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BULLETIN

EXPERIMENTAL ALTERATION OF THE NAUTILUS SHELL BY FACTORS INVOLVED IN DIAGENESIS AND METAMORPHISM

Part I. — Thermal changes in conchiolin matrix of mother-of-pearl

BY

Charles GRÉGOIRE (Liège)

(with 2 tables and 95 Figures)

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INTRODUCTION.

The electron microscope supplied the first direct evidence of structurally preserved nacreous conchiolin in shells of more than 200 species of fossil molluscs, ranging from Ordovician to Cenozoic (GRÉGOIRE, 1958, 1959 ab, 1966, and unpublished observations).

Original patterns of nacreous conchiolin matrix (lace-like reticulated sheets), closely similar or identical to those described previously in modern molluscs (GRÉGOIRE, DUCHÂTEAU and FLORKIN, 1950, 1955, GRÉGOIRE, 1957, 1959, 1962) were remarkably well preserved in a few materials, such as unweathered portions of cephalopod shells buried in the asphaltic sandstones of Oklahoma (GRÉGOIRE, 1959 b, 1966 b; GRÉGOIRE and TEICHERT, 1965). In many shells from various ages, these patterns were generally destroyed or considerably altered. In these specimens, identification of the organic residues as remnants of original conchiolin fabrics is uncertain. The limits of the shell layers, blurred by calcitic epigeny and by other metamorphic changes, are frequently imprecise, and materials from the adjacent layers can be mixed with the nacreous substance. Organic remnants of foreign contaminants, modified by diagenesis, fragments of epibionts and especially of boring predators contemporaneous of the specimen, may present aspects resembling those of altered conchiolin.

Experimental reproduction in a modern shell of the alterations recorded in fossils would aid in the identification of the modified structures. In a modern shell, contamination by foreign materials can easily be controlled.

It has long been known that temperature and pressure play an important role in fossilisation. In the first part of this study, the alterations of the organic components in the nacreous layer of the *Nautilus* shell have been examined in the electron microscope on samples heated in the presence and in the absence of oxygen to temperatures ranging from 150 °C to 900 °C. Other samples were boiled in mixtures of sea mud and sea water.

The shell of the modern *Nautilus* has been selected for two reasons : this animal, as the only survivor of long extinct large groups of cephalopods, has a considerable importance as a stratigraphic indicator and the characteristic ultrastructure of its nacreous conchiolin has been investigated with the electron microscope.

The changes observed in the pyrolysed mother-of-pearl of *Nautilus* have been compared with those recorded in residues of decalcification of nacreous layers in Paleozoic and Mesozoic nautiloids and ammonoids.

Studies with the electron microscope of thermally altered conchiolin might also contribute to identify on the ultrastructural scale the biochemical breakdown products of the conchiolin complex.

Finally such studies are able to furnish information on the modifications developed in the brick wall architecture of mother-of-pearl during thermal conversion of aragonite into calcite, which occurs at temperatures of 400 °C and above.

The alterations in biochemical composition of the samples will be analyzed in Part II of this study. Part III will deal with the architecture of pyrolysed mother-of-pearl, and especially with the changes recorded on replicas in the interlamellar conchiolin matrices preserved in their original position. These changes differ in part from those observed in conchiolin suspensions of decalcified mother-of-pearl. Part IV will be devoted to the combined effects of elevated temperatures and high pressures in dry and wet environments. In part V, experimental changes in environmental conditions will be analysed with regard to their repercussions on ultrastructure of mother-of-pearl during pyrolysis.

Fragmentary results have been summarized in *Nature* (London) (1964), in Bull. Inst. roy. Sc. natur. Belg. (1966 b) and presented at the Third International Meeting of Geochemistry (London, Sept. 26-29, 1966 a).

MATERIAL AND METHODS.

Fragments of mother-of-pearl, of the same thickness, from the shell wall in the living chamber of *Nautilus pompilius* LINNÉ and of *Nautilus macromphalus* SOWERBY were cleaned by polishing from the outer, porcelaneous layer. The organic debris which adhered to the inner surface of the shell in the living chamber were removed with portions of the innermost nacreous layers.

Three groups of experiments have been performed.

In group 1, fragments of mother-of-pearl, some embedded in alumin and in graphite powders, were placed in ceramic boats and dry heated in electric ovens and muffle furnaces to temperatures ranging from 150 °C to 800 °C for various lengths of time (5 minutes to 21 days).

In group 2, fragments, mixed with sea mud consisting of sand grains and of shell debris from various pelecypods (mostly *Mytilus edulis, Donax* and *Arca*) were boiled in sea water for several periods of from 3 to 10 hours, separated by intervals during which the fragments were maintained buried in this mixture at room temperature. In an attempt to evaluate the effects of time on the alterations, one experiment lasted 2 years.

In group 3, quartz tubes (vitriosil), containing fragments of mother-of-pearl, were sealed under vacuum or under argon, then heated in electric furnaces to temperatures ranging from 150 °C to 900 °C for various lengths of time (5 minutes to 21 days).

The shell fragments were decalcified in saturated aqueous solutions of the disodium salt of ethylene-diamine-tetraacetic acid (E. D. T. A.) (titriplex III Merck, Darmstadt), at pH 4.0 and pH 8.0 (GRÉGOIRE et al., 1955), and washed by centrifugation. The samples heated in open vessels in the ranges of 600 °C to 800 °C could not be demineralized in titriplex and were dissolved in 25 per cent solutions of hydrochloric acid.

In several preparations of groups I and III, the pyrolysed conchiolin matrices spontaneously cleaved during decalcification into fragments of single interlamellar sheets, were sufficiently permeable to the electron beam, and were mounted directly on coated screens (see below). Other interlamellar sheets, agglutinated after disappearance of the mineral components which alternate with them, or fixed together by coalescence, were delaminated into single sheets in aqueous suspensions by means of ultrasonic irradiation (Headland « Electrosonic » Ultrasonic Cleaning Equipment, H 55 Generator, Frequency 80 Kc/s, Headland Engineering Developments Ltd, London).

The biuret reaction was applied to all the samples on residues of decalcification suspended in distilled water. Variations in intensity of the pink-violet (lilac), positive reaction in the residues were appreciated under a conventional microscope on thin films of these suspensions spread out between slide and coverglass. These variations are indicated in table 1 as follows : + : pale pink flakes; ++ : violet flakes; +++ : strongly violet flakes.

Drops of the suspensions were deposited on copper screens coated with films of formvar or of carbon, then drained, dried and examined in the electron microscope, either directly or after staining with P. T. A. (positive staining : 2 and 3 per cent solutions of sodium and/or potassium phosphotungstate at pH 4.0; negative staining (BRENNER and HORNE, 1959) : 2 and/or 3 per cent solutions at pH 6.5-7.0). Other preparations were shadowed with palladium and platinum, at angles of 15°-30 °C.

Electron microscopy was carried out with a R. C. A. - E. M. U. - 2 electron microscope and mostly with a Siemens Elmiskop - I, using a double condenser, a 200 μ condenser aperture, a 30 μ objective aperture and a cooling stage for a part of the material.

The results are based on examination of 4.000 electron micrographs. 8.000 micrographs recorded on fossil shells were used for comparison.

OBSERVATIONS.

A stepwise description of the thermal alterations in mother-of-pearl of the shell wall of *Nautilus* is given in table 1.

Group 1 : Dry heat in open vessels (1).

Mineral components.

X-ray powder diffraction analysis revealed preservation of original aragonite in the 150 °C - 300 °C samples, and transformation into calcite in the 400 °C and above samples. Calcium hydroxide, with decreasing amounts of calcite, was recorded in the 600 °, 700 °C, and 800 °C samples respectively.

Normal mother-of-pearl of *Nautilus* is a hard substance, which breaks without cleavage, except on the outer margin of the fragments. The effects of dry heat on that material consist of progressive increase in brittleness and easier cleavage into thin mineral sheets and flakes (200 °C and above). At 500 °C and above (600 °C, 700 °C - 800 °C), the nacreous matter is transformed into a snow-white powdery substance.

Unpolished nacreous layer of the living chamber in *Nautilus* shell is faintly iridescent, with pale pink-greenish hues. The inner, unweathered surfaces of the shell wall in the camerae are intensely iridescent.

A slight burnishing of iridescence appears on the exposed surfaces at 150 °C and develops with elevation of temperature. Between 200 °C and 300 °C, the cleaved lamellae and flakes exhibit intense metallic colours. Protracted exposure to 150 °C produced the same changes. Iridescence disappeared above 400 °C, and the samples show a bright ash-grey colour which becomes lustreless above 600 °C.

Differences in colour appeared between central, freshly cleaved portions, and outer surfaces, directly exposed to the air.

(1) Fragments of the outer porcelaneous layer of the shell wall exposed in open vessels for 5 hours to a temperature of 300 °C, were brittle and still aragonitic. Decalcification of these fragments left black-brown particles. In the electron microscope, these residues consisted chiefly of veils and fibrillar membranes associated with clusters of pebble-shaped spheroidal bodies and granules. The latter structures were possibly organic remnants of nacreous indentations in the porcelaneous substance (See GRÉGOIRE, 1962).

Organic components (conchiolin).

The samples heated in the ranges of 150 °C - 500 °C dissolved rapidly in titriplex and smelled of petroleum or of putrid organic matter. The samples heated to 600 °C, 700 °C and 800 °C, immersed in titriplex or in 3 per cent solutions of hydrochloric acid, left an insoluble grey (600 °C) or white (700 °C, 800 °C) mud, composed chiefly of calcium hydroxide (see discussion). This mud dissolved with considerable effervescence and emission of H2 S in 25 per cent solutions of hydrochloric acid.

Decalcification of the nacreous portion of the normal *Nautilus* shell leaves abundant, soft, transparent, highly iridescent membranes. The appearance of these membranes did not change in the residues of the samples heated to 150 °C for 5 hours. In the 200 °C - 300 °C samples, the residues of decalcification appeared in the form of mahogany-brown shreds. In the 400 °C and 500 °C samples, the shreds were transformed into brown-black particles, and at 600 °C, 700 °C and 800 °C into a scum of black particles.

In all the samples (150 °C - 800 °C) (Fig. 35 b), the biuret-positive shreds of nacreous conchiolin appeared mostly in the form of transparent, rounded or polygonal, pink-violet (lilac) flakes, scattered or still assembled into fragments of flaggings. These flakes are portions of the original interlamellar conchiolin matrix which, in architecture of mother-of-pearl, stands opposite the tabular 001 planes of the aragonite crystals disposed in flaggings. A few lilac-coloured flakes were speckled with bright red dots or larger, purple spots and stripes. Clusters of dark violet and ruby-red grains were embedded in a colourless or yellow jelly.

Electron microscopy.

A described previously (GRÉGOIRE et al., 1950, 1955; GRÉGOIRE, 1957, 1962, (Fig. 39), 1966 (Figs. 1-3)), the nacreous conchiolin matrix consists in *Nautilus* of sturdy irregularly cylindrical trabeculae, studded with scattered protuberances, and separated by an elongated or polygonal fenestration (nautiloid pattern : Fig. 1).

In unstained preparations, the trabeculae of this matrix appear in the electron microscope to be composed of a pale, uniformly amorphous or granular matter. Negative staining reveals ill-defined, unoriented fibrils (see GRÉGOIRE, 1967, Pl. 6, Fig. 1).

Heating of mother-of-pearl to 150 °C for 5 hours, 11, 13 and 19 days, to 200 °C and to 225 °C for 5 hours modified only slightly the appearance of the matrix in shadowed preparations (Figs. 2, 3, 4, 5, 6, 7 and 8). Electron diffraction patterns of these samples showed only concentric rings with diffuse boundaries. Shrinkage, shortening and increase in density, accompanied by rounding up of fenestration, affected locally groups of trabeculae (Figs. 4 and 8), around which the nautiloid pattern still had a normal appearance. In samples heated to 225 °C for 21 days

(Fig. 10) to 250 °C (Fig. 17) and to 275 °C for 5 hours (Figs. 18 and 19), some of these groups were transformed into large spheroidal corpuscles in which the trabeculae were considerably flattened and filled with microvesicles (Figs. 12, 13 and 15). Protracted exposure to the electron beam during examination produced increase in size and coalescence of these vesicles. Some of these corpuscles, in which the trabeculae were disposed radially, resembled spherulites or cartwheels. Other corpuscles were transformed into rings by disappearance of their central portion (Fig. 13). Electron diffraction patterns of these structures (Fig. 15) revealed either concentric rings with diffuse boundaries (Fig. 14) or rings and oriented spots (Fig. 16).

Apart from these particular structures, swellings separated by constrictions were the first signs of fragmentation of the trabeculae in the 150 °C - 250 °C samples (Figs. 5, 6, 7 and 8). Vesicles developed in the bloated portions appeared in P. T. A. stained preparations in the form of opaque, rounded speckles, disposed in mosaics (Fig. 9). The X-ray diffraction patterns of these speckles (not shown) were identical to those of the stain patches. Similar mosaics of spots were observed in P. T. A. stained trabeculae of nacreous conchiolin in Pennsylvanian nautiloids of Buckhorn asphalt (not shown).

In samples heated to 225 °C for 21 days (Fig. 17) and to higher temperatures (300 °C to 800 °C) (Figs. 21, 22, 23 and 24), the nautiloid pattern was destroyed by general disintegration of the trabeculae into pebble-shaped spheroidal corpuscles and into other small debris. These corpuscles were structureless, thinly granular or pitted by holes (Figs. 28, 29, 31 and 36). Presence of PTA within corpuscles suggests that a part of them (Fig. 28) could be hollow spheroids similar to those shown in Fig. 38, with translucent centres and dense walls.

In the samples heated to 700 °C - 800 °C, sturdy fibers (Figs. 33 and 35) and thinner filaments, scattered or associated in bundles (Figs. 30 and 32), were mixed, sometimes in substantial amounts, with the clustered conchiolin debris, fused by coalescence into membranes.

Group 2: Protracted boiling in sea mud and sea water.

Mineral components.

Under the conditions indicated in table 1 (group 2) boiling did not alter the crystallographic nature of the samples of nacreous substance, which remained aragonitic throughout.

The hardness of mother-of-pearl remained also unmodified except in some samples which had been accidentally exposed to dry heat for 30 minutes at the end of the treatment in one experiment (761 C). These samples were as brittle as those heated in open vessels.

A slight burnishing of iridescence with pink-violet hues developed on the surfaces in direct contact with the mud. The inner portions were unchanged in colour.

Organic components.

In remnants of decalcification of the boiled samples, the biuret-positive conchiolin shreds were rigid, in contrast with the soft residues of unheated (control) material. Their colour remained unchanged. On the other hand, the shreds from fragments dry heated accidentally appeared as mahogany-brown particles, as in many conchiolin remnants in group 1.

Electron microscopy. — Preservation of the nautiloid pattern, various degrees of coalescence and of flattening (Figs. 39 and 43), general shrinkage of the conchiolin structures (Figs. 41 and 42) were the most characteristic changes which affected the conchiolin matrix in this group.

In unshadowed material, the substance of the trabeculae appeared to be amorphous, or marbled by rounded, dense islands indicating the sites of the protuberances. Tight networks of ill-defined filaments are shown in P. T. A. stained trabeculae of the nacreous substance in a fragment boiled for 58 hours in 47 days (Fig. 40).

Group 3 : Dry heat under vacuum, in sealed tubes.

Mineral components.

As in mother-of-pearl heated in open vessels, calcite had replaced aragonite in the 400 °C - 900 °C samples. In the samples heated above 700 °C, small amounts of calcium hydroxide were mixed with calcite. Conversion of aragonite took place rapidly : the samples exposed to 600 °C (813) and to 800 °C (816) for 5 minutes, after a warming period of 15 minutes, already consisted of calcite (see table 1).

In the ranges of 150 °C to 500 °C, alterations in hardness, cleavability and colour of mother-of-pearl did not differ distinctly in the samples of group 3 from those of group 1. On the other hand, in the absence of oxygen, iridescence subsisted in the 500 °C and 600 °C samples, and was still visible in the fragments heated to 800 °C for 5 minutes (table 1: 816).

Organic components. — All the samples, including those heated to 700 °C, 800 °C and 900 °C, dissolved completely in titriplex, in contrast with the 600 °C, 700 °C and 800 °C samples of group 1 (see note in discussion).

The organic remnants of decalcification appeared in the form of iridescent (150 °C), mahogany-brown (200 °C - 300 °C) and black

(400 °C - 900 °C) shreds and particles, which were relatively resistant to ultrasonic dissociation.

In all the samples of this group (150 °C - 900 °C: Fig. 87), these shreds were biuret-positive and consisted of polygonal flakes stained in pink-violet and violet with various grades in intensity of the reaction. Speckles of various colours, including bright purple, marbled the uniform lilac background of the flakes. Transparent jellies contained lilac-coloured rods, grains and filaments.

Electron microscopy. — In the 150 °C samples heated for 5 hours, the modifications in structure of the conchiolin matrix consisted of diffuse shrinkage and shortening of trabeculae, with rounding up of fenestration. Local swelling and constriction appeared in other trabeculae (Fig. 44). Coalescence, accompanied by swelling (Fig. 46), coalescence and flattening (Figs. 47, 48, 49 and 50), fragmentation into elongated, contorted blocks and spheroidal corpuscles (Fig. 45) characterized the alterations in the matrix of the samples heated to 200 °C, 250 °C, 275 °C for 5 hours and to 225 °C for 21 days. In the 300 °C samples, fragments of matrix exhibiting the nautiloid pattern only slightly modified were mixed with other residues considerably altered, as described here below.

The changes observed in conchiolin structures of samples heated in the absence of oxygen in the ranges of 300 °C to 800 °C differed thoroughly from those produced by the same temperatures in open vessels. Fusion and flattening of the interlamellar reticulated sheets of nacreous conchiolin into continuous membranes and into loose plane networks with broad perforations were the predominant alterations (300 °C - 5 hours : Fig. 51; 500 °C - 5 hours : Figs. 67, 68 and 72; 600 °C - 5 minutes : Figs. 69 and 70; 600 °C - 30 minutes : Figs. 73 and 74; 600 °C - 5 hours : Figs. 75 and 76; 700 °C - 5 hours : Fig. 77). Disruption of the conchiolin trabeculae into pebble-shaped corpuscles, predominant in group 1 at these temperatures, was less frequent or absent. In the 800 °C samples, some of the perforated membranes were relatively thick (Figs. 78, 80 and 85) and had preserved structural features of the nautiloid pattern (Fig. 80). Other membranes were extremely thin, soft, transparent, wrinkled veils (Fig. 82), perforated by broad openings (Fig. 85).

Constitution of membranes was followed or accompanied either in the sample itself during heating, or during preparation of the material, by dislocation of portions of these membranes into flat, sharp-edged structures in the form of polygonal, wedge-shaped, angular blades and flakes (300 °C - 5 hours : Figs. 52 and 53; 400 °C - 60 minutes : Figs. 55, 57 and 59; 400 °C - 5 hours : Fig. 56; 400 °C - 21 days : Figs. 58 and 61), and by separation of the intercrystalline conchiolin bridges from the interlamellar sheets in the form of bars, girders, cords and ribbons (Fig. 51) overlying the membranes (Fig. 52).

Viewed on transverse section, along their edges, many wedge-shaped blades and flakes reveal cleavage lines and seem to be composed of more than one layer (Figs. 52, 53, 54, 55, 56, 58 and 61). In Fig. 59, a thick flake shows cleavage lines on its sharp edge appearing as an oblique cliff, and seems to consist of several layers, piled on top of each other.

Thickenings in the form of bulging, cylindrical, ring-shaped pads (Figs. 68, 69, 70, 75, 76, 77, 78, 80 and 83) surround the perforations in the membranes and in their fragments.

Examined in unshadowed and negatively stained preparations, the membranes and their debris appeared generally amorphous or granular (Figs. 59, 60, 72, 73, 74, 79, 81, 83 and 84). Vesicles of various sizes developed within these structures, especially at high temperature (Fig. 84). Clefts located in the bulk of some fragments are visible in the form of crescents and half-circles (Fig. 75). Dense filament-like structures were scattered or assembled in bundles in other fragments of membranes (Fig. 81).

In unshadowed preparations, concentric rings of dense lines, about 13 Å in width, are visible in the pads around the perforations (Fig. 79).

In the conchiolin remnants of mother-of-pearl heated in sealed tubes to 900 °C, the membranes resulting from coalescence of conchiolin shown in Figs. 86, 92 (left centre and bottom) and 93, were mostly disintegrated into corpuscles, 65 Å in average diameter. These corpuscles were grouped into networks, contorted chains and rings or assembled in clusters (Figs. 86 and 94). Several clusters of these debris assumed polygonal shapes (Figs. 86, 92, 94 and 95), which reflect the outlines of the dissolved original aragonite crystals disposed in flaggings in the mineral lamellae. The opaque strands which circumscribe the polygonal structures shown in Figs. 86 and 92 are remains of the original intercrystalline systems of conchiolin.

Electron diffraction diagrams of these polygonal assemblages consisted of concentric rings with diffuse boundaries (Figs. 90 and 91), some with scarce oriented spots(Fig. 90).

As in conchiolin remnants of samples dry heated in open vessels, substantial fibers and filaments were mixed with the conchiolin residues of the 800 °C and the 900 °C samples of group 3 (Fig. 88).

In samples recovered after a short exposure to heat, the alterations in conchiolin had already developed and seemed to be stabilized without further important degradation during protracted heating. See table 1 : 771. Compare Figs. 54, 57, 59 (400 °C - 60 minutes) with Figs. 55 and 56 (400 °C - 5 hours) and with Figs. 58, 60 and 61 (400 °C - 21 days); also Figs. 69 and 70 (600 °C - 5 minutes) with Figs. 73 and 74 (600 °C - 30 minutes) and with Figs. 75 and 76 (600 °C - 5 hours); also Figs. 78 and 81 (800 °C - 5 minutes) with Figs. 79 and 80 (800 °C - 30 minutes) and with Figs. 82, 83, 84 and 85 (800 °C - 5 hours).

DISCUSSION.

Reliability of the method of preparation.

The accuracy of the procedures used in the present study for examination by direct transmission in the electron microscope of the pyrolysed organic material has already been discussed elsewhere concerning fossil conchiolin prepared by the same procedures (GRÉGOIRE, 1966, p. 13).

After decalcification of normal or of moderately heated (150 °C) mother-of-pearl, numerous interlamellar sheets of matrix, collapsed onto each other after dissolution of the mineral lamellae, remain fastened together by their intercrystallinic bridges. This agglutinated material is opaque to the electron beam.

In the samples heated to high temperatures (600 °C - 900 °C), the scum of black particles which constitutes the organic remnants of decalcification (see table 1), results from condensation, agglutination and coalescence of conchiolin substance. This material is also opaque to the electron beam.

In order to obtain an adequate degree of electron permeability requested for observation in the electron microscope, it was necessary to break the intercrystallinic bridges, either by shaking the suspensions containing the conchiolin shreds, or by applying ultrasonic irradiation. These procedures separate single interlamellar sheets permeable to the electron beam, but are responsible in part for a certain degree of fragmentation of the brittle fossil and pyrolysed conchiolin matrices, illustrated in the present and in previous studies (GRÉGOIRE, 1959 b, 1966). However, control tests performed on 300 °C samples from group III showed that the appearance of the remnants of matrix did not distinctly differ in thin fragments of matrix observed directly after decalcification along the edges of the thick shreds, in fragments dissociated by shaking or by teasing, and in fragments exposed to the ultrasonic irradiation.

As will be shown in Part III of this study, etching of mother-of-pearl polished in tangential orientation, parallel to the tabular planes 001 of the aragonite crystals, reveals fragments of interlamellar conchiolin matrix which have been replicated or which lay as pseudoreplicas on the aragonite crystals of the underlying lamella. In samples heated to 200 °C for 5 hours, to 225 °C for 5 hours and 21 days, to 400 °C for 5 hours, for example, the conchiolin remnants are mechanically undisturbed or less disturbed than in suspensions. In these remnants, the various products of conchiolin dislocation, namely pebble-shaped corpuscles identical to those obtained after decalcification, appear to be loosely assembled in networks of ribbons in which the outlines of the nautiloid pattern of structure is occasionally recognizable. On the other hand, in other portions of the same replicas, clusters or imprints of corpuscles identical to those recorded in suspensions appear on the mineral background.

In the various procedures used, the disintegration of fossil and of pyrolysed conchiolin reflects the increase in brittleness of the matrix remnants (2).

Diagenesis, metamorphism and experimental pyrolysis of mother-of-pearl (3).

Biochemical factors, among which enzymatic autolysis, hydrolysis, oxidation, solubility in water, microbiological decomposition, pH of environmental sediment, influenced by selective physical agents such as gravity (MÜLLER, 1957; VALLENTYNE, 1962, 1964; BATHURST, 1964; LOWENSTAM, 1964) are especially operative during the initial stages of diagenesis in organic substances. The postdepositional changes in these substances develop generally at temperatures and pressures similar to those at the surface of the earth (Prof. R. G. C. BATHURST, personal communication). Geophysical factors, such as static and tectonic pressures, and temperature, in the absence of oxygen, are predominantly involved in the subsequent metamorphic stage. A clear cut distinction between the two stages is however difficult to establish, because of the intermingling of the two groups of processes (PETTIJOHN, 1957).

(2) (Addition on galley proofs).
The reliability of these methods has been recently questioned by ERBEN, FLAJS and SIEHL (1968, p. 12) :

« Die zur Untersuchung der organischen Bestandteile angewandte Methode hat den Nachteil, dass das Conchiolin durch Ultraschallbehandlung in dünne, unzusammenhängende Fetzen zerrissen wird, deren ursprüngliche Orientierung nicht rekonstruierbar ist. Auch bleibt die Abhängigkeit der nach dieser Behandlung beobachteten Strukturen von der mechanischen Beanspruchung zunächst unbekannt. Da überdies die Präparation niemals exakt reproduzierbar ist, wurde von einer weiteren Auswertung der obigen Ergebnisse abgesehen. »

Destruction of the conchiolin matrices by ultrasonic irradiation into unrecognizable, torn shreds only takes place after protracted exposure and use of too high intensities.

In this and former studies, ultrasonic irradiation has been used merely in order to delaminate the interlamellar conchiolin sheets of mother-of-pearl, firmly adhering to each other after decalcification, as reported above. Fragmentation of these sheets into shreds did not conceal the pattern of structure, especially in modern materials.

Original orientation of conchiolin in the shell architecture has been routinely and simultaneously appreciated by using replication procedures (GRÉGOIRE, 1957, 1962, 1966). Comparison of the results obtained by the two methods has mostly shown identity between the conchiolin matrices liberated by decalcification and those revealed by etching, and lying undisturbed on the original mineral background. The two methods are complemental. Compare pl. 2, Figs. 1-6; pl. 3, Figs. 1 and 2; pl. 4 (GRÉGOIRE et al., 1955); Fig. 39 (GRÉGOIRE, 1962); pl. 1, Fig. 1 (GRÉGOIRE and TEICHERT, 1965); Fig. 1 (GRÉGOIRE, 1966) with pl. 251, Figs. 1-3; pl. 252, Figs. 4-6 (GRÉGOIRE, 1957) and especially with Fig. 80 (GRÉGOIRE, 1962).

Examination of the above mentioned figures of conchiolin matrices recorded during the last 19 years using the questioned procedure shows that the preparations are consistently reproducible.

(3) The term « paleization », introduced by FLORKIN (1966), defines the sum of biochemical alterations undergone since death by the organic, especially protidic substances of a fossil. It includes all the changes developed during diagenesis and metamorphism.

In contrast with many organic fossil structures, the conchiolin matrix, sheltered between the mineral layers which alternate with it in architecture of mother-of-pearl, escaped the influence of several of the diagenetic factors, as long as its mineral shielding remained intact. On the other hand, in spite of their mineral protection, increase in temperature, one of the chief factors of metamorphism, influences rapidly, if not homogeneously (see below), the conchiolin structures.

On the basis of data furnished by the geothermal gradient, many shells were exposed during fossilisation to temperatures not exceding the ranges of 150 °C to 250 °C. Temperatures in the ranges of 400 ° to 900 °C, used in the present study, are found only in close proximity to the igneous material of the earth crust (BIRCH, 1965; MAXWELL, 1960). However, as pointed out by GRIGGS (1940) in his experimental investigations on rock formation, changes similar to those found in nature, could be realized in experimental conditions which were not necessarily identical.

In pyrolysis in open vessels (group 1), oxidative processes play a role in conchiolin degradation when the hard, impermeable nacreous substance becomes brittle and cleavable into sheets composed themselves of various numbers of mineral lamellae (300 °C - 400 °C samples), and are further frayed into booklets of diverging elements (500 °C - 800 °C samples).

In fragments exposed to protracted ebullition in open vessels (group 2), only the conchiolin shreds at the edge of the fragments underwent influence of oxidation, whereas temperature alone affected the organic substance in the central portions of these fragments.

In pyrolysis in the absence of oxygen (group 3), temperature and a certain degree of pressure (4) (not measured) developed by volatile constituents resulting from decomposition of the organic substances (see table 1), were the factors involved in the alterations. In this group, the changes in the samples heated above 300 °C were related to metamorphism rather than to diagenesis.

The present results illustrate the role of oxidation in conchiolin breakdown, already established in former biochemical investigations (5) : under identical conditions of temperature, the structural alterations were distinctly more intense in group 1 than in groups 2 and 3, especially in the samples heated above 300 °C. In fragments of mother-of-pearl boiled for 58 hours in sea mud and sea water, and dry heated accidentally for a few minutes at the end of the treatment (see table 1, group 2, 761 C), conchiolin was disintegrated into corpuscles, as in the 300 °C samples heated in open vessels (Fig. 21), whereas in the fragments still buried in the wet

(4) Flattening of the remnants could possibly be caused by compression of the interlamellar and intercrystalline conchiolin matrices under the combined action of expansion in volume of the mineral phase during conversion of aragonite into calcite and of the pressure exerted by the volatile constituents.

(5) Amino acid degradation is greatly enhanced in the presence of oxygen (ABELSON, 1957). Biochemical composition differs in shells heated in open vessels and under vacuum in sealed tubes (JONES and VALLENTYNE, 1960).

mud, the nautiloid pattern was only slightly altered (see Figs. 39, 41 and 43).

Similarities in structures of pyrolysed and fossil mother-of-pearl.

Alterations in mineral components.

In agreement with former observations of KLEIN (1883: quoted by MÜGGE), MÜGGE (1901), HINTZE 1930), and LANDER 1949), conversion of aragonite into calcite occurred in mother-of-pearl heated above 400 °C, in open vessels and in sealed tubes (6).

Preservation of aragonite in samples boiled for 17, 42, 53 and 58 hours in sea mud and in sea water exemplifies the greater stability of skeletal aragonite compared with that of inorganic aragonite. The latter is rapidly transformed into calcite at temperatures lower than 100 °C (WRAY and DANIELS, 1957; HALL and KENNEDY, 1967). As suggested by these authors, the presence of an organic matrix of conchiolin might explain in part preservation of aragonite in many Mesozoic shells (GRANDJEAN et al., 1964, HALL and KENNEDY, 1967).

Increase in brittleness and in cleavability, change of pale, pink and green iridescence into glowing dark metallic tints, observed in the nacreous fragments of *Nautilus* heated in open vessels and under vacuum in the ranges of 200 °C - 300 °C closely resembled the modifications of mother-of-pearl in shells of several Cretaceous nautiloids and ammonoids from various formations (e.g. RIPLEY formation: CONRAD, 1858; WADE, 1926).

On the other hand, dry heat alone was unable to reproduce in the nacreous layer of *Nautilus* the hardness and honey-brown colours which characterize the alterations of the shell wall in several Devonian nautiloids (e.g. large specimens from Eifel) and in Jurassic ammonites (e.g. *Harpoceras, Arietites, Pleuroceras, Phylloceras, Androgynoceras, Eoderoceras, Ovaticeras, Hildoceras, Porpoceras, Eleganticeras, Tragophylloceras,* Ammonites from « Marston ammonite marble »). These kinds of alterations were simulated to a certain degree in experiments in which temperature and pressure were applied simultaneously (GRÉGOIRE and LORENT, unpublished).

(6) Calcium hydroxide, recorded in the 600 °C - 800 °C samples resulted probably from hydration of calcium oxide formed by pyrolysis during cooling and preparation of the samples for X-ray diffraction.

As shown in description, titriplex dissolved completely the fragments heated in sealed tubes to temperatures of 600 °C - 900 °C, whereas in the samples heated in these ranges of temperatures in open vessels, an abundant white mud left after immersion of the fragments in titriplex or in 3 per cent solutions of hydrochloric acid could only be dissolved in large amounts of 25 per cent solutions of hydrochloric acid. These differences are possibly due to variations in the amounts of calcium hydroxide in the samples of the two groups. However, these variations were not measured. X-ray diffraction revealed the presence of small amounts of calcium hydroxide within the organic residues of a few samples (778, 779 in table 1).

Alterations in organic components.

Denaturation, melting and expansion are among the chief thermal effects on proteins reported in literature (see POLLARD, 1964).

Part I of this study is limited to the morphological aspect of pyrolysis in conchiolin matrix of mother-of-pearl on the electron microscope scale. The literature on artificial simulation by temperature in modern materials of changes in biochemical composition of fossil shells will be reviewed in Part II of this study.

The present data (see table I) show that pyrolysed conchiolin of mother-of-pearl from the modern *Nautilus* shell and the residual matrix of fossil mother-of-pearl have in common several characteristics, listed below:

1. As in fossil shells, decalcification of the pyrolysed nacreous substance took place with emission of various pungent smells.

2. As in fossil shells, conversion of aragonite into calcite did not destroy the organic components in the heated samples.

3. The mahogany-brown (in samples heated to 200°C - 300 °C) and black (in samples heated to 400 °C and above) colours are constant findings in the organic residues of decalcification in fossil shells.

4. Biuret - positive shreds were uniformly recorded, with variations in intensity of the reaction, in the residual matrix of nacreous layers from fossil shells of various ages, including Ordovician, and in pyrolysed conchiolin of modern mother-of-pearl, including samples heated to 900 °C.

In agreement with the results of the biuret reaction, Mrs. VOSS-FOUCART has detected polypeptide assemblages in the present pyrolysed material, including the samples heated to 900 °C for 5 hours (see Part II).

These findings are consistent with biochemical data concerning preservation, in fossil shells of various ages, of residues of organic matter in the form of peptides, polypeptides and assemblages of amino acids characteristic of conchiolin scleroproteins (Pleistocene : JONES and VALLENTYNE, 1960; Pliocene and Recent : TONG YUN HO, 1966; Tertiary : DEGENS and LOVE, 1965; Eocene and Oligocene : FLORKIN, GRÉGOIRE, BRICTEUX-GRÉGOIRE and SCHOFFENIELS, 1961; Pennsylvanian, Hare, quoted by LOWENSTAM, 1963; Jurassic and Silurian, in Brachiopods : JOPE, 1967).

Thermal energy has been used for polymerization of free amino acids to polypeptides. The resulting products can contain the eighteen amino acids common to proteins (FOX and MIDDLEBROOK, 1954; HARADA and FOX, 1964; FOX, 1964; HARADA, 1967; ROHLFING, 1967). One might suppose that a part of the organic structures detected in the samples heated in the ranges of 700 °C and 900 °C, could be similar products of repolymerization of amino acids and not true residual conchiolin. However, records of the successive steps of degradation of the nacreous matrix from 150 °C to 900 °C and presence in the 800 °C and 900 °C samples of remains, still recognizable, of the original nautiloid pattern (e.g. Fig. 80) preclude this interpretation.

Other data in litterature suggest that the remarkable resistance of conchiolin to pyrolysis might be explained by a kind of stabilization caused by the surrounding mineral matter (see above in this discussion). Thermal stabilization of amino acids is considerably enhanced when these acids are heated in the open air in presence of minerals such as kaolinit and especially montmorillonit (BRODMEIER, 1963; KROEPELIN, 1962, 1967). These data will be discussed in Part IV of this study.

5. Several alterations produced by pyrolysis in conchiolin structure of mother-of-pearl are closely similar in their morphological features to those described previously in organic remnants of fossil mother-of-pearl prepared by the same procedures (see table 1 and 2).

In fossil materials, these alterations consist of flattening, broadening, thinning, curling, shrinkage and conversely of swelling of the trabeculae in the conchiolin matrix. In more advanced stages of degradation, the trabeculae are fragmented into twisted segments and finally dislocated into lenticular or spheroidal, pebble-shaped corpuscles of various sizes. In another type of alteration, the matrix is fused into membranes, frequently perforated, and the products of disintegration of these membranes appear in the form of ribbons, strands and blades.

In some shells, substantial bundles of fibrils formed large portions of the residues of conchiolin breakdown.

The type of alteration of nacreous conchiolin in the form of spheroidal pebble-shaped corpuscles, predominant in samples heated in open vessels, has been found in remnants of mother-or-pearl from fossil shells of all ages and formations (see tables 1 and 2; Figs 21-27) and especially in weathered shell fragments.

The kind of alteration in the form of fragments of perforated membranes, which characterizes the pyrolysed conchiolin matrices in the samples heated in the absence of oxygen seems to be frequent in Paleozoic and in Jurassic shells (Figs. 52-72; see also GRÉGOIRE, 1966, Figs. 5, 6, 7, 12 and 14).

In several instances, the similarities between fossil and pyrolysed material aided in identification of structures of doubtful origin, such as the organic components of the cameral deposits in Paleozoic nautiloids (7) (see table 2, p. 56).

(7) Among the biuret-positive remnants of decalcification of the soft, crumbly substance filling the central portion of the cameral deposits in the Pennsylvanian nautiloid *Pseudorthoceras knoxense*, were clusters of pebble-shaped corpuscles (Fig. 11), identical to those obtained artificially in conchiolin from samples heated in open air to 225 °C for 21 days (Fig. 10), and perforated membranes, ribbons and flakes (Fig. 62), resembling those recorded in samples heated to 275 °C, 300 °C and 400 °C for 5 hours in tubes sealed under vacuum (Figs. 50, 52, 58).

These observations support the former interpretation (GRÉGOIRE and TEICHERT, 1965) that at least a part of these structures would result from exfoliation of nacreous substance from the mural and septal surfaces of the camerae.

6. As in fossil shells (mineral components : TUREKIAN and ARMSTRONG, 1961; organic components : GRÉGOIRE, 1966) the degrees in alteration of pyrolysed mother-of-pearl varied in the different samples and in different portions of the same sample.

Differences in intensity of the biuret reaction in limited portions of conchiolin matrix, scattering of dark violet and purple speckles in the homogeneous lilac background of the conchiolin shreds reflect local variations on the microscope scale in the degree of degradation of the peptide bonds. The paradoxical increase in intensity of the lilac tints noted in the shreds from the samples heated to 800 °C and 900 °C (table I) might be explained by limited local coalescences, condensations and shrinkages of conchiolin debris still containing peptide bonds.

In fossil as in pyrolysed materials, the samples constitute « complexes of alterations products ». Results obtained on single fragments might not be representative.

In spite of the close similarities between fossil and pyrolysed organic materials, the complexities of interaction between the multiple factors involved in fossilisation (paleization) (see note 3, p. 11) preclude any direct extrapolation of the conditions realized artificially in part I of the present study, limited to a single factor, to those operative during diagenesis and metamorphism.

Nature of some particular structures in pyrolysed nacreous conchiolin.

The Spherulite-like corpuscles observed in the 225 °C - 21 days, 250 °C - 5 hours and 275 °C - 5 hours samples (Figs. 12-16) seem to derive from the rounding up of dense portions of matrix preserved with their nautiloid pattern intact in limited islands among the other products of disintegration of the trabeculae. Most of these structures are purely organic (Fig. 14). Others may contain crystalline material (Fig. 16), possibly entrapped in the trabeculae and escaping demineralization.

The fragmentary data so far collected on the inner structure of the trabeculae in nacreous conchiolin matrix have been reviewed elsewhere (GRÉGOIRE, 1966b, 1967). Biochemical separation of conchiolin fractions (GRÉGOIRE, DUCHÂTEAU and FLORKIN, 1955) and observations in the electron microscope (GRÉGOIRE, and al., 1955; GRÉGOIRE, 1960; TRAVIS, FRANÇOIS, BONAR and GLIMCHER, 1967) *suggest that fibrils are involved* in the constitution of the lamellar reticulated sheets of conchiolin matrix. The relations of these fibrils dispersed outside the fragments of matrix, with ill-defined, tight networks of unoriented microfibrils observed within the trabeculae (see Fig. 40) are not elucidated. Fibrils scattered or grouped in bundles of parallel elements, have been also recorded in nacreous organic remnants of fossil shells of various ages, including Ordovician (GRANDJEAN and al., 1964; GRÉGOIRE, 1966b).

As shown in the descriptive part of this study, fibrils were found among the various debris of conchiolin pyrolysis (Figs. 30, 32, 33, 34), especially in the samples heated to high temperatures (700 °C - 900°C : Figs. 35 and 88). The origin of these fibrils is not clear. In the material heated in open vessels, these structures could be contaminants, such as air-borne dust adsorbed during cooling of the samples on the pyrolysed, highly porous or powdery nacreous substance. However, identical fibrillar materials were recorded in samples heated in sealed tubes, used immediately after tube breaking, which rules out possibility of contamination. These fibrils could be original conchiolin components, concealed in intact trabeculae by coatings of other substances, and revealed in pyrolysed materials by destruction of unstable conchiolin fractions.

Examined in unshadowed and in stained preparations, the various products of conchiolin pyrolysis were mostly amorphous (Figs. 28, 29, 31, 57, 58, 71, 73, 74, 79, 83), thinly granular (Fig. 60), or pitted by vesicles developed under the action of volatile constituents (Figs. 9, 83 and 84). Filament-like structures, about 10-20 Å in width, observed also in debris of fossil conchiolin (Fig. 72), were scattered at random (Fig. 81), or assembled in parallel arrays (Figs. 63. 73 and 74) in the fragments of membranes and along their edges (Fig. 79).

In view of the uncertainties concerning the organization of the normal conchiolin matrix (see legend of Fig. 40), the origin of these structures could not be determined. A granular appearance of membranes and of their fragments might be due to phase contrast effects associated with underfocusing. This explanation is not valid with regard to Figs. 29 and 89, in which opaque granules seem to form micronetworks. Folds in extremely thin veils could simulate fibrils (Figs. 73-74). Some of these microfilaments could be optical artifacts, due to association of layers of contamination by the beam and local defocusing (positive Fresnel fringes). Interference patterns in overlying membranes could also simulate fibrils (Fig. 63).

The concentric arrays of dark lines included in the ring-shaped thickenings which surround perforations in the membranes from samples heated to 700 °C - 800 °C in the absence of oxygen, could possibly indicate a layered organization of these membranes and of their fragments, visible in shadowed preparations (Figs. 53, 54, 55, 56, 58, 59, 61 and 80). Pressure of volatile constituents and expansion in volume of crystals during conversion of aragonite into calcite could produce flattening of the matrix, followed, after dissolution of the mineral lamellae, by collapse and subsequent coalescence of adjacent interlamellar sheets of conchiolin into stratified membranes.

As shown in description, the organic debris of the samples heated to 900 °C in sealed tubes appear to be included within polygonal systems. These systems represent ghosts of the former flaggings of aragonite crystals. Dissolution of these crystals left the residues of pyrolysed conchiolin as if they had been stiffened by heat in their original topography and orientation with regard to the crystals (Fig. 95). Arrangement of the conchiolin remnants on a membrane within a rectangular area (Fig. 86) could possibly be related to changes in mineral topography following conversion of aragonite into calcite.

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SUMMARY.

1. This paper is an electron microscope study of the alterations produced by temperatures in the ranges of 100 °C to 900 °C in mother-of-pearl of the modern *Nautilus* shell.

2. Fragments of nacreous layers of the shell wall in the living chamber were exposed for 5 minutes to 21 days to dry heat in open vessels and in quartz tubes sealed under vacuum or argon. Other fragments were boiled in sea mud and sea water.

3. In open vessels and in sealed tubes, conversion of aragonite into calcite took place in the samples heated at 400 °C and above. In the 600 °C - 900 °C samples, calcite was mixed with varying amounts of calcium oxide.

With elevation of temperature, the originally hard, compact and stratified mother-of pearl became progressively brittle, porous and cleavable into booklets of mineral sheets, each of them composed of groups of nacreous lamellae.

In the 200 °C - 300 °C samples, iridescence increased in intensity with glowing metallic tints. Iridescence disappeared above 400 °C in the open air, and persisted at higher temperatures in sealed tubes.

4. Demineralization of the pyrolysed fragments including the 800 °C (in open vessels) and 900 °C (in sealed tubes) samples, left biuret-positive conchiolin shreds.

The present results give evidence of the considerable resistance to thermal stress of conchiolin, sheltered between mineral lamellae.

5. Heated at the same temperature, the conchiolin structures were differently and distinctly less altered in the fragments pyrolysed in the absence of oxygen than in those heated in open vessels, in which the alterations were enhanced by oxidation.

Progressive fragmentation of the trabeculae of the matrix into branched rods and into spheroidal pebble-shaped corpuscles characterized the alterations in the conchiolin residues of the samples heated in open vessels.

Fusion and flattening of the interlamellar matrix into membranes, followed by dislocation of these membranes, were the predominant modifications in the fragments pyrolysed in the absence of oxygen.

In both groups of preparations, fragmentation of the matrix residues occurred, either spontaneously in the suspensions of the decalcified samples, or was slightly enhanced by mechanical dissociation (shaking, ultrasonic irradiation). The latter procedures were used in order to obtain structures permeable to the electron beam from condensed or firmly agglutinated organic shreds.

6. Protracted ebullition of mother-of-pearl in sea mud and in sea water for 17, 42, 53 and 58 hours did not destroy the nautiloid pattern of structure and caused only diffuse alterations in the trabeculae of the matrix.

7. The various kinds of alteration in ultrastructure of conchiolin matrix produced in mother-of-pearl of modern *Nautilus* by heat and oxidation (in open vessels), by heat and a certain degree of pressure (in tubes sealed under vacuum), were similar or identical to those recorded previously in residues of nacreous conchiolin matrix of Paleozoic and Mesozoic nautiloids and ammonoids. In the samples heated to 800 °C and 900 °C, new structures developed, which had not yet been detected in the organic debris of fossil mother-of-pearl.

8. Pyrolysis of shells of modern molluscs can furnish information for identification of fossil remnants of conchiolin matrix in which the original structure pattern is no more recognizable and could be confused with foreign organic contaminants.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	Description
1. *Dry heat in open vessels.*			
(721) 20 °C (control)	Aragonite	Very hard. Fragments break without cleavage. Iridescent with pale, greenish, and pink hues. Inodorous during and after sample decalcification.	Abundant, soft, transparen[t] iridescent shreds.
(721) 150 °C 5 hours See group 3 : (801) Fig. 44	Aragonite	Hard. Fragments break with moderate cleavage. Slight, diffuse burnishing with increase of green and pink hues in iridescence. Smell of petroleum during decalcification.	Abundant, transparent an[d] whitish, iridescent shred[s]
Fossil records of similar alterations.			
(731) 150 °C 11 days	Aragonite	Moderately brittle. Fragments easily cleavable into bronze-coloured, strongly iridescent sheets with intense metallic (red, violet and green) hues. Putrid smell during decalcification.	Abundant, mahogany-brow[n] strongly iridescent shred[s]
Fossil records of similar alterations.			

in mother-of-pearl *(Nautilus)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets).
+ to +++	Conchiolin Matrix : Nautiloid pattern : sturdy, irregularly cylindrical trabeculae or cords, studded with hemispheric protuberances; mostly elongated fenestration (see GRÉGOIRE *et al.*, 1955 (Pl. 3 and 4); GRÉGOIRE, 1962 (Fig. 39); 1966 (Figs. 1, 2 and 3); (Fig. 1)).
+ to ++	Nautiloid pattern unchanged. Diffuse swelling of portions of trabeculae (Fig. 2).
	Matrix of nacreous conchiolin of Buckhorn asphalt nautiloids (Pennsylvanian).
-	Nautiloid pattern preserved. Swelling of trabeculae in certain areas of the matrix, shrinkage in other portions, the latter modifications accompanied by increase in contrast of the trabeculae in these portions (Fig. 4).
	Matrix of nacreous conchiolin of Buckhorn asphalt nautiloids (Pennsylvanian). See also below, 225 °C samples (Figs. 5 and 6).

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples: degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(734) 150 °C 13 days	Aragonite	Hard. Breaks with moderate cleavage. Burnishing of iridescence on outer surfaces of fragments. Bright metallic hues on freshly cleaved surfaces.	Abundant, rigid, yellowis[h] shreds.
(731) 150 °C 19 days	Aragonite	Brittle. Fragments easily cleavable into strongly iridescent sheets, with intense metallic hues. Putrid smell during sample decalcification.	Mahogany-brown shreds.
(721) 200 °C 5 hours See group 3 (802)	Aragonite	Brittle. Fragments easily cleavable into bronze-coloured, iridescent sheets with bright metallic hues. Putrid smell during sample decalcification.	Abundant, mahogany-brow[n] soft shreds.
Fossil records of similar alterations.		As in the 150 °C-200 °C samples: appearance and consistency of undecalcified nacreous substance of the shell wall in many Cretaceous ammonites (e.g. *Placenticeras, Baculites*)	
(721-225-15) Preheating: 20 °C to 225 °C: 2 minutes 30 seconds. 225 °C: 10 minutes.	Aragonite	Brittle. Fragments cleaved in part into thin sheets. Diffuse burnishing of iridescence on outer and freshly cleaved surfaces. Smell of petroleum during sample decalcification.	Rigid, iridescent shreds.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix *(trabeculae of the reticulated sheets)*
+	1. Nautiloid pattern unchanged in portions of matrix. 2. In other portions, shrinkage of trabeculae resulting in increase of contrast and rounding up of fenestration. 3. In other portions, predominant alteration of trabeculae consisting of swellings separated by constrictions.
+	Alterations as in (734) Beginning of fragmentation of trabeculae by separation of their swollen parts into irregularly spheroidal corpuscles, about 70 millimicrons in diameter. (Fig. 3).
+ and ++	1. Nautiloid pattern unchanged in portions of matrix. 2. In other portions, swelling of trabeculae and fragmentation into spheroidal corpuscles. 3. In many other fragments, constriction and increase in density of trabeculae, resulting in broadening of fenestration.
	As in (734) (731) (721 - 200 °C) : Matrix of nacreous conchiolin of Buckhorn asphalt nautiloids.
++	Alterations as in (721) - 200 °C sample 1, 2, 3. Local shrinkages and alternating swellings and constrictions in trabeculae, frequently associated in the same regions of reticulated sheets.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(721) 225 °C 5 hours	Aragonite	Brittle. Scattered lenticular swellings on the exposed surfaces. Beginning of spontaneous cleavage. Burnishing of iridescence on the exposed surfaces. Intense metallic hues on the cleavage surfaces. Putrid smell during sample decalcification.	Mahogany-brown shreds.
(721) 225 °C 21 days (3 different samples) See group 3 : (770, 772) Figs. 45, 46, 47, 48	Aragonite	Very brittle : fragments spontaneously cleaved into sheets. Exposed surfaces : smoke-brown. Cleavage surfaces : intense metallic hues.	Mahogany- and orange- coloured shreds.
Fossil records of similar alterations.			
(721) 250 °C 5 hours (4 samples) See group 3 : (803)	Aragonite	Brittle. Fragments cleavable into thin mineral sheets. Burnishing of iridescence on exposed surfaces. Cleaved sheets strongly variegated. Intense smell of petroleum during sample decalcification.	Mahogany-brown shreds.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
++	Alterations as in (721) - 200 °C - 5 hours and (721) - 225 °C - 10 minutes samples. Beginning of fragmentation of swollen trabeculae into rods and spheroidal corpuscles. Dissociation of these corpuscles into thinly granular materials (Figs. 5, 6, 7 and 8).
+	1. Disappearance of the nautiloid pattern, except in fragments of reticulated sheets characterized by highly contrasted, shrunk trabeculae and broadened fenestration, as in the 150 °C, 200 °C, and 225 °C - 5 hours samples. 2. In other regions of the matrix, general dissociation of the trabeculae into rods, spheroidal or lenticular corpuscles and into small, pebble-shaped bodies and granules. 3. Large, spherulite-like, oval or spheroidal corpuscles, composed of branched, frequently diverging trabeculae (Figs. 12, 13, 14, 15 and 16).
	As in 225 °C - 21 days samples, alterations in organic remnants of the soft, central, crumbly, cocoa-brown matter of the cameral deposits in *Pseudorthoceras knoxense* McChesney, nautiloid, Buckhorn asphalt, Pennsylvanian. See Table 2. Compare Fig. 11 with Fig. 10. (see also Grégoire and Teichert, 1965, Pl. VI, Fig. 2).
++ Bright, brick-red spots scattered in the violet flakes.	Nautiloid pattern preserved in fragments of reticulated sheets, including those characterized by dense trabeculae. Transitional structures between these fragments and the spherulite-like bodies observed in the (721) - 225 °C - 21 days samples. Other trabeculae variously dissociated into branched rods and corpuscular structures. Pitted appearance of many of these structures.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
Fossil records of similar alterations.			
(721) 275 °C 5 hours See group 3 : (804) Figs. 49 and 50	Aragonite	Brittle. Portions of fragments cleaved into iridescent sheets. Strong metallic hues on the cleavage surfaces. Smell of petroleum during sample decalcification.	Rust-coloured and black-brown shreds.
Fossil records of similar alterations.			
(721) 300 °C 5 hours (4 samples) See group 3 : (782) (Figs. 51, 52, 53)	Aragonite	Very brittle. Fragments easily cleavable into sheets. Burnishing of iridescence on exposed surfaces. Surfaces of cleavage strongly iridescent with intense metallic hues. Smell of petroleum during sample decalcification.	Reddish and bright mahogany-coloured particles.

in mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets).
	As in the 250 °C - 5 hours samples: pitted appearance of rod-like or pebble-shaped corpuscles in conchiolin remnants of samples of *Aturia* sp. (Oligocene). (See GRÉGOIRE 1959, Figs. 15 and 16).
+ + Yellow flakes with scattered purple and violet speckles. Red blocks and clusters of filaments.	Nautiloid pattern preserved in a few fragments. Predominantly fragmentation of trabeculae into branched rods and irregularly spheroidal corpuscles, including small pebble-shaped bodies (see GRÉGOIRE, 1966, Fig. 23).
	Alterations as in 225 °C - 21 days, 250 °C and 275 °C - 5 hours samples in conchiolin remnants of mother-of-pearl from Paleozoic and Mesozoic nautiloids and ammonoids, e. g. *Harpoceras mulgravium* (SIMPSON, YOUNG and BIRD), Jurassic (see GRÉGOIRE, 1966, Figs. 40 and 41); *Eoasianites hyattianus* (GIRTY), Buckhorn asphalt, Pennsylvanian (see GRÉGOIRE and TEICHERT, 1965, Pl. XI, Fig. 1; GRÉGOIRE, 1966, Fig. 35). Compare Figs. 17, 18 and 19 (250 °C and 275 °C samples) with Fig. 20 (unidentified cephalopod from Buckhorn asphalt). Trabecular remnants of mother-of-pearl of the Eocene nautiloid *Aturia* sp. have a pitted appearance as some debris of trabeculae in the 250 °C sample (see GRÉGOIRE, 1959 a, Figs. 15 and 16).
+ + Pale, pink granules and purple spots scattered in a transparent jelly.	Clusters of lenticular and spheroidal bodies (Fig. 21). Scattered fibrils.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
Fossil records of similar alterations.		Alterations as in the 150 °C-19 days, 200 °C, 225 °C, 225 °C - 21 days, 275 °C, and especially 300 °C samples : Mother-of-pearl of the shell wall of many ammonoid and nautiloid genera from various ages, e.g. : 1. Jurassic (*Rasenia, Dactylioceras, Paltopleuroceras, Amaltheus, Quenstedticeras, Psiloceras, Leioceras*), also including several specimens from the russian Jurassic horizons (e.g. *Virgatites, Craspedites, Garniericeras, Perisphinctes, Proplanulites*). 2. Cretaceous, including many ammonoid and nautiloid genera from S. Dakota, Montana, Mississippi, Kansas (e.g. *Baculites, Sphenodiscus, Acanthoscaphites, Discoscaphites, Scaphites, Hoplites, Placenticeras, Collignoniceras, Eutrephoceras*). 3. Eocene (*Nautilus, Aturia*). In all the fossil shells listed above, the nacreous substance is generally of harder consistency than the heated modern material.	As in the 225° C — 21 days 250 °C, 275 °C and 30[illegible] °C - 5 hours samples, similar mahogany-brown remnants of mother-of-pearl i[illegible] many Paleozoic and Mesozoic ammonoids and nautiloids, some listed in th[illegible] adjacent column.
(721) 150 °C (5 hours) 300 °C (4 hours)	Aragonite	As in the 300 °C sample (stronger metallic hues).	Mahogany-brown particles

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
	Clusters of mostly small granules and a few larger pebble-shaped corpuscles.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples: degree of hardness, cleavability, colour, smell before or during decalcification	Description
(721) 400 °C 5 hours (3 samples) See group 3: (783) Figs. 55 and 56	Calcite	Very brittle. Fragments cleaved into booklets of iridescent steel-coloured sheets, with faint metallic hues.	Brown-black shreds an particles.
Fossil records of similar alterations.		Poorly preserved nacreous layers of Jurassic (e.g. Oxfordian *Kosmoceras, Cardioceras* and *Gulielmiceras*) and Cretaceous (e.g. *Baculites, Discoscaphites, Scaphites, Hoplites*) specimens.	
(721) Preheating (20 °C to 500 °C): 2 min. 30 sec. 500 °C: 10 min.	Calcite	Very brittle. Fragments cleaved into booklets of uniformly slate-coloured and ash-grey, bright or lustreless sheets. Faint traces or iridescence. Smell of cyanhydric acid and of H_2S during sample decalcification.	Brown-black particles.
Fossil records of similar alterations.	As in (721) 500 °C - 10 min. X-ray type of calcite in some Ordovician (454) Permian 422 A 80) and Jurassic (529, 538, 540) undecalcified mother-of-pearl.		

in mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
- aintly pink and bright purple granules scattered or clustered in a yellow jelly.	Clusters of pebble-shaped bodies, 10-72 mμ in diameter, and granules of smaller size (Fig. 22).
-+ lusters of pink grains.	Alterations as in the 400 °C sample : Pebble-shaped, spheroidal bodies of various sizes, clustered in microflocs.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(721) 500 °C 5 hours *(5 samples)* See group 3 : (780) Figs. 67, 68 and 72	Calcite	Very brittle. Cleaved into lustreless limestone — coloured sheets. Strong smell of petroleum *during sample decalcification.*	Black, dark smoke-brow and grey-brown particle
(721) 600 °C 5 hours (3 samples) See group 3 : (779) Figs. 75 and 76	Calcite and $Ca(OH)_2$	Brittle. Fragments cleaved into lustreless, snow-white (outer portion) and ash-grey (inner portion), sheets, disintegrating into powder. Smell of H_2S during sample decalcification.	A few dark-brown and blac particles. Abundant mineral remnan appearing in the form c black and grey muds.
Fossil records of similar alterations.			

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets).
– right purple spots scattered in the violet particles. Many colourless flakes.	As in the 500 °C - 10 minutes stage. (Fig. 23).
– Clusters of faintly pink grains.	Clusters or irregularly spheroidal corpuscles of various sizes (Fig. 24), some appearing as if thinly perforated by a network of holes. Unidentified bundles of fibrils. Crystals resisting decalcification.
	Pebble-shape type of alteration (300 °C - 600 °C samples). Under the conditions of preparation selected in the present studies, the kind of alteration of the nacreous reticulated sheets of conchiolin consisting of dislocation of the trabeculae into pebble-shaped corpuscles has been found, mixed with other kinds of alteration (see GRÉGOIRE, 1966) in nacreous conchiolin remnants of nautiloids and ammonoids from all ages, e. g. in the nautiloid *Faberoceras* sp., Upper Ordovician (see GRÉGOIRE, 1966, Fig. 5), in several Devonian, Carboniferous, Permian, Jurassic and Cretaceous specimens. (GRÉGOIRE 1966, Figs. 11, 13, 14, 21, 24, 25, 35-37, 40, 41). Similar alterations are frequent in diagenetically weathered portions of nacreous layers of various nautiloids and ammonites from Buckhorn asphalt, in which lace-like reticulated sheets of conchiolin are remarkably preserved in other portions.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(806) Preheating (20 °C to 700 °C) : 15 min. 700 °C : 10 min	Calcite	Brittle. Fragments cleaved into booklets of ash-grey, lustreless sheets, disintegrating into powder. Smell of H2S during sample decalcification.	Black-brown particles.
(807) 700 °C Preheating (20 °C to 700 °C) : 15 min. 700 °C : 60 min.	Calcite	As in the 10 min. stage (806)	Black particles.
Fossil records of similar alterations.			
(721) 700 °C 5 hours (4 samples) See group 3 : (778) Fig. 77	$Ca(OH)_2$ and traces of calcite.	Brittle. Fragments thoroughly cleaved into snow-white, powdery sheets with faintly yellowish tints.	Scarce, brown and gre particles. No residue in one sample.

in mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets).
+	Clusters of pebble-shaped, irregularly spheroidal corpuscles of various sizes (7 mμ - 100 mμ), appearing as pitted by networks of cavities.
+	Figs. 29, 30, 31, 32 and 33. Alterations as in (806). Substantial bundles of fibrils associated with the corpuscles (Figs. 30, 32 and 33).
	As in (806) and (807) samples. Similar associations of fibrils and corpuscles were observed e.g. in *Harpoceras mulgravium* SIMPSON, YOUNG and BIRD, ammonoid, (524), Lower Jurassic (Fig. 34) (see also GRÉGOIRE, 1966, Fig. 41, same specimen), in nacreous organic remnants of *Agoniatites vanuxemi* (704 — 10 E) (goniatite) Middle Devonian, of *Orthonybyoceras duseri,* nautiloid, Upper Ordovician, of *Faberoceras* sp., nautiloid, Upper Ordovician (GRÉGOIRE, 1967, Pl. 6, Figs. 5 and 6).
+	Alterations as in (806) and (807). Granular membranes resulting from coalescence of spheroidal bodies.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(808) Preheating (20 °C to 800 °C) : 15 min. 800 °C : 10 min. See group 3 : (817) Figs. 79 and 80	Calcite	Grey-white powder with traces of lamellation. Smell of H_2S during sample decalcification.	Scarce brown-black particles Filaments (see discussion)
(809) Preheating (20 °C to 800 °C) : 15 min. 800 °C : 60 min. See group 3 : (818)	Calcite $Ca(OH)_2$ (Portlandite)	Snow-white powder with grey patches of substance.	Scarce, black particles. Filaments resisting ultrasonic dissociation.
(721) 800 °C 4 hours (5 samples) See group 3 : (775) (776) Figs. 82, 83, 84 and 85	$Ca(OH)_2$	A few booklets of cleaved sheets and snow-white powder.	No residue or scarce dark brown particles.
Fossil records of similar alterations.			As in the 400 °C - 800 °C samples, dark brown and black particles in organic remnants of mother-of-pearl of Devonian shells (e.g. *Cyrtoceras, Striacoceras*).

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
+ Pink granular jelly.	Nautiloid pattern recognizable in a few fragments (not shown). Trabeculae of the nacreous reticulated sheets dissociated predominantly into clustered pebble-shaped corpuscles, many appearing as pitted by cavities or microvesicles (Fig. 36). Coalescence of the organic remnants into membranes and flakes. Substantial bundles of fibrils and of filaments.
+ (Fig. 35b)	Clusters of small pebble-shaped corpuscles associated with sturdy fibers, fibrils and microfilaments. Coalescence of the organic remnants into membranes. Vesicles of large size resulting possibly from local swellings in these membranes (not shown).
+ A few pink-violet flakes with scattered bright red spots. Red blocks. Spongy colourless networks.	Agglutinated trabeculae in which the nautiloid pattern is still recognizable (Fig. 37). Clusters of pebble-shaped bodies, vesicles, ovoid knobs (see GRÉGOIRE, 1966, pp. 6 and 15) and membranes resulting from coalescence of these structures. Abundant bundles of filaments and fragments of fibrillar networks mixed with the clusters of pebbles. Crystals resisting decalcification.
	As in the 800 °C (10 minutes to 4 hours) samples. Vesicles, some of very large size, others described previously as « knobs » in remnants of nacreous conchiolin from several Paleozoic nautiloid and ammonoid shells, e. g. *Eoasianites* sp., ammonoid, Buckhorn asphalt, Pennsylvanian (see GRÉGOIRE and TEICHERT, 1965, Pl. IX, Fig. 2; GRÉGOIRE, 1966, Fig. 34).

TABLE 1. — Thermal change

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples: degree of hardness, cleavability, colour, smell before or during decalcification	Description
2. *Repeated boiling of mother-of-pearl in mixtures of sea mud and sea water, alternating with*			
(886-2) Total boiling time: 42 hours. Total duration of the treatment: 47 days.	Aragonite	Very hard. Slight burnishing of iridescence (pink violet hues) on exposed surfaces.	Bluish particles
(886-1) Total boiling time: 58 hours. Total duration of the treatment: 47 days.	Aragonite	Very hard. Fragments iridescent with pink hues.	Many transparent bluis particles, more resistant ultrasonic dissociation tha particles in 886-2.
(761 A) Total boiling time: 17 hours. Total duration of the treatment: 26 months.	Aragonite	Very hard. Slight burnishing of iridescence on exposed surfaces (pink hues). Colours unchanged on surfaces of fracture. Inodorous during sample decalcification.	Rigid, transparent shre resisting ultrasonic diss ciation.
(761 C) Total boiling time: 53 hours. Total duration of treatment: 28 months At the end of experiment, accidental dry heating (250 °C-300 °C) for approximately 30 minutes, followed by rapid cooling in sea water, with intense emission of vapour.	Aragonite	Moderately hard to very brittle. Slight burnishing of iridescence to intensely iridescent with green hues. Smell of petroleum during sample decalcification.	Rigid, transparent, iridesce and bluish flakes resisti ultrasonic dissociation. Bright, iridescent and mah gany-brown particles.

n mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
sedimentation at 20 °C in the same environments for various lengths of time.	
+	Nautiloid pattern preserved (Figs. 41 and 42) Alteration of the nacreous matrix consisting of diffuse shrinkage and transformation into membranes by coalescence of the trabeculae and obturation of the openings. The hemispheric protuberances appear as sharply delimited, flattened domes on the trabecular surfaces.
+	Alterations as in 886-2 (Fig. 43).
+ to ++	Nautiloid pattern preserved. Alteration of the reticulated sheets in the form of diffuse flattening and fusion of the trabeculae. Protuberances still visible (Fig. 39).
+	Nautiloid pattern preserved in many fragments in which alterations are diffuse and consist of moderate flattening and coalescence of trabeculae. In other fragments, exposed to dry heat for 30 minutes at the end of the treatment, the organic remnants appear variously disintegrated, as in group 1, 250 °C - 300 °C samples.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples: degree of hardness, cleavability, colour, smell before or during decalcification	Description
3. *Dry heat in the absence of oxygen or in argon atmosphere (sealed quartz tubes)*			
(801) 150 °C 5 hours See group 1: (721)-150 °C Fig. 2	Aragonite	Faint smell of H_2S on breaking tube. Hard. Fragments break without cleavage. Slight burnishing of iridescence on exposed surfaces.	Iridescent shreds.
(802) 200 °C 5 hours See group 1: (721) 200 °C Fig. 4	Aragonite	On breaking tube, pungent smell of H_2S and of burned horn. Decrease in hardness. Fragments cleavable into iridescent sheets with intense bronzed and green tints on the cleavage surfaces. Smell of petroleum during sample decalcification.	Yellow to mahogany-coloured shreds.
(770-772) 225 °C Argon 21 days See group 1: (721)-225 °C 21 days Figs. 10, 12, 13, 15.	Aragonite	On breaking tube, pungent smell of H_2S, burned horn and NH_3 Decrease in hardness. Fragments cleavable into iridescent sheets, with intense metallic hues on the freshly cleaved surfaces. Strong putrid smell during sample decalcification.	Brown shreds.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
++	Slight diffuse alteration of the nautiloid pattern in portions of matrix: shortening and condensation of trabeculae, hypertrophy of protuberances, rounding up of fenestration. (Fig. 44). In other areas of the matrix, no distinct change or some degree of coalescence of trabeculae with local disappearance of fenestration.
++	Nautiloid pattern preserved over large areas of the reticulated sheets. Alterations consisting of general shortening and condensation of trabeculae and rounding up of fenestration. Beginning of fragmentation of trabeculae into rods and irregularly spheroidal particles. Scattered fibrils.
+ and ++ straw-coloured particles.	Nautiloid pattern recognizable. Alteration in trabeculae of matrix consisting predominantly of coalescence (Figs. 46, 47, 48), flattening into ribbons, (Figs. 46, 47, 48) and fragmentation (Fig. 45). The protuberances seem to have disappeared (Fig. 47) or to be reduced in number and swollen into spheroidal corpuscles, which protrude onto the ribbons or are detached from the trabecular surfaces. (Figs. 45 and 48).

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
Fossil records of similar alterations.		As in the 225 °C - 21 days sample (770-772 : group 3) and in the 150 °C - 19 days to 300 °C samples of group 1 (see above), intense metallic hues in nacreous layers of Jurassic and Cretaceous ammonites from various formations.	
(803) 250 °C 5 hours See group 1 : (721)-250 °C Fig. 17	Aragonite	On breaking tube, pungent, persisting smell of burned horn. Decrease in hardness. Fragments moderately cleavable. Bronzed iridescence on the exposed surfaces. Intense metallic tints on freshly cleaved surfaces. Smell of petroleum during sample decalcification.	Mahogany-coloured shreds.
(804) 275 °C 5 hours See group 1 : (721)-275 °C Figs. 18 and 19	Aragonite	On breaking tube, pungent smell of burned horn. Persisting fishy smell. Very brittle and cleavable. Burnishing of iridescence with metallic hues on the cleavage surfaces. Smell of petroleum during sample decalcification.	Brown shreds.
Fossil records of similar alterations.			As in the 225 °C - 275 °C samples of groups 1 and 3, mahogany-brown particles constitute the organic remnants of mother-of-pearl in many Paleozoic and Mesozoic (especially Jurassic) shells.

in mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
	As in (770-72) (225 °C - 21 days), alterations in remnants of nacreous conchiolin of Pennsylvanian cephalopods from Buckhorn asphalt (compare Fig. 45 of the present paper with GRÉGOIRE and TEICHERT, 1965, Pl. I, fig. 2 (orthoconic nautiloid), Figs. 46, 47 and 48 with GRÉGOIRE and TEICHERT, Pl. II, Fig. 2 (*Pseudorthoceras knoxense*) and Pl. III, Figs. 1 and 2 (unidentified nautiloid).
+	See below: (804)
+	Nautiloid pattern recognizable: persistance of the reticulated structure. Trabeculae flattened into contorted ribbons, rounding up and broadening of fenestration, swelling of the protuberances into spheroidal corpuscles bulging like buds on the trabeculae (Fig. 49). Scattered fragmentation of trabeculae into pebble-shaped bodies (not shown).

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	 Description
(782) 300 °C 5 hours See group 1 : (721)-300 °C Fig. 21	Aragonite	On breaking tube, pungent smell of burned horn. Persisting fishy smell. Decrease in hardness. Portions of fragments cleaved into silvery-brown, iridescent sheets. Smell of bitumen and of burned rubber during sample decalcification.	Rust-brown particles. X-ray diffraction of th sediment : broad ring with diffuse boundaries.
(811) Preheating (20 ° to 400 °C) : 15 min. 400 °C : 30 min.	Calcite	On breaking tube, smell of H_2S, tar and NH_3 (still pungent after several weeks). Brittle. Fragments cleaved into booklets of slate-coloured, slightly iridescent sheets.	Rust-brown particles.
(812) Preheating (20 ° to 400 °C) : 15 min. 400 °C : 60 min.	Calcite	On breaking tube, intense smell of petroleum and of tar, still pungent after several weeks. Brittle, as in (811).	Black particles.
(783) 400 °C 5 hours See group 1 : (721)-400 °C Fig. 22	Calcite	Brittle, as in (811) and (812). Fragments cleaved into mostly lustreless, grey-black sheets. Faint traces of iridescence. Smell of petroleum during sample decalcification.	Dark-brown and black par ticles. X-ray diffraction of the sedi ment : a single broad ring with diffuse boundaries.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
+ curved, yellow rods and dots.	All transitions between slightly altered matrix (flattening of trabeculae into ribbons, preservation of the protuberances) (not shown), various degrees of coalescence (see 225 °C - 21 days stage: Figs. 45, 46 47 and 48) and general coalescence of the conchiolin matrix into membranes in the interlamellar spaces of the heated fragments. Condensation of the intercrystalline conchiolin into sturdy opaque cords (Fig. 51). Dislocation of these structures into fragments assuming the most various forms: wedge-shaped blades and flakes, cords, ribbons, strands, discs, rings and horseshoe-like structures. (Figs. 52 and 53). Scattered unidentified fibers with traces of periodical structures (not shown).
++	Nautiloid pattern destroyed. As in (782) (300 °C - 5 hours) the conchiolin debris of pyrolysed mother-of-pearl consist of irregularly polygonal membranes, stratified wedge-shaped blades with cleavage lines visible on their edges, ribbons, discs, rings and spheroidal bodies.
++ Red granules and particles embedded in a lilac-coloured jelly.	Nautiloid pattern destroyed. Alterations as in (811) (Figs. 54, 57 and 59).
+	Nautiloid pattern destroyed. Alterations of conchiolin, as in (811) and in (812), in the form of membranes perforated by large, rounded openings, polygonal blades (Figs. 55 and 56), cords, contorted ribbons, discs and pebble-shaped corpuscles.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	Description
(879) 400 °C 21 days	Calcite	Explosion on breaking tube. Strong, persisting smell of tar and transient smell of H_2S. Fragments cleaved into booklets of dark-grey, slate-coloured, lustreless sheets.	Abundant, black particles
Fossil records of similar alterations.			
(771) Argon Explosion after 5 min. during Preheating to 500 °C	Aragonite	Beginning of cleavage. Bronze-coloured fragments, strongly iridescent with intense metallic hues.	Mahogany-brown shreds.

in mother-of-pearl *(Nautilus) (contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
++	Nautiloid pattern destroyed. Conchiolin alterations not differing distinctly after 21 days, at least in the depicted areas (Figs. 58, 60 and 61), from those recorded after exposure to the same temperature for 30 minutes (811), 60 minutes (812) and 5 hours (783).
	As in the 300 °C - 400 °C samples, alterations in conchiolin remnants (perforated membranes, cords, ribbons, blades) of fossil mother-of-pearl from specimens of various ages, especially Paleozoic nautiloids and ammonoids: e.g. *Cyrtoceras* sp., nautiloid (680), Upper Middle Devonian, Givetian, Gerolstein, Eifel; *Hudsonoceras proteum (*BROWN), goniatite (664), Upper Carboniferous, Lisdoonvarna, Ireland, probably mixed with remnants of a boring organism (see GRÉGOIRE, 1966 and disc.); *Pronorites* sp. (?) and other unidentified ammonoids (754, 755), Pennsylvanian, Buckhorn asphalt; *Pseudorthoceras knoxense* (MCCHESNEY), nautiloid (530-36 a): decalcified, soft, crumbly, cocoa-brown, stratified matter of the cameral deposits (Fig. 62) (see also GRÉGOIRE and TEICHERT, 1965, Pl. VII, Figs. 1 and 2, Pl. VIII, Figs. 1-3) *Domatoceras* or *Stearoceras,* nautiloid (422-A-80), Permian, San Andres limestone, Rio Penasco River, Alamogordo, New Mexico, U. S. A. (Fig. 67); *Rhacophyllites neojurensis* QUENSTEDT, ammonoid (794-3), Trias (Geol. Museum, University of Tübingen); unidentified specimen from Ammonite Marble (823-1), Jurassic, Lower Lias, Marston Magna near Yeovil, Somerset, England (Fig. 65); *Hildoceras* sp., ammonoid (826). Jurassic, Upper Lias, Yorkshire, England, *Eleganticeras* sp., ammonoid (832), Jurassic, Upper Lias, Whitby, Yorkshire, England (Fig. 66): *Eutrephoceras* sp., nautiloid (398), Cretaceous; *Nautilus* sp. (555), Upper Eocene, Plainberg, Becken Reichenhall, Salzburg, Austria (Fig. 64). Similar alterations in nacreous conchiolin of fossil shells have been illustrated in a previous paper (GRÉGOIRE 1966): in *Faberoceras* sp., nautiloid (699) Upper Ordovician, Figs. 6, 7, and 12; *Rutoceratidae* sp., nautiloid (685), Upper Middle Devonian, Givetian, Fig. 14; *Domatoceras* or *Stearoceras,* nautiloid (422), Permian, Fig. 38 (compare with Fig. 67 of this paper, see above); *Baculites* sp., ammonoid (395), Cretaceous, Senonian, Fig. 44.
+	Nautiloid pattern preserved, with swellings in the trabeculae, in portions of nacreous matrix. Membranes resulting from coalescence of matrix in the interlamellar spaces, in other portions. In still other portions, dislocation of the matrix by fragmentation of the trabeculae into spheroidal pebble-shaped bodies, possibly caused by exposure to the open air at high temperature, immediately after explosion.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	Residues
Fossil records of similar alterations.		As in (771), mother-of-pearl intensely variegated in specimens from various ages : e. g. Pennsylvanian (Buckhorn asphalt nautiloids), Jurassic *(Leioceras, Garniericeras)* and Cretaceous (*Baculites, Collignoniceras, Scaphites, Sphenodiscus, Placenticeras*). See also group 1, above, (150 °C - 19 days to 300 °C). Mother-of-pearl harder in fossils.	As in (771), mahogany-brown organic remnants of mother-of-pearl in many Paleozoic and Mesozoic, especially Jurassic, shells.
(780) 500 °C 5 hours See group 1 : (721)-500 °C Figs. 23 and 28	Calcite	On breaking tube, pungent smell of tar and of lighting gas. Brittle. Fragments cleaved into booklets of dark, slate-coloured sheets, with traces of iridescence. Smell of tar during sample decalcification.	Black particles.
(813) Preheating (20 °C to 600 °C) : 15 min. 600 °C : 5 min.	Calcite	On breaking tube, pungent smell of tar. Very brittle. Fragments cleaved into booklets of black, iridescent mineral sheets with intense metallic hues.	Scum of black particles floating over the supernate, and resisting ultrasonic treatment.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
+	Nautiloid pattern destroyed. Perforated membranes and veils: holes surrounded by thickenings in the form of bulging, cylindrical, ring-shaped pads, with circular clefts. Similar clefts run at some distance of the edges, along the limits of blades and cords (Figs. 67, 68 and 72). Polygonal blades, cords, contorted ribbons and strands (as in the 400 °C sample). Discs, lenticular bodies, complete and incomplete rings. The latter structures result from perforation of the thin centres of membraneous blades and discs. Traces of periodicity in unidentified ribbons.
++	Nautiloid pattern destroyed. Alterations as in (780): perforated membranes studded with hemispheric granules. Openings in the membranes surrounded by thickenings in the form of rings (Figs. 69 and 70). Contorted cords and ribbons, polygonal blades, rings, discs.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(814) Preheating (20 °C to 600 °C) : 15 min. 600 °C : 30 min.	Calcite	Explosion on breaking tube : smell of H_2S and of tar. Persistent ammoniacal smell. Very brittle. Fragments cleaved into booklets of grey-black, iridescent sheets, with dark metallic hues. Naphtalene smell during sample decalcification.	Scum of agglutinated black particles.
(815) Preheating (20 °C to 600 °C) : 15 min. 600 °C : 60 min.	Calcite	Explosion on breaking tube. Strong smell of H_2S. Very brittle. Fragments cleaved into booklets of dark-grey, iridescent sheets with metallic hues.	Abundant scum of black particles resisting ultra-sonic dissociation.
(779) 600 °C : 5 hours See group 1 : (721)-600 °C Fig. 24	Calcite	On breaking tube, transient smell of H_2S and persisting ammoniacal smell. Very brittle. Fragments cleaved into booklets of grey-black, strongly iridescent sheets, with intense metallic hues.	Scum of black particles.
(778) 700 °C : 5 hours See group 1 : (721)-700 °C Figs. 29, 30, 31, 32 and 33	Calcite	Explosion on breaking tube : strong persisting ammoniacal smell and transient H_2S smell Brittle. Sample cleaved into lustreless, black sheets.	Black particles.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
++	Alterations as in (813) (Figs. 73 and 74). In the perforated membranes, the pads which surround the holes reveal parallel, concentric, linear structures (not shown, see Figs. 69 and 70).
++	Alterations as in (813) and (814), including many ring-shaped cords and perforated membranes with bulging pads encircling holes.
+	Alterations as in (813) (814) and (815). Perforated membranes and veils, with holes surrounded by cylindrical thickenings. Ring-shaped cords and discs (Figs. 75 and 76).
+ Clusters of black rods and dots.	Nautiloid pattern destroyed. Conchiolin alterations in the form of soft membranes and veils, some wrinkled, others perforated by rounded or oval openings and clefts of various shapes (Fig. 77). As in the samples heated to 600 °C, pads around the holes. Products of fragmentation of the membranes : blades, cords, ribbons, discs and lenticular bodies. Parallel fibrils (30 Å in diameter), frequently grouped in bundles, are scattered in the cords, ribbons and blades. A periodicity of alternating light (37 Å) and dark (50 Å) bands has been observed in a fiber (not shown). Crystals in the form of oblong, elongated rods, with longitudinal striation (not shown).

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples : degree of hardness, cleavability, colour, smell before or during decalcification	Description
(816) Preheating (20 °C to 800 °C) : 15 min. 800 °C : 5 min.	Calcite	Violent explosion on breaking tube : intense smell of H_2S. Very brittle. Fragments cleaved into booklets of grey-black, pulverulent sheets, with scattered, intensely iridescent areas. Faint smell of H_2S during sample decalcification.	Scum of black particles resisting ultrasonic disso- ciation.
(817) Preheating (20 °C to 800 °C) : 15 min. 800 °C : 30 min. See group 1 : (808) Fig. 36	Calcite	Very brittle. Fragments cleaved into lustreless, bloated, black and dark-grey pulverulent sheets. Strong smell of H_2S during sample decalcification.	Scum of black particles.
(818) Preheating (20 °C to 800 °C) : 15 min. 800 °C : 60 min. See group 1 : (809) Fig. 35	Calcite	Strong explosion on breaking tube. Intense smell of H_2S. Very brittle. Fragments cleaved into lustreless, powdery ash-grey sheets. Smell of H_2S during sample decalcification.	Scum of black particles.

in mother-of-pearl *(Nautilus)* *(contd.)*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
+	Nautiloid pattern destroyed. Perforated membranes (Fig. 78) and veils with ring-shaped thickenings around the holes as in the (778) (700 °C - 5 hours) and (817) (800 °C - 30 minutes) samples. Filament-like structures, 20-30 Å in width, scattered in the veils (Fig. 81) (see discussion). Substantial bundles of fibrils (not shown) mixed with the debris of the membranes.
+ Some violet flakes speckled with black rods, black grains, blue and yellow spots. Clusters of pink filaments (see discussion)	Predominant conchiolin alterations in the form of membranes and veils, perforated by irregularly rounded, mostly elongated openings (Figs. 79 and 80). Fig. 80 shows a loose network, made up of flat and broad strands, which has kept some of the features of the nautiloid pattern. In Fig. 79, the openings in the membranes are surrounded by concentric, 10 mμ broad thickenings (also visible in Fig. 80), in which alternating dense and light lines are visible. Some of the white lines, at some distance of the edge of the openings, seem to be linear clefts connected with small vesicles (See Fig. 83). Structures resembling flattened vesicles, superimposed on the perforated membranes (Fig. 80) might be remnants of swollen fragments detached from the trabeculae. Fibrils, 16 Å in width, scattered or forming networks and bundles, in the substance of the trabeculae (not shown).
+ Abundant, contorted, dark-brown rods, grains and fragments of filaments scattered in the violet flakes.	Alterations as in (817). Bundles of parallel fibrils scattered within soft, granular or amorphous veils containing many microvesicles.

TABLE 1. — Thermal changes

File number (in brackets) Temperature (in °C) Exposure time	Mineral composition of the samples (X-ray powder diffraction)	Physical characteristics of the undecalcified samples: degree of hardness, cleavability, colour, smell before or during decalcification	
			Description
(775) (776) 800 °C 5 hours (2 samples) See group 1: (721)-800 °C Figs. 35, 36, 37, 38.	Calcite	Strong detonation and smell of H_2S on breaking tube. Ash-grey, powdery substance marbled with black areas. Strong smell of H_2S during sample decalcification.	Scum of black particles.
(1000) (880) (805) 900 °C 5 hours (4 samples)	Calcite	In two samples, explosion on breaking tube. Smell of H_2S and KCN. Brittle. Glistening, swollen, snow-white flakes and white powdery substance. Strong smell of H_2S during sample decalcification.	Scarce, black particles.

in mother-of-pearl *(Nautilus) (contd. and end).*

Residues of decalcification	
Biuret test (see Materials and Methods)	Alterations in ultrastructure of the pyrolysed nacreous conchiolin matrix (trabeculae of the reticulated sheets)
+ right purple spots in some violet flakes. Clusters of pink rods and grains.	Alterations as in (817) and (818), predominantly in the form of perforated membranes and thin veils (Figs. 82 to 85). Numerous vesicles of various sizes scattered at random (Fig. 84) in the membranes or alined in or behind the thickenings along the edges of the openings. As in (778), crystals in the form of oblong cucumber-shaped rods with longitudinal striation (not shown).
- and ++ (see discussion and Fig. 87). Violet flakes speckled with yellow and blue spots.	Disintegration of the original conchiolin matrix predominantly into pebble-shaped corpuscles (Figs. 86 and 89), contorted cords (Fig. 94) and, less frequently than in the preceding stages, into wrinkled membranes (Fig. 93). In several preparations, the debris have not been displaced from their original position in the interlamellar conchiolin sheets. They appear to be included in polygonal figures of large size (Figs. 86, 92 and 95) in which the outlines of the original aragonite crystals or groups of crystals, dissolved by decalcification, are traced by remnants of intercrystalline conchiolin in the form of opaque straight ribbons (Figs. 86, 92 and 95). Some degree of crystallinity is revealed by electron diffraction in some of these remnants (Fig. 90), not in others (Fig. 91). Fibrils in substantial amounts were mixed with these structures. (Fig. 88).

TABLE 2.

Similarities shown in the micrographs, between thermal changes produced artificially in nacreous conchiolin of modern *Nautilus*, and alterations in ultrastructure of organic remnants of fossil mother-of-pearl.

Pyrolysed mother-of-pearl (modern *Nautilus*)	Alterations in conchiolin structures	Fossil mother-of-pearl (nautiloids and ammonoids)
Group 1. (Dry heat in open vessels)		
Fig. 10. Sample heated to 225 °C for 21 days.	Spheroidal pebble-shaped corpuscles.	Fig. 11. *Pseudorthoceras knoxense* McCHESNEY (nautiloid) Pennsylvanian. Soft, stratified matter of the cameral deposits (central portion).
Figs. 17, 18 and 19. Samples heated to 250 °C and 275 °C for 5 hours.	Clusters of corpuscles and of granular material.	Fig. 20. Unidentified cephalopod. Pennsylvanian. Outermost, weathered, portion of the inner nacreous layer of the shell wall.
Figs. 21 to 24. Samples heated for 5 hours to 300 °C (Fig. 21), 400 °C (Fig. 22), 500 °C (Fig. 23) and 600 °C (Fig. 24).	General disintegration into pebble-shaped bodies.	Fig. 25. *Agoniatites vanuxemi* HALL, goniatite, Middle Devonian. Fig. 26. *Leioceras (Harpoceras) opalinum* REINECKE (ammonoid), Middle Jurassic. Fig. 27. *Amaltheus spinatus* BRUGUIÈRE (ammonoid), Lower Jurassic.
Figs. 29 to 33. Samples heated for 60 minutes to 700 °C.	Clusters of spheroidal corpuscles associated with groups of fibrils and filaments.	Fig. 34. *Harpoceras mulgravium* SIMPSON, YOUNG and BIRD (ammonoid) Lower Jurassic.
Group 3. (Dry heat in tubes sealed under vacuum)		
Samples heated to 275 °C (Fig. 50) and to 300 °C (Fig. 52) for 5 hours, to 400 °C (Fig. 58) for 21 days.	Loose networks of flattened trabeculae. Membranes and their fragments (blades and flakes).	Fig. 62. *Pseudorthoceras knoxense* McCHESNEY (nautiloid), Pennsylvanian. Soft, stratified, central matter of cameral deposits.
Samples heated to 300 °C for 5 hours (Fig. 53), to 400 °C for 60 minutes (Figs. 54, 57 and 59), 5 hours (Figs. 55 and 56) and 21 days (Figs. 58, 60, 61).	Coalescence of interlamellar conchiolin matrix into perforated membranes, fragmented into blades, flakes, ribbons and cords.	Figs. 63, 65 and 66. Lower Jurassic ammonoids: *Androgynoceras*, Specimen of MARSTON « Ammonite Marble », *Eleganticeras*. Fig. 64. *Nautilus* sp. Upper Eocene.
Fig. 72. Sample heated to 500 °C for 5 hours.	Perforated membranes.	Fig. 71. *Pronorites* sp. ammonoid, Pennsylvanian.

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EXPLANATION OF FIGURES.

The electron micrographs depict the progressive degradation of conchiolin in fragments of mother-of-pearl (shell wall in the living chamber : *Nautilus pompilius* LINNÉ, *Nautilus macromphalus* SOWERBY (Fig. 3)) heated to temperatures ranging from 100 °C to 900 °C in open vessels (Figs. 2-10, 12-19, 21-24, 28-33 and 35-38), in mixtures of sea mud and sea water (Figs. 39-43) and in absence of oxygen, in tubes sealed under vacuum and argon (Figs. 44-61, 67-70, 72-95).

The organic residues of decalcification, deposited on supporting films, have been examined directly, after staining and after shadowing with palladium and platinum.

Structural alterations in organic remnants of nacreous layers in fossil Cephalopods (nautiloids and ammonoids), similar to the pyrolytic changes produced experimentally in nacreous conchiolin of the modern *Nautilus* shell, are shown in Figs. 11, 20, 25-27, 34, 62-66 and 71.

The illustrations of shadowed material are of two types :

(a) Direct prints made from the original negatives (white shadows directed upward or to the left).

(b) Reversed prints obtained through intermediary direct prints on plates (black shadows directed downward or to the right).

Fig. 1.

Nautilus pompilius LINNÉ (modern) (449-123).

Control of the pyrolytic alterations.
Fragment of conchiolin matrix from the median portion of the decalcified nacreous layer of the shell wall in the living chamber.
The nautiloid structure pattern of conchiolin consists of sturdy, irregularly cylindrical trabeculae or cords, studded with hemispheric protuberances of various sizes (8-35 mμ). The generally elongated openings which separate the trabeculae have irregular outlines. Variations in shape and in size of fenestration depend in part upon degrees in stretching and in spreading of the organic fragments during desiccation on the supporting films (See GRÉGOIRE, DUCHÂTEAU and FLORKIN, 1955, plates 3 and 4; GRÉGOIRE, 1962, Fig. 39; 1966, Figs. 1-3).
Shadowed with palladium.
Direct print : $\times$ 42.000.

Fig. 2.

Nautilus pompilius LINNÉ (modern) (721-150).

Nacreous layer of the shell wall, heated in an open vessel to 150 °C for 5 hours.
In the sheets of conchiolin left by decalcification, the nautiloid pattern has been preserved. The alterations in the trabeculae are diffuse and consist predominantly of scattered swelllings separated by constrictions.
Shadowed with palladium.
Direct print : $\times$ 21.000.

Fig. 3.

Nautilus macromphalus SOWERBY (modern) (731-19).

Nacreous layer of the shell wall, heated in an open vessel to 150 °C for 19 days.
Conchiolin residues of decalcified fragments. In a portion of matrix, the process of fragmentation of the trabeculae consists of separation of their swollen portions into irregularly spheroidal corpuscles of various sizes.
Shadowed with palladium.
Direct print : × 42.000.

Fig. 4.

Nautilus pompilius LINNÉ (modern) (721-200).

Nacreous layer of the shell wall, heated in an open vessel to 200 °C for 5 hours.
Conchiolin residues of decalcified fragments.
The modifications in this portion of matrix are characterized by shrinkage and increase in density of the trabeculae and by rounding up and broadening of fenestration. In another region (bottom centre) the alterations in trabeculae consist of swellings separated by constrictions.
Shadowed with palladium.
Direct print : × 42.000.

Figs. 5-8.

Nautilus pompilius LINNÉ (721-225).

Nacreous layer of the shell wall heated in an open vessel to 225 °C for 5 hours.
Organic remnants of decalcified sample. These four micrographs show variations in the alterations in representative pictures of four different preparations.
The nautiloid pattern, variously modified, is still recognizable in most regions of the matrix. The alterations in the trabeculae consist of swellings (Fig. 5, bottom), and conversely of shrinkages (Figs. 6, 7 and 8), accompanied by protrusion of the protuberances (Fig. 6), and fragmentation into spheroidal corpuscles and granules (Fig. 5).
Shadowed with palladium.
Direct print : × 42.000.

Fig. 9.

Nautilus pompilius LINNÉ (721-200).

Nacreous layer of the shell wall heated in an open vessel to 200 °C for 5 hours.
Conchiolin residues of decalcification stained with a 3 per cent solution of potassium phosphotungstate (pH 7.0).
Opaque, irregularly rounded islands disposed in mosaics within the trabeculae.
× 150.000.

Fig. 10.

Nautilus pompilius LINNÉ (721-225-21).

Nacreous layer of the shell wall heated in an open vessel to 225 °C for 21 days.
Conchiolin residues of decalcified fragments.
Alteration of the conchiolin trabeculae consists of general disintegration into spheroidal corpuscles (see Fig. 11).
Shadowed with palladium.
Direct print : × 42.000.

Fig. 11.

Pseudorthoceras knoxense MC CHESNEY (530-33) nautiloid, Pennsylvanian, Buckhorn asphalt, Oklahoma, U. S. A.

Remnants of decalcified, soft, crumbly, cocoa-brown, stratified matter of the central portion of the cameral deposits. The organic structures recorded in this micrograph consist mostly of spheroidal pebble-shaped bodies which appear to be identical or closely

similar to those depicted in Fig. 10 at a slightly higher magnification, in pyrolysed modern nacreous substance.
Shadowed with palladium.
Direct print : × 16.000.

Figs. 12-16.

Nautilus pompilius LINNÉ (721-225-21 M).

Nacreous layer of the shell wall, heated in an open vessel to 225 °C for 21 days.
Conchiolin residues of decalcified fragments. Among these residues were spheroidal corpuscles of large size (Fig. 12 : 1,5 μ in diameter), composed of a network of ribbon-shaped trabeculae, frequently diverging as in spherulitic structures. In spite of the alterations, some features of the nautiloid pattern can be recognized in these structures.
The trabeculae appear to be filled with microvesicles (Fig. 12) which increase in size under the electron beam (Fig. 15). The corpuscles are transformed into rings (Fig. 13, right) and crescents (Fig. 13, bottom left), by disappearance of their central portion. Figs. 14 and 16 show two types of electron diffraction patterns recorded in these large bodies (Fig. 15).
Unshadowed material.
Figs. 12 and 13 : × 50.000. Fig. 15 : × 30.000.

Figs. 17, 18 and 19.

Nautilus pompilius LINNÉ (721-250, 721-275).

Nacreous layer of the shell wall, heated in open vessels for 5 hours to 250 °C (Fig. 17) and 275 °C (Figs. 18 and 19).
In the depicted areas, the nautiloid pattern of conchiolin structure has been destroyed. Fragmentation of the trabeculae is the predominant alteration. The remnants consist of branched rods. (Fig. 18 : top right; Fig. 19 : centre left) and of corpuscles of various sizes, including small granules.
Shadowed with palladium.
Direct prints. Fig. 17-19 : × 42.000.

Fig. 20.

Weakly curved fragments of mother-of-pearl from the shell of an unidentified large cephalopod (nautiloid or ammonoid) (385-4 C), Pennsylvanian, Upper Atoka formation, Buckhorn asphalt, Sulphur, Oklahoma, U. S. A.
Fragment of the outermost portion of the inner nacreous layer of the shell wall. These fragments appear to have been directly exposed to weathering factors after exfoliation of the outer shell layers.
The biuret test applied to the organic remnants shown in Fig. 20, gave pink violet flakes and slightly violet shreds. In shadowed preparations, this organic material appears to consist, as in the modern material pyrolysed experimentally (Figs. 17, 18 and 19) of corpuscles and of granules of various sizes. The poor state of preservation of this conchiolin material from weathered fragments of the shell contrasts with that of nearly intact nacreous matrix recorded in the sheltered inner portions of the shell, and shown in former papers (GRÉGOIRE, 1959 b, 1966; GRÉGOIRE and TEICHERT, 1965).
Shadowed with palladium.
Direct print : × 42.000.

Figs. 21-24.

Nautilus pompilius LINNÉ (721-300-400-500-600).

Nacreous layer of the shell wall, heated in open vessels for 5 hours to 300 °C (Fig. 21), 400 °C (Fig. 22), 500 °C (Fig. 23) and 600 °C (Fig. 24).
The alterations in the conchiolin residues consist of general disintegration of the matrix into spheroidal bodies of small size. Shadowed with palladium.
Direct prints. Figs. 21, 23 and 24 : × 42.000; Fig. 22 : × 21.000.

Figs. 25-27.

Pebble-shaped corpuscles similar to those seen in Figs. 21-24 (and in Fig. 10), characterize the decalcified organic remnants of fossil mother-of-pearl in shells of various ages and formations (see GRÉGOIRE, 1959, 1966; GRANDJEAN et al., 1964).

Agoniatites vanuxemi HALL (Fig. 25) (704-9), goniatite, Middle Devonian, Cherry Valley limestone, Stockbridge Falls, New York, U. S. A. Mineral composition of the sample : calcite (GRANDJEAN et al., 1964).

Leioceras (Harpoceras) opalinum REINECKE (Fig. 26) (405-9), ammonoid, Middle Jurassic, Lower Dogger (Opalinus-Ton), Boll, Württemberg, Germany. Mineral composition of the samples : aragonite and principal ray of calcite (GRANDJEAN et al., 1964).

Amaltheus spinatus BRUGUIÈRE, var. *spinata* BR., stad. *costatum* REIN. (Fig. 27), Lower Jurassic, Lias δ, Schloss Banz, Bayern, Germany. Mineral composition of the sample : aragonite (GRANDJEAN et al., 1964).
Shadowed with palladium (Fig. 25) and with platinum (Figs. 26 and 27).
Direct print : × 42.000.

Fig. 28.

Nautilus pompilius LINNÉ (721-500-3).

Nacreous layer of the shell wall heated to 500 °C in an open vessel for 5 hours.
Conchiolin shreds lying on carbon films. Negative staining (3 per cent solution of sodium phosphotungstate, pH 7.0). The conchiolin debris, of very small size, are seen in white in the opaque stain and assume the most various shapes, such as spheroidal bodies, rings, doughnuts, contorted rodlets, commas, horse-shoes, crescents, brackets, dots, micronetworks of vermicular elements and granules. Presence of stain within spheroidal bodies (bottom right) suggests that a part of the pebble-shaped structures shown in shadowed preparations (Figs. 21-24) could be hollow spheroids.
× 176.000.

Figs. 29 to 33.

Nautilus pompilius LINNÉ (807).

Nacreous layer of the shell wall heated to 700 °C in an open vessel for 60 minutes.
Fig. 29, In this unstained and unshadowed preparation, the conchiolin remnants, including small spheroidal corpuscles or vesicles seem to contain opaque granules possibly arranged in networks. Fig. 31, Clustered spheroidal bodies without distinct inner structure, and other conchiolin debris. Figs. 30 and 32, Substantial bundles of fibrils (16 Å in width) have been frequently found among the organic remnants of samples heated to high temperatures (700 °C-800 °C) (see discussion). Fig. 33. The structures seen in Figs. 29-32 are shown here after shadowing with platinum : clusters of spheroidal corpuscles, a fragment of membrane (bottom left) and groups of fibrils and filaments (bottom right and top middle).
Fig. 29 : unstained, unshadowed. × 75.000.
Figs. 30, 31 and 32. Negative staining. Fig. 30 : × 90.000.
Fig. 31 : × 126.000; Fig. 32 : × 168.000.
Fig. 33 : shadowed with platinum. × 60.000.

Fig. 34.

Harpoceras mulgravium SIMPSON, YOUNG and BIRD (524-1) ammonoid.

Lower Jurassic, *Falciferum* subzone, Whitby, Yorkshire, England.
Outer portion of the inner nacreous layer of the shell wall. Mineral composition : calcite (GRANDJEAN et al., 1964).
This micrograph shows in the biuret positive organic residues of decalcification of this sample, an assemblage, similar to that found in the pyrolysed material of Fig. 33, composed of clustered corpuscles of various sizes, of fibrils, of fragments of ribbons and angular blades (centre and bottom centre).
Other aspects of the conchiolin remnants in this specimen have been shown in a previous paper (GRÉGOIRE, 1966, Figs. 40 to 43).
Shadowed with platinum.
Direct print : × 42.000.

Figs. 35-38.

Nautilus pompilius LINNÉ (808, 809, 721-800, 721-800-5).

Nacreous layer of the shell wall, preheated in open vessels from 20 °C to 800 °C for 15 minutes and maintained at this temperature for 10 minutes (Fig. 36), 60 min. (Figs. 35 and 35 b) and 4 hours (Figs. 37 and 38).

Remnants of decalcification of the samples. The nautiloid pattern has been rapidly destroyed (Fig. 36). However, in the 4 hours sample (Fig. 37), fragments of stretched and agglutinated trabeculae are still recognizable. The organic remnants consist of clusters of pebble-shaped corpuscles of various sizes, associated with substantial bundles of fibrils (Fig. 35). Note the pitted appearance of several spheroidal bodies in Fig. 36. Fig. 38 shows coalescence of conchiolin into a membrane in which spheroidal corpuscles seem to consist of an electron-transparent centre encircled by an opaque wall.

Shadowed with platinum (Fig. 35) and palladium (Figs. 36 and 37).

Direct prints. Figs. 35-38 : × 42.000.

Fig. 35 b. This phase contrast photograph (× 600) shows in white and black a biuret-positive (pink violet) shred. This remnant of decalcification of a sample heated to 800 °C for 60 minutes in an open vessel consists or four or five clustered, rounded, polygonal flakes. These flakes are fragments of interlamellar conchiolin matrix which has preserved the imprints of the 001 facets of the tabular crystals of aragonite between which this matrix was compressed in the normal architecture of mother-of-pearl.

Figs. 39-43.

Nautilus pompilius LINNÉ (761 A, 886-1, 886-2).

Nacreous layer of the shell wall, boiled in mixtures of see mud and sea water for various lengths of time, separated by intervals during which the samples remained buried at room temperature in the wet mud.

The total duration of the treatment amounted to 17 hours in 26 months (Fig. 39), 58 hours in 47 days (Figs. 40 and 43), and 42 hours in 47 days (Figs. 41 and 42).

In the conchiolin matrix left by decalcification of the samples, the nautiloid pattern has been preserved. The alterations in thix matrix consist of diffuse shrinkage and flattening of the trabeculae on which the protuberances are visible in the form of dome-shaped elevations.

In negatively stained preparations (Fig. 40), ill-defined, densely entangled fibrils seem to form a network inside the trabeculae.

Shadowed with platinum.

Direct prints. Figs. 39, 41, 42 : × 48.000; Fig. 43 : 69.000.

Fig. 40 : × 160.000.

Fig. 44.

Nautilus pompilius LINNÉ (801-2).

Nacreous layer of the shell wall, heated to 150 °C for 5 hours in a quartz tube sealed under vacuum.

Decalcification of the samples left the conchiolin matrix nearly unchanged. Alterations are diffuse and consist of moderate shortening and condensation of the trabeculae, rounding up of fenestration, swelling of protuberances.

Compare with the material heated in open vessels : Fig. 2.

Shadowed with platinum.

Direct print : × 42.000.

Figs. 45-48.

Nautilus pompilius LINNÉ (772-770).

Nacreous layer of the shell wall, heated to 225 °C for 21 days in a quartz tube sealed under argon.

In the remnants of decalcification of the samples, the nautiloid pattern, still recognizable, has been variously altered by pyrolysis. The modifications in the trabeculae of the matrix consist of swellings (Fig. 46), conversely of flattenings (Figs. 47 and 48), dislocation into blocks and corpuscles with scattering of protuberances (Figs. 45 and 48) and coalescence into membranes (Figs. 46 and 47).

Compare with the same material heated in open vessels : Fig. 10.

Shadowed with platinum.

Direct print. Fig. 48 × 42.000.

Reversed prints. Figs. 45, 46 and 47 × 42.000.

Figs. 49 and 50.

Nautilus pompilius LINNÉ (804).

Nacreous layer of the shell wall heated to 275 °C for 5 hours in a quartz tube sealed under vacuum.

In the remnants of decalcification of the samples, the predominant alterations in conchiolin matrix were flattenings and shrinkages of the trabeculae into contorted ribbons (Fig. 49). Superimposition of two reticulated sheets shown in these micrographs is due to collapse and coalescence of adjacent interlamellar matrices after dissolution of the aragonitic lamella interposed between them.

Compare with samples heated in open vessels : Figs. 18 and 19.

Shadowed with platinum.

Fig. 49, reversed print : × 42.000; Fig. 50, direct print : × 66.000.

Figs. 51, 52, 53.

Nautilus pompilius LINNÉ (782).

Nacreous layer of the shell wall heated to 300 °C for 5 hours in a quartz tube sealed under vacuum.

Fig. 51 shows the fusion of portions of interlamellar conchiolin matrix into membranes in the form of three polygonal fragments. These fragments are imprints of tabular 001 facets of the original aragonite crystals which have been dissolved by decalcification, and between which the reticulated sheets of nacreous conchiolin were originally sandwiched.

Hemispheric bodies scattered on the surface of the membranes could be remnants of protuberances. The straight opaque strands which delimit the polygonal fragments (on the right) or are detached from them (in centre) are remnants of intercrystalline conchiolin bridges that wrapped before decalcification the side — facets of the aragonite crystals.

Mechanical dislocation of these membranes in situ or during preparation of the material for electron microscopy gave rise to fragments assuming the most various shapes (Figs. 52 and 53) : Curled, polygonal flakes and blades, rings, discs, crescents, cords, bars, ribbons. Blades and flakes are wedge-shaped in cross section. They are thicker on their edges and become progressively thinner towards their centre, which is nearly transparent (Fig. 52 : top; Fig. 53 : top and centre left). Examination of the edges which project upward from the curled flakes and show the material in cross section reveals a stratified structure with cleavage lines (Figs. 52 and 53 : top right).

Disappearance of the thin central portion of the wedge-shaped blades leaves the thick peripheral portion in the form of irregular rings (Fig. 52 : centre left and right, bottom right).

A part of the cords, ribbons, and bars are remnants of intercrystalline conchiolin bridges. In Figs. 52 and 53 (top centre and right), erected ridges, which protrude on polygonal flakes, are probably remnants of these intercrystalline bridges still fixed to fragments of interlamellar conchiolin.

Compare with material heated in open hair : Fig. 21.

Shadowed with platinum.

Direct prints. Figs. 51 and 53 : × 42.000.

Reversed print. Fig. 52 : × 42.000.

Figs. 54 to 61.

Nautilus pompilius LINNÉ (812, 783, 879).

Nacreous layer of the shell wall heated in quartz tubes sealed under vacuum to 400° C for 60 min (Figs. 54, 57 and 59), 5 hours (Figs. 55 and 56) and 21 days (Figs. 58, 60 and 61).

As in the 300° C stage, the conchiolin structures of these samples were chiefly relatively dense, polygonal blades and flakes and the modifications of the latter in the form of cords, contorted ribbons and rings. Cleavage lines are distinctly visible along the edges of the flakes and of their perforations (e.g. Fig. 54, right edge of the central flake; Fig. 55, centre). The flake shown in Fig. 59 seems to be composed of several, tightly stratified, 16 Å thick lamellae. The edges of these lamellae appear as faint grey lines. Except for these structures, the substance of the flakes and blades is amorphous (Figs. 57 and 60).

Protracted heating (21 days : Figs. 58 and 61) does not seem to have distinctly modified alterations already developed after 60 minutes (Fig. 54) and 5 hours (Fig. 55).

Shadowed with platinum : Fig. 54 (× 60.000), Fig. 55 (× 42.000), Fig. 56 (× 42.000), Fig. 58 (× 60.000) and Fig. 61 (× 60.000). Unshadowed preparations : Fig. 57 (× 126.000), Fig. 59 (× 126.000) and Fig. 60 (× 110.000). Figs. 54, 55, 56 and 61 : reversed prints.Fig. 58 : direct print.

Fig. 62.

Pseudorthoceras knoxense McCHESNEY, nautiloid (530-36 α), Pennsylvanian, Buckhorn asphalt, Sulphur, Oklahoma, U. S. A.

Decalcification remnants of the soft, crumbly, stratified, cocoa-brown, central matter of the cameral deposits. Biuret test : pink violet particles.

The three portions of this electron micrograph show another type of alteration in organic remnants of cameral deposits (see Fig. 11), which consists of polygonal blades and flattened ribbons resembling those produced by artificial pyrolysis of modern conchiolin under vacuum at 275 °C, 300 °C and 400 °C.

Shadowed with platinum.

Direct print : × 48.000.

Fig. 63.

Androgynoceras sp., ammonoid (828-3), Lower Jurassic, Lower Lias, Lyme Regis, Dorset, England.

Inner nacreous layer of the shell wall. Mineral composition of the sample : calcite.

Biuret-positive remnants of decalcification : lilac and violet flakes.

In this unshadowed preparation, soft, torn membranes and ribbons appear amorphous or thinly granular, as in pyrolysed material shown in Figs. 57, 59 and 60. Parallel dark lines, 14 Å in width, might be either filaments, or interference patterns of granular material in superimposed (left) or torn (right) sheets. (see discussion).

× 160.000.

Fig. 64.

Nautilus sp. (555), Upper Eocene, Plainberg im Becken Reichenhall, Salzburg, Austria.

Nacreous layer of the shell wall.

Remnants of decalcification (biuret test : violet flakes).

Alterations in nacreous conchiolin recorded in this specimen (fragments of membranes, cords, flattened ribbons) are similar to those produced by pyrolysis at 300° C-400 °C in the absence of oxygen in nacreous conchiolin of the modern *Nautilus* shell (see Figs. 52-61).

Shadowed with platinum.

Direct print : × 60.000.

Fig. 65.

Unidentified ammonoid from « Ammonite Marble » (823-1) probably *Promicroceras marstonense* Spath, Lower Jurassic, Lower Lias, Marston Magna, near Yeovil, Somerset, England.

Nacreous layer of the shell wall. Mineral composition : calcite.

This electron micrograph showns the organic remnants of decalcification of the samples (biuret test : violet flakes) in the form of a loose network of ribbons, polygonal flakes and fragments of membranes, which resemble the structures produced by pyrolysis at 300° C and 400° C in the absence of oxygen in nacreous conchiolin matrix of the modern *Nautilus* shell (see Figs. 52-61).

Shadowed with platinum.

Reversed print : × 54.000.

Fig. 66.

Eleganticeras sp., ammonoid (832-1), Lower Jurassic, Upper Lias, Whitby, Yorkshire, England.

Nacreous layer of the shell wall. Mineral composition : calcite.

The remnants of decalcification of the samples (biuret test : violet flakes) are composed of fragments of branched rods, cords, ribbons and perforated flakes (bottom centre), which resemble the structures shown in Figs. 52-61.
Shadowed with platinum.
Reversed print : × 60.000.

Fig. 67.

Domatoceras or *Stearoceras* sp. (nautiloid) (422-A-80), Permian, San Andres limestone, Rio Penasco River, east of Alamogordo, New Mexico, U. S. A.

The biuret-positive structures detected in the residues of decalcification of this specimen included spheroidal and lenticular corpuscles and debris of networks composed of branched, flattened fragments resembling those obtained in pyrolysed modern material (e.g. Figs. 58 and 61 : 400 °C-21 days). (See also GRÉGOIRE, 1966b, Figs. 37, 38, 39).
Shadowed with palladium.
Reversed print : × 44.000.

Figs. 68 and 72.

Nautilus pompilius LINNÉ (780).

Nacreous layer of the shell wall heated to 500 °C for 5 hours in quartz tubes sealed under vacuum.

Remnants of decalcification of the samples chiefly in the form of folded and perforated membranes, onto which various structures, including contorted cords and flat, lenticular or rounded corpuscles are lying. The perforations are delimited by thickenings in the form of bulging, irregularly cylindrical, ring-shaped pads (Fig. 68). Small clefts or holes are alined at some distance of the edge of several structures, namely in pads and in the lenticular corpuscle lying on the membrane at the right upper portion of Fig. 68.

In negative contrast, the substance of the membranes and blades appears amorphous (Fig. 72) (Compare with Fig. 71). Shadowed with platinum : Fig. 67 (reversed print) × 42.000.
Fig. 68 (direct print) : × 42.000.
Fig. 72 : × 126.000.

Fig. 71.

Pronorites sp., ammonoid (754), Pennsylvanian, Buckhorn asphalt, Oklahoma, U. S. A.

One of the types of structure in the form of perforated amorphous membranes similar to those produced in experimental pyrolysis (see Fig. 72), recorded in biuret-positive remnants of decalcification of nacreous layers from this specimen. Well preserved matrix with a typical nautiloid pattern has been seen in other portions of the nacreous layers.
Direct print : × 42.000.

Figs. 69, 70 and 73 to 76.

Nautilus pompilius LINNÉ (813, 814, 779).

Nacreous layer of the shell wall heated in quartz tubes sealed under vacuum to 600 °C for 5 min. (Figs. 69, 70), 30 min. (Figs. 73 and 74) and for 5 hours (Figs. 75 and 76).

As in the 500 °C stage, the predominant structures in the conchiolin residues of these samples were *soft membranes and thin veils with holes surrounded by ring-shaped pads* (Fig. 69 : bottom and centre; Fig. 75 : right; Fig. 76 : bottom centre). Various structures, including entangled fragments of cords, twisted and contorted ribbons (Fig. 70 : upper half), discs and lenticular corpuscles (Figs. 75 and 76) are lying on the membranes and veils. Folds in the membranes may simulate cords or fibers. In Fig. 75, note clefts assuming a semi-circular shape, and appearing as white lines in direct print (Fig. 70 : bottom) and as dark cracks in thick fragments of cords, in reversed print (Fig. 75 : centre).

Unshadowed preparations (Figs. 73 and 74) reveal the presence within the amorphous substance of the membranes and of their fragments, of bundles of extremely thin, parallel, dark lines, 14 Å in width. Identical lines are visible at the edges of the structures, where it is difficult to distinguish them from optical artifacts (see discussion).

Compare with the 600 °C stage in open vessels (Fig. 24).

Shadowed with platinum. Direct prints : Figs. 69 and 70 (× 54.000).
Reversed prints : Figs. 75 and 76 (× 42.000).
Unshadowed material : Figs. 73 and 74 : × 126.000.

Fig. 77.

Nautilus pompilius LINNÉ (778).
Nacreous layer of the shell wall heated in tubes sealed under vacuum to 700 °C for 5 hours.
As in the 500 °C and 600 °C samples, the predominant alterations in the conchiolin remnants consisted of perforated membranes and thin veils. In Fig. 77, folds in the membrane simulate fragments of cords. The white vertical contorted cord (centre right) seems to be composed of parallel filaments. Opaque spheroidal knobby bodies are lying on the membrane.
Shadowed with platinum.
Reversed print :× 42.000.

Figs. 78-85.

Nautilus pompilius LINNÉ (816-1; 817-1, 775, 776).
Nacreous layer of the shell wall heated in quartz tubes sealed under vacuum to 800 °C for 5 min. (Figs. 78 and 81), 30 min. (Figs. 79 and 80) and 5 hours (Figs. 82, 83, 84 and 85).
As in the preceding stages (600° C, 700° C), perforated membranes and veils are the predominant alteration recorded in conchiolin in these samples. This kind of alteration develops rapidly (Figs. 78 and 81 : preheating 20° C to 800° C : 15 min.; heating at 800° C : 5 min.), and the structural modifications remain relatively stable with protracted heating. Some membranes are thick (Fig. 80), composed of networks of flattened ribbon-like trabeculae which still resemble the matrix of the original nautiloid pattern. The peculiarities of structure recorded in previous stages in perforated membranes along the edges of the holes appear more distinctly : parallel concentric dark lines (10-14 Å in width) are visible in the thickenings which surround these holes (Figs. 78, 79 and 80). As shown in Fig. 80, and more distinctly in Fig. 83, vesicles or pits of irregular size are alined in the trabecular substance in or behind the pads surrounding the holes.
In Fig. 85, extremely thin, transparent veils, perforated by oval or rounded large windows encircled by sharp white lines, are lying on sturdy, possibly swollen, perforated membranes. Similar superimposed veils appear folded in Fig. 82, and filled with vesicles of the most various sizes in Fig. 84. Filament-like elements, 15-20 Å in width, scattered of grouped in bundles, are visible in some of these veils (Fig. 81) (see discussion).
Shadowed with platinum. Direct prints : Fig. 78 (× 60.000). Reversed prints : Fig. 80 (× 60.000), Fig. 85 (× 42.000).
Unshadowed preparations : Fig. 79 (× 160.000); Fig. 81 (3 micrographs) (× 114.000); Fig. 82 (× 56.000); Fig. 84 (× 42.000).
Negative staining : Fig. 83 (× 66.000).

Figs. 86-95.

Nautilus pompilius LINNÉ (805, 880, 1000).
Nacreous layer of the shell wall heated in quartz tubes sealed under vacuum to 900 °C for 5 hours.
In the 900 °C stage, the remnants of nacreous conchiolin still present a positive biuret reaction : Fig. 87 is a phase contrast photograph recorded at low magnification (× 600) of four polygonal organic flakes from the nacreous interlamellar conchiolin system, which stained in violet. Soft membranes due to coalescence of the original interlamellar conchiolin systems and predominant in the preceding stages (600 °C to 800 °C), were seen only exceptionally in the 900 °C samples : Fig. 93 shows such a membrane considerably folded. In most preparations, the residues of these membranes appeared as opaque flakes (Fig. 92 : left portion of the micrograph). Dissociation of the membranes into small corpuscles with a pitted appearance seems to be predominant in these preparations. The corpuscles are scattered or clustered into flocs (Fig. 86, top), into

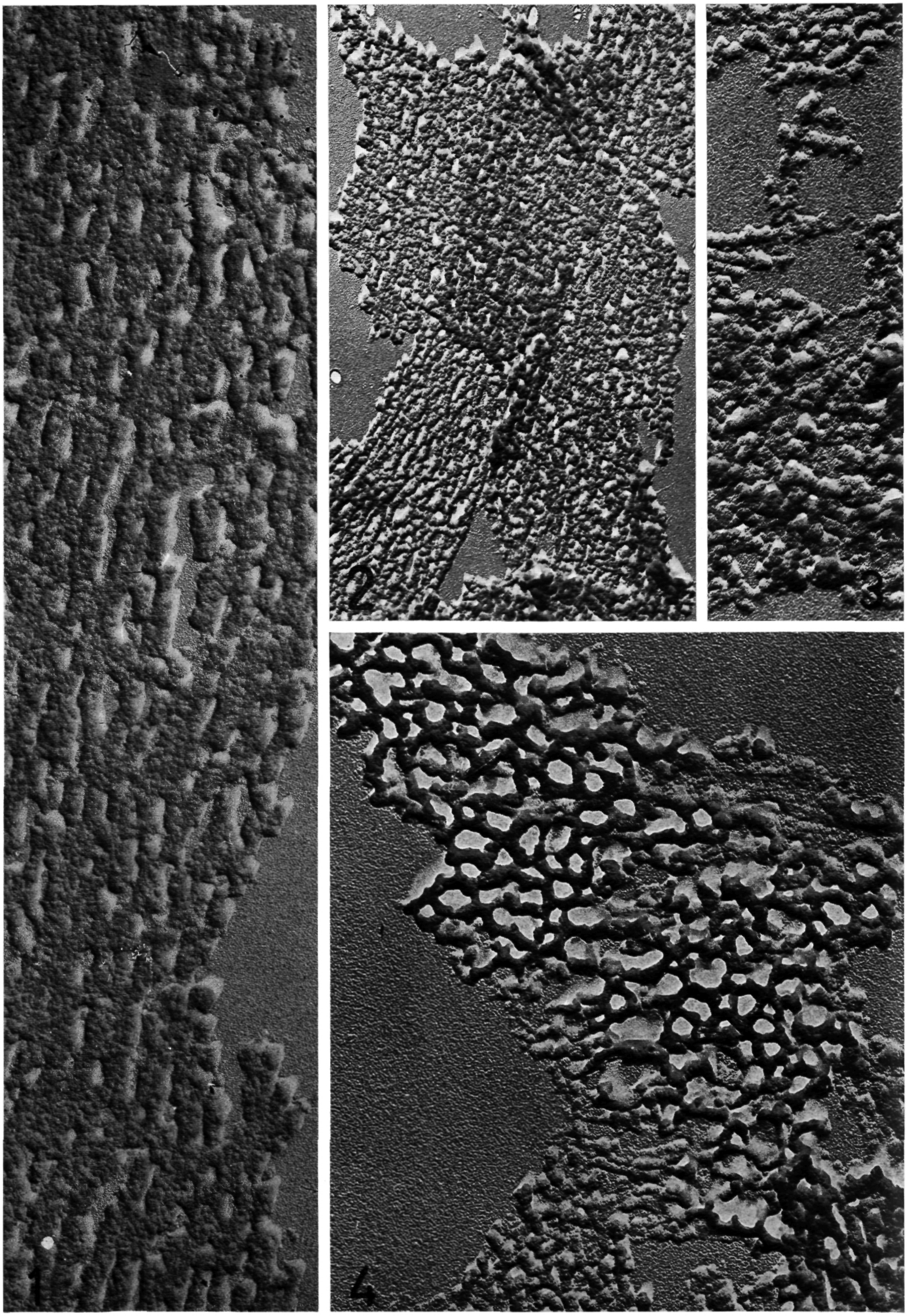
vermicular cords and rings (Fig. 94), and are seen arranged with a certain degree of regularity in parallel rectangular structures (Fig. 86). The outlines of the original aragonite crystals between which the interlamellar sheets of conchiolin were sandwiched in the normal layers of mother-of-pearl are traced by coarse dense strands (Figs. 92, 94 and 95), which represent remnants of intercrystalline conchiolin. Electron diffraction diagrams of these geometrical structures were composed of rings with diffuse boundaries (Fig. 91) or revealed a certain degree of crystallinity (Fig. 90). Crystal « ghosts » (Fig. 95) with an electron diffraction diagram similar to that shown in Fig. 91, contained altered remnants of reticulated sheets in their original orientation, seen in the middle portion of the hexagonal figure.

Fibres and fibrils were observed in several preparations (Fig. 88).

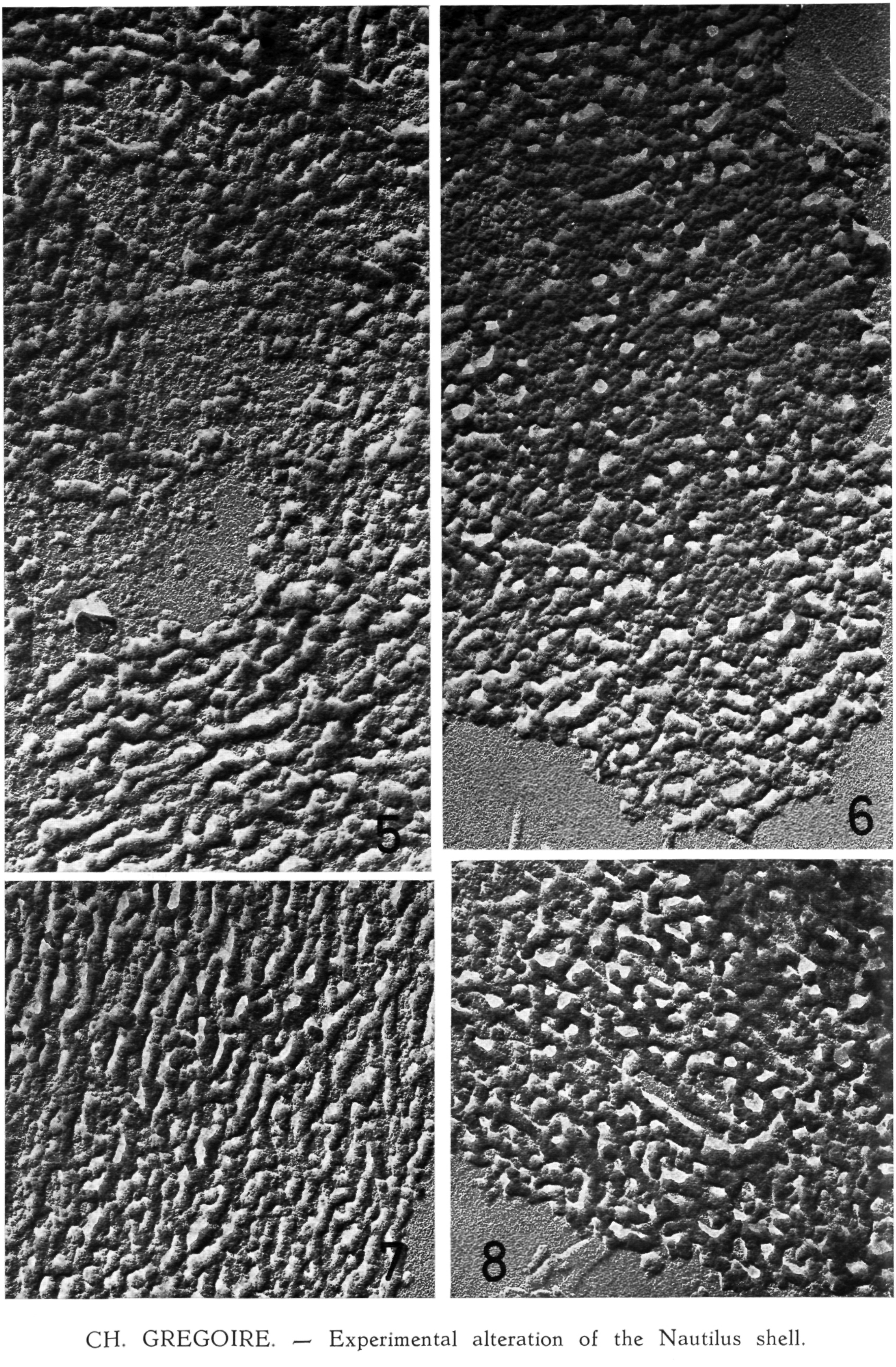
In unshadowed material (Fig. 89), the small corpuscles appear to contain sharply outlined, opaque grains, about 10 Å in diameter.

Shadowed with platinum. Direct prints: Fig. 86 (×60.000); Fig. 88 (× 60.000), Fig. 92 (× 60.000); Fig. 93 (× 70.000).

Unshadowed material : Fig. 89 (× 96.000); Fig. 94 (× 48.000) and Fig. 95 (× 42.000).



CH. GREGOIRE. — Experimental alteration of the Nautilus shell.



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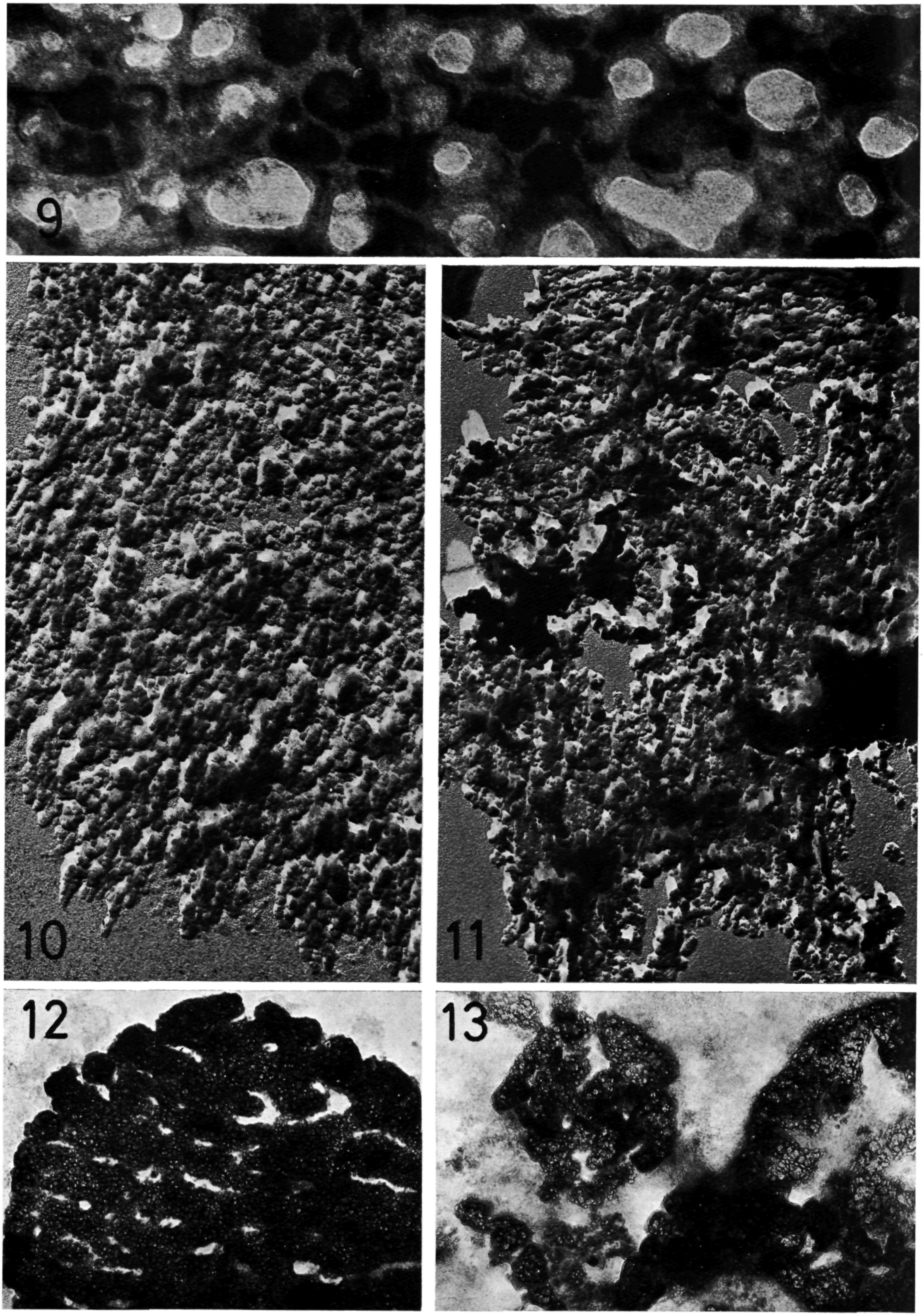

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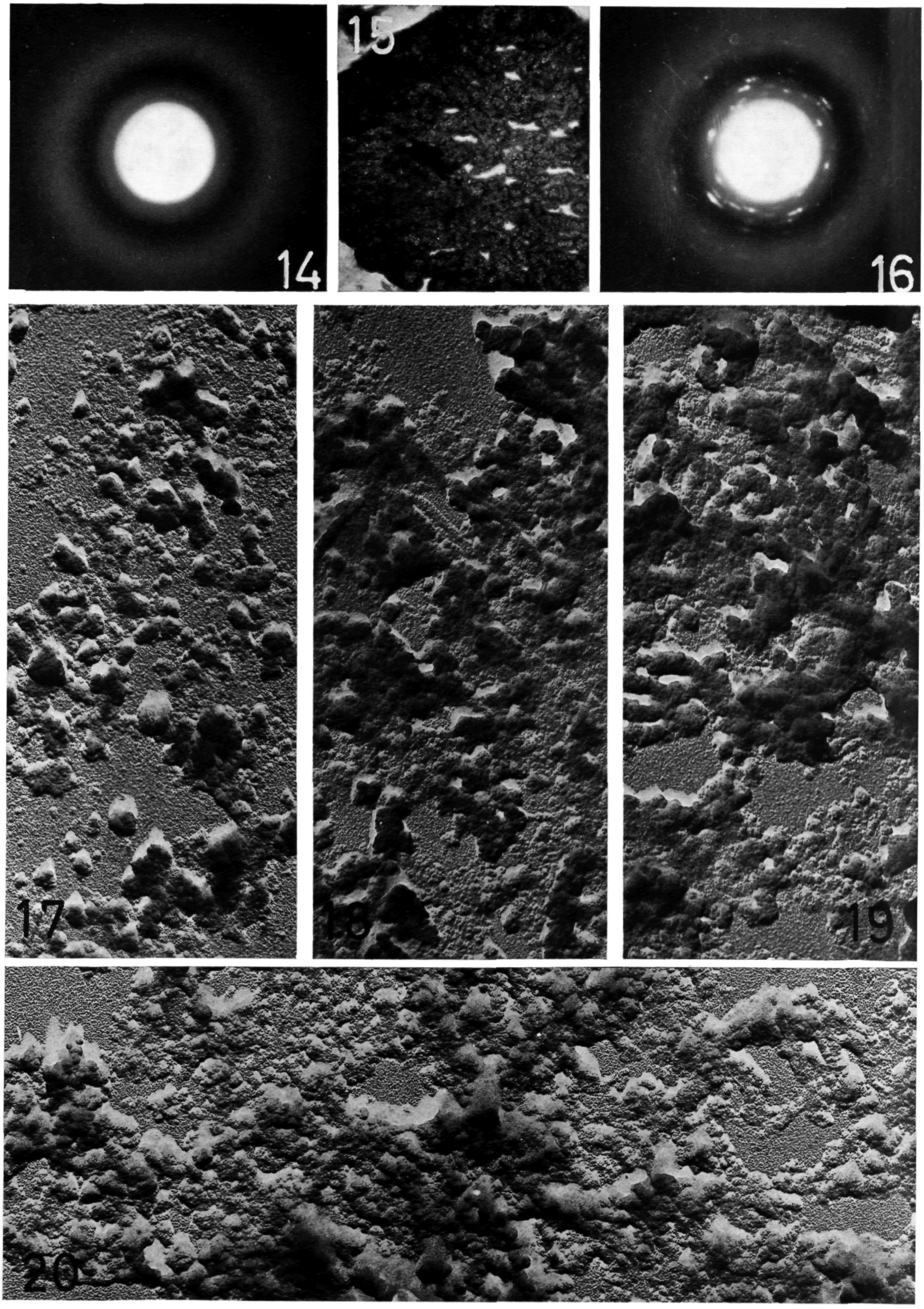

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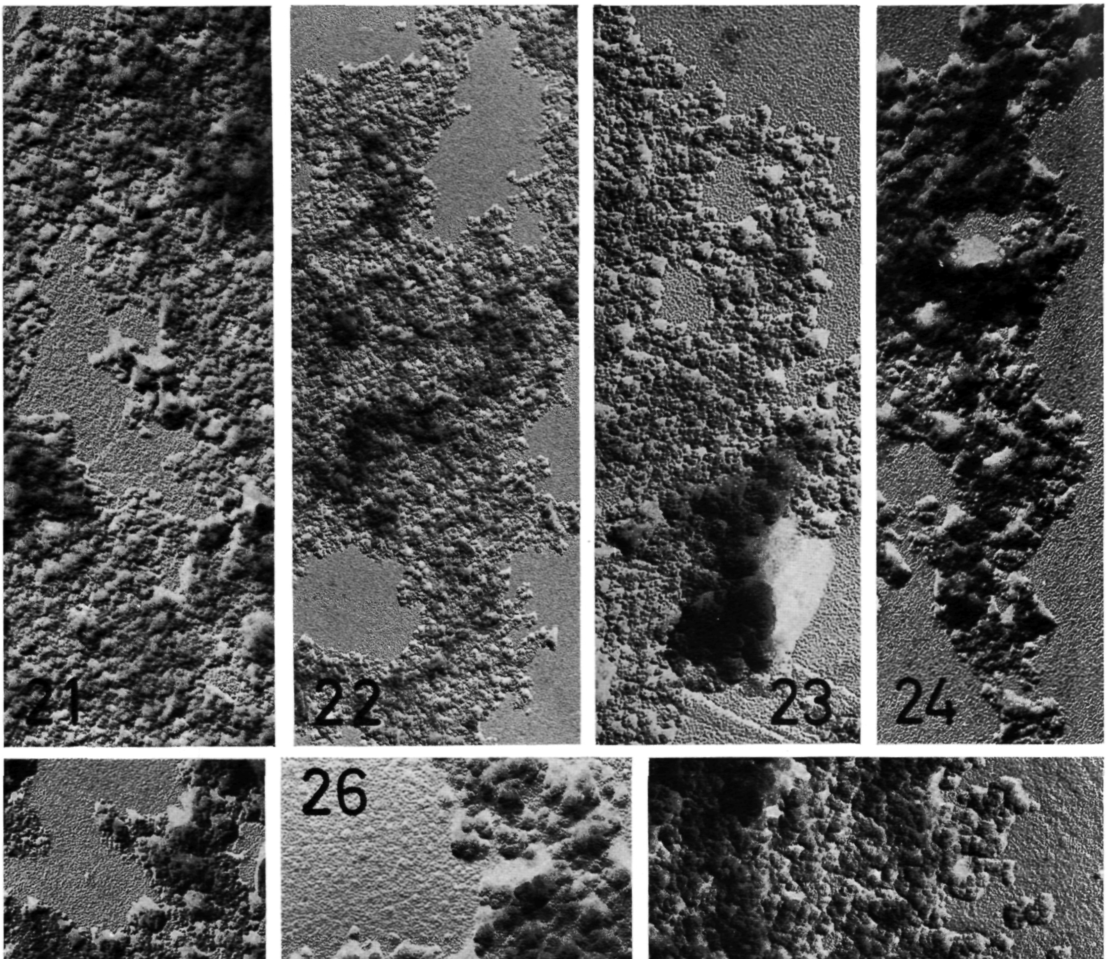

ÇH. GREGOIRE. — Experimental alteration of the Nautilus shell.

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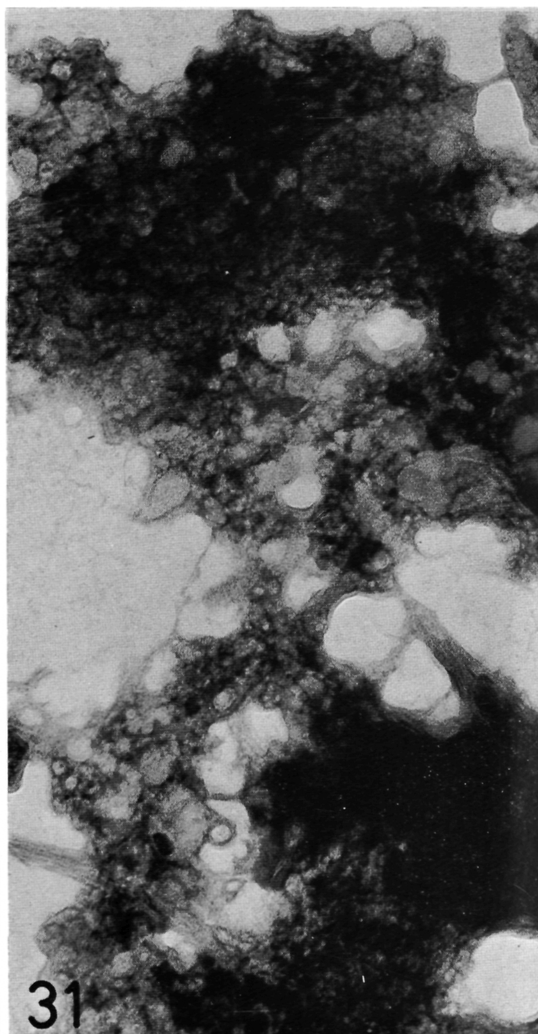

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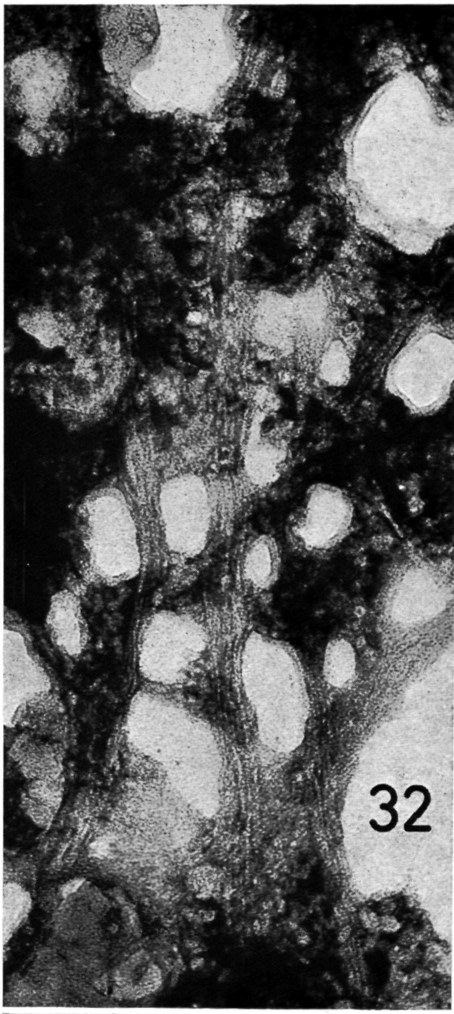

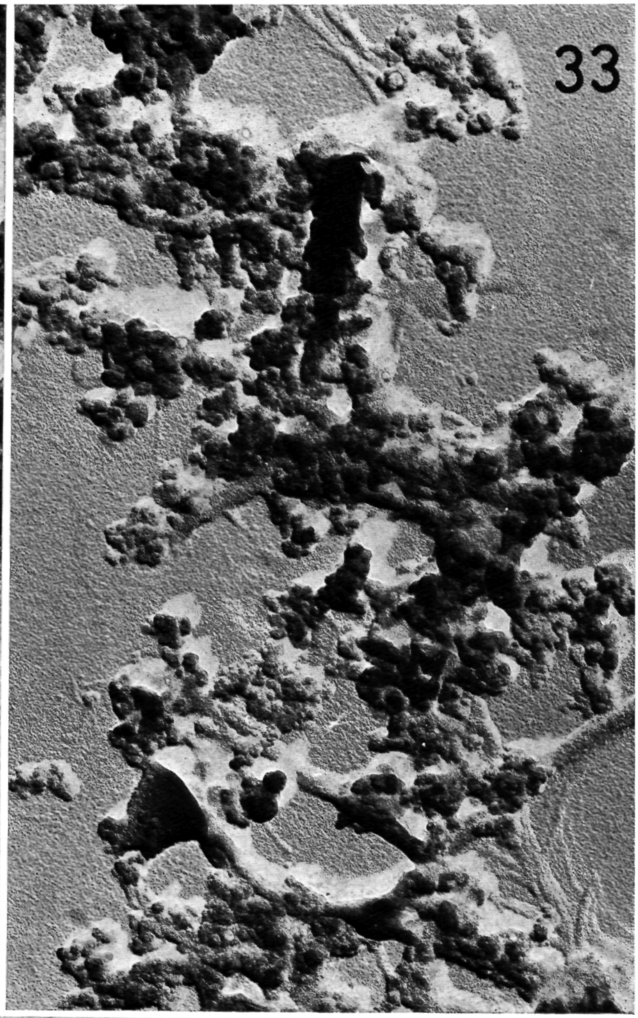

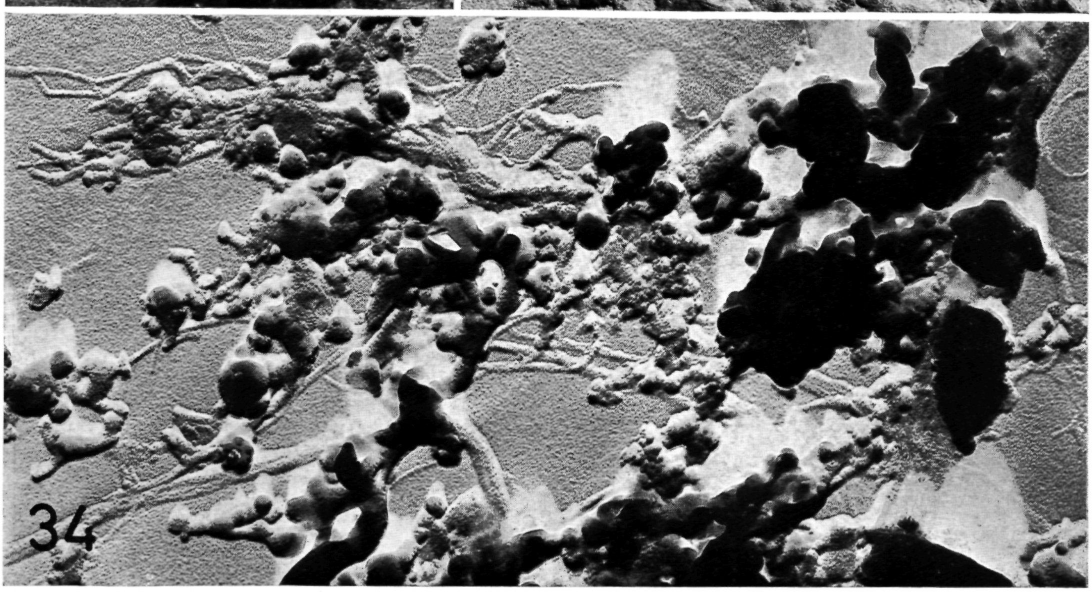

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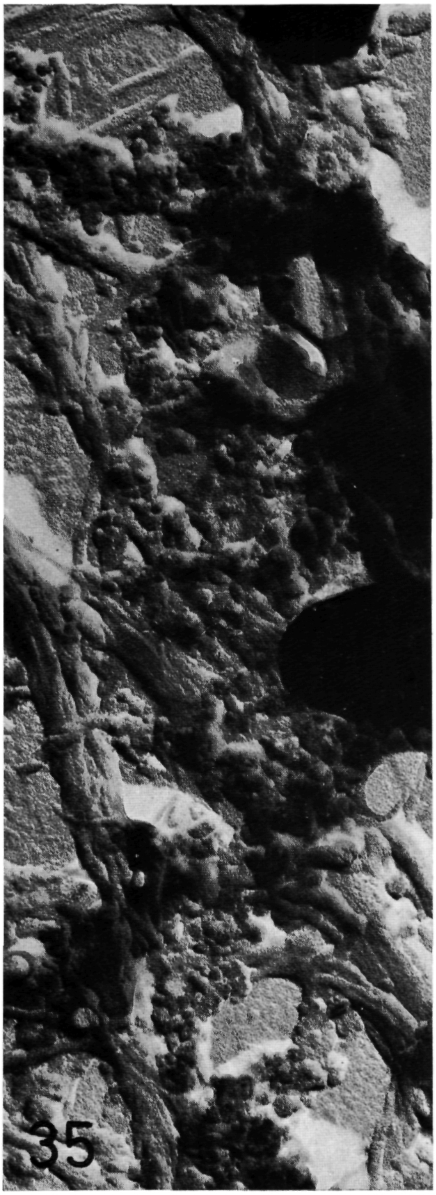
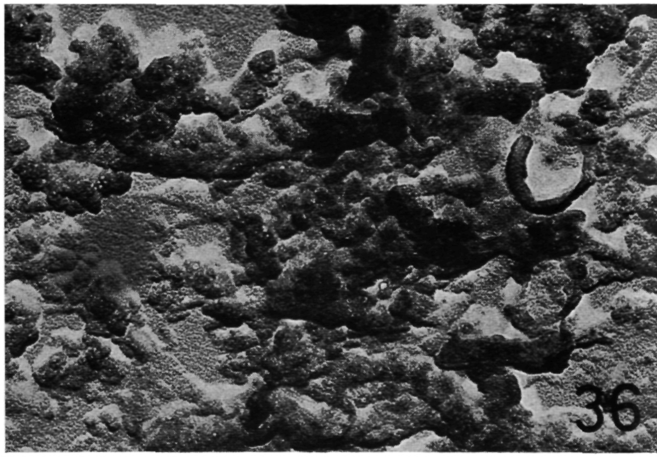
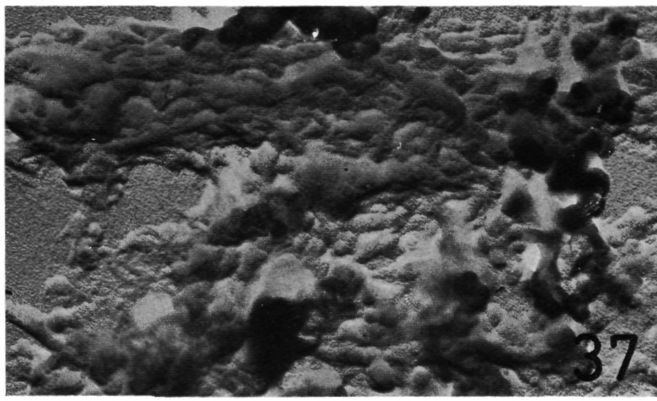
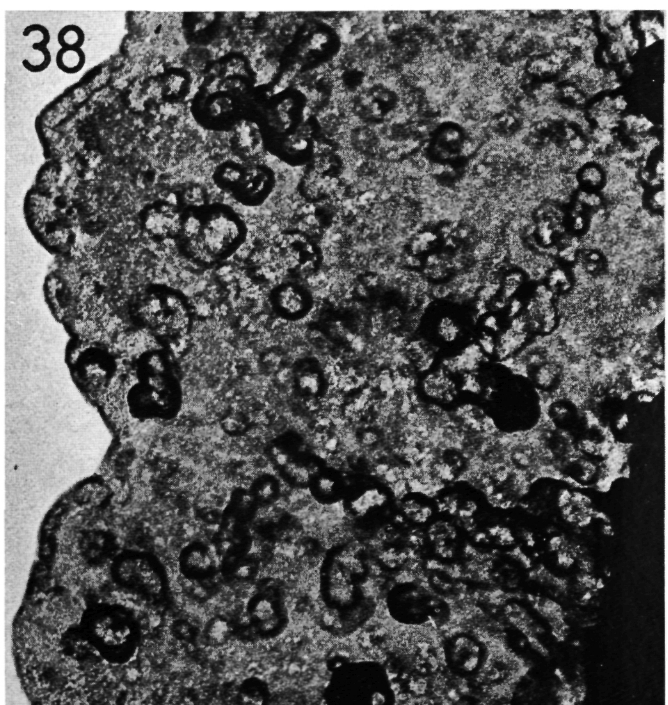
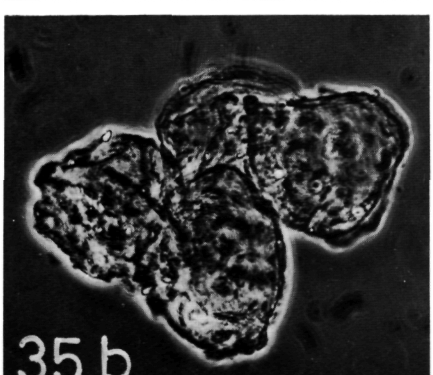


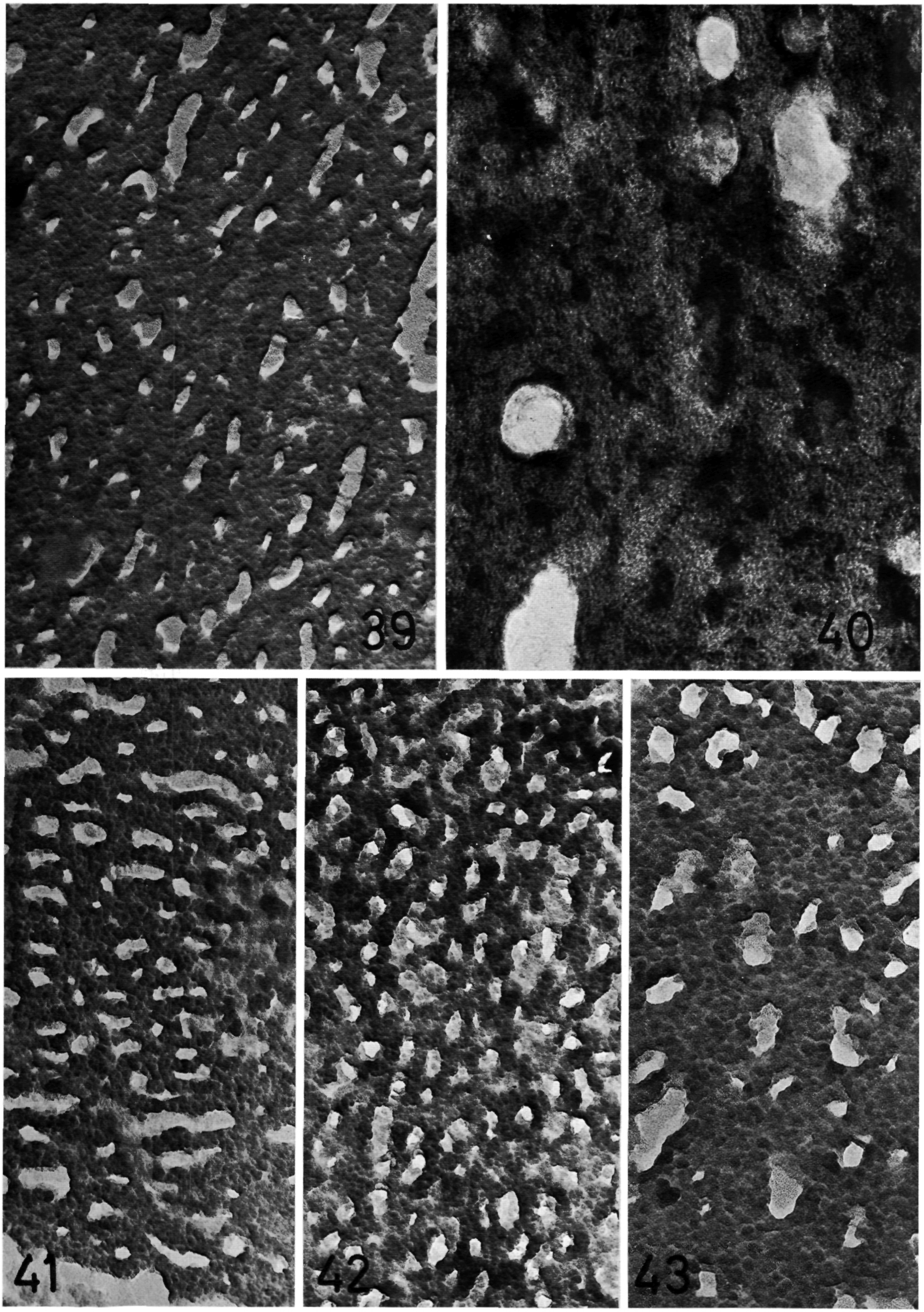








CH. GREGOIRE. — Experimental alteration of the Nautilus shell.



CH. GREGOIRE. — Experimental alteration of the Nautilus shell.

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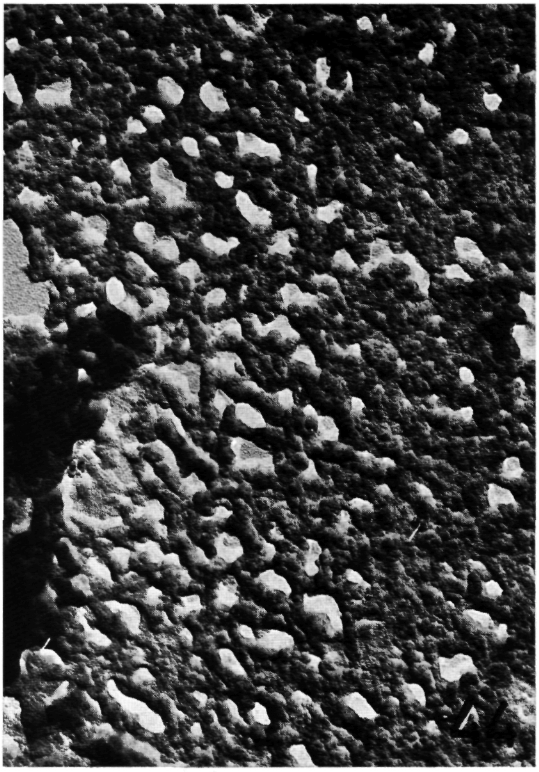
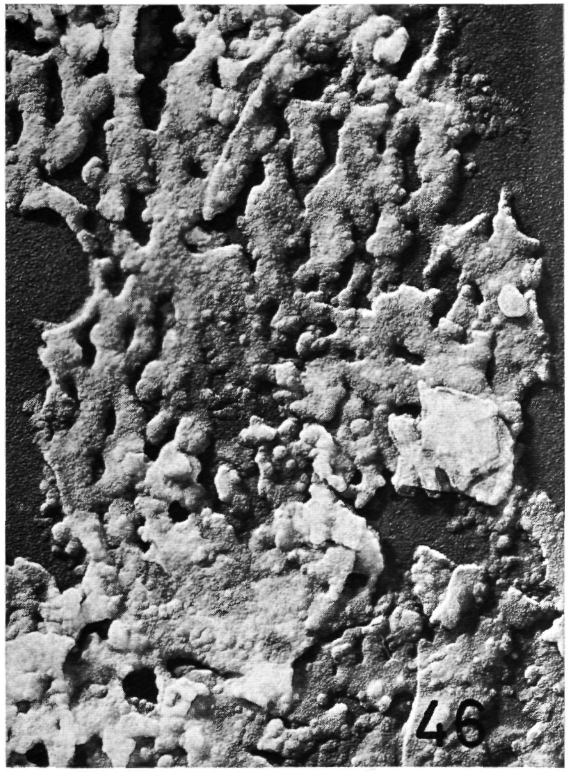
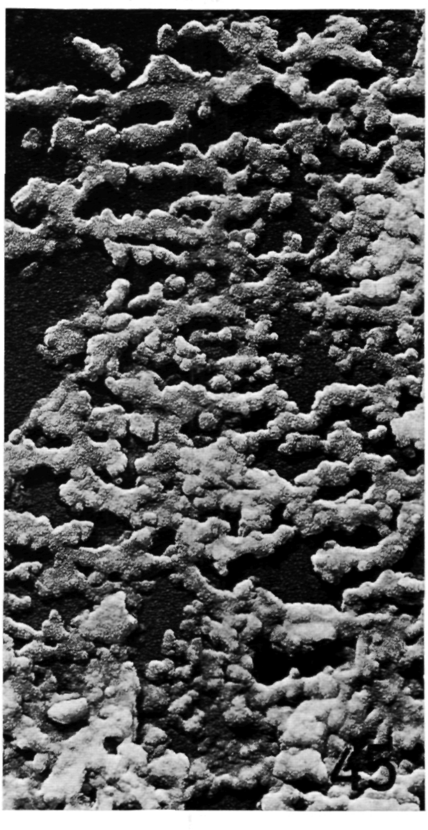
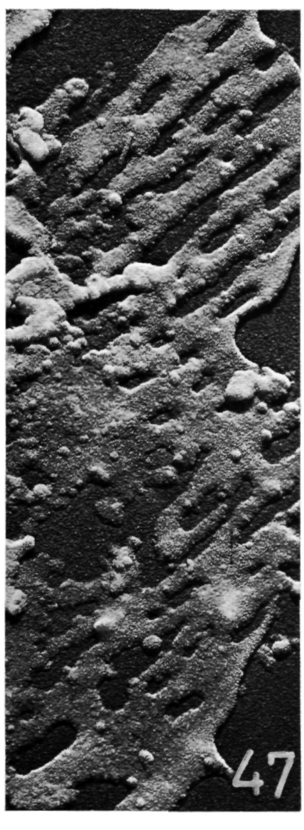
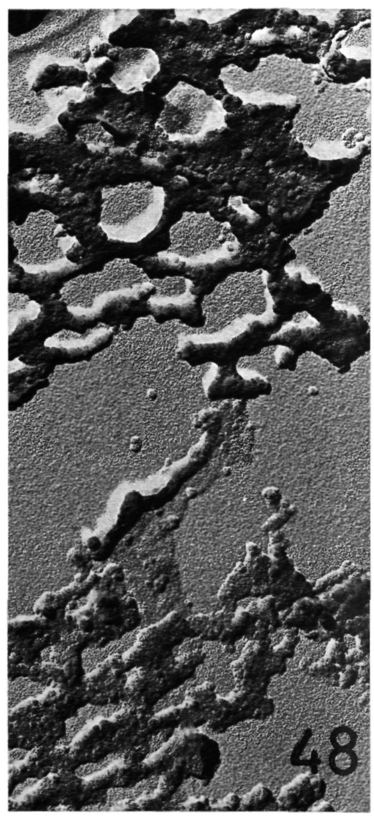
Bull. K. Belg. Inst. Nat. Wet. — D. **44**, Nr 25, 1968.











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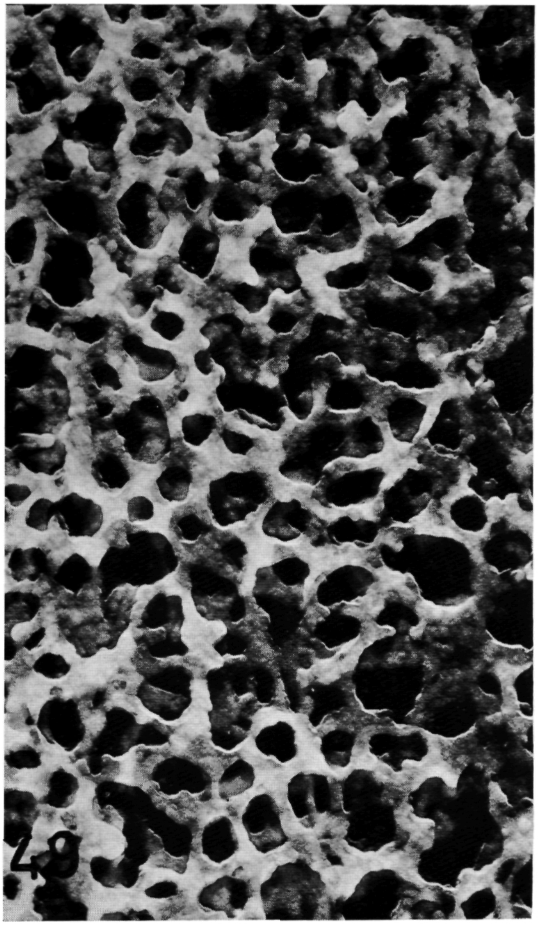

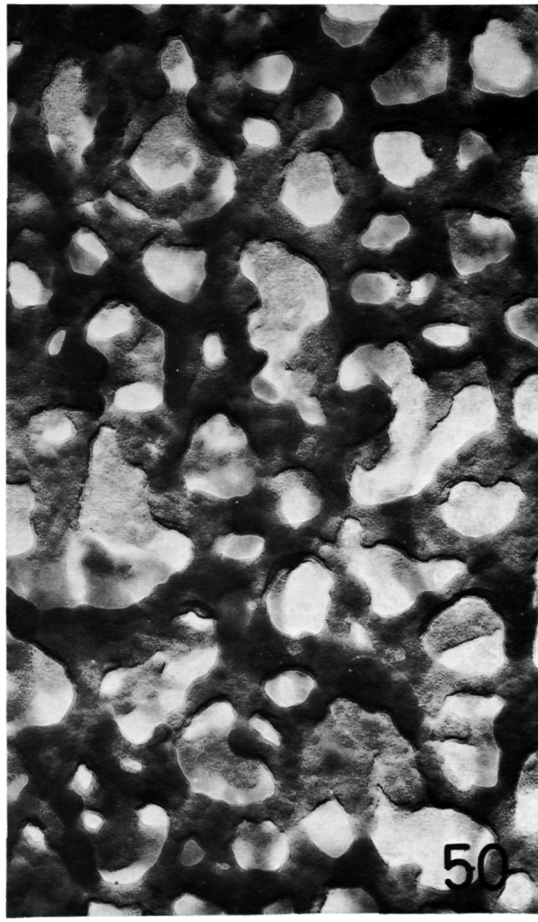

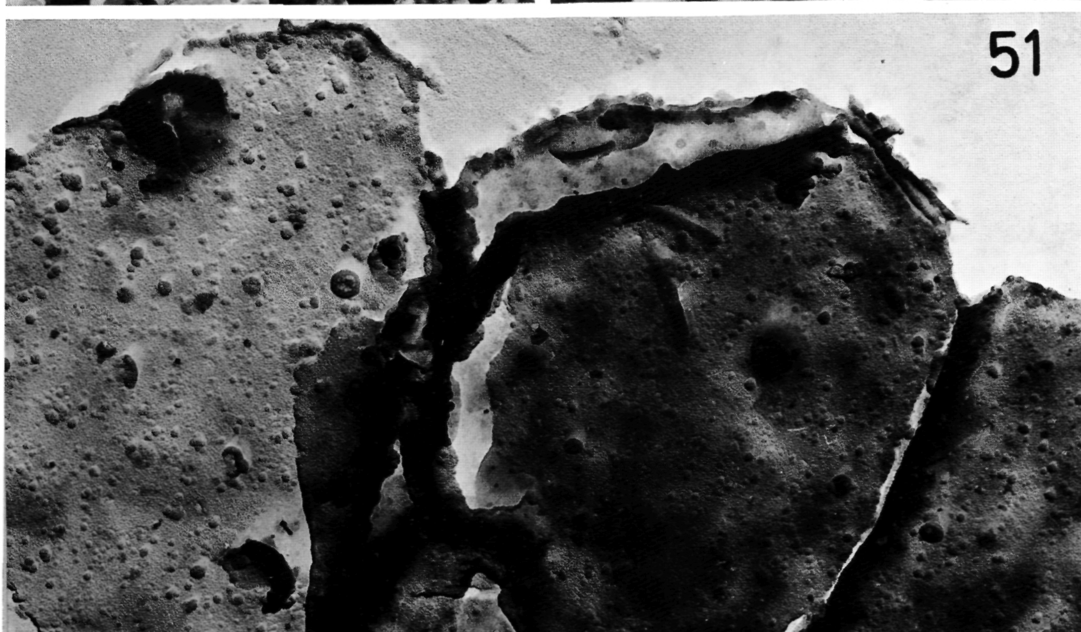

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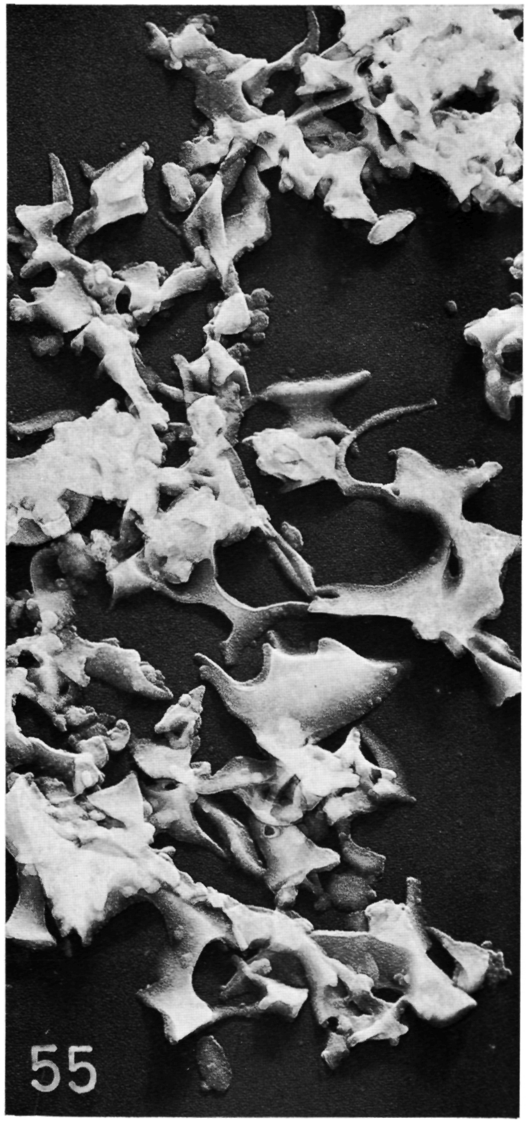

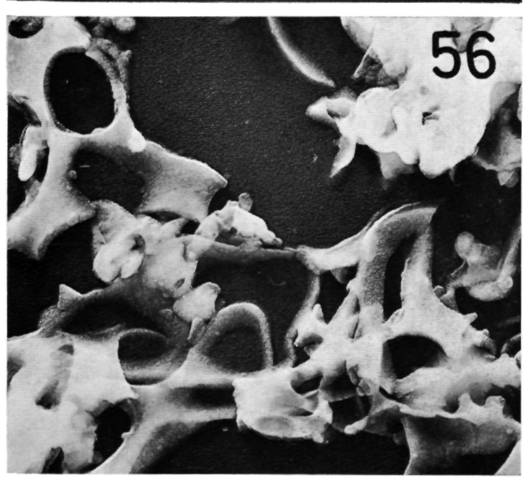

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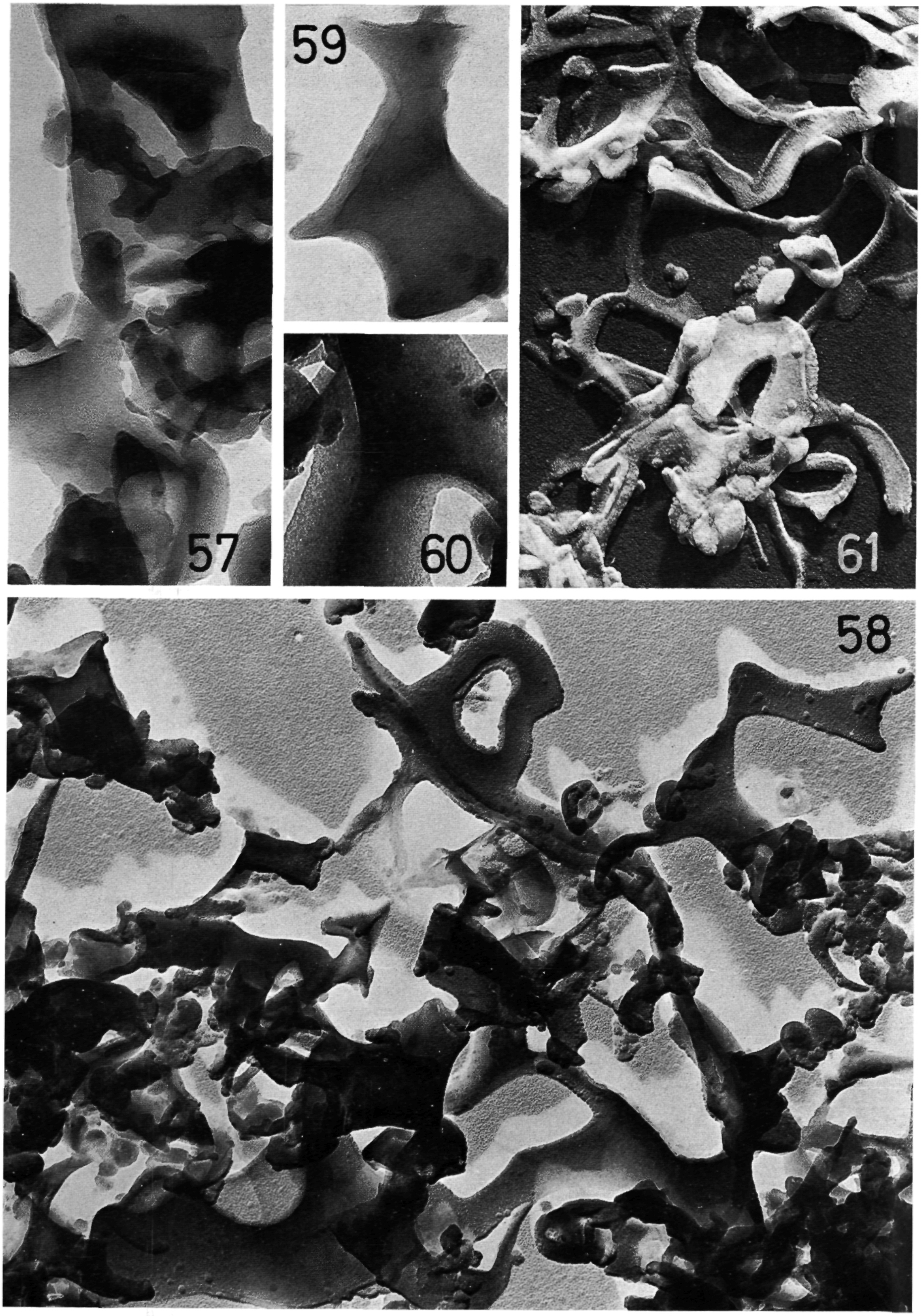

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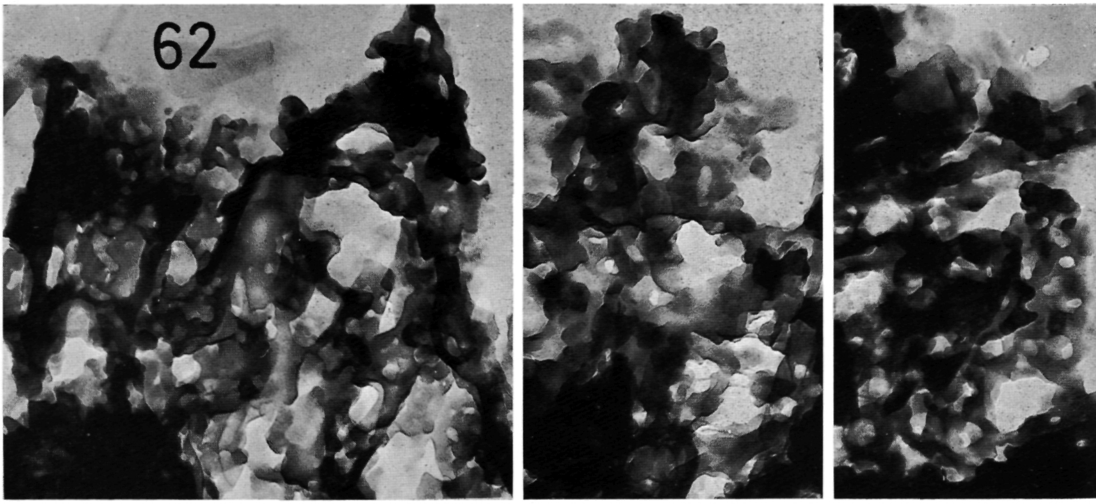

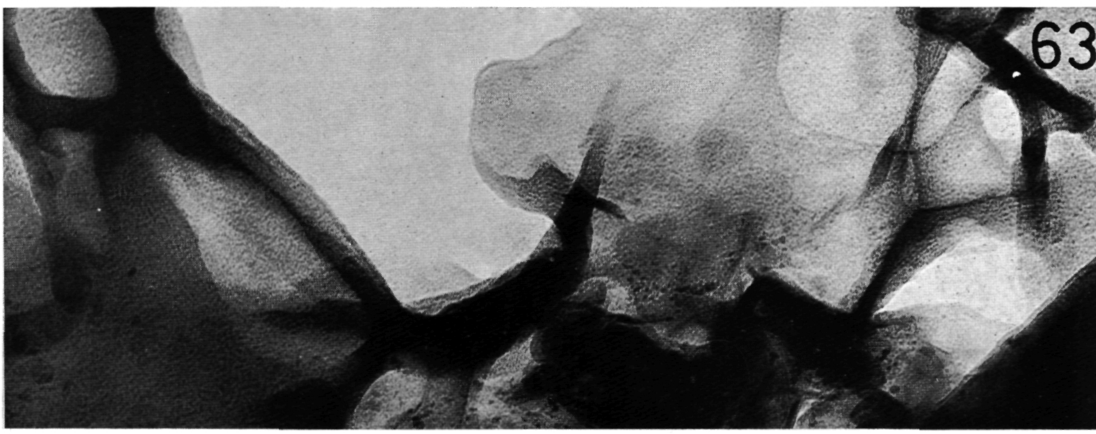

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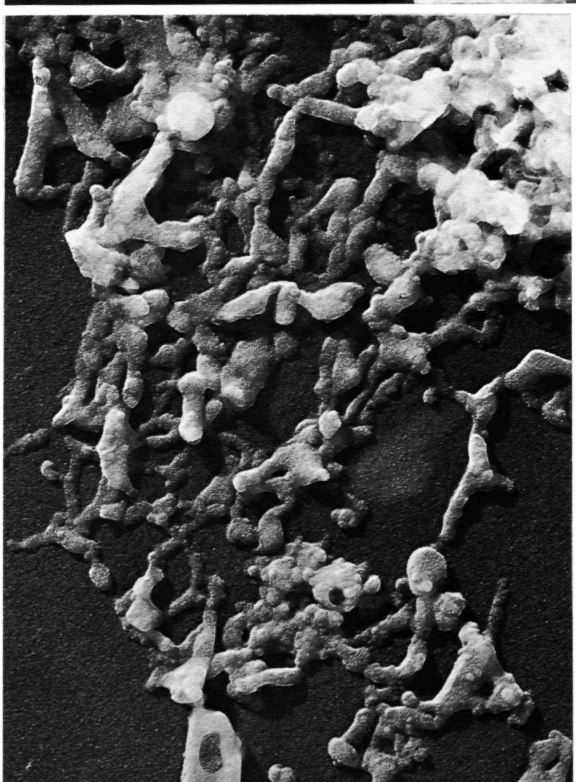
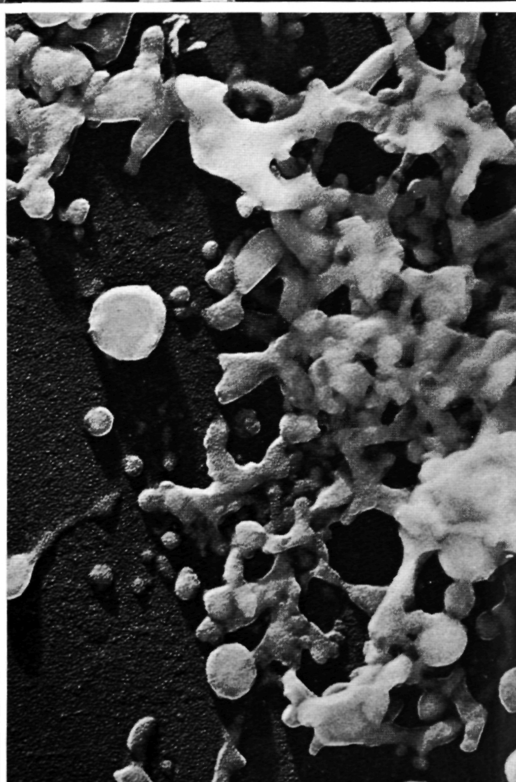
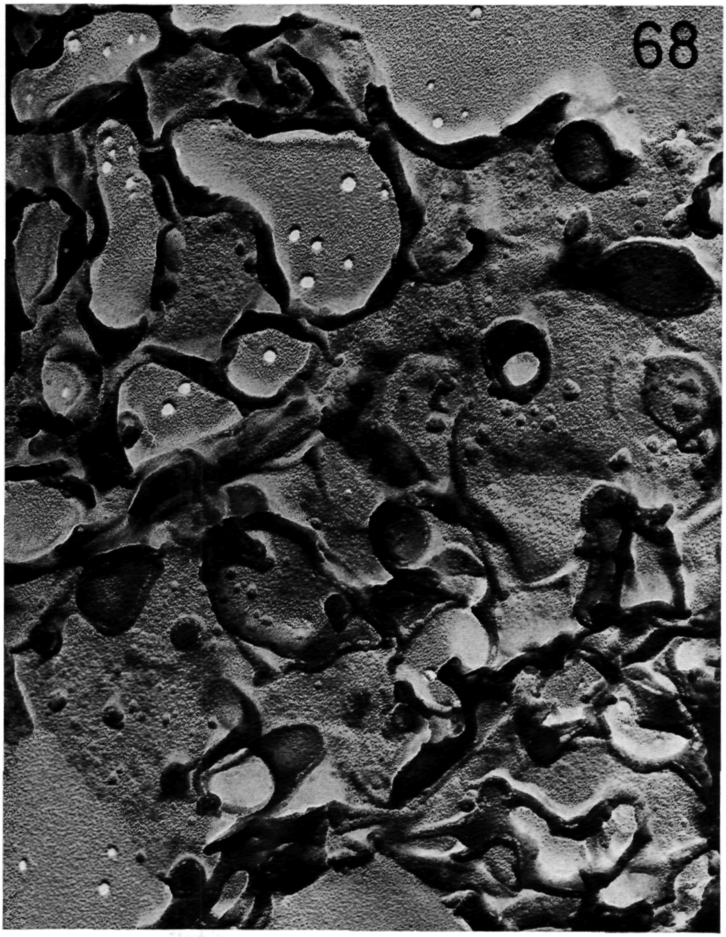
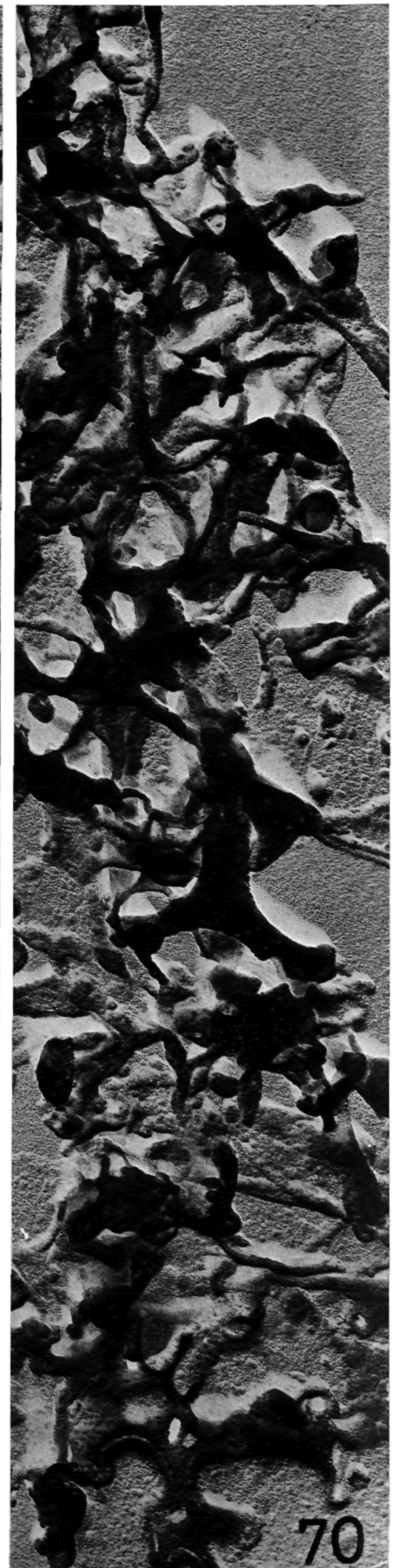




ÇH. GREGOIRE. — Experimental alteration of the Nautilus shell.





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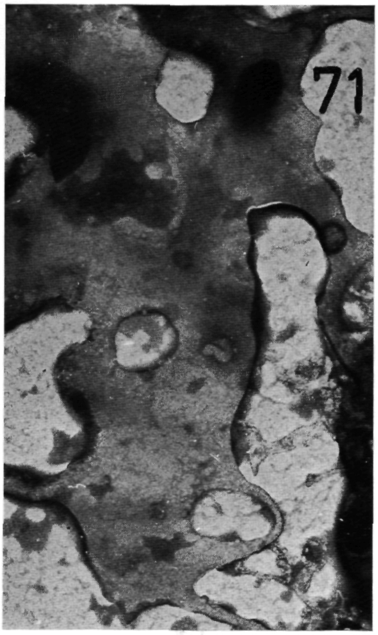
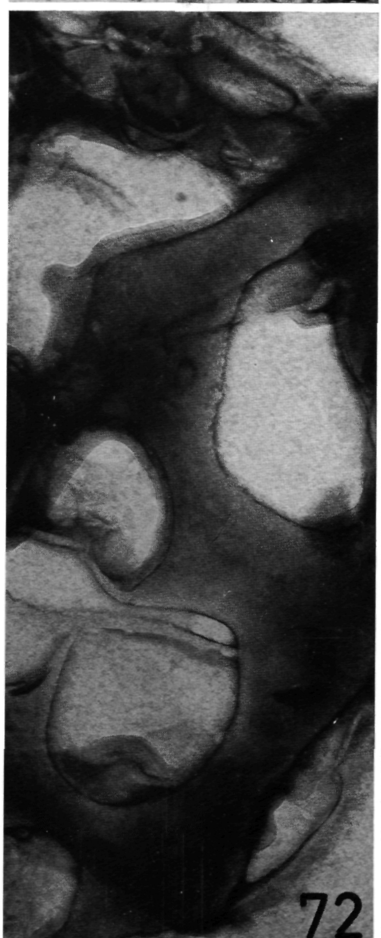

71


73


72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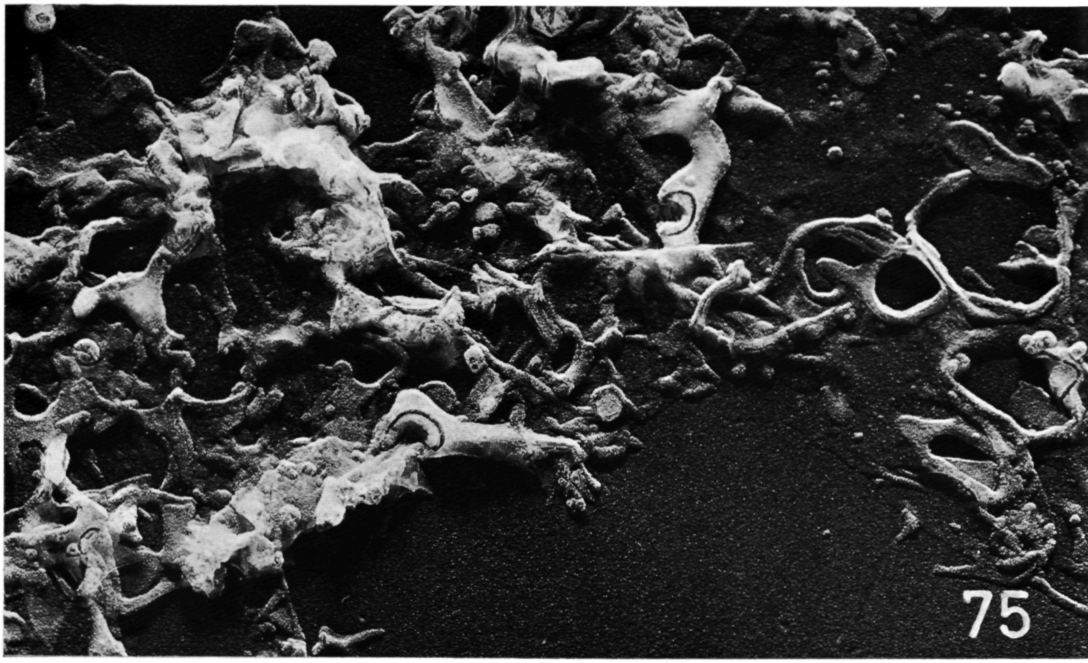

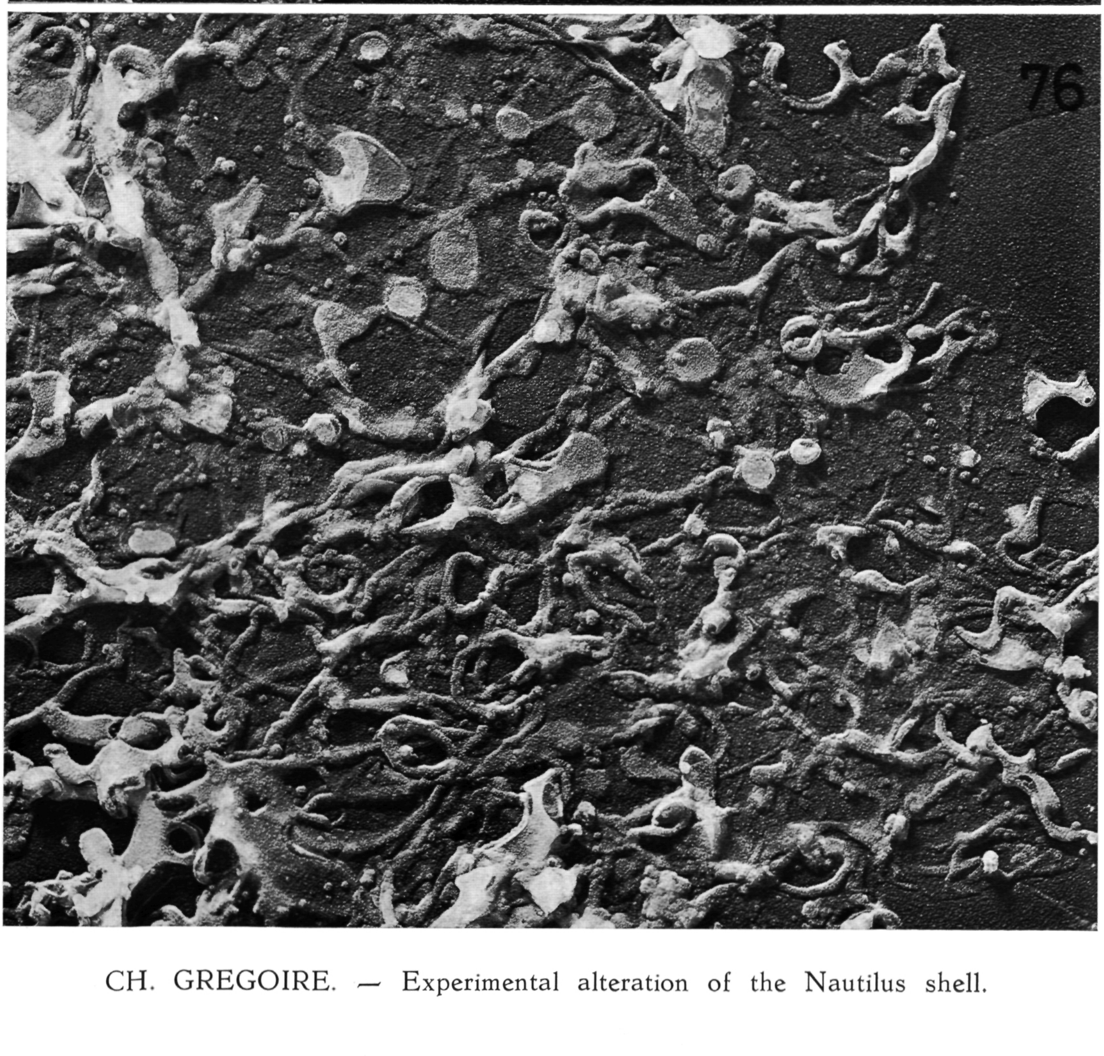

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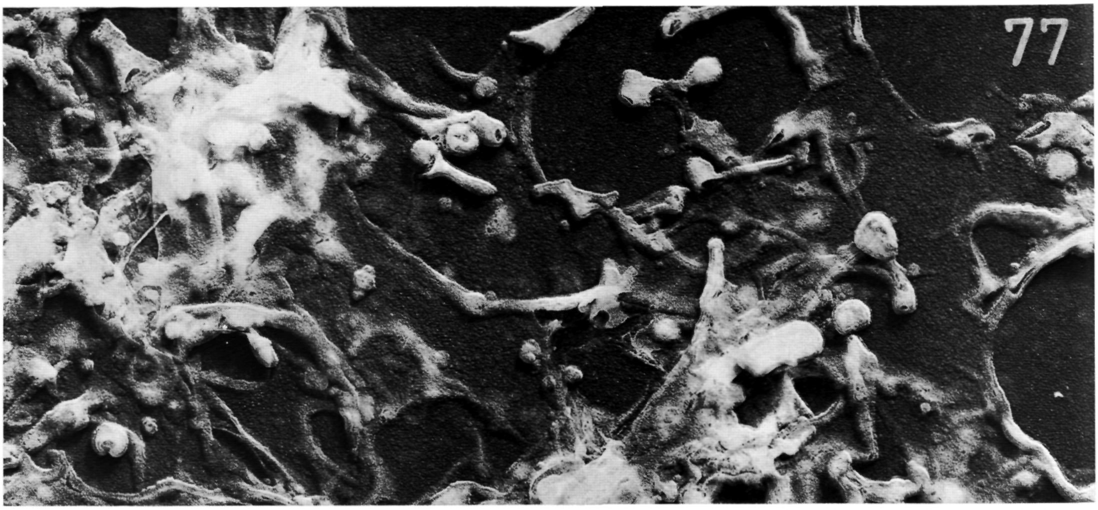

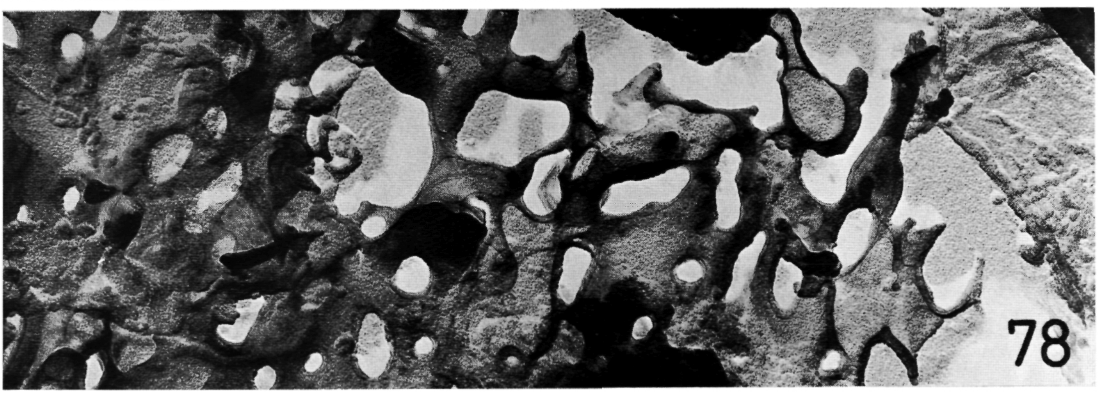

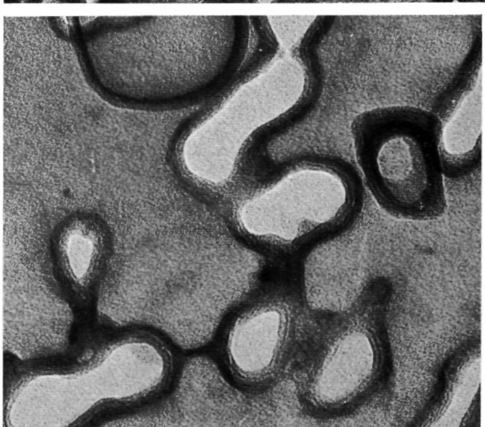

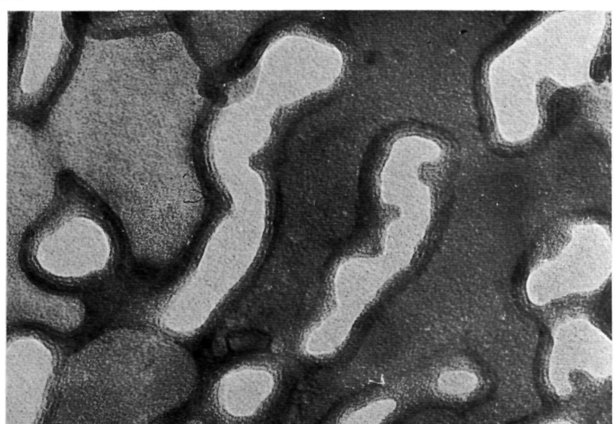

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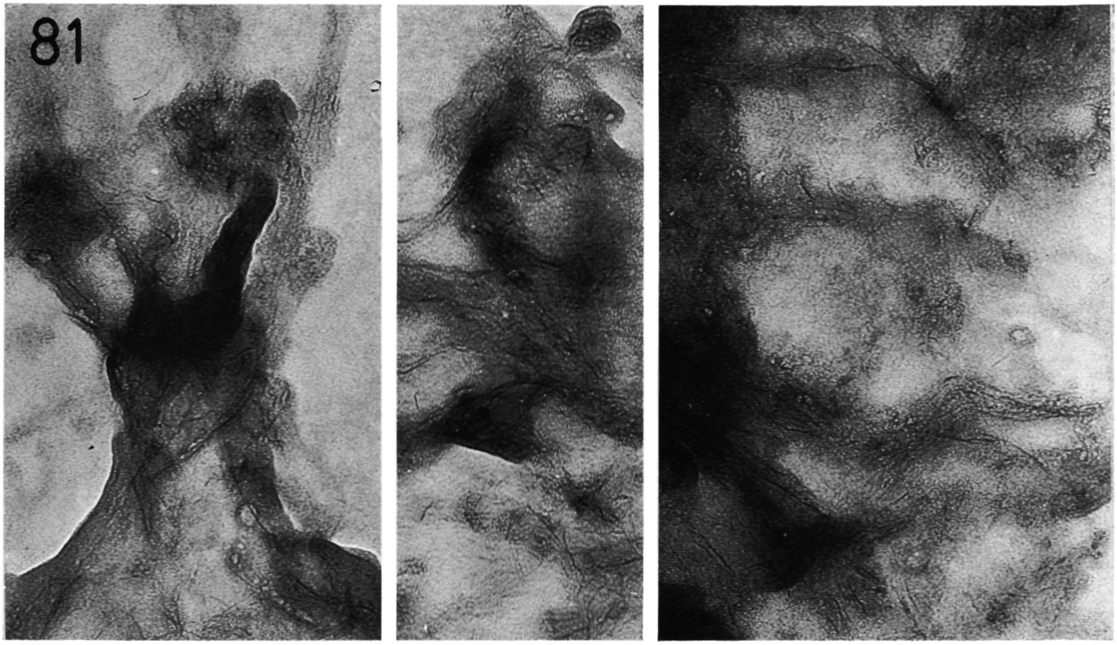
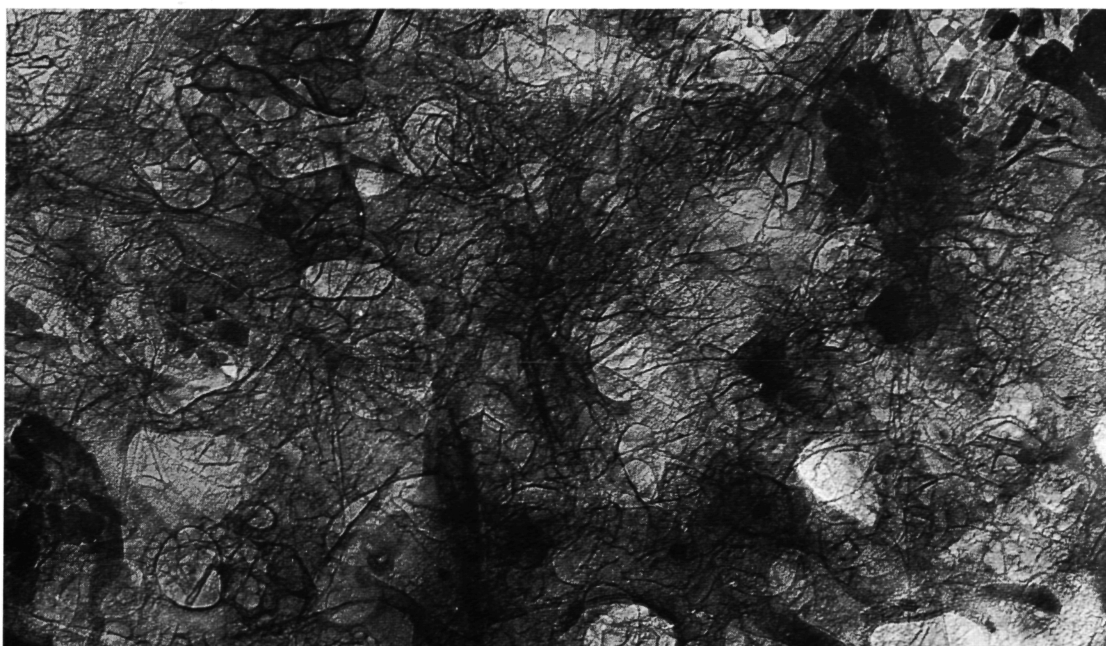


81



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CH. GREGOIRE. — Experimental alteration of the Nautilus shell.

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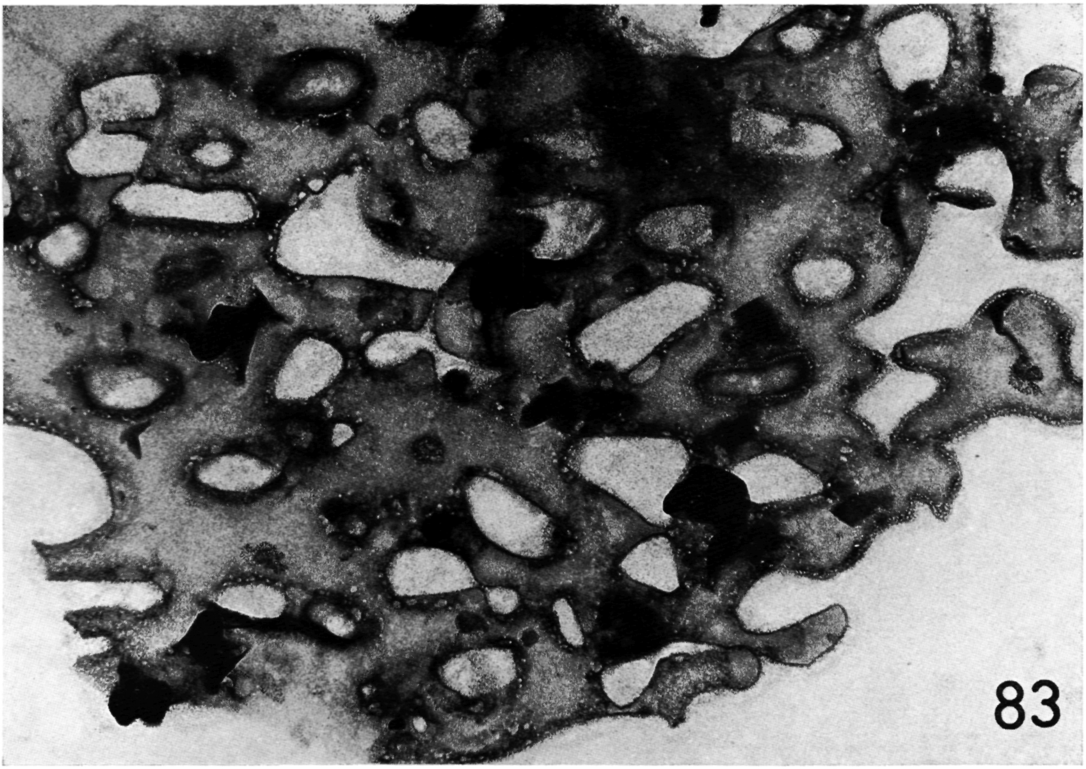

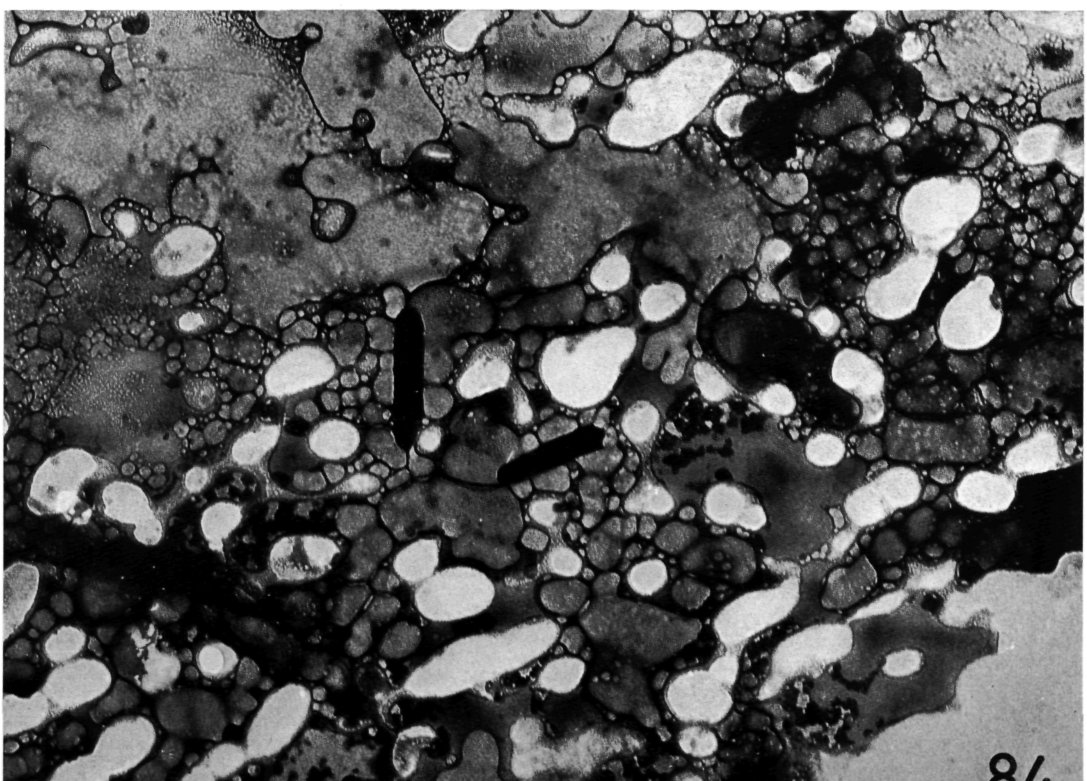

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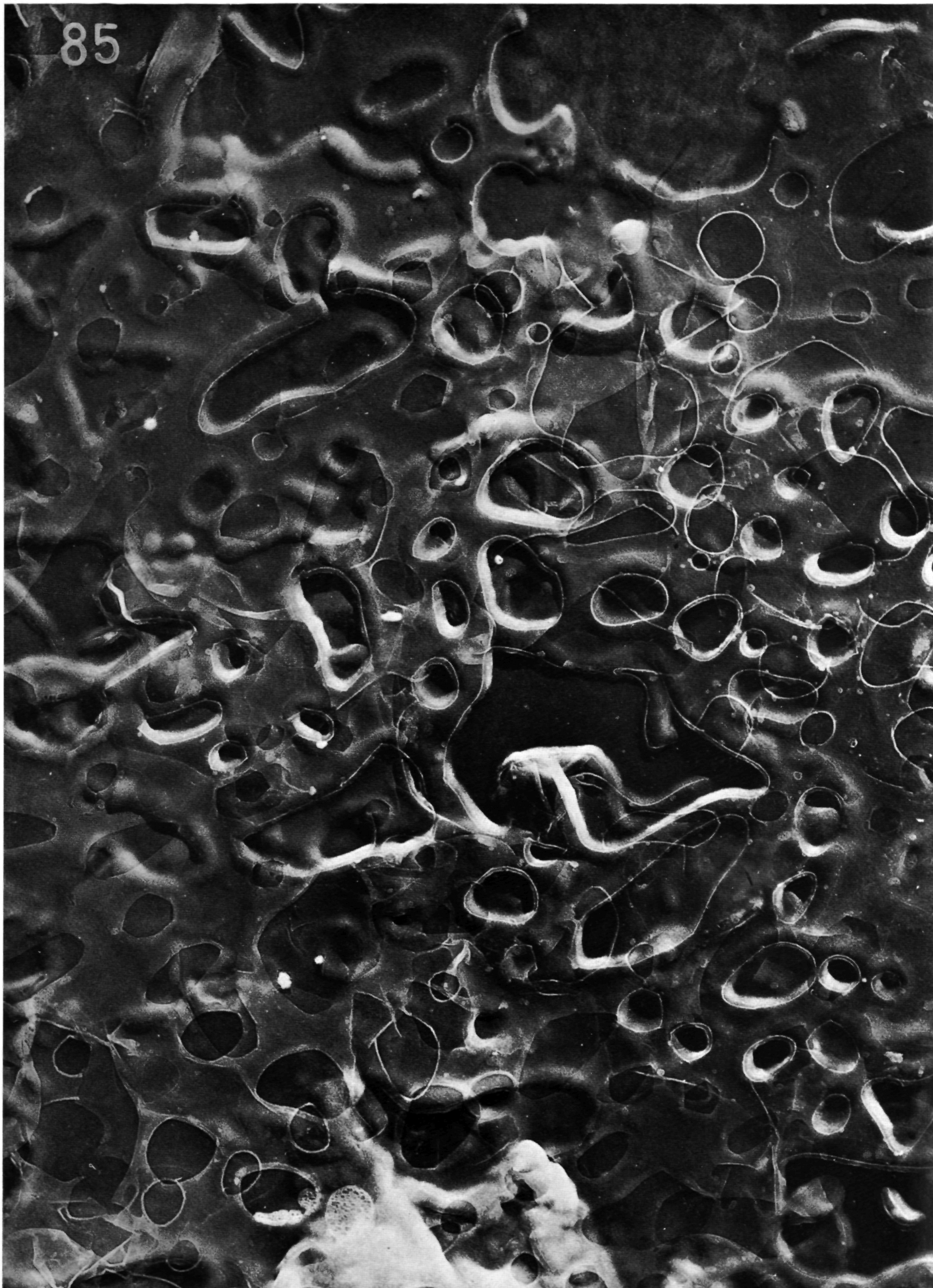

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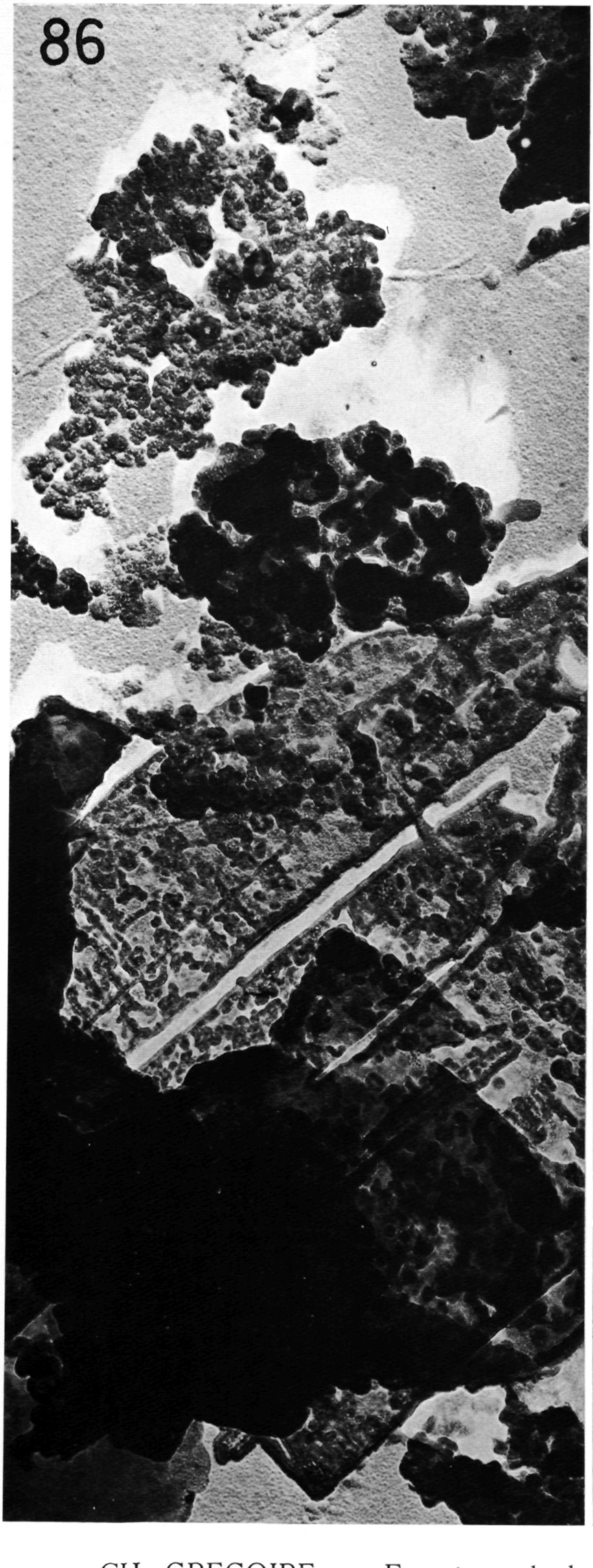

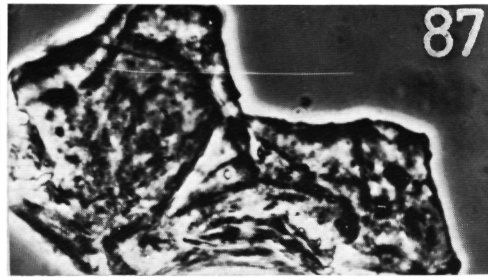

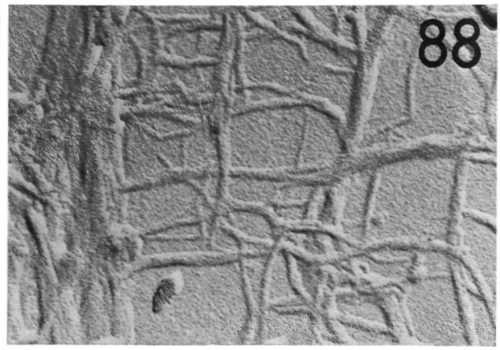

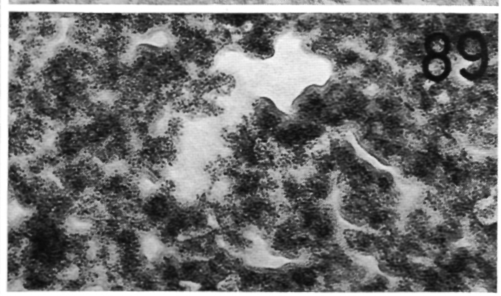

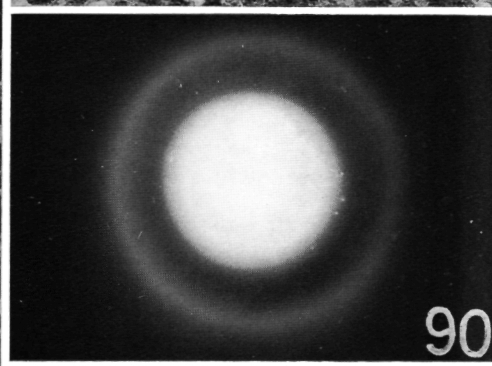

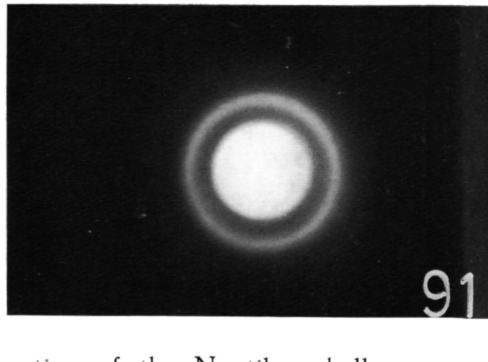

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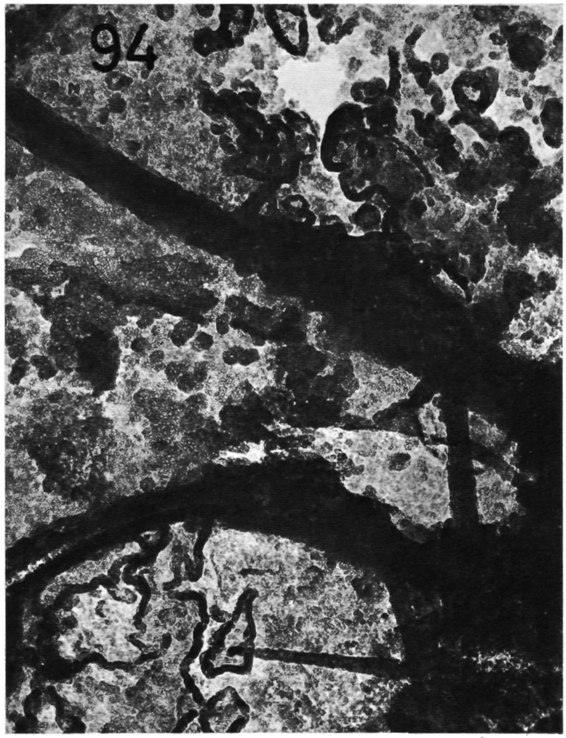

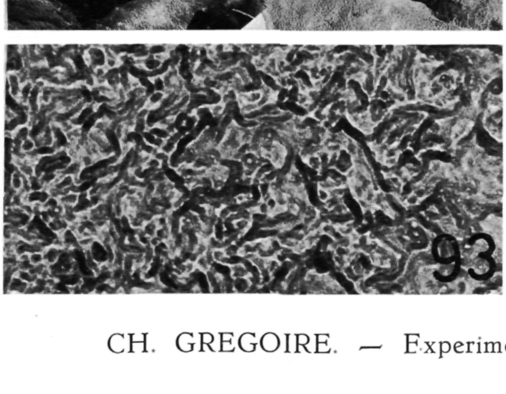

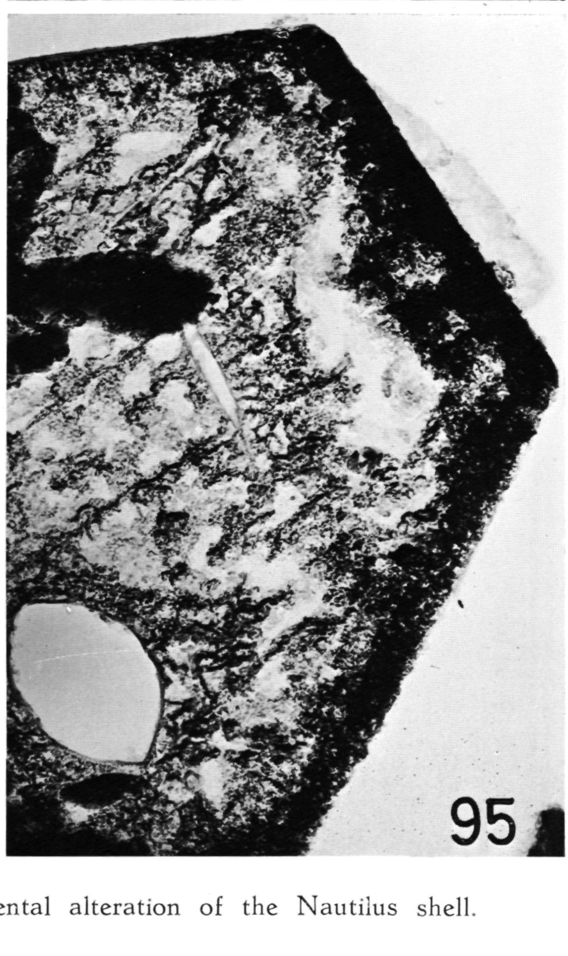

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AD. GOEMAERE, Imprimeur du Roi, 21, rue de la Limite, Bruxelles 3