUDSON, carbon-nitrogen ratio, 1967; GRÉGOIRE and VOSS-FOUCART, 1970 : preservation of polypeptides). Besides, as reported recently (GRÉGOIRE and LORENT, 1971), in the whole cephalopod material so far investigated, (GRÉGOIRE, 1958, 1959ab, 1966ab, 1968 and unpublished data; GRANDJEAN et al., 1964; GRÉGOIRE and TEICHERT, 1965; the present material) the different types of ultrastructural alterations described in the fossil remnants of the conchiolin matrices are distributed without appreciable predominance of one or more types in the still aragonitic or in the recrystallized mother-of-pearl. An example is furnished in the present study by the Jurassic nautiloid *Cenoceras* from Lyme Regis (see table 4 : 949-1; 949-2, and Fig. 11; compare with GRÉGOIRE and VOSS-FOUCART, 1970, Plate 11) in which still aragonitic and recrystallized portions of mother-of-pearl coexisted in the shell wall. In the samples of both materials alterations in the trabeculae of the conchiolin matrices were identical. Other observations have also shown that conchiolin remnants of Paleozoic (including Ordovician) and Jurassic samples can be less altered than certain Cretaceous and Tertiary materials.

The combined results suggest that the alteration in the conchiolin matrices are probably caused by other factors than the crystallographic reorganization of the mineral shell components during the direct conversion of aragonite into calcite.

We are indebted to the following persons who generously supplied several specimens used in this study : Mr S. BARNEY-HANSFORD, Dr. J. BOUCKAERT, Prof. C. C. BRANSON, The British Portland Cement Manufacturers Ltd in Smalldole, Steyning, Sussex, Dr. G. Arthur COOPER, Dr. Thomas A. DARRAGH, Prof. ROUSSEAU H. FLOWER, Prof. A. F. DE LAPPARENT, Dr. J. B. REESIDE, Prof. O. H. SCHINDEWOLF, Prof.

Ad. Seilacher, Dr. N. F. Sohl, Prof. A. G. Unklesbay, The United States Geological Survey, Dr. F. Westphal.

This work is part of a research program financed by the Fonds de la Recherche Fondamentale Collective (Crédit 267) and by the Fonds National de la Recherche Scientifique (Crédits aux Chercheurs). The help of these Organizations is gratefully acknowledged.

SUMMARY

1. The amino-acid patterns of the nacreous polypeptidic remnants have been recorded in decalcified shell walls of 30 samples of Devonian, Pennsylvanian, Permian, Jurassic, Cretaceous, Eocene and Miocene nautiloids and ammonoids.

2. In all the samples investigated, in which the original aragonite has been preserved or replaced by calcite, polypeptidic structures have been detected with the electron microscope and by biochemical analysis.

3. The amino-acid patterns of the fossil polypeptidic residues distinctly differed by their chemical composition from the conchiolin patterns of mother-of-pearl in modern *Nautilus*.

These amino-acid patterns were closely similar in all the fossil samples, independently of age (Devonian to Miocene), locality (scattered on three continents) and taxonomy (nautiloids and ammonoids).

5. The nature of these protidic structures has been discussed namely with regard to possible sources of contamination. The results suggest that these structures are genuine remnants of the original conchiolin. This conclusion is supported by the detection with the electron microscope in this material of submicroscopic structures identified in former observations and experimental studies as the remnants of the original conchiolin matrices altered diagenetically.

6. The similarities in the degree of degradation of the conchiolin matrices studied in the present paper suggest that the diagenetic alterations develop chiefly in the early stages of diagenesis and that these organic residues remain stabilized throughout the further geologic ages, in spite of possible accidental modifications induced by metamorphism. Experimental simulation of the diagenetic alterations in pyrolyzed modern *Nautilus* shell, reported in the previous investigations and in a later paper seems to confirm these conclusions.

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EXPLANATION OF FIGURES.

Figs. 1 and 2.

Eutrephoceras balcombensis (CHAPMAN, 1915) (1076). Nautiloid, Fyansford Formation, Balcombian, Middle Miocene, Heatherton, Melbourne, Australia, Specimen supplied by Dr Thomas A. DARRAGH.

Mineral composition of the samples : aragonite.

Double stage carbon-platinum replica of mother-of-pearl polished in tangential orientation parallel to the interlamellar spaces, and etched with E. D. T. A.

The remnants of the conchiolin matrices appear in the form of pseudoreplicas : polygonal areas delimited by the intercrystalline matrices (opaque cords : black, Fig. 1; white : Fig. 2) enclose loose networks of flattened trabeculae, fused into membranes (arrows). See also GRÉGOIRE and VOSS-FOUCART, 1970, Plate 13.

Fig. 1 : direct print; Fig. 2 : reversed print. × 24.000.

Figs. 3 and 4.

Nautiloid sp. (1022). Eocene, Wemmelian, Baeleghem, Flanders.

Mineral composition of the samples : aragonite.

Decalcification of mother-of-pearl left substantial debris composed of cylindrical or flattened trabeculae fused into membranes (e.g. Fig. 3 : middle left hand) and of vesicle-like hemispheric nodules.

Directs prints. Fig. 3 : × 6.000; Fig. 4 : × 48.000.

Fig. 5.

Cymatoceras sp. (478). Nautiloid, Cretaceous, Gault-Albian, Vöhrum, Hannover, Germany.

Mineral composition of the samples : aragonite (GRANDJEAN & al., 1964).

One of the aspects of the residues of decalcification of mother-of-pearl : disintegration of the conchiolin matrices into pebble-shaped corpuscles.

Shadowed with platinum. × 48.000.

Figs. 6 and 7.

Eutrephoceras sp. (999). Nautiloid, Cretaceous, Eutaw Formation, Menabites, Alabama, U. S. A. Specimen supplied by Dr. N. F. SOHL. (U. S. G. S. 27 0 65).

Substantial remnants of decalcification of mother-of-pearl composed of loose networks of sturdy, flattened or inflated, partly fused, trabeculae, and of clusters of spheroidal, vesicle-like corpuscles, some of large size (« knobs »), shown in Fig. 7 mixed with another type of alteration in the form of pebble-shaped corpuscles.

Shadowed with platinum. Fig. 6 : × 48 000; Fig. 7 : × 36 000.

Fig. 8.

Nautiloid sp. (990). Jurassic, Lias, Whitby, Yorkshire, England. Specimen of large size.

Mineral composition of the samples : aragonite.

Residues of decalcification of the nacreous layer. Dislocation of the nautiloid pattern : fragmentation of cylindrical or flattened trabeculae with spheroidal bud-like expansions.

Shadowed with platinum. × 48.000.

Figs. 9 and 10.

Cenoceras sp. (948). Jurassic, Lias, region of Lyme Regis Charmouth, Dorset, England. Specimen supplied by Mr. S. Barney HANSFORD.

Brown substance of the recrystallized mother-of-pearl.

Mineral composition of the samples : calcite.

Two of the different types of alteration of the conchiolin matrices are shown : disintegration of the trabeculae into corpuscles (Fig. 9), flattened trabeculae, fused into membranes and fragmented into corpuscles (Fig. 10).

Shadowed with platinum. × 48.000.

Fig. 11.

Cenoceras sp. (949-1). Nautiloid of large size, Lower Jurassic, Lower Lias, Region of Lyme Regis Charmouth, Dorset, England. Specimen supplied by Mr. S. Barney HANSFORD.

Nacreous layer of the shell wall, recrystallized into calcite.

The remnants of decalcification consist of flattened trabeculae, fragmented into pebble-shaped corpuscles, fused in part into membranes.

Shadowed with platinum. × 48.000.

Fig. 12.

Domatoceras or *Stearoceras* (nautiloid) (422-A-80). Permian, San Andres limestone, Rio Penasco River, east of Alamogordo, New Mexico. Specimen supplied by Dr. ROUSSEAU H. FLOWER.

Fragment of the former nacreous layer of the shell wall : calcite (GRANDJEAN & al., 1964).

Residues of decalcification in the form of twisted fragments of smooth cylindrical trabeculae and spheroidal corpuscles agglomerated into masses (in white). Other aspects (loose networks of smooth, flattened, ribbon-like trabeculae) were illustrated in GRÉGOIRE, 1966a, Figs. 37 and 38.

Shadowed with platinum. × 42.000.

Figs. 13 and 14.

Unidentified nautiloid (orthoconic brevicone) (607-3).

Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma, U. S. A., Specimen supplied by Prof. C. C. BRANSON.

Fragment from the inner portion of the shell wall : violet slabs with intense metallic hues.

Mineral composition of the samples : aragonite and very weak principal ray of calcite (GRANDJEAN & al., 1964).

Fig. 13. Nautiloid pattern slightly altered : trabeculae smooth, cylindrical or moderately flattened. Comparison with GRANDJEAN & al., 1964, Plate I, shows that the rounded, transparent spots on the trabeculae are additional sharp-edged perforations of these trabeculae, which are unrelated with the characteristic elongate fenestration of the nautiloid pattern. The arrow indicates fragments of a cylindrical intercrystalline cord. (See also GRÉGOIRE and VOSS-FOUCART, 1970, Plates 4 and 5).

Shadowed with platinum. × 48.000.

Fig. 14. Remnants of decalcification of the grey-white material collected from the internal mould (607-6) a few millimeters away from the inner surface of the nacreous layer of the shell wall. The preserved nautiloid pattern indicates that these organic net-

works proceed from conchiolin matrices of splinters of fracture exfoliated from the shell wall.

Shadowed with platinum. × 36.000.

Figs. 15-18.

Unidentified nautiloid, with gyroconic conch (diameter of the outer whorl : 21 cm.) (713). Middle Devonian, Couvinian, region of Dinant, Belgium. Specimen supplied by J. BOUCKAERT.

Mineral composition of the samples : predominance of calcite (GRANDJEAN & al., 1964).

Fig. 15. This phase contrast photograph shows in white and black a cluster of biuret-positive (pink violet) flakes. These flakes are fragments of preserved interlamellar conchiolin delimited by black cords of intercrystalline conchiolin (crystal imprints). × 400.

Fig. 16. Residues of decalcification of the shell wall in which the altered conchiolin matrices appear in the form of polygonal areas encircled by remnants of intercrystalline conchiolin (arrows). Note the coalescence of the flattened trabeculae into membranes at the periphery of the polygonal area and the trabecular shreds with bud-like expansions protruding into the central portion, which is empty. Shadowed with platinum. × 32.000.

Fig. 17. Residues of decalcification of another sample from the shell wall of the same specimen. Clustering of rounded corpuscles, including vesicle-like structures encircled by turban-like rings more opaque than the centre (« knobs ») and differing considerably in size, is a highly predominant alteration recorded in this Devonian specimen (see also GRÉGOIRE, 1966a, p. 29 and Figs. 11 and 13; GRÉGOIRE and VOSS-FOUCART, 1970, Plate 2). Shadowed with platinum. × 48.000.

Fig. 18.

Double stage, carbon-platinum replica of the shell wall polished in tangential orientation and etched with E. D. T. A. Adhering to the replica, in the form of pseudoreplicas, the interlamellar conchiolin matrix appears to be composed of loose networks of flattened and partly fused trabeculae. Several of these trabeculae are fragmented into the corpuscles shown in Fig. 17, but the dispersion into free elements has not taken place in this area (middle left hand). × 60.000.

Fig. 19.

Hoplitaceae (?) Ammonoid (911). Cretaceous, Gault, Seaton, Golden Cap, Dorset, England.

Mineral composition of the samples : aragonite and an unidentified ray.

Residues of decalcification of the very brittle, pink creamy nacreous layer in the form of fragments of membranes and of corpuscles.

Shadowed with platinum. × 48.000.

Fig. 20.

Baculites claviformis STEPHENSON. Ammonoid (998, 393-14). Cretaceous, Senonian, Ripley Formation, Coon Creek Member, near Enville-Adamsville, McNairy Co, Tennessee, U. S. A. Specimen supplied by Dr. N. S. SOHL (U. S. G. S. 25406) and Dr. G. Arthur COOPER.

Mineral composition of the samples : aragonite (GRANDJEAN & al., 1964).

Coalescence of flattened trabeculae into membranes characterize the remnants of decalcification of the nacreous layer of the shell wall in this specimen. Local inflation of the substance of the flattened trabeculae appear in the form of vesicle-like structures. See also GRÉGOIRE and VOSS-FOUCART, Plate 15.

Shadowed with platinum. × 48.000.

Fig. 21.

Placenticeras sp. Ammonoid (386). Cretaceous, Coffee Sand, Ratliff, Lee Co, Mississippi, U. S. A. Specimen supplied by Dr. N. F. SOHL (U. S. G. S. 17809) and Dr. G. Arthur COOPER.

Mineral composition of the sample : aragonite.

Double stage, carbon-platinum replica of the nacreous layer of the shell wall polished in tangential orientation and etched with E. D. T. A.

Adhering to the replica in the form of pseudoreplicas, enclosed in polygonal areas delimited by white cords and filaments (intercrystalline conchiolin), the interlamellar conchiolin matrices appear to be composed of dislocated networks of contorted ribbon-shaped structures. × 36.000.

Figs. 22 and 23.

Baculites sp. Ammonoid (553-70). Upper Cretaceous, Ripley, Coon Creek Formation, McNairy Co., Western Tennessee, U. S. A. Specimen supplied by Prof. A. G. UNKLESBAY.

Mineral composition of the samples : aragonite.

Remnants of conchiolin matrices from different samples are composed of fenestrate membranes and of fragments of flattened trabeculae.

Shadowed with platinum. × 48.000.

Figs. 24 and 25.

Pseudoamaltheus engelhardti D'ORB. (962). Ammonoid. Lower Jurassic, Middle Lias, Domerian, Dörnten bei Goslar, Harz, Germany.

Mineral composition of the samples : aragonite.

Conchiolin remnants in which corpuscular fragments of the trabeculae appear agglutinated (Fig. 24) or fused into membranes and nodules (Fig. 25). See also GRÉGOIRE and VOSS-FOUCART, 1970, Plate 8.

Shadowed with platinum, × 48.000.

Fig. 26.

Pleuroceras sp. (501). Ammonoid. Lower Jurassic, Middle Lias, Schloss Banz, Franken, Bayern, Germany.

Mineral composition of the samples : aragonite (GRANDJEAN & al., 1964).

Remnants of nacreous conchiolin matrices : three or four superimposed loose networks of smooth, flattened, ribbon-like trabeculae are shown.

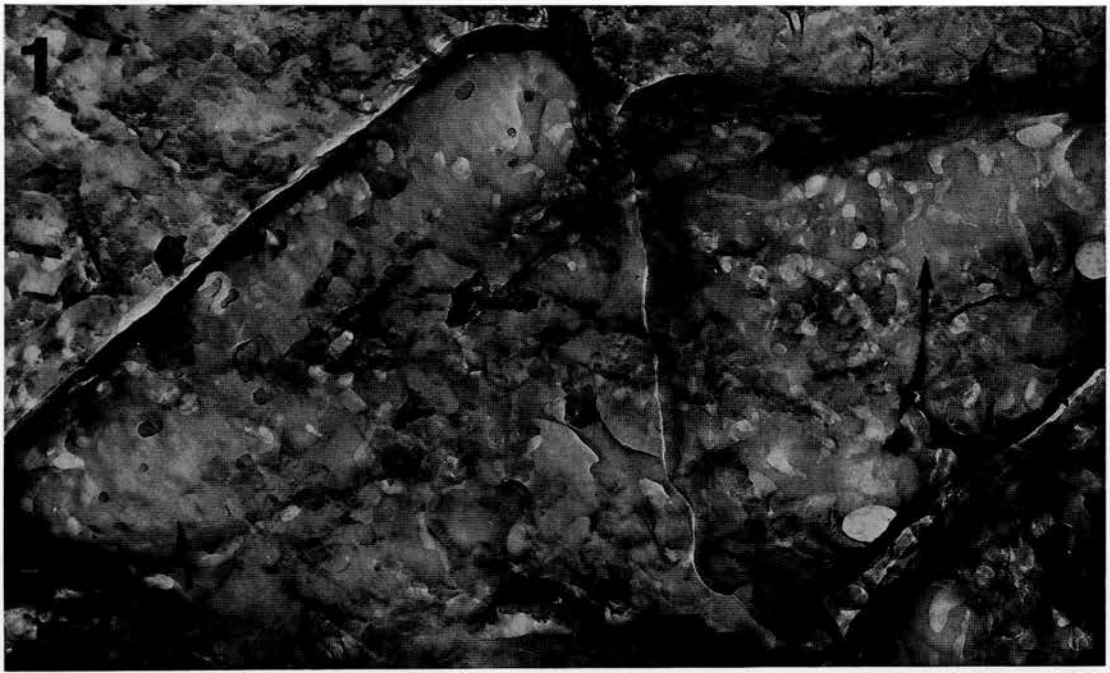
Shadowed with platinum. × 48.000.

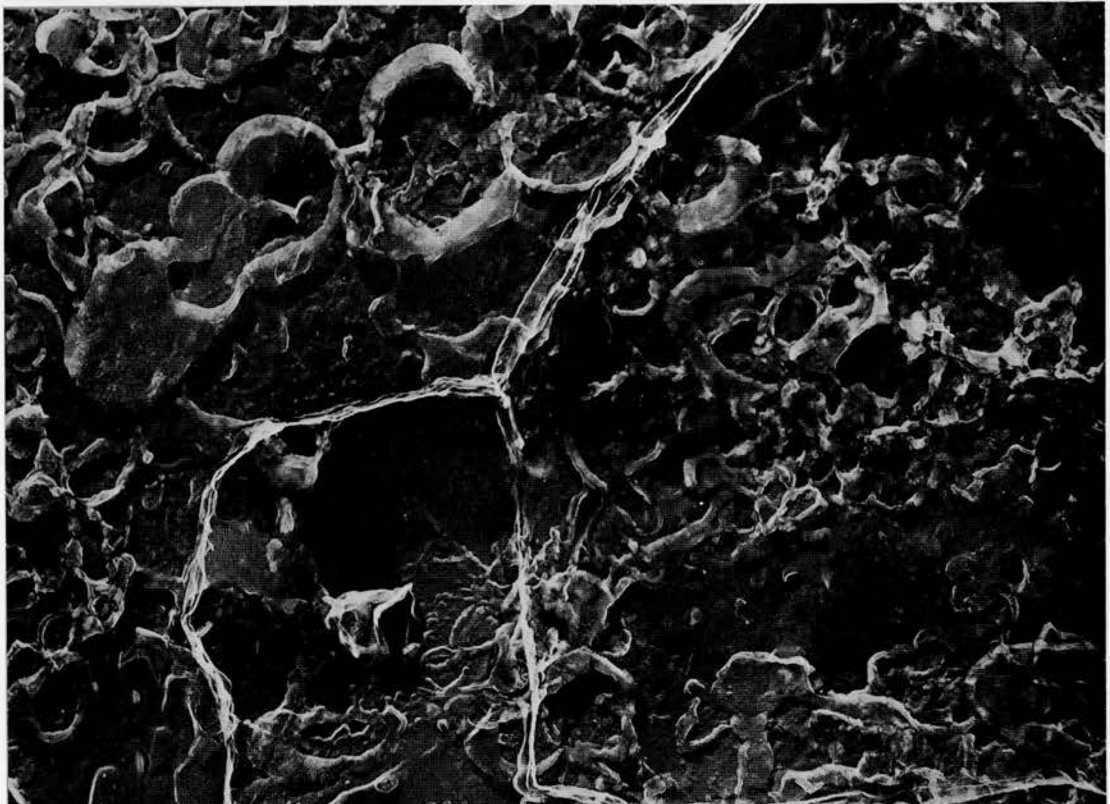
Fig. 27.

Psiloceras planorbis (J. DE SOWERBY). Ammonoid (988). Jurassic, Lower Lias, *Planorbis* Zone Range, Hettangian, probably from Watchet, Somerset, England.

Mineral composition of the samples : aragonite.

Double stage, carbon-platinum replica of the nacreous layers of the shell wall polished in tangential orientation and etched with E. D. T. A. Pseudoreplicas of the altered trabeculae, fragmented into corpuscles, without dispersion, and lying on the tabular 001 faces of three rounded polygonal crystals of the lamellar flagging. The original reticular disposition of the trabeculae and the fenestration are still distinguishable in some areas. The remnants of the intercrystalline conchiolin are visible in the form of white threads anchored in the intercrystalline grooves. × 48.000.





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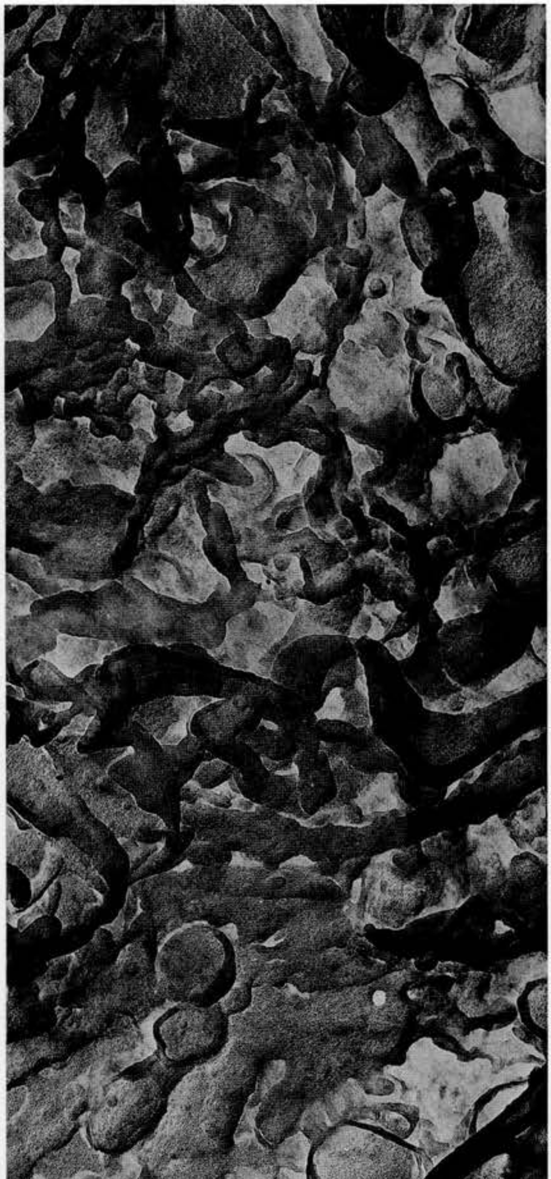

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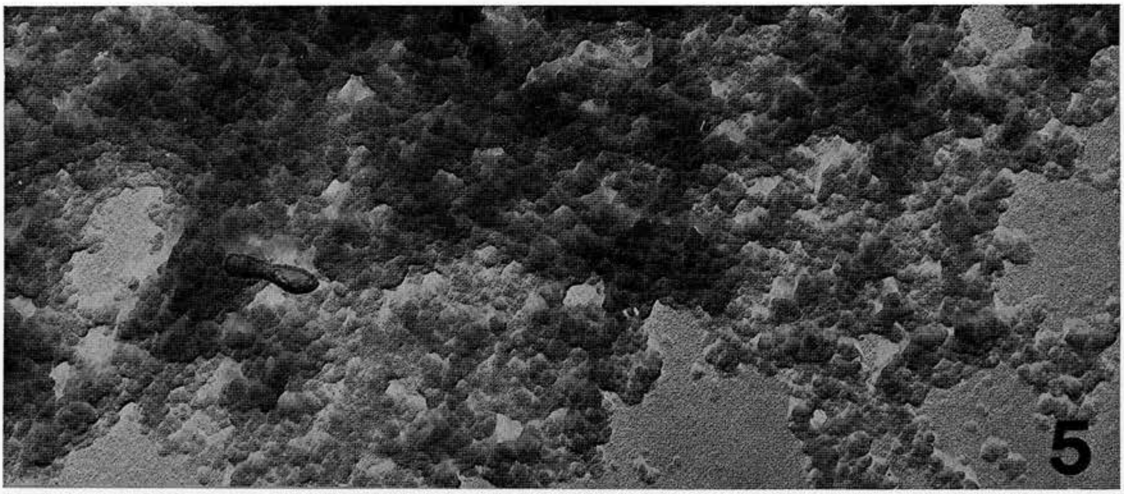
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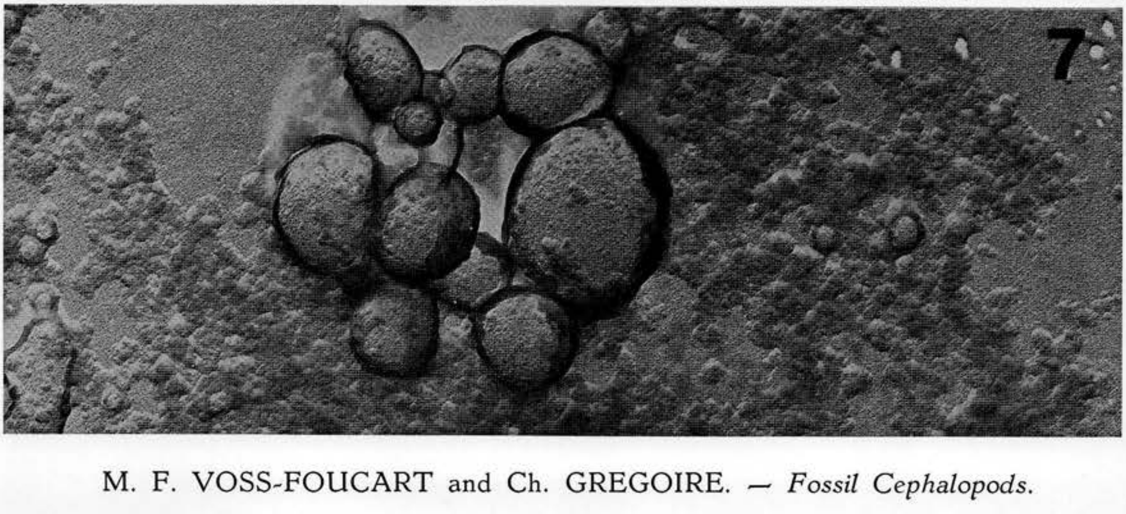
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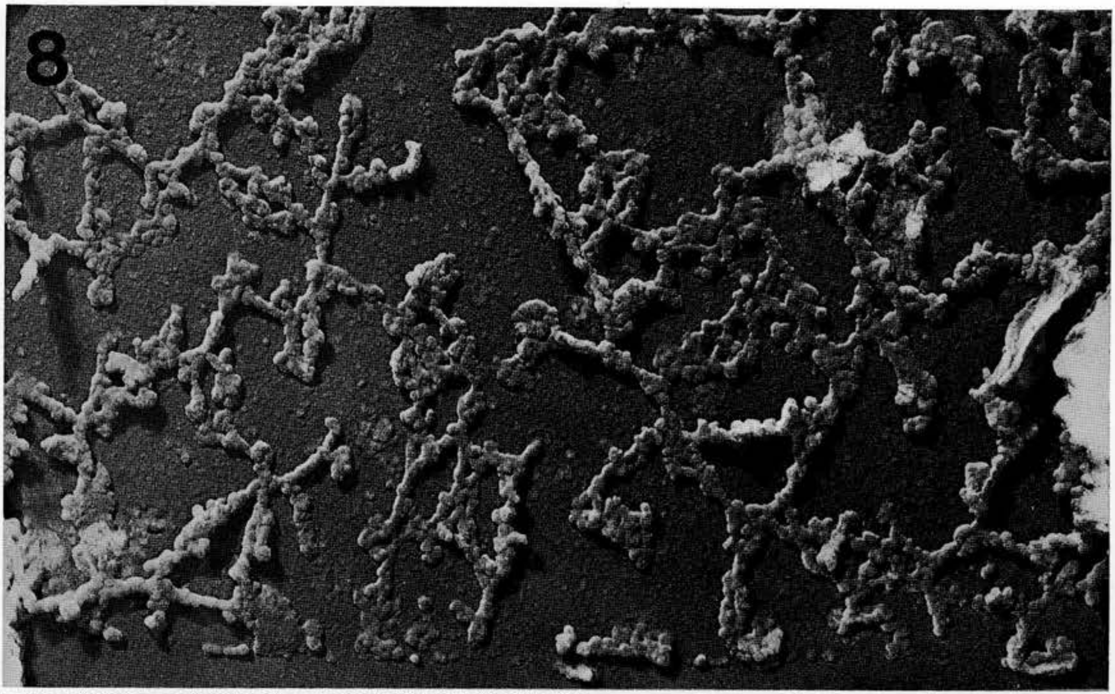
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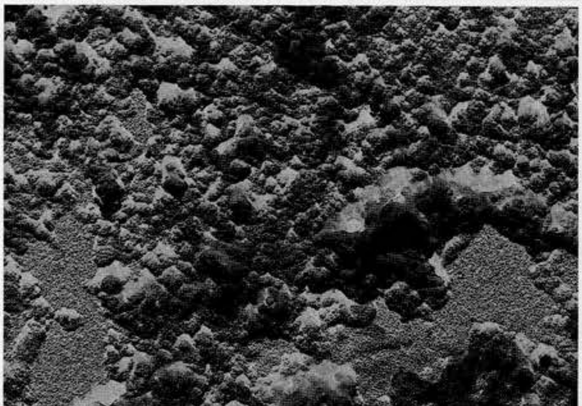
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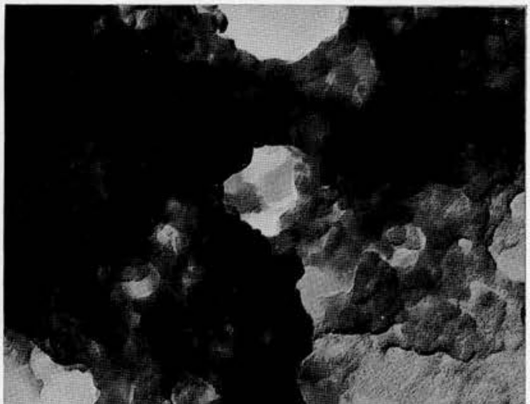
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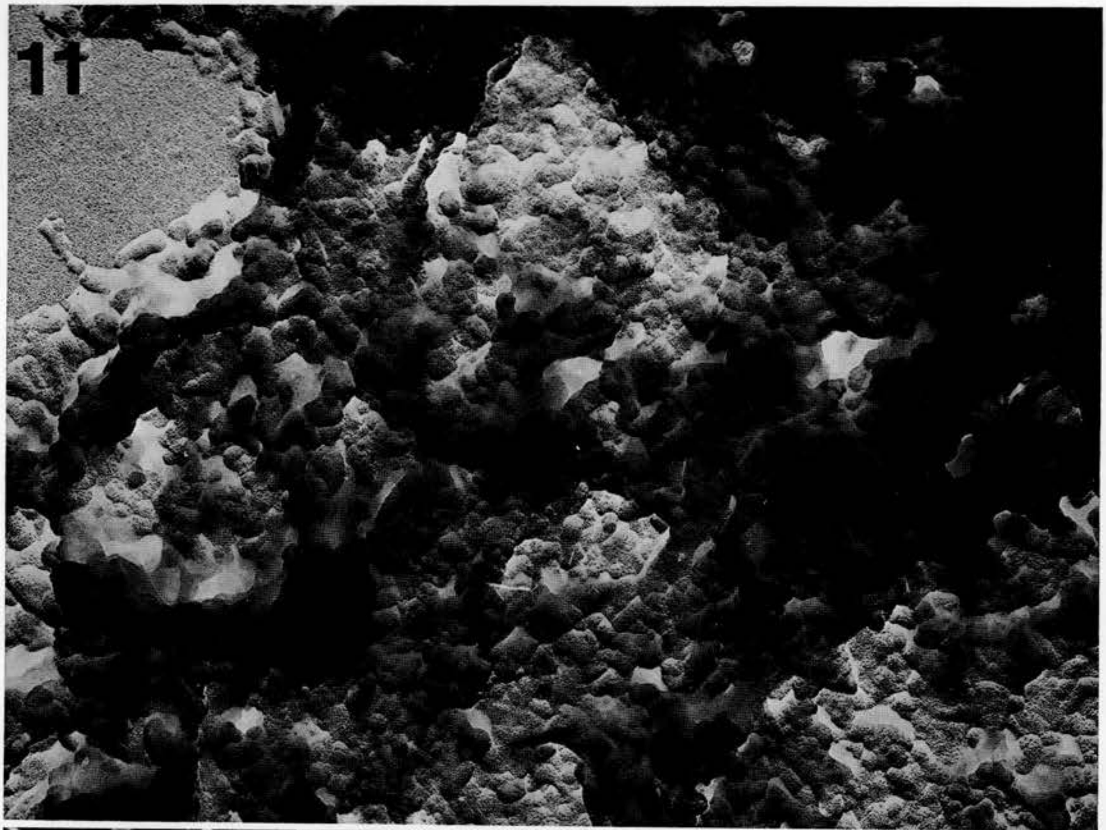
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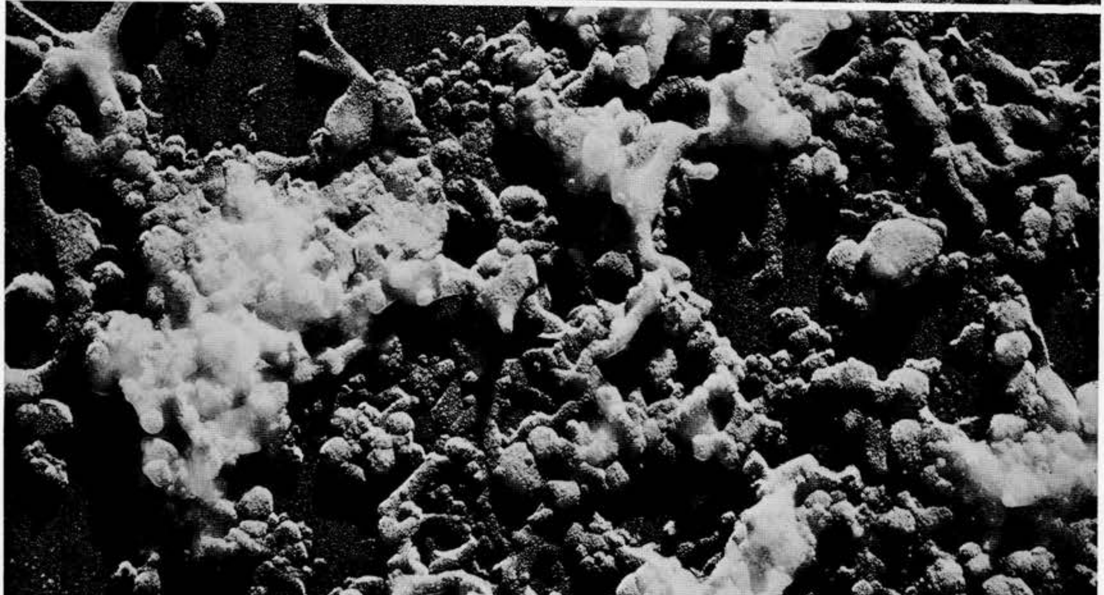
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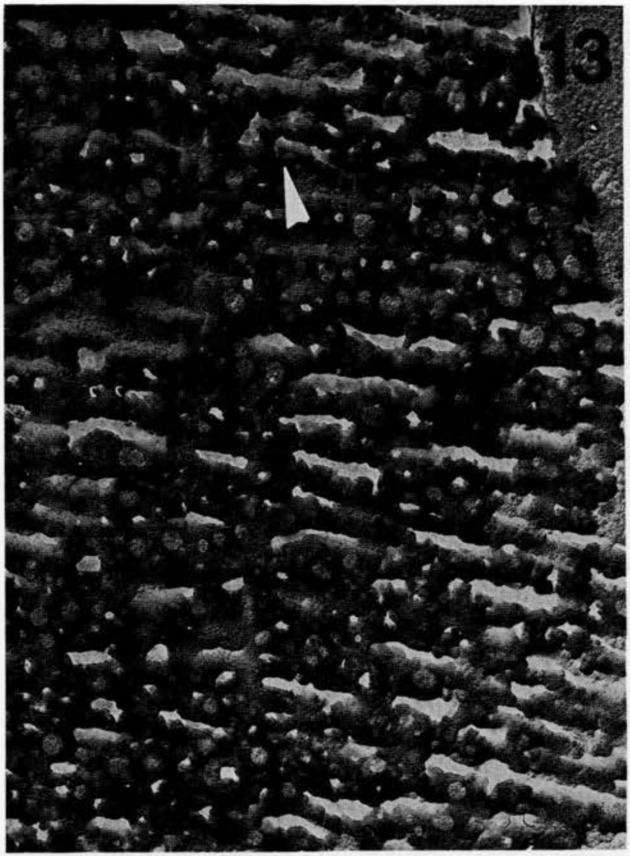

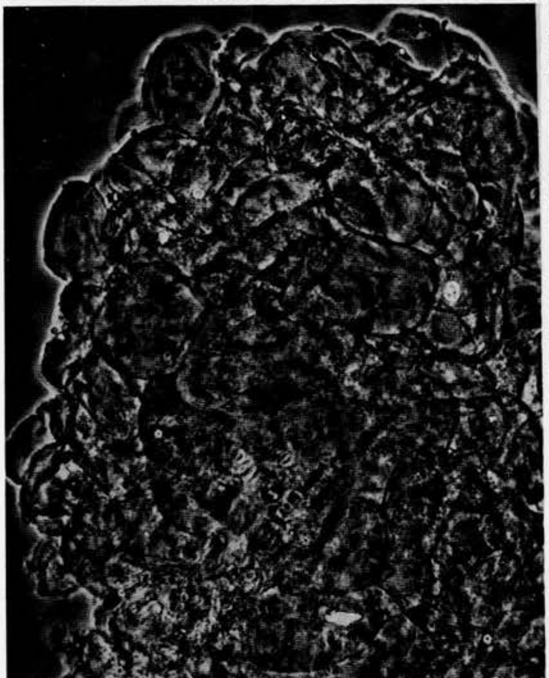

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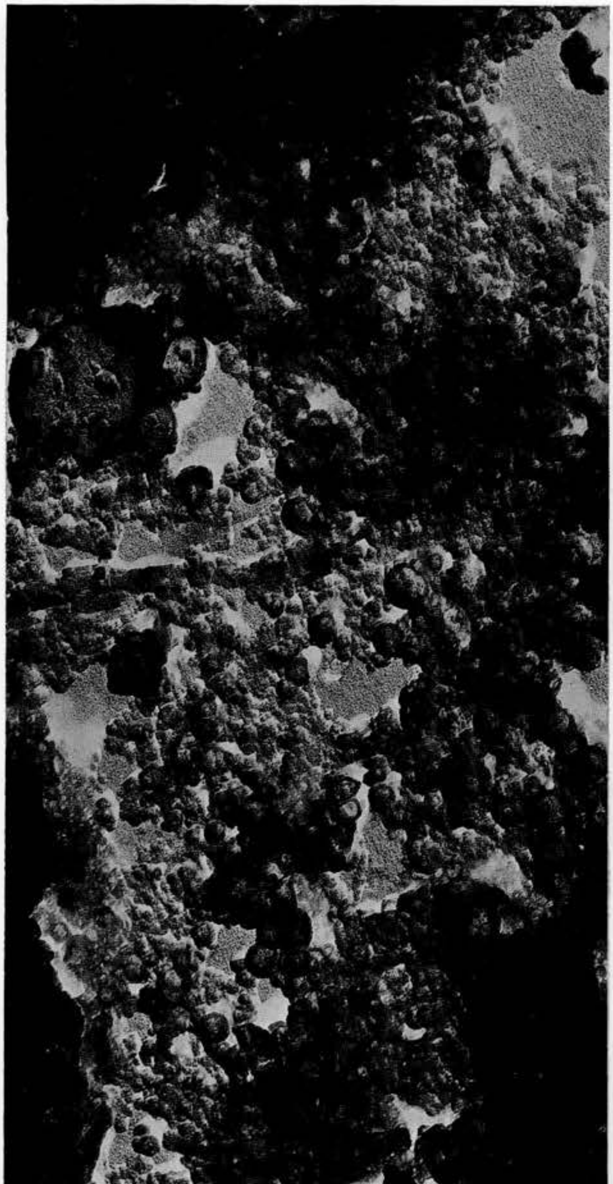

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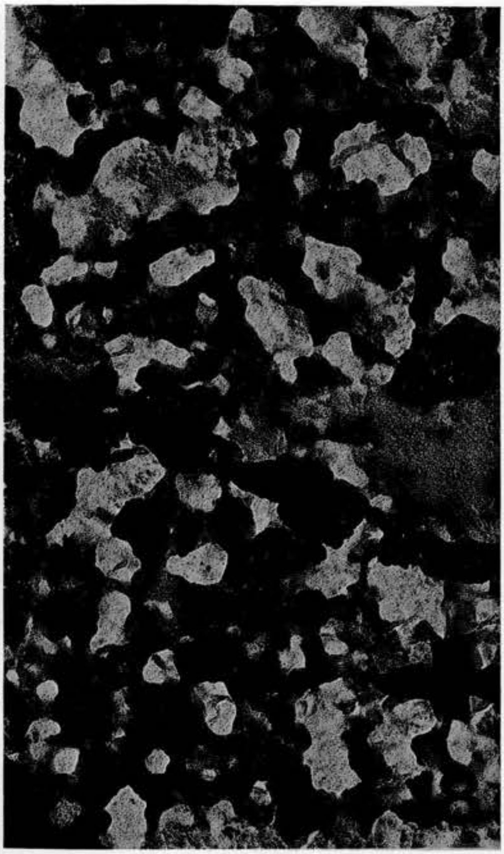

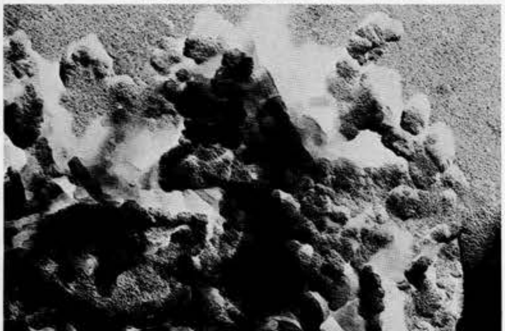

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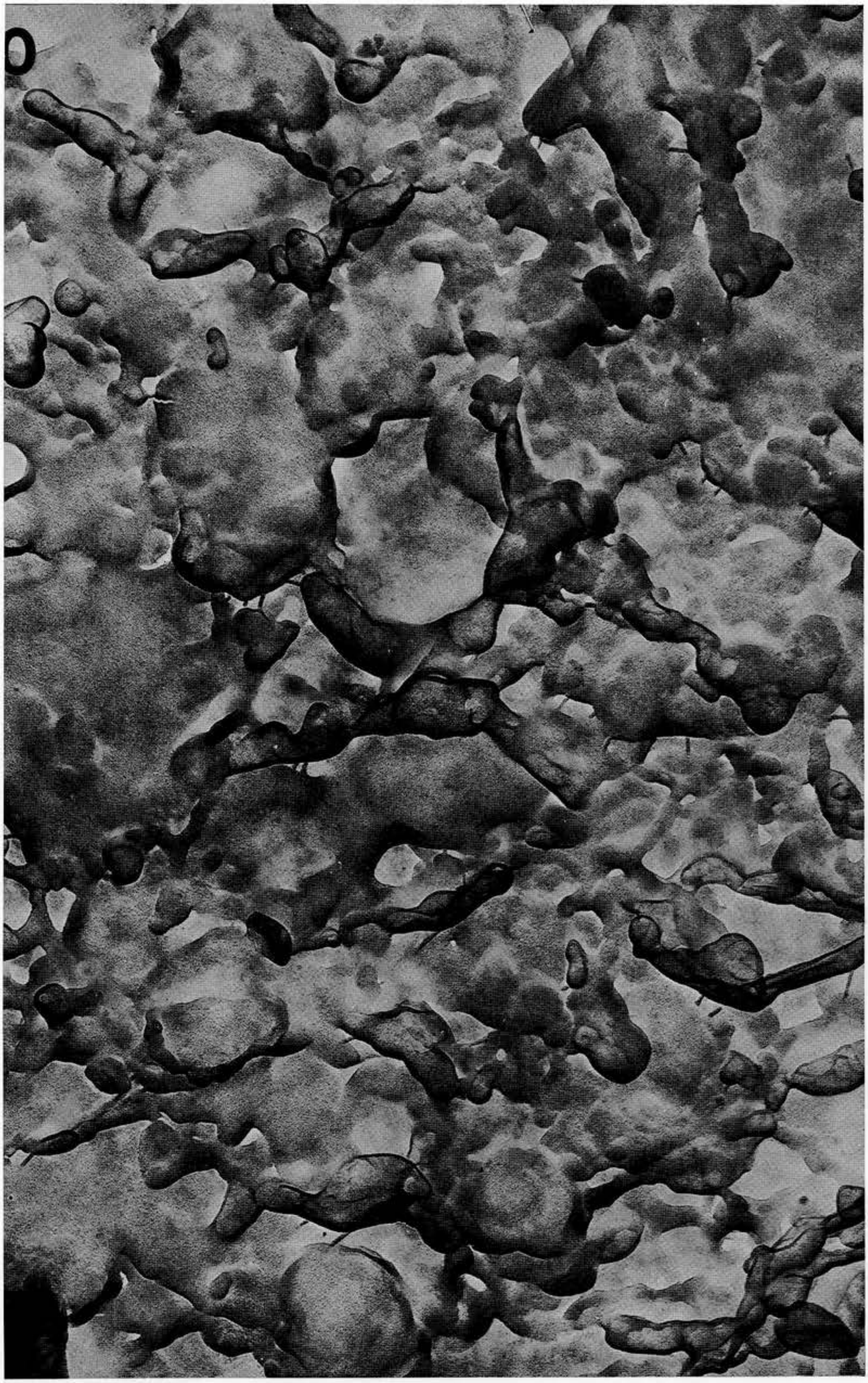

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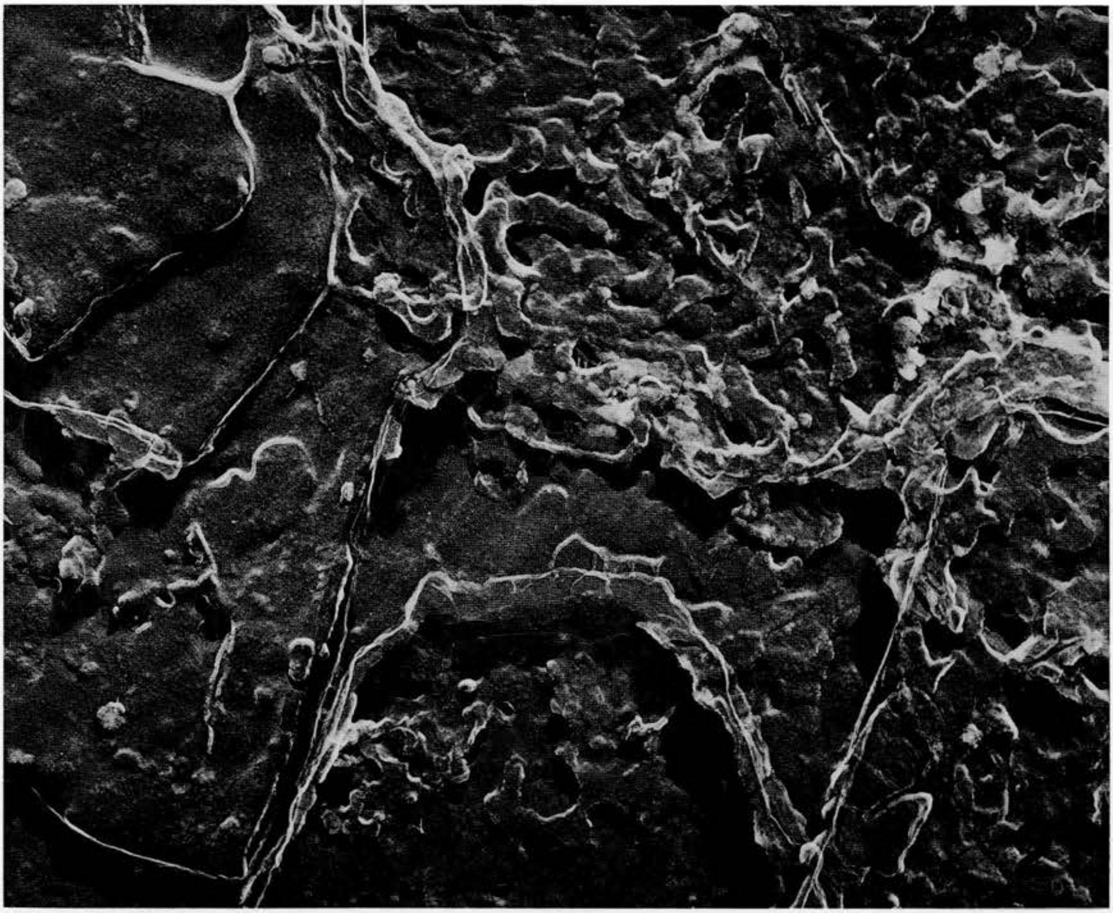

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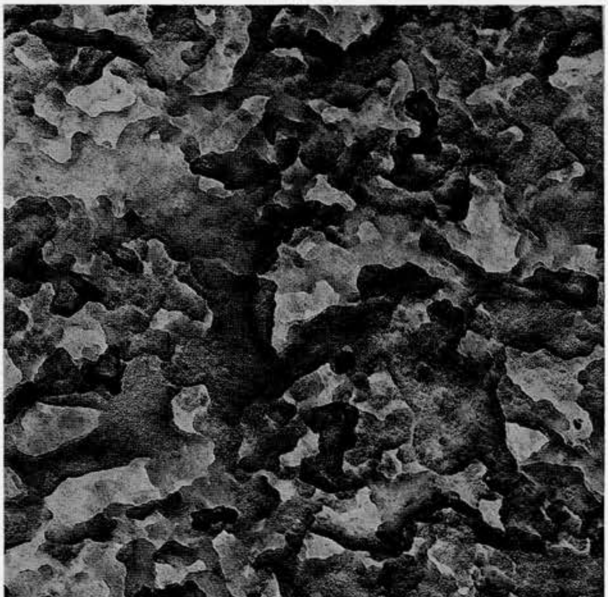

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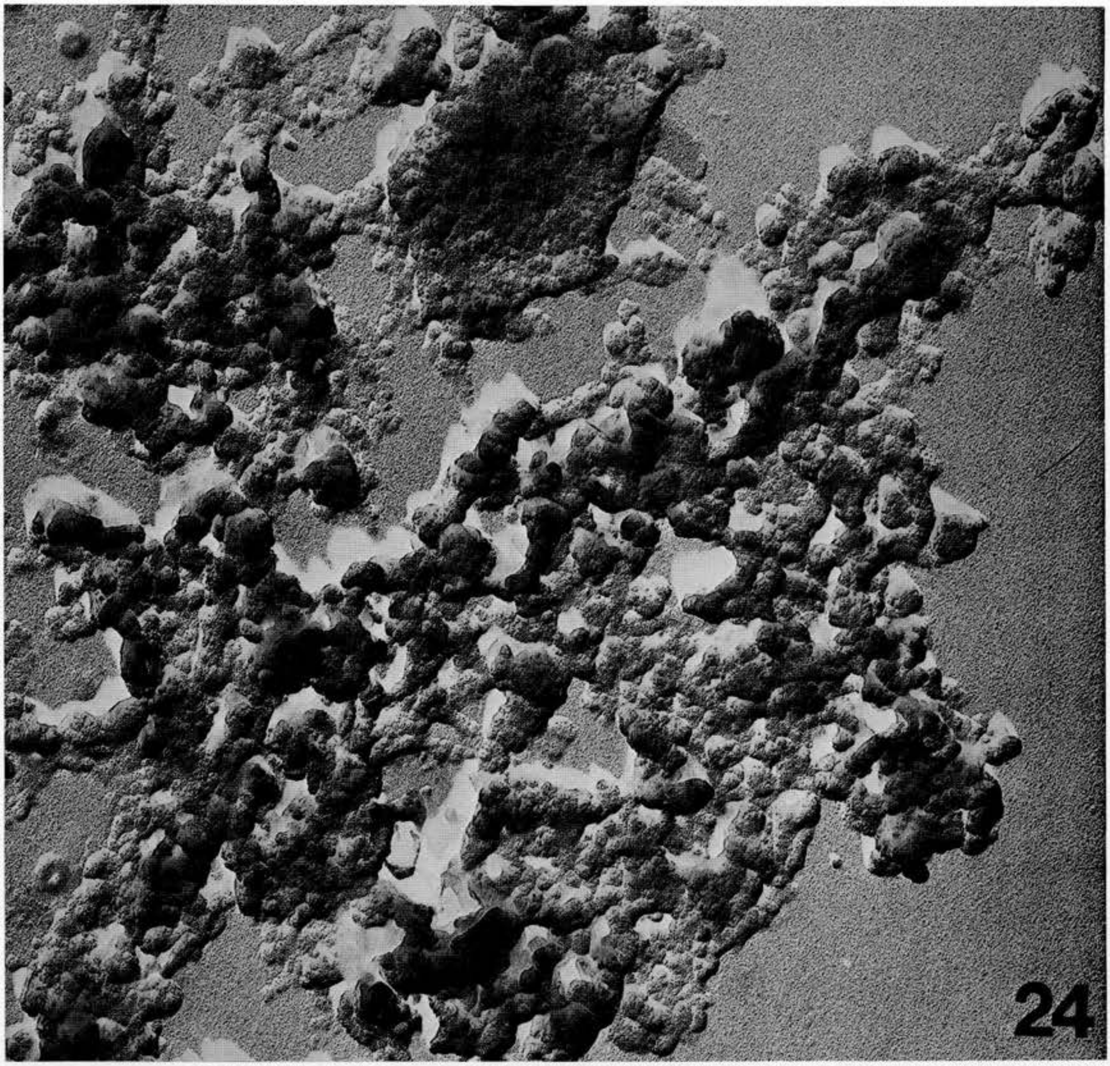

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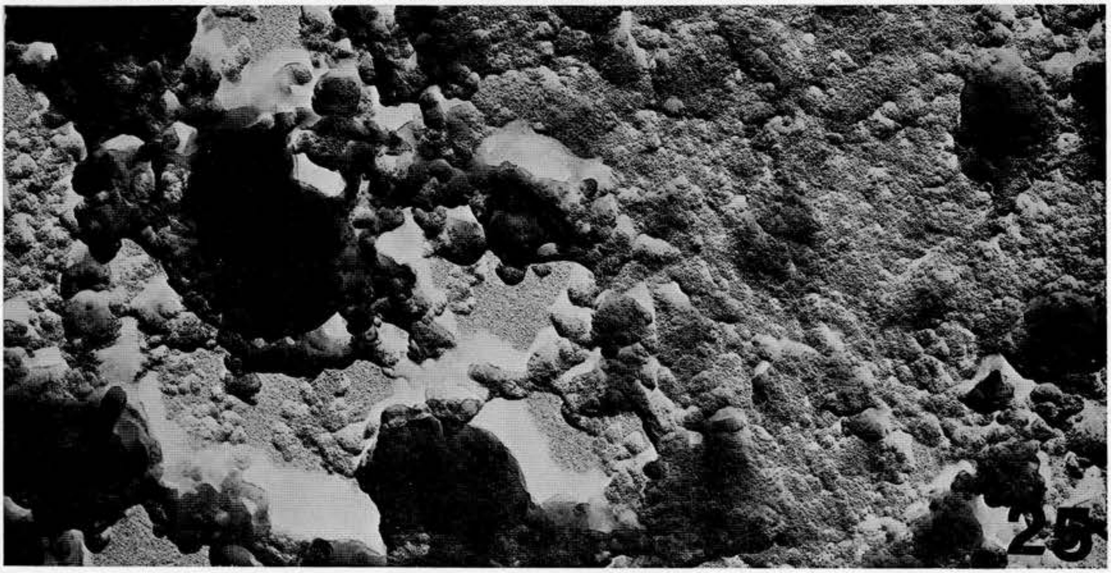

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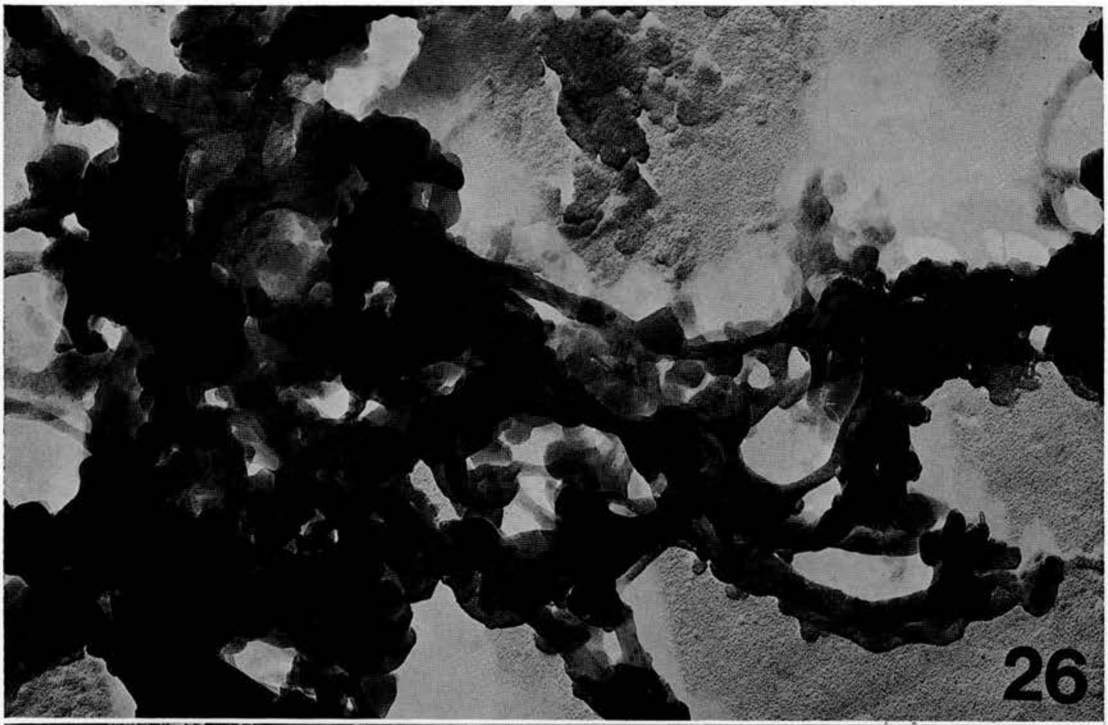

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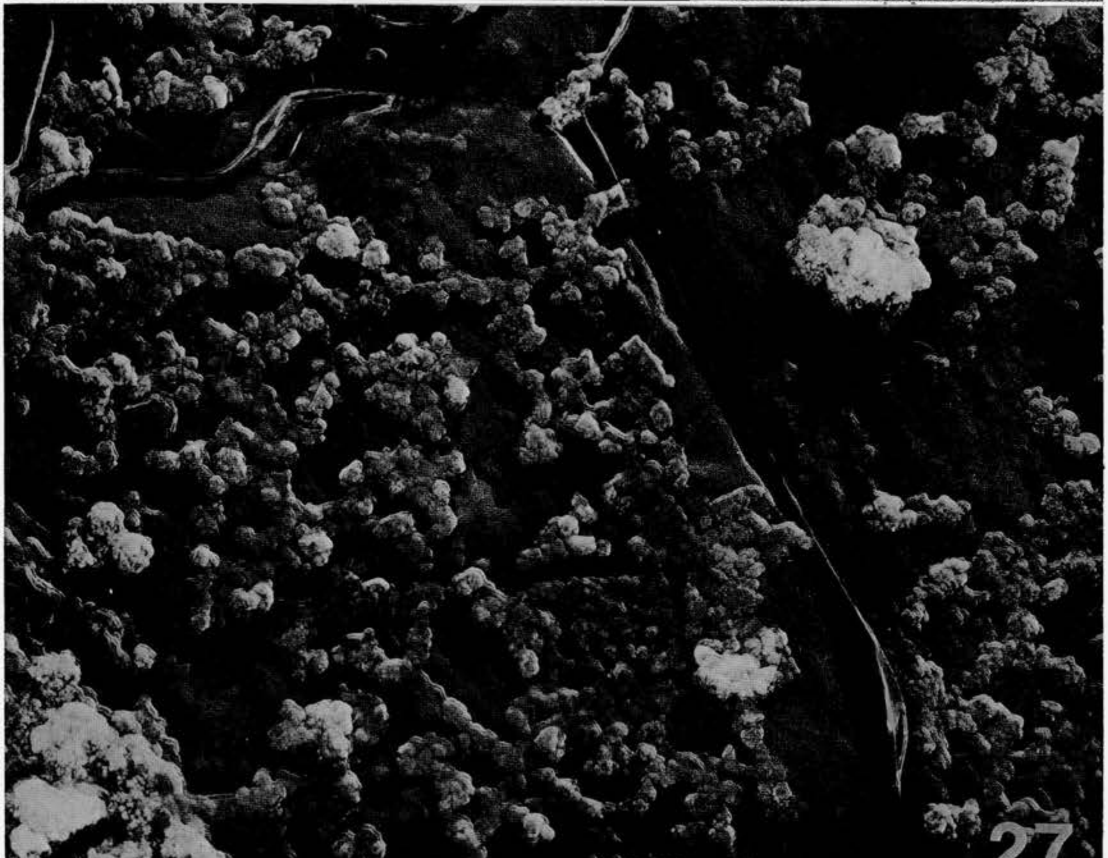

27

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