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BULLETIN

ON ORGANIC REMAINS IN SHELLS OF PALEOZOIC AND MESOZOIC CEPHALOPODS (NAUTILOIDS AND AMMONOIDS)

BY

Charles GRÉGOIRE (Liège)

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INTRODUCTION.

As shown in previous investigations with the electron microscope (41, 42), nacreous conchiolin left by decalcification of shells of Recent molluscs consists of reticulated sheets, resembling laces. The fabric of these structures varies with the class of molluscs. Three patterns — nautiloid, gastropod and pelecypod — have been provisionally described. Detailed studies on pelecypods have shown that statistically significant differences may be detected at the family level of taxonomy (37).

In further observations, shreds of substance still presenting structural characteristics of the conchiolin pattern in corresponding groups of Recent molluscs have been detected with the electron microscope in residues of decalcified fossil mollusc shells of various ages (34, 35, 36).

As it is known, the shells of fossil molluscs, especially those of cephalopods (nautiloids, ammonoids), play an important role in the determination of geological formations. The criteria so far applied for identification of these shells cannot always be used because of the poor state of preservation of many crushed and weathered specimens.

Occurrence of conchiolin remnants in fossil shells suggested use of these remnants for different purposes, including specimen identification, detection of taxonomic differences at the ultrastructure level, determination of the conchiolin pattern, and perhaps of bygone types of organization, in extinct groups, such as the ammonites, control of composition of samples used for biochemical analyses, and study of the morphological counterpart of biochemical alterations recorded in the original proteins.

The investigations with the electron microscope on the shells of fossil molluscs have been extended to samples of nacreous substance of 150 species, a few millions to 450 millions years old. Except for fragmentary reports (32, 43), the results, based on examination of more than 9.000 electron micrographs, have not been published.

The present paper is a survey on the structure of decalcification remnants of nacreous substance in a selection of Ordovician, Devonian, Carboniferous (including Pennsylvanian), Permian, Jurassic, and Cretaceous, nautiloid and ammonoid shells.

In many specimens, the conchiolin sheets had undergone considerable alterations, resulting from diagenetic changes. In order to aid in identification of conchiolin, in spite of these changes, and in order to decrease the risk, always present in fossils, of confusion with structures from foreign contaminating organisms, attemps were made, in studies still in progress, to reproduce artificially these diagenetic alterations. Nacreous fragments of Recent *Nautilus* shells, the only living survivor of the groups of fossils examined in the present investigation, were exposed to a few of the many factors involved in the diagenetic processes, such as heat, and pressure, and the alterations produced in conchiolin were compared with those observed in fossil materials.

MATERIALS AND METHODS.

The inner, nacreous layer of the shell wall from the following cephalopods has been selected for the present study (file number in brackets) :

Isorthoceras sociale FLOWER (26) (formerly *Dolorthoceras sociale* HALL), nautiloid (Orthocerida), Upper Ordovician Lower Maquoketa Formation, Graf, Iowa, U. S. A. (357). *Faberoceras* sp., nautiloid (Discosorida) (28, 72), Upper Ordovician, Leipers Beds, Cumberland River Valley near Rowena, Kentucky, U. S. A. (699). *Striacoceras typus* (SAEMANN) (23), nautiloid (Orthocerida), Devonian, Cherry Valley limestone, Stockbridge Falls, N. Y., U. S. A. (703). Unidentified gyroconic nautiloid of large size (*Rutoceratidae* ?, 54), Middle Devonian (Couvinian), Dinant, Belgium (713). *Rutoceratidae* sp., nautiloid, Upper Middle Devonian (Givetian), Sötenicher Mulde, Sötenich, Eifel, Germany (685). Several Pennsylvanian cephalopods from Buckhorn asphalt, Sulphur, Oklahoma, U. S. A. : *Pseudorthoceras knoxense* (MCCHESNEY), nautiloid, (421-33); unidentified nautiloid, septal material (751); unidentified cephalopod (nautiloid ? ammonoid ?), curved fragment of shell wall (749); four unidentified ammonites (whorl fragments) (421-26; 421-39; 421-47; 755); *Eoasianites hyattianus* (GIRTY) (676-7) and *Eoasianites* sp. (358), both goniatites. *Beyrichoceratoides* sp., *goniatite*, Lower Carboniferous, Cot Castle shell Beds, Bore Baads Mine, Scotland (662). *Hudsonoceras proteum* (BROWN), goniatite, Upper Carboniferous, Coolagh River, Lisdoonvarna, Co Clare, Ireland (664). *Homoceras beyrichianum* (DE KONINCK), goniatite, Upper Carboniferous, Chokier-Flémalle, Belgium (668). *Domatoceras* or *Stearoceras*, nautiloid, Permian, San Andres limestone, Rio Penasco River, east of Alamogordo, New Mexico, U. S. A. (422). *Harpoceras mulgravium* (SIMPSON, YOUNG, and BIRD), ammonoid, Jurassic, Lias, *Falciferum* Subzone, Whitby, Yorkshire, England (524). *Baculites* sp., ammonoid, Cretaceous (Senonian), Ripley Formation, Coon Creek, near Enville, Tennessee, U. S. A. (395). *Nautilus pompilius* L., Recent.

Methods. — The nature of the minerals composing the samples used has been determined previously by X-ray powder diffraction analysis (32). However, with the diffractometer available, minerals in lesser amounts than about 3 per cent could not be recorded, and the data reported in brackets, in the legends of figures, indicate in fact the predominant substance found in the samples.

When possible, the samples were collected from nacreous material freed by fracture of the embedding sediment, immediately before use. This procedure decreases the risk of contamination by Recent organisms, but not that contemporaneous of the specimen burial, especially by boring predators. In other cases, the weathered portions of the samples were removed by filing off and polishing off, and only the inner portions of the samples were used. In several ammonites, thinness of the test did not permit to separate the outer and inner shell layers.

The samples were decalcified by chelation (saturated aqueous solutions of EDTA disodium salt, titriplex III Merck, at pH varying from pH 4.0 to pH 7.0) (34-43). The residues, rinsed several times and recovered by centrifugation, were mounted on copper screens coated with films of formvar or of carbon. Agglutinated shreds of substance, opaque to the electron beam, were dissociated and thinned by moderate exposure (in distilled water) to ultrasonic waves (Headland Ultrasonic Equipment).

Inorganic salts of low solubility resisting decalcification were found in many samples, especially in Paleozoic material. Sedimentation on the supporting films of such crystals, mingled with the organic remnants, is responsible for frequent object-drifting under the beam. In order to dissolve these salts, or to decrease their amount, portions of the residues were allowed to stand in contact for one to six days and under intermittent agitation, with mixed-bed ion-exchange resins (including Amberlite MB - 3). As reported recently (6, 49), many inorganic salts of lower solubility are dissolved by this procedure, but even the most delicate structures should be left wholly unaffected.

The biuret reaction was routinely performed, in all the samples, on residues suspended in distilled water and the staining reaction of the fragments was observed under a conventional microscope. The dried preparations were examined in the electron microscope either directly, or after shadowcasting with palladium or platinum, at angles of 15-28°. The negative staining method of Brenner and Horne (17) with its various modifications reported in literature, was also used (86, 87).

Positive carbon replicas (double stage method of Bradley, 14, 15), shadowcast with palladium or platinum, were prepared, before and after etching, from various surfaces of the specimens, freshly exposed by disection of the surrounding moulds, from surfaces of fracture and from surfaces of polished and etched, tangential and transverse sections of the samples.

Electron microscopy was carried out with a R. C. A. - EMU - C electron microscope and with a Siemens Elmiskop - 1 using a double condenser, a 200 μ condenser aperture and a 30 μ objective aperture. Absence of a cold stage in the electron microscope was responsible for contamination of some preparations in the form of carbonaceous deposits appearing as grey layers around several structures (figs 15 and 18).

OBSERVATIONS.

Types of structures observed in remnants of decalcification of fossil nacreous layers.

In the brickwall architecture of mother-of-pearl (21, 63, 64, 65), the fragments of reticulated sheets of conchiolin shown in figs 1, 2, 3 are portions of the pericrystalline and of the interlamellar conchiolin systems that alternate in the nacreous stratification with the lamellae or layers of aragonite crystals (33, 77, 78). Sturdy trabeculae, studded with hemispheric protuberances or tuberosities, and a generally elongated fenestration, characterize, in shadowcast preparations, these conchiolin structures in shells of Recent *Nautilus* (nautiloid pattern : 41, 42, 33, 39). As pointed out previously (33), the trabeculae appear as knobby cords resembling rhizomes of the garden iris or beachtree roots.

Decalcification of nacreous regions of fossil shells of different ages and from different stratigraphic levels leaves shreds or flakes of soft substance, differing in colour and consistency, and frequently mixed, especially in Paleozoic materials, with various amounts of undissolved mineral salts. Under the phase contrast microscope (fig. 10), these shreds appear in the form of transparent, polygonal, rounded, scattered or clustered flakes, still partly assembled into fragments of flaggings. Each flake represents a portion of conchiolin sheet which covers a polygonal crystal facet in the original nacreous configuration. The straight ridges that delimit the polygonal areas are remnants of intercrystalline conchiolin bridges that wrapped before decalcification the side facets of crystals. Small particles, frequently embedded in jellies, were found to be associated with the flakes.

Biuret reaction stained homogeneously a part of these structures (such as those shown in fig. 10) in pink-violet (lilac), with various grades of intensity. In samples from various fossils, violet or purple speckles marbled the uniformly lilac background of the flakes and appeared also on straw-coloured, unstained flakes.

In the electron microscope, the components of these remnants of decalcification assume different aspects, which may be roughly ranged into the following groups of structures, frequently assembled in a same preparation :

1. Reticulated sheets, in which the structural characteristics of the nacreous sheets in the Recent *Nautilus* shell are recognizable (figs. 27, 28, 29, 31). Such structures were especially observed in shell fragments of Upper Pennsylvanian nautiloids (about 300 million years old) entombed in asphaltic sandstones of Oklahoma and which have retained their original mineral (69, 32) and organic components (32, 43) nearly unchanged in their structure and composition. These fossil sheets of nacreous conchiolin differ from those of the Recent *Nautilus* by disappearance of the tuberosities covering their trabeculae and by some degree of flattening of the latter (compare figs. 1, 2, and 3 with figs. 27 and 28). As in Recent *Nautilus* shells (39), the fabric of the septal organic material of these specimens is slender, in contrast with that of the wall conchiolin (compare figs. 27 and 28 with fig. 29).

The organic, ammonoid shell material buried in the same Buckhorn asphalt formation as the nautiloids appeared to be less preserved and fragments of recognizable reticulated sheets were recorded only incidentally (fig. 36). In these sheets (figs. 30, 32, 35 and 36), the trabeculae are short, frequently barrel-shaped. Difference in texture between wall and septal nacreous conchiolins seems also to exist in ammonite shells (compare figs. 30 and 32 with fig. 31).

In many other preparations, the pattern of ammonite conchiolin had been considerably modified and debris of trabeculae show the kinds of alteration described below (figs. 35 and 36).

2. Scattered or clustered flat discs, lenticular and spherical bodies, measuring from 20 to 200 $m\mu$ in diameter, and resembling pebbles in shadowcast preparations (figs. 4, 5, 11, 14, 21, 24, 25, 35, 37, 40, 41, 44) were found among the decalcification remnants of the nacreous layers of nearly all Paleozoic and Mesozoic shells so far investigated (35). In some of these structures, faint polygonal outlines are recognizable. Similar pebble-shaped bodies appear occasionally at the margins of mechanically dissociated reticulated sheets of conchiolin of Recent *Nautilus* (fig. 2) and in scattered areas of otherwise well preserved sheets of the Buckhorn asphalt nautiloids.

3. Other spheroidal bodies of widely varying size (20-300 $m\mu$), are composed of a relatively transparent center, encircled, when the structures are viewed in vertical projection, by a denser, apparently membraneous envelop (figs. 13, 14, 26, 34, 36, 39, 40) which appears as a turban-shaped ring. These structures, provisionally labelled knobs, were detected in varying amounts in samples from all ages and deposits. These knobs were especially numerous in nacreous samples of a Devonian nautiloid from Eifel (fig. 13), in samples of Carboniferous goniatites (fig. 26) and of Pennsylvanian ammonites (figs. 34 and 36). In the latter specimens, some knobs (not shown) reached much greater sizes than that illustrated in fig. 34.

4. Twisted ribbon-like strips, with variously elongated budding expansions, and thong-shaped membranes were detected among the decalcification remnants of nacreous substance in specimens from various ages and deposits, especially in shells in which original aragonite had been diagenetically recrystallized into calcite or had been replaced by other minerals. Several membranes were perforated either by broad polygonal fenestration (fig. 6) or by oval or rounded openings (fig. 7). In several of these structures, the nautiloid pattern, though deeply altered, was still recognizable (fig. 7).

5. In a Devonian nautiloid and in Carboniferous goniatites from different deposits and geographic origins *(Homoceras, Hudsonoceras, Gastrioceras)*, decalcified nacreous samples included, aside the ubiquitous clustered pebble-shaped bodies consistently recorded in fossil nacreous samples (type 2 : figs. 20, 24 and 25), other structures, such as large spherical and pear-shaped corpuscles, resembling knobs (figs. 17 and 26), and extremely polymorph, branched and club-shaped, flattened strands

of elongated membraneous fragments (figs. 17 and 18). These structures were associated with 1.1 to 1.4 μ large, ovoid or spheroidal, spore-like corpuscles. As shown in fig. 15, two kinds of elements, irregularly oval or spheroidal structures, about 70 mμ in size (also shown in fig. 18), and smaller, spherical granular bodies, about 20-25 mμ in size (also shown in fig. 16), seem to be discharged from a spore-like corpuscle.

6. Fibrils, 10-40 Å in width, scattered or assembled in bundles, were mixed incidentally with the nacreous organic remnants described above, in nacreous samples of several shells, especially in *Orthonybyoceras duseri* (nautiloid) (Upper Ordovician, Cincinnatian), in *Faberoceras* sp. (nautiloid) (Upper Ordovician), in *Agoniatites vanuxemi* (goniatite) (Middle Devonian), in *Cyrtoceras* sp. (nautiloid) (Middle Devonian, Couvinian), in *Eoasianites hyattianus* (goniatite) (Pennsylvanian), in *Domatoceras* or *Stearoceras* (nautiloid) (Permian) and in *Harpoceras mulgravium (ammonite)* (Jurassic). In several preparations, these microfibrils seemed to be composed of chains of beads.

Inner structure of remnants of trabeculae in fossil nacreous conchiolin.

In the Paleozoic and Mesozoic organic remains described in the present study, the various kinds of structures (discs, pebbles, fragments of trabeculae, membranes, knobs), examined on the supporting films without other treatment, appeared to be composed, as conchiolin from Recent material (see discussion) of a relatively transparent and amorphous, incidentally slightly granular material (see figs. 12, 20 and 39). Remains from other samples were marbled with scattered grains and small twisted rods, possibly residues of microcrystals (not shown).

Electron diffraction diagrams of clusters of discs, of pebble-shaped bodies and of knobs, consisted of concentric rings with diffuse boundaries, on which a few spots were irregularly disposed.

Fragments of trabeculae from all the shells investigated, stained with phosphotungstic acid (positive and negative contrast : 17, 86, 87) appeared also generally amorphous or thinly granular (figs. 43 and 46). In some preparations, microfibrils, mostly ill-defined, unoriented, disposed in bundles or forming networks, were observed in these trabecular fragments (figs. 42 and 45).

Architecture of fossil mother-of-pearl and topography of conchiolin remains.

In the shell of the Recent *Nautilus,* configuration of mother-of-pearl differs from the brickwall arrangement of the aragonite crystals in many other shells by the columnar stacking of its crystals. The margins of these crystals coincide in consecutive lamellae (64, 5, 39).

In former studies on topography of conchiolin in mother-of-pearl in various mollusc shells (*Nautilus*, gastropods and pelecypods) (33), interlamellar (possibly composed of several sheets) and intercrystallinic conchiolin sheets had been observed with the electron microscope in the nacreous configuration.

Recent observations by Watabe (77, 78), on thin sections of mother-of-pearl in the Recent pelecypod *Elliptio complanatus*, examined with the electron microscope before and after decalcification of the sections, revealed new aspects of mollusc shell structure. In mother-of-pearl, the single crystals of aragonite are composed of many small oriented blocks and the organic matrix not only surrounds the single crystals, but is also present within them. The *Nautilus* shell material does not seem to have been so far investigated for presence of similar subcrystalline elements in its nacreous substance.

In the present state of research on mollusc shells, three systems of conchiolin seem to exist in the nacreous architecture : 1. Interlamellar matrix lying horizontally between consecutive lamellae (33, 78). 2. Intercrystalline matrix, surrounding the tabular crystals of aragonite disposed side by side in a single layer in each lamella. The intercrystalline matrix forms vertical bridges of substance which separate the side facets of the crystals (33, 78) and covers also the tabular facets of these crystals in the horizontal interlamellar spaces, thus duplicating the interlamellar matrix in front of each tabular facet (33, 78). Consequently, the interlamellar conchiolin is composed of three horizontal sheets, the interlamellar sheet mentioned above sandwiched between two pericrystalline sheets, the latter structures being conchiolin portions covering the tabular facets of the crystals. As pointed out by Watabe (78), the horizontal portions of intercrystalline matrix mostly cannot be distinguished. 3. Intracrystalline conchiolin sheets disposed horizontally and vertically between the crystalline subunits (78).

The results of a study in progress with the electron microscope on shell architecture in fossil mollusc shells of different ages and deposits will be reported later. Two examples, selected from this material, illustrate some relations between organic and mineral components of mother-of-pearl in shells in which X-ray powder diffraction analysis (32) revealed either preservation of original aragonite in nacreous substance or its recrystallization into calcite or/and replacement by other minerals.

A. Shells with preservation or slight alteration of aragonite in nacreous layers.

Several Pennsylvanian nautiloid and ammonoid shells from Buckhorn asphalt are still composed predominantly of original aragonite (69, 69A, 32), mixed in some specimens with small amounts of calcite (32). In the nacreous layers of these shells, the architecture of mother-of-pearl described previously with the electron microscope in the shell of the Recent *Nautilus* (39) has been preserved nearly integrally in some areas and has undergone distinct modifications in others (figs. 47, 49 and 51 : unidentified ammonite and *Eoasianites* sp., goniatite; figs. 48 and 50 : *Pseudorthoceras knoxense*, nautiloid).

Piling up in columns of aragonite crystals with coincidence of their margins in successive nacreous lamellae, which characterizes *Nautilus* mother-of-pearl, can also be found in ammonoid shells and is shown in fig. 47 (extreme right). In this preparation, measurements of 30 successive lamellae revealed an irregular alternation of layers of thicker and of thinner crystals in the nacreous stratification. As in the pelecypod *Elliptio complanatus* (77, 78), the nacreous aragonite crystals of nautiloids and ammonites seem to be composed of subunits consisting of microblocks, revealed in figs. 47 and 48 in the form of vertical furrows, partly filled with intracrystalline soft shreds of conchiolin, and shown across the crystal thickness. Moderate alteration of the mineral components of mother-of-pearl in these fossil specimens, which precede or accompany local recrystallization of aragonite into calcite, consists of coalescence of adjacent lamellae (figs. 47 and 48, left). This coalescence proceeds from fusion of the crystals along a part of their subunits or microblocks (fig. 47) in adjacent lamellae. The fusion process results in formation of elongated and imbricated tablets, disposed in parallel arrays at right angles to the nacreous lamellae (fig. 48, left). In other regions of this preparation (not shown), the systems of parallel, elongated tablets, disposed vertically, have completely replaced and concealed the original stratification, which is still indicated incidentally by preservation of scattered groups of crystals exhibiting the primitive horizontal brickwall disposition. In these regions in which the mineral architecture has been modified, the conchiolin components have not disappeared (black and grey shreds in fig. 48 left).

Preservation in fossil shells of whole systems of nacreous conchiolin identical to those described in Recent shells (33, 78) is illustrated in ammonoid (figs. 49 and 51) and nautiloid (fig. 50) materials, on preparations of polished and etched transverse sections of mother-of-pearl. In these preparations, the conchiolin remnants appear in the form of cylindrical cords. These cords are mostly pseudoreplicas detached with the negative replica from the mineral background on which they protruded, then were transferred to the positive replica and were subsequently shadowed with the latter.

Figure 50 shows, in the shell of *Pseudorthoceras knoxense*, a preserved conchiolin system in nine consecutive nacreous lamellae (presented vertically in the figure). The interlamellar matrix (ilm), mostly soldered to the neighbouring parallel pericrystalline layers, appears in the form of variously thick cords interposed between crystalline layers. Instead of running continuously between lamellae as in unaltered shells, this fossil matrix is broken into variously long segments. A substantial system of short cords (about 25 mμ thick), crosses at right angles the elements of the interlamellar matrix. These cords are intercrystalline and intracrystalline matrix.

In figures 49 and 51 *(Eoasianites)*, conchiolin elements, lying in pits or disposed behind protruding structures, have been protected from the impact of the shadowing metal. Tongue-shaped cords (arrows) of intercrystalline and of intracrystalline matrix, shown in cross section, appear as triple-layered structures, composed of a central, 4-5 mμ thick, opaque, threadlike core in cross section, bisecting the cord and surrounded on both sides by 8-10 mμ thick, relatively transparent, strands of substance.

B. Shells with recrystallization or replacement of original aragonite in nacreous layers.

In specimens of the Upper Ordovician nautiloid *Isorthoceras sociale*, recrystallization of the original aragonite into calcite or its replacement by other substances, including quartz and carbonate apatite (dahlite), has been recorded by X-ray powder diffraction analysis (Clifford FRONDEL, 1947, quoted by CLOUD and BARNES, 18; 32).

In replicas of polished and etched sections of different portions of the shell wall corresponding to the topography of the original nacreous layers, traces of the original lamellar configuration of mother-of-pearl are still visible (figs. 52 and 53) and consist of scattered groups of straight, irregularly parallel channels and ridges. Recrystallization or replacement of original nacreous aragonite is illustrated by disappearance of the brickwall structure, which has been replaced by large blocks of crystals. The crystalline subunits of this new material are indicated by shadows projected on parallel elongated grooves (fig. 52). Development of large crystals has disturbed orientation of the former interlamellar spaces and structures in some areas and destroyed them in other regions (fig. 52, bottom right; fig. 53, right upper quarter). On the other hand, as shown in figure 53, original columnar stacking of the crystals, with coincidence of their margins, a characteristic feature of mother-of-pearl in the Recent *Nautilus*, has been preserved in limited regions. The remnants of conchiolin systems consist of intercrystalline filaments which surround the piled crystals (fig. 53) or which run along the ridges and channels (figs. 52 and 53). In the latter structures, the conchiolin remains are composed of pairs of thin, parallel membranes which appear as threadlike structures in cross section. These membranes seem to encircle elongated, rod-shaped crystalline structures and their pseudoreplicas (white strands in fig. 52; black strands in fig. 53). These membranes occupy the position of pericrystalline conchiolin sheets in the original conchiolin systems. In these areas, the interlamellar sheets, originally sandwiched between two pericrystalline sheets, seem either to have disappeared or to have been displaced and agglutinated to one of the lateral sheets. In any case, the voids left by disappearance or displacement of interlamellar sheets seem to have been occluded subsequently by crystals growing in the elongated cavities.

Another aspect of the diagenetic changes induced in this Ordovician shell, in the form of spherulite-like arrangement of crystals, is illustrated in figure 54. This type of structure characterizes dahlite (60), recorded by X-ray powder diffraction analysis in the present samples (32).

DISCUSSION.

Occurrence of organic remnants in fossils has long been reported (75, see lit. in 35). Preserved microfossils have been found in Precambrian rocks and in two billion years old Precambrian Gunflint chert (74, 8, 66). Amino acids (1, 2, 3) and remains still presenting the amino acid pattern of conchiolin scleroproteins (53, 22, 45, 20) have been detected in biochemical studies on fossil shells. Similar results on preservation of organic compounds have also been reported in bones and teeth from various ages (50, 85) and recently in graptolites (29). Luminescence and fluorescence microscopy (79, 81, 57, 88) have been employed to detect organic substances in fossil molluscs. Use of the electron microscope has permitted to observe preservation of original organic ultrastructures in fossil mollusc shells (34, 35, 36, 32, 43), in fossil bones and teeth (58, 84, 68, 51, 59).

Identification of structures escaping decalcification.

Identification of the remnants of decalcified fossil mother-of-pearl, in which the original nacreous pattern has been considerably altered, is hazardous. Confusion with fragments of foreign organisms contaminating the samples, is a permanent danger.

Evidence of conchiolin nature of the different types of structures recorded with the electron microscope in the present material, such as discs, spheroidal pebble-shaped bodies, a part of the knobs, and perforated membranes, is based on the following records :

1. Similar types of alterations occur at the margins of nacreous reticulated sheets of the Recent *Nautilus* shell (fig. 2) and in portions of otherwise well preserved conchiolin membranes of nautiloid material entombed in Buckhorn asphalt (43).

Salt residues escaping decalcification and dissolution by mixed-bed ion exchange resins assume occasionally a discoidal or spheroidal shape resembling that of the bodies found in conchiolin remnants. However, uniform size and diameter, and electron diffraction analysis permit to distinguish these salts from the shell structures.

2. Topography of the fossil nacreous remnants of decalcification in interlamellar, intercrystallinic and intracrystallinic spaces coincides with that of conchiolin in shell architecture of Recent materials.

3. Biuret-positive flakes of substance, indicating preservation of peptide bonds, were observed in all remains of decalcification investigated in this study. The biuret-positive structures from the Ordovician nautiloid *Faberoceras,* illustrated in figure 10, are unequivocally fragments of preserved interlamellar and intercrystalline systems of conchiolin. These remains were associated in the preparations with the other types of alteration observed consistently in the nacreous residues of the fossil shells so far investigated.

4. Discs and pebble-shaped bodies, identical to those illustrated in the present material, were frequent or predominant in the remnants of decalcified nacreous substance from shells of Eocene and Oligocene nautiloids (*Nautilus* sp., *Aturia* sp., 34, 35) and from organic components of cameral deposits of *Pseudorthoceras knoxense* (Pennsylvanian, 43) in which specific protidic components of conchiolin have been subsequently recorded with biochemical methods (22, 45).

5. In studies in progress on factors involved in the process of diagenesis during fossilisation, such as temperature and pressure, in open air or in sealed vessels, types of alteration recorded in fossil shells, namely discs and pebble-shaped bodies (figs. 19, 22, 23), knobs (fig. 33), twisted ribbon-shaped strips and perforated membranes (fig. 8, 9) could be reproduced artificially in sheets of nacreous conchiolin from samples of Recent *Nautilus* shells free from any contamination.

Foreign contaminants of fossil conchiolin remnants.

Colonies of epibionts (diatoms, algae) are frequently anchored on the rough surfaces of the shells of Recent *Nautilus,* especially in the region of the umbilical callus (39). Contamination of the shells of fossil molluscs during life or after death by commensal or parasitic organisms (algae, fungi, sponges and especially boring predators) has long been observed (56, 80, 24, 61, 62, 82). Contaminants were recorded with the electron microscope in the form of densely entangled, worm-shaped ribbons or cords in and around layers of Pennsylvanian nautiloid and ammonoid shells (43, Plate IV, fig. 3). In that material, however, the size of the huge contaminating structures was distinctly out of proportion with that of the original shell structures, and could easily be recognized.

In the present material, contamination of conchiolin samples by foreign elements was suggested by the presence, among the ubiquitous pebble-shaped remnants of conchiolin decalcification, of unusually composite structures (figs. 15 and 17). From these structures, detected in a Middle

Devonian nautiloid and in several Carboniferous goniatites from wide geographic dispersion (Ireland, England, Belgium, Oklahoma), spore-like, ellipsoidal or spheroidal corpuscles (fig. 15), obviously do not belong to the organic shell components. Other structures, such as small granular bodies (figs. 15 and 16), knobs (figs. 13 and 26), twisted and contorted membraneous strips (figs. 17 and 18), discharged from the spore-like corpuscles (fig. 15) or connected with them, exhibit a deceptive resemblance with the various types of altered conchiolin, either mingled with the foreign structures in the same contaminated shells (figs. 11, 20, 24 and 25), found in shells apparently free from contaminants (figs. 2, 5, 6, 7, 14, 21), or reproduced experimentally in conchiolin from Recent *Nautilus* (figs. 8, 9, 19, 22 and 23).

The presence of unusually large spheroidal pebbles in the decalcified nacreous samples of the Permian nautiloid *Domatoceras* (figs. 37 38, 39), suggests that some foreign contaminant might be mingled with the remnants of original nacreous conchiolin. However, all transition stages between pebbles of nacreous origin and these spherical corpuscles of large size are clearly visible in figs. 37 and 39. Spore-like spheroids or other doubtful structures were not detected in that material. As the weathered portions of this shell were removed by polishing before decalcification, a contingent contamination could only have been caused by a boring organism, contemporaneous with the burial of the specimen.

Comparison with the data obtained in literature with the electron microscope on fossil algal and fungal structures and on fossil microorganisms (9, 74, 31, 7, 19, 8, 66, 83) did not reveal close resemblance between these structures and the enigmatic elements detected in the contaminated shells of the present material.

Mechanism and nature of structural alterations in fossil nacreous conchiolin.

In contrast with the relatively tough nacreous reticulated sheets of Recent conchiolin, fossil conchiolin is brittle (34, 35). This change in consistency reflects degrees in degradation of original conchiolin protidic components, namely loss of certain amino acids, less stable than others (1, 2, 3), to diagenetic factors such as temperature, whereas in other shells the specific protidic constitution of conchiolin has been retained (53, 22, 45, 20). Considering this fragility of fossil conchiolin, it might be objected that artifacts inherent to each of the procedures of preparation used, and which probably occur in a part of the material, might affect differently ultrastructure of the fragile fossil conchiolin elements. For example, the pebble-shaped bodies contained in aqueous suspensions might result rather from mechanical disintegration after decalcification than from diagenetic processes. On the other hand, networks with short, broad, standlike trabeculae, detected as pseudoreplicas, on the mineral background of etched surfaces of mother-of-pearl polished tangentially (35, fig. 17, and unpublished results), might result in part from artifacts of another kind, such as shrinkage and coalescence of a malleable organic material. However, simultaneous presence in a same preparation of the different types of conchiolin alterations (fig. 14), suggests that the structures obtained by the procedures used are representative of many morphological changes in fossil conchiolin.

Artificial reproduction of several alterations observed in fossil conchiolin by exposure of nacreous shell material from Recent *Nautilus* to diagenetic factors such as temperatures ranging from 150 ° to 800 °C (40, 89, unpublished results), combined in experimental sets with pressure (GRÉGOIRE and LORENT, unpublished), provided information on the probable mechanism of alteration in the reticulated sheets of conchiolin in fossils.

Recent conchiolin is transformed by heat into a fragile substance. Bloating and shrinkage of portions of trabeculae of reticulated sheets, which occur in the material exposed in the open air to 225 °C for 5 hours, are the first signs of alteration. Protracted exposure to this temperature for 21 days or exposure to increased temperatures for 5 hours induced progressively disappearance of the nautiloid pattern by fragmentation of the trabeculae, followed by rounding up and possibly inflation of the debris into spherical or lenticular, pebble-shaped bodies. Detached protuberances might also be involved in the alterations. These modifications, which precede recrystallization of the original aragonite to calcite, resemble those consistently detected in many Paleozoic and Mesozoic shells, illustrated in the present and former papers (35, 32, 43). For example, closely similar pebble-shaped types of alteration in nacreous conchiolin are shown in a Devonian nautiloid (fig. 21) and in fragments of the Recent *Nautilus* shell, heated (fig. 23) and heated under pressure (fig. 22). In experiments still in progress on reactions of *Nautilus* conchiolin heated in vacuum in sealed quartz tubes, or heated under high pressures, such as 60 Kilobars per square cm (GRÉGOIRE and LORENT, unpublished), the third type of alteration observed in fossil shells, especially in Paleozoic specimens, consisting of coalescence of original trabeculae of nacreous conchiolin into membraneous strips, could be reproduced (compare fig. 7, Ordovician *Faberoceras* sp., with fig. 8, mother-of-pearl of Recent *Nautilus* heated under pressure).

These preliminary results of experimental diagenesis suggest that fragmentation, inflation, and coalescence of conchiolin trabeculae took place in fossil shells as in the Recent nacreous fragments exposed to diagenetic factors.

The type of diagram recorded by electron diffraction of the pebble-shaped corpuscles indicated a certain degree of crystallinity. However, as the small areas selected for diffraction contained occasionally microcrystals of minerals such as silica, escaping decalcification, it remains to be determined if mineral is still associated with the biuret-positive substance of these pebbles.

The nature of the lenticular, spheroidal, or hemispheric, vesicle-shaped bodies referred to as knobs in description, and as papillae in former papers (35, 38) and the mechanism of their formation are still unexplained. In the fossil material so far investigated, these bodies were detected in varying amounts in specimens of different ages, and from deposits of wide geographic distribution. As reported above, they were especially numerous among residues of shell decalcification in a Devonian nautiloid, in the Pennsylvanian goniatite *Eoasianites* sp. from Oklahoma, and in several european Carboniferous goniatites.

These knobs might result from three sources : diagenetic alteration of original conchiolin, artifacts of preparation, foreign contamination (see above).

1. Some knobs might reflect diagenetic changes observed in fossil conchiolin, such as inflation and vesiculation of trabecular fragments, and, possibly, hypertrophy of detached protuberances, as previously suggested (43). The knobs illustrated in figures 32, 34, 35 and 36 probably belong to this category. Knobs were produced artificially (fig. 33) by exposing mother-of-pearl of Recent *Nautilus* shells to a temperature of 800 °C for 5 hours.

2. Corpuscles identical to knobs have been illustrated, sometimes without being mentioned, in various materials, such as replicas of photographic grains decomposed by the action of the electron beam (15), replicas of siliceous algal scales (46), replicas of polished and etched transverse sections of prisms in *Ostrea edulis* (38, fig. 36), replicas of surfaces of the innermost nacreous layer in a Jurassic ammonite (*Dactylioceras* sp., 35 : figs. 4 and 5). Their resemblance with crystal seeds surrounded by membraneous material, and developed on nacreous growth surfaces of Recent shells has been noted (35). It has been suggested that these knobs could be artifacts formed by recrystallization during desiccation on the supporting film of dissolved mineral remnants (35). On the basis of recent data on the presence within the nacreous aragonite crystals of an organic matrix separating crystalline subunits in the form of microblocks (WATABE, 77, 78), it might be tentatively suggested that some knobs, at least in the shells having preserved their aragonitic equipment, might result from rounding up after etching of subunit fragments of the original aragonite crystals. These fragments, enclosed in portions of intracrystalline conchiolin interposed in the normal shell between the crystalline subunits, might have escaped, in part, action of the decalcifying agent. Some of these bodies still show blurred polygonal outlines. However, as reported above, electron diffraction diagrams did not reveal conclusively presence of crystalline material within these knobs.

3. The third possible source of knobs, foreign contamination, has been discussed above.

Inner structure of remnants of trabeculae in fossil nacreous conchiolin.

The structural organization of trabeculae in reticulated sheets of nacreous conchiolin is still largely unknown. Association of fibrils with the trabeculae has long been detected with the electron microscope in shells of Recent (42) and of fossil (35, 32) molluscs (1). The presence of these fibrils is frequently indicated by alignments of small tuberosities on trabecular surfaces. Relatively substantial fibrillar material was unmasked after protracted ultrasonic disintegration (37). Successive extractions of watersoluble, protidic, and of scleroprotidic fractions from Recent nacreous conchiolin left bundles of fibrillar material (42). Use of quantitative enzymatic methods for detection of chitin (52) has shown that this fibrillar fraction is a mucoprotidic complex in which fragile polypeptides are combined with more stable polyamino-saccharides (30).

In unstained conchiolin sheets of Recent mollusc shells (see 42 : plate 2, Figs. 1, 2 and 4, in *Nautilus;* plate 6 to 22, in other molluscs), the nacreous trabeculae appear as homogeneous, amorphous or granular material. In some preparations, small, rounded, faintly outlined, darker areas gave these trabeculae a flecked aspect. Similar observations have been made on nacreous matrix of the pearl oyster *Pinctada martensii* (76, 70) and, in the present study, on debris of trabeculae of fossil shells of various ages (figs. 12, 20 and 39).

In former studies, osmium tetroxide, phosphotungstic acid, uranium acetate, at various pH and concentrations, produced an increase in the general contrast of the trabecular substance (see 42 : plate 2, figs. 5 and 6; plate 7 : fig. 2; plate 16 : figs. 2 and 4). Staining revealed only incidentally ill-defined microfibrillar networks inside the trabeculae, as if these elements had been concealed by other substances.

The nature and origin of the microfibrils, mostly located outside trabecular remnants, are still conjectural. As similar structures were found in unstained material, (fig. 41), a contamination of the preparations by infected staining fluids seems to be ruled out. Contamination of the samples by foreign structures contemporaneous of the specimen presents other aspects (figs. 15-18). Incidental occurrence of these extratrabecular fibrils suggests that a part of them might be organic components from layers adjacent to mother-of-pearl, such as the outer porcelaneous layer of the wall. As pointed out elsewhere (39), this layer sends tongue-shaped indentations into the nacreous layer. After cleaning of mother-

(1) Recent material (42, 37) : *Nautilus macromphalus* SOWERBY, *Nautilus pompilius* L. (Cephalopods) : *Astraea, Turbo* (Gastropods); *Brachyodontes bilocularis* L., *Dreissena polymorpha* PALLAS, various *Aetheriidae*, *Hyriopsis schlegeli* VON MARTENS, *Grandidieria burtoni* WOODWARD, *Trigonia lamarckii* REEVE, (Pelecypods).

Fossil material (32, 35) : *Trigonia papillata* AGASSIZ (32 : plate 5, fig. 8), *Trigonia booni* CHAVAN (32 : plate 4, fig. 7), and *Leioceras opalinum* REINEKE (Jurassic); *Nautilus* sp. (Eocene); *Aturia* sp. (Oligocene); *Bolma rugosa* (Pliocene); *Iridina spekii* WOODWARD (Holocene).

of-pearl by polishing off the neighbouring layers, microscopic fragments of indentations might subsist and their organic components, composed of fibrils (39) freed by decalcification, might be mixed with the remnants of trabeculae.

Recent data suggest a layered structure of conchiolin.

In sheets components of intercrystalline and intracrystalline organic matrix in the shell of the Recent *Crassostrea virginica,* composed of calcitostracum, WATABE (78) described recently three elemental layers, illustrated in figures 12 b and 14 of his paper. This arrangement closely resembles that described in nacreous conchiolin matrix preserved on replicas of cross sections of the shell wall in the Pennsylvanian *Pseudorthoceras knoxense* (nautiloid), in *Eoasianites hyattianus* (ammonoid), and shown in figs. 49 and 51 of the present paper.

The triple-layered appearance of conchiolin trabeculae in that material does not seem to be due to an artifact, in which the dense line bisecting several trabecular cords would be a real structure surrounded by contamination layers. It might rather illustrate phase discontinuities in the substance of the trabeculae, and indicate the presence, as in calcitostracum conchiolin, of a layered structure consisting of a core, denser than surrounding coating muffs.

Significance of variations in conchiolin pattern of fossil nautiloids.

In this and former studies (35, 32, 43), the chief characteristics of the nautiloid pattern were recognized in nacreous conchiolin of fossil nautiloids of various ages, especially of those entombed in the Buckhorn asphalt. Slight differences in the conchiolin fabrics, noted between different specimens, concerned size and shape of the trabeculae, variations in number of hemispheric tuberosities protruding on these trabeculae, and form of fenestration. Many more observations are needed before one might conclude that the differences so far recorded in the nacreous pattern of conchiolin in fossil nautiloids possess a taxonomic significance or merely reflect diagenetic variations of an unique pattern, induced by degrees in flattening, shrinkage or conversely stretching, coalescence or dislocation of the trabeculae, reduction in number or disappearance of the tuberosities.

Nacreous conchiolin pattern in ammonites.

A considerable literature has been devoted to the still controversial relationships between nautiloids and ammonites (4). In the present and former studies (35, 32, 43), attempts have been made to establish with the electron microscope the pattern of ammonite conchiolin. The conchiolin pattern of the Jurassic ammonite *Dactylioceras* sp. (34; 35 : fig. 2) resembles that so far detected in nautiloids. On the other hand, in agreement with previous results (43), the present observations have shown that the type of fabric of nacreous conchiolin recorded in several Pennsylvanian specimens of ammonites from Buckhorn asphalt differs by structural peculiarities from that of the nautiloid material from the same deposit, namely by broader and shorter trabeculae, and by a more « dumpy » aspect of the conchiolin fabrics than in nautiloid reticulated sheets (figs. 30 and 32). Inflation of portions of fragmented trabeculae into knobs (fig. 34) or vesicles, frequently of considerable size, was another characteristic of the conchiolin remnants in the Buckhorn asphalt ammonites. Most of the remnants of ammonoid conchiolin from this deposit seemed to be much more altered (figs. 35, 36) than the nautiloid material (figs. 27, 28). The factors responsible for this difference in preservation of shells from two different groups of cephalopods buried and mingled in the same deposit and therefore exposed to identical diagenetic conditions, are unknown.

Splinters from crushed specimens of the same Buckhorn asphalt deposit, too small to be identified as nautiloid or as ammonoid material by means of megascopic criteria, could be determined with the electron microscope as nautiloids, thanks to the characteristic nautiloid pattern of conchiolin (figs. 27, 28).

Variations in alterations of conchiolin ultrastructure in samples from single specimens, or from different specimens of a same genus or species.

Analytical data on specimens of the Cretaceous ammonite *Sphenodiscus* presented by Turekian and Armstrong (73) indicate that a wide range of values for all chemical and mineral parameters exists both for samples from a single specimen and for a large number of specimens of the same genus. No single observation on a fossil shell guarantees uniformity on the original composition of the shell. The results of the authors (73) suggest that the composition of a fossil shell of any age is a complex of alteration products.

From the present and former observations, it seems that the conclusions of Turekian and Armstrong are also valid with regard to the conchiolin components. In the present material, several samples from various regions of nacreous layers of a single or of different specimens of the same species were collected, when possible, for the study of conchiolin and of its topography. As already noted, the various kinds of structures recorded among the remnants of decalcification, such as fragments of trabeculae, pebble-shaped corpuscles, ribbon-shaped fragments or perforated membranes, which represent different stages in conchiolin degradation, coexist frequently in the same region of a sample (fig. 14), or they were observed in different samples of the same genus (35 : figs. 1-6, 8; 32 : Pl. VII, figs. 16-19). Similar associations of alteration structures were recorded in samples of *Nautilus* mother-of-pearl exposed to artificial diagenesis (see fig. 9). Different grades of intensity in the biuret reaction observed in polygonal flakes of interlamellar conchiolin, and presence of dark violet and bright red speckles scattered in the lilac-coloured organic flakes probably indicate local differences in the degree of structural and biochemical alteration of the remnants of original conchiolin. In contaminated shell materials, some of these biuret-positive speckles might be fragments of foreign elements, mingled with conchiolin residues. However, similar structures were also observed in biuret-positive flakes of conchiolin of Recent *Nautilus* altered artificially.

Fossil conchiolin and diagenetic alterations in mineral composition of mother-of-pearl.

A. Shells with preservation or slight alteration of original nacreous aragonite.

In the present material (figs. 49, 50, 51), whole conchiolin systems, including interlamellar, intercrystalline, and intracrystalline sheets, subsist in nacreous layers of Pennsylvanian, nautiloid and ammonoid shells from Buckhorn asphalt, in which aragonite had been integrally preserved or had undergone moderate recrystallization into calcite. The present results extend to nautiloid and ammonoid shells, 300 million years old, the recent findings of WATABE (77, 78) on shells of Recent Pelecypods, concerning the presence of an organic matrix within aragonite crystals as well as around them (33, 78). As reported in description of results, the first stages of alteration in the original brickwall architecture seem to be characterized by soldering of crystalline subunits in successive lamellae. This change, leading to replacement of the horizontal nacreous stratification by a secundary vertical arrangement of prismlike, parallel pillars, disposed at right angle to the original lamellae, might confuse interpretation of the different layers so far described in fossil shell architecture. This problem will be examined in detail elsewhere, in relation to data obtained with the conventional microscope (BØGGILD, 13; HÖLDER, 47).

B. Shells with recrystallization or replacement of original nacreous aragonite.

Former studies with the conventional and polarisation microscopes have shown that the large, coarse crystals of secondary calcite, which replaced aragonite in shell layers, are recognizable from the original aragonite crystals by their fabric and orientation (BØGGILD, 13; BATHURST, 10;

see also LOWENSTAM, 55). In recrystallized shells, HUDSON (48) observed traces of the original growth layers, marked by lines of inclusion passing through the calcite crystals. The new crystal boundaries often follow these layers for part of their length and then cross abruptly to another layer. In HUDSON's material, the replacement of aragonite by calcite was a slow, step-by-step process, preserving delicate traces of the original shell structures. Similar relics of original shell fabrics have been described and illustrated with the conventional microscope by BATHURST (10), who analysed crystallographically the relations between fossil shells and calcite crystals involved in the process of recrystallization. In thin sections of the recrystallized shell of *Faberoceras,* an Ordovician nautiloid (figs. 5, 6, 7, 10, 12), FLOWER (personal communication, 1961) also found traces of the original textures of the shell wall. These findings have been confirmed in the present study with the electron microscope : electron micrographs presented in figures 52 and 53, showing vestiges of original nacreous architecture, illustrate clearly the modifications described by preceding authors with the conventional microscope.

Disappearance of the organic components in fossil shells in which original aragonite has recrystallized into calcite or has been replaced by other minerals has been reported in literature. From the present results, it appears that the conchiolin material is not destroyed by recrystallization into calcite or by replacement, but undergoes a series of modifications in its structure illustrated in the present paper (figs. 4-7, 10, 14, 20, 21, 24, 25, 37-43). Among these modifications, coalescence of reticulated sheets into thin membranes perforated by polygonal holes (figs. 6, 7) seems to occur frequently. The latter modifications of the conchiolin structure are probably closely connected with the crystallographic reorganization of the mineral nacreous components.

CONCLUSIONS.

1. The nautiloid pattern of nacreous conchiolin, though altered, is still recognizable in the 430 million years old Ordovician nautiloid *Isorthoceras sociale* FLOWER (fig. 4). Fine details of mother-of-pearl structure, identical to those existing in Recent mollusc shells, such as constitution of aragonite crystals with crystalline subunits, presence of interlamellar, intercrystalline and intracrystalline sheets of conchiolin, triple-layered ultrastructure of intercrystalline and intracrystalline conchiolin trabeculae, are preserved in 300 million years old Pennsylvanian cephalopod shells from the Buckhorn asphalt. These findings indicate a great stability throughout the ages of the structural pattern of nacreous conchiolin. They suggest that the nacreous architecture of Recent mollusc shells was already established in Ordovician shells. More archaic patterns of shell structure must be searched for earlier in the geologic scale, possibly in the group of Ellesmeroceratida (25, 27) and other Cambrian forms.

2. In many fossil mollusc shells, conchiolin has been considerably altered in its structure. Several kinds of alterations, in the form of discs, lenticular or spheroidal, pebble-shaped bodies, corpuscles in the form of knobs, perforated membranes, have been consistently recorded with the electron microscope in decalcified residues of fossil nacreous substance from shells of different ages. Such remnants were found not only in shells with preserved original nacreous aragonite, but also in shells in which aragonite had recrystallized into calcite or had been replaced by other minerals. Identification of these structures as altered remnants of the original conchiolin networks and discrimination with elements from foreign organisms contaminating the samples have been discussed.

3. Preliminary results based on analysis of 2.700 electron micrographs, from studies in progress (40; 87; GRÉGOIRE and LORENT, unpublished) on experimental diagenesis of the shell of Recent *Nautilus*, in which absence of contamination by foreign elements can be controlled, have been used as an aid for identification of the structures escaping decalcification recorded in fossil mother-of-pearl. These results have so far shown that heat alone in open air, or associated with pressure, produced various stages of ultrastructural degradation of conchiolin, similar or identical on the electron microscope scale to those observed consistently in remnants of decalcification of Paleozoic and Mesozoic nautiloid and ammonoid shells. The implications of these results for the paleontological record will be discussed elsewhere in a detailed study. The experimental conditions of temperature and of pressure that were realized in these investigations were rather crude and simplist. Considering the extreme complexity of the diagenetic processes of the organic (16) and mineral (60, 11) shell components, these conditions did not probably exactly reflect the actual diagenetic circumstances at the time of deposition of the fossil specimens presenting the same structural alterations of their conchiolin. Some of these conditions (for example 800 °C, 60 Kilobars), to which many altered fossil shells were obviously not exposed, are found only in close proximity of the igneous material of the earth crust (12).

4. Contamination by microstructures from unidentified organisms has been observed with the electron microscope among the remnants of decalcification of several shell samples, used immediately after fracture of the embedding sediment. As samples of nacreous substance from Recent *Nautilus* shells, undergoing the same successive steps of preparation as the fossil specimens, never contained such foreign structures, it is suggested that the contaminants were fossil organisms contemporary of the molluscs which they had invaded before entombment in the sediment. Frequent occurrence of contaminants in samples suggests cautious interpretation of results of microbiochemical analysis of protidic structures in random samples, in which possibility of contamination by epizoans, parasites, and especially boring predators, has not been ruled out

by thorough control by means of the electron microscope. The uncertainty of identification with the electron microscope of heterogeneous intermingled structures, proceeding from different sources, has been pointed out. The difficulties are enhanced by the fact that the fossil contaminants were themselves altered by diagenesis.

On the other hand, a systematic study with the electron microscope of structure of epibionts of ultramicroscopical size associated with weathered shell portions, might provide, as the study of much larger other epizoans (67), additional information concerning paleoenvironments.

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SUMMARY.

Remnants of decalcified nacreous layers from Ordovician, Devonian, Carboniferous (including Pennsylvanian), Permian, Jurassic and Cretaceous, nautiloid and ammonoid shells, examined in the electron microscope, consist of various, biuret-positive structures, which reflect degrees in degradation of the original conchiolin sheets. Identification of these structures as altered nacreous conchiolin and discrimination from contaminating structures of foreign organisms, a frequent finding in fossil shells, were based on detection of similar structural modifications in the Recent *Nautilus* shell, in well preserved shells of Pennsylvanian and Mesozoic cephalopods and in alterations produced artificially in experimental diagenesis of the Recent *Nautilus* shell. Nacreous organic remnants subsisted in recrystallized shells. The mechanism of the conchiolin alterations, the significance of variations in the structural patterns of nautiloid conchiolin, the structural pattern of ammonoid nacreous conchiolin, and modifications in configuration of the nacreous layers in shells with preserved original aragonite and in recrystallized shells, have been discussed.

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EXPLANATION OF FIGURES.

Figs. 1-46 illustrate appearance of nacreous conchiolin in the shell of the Recent *Nautilus pompilius* L. (Figs. 1-3), and in remnants of decalcification of the nacreous layers of fossil cephalopods (nautiloids and ammonoids), selected among specimens from various ages and stratigraphic levels : Ordovician (about 425 to 450 million years : Figs. 4-7, 10 and 12), Devonian (about 325 to 350 million years : Figs. 11, 13, 14, 15, 16, 21), Carboniferous, including Pennsylvanian (about 280 to 300 million years : Figs. 17, 18, 20, 24-32, 34-36), Permian (about 230 to 250 million years : Figs. 37-39), Jurassic (about 140 to 160 million years : Figs. 40-43), Cretaceous (about 70 to 100 million years : Figs. 44-46). Figs. 47 to 54 show nacreous architecture in fossil shells with preserved or moderately altered mineral composition (Figs. 47-51) and in fossil shells in which original aragonitic structure of mother-of-pearl has recrystallized into calcite, or has been replaced by other minerals (Figs. 51-54). Reproduction of structural alterations in fossil conchiolin, obtained experimentally by exposing fragments of mother-of-pearl of the Recent *Nautilus* shell to heat and to pressure, is illustrated in Figs. 5, 8, 9, 19, 22, 23 and 33.

Figs. 1, 2, 3.

Nautilus pompilius L. (Recent) (721, 449). Fragments of reticulated sheets of nacreous conchiolin from decalcified nacreous layer of the shell wall in the living chamber. Biuret reaction : pink-violet flakes.

As described previously (41, 42, 39), the nautiloid pattern consists of robust, irregularly cylindrical trabeculae or cords, of variable diameter (30-100 mμ), studded with hemispheric protuberances of various sizes (about 8-35 mμ). The generally elongated openings which separate the trabeculae have irregular outlines. Variations in shape and in size of fenestration depends in part upon degrees in stretching and in spreading of the organic fragments during desiccation on the supporting films. In Fig. 2, mechanical disintegration of trabeculae at the margin of a fragment of reticulated sheet exposed to the ultrasonic waves left clusters of rounded bodies composed in part of tuberosities. Shadowcast with palladium. Fig. 1 : reversed print; × 42.000. Fig. 2 : reversed print : × 50.000. Fig. 3 : direct print, × 42.000. (In this figure, white shadows fill large portions of the openings).

Fig. 4.

Isorthoceras sociale FLOWER (26) [formerly *Dolorthoceras sociale* (HALL) (nautiloid) (357)]. Free and telescoped orthoceracones. Upper Ordovician, Maquoketa Formation, Graf, Iowa, U. S. A. Specimens supplied by Prof. W. M. Furnish and Prof. B. F. Glenister.

The samples are middle and inner portions of the wall, collected from the concave surface of a shell fragment and composed of slate-coloured and highly iridescent, golden-blue sheets and of brown powdery substances. Preservation in this material of coloured powdery films of the original nacreous substance has been reported by TASCH (71). X-ray diffraction analysis revealed in this material a mineral mosaic composed of carbonate apatite, navajoite and calcite (32).

The sediments left by decalcification of this material were placed in contact with Amberlite M B-3 for 30 hours, under intermittent agitation. After this treatment, the residues appeared in the form of transparent brown-yellowish particles and rounded polygonal flakes (see Fig. 10). Biuret reaction : faintly pink-violet shreds.

This electron micrograph shows a fragment of a variously altered reticulated sheet of conchiolin. A parallel array of flattened trabeculae, resulting possibly from accidental stretching on the supporting film, appears in the lower central portion of the fragment. In peripheral parts of this fragment, other trabeculae, partly fragmented into hemispheric or lenticular bodies of various sizes (15 to 63 mμ), delimit a fenestration exhibiting features of the nautiloid pattern (arrow). In some areas (middle right), the fenestration has been obliterated by coalescence of the trabeculae into membrane-shaped structures or by clustering of their pebble-shaped debris. The opaque areas scattered in the fragment consist of thickly agglutinated conchiolin substance made up of the same structures. Shadowcast with palladium. Direct Print : × 42.000.

Figs. 5 and 6.

Faberoceras sp. (nautiloid, Discosorida : 28) (699-2). Upper Ordovician, Leipers beds, Cumberland River Valley, near Rowena, Kentucky, U. S. A. Specimens supplied by Dr. Rousseau H. FLOWER.

The samples consisted of grey-brown and blue-grey dust filed off from the shell wall. Mineral composition : calcite (32).

The sediments left by decalcification of portions of this material were placed in contact with Amberlite M B-3 for 41 hours, under intermittent agitation, and appeared after this treatment as brown-black muds. Ultrasonic waves were applied for a few seconds to a part of this material. Biuret reaction : many homogeneously pink-violet flakes, clusters of dark ruby-red, rounded particles and bright brick-red speckles scattered within yellow flakes (see legend of Fig. 10).

Fig. 5 shows clusters of pebble-shaped, mostly spheroidal bodies of various sizes (40-100 mμ) and debris of short, dumpy, cylindrical trabeculae. Fig. 6 illustrates another type of structure found among the decalcification remains of the same specimen, in the form of membranes perforated by a broad polygonal fenestration, in which the openings, about 0.7 to 1 μ in diameter, are the site of dissolved crystals. Clusters of small granules, 6 mμ-31 mμ in diameter, some with a clear center surrounded by a dark ring (Fig. 6 : centre right) are anchored to a strip of the perforated membrane. Similar bodies are scattered on the thin transparent membrane, through which the background granulations are visible. Shadowcast with palladium. Direct prints. Fig. 5 = × 42.000; Fig. 6 : × 20.500.

Fig. 7.

Faberoceras sp. (nautiloid, Discosorida) (697-1).

This electron micrograph shows remnants of shell wall decalcification in the form of a perforated membrane presenting the same characteristics as those illustrated in Fig. 6. The left portion of the structure consists of a coarse network of broad and flattened trabeculae, which delimit rounded, polygonal openings, and represents an altered nautiloid pattern. The characteristic tuberosities of the *Nautilus* trabeculae (see Figs. 1-3) have disappeared, leaving smooth surfaces. Compare with alterations, illustrated in Figs. 8 and 9, induced experimentally in Recent *Nautilus* conchiolin. Shadowcast with palladium. Direct print : × 46.500.

Fig. 8.

Nautilus pompilius L. (DB 13).

Fragment of mother-of-pearl from the inner layer of the shell wall in the living chamber, immersed in sea water and exposed in a steel vessel to a temperature of 500 °C for 5 minutes under a confining pressure of 60.000 kilogs per sq. cm (GRÉGOIRE and LORENT, unpublished).

Comparison with Figs. 1-3 indicates considerable alteration in the nautiloid pattern of conchiolin : a transparent membrane perforated by irregular holes is shown in the center of the figure. This membrane is connected with other, irregularly shaped, dumpy, membraneous strips protruding above the background. These strips result from coalescence of original trabeculae. Compare with similar alterations recorded in fossil material : Figs. 6 and 7. Shadowed with palladium. Direct print. × 42.000.

Fig. 9.

Nautilus pompilius L. Recent (721-225-21).

Mother-of-pearl from the inner layer of the shell wall in the living chamber, exposed for 21 days to a temperature of 225 °C in open air, in a dry furnace (40). In this sample, the original hard, opalescent, nacreous substance was transformed into a brittle, cleavable and brightly variegated, still aragonitic material, with metallic violet and salmon-colored hues.

This electron micrograph shows pseudoreplicas of an altered reticulated sheet of conchiolin, lying on a positive carbon-palladium replica of a polished and etched surface of a tangential section of the inner nacreous layer. This reticulated sheet of conchiolin, freed by the decalcifier, has been detached from the specimen with the intermediary negative replica and has been transferred as a pseudoreplica to the positive replica. In this reticulated sheet of conchiolin, the alteration in the nautiloid pattern consists of considerable flattening and coalescence of conchiolin into a system of broad membraneous trabeculae on which protuberances have disappeared. In the central portion of this structure, however, the nautiloid pattern is still recognizable, and the trabeculae are fragmented into spheroidal pebble-shaped bodies, measuring 10-50 mμ in diameter. Simultaneous presence of different types of conchiolin alteration in a same specimen, as shown in this artificially altered structure, has been observed in several fossils (see 35 : Figs. 1, 3, 6, 7; 32 : Plate VII, Figs. 16-19, and below, Fig. 14). Direct print : × 33.000.

Figs 10 and 12.

Faberoceras sp. (nautiloid, *Discosorida*), (699-8), Upper Ordovician, Leipers beds, Cumberland River Valley, Kentucky, U. S. A. A third specimen supplied by Dr. Rousseau H. FLOWER.

The sample consisted of grey dust filed from shell wall. Mineral composition : calcite, 32.

The brown mud left by decalcification was exposed for a few seconds to ultrasonic waves. Biuret reaction : many groups of distinctly pink-violet, polygonal flakes, some speckled with bright red spots.

This phase contrast photograph (fig. 10) shows in white and black a cluster of such biuret-positive polygonal flakes, about 27-38 μ in size. Some flakes are still associated in portions of flagging. These flakes are fragments of preserved interlamellar sheets of conchiolin, originally sandwiched in the nacreous layers between the lamellae made up of tabular crystals of aragonite. Portions of pericrystalline conchiolin, which, in shell architecture, coat the tabular facets of the aragonite crystals and which parallel the interlamellar sheets, might also be involved in that cluster. Intercrystaline conchiolin, which delimits the crystals in the lamellae, appears on the picture in the form of straight, black lines, separating the flakes. (× 600.)

The electron micrograph. Fig. 12 represents an unshadowed fragment of membrane identical to those shown in Figs. 6 and 7 on shadowcast preparations. Except for scattered opaque grains and polygonal rounded bodies, probably remnants of microcrystals, the substance of this membrane appears to be amorphous or thinly granular. Fig. 12 : direct print. (× 80.000.)

Figs. 11 and 13.

Unidentified nautiloid of large size, with gyroconic conch (diameter of the outer whorl : 21 cm; diameter of the adoral portion of the shell : 6 cm) (713), Middle Devonian, Couvinian, Dinant area, Belgium. Specimen supplied by Dr. J. BOUCKAERT.

The samples consisted of substance from the coal-black, 1-2 mm thick, inner portion of the shell wall from the outer whorl. Mineral composition : predominance of calcite (32).

Decalcification left a black mud. Biuret reaction : pink-violet and yellow flakes speckled with bright red or dark ruby-red particles (see legend of Fig. 10). X-ray powder diffraction analysis of this mud revealed presence of traces of silica.

Figs. 11 and 13 are two representative pictures of the structures found among the remnants of decalcification of ten samples from different parts of the shell wall of this specimen. The samples contained clusters of pebble-shaped, irregularly spheroidal bodies, consistently found in fossil conchiolin remnants of all ages (Fig. 11), and other spheroidal elements encircled by a turban-like ring, more opaque than the center. The cluster shown in Fig. 13 consists predominantly of tightly agglomerated similar tiny elements (22-88 mμ in size), referred to as knobs in description. Palladium shadowcast. Fig. 11 : direct print. Fig. 13 : reversed print. (× 31.000.)

Fig. 14.

Rutoceratidae sp. (54) (nautiloid). A 60 mm long, strongly curved segment of a gyrocone or cyrtocone, 3 cm in diameter, showing signs of multiple fractures and displacements of wall and septa (685-2), Upper Middle Devonian (Givetian), Sötenicher Mulde, Sötenich, Eifel, Germany.

The samples consisted of fragments of the dark-brown or coal-black, inner nacreous region of the 1-6 mm thick, recrystallized shell wall. Mineral composition : calcite, 32.

Abundant residues of decalcification in the form of a brown sediment containing many shreds. Biuret reaction : pink flakes and red particles (see legend of fig. 10).

The different types of structures listed in description : spheroidal pebble-shaped bodies (p), knobs (k), fragments of reticulated sheets with debris of flattened, smooth trabeculae deprived of their tuberosities (r s), perforated membranes (m) are assembled in this preparation. The nautiloid pattern is recognizable in portions of the material (r s). Palladium shadowed. Direct print. (× 42.000.)

Figs. 15 and 16.

Unidentified nautiloid of large size with evolute conch, Middle Devonian (Couvinian), Dinant area, Belgium (see Figs. 11 and 13).

In Fig. 15, an irregularly spheroidal corpuscle, about 340 mμ in size, seems to discharge small granular rounded bodies, 20-50 mμ in diameter, and larger, about 70 mμ in diameter, spheroidal, oval and pear-shaped elements. Fig. 16 shows a cluster of similar small bodies. These bodies are difficult to distinguish from true remnants of altered fossil conchiolin (Fig. 20) and from those obtained artificially from Recent *Nautilus* conchiolin in experimental diagenesis (Fig. 19). Unshadowed preparation : × 100.000.

Figs. 17, 18 and 20.

Hudsonoceras proteum (BROWN) (goniatite) (664-6), Upper Carboniferous, Coolagh River, Lisdoonvarna, Co Clare, Ireland. Specimen supplied by Dr. J. BOUCKAERT.

The samples consisted of debris of the 0.2 to 0.4 mm thick, brown to coal-black, recrystallized shell wall. Mineral composition : calcite (32). Fracture of the rock embedding this shell revealed the presence on the outer shell surface of a network of mahogany-brown filaments, obviously proceeding from a contaminating foreign structure, probably contemporaneous to the specimen (see discussion). The shell was cleaned from this material before being decalcified. The residues of decalcification consisted of biuret-positive (pink-violet) clusters of polygonal flakes, mingled with biuret-negative, yellow-stained, large spore-shaped bodies (not shown). Contamination of the sample, probably by a boring (algal ?) organism was confirmed in electron micrographs by the presence of composite structures, such as those illustrated in Figs. 17 and 18. These structures were mingled with clusters of the small pebble-shaped bodies, 20-25 mμ in size, appearing as granular vesicles in unshadowed preparations, and which characterize the organic remnants of fossil nacreous conchiolin (Fig. 20). The suspected contaminating elements consist of entangled, twisted, elongated, flattened, sturdy ribbons and strands, with expansions in the form of irregular cords ending in buds (Fig. 18, upper right) and closely associated with spheroidal or oval structures (Figs. 17 and 18). As in the Devonian material shown in Fig. 15, all these structures were frequently attached to large (1.1 to 1.4 μ in size), oval, spore-shaped corpuscles. In Fig. 18 (as in Fig. 15), grey layers which coat the structures are carbonaceous deposits developed under the electron beam. Unshadowed material. Fig. 17 : 56.000; Fig. 18 : × 112.000; Fig. 20 : × 80.000.

Fig. 19.

Nautilus pompilius L. Recent.

Mother-of-pearl from the inner layer of the shell wall in the living chamber, exposed in open air in a dry furnace to a temperature of 500 °C for 5 hours (40). Heating transformed the iridescent nacreous substance into a chalky, grey-white, lustreless, brittle, calcitic (32) substance. Decalcification of this material left a sediment composed of a brown-black mud. The biuret reaction applied on this sediment showed, as in fossil material (see Fig. 10), clusters of pink-violet polygonal flakes, some speckled with bright red, rounded particles.

The residues of decalcification of this material, stained with a 3 percent solution of P. T. A. (pH 6.0) and examined in the electron microscope, consisted of dense clusters of spheroidal, pebble-shaped, granular bodies, about 20-27 mμ in size, closely resembling those of about the same size (20-25 mμ) recorded in fossil material and illustrated in Fig. 20. Unshadowed material. (× 102.000.)

Fig. 21.

Striacoceras typus (SAEMANN). (FLOWER, 23). (nautiloid). (703-1), Middle Devonian, Cherry Valley limestone, Stockbridge Falls, New York, U. S. A. Specimen supplied by Dr. Rousseau H. FLOWER.

The sample used was a fragment of the 1 mm thick, coal-black shell wall. Mineral composition : calcite (32).

The brown-black remnants of decalcification were placed for 41 hours in contact with Amberlite M B-3 under intermittent agitation. Biuret reaction : pink-violet flakes and free granules, ring- and comma-shaped, unidentified, violet to ruby-red particles (see Fig. 10).

This electron micrograph shows a large cluster of agglomerated small particles. A few fragments of trabeculae are visible (center). Compare with similar alterations produced artificially in the Recent *Nautilus* shell : Figs. 22 and 23. Palladium shadowcast. Direct print. (× 42.000.)

Fig. 22.

Nautilus pompilius L. Recent (DB 10).

Fragment of mother-of-pearl from the inner layer of the shell wall in the living chamber, immersed in wet sea mud and exposed in a steel vessel to a temperature of 200 °C for 30 minutes under a confining pressure of 7.500 kilogs per square cm.

As shown in this electron micrograph of the decalcified material (compare with Figs. 1-3), the conchiolin alterations consist of fragmentation of the trabeculae into spheroidal bodies similar to those found in many fossil preparations (see Fig. 21). Debris of less disintegrated trabeculae appear scattered among the debris (upper right). Palladium shadowed. Direct print. (× 42.000.)

Fig. 23.

Nautilus pompilius L. Recent. (721-275-2).

Fragment of mother-of-pearl from the inner layer of the shell wall in the living chamber, exposed in open air in a dry furnace to a temperature of 275 °C for 5 hours (40). The nacreous material was dissociated in part into very brittle brown mineral sheets, with metallic silvery, red and green hues. Mineral composition : aragonite (32).

Decalcification left rust-coloured material, which was exposed to the ultrasonic waves for 6 minutes. Biuret reaction : many pink-violet flakes, some speckled with bright red elements. Other flakes appeared yellow with red and violet spots.

This electron micrograph shows a dense cluster of spheroidal bodies and particles of various sizes (9-100 mμ in diameter), which result from fragmentation of conchiolin trabeculae (compare with Fig. 21). Palladium shadowed. Direct print. (× 42.000.)

Fig. 24.

Beyrichoceratoides sp. (goniatite). (662), Lower Carboniferous, Cot Castle shell Bed, 263 feet in n° 1 Bore Baads Mine, Scotland. Specimen supplied by Dr. R. B. WILSON (H. M. Geological Survey : M 2135 L).

Brittle, pink-white fragments of the shell wall. Mineral composition of the sample : aragonite (44, 32).

After decalcification, the residues, consisting of a few glistening rigid flakes, were exposed for 92 hours to Amberlite MB-3 under intermittent agitation. Biuret reaction : very pale pink flakes (see legend of Fig. 10).

In the electron microscope, the remnants consisted of fragments of membranes (not shown) and of agglutinated small pebble-shaped bodies, illustrated in this figure. Palladium shadowed. Direct print : × 52.000.

Figs. 25 and 26.

Homoceras beyrichianum (DE KONINCK). (goniatite). (668 : 34 specimens used). Upper Carboniferous, Etage de Chokier-Flémalle, Belgium. Specimens supplied by Dr. J. BOUCKAERT.

The samples consisted of brown debris of the shell wall. Mineral composition : Calcite (32).

Decalcification left grey-black sediments. Biuret reaction : pink-violet flakes, some of them marbled with darker, bright red speckles.

Among the structures found in these remnants were clusters of spheroidal, pebble-shaped bodies, generally of small size (Fig. 25), mingled (in Fig. 26) with structures referred to as knobs in description. The size of the knobs varies between 40 mμ and 230 mμ. Two oval bodies still reach a greater size. These enigmatic structures appear in the picture as granular vesicles encircled by a relatively opaque ring-shaped membrane. Palladium shadowed. Reversed prints. (Fig. 25 : × 42.000. Fig. 26 : × 52.000).

Figs. 27 and 28.

The specimen was a curved, dark-brown, iridescent flake, with green hues, of a crushed cephalopod shell, either a nautiloid or an ammonoid (749), Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Dr. C. C. BRANSON.

Decalcification left abundant brown shreds. Biuret reaction : pink-violet and brick-red flakes.

In this well preserved conchiolin sheet (compare with Figs. 1-3), the nautiloid pattern has been only slightly altered. In Fig. 27, some degree of coalescence and of flattening of the trabeculae is visible, especially in the left portion of the picture. Some hemispheric tuberosities are scattered on the trabecular surfaces. In Fig. 28, shrinkage and shortening of the trabeculae took place along their length. Slight variations in the fabric of the nautiloid pattern, as they appear in Figs. 27 and 28, might be due either to local differences in the diagenetic processes, or to small differences in desiccation conditions to which the fragile structures were exposed on the supporting films. Fig. 27 : platinum shadowed, × 42.000; Fig. 28 : palladium shadowed, × 42.000.

Fig. 29.

Dark brown, iridescent, dome-shaped septum of an unidentified nautiloid shell (751). Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Dr. C. C. BRANSON.

In this fragment of conchiolin, the texture of the septal reticulated sheets is tighter, the trabeculae are more slender than those from shell walls shown in Figs. 27 and 28. Comparison of these three pictures indicates that differences recorded previously in the shell of the Recent *Nautilus* between mural and septal nautiloid patterns (39) appear also in well preserved fossil material. Palladium shadowed. (× 42.000.)

Fig. 30.

Iridescent, brown-violet shell splinter of an unidentified ammonite (421-26-3). Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. F. G. Stehli.

Decalcification of the inner layer of the shell wall left soft brown shreds. Biuret reaction : faintly violet flakes and clustered red particles (see legend of Fig. 10).

This electron micrograph shows a coarse, lace-like network of conchiolin, which differs from the texture of the nautiloid pattern by several peculiarities, namely by shorter, dumpier and thicker trabeculae, and by an irregularly polygonal fenestration. Palladium shadowed. (× 42.000.)

Fig. 31.

Unidentified ammonite (755). Pennsylvanian, Buckhorn asphalt, Oklahoma. Specimen supplied by Dr. C. C. Branson (Oklahoma, G. S. 3768). Septal material (saddles and lobes).

Shreds left by decalcification were biuret-positive (many pink flakes and red-violet particles : see legend of Fig. 10).

This well preserved reticulated sheet of septal conchiolin has a more slender texture than that of the shell wall, illustrated in Figs. 30 and 32. This finding indicates that the structural differences between mural and septal conchiolin, first observed in the shell of the Recent *Nautilus* (39), in fossil nautiloids (see Figs. 27 and 29), existed also in ammonites. Palladium shadowed. (× 42.000.)

Figs. 32 and 34.

Curved fragments of whorl of an unidentified ammonite (421-47, 421-37). Pennsylvanian. Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. F. G. Stehli.

Decalcification of the inner layer of the shell wall left biuret-positive shreds (pale pink flakes and brick-red particles : see legend of Fig. 10). In Fig. 32, alteration in trabeculae of a conchiolin reticulated sheet consists of flattening (centre), beginning of fragmentation into lenticular bodies (right), inflation and coalescence (left). Fig. 34 shows a knob, about 700 mμ in diameter, which consists of a spherical, central corpuscle, partly wrapped in a circular membrane. Similar structures, some of considerable size (3 μ), characterize several organic remnants of ammonitic shells in the Buckhorn asphalt material (see Fig. 36 and discussion). Knobs were reproduced artificially (see Fig. 33). Palladium shadowed. Fig. 32 : × 20.500; Fig. 34 : × 42.000.

Fig. 33.

Nautilus pompilius L. Recent. (721-800-5).

Fragment of mother-of-pearl of the inner layer of shell wall in the living chamber, exposed in open air in a dry furnace for 4 hours to a temperature of 800 °C. After this treatment, the nacreous material appeared to be cleaved in many extremely brittle sheets, composed of a snow-white and powdery substance. The mineral components of the samples, identified by X-ray diffraction analysis as Ca(OH)2 (see 40), could not be dissolved by chelation, but only in a 25 per cent solution of hydrochloric acid.

The scarce residues of decalcification consisted of a few grey shreds. Biuret reaction : clusters of faintly pink flakes.

Among the various structures detected in the remnants of decalcification, this ovoid knob, measuring about 800 mμ, consists, as the fossil structure shown in Fig. 34, of a dome-shaped central elevation encircled by a ring-like membrane. Palladium shadowed. (× 33.000.)

Fig. 35.

Eoasianites hyattianus (Girty). (Goniatite). (676-7).

Lower Middle Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. W. M. Furnish and Prof. B. F. Glenister (State University of Iowa, Fig. spm. 8, 888).

The sample was a 3-5 mm thick flake, composed of bronze-coloured layers of nacreous substance, with irregular interposition of presumably altered powdery white matter.

Before decalcification, the sample was immersed for five days in pyridine, in order to remove oil, impregnating the specimens entombed in Buckhorn asphalt. (Prof. Stehli :

personal communication). This treatment did not modify the organic structures, as shown by comparison with untreated samples of the same specimens. The soft brown shreds left by decalcification of the shell wall were biuret-positive (pink-violet flakes and ruby-red grains, or violet grains embedded in a transparent jelly).

These remnants of conchiolin reticulated sheets are composed of pebble-shaped, irregularly spheroidal particles, mingled with fragments of sturdy trabeculae such as those illustrated in Fig. 32. In areas protected from impact of the metal used for shadowing (bottom left), the pebbles appear to be composed of an amorphous or thinly granular material. Identical alterations in conchiolin texture were recorded in other samples of the same specimen (see 43 : Plate XI, Fig. 1). Palladium shadowed. (× 42.000.)

Fig. 36.

Shell wall of an unidentified ammonite from the same deposit as in Fig. 35.

This electron micrograph shows, in the form of spheroidal knobs, a typical alteration observed in conchiolin of many ammonitic shell samples from Buckhorn asphalt. In this preparation, the knobs, more than a hundred in number, appear to be inflated portions of agglutinated conchiolin trabeculae. Note (bottom center) a fragment of conchiolin reticulated sheet in which the nautiloid pattern in recognizable, in spite of considerable flattening of the trabeculae. Palladium shadowed. (× 25.000.)

Figs. 37, 38 and 39.

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

The samples were fragments of the shell wall (calcite, 32) and consisted of 1-6 mm thick, coarsely recrystallized, brown slabs. The substance used for decalcification was collected by filing or by fracture of different regions of the slabs, including innermost portions, cleaned by polishing off all possibly contaminated surfaces. The residues of decalcification were composed of abundant biuret-positive shreds (many violet and pink flakes mixed with red particles).

The structures consistently detected with the electron microscope in all the residues of this specimen were clustered, spheroidal and lenticular corpuscles, measuring from 12 mμ to 180/200 mμ (Fig. 37), fragments of networks composed of smooth, ribbon-like trabeculae, delimiting an irregularly polygonal fenestration (Fig. 38), and knobs (Fig. 39). In unshadowed preparations, all these structures seemed to be composed of an amorphous substance (Fig. 39). Alignements in chains of spheroidal pebble-shaped bodies, shown in several areas of Fig. 37, suggest that these structures result probably from dislocation of trabeculae, followed by rounding up of the fragments. Figs. 37 and 38 : Palladium shadowed, reversed prints. Fig. 37 : 42.000; Fig. 38 : × 33.300.

Fig. 39 : unshadowed, × 88.000.

Figs. 40, 41, 42, 43.

Harpoceras mulgravium SIMPSON, YOUNG and BIRD (ammonite) (524). Lower Jurassic, *Falciferum* subzone, Whitby, Yorkshire, England. Honey-brown, recrystallized substance of the shell wall. Mineral composition : calcite (32).

The samples consisted of portions of the outer part (Figs. 40 and 43) and of the inner part of the nacreous layers of the shell wall (Figs. 41 and 42), separated from each other by a pyritized golden-coloured layer. Decalcification left biuret-positive shreds (pink-violet flakes and pink dots in a colourless jelly).

As shown in Figs. 40 and 41, the debris left by decalcification consisted of discs, of scattered or of clustered spheroidal or lenticular bodies, mingled with abundant, smooth, flattened and twisted fragments of trabeculae ,remnants of a reticulated sheet. Typical knobs appear at the extreme top right and bottom left of Fig. 40. Bundles of fibrils shown in Fig. 41 could not be identified. In the Recent *Nautilus* shell, similar fibrils characterize ultrastructure of porcelaneous substance (39). In this sample, small portions of the outer layer were possibly mixed with the nacreous substance. Debris of trabeculae, stained with PTA, reveal delicate networks of unknown nature (Fig. 42). Such structures were absent in the spheroidal corpuscles and in other trabeculae, which appeared amorphous or thinly granular (Fig. 43). Figs. 40 and 41 : direct prints : × 42.000; Fig. 42 : × 128.000; Fig. 43 : × 160.000.

Figs. 44, 45 and 46.

Baculites sp. (ammonite) (395). Cretaceous (Senonian), Ripley formation, Coon Creek, Tennessee, U. S. A. The specimen, supplied by Dr. Arthur G. COOPER, was a chalky, strongly iridescent fragment of an orthocone with bright metallic hues. Mineral composition : aragonite (32).

The samples were residues of decalcification of the inner nacreous portions of the shell wall. Biuret reaction : pink flakes and brick-red grains.

Fig. 44 shows broad fragments of interlamellar conchiolin. In the central portions of these fragments, coalescence obliterated fenestration and inverted the original reticulated sheets of conchiolin into membranes. Presence of ridges protruding on the membranes and delimiting polygonal areas identifies unequivocally these membranes as organic nacreous material. These ridges are remnants of former intercrystalline conchiolin which originally separated the polygonal tabular crystals of aragonite disposed in a single flagging in each nacreous lamella. At the margins of these membranes, spheroidal bodies result from fragmentation of trabeculae. In Fig. 45, representing PTA (0.1 per cent solution, pH 5.4) stained conchiolin material from the same sample, networks of a dark substance appear inside thin fragments of conchiolin sheets superimposed on thicker portions of an amorphous material. This dark substance is absent on the supporting film outside the conchiolin structures. In negatively stained preparations, no particular organization could be detected in the conchiolin fragments (Fig. 46). Fig. 44 : palladium shadowed. Direct print : × 33.000; Fig. 45 : × 112.000; Fig. 46 : × 108.000.

Fig. 47.

Unidentified ammonite (421-39). Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. F. G. STEHLI.

Positive carbon replica, shadowcast with palladium, of a polished and etched transverse section of the inner nacreous layer of the shell wall. Eight nacreous lamellae are shown. The thickness of their crystals varies between 0,46 and 0,63 μ. Columnar stacking of the crystals with their margins coinciding in successive lamellae is visible on the right portion of the figure (arrow). Interlamellar conchiolin matrix (ilm), intercrystalline and intracrystalline conchiolin matrices (icm) appear in the form of grey-black, horizontal and vertical shreds respectively. Parallel vertical furrows, partly filled with these shreds, and shown across the thickness of the crystals, separate crystalline subunits, appearing in the form of parallel microblocks resembling those described by WATABE (78 : Fig. 5 A) in the nacreous substance of *Elliptio complanatus* (Recent pelecypod). Moderate alteration in configuration of mother-of-pearl consists of scattered coalescence of crystalline subunits across several crystals belonging to successive lamellae. This alteration results in disappearance of portions of the interlamellar spaces, and gives the surface a streaming appearance disposed at right angle to nacreous stratification. Streaming or washed out aspects are common artifacts of replication methods, especially when etchants are applied on greasy or oily surfaces. In the present material, such artifacts might be caused by oil soaking the Buckhorn asphalt specimens. However, such artifacts are characterized in the electron microscope by random distribution of the surfaces on which the etchant did not take. (× 25.000.)

Fig. 48.

Pseudorthoceras knoxense MCCHESNEY (nautiloid) (421-33). Upper Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. F. G. STEHLI.

Positive carbon replica, shadowcast with palladium, of a polished and etched transverse section of the shell wall. Alteration in nacreous configuration consists (left part of the figure) of coalescence of two and more crystals belonging to successive lamellae. The fragments of interlamellar (ilm), intercrystalline and intracrystalline (icm) conchiolin appear in the form of undulating black lines. Note (extreme bottom right) the presence in the interlamellar space of fragments of three conchiolin sheets, composed probably of an interlamellar sheet sandwiched between two pericrystalline sheets, the latter wrapping the tabular faces of the adjacent crystals (see also Fig. 51, bottom). (× 25.000.)

Figs. 49 and 51.

Eoasianites sp. (goniatite) (358), Lower Middle Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. W. M. FURNISH and Prof. B. F. GLENISTER.

Positive carbon replica, shadowcast with palladium, of a polished and etched transverse section of a bronze-coloured, 1-5 mm thick slab, splinter of fracture from the shell wall, and including nacreous layers.

Figs. 49 and 51 illustrate the topography and the inner structure of nacreous conchiolin systems in pits of microfracture, where interlamellar ,intercrystallinic and intracrystallinic sheets appear as grey-black cords in transverse projection. These cords, freed from the mineral background by the etching process, were detached and transferred as pseudoreplicas from the first-negative-replica to the positive replica, and were protected from the impact of the shadowing metal by interposed protruding structures. In several areas, especially in the rectangular pit shown in central portion of Fig. 49, and in Fig. 51 (bottom), three fragments of parallel sheets appear in the interlamellar space (il). These fragments seem to bend at right angle into intercrystallinic and intracrystallinic sheets, or to be crossed by similar elements. The triple-layered structure of the latter components (arrows) consists of a central, 4-5 mμ thick, dense, threadlike core, sandwiched between two, 8-10 mμ thick, less opaque strands of substance. The three pictures of Fig. 51 illustrate these details of structure (arrows) at higher magnification. Direct prints. Fig. 49 : × 50.000; Fig. 51 : × 80.000.

Fig. 50.

Pseudorthoceras knoxense Mc CHESNEY (nautiloid). (530-35). Upper Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma. Specimen supplied by Prof. A. G. FISCHER.

Positive carbon replica, shadowcast with palladium, of a polished and etched transverse section of the nacreous layer in a septum. Etching revealed, in ten successive nacreous lamellae disposed vertically in the picture, preservation of a whole system of conchiolin, in the form of white cords (pseudoreplicas, see legend of Figs. 49 and 51). In the figure, the cords are arranged as the uprights and rungs of parallel ladders. The conchiolin system includes interlamellar and pericrystalline cords, soldered together in this preparation (vertical cords), intercrystallinic and intracrystallinic cords (horizontal short cords, undistinguishable from each other in this picture). The rectangular areas formed by intersection of vertical and of horizontal cords were occupied before etching by subunits of aragonite crystals (microblocks : see Fig. 47). The outlines of whole crystals appear at the upper part of the picture (arrow). Pits, in which conchiolin cords form loops frequently disposed concentrically (bottom right), are randomly scattered among the other structures. Reversed print. (× 42.000.)

Figs. 52, 53 and 54.

Isorthoceras sociale FLOWER (nautiloid) (357-C: 357-B 12). Upper Ordovician, Maquoketa Formation, Graf, Iowa. Specimen supplied by Prof. W. M. FURNISH and Prof. B. F. GLENISTER.

Figs. 52 and 53.

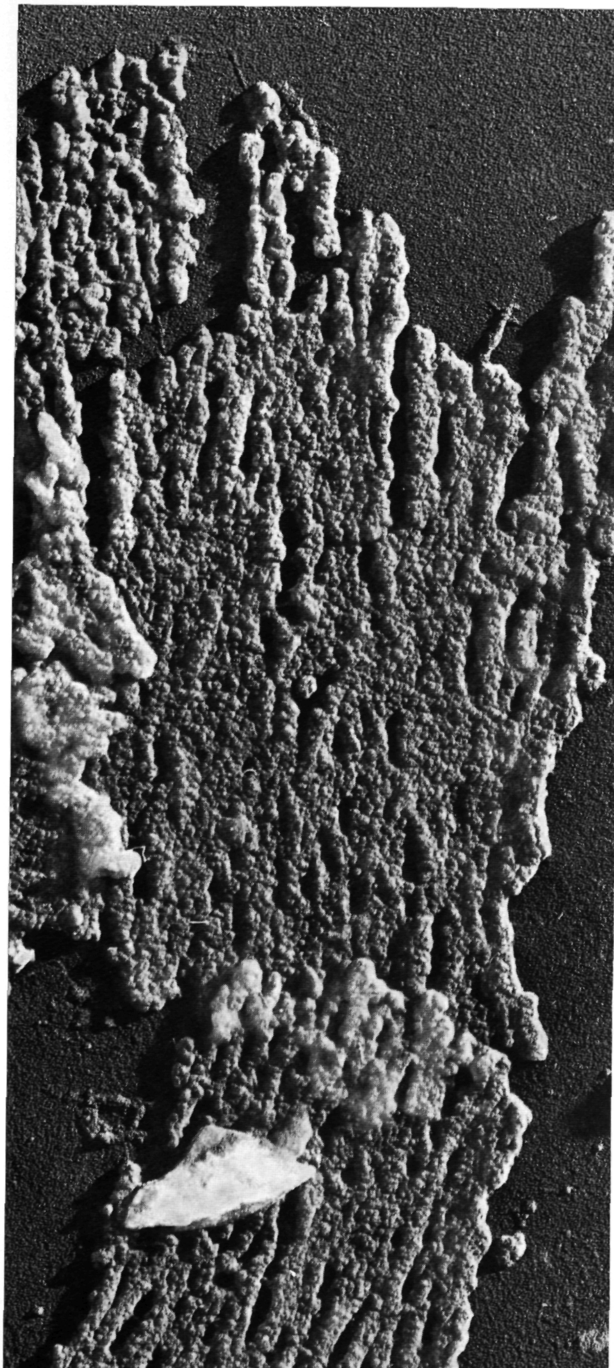
Positive carbon replica, shadowcast with palladium, of a polished and etched transverse section of the inner nacreous layer of the shell wall. The sample was collected in portions of the shell having undergone recrystallization and replacement of aragonite by other minerals, including dahlite and SiO2 (32).

Traces of original lamellar stratification and of interlamellar and intercrystalline conchiolin systems appear in the form of irregularly parallel arrays of straight, broken, elongated strands (white in reversed print : Fig. 52; black in direct print : Fig. 53). In Fig. 52 (center) the conchiolin remnants appear to be located in the former interlamellar spaces as pairs of parallel filamentous and membraneous structures, which delimit elongated, 80-120 mμ wide areas filled with mineral substance. The straight strands end abruptly against mineral blocks. The original parallel orientation of a part of the interlamellar spaces has been slightly altered. This alteration is especially distinct in central portion of Fig. 53, where two interlamellar spaces have been displaced and form an acute angle with the neighbouring interlamellar space. Columnar stacking of crystals, with coincidence of their margins, is shown in the right bottom part of Fig. 53, where the traces of 6 superimposed crystals with their intercrystalline conchiolin sheets (black filaments) are still apparent.

The direction of the crystalline subunits of the mineral replacing aragonite in the lamellae is indicated by orientation of shadows in parallel grooves which intersect the conchiolin interlamellar systems at angles varying between 35° and 55°. Fig. 52 : reversed print, × 25.000; Fig. 53 : direct print, × 16.000.

Fig. 54.

Positive carbon replica, shadowcast with palladium, of the iridescent, golden-coloured surface of a concave region of cleavage in the inner nacreous layer of the shell wall, in which X-ray powder diffraction analysis had revealed replacement of aragonite by *carbonate apatite* (32). *Fig. 54 shows about four superimposed and interlocked arrays* in form of discs composed of radially oriented, imbricated, elongated tablets. In this preparation, disappearance of the original nacreous topography does not permit to identify conclusively the nature of the filaments which encircle the wheel-shaped discs. These filaments might be replicas either of remains of original conchiolin or of cracks in the surfaces, a common artifact of replication methods. However, as the fragments of reticulated sheets shown in Fig. 4 were obtained from shell material which had undergone the modifications illustrated in Figs. 52-54, these filamentous structures are probably replicas of true conchiolin remains displaced by mineral reorganization. Reversed print, × 22.000.



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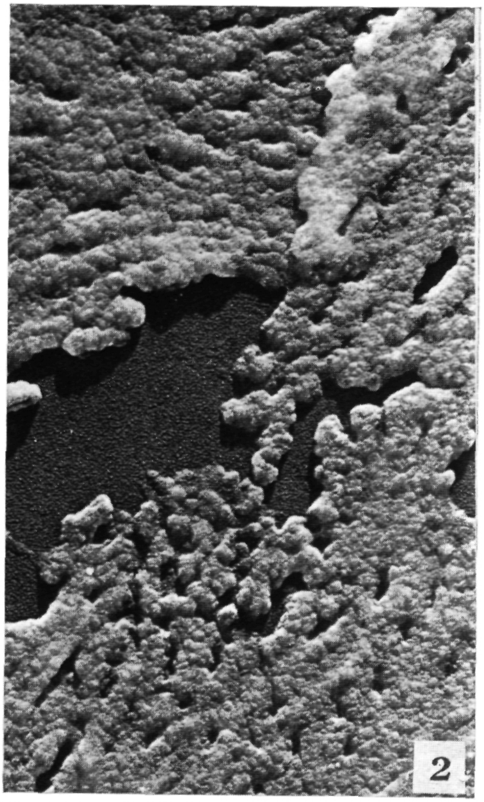

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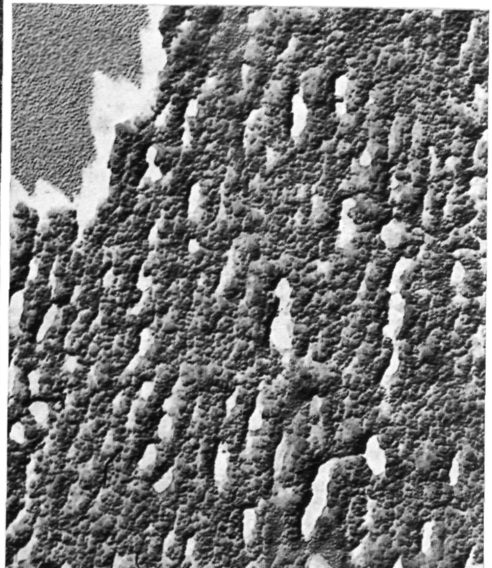

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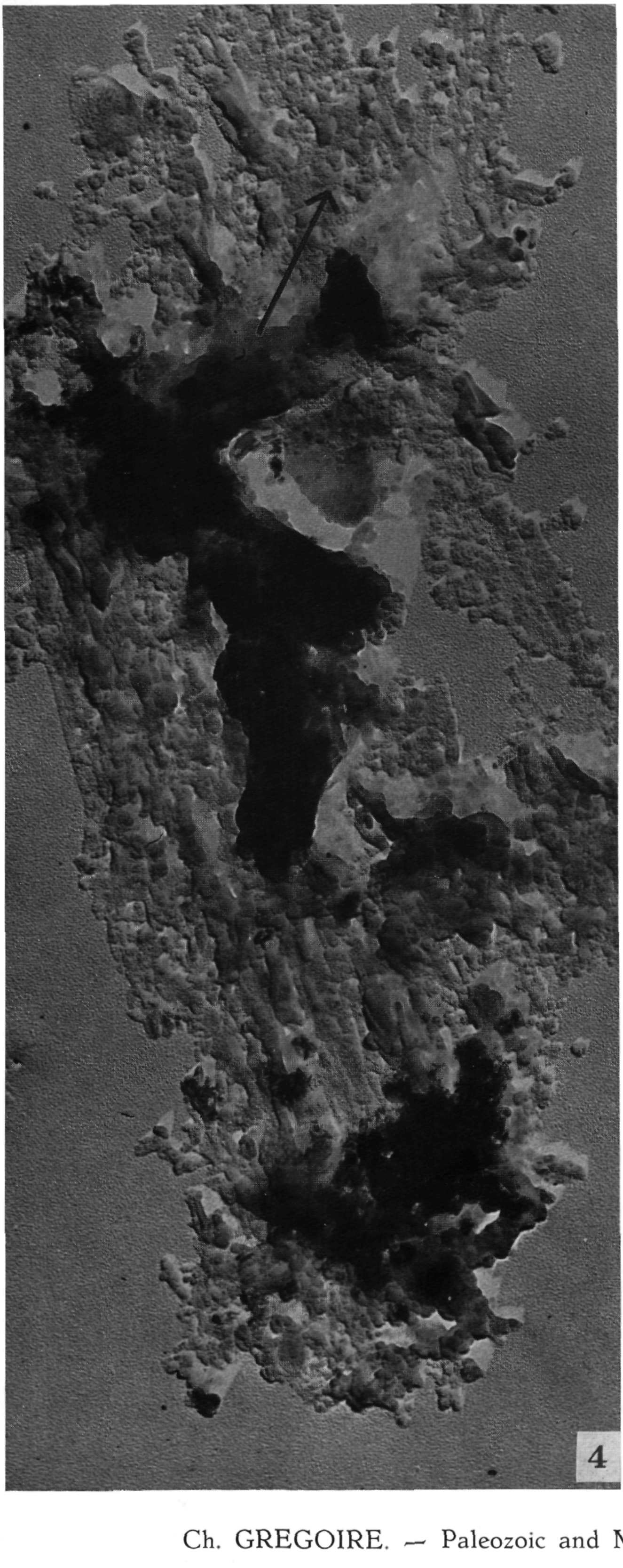
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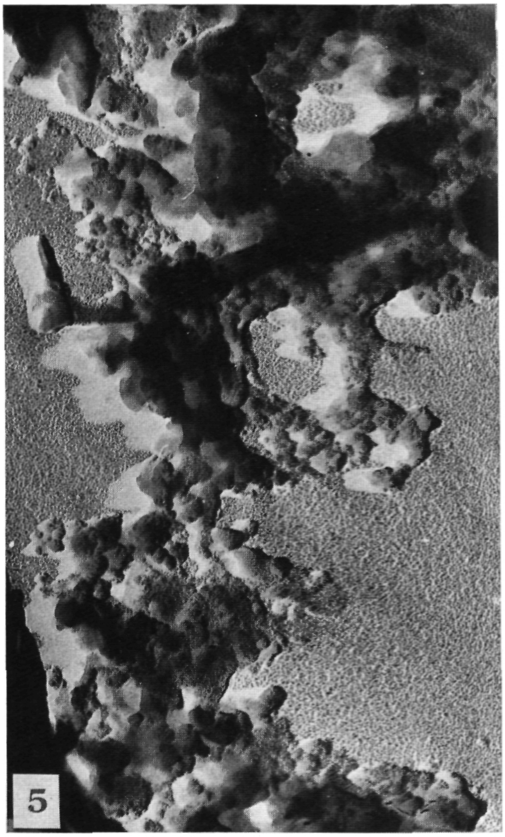
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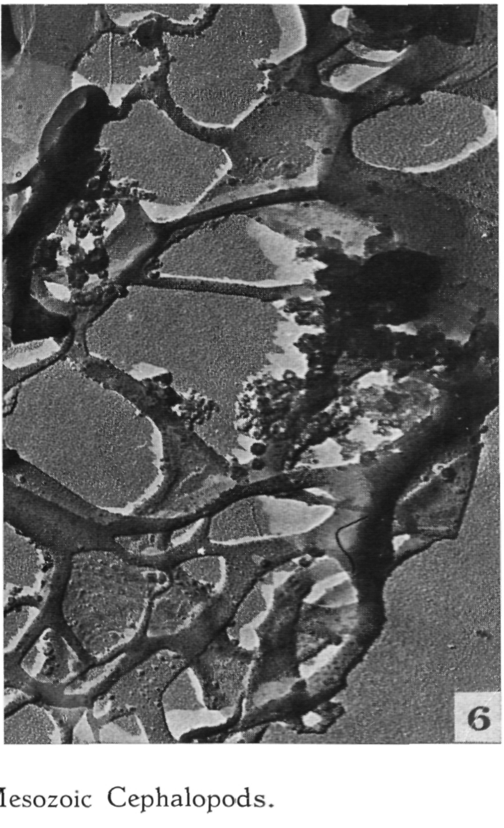
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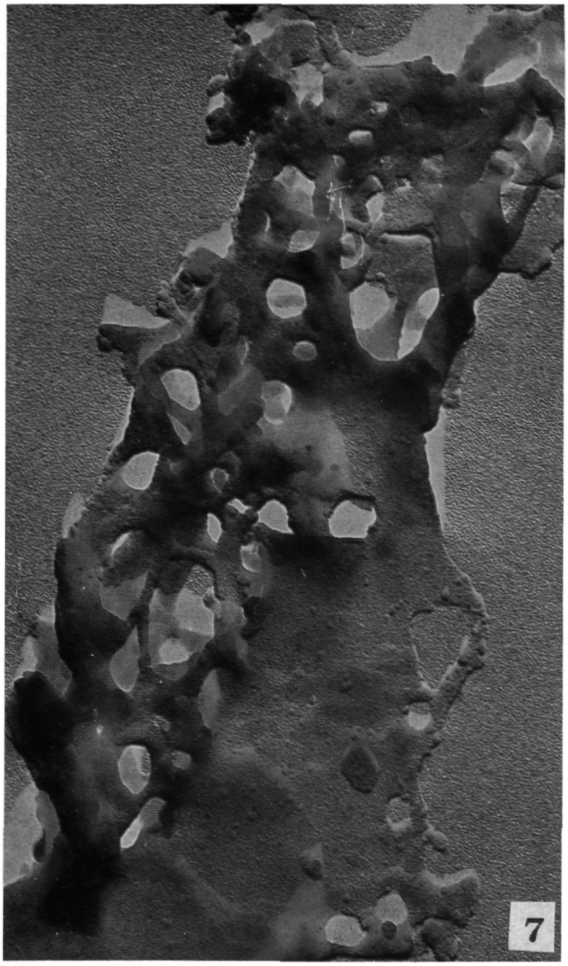

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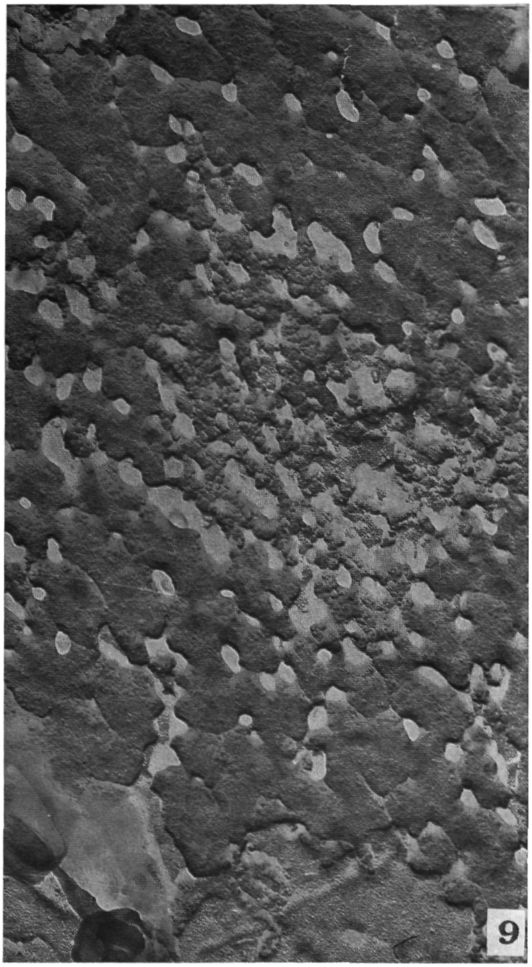

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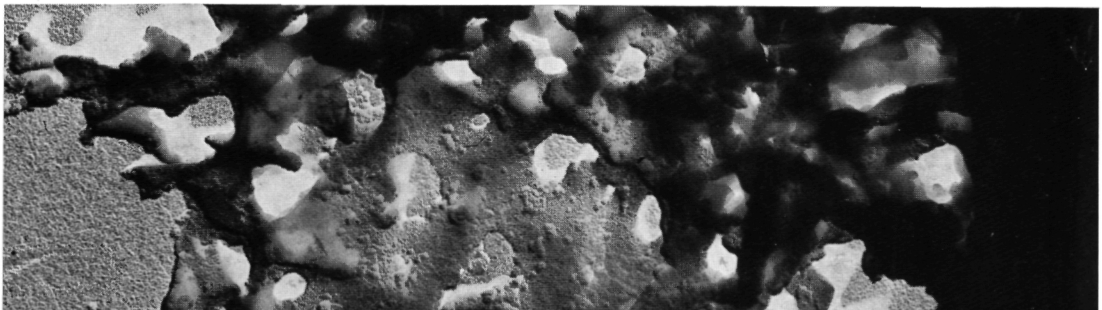

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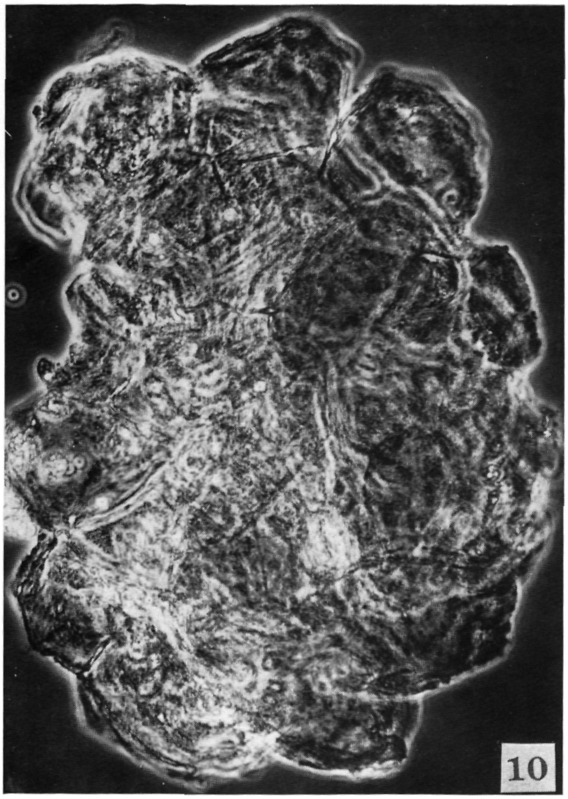
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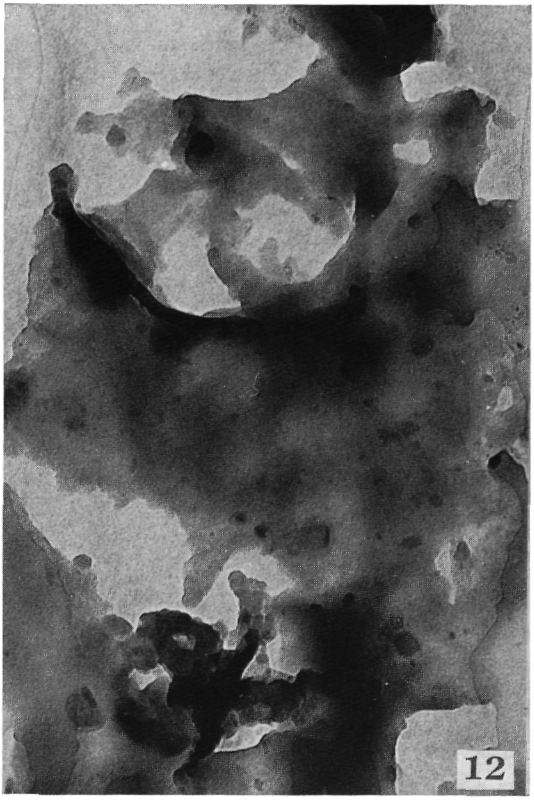
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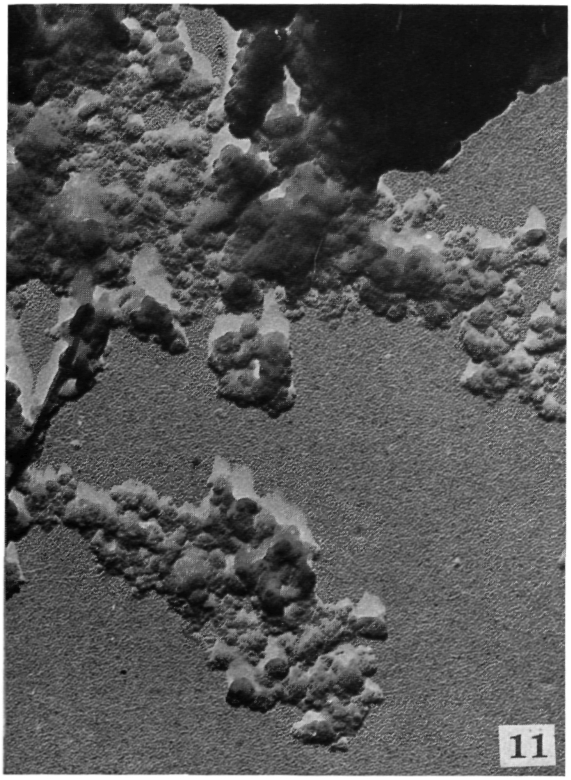
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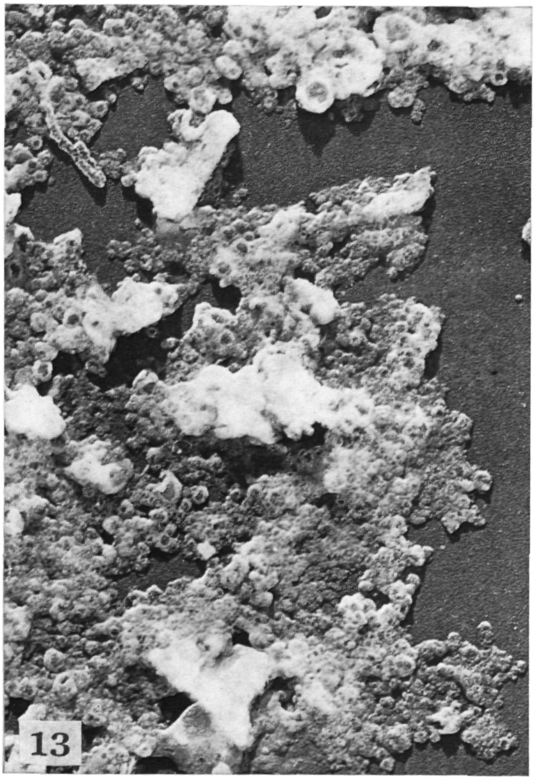
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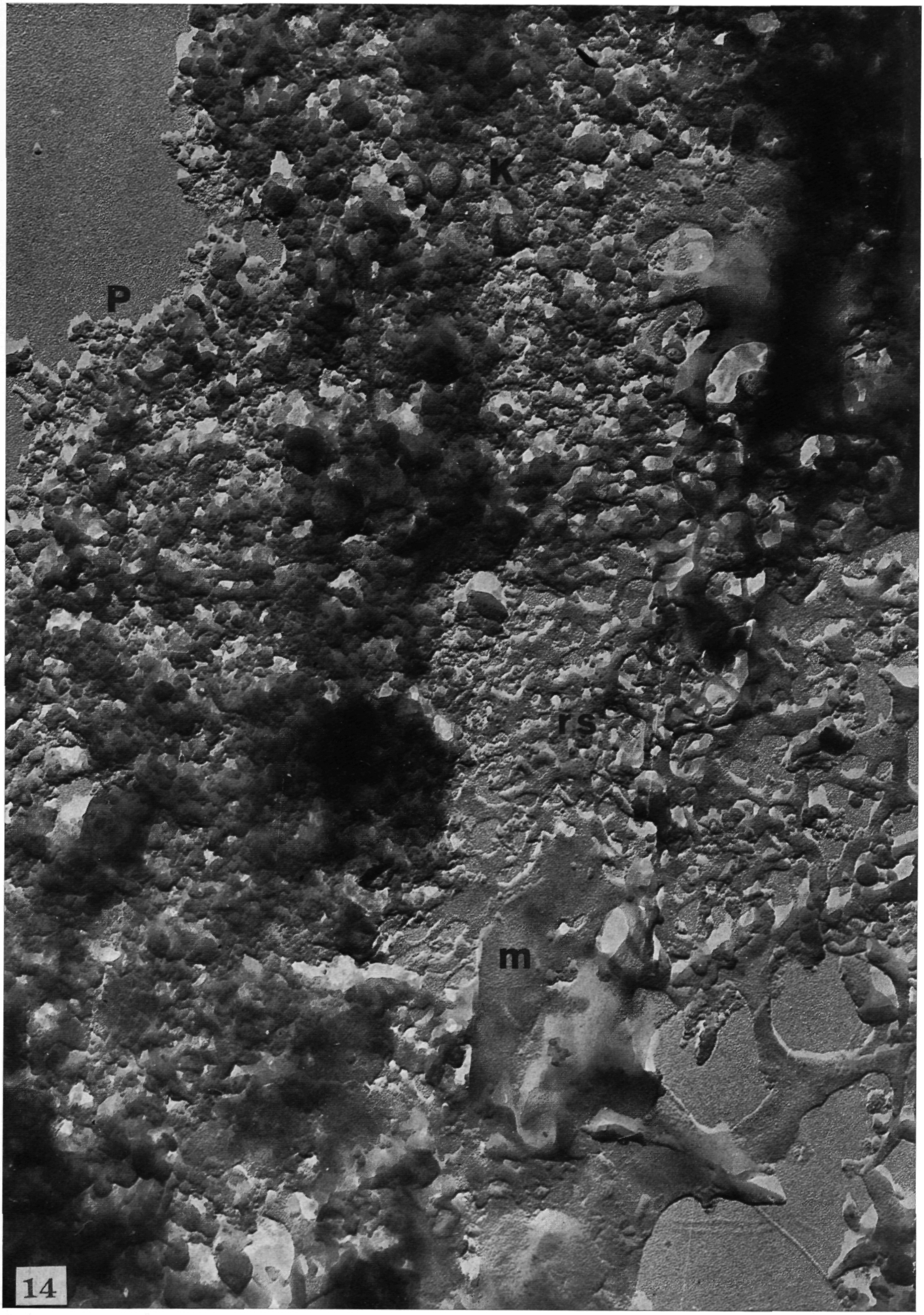

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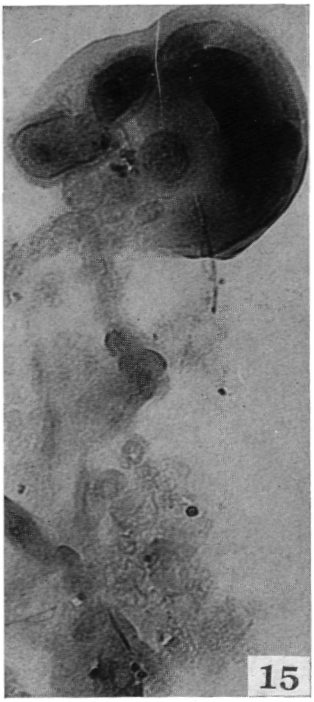
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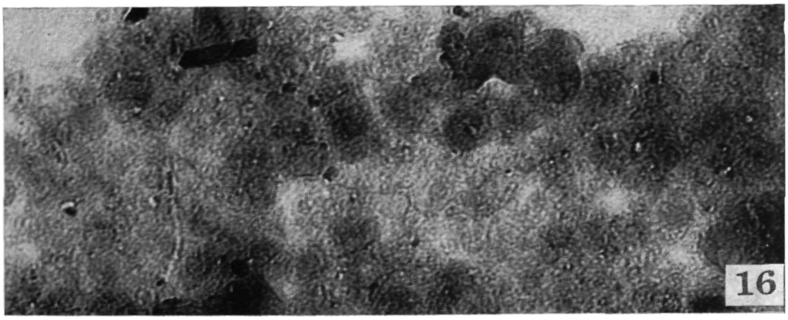
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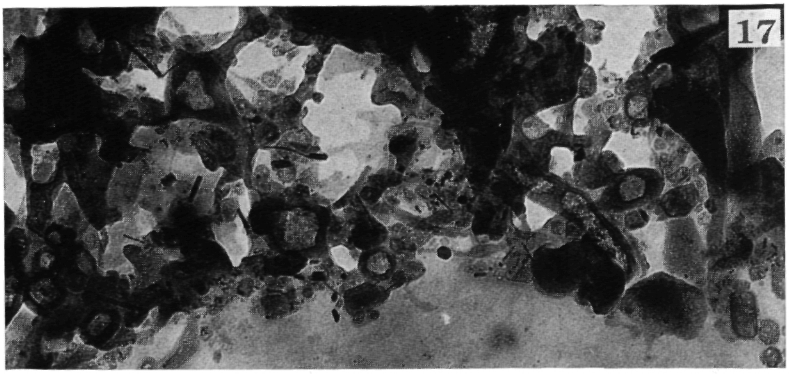
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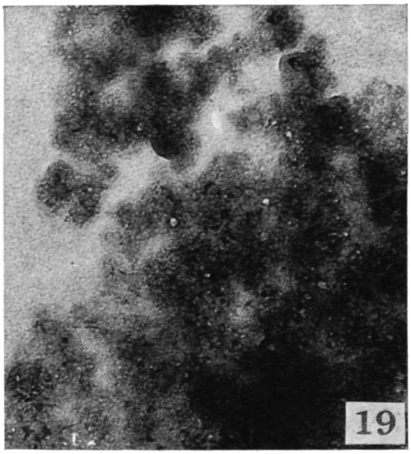
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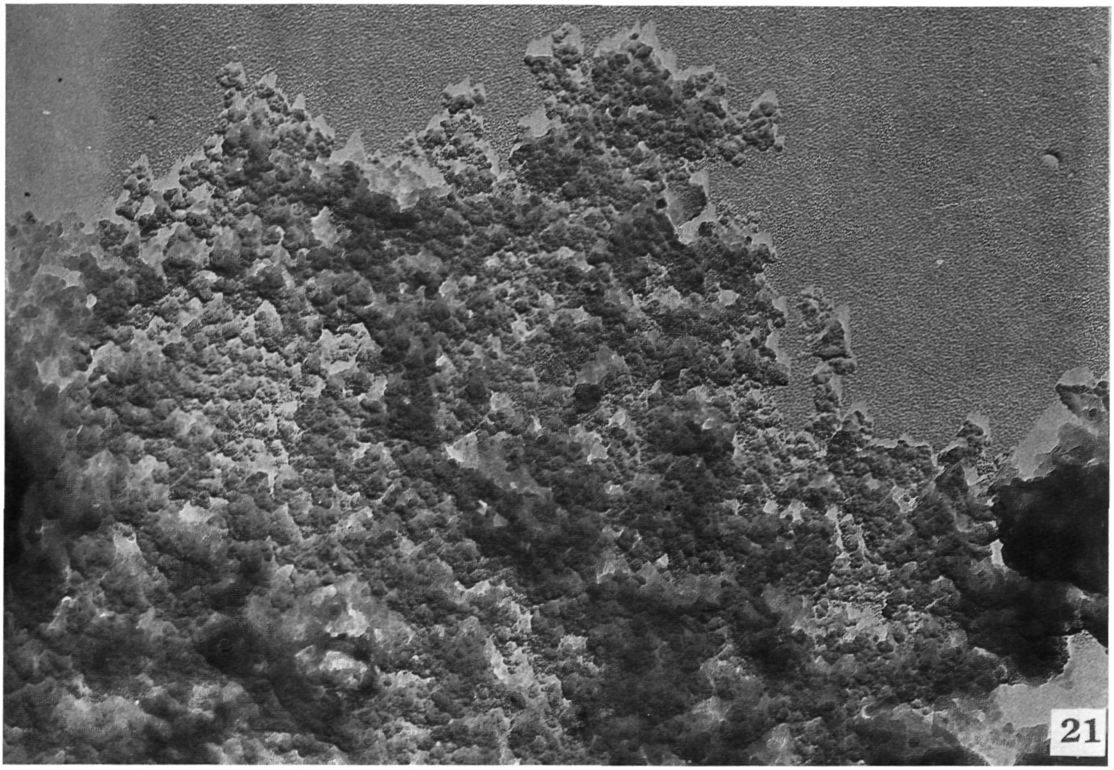

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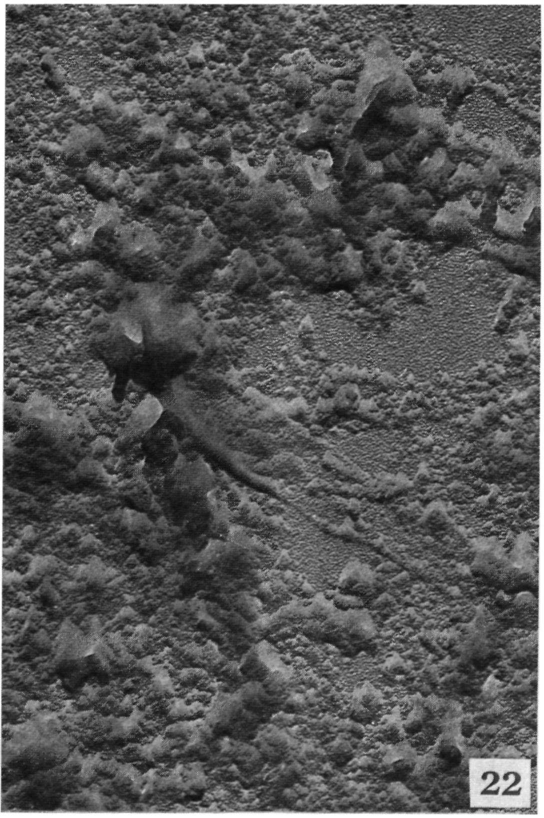

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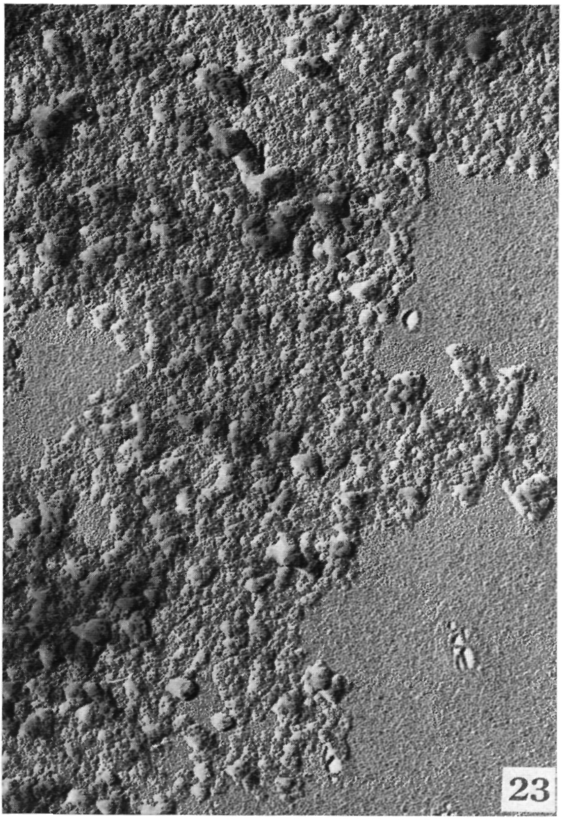

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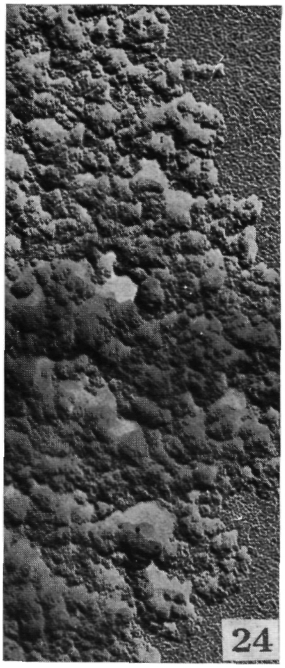
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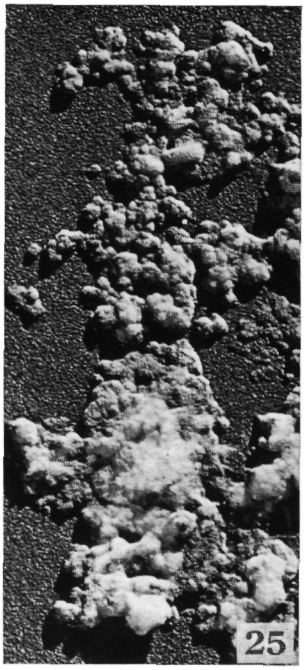
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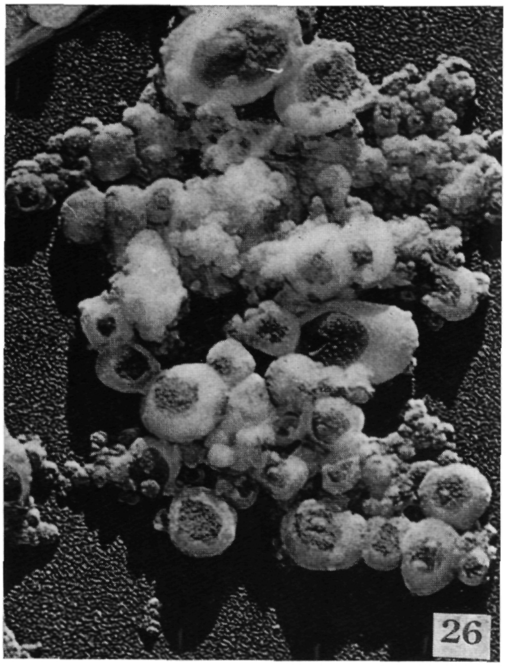
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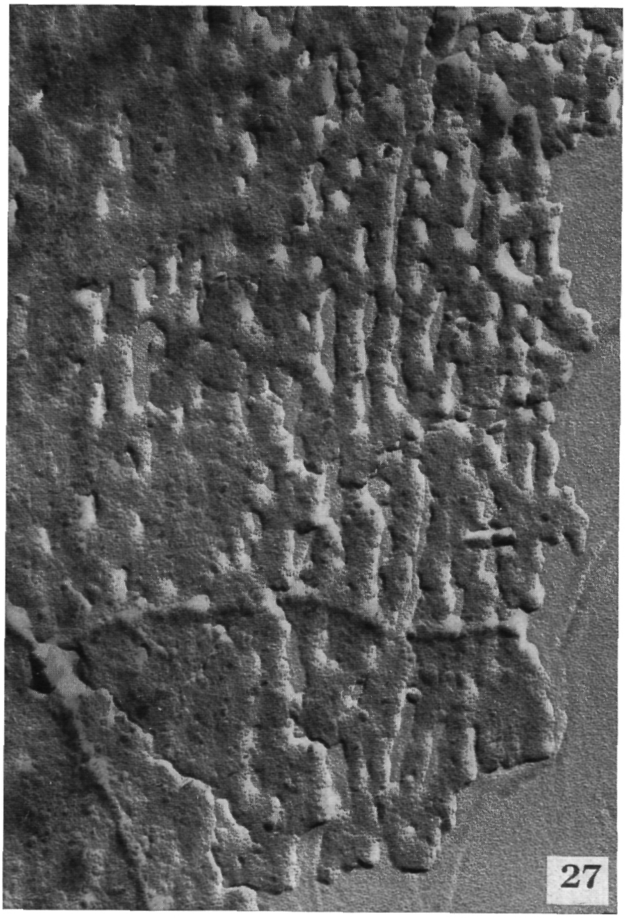
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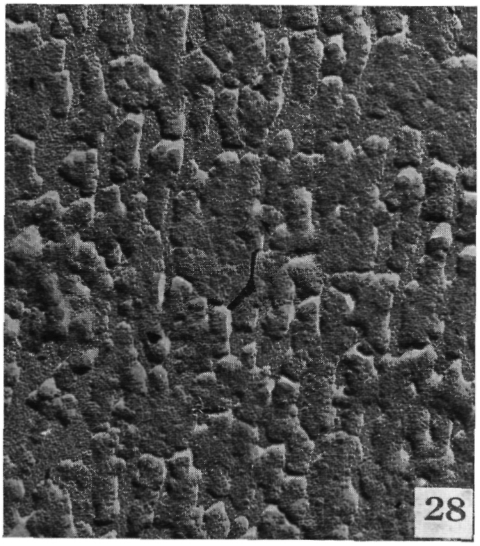
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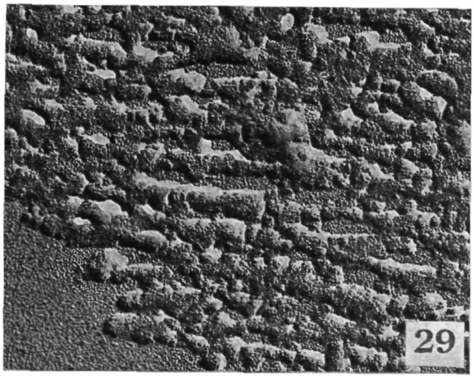
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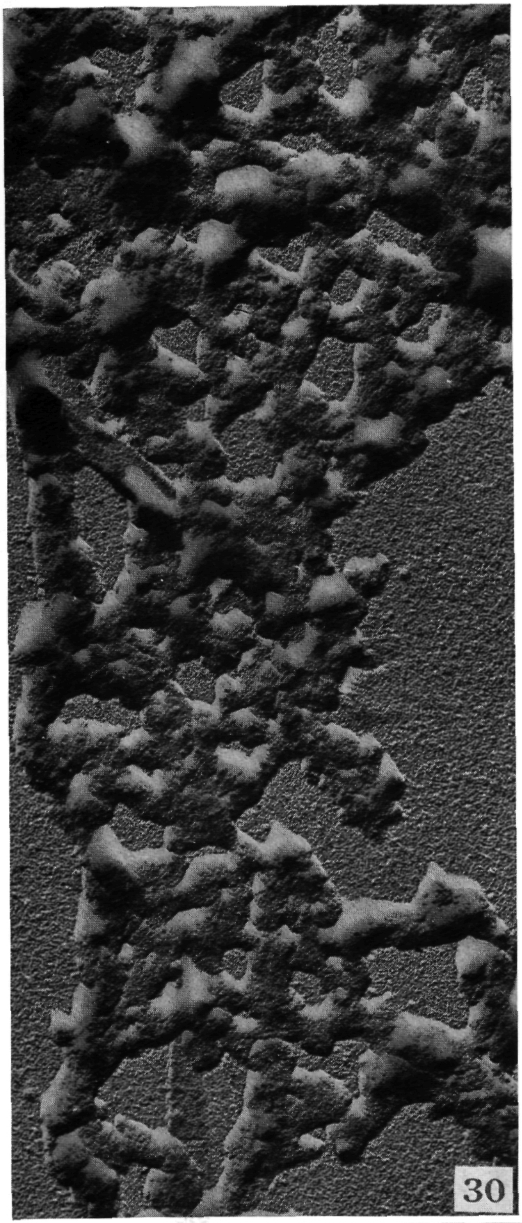
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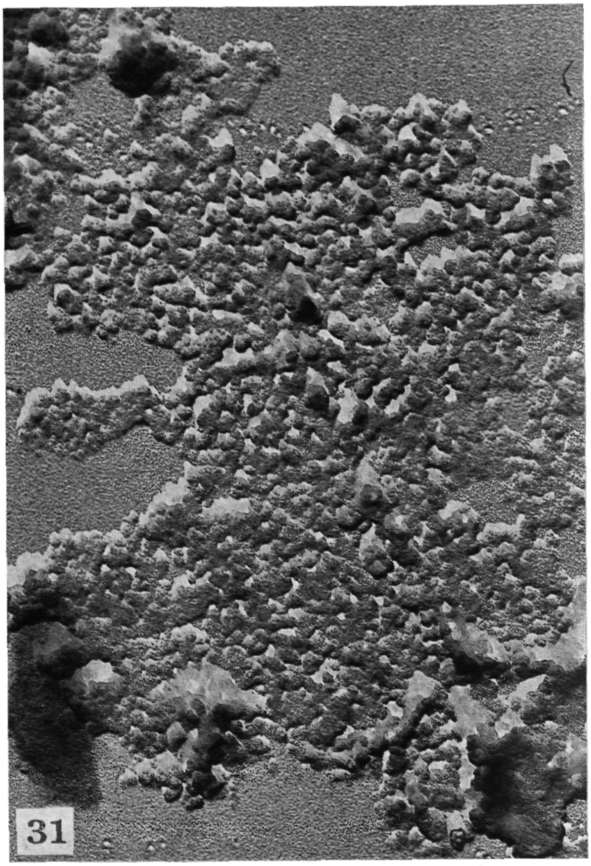
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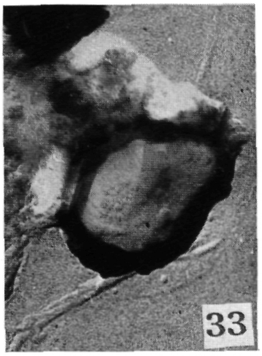
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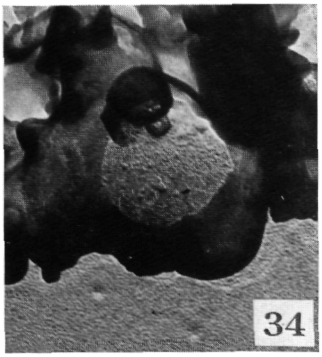
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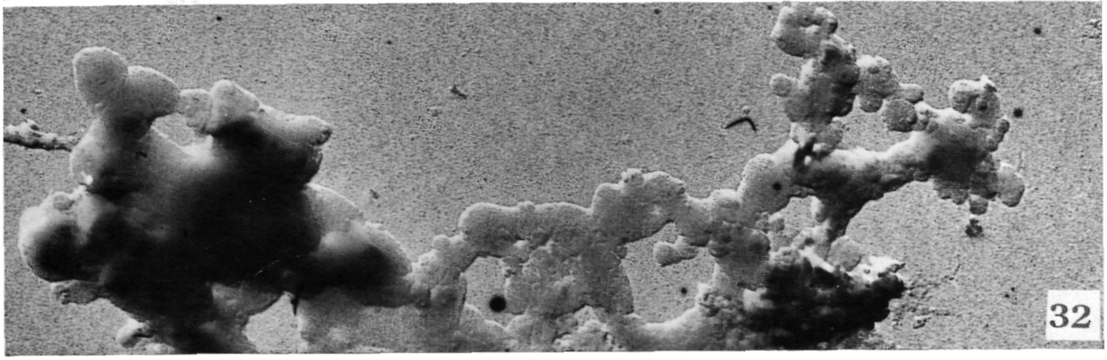
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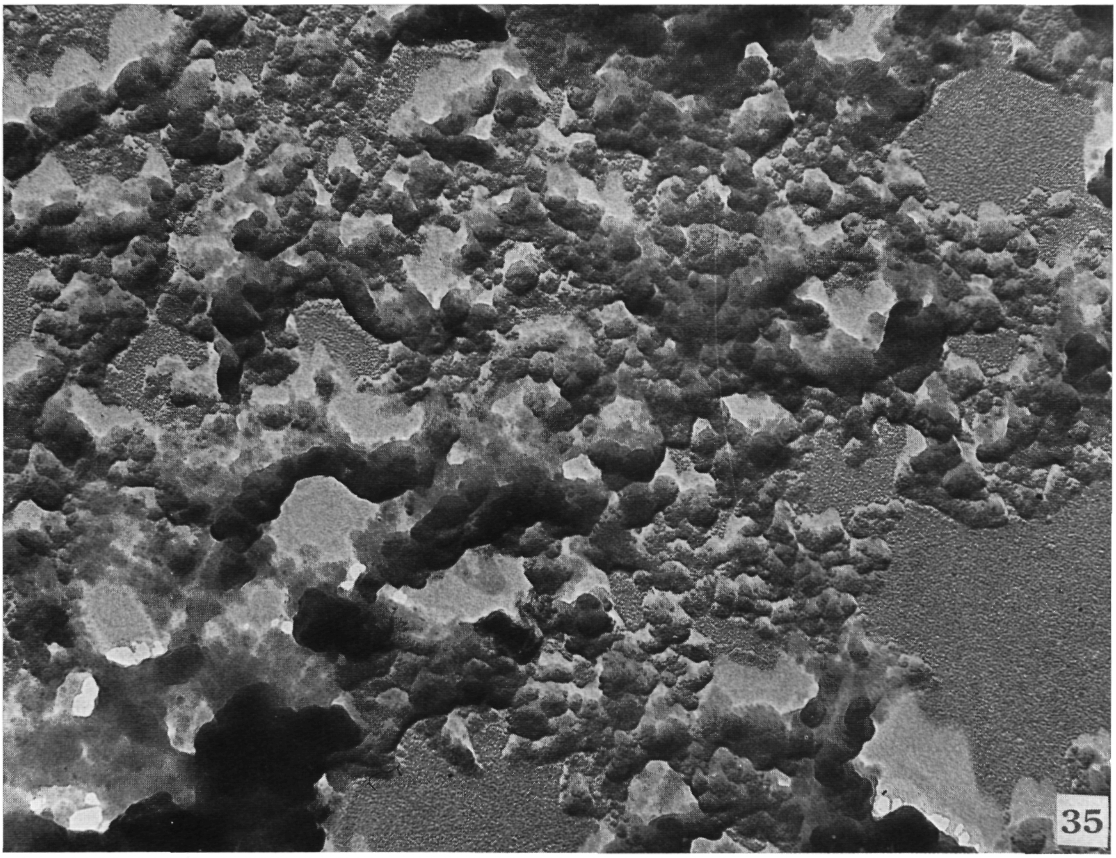

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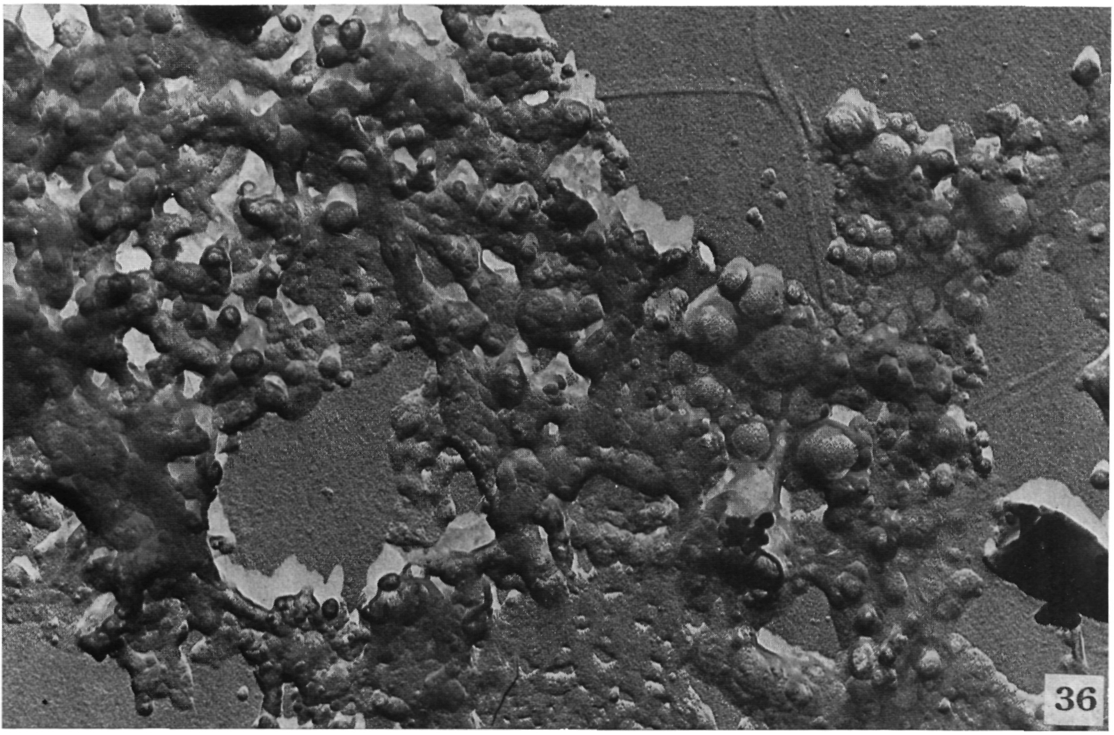

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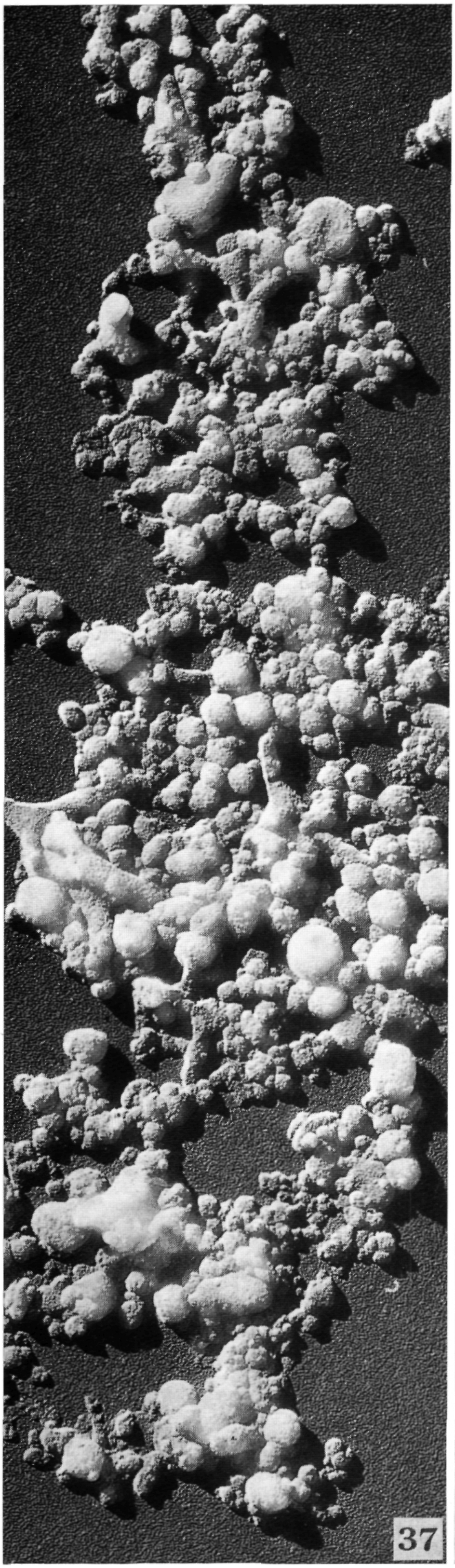

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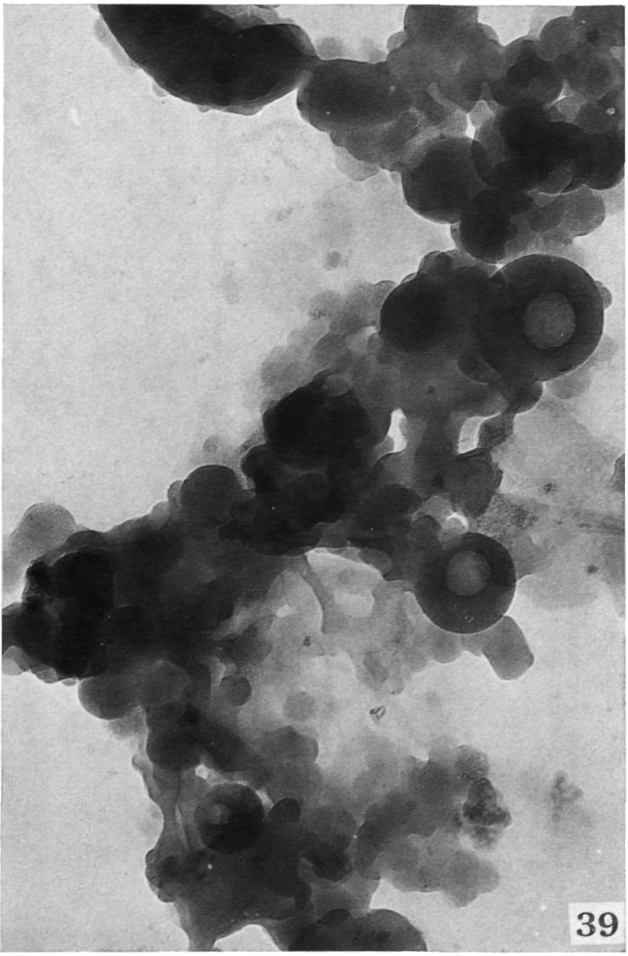

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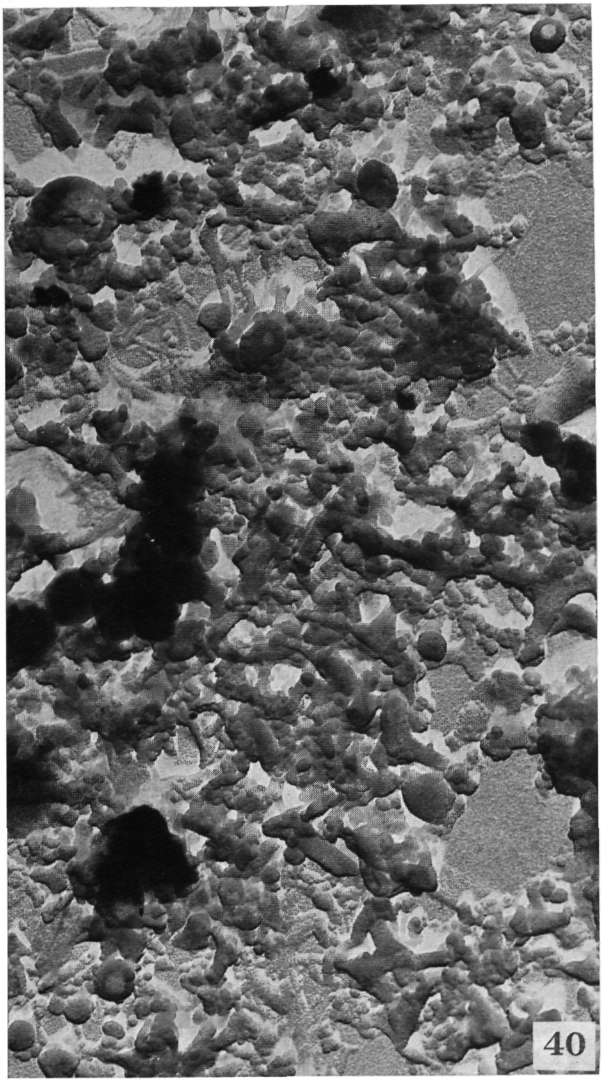
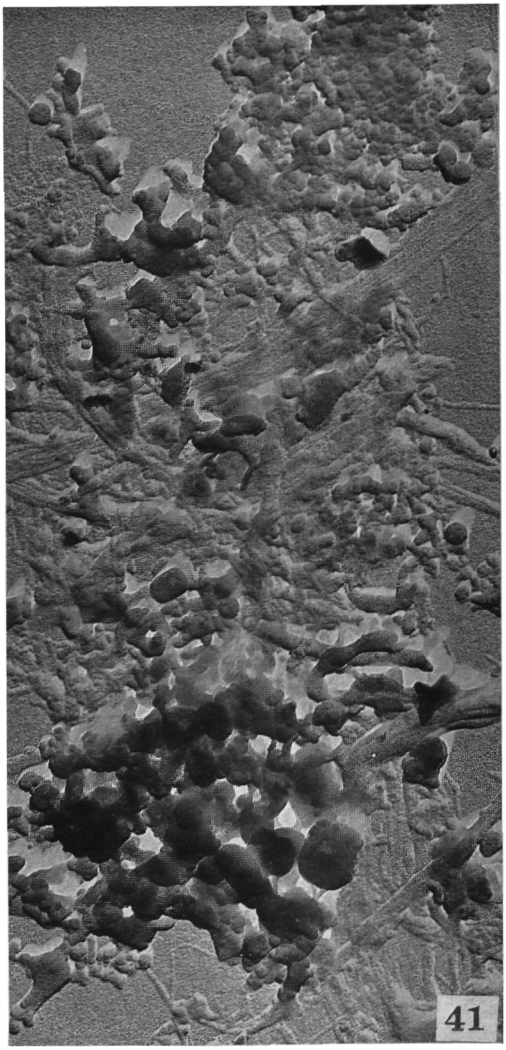
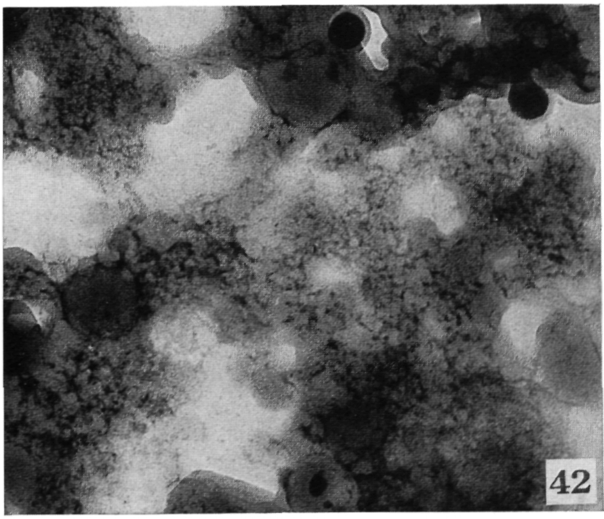
Ç̦h. GREGOIRE. — Paleozoic and Mesozoic Cephalopods.



40



41



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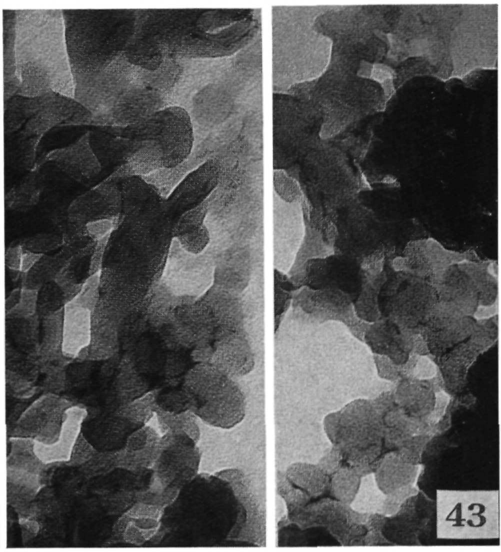

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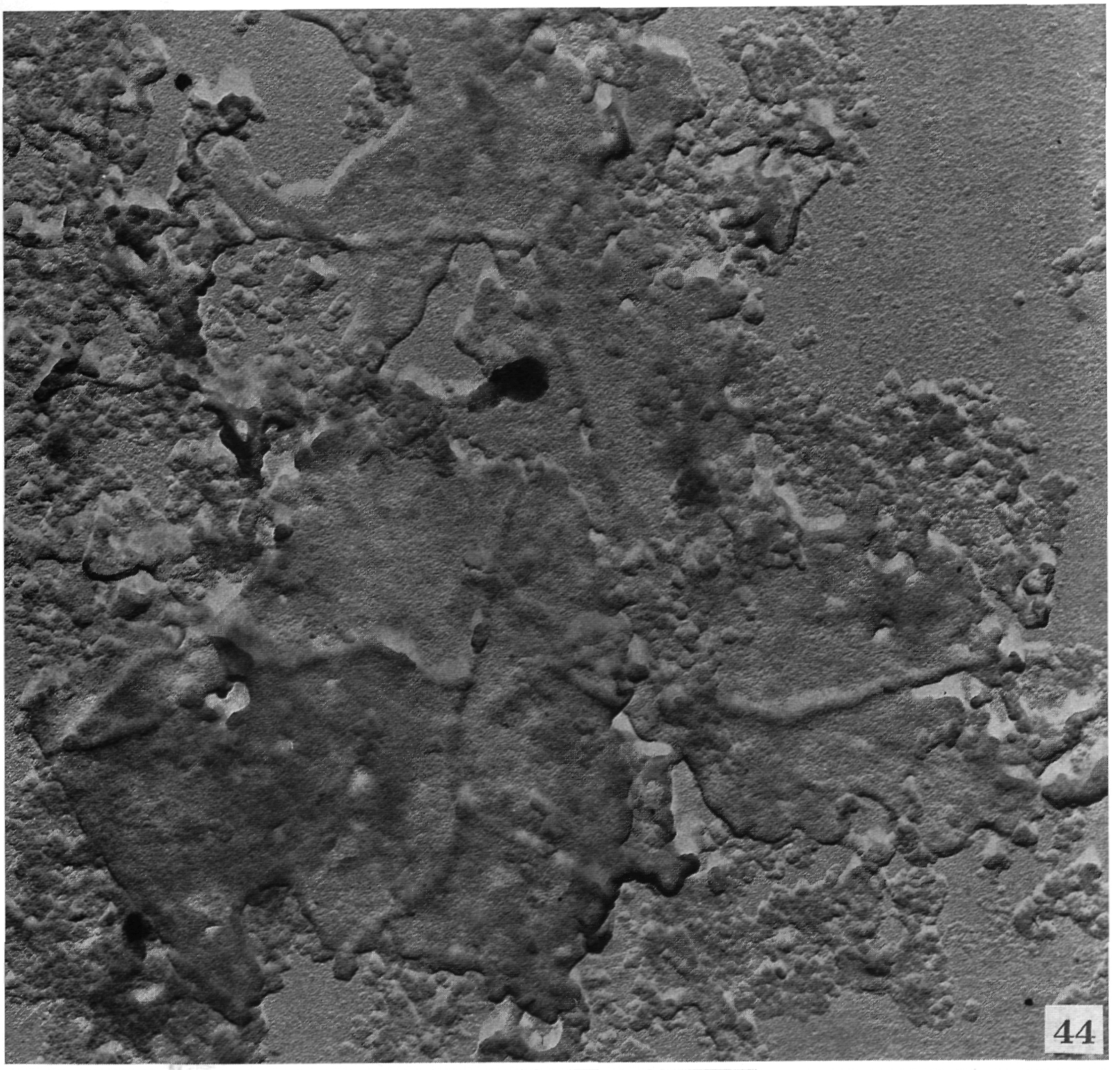
Ch. GREGOIRE. — Paleozoic and Mesozoic Cephalopods.

Inst. Roy. Sc. Nat. Belg. — Bull. T. **42,** N° 39, 1966.
Kon. Belg. Inst. Natuurw. — Bull. D. **42,** Nr 39, 1966.



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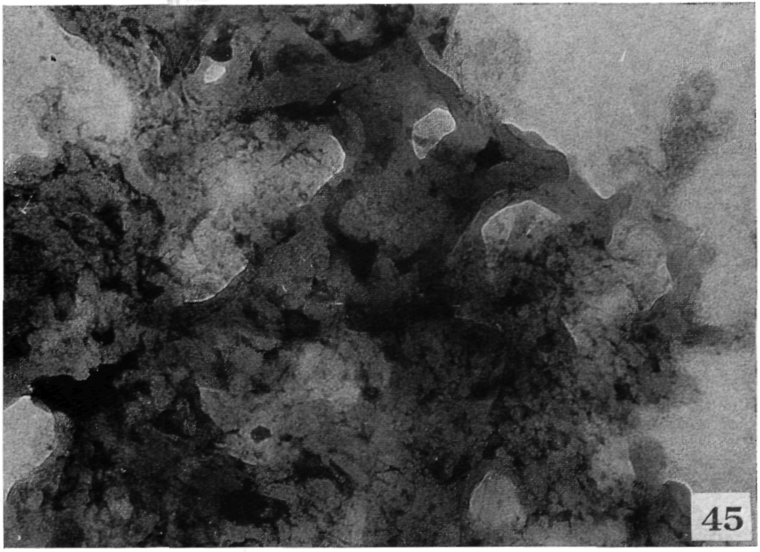
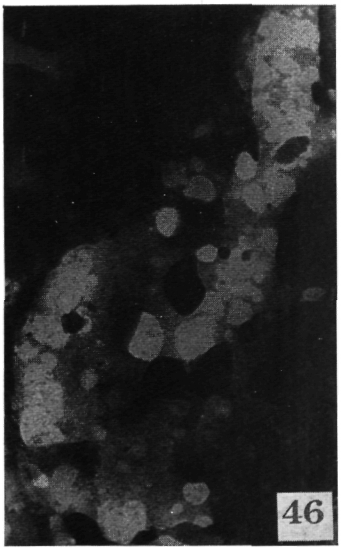


45



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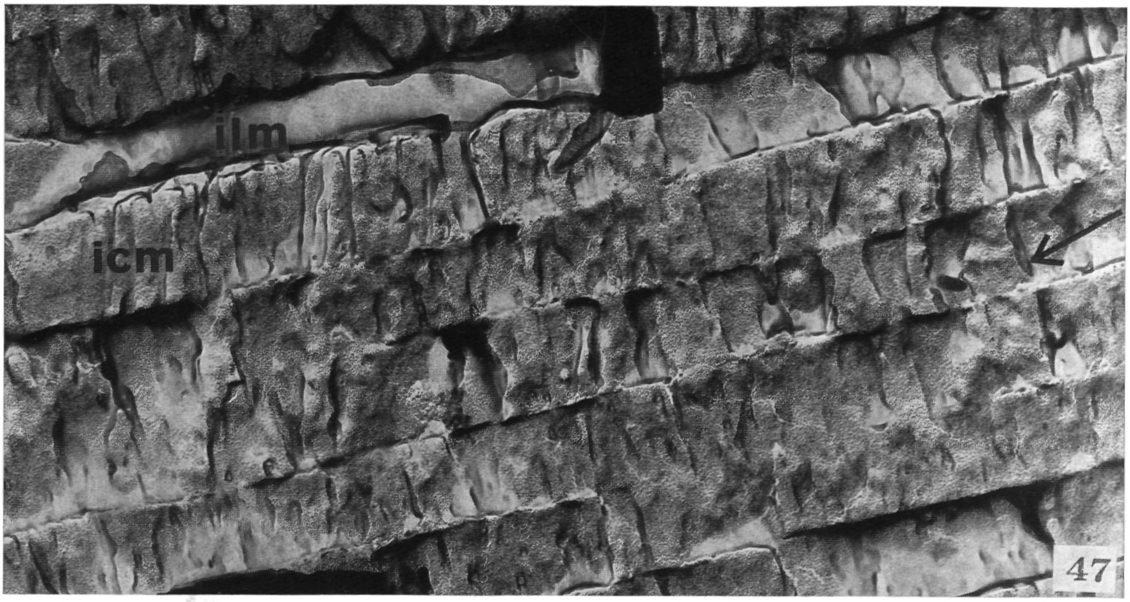
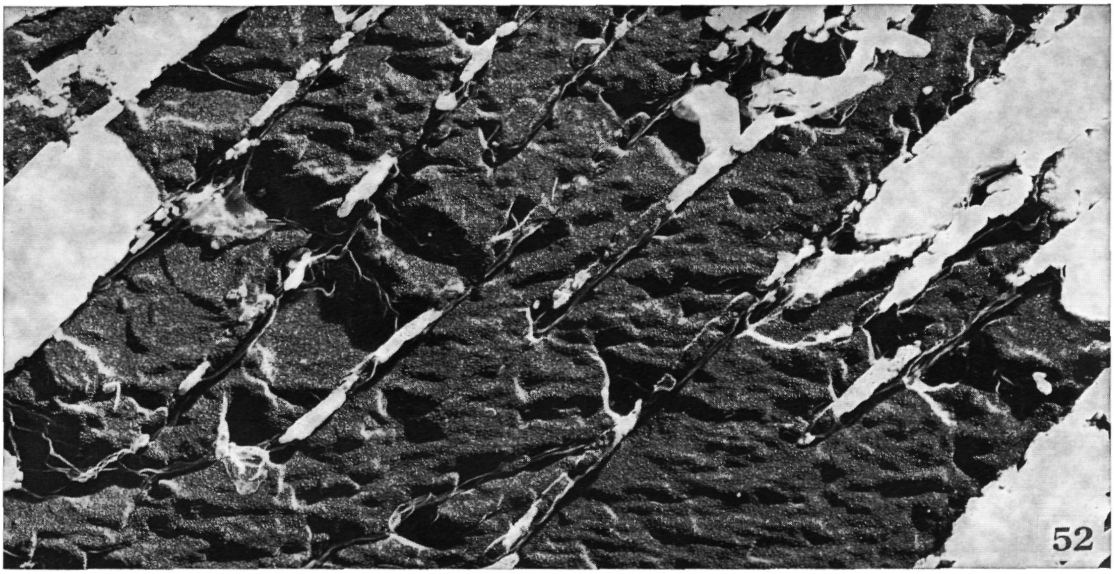
Ch. GREGOIRE. — Paleozoic and Mesozoic Cephalopods.

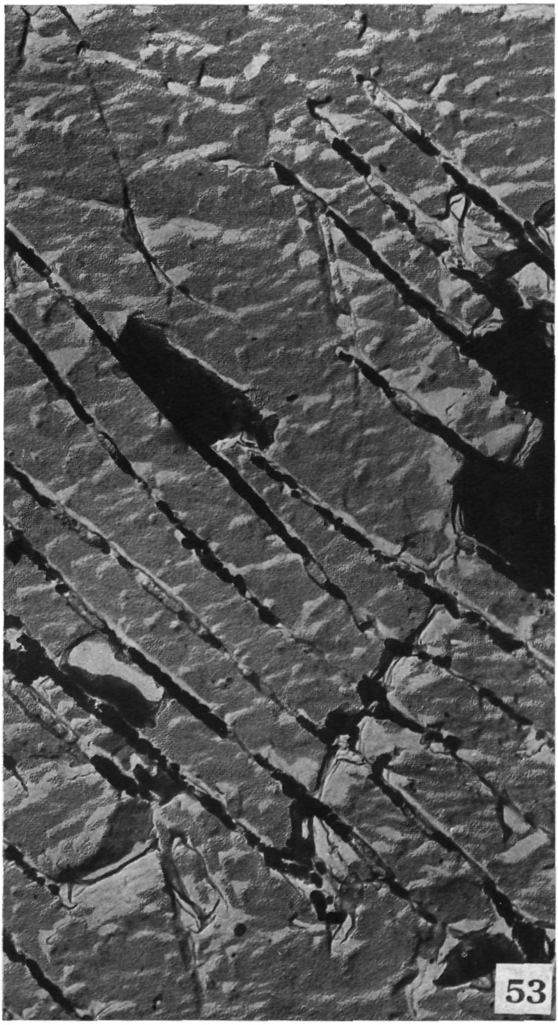


Ch. GREGOIRE. — Paleozoic and Mesozoic Cephalopods.

Inst. Roy. Sc. Nat. Belg. — Bull. T. 42, N° 39, 1966.
Kon. Belg. Inst. Natuurw. — Bull. D. 42, Nr 39, 1966.



52



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Ch. GREGOIRE. — Paleozoic and Mesozoic Cephalopods.