Mitt. Geol.-Paläont. Inst. Univ. Hamburg	Heft 61	ULRICH LEHMANN Festband	S. 21–33	Hamburg Dezember 1986

Unusual transformation of $CaCO_3$ into $CaSO_4$ with preservation of original structure

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With 3 plates and 1 text-figure

Contents

Zusammenfassung

Kalkschalen von Mollusken und Echinodermen, die während der Ablagerung miozäner Sedimente in der Sahabi Region des Sirte Beckens Libyens entstanden, wurden anschließend in Gips umgewandelt. Dieser Diagenesevorgang steht im Zusammenhang mit dem Übergang von normal marinem Flachwassermilieu zu salineren Verhältnissen in der „Messinischen Phase". Lokal blieben bei der Umwandlung von Kalziumkarbonat zu Kalziumsulfat sowohl die Kreuzlamellenstruktur der Mollusken wie die wohlgeordnete Gitterstruktur der Echinodermen und sogar die optische Ausrichtung der Biokristalle erhalten. Kalzit wie Aragonitstrukturen wurden an anderer Stelle beim Übergang in Gips verändert oder verschwanden.

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Abstract

Calcareous shells of molluscs and echinoderms grown during the deposition of Miocene sediments at the Sahabi area, Sirti Basin, were transformed into gypsum. Diagenetic alteration is connected with the switch from shallow normal marine environment to salinal conditions of the Messinian stage. The original crossed lamellar structure of the aragonite and the spongeous well ordered structure of the calcite were preserved in parts of the shells, altered in other parts of the same shells, or totally destroyed. In well preserved portions of the shell even primary optical orientation of the aragonitic and calcitic biocrystallites survived the transformation from calcium carbonate to calcium sulphate.

I. Introduction

The diagenetic observations discussed in this paper occur in calcareous shells of invertebrates which have been collected during field works in the Sahabi area in Libya. The exact locality is P 53 by the International Sahabi Research Project (DE HEINZELIN et al. 1980) (Fig. 1).

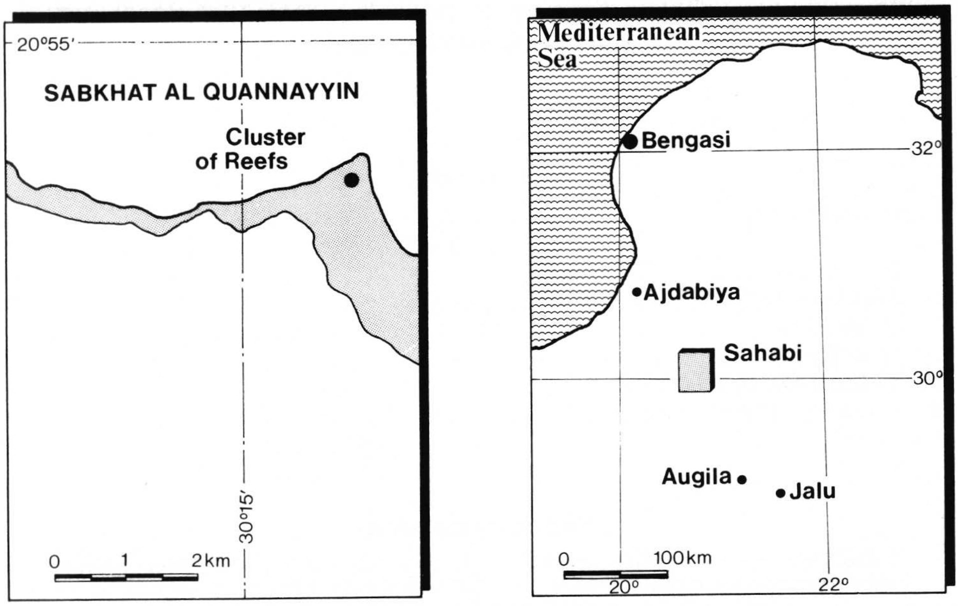

Fig. 1: Maps showing the location where studied fossils were collected. The gray area shows outcropping Formation M and the collecting site (dot).

The Sahabi area is located on the eastern margin of the Sirte Basin and is situated about 100 km south of the town Ajdabiya on the road to the oasis of Jalu. The eastern margin of the study area includes a part of the depression of Sabkhat al-Quannyyin lying around 25 m below sea level (DE HEINZELIN et al. Ibid.). Near the ruins of the Qasr as-Sahabi, an ancient fort used at Roman, Byzantine, and Turkish time, in the early thirties fossil bones of vertebrates were discovered (see historical review of this site in: DE HEINZELIN et al. 1980) that made this site well known to science.

According to the results of the geological mapping carried out in this area (DE HEINZELIN & EL-ARNAUTI, 1982) three formations can be distinguished here. These are:

Sahabi Formation
Formation P
Formation M

According to DE HEINZELIN and EL-ARNAUTI (1982: 5–9), Formation M is exposed in the floor of the Sebkhat al-Quannayyin with an accessible thickness of about 10 m. It consists of sandy detrital material which includes single coral patch reefs as well as clusters of reefs associated with numerous invertebrate fossils belonging to bivalves, gastropods, and echinoids as well as vertebrate remains like bones of sirenians and cetaceans.

According to DE HEINZELIN and EL-ARNAUTI (1982), Formation M was deposited on a shallow shelf in normal open-sea marine conditions and it can be correlated with the Upper Ar-Rajmah Formation of Middle Miocene age as exposed in the Benghazi area (see also MEGERISI & V. D. MAMGAIN, 1980: 72).

Formation M is overlain by evaporitic sediments of Formation P. Its observed thickness ranging from 0 to 25 m contains gypsum and clastic grains intercalated with dark sand and clay. It is presumed that Formation P was deposited during the time of the salinity crisis of the Mediterranean Sea at the Messinian stage of the Late Miocene (DE HEINZELIN & EL-ARNAUTI 1982).

In the Sahabi area, the youngest rocks exposed consist of the Sahabi Formation that had been deposited on a shallow continental shelf. Its facies indicate deposition in a transgressive neritic to littoral-deltaic base and a continental top. Sahabi Formation according to DE HEINZELIN & EL-ARNAUTI (1982: 10-11) is of Early to Middle Pliocene (Zanclian) age.

The discussed shells of pelecypods, gastropods, and echinoids have been extracted from the top beds of Formation M and have been collected from the locality P 53 (Fig. 1).

II. Structures before diagenesis

The shells studied consist of two basically different structural and compositional types. Those providing most details are molluscan shells coming from gastropods like *Vasum*, *Stromus* and *Turritella* and from heterodont bivalves. These shells represent the external skeleton of molluscs and have been secreted by the molluscan mantle. The second type of structure discussed was formed within the body of a sea-urchin (Echinodermata) and represents individual plates that compose the internal skeleton (corona). Both shell structures can be considered as biocrystals which have formed under very intense control of the organism.

a) Molluscs

The original material of the molluscan shells, presented here, consisted of aragonitic biocrystallites enwrapped with minute amounts of organic shell material. The structure of the shell is quite well known since the study of BIEDERMANN (1902) and the systematic review of molluscan shell structures by BØGGILD (1930). Additional details, seen when smaller dimensions are viewed with the scanning electronic microscope (SEM), were added by BANDEL (1975, 1979).

The smallest units of these aragonitic biocrystallites are the 0.2 micron large basal elements (BANDEL 1979), each of which is enwrapped by organic sheets. Basal elements are arranged into needles of 0.2 micron width. The smallest structural units seen in the diagenetically altered material, figured here, are these needles (Pl. 1, Figs. 4, 5; Pl. 2, Fig. 5) which may compose prismatic layers or the more complex crossed lamellar structure. In the latter, needles (lamellae of 3rd order) are united into plates (lamellae of 2nd order) of the width of a needle (Pl. 1, Figs. 1, 4). Such lamellae of the 2nd order, like a pile of sheets of paper of the same size, form rods, the lamellae of first order. Within lamellae of first order, all needles (lamellae of 3rd order) and, within these, all basal elements have the same crystallographic arrangement of the C-axis, that under polarizied light (crossed nicols) have the same direction of extinction.

Lamellae of the first order lying side by side are inclined to each other with an angle which is the same within an individual layer of the shell (Pl. 1, Figs. 1, 4; Pl. 2, Figs. 1, 2, 5). The result is a regular pattern seen in fractured shells as well as in thin-section. Under SEM we see a pattern of needles with two needle directions, in thin-section we see a zebra-like pattern of lamellae of the first order, most prominent unter polarized light (Pl. 2, Fig. 6 and Pl. 3, Figs. 1, 2, 4, 5). In sections we commonly see lamellae of the first order split or cut parallel or perpendicular to their needles (Pl. 3, Fig. 4) since crossed lamellar layers within the shell wall lie on top of each other with a 90 degree angle (BANDEL, 1979). When prismatic layers are intercalated, needles are arranged vertically to growth surface, with optical axis usually parallel to needle axis.

b) Echinoids

The primary mineralogy of the echinoid plates is high-Mg calcite (HMC). During freshwater diagenesis this mineral phase is transferred into low-Mg calcite (LMC) in two ways. First via a solution precipitation process during which the original microstructure is being lost. Second via incongruent leaching which preserves original microstructures (BATHURST, 1971). In contrast to aragonitic molluscs the microstructure of the HMC shell of seaurchins has therefore a better potential of record. The echinoid stereom (plate of corona) consists of a porous material, which has in detail been studied by SMITH (1980). It is formed within the tissue of the animal, thus represents an internal skeleton, and was surrounded by living tissue throughout life. Each plate consists of a network of rods and pillars (Pl. 3, Figs. 6, 7) connected to each other and usually arranged that one individual plate of the corona shows only one crystallographic orientation of the axes. Thus each plate under polarized light reacts as one unit, like a monocrystal. The crystalline matrix is free of organic sheets but, during life, was interwoven with living tissue.

After death, the shells of sea-urchins and molluscs alike may have become invested by boring organisms like fungi, cyanobacteria, clionid sponges and others. These produced minute to large bore holes, but did not change the original micro-structures.

III. Structures after diagenesis

We studied gastropod, bivalve and echinoid shells from the Sahabi Formation M by two methods. We prepared thin sections that were viewed with optical microscope and we fractured shells to view them under the SEM. Soon it was evident from data provided by both approaches and additional ones from X-ray analysis that not a trace of original aragonite or calcite has survived in these shells, and that all shell material now consists of $CaSO_4$ either as gypsum, anhydrite or both.

Preservation of original shell structure is only present in those parts of the shell, where the coloration is whitish or grey. Where the gypsum that represents the former shell is totally transparent, no traces of the original shell structures are preserved. Within an individual conch or corona, parts of the shell may be preserved only as clear gypsum, while others are gypsum with shell structures still present. Within an individual shell, an exchange of molecule by molecule of the original $CaCO_3$ into the $CaSO_4$ of the fossil resulted in the preservation of the needle structure of the lamellar structure (pl. 1, fig. 4, 5; pl. 2, fig. 5). At other places, larger solution cavities were filled with growth of statistically arranged crystals of gypsum with blocky morphology. Where molecule by molecule was replaced, even the optical pattern was preserved (pl. 2, figs. 3–6), with its characteristic zebra pattern of the lamellae of first order, each consecutive one showing a different arrangement of needles and optical axes. The striped appearance is not only seen when light optical methods are used (pl. 2, figs. 3–6) and here under crossed nichols in polarized light, but can also be made out from the SEM pictures (pl. 1, figs. 1–4; pl. 2, fig. 1). Lamellae in pl. 1 fig. 5 are well preserved in one part of the photographed section as is seen in detail (pl. 1, fig. 6) with endolithic bore holes still open and needles (lamellae of 3rd order) clear. But some needles have become fused to larger rods, as is seen in better details in pl. 2 figs. 1 and 2. These small crystallites still faithfully follow the original orientation of the aragonitic biocrystallites, but their width is larger, and they consist of 100 % gypsum.

The SEM photographs in pl. 1, figs. 2, 3, 4 clearly show areas in which the original structure has disappeared and been replaced by larger crystals of gypsum. Optical survey of this section reveals that we can observe all transitions from the concentration of needles of the 3rd lamella into thicker needles of the same arrangement (pl. 1, fig. 6; pl. 2, fig. 2) into areas within the lamella of first order, where original structures of the aragonitic cross-lamellar pattern are destroyed (pl. 1, fig. 4; pl. 2, fig. 1).

Pl. 2, fig. 1 demonstrates the transition from preservation of structure to total destruction of structure from one layer to the next layer in SEM view, as seen in optical view in pl. 3, fig. 5. A coarsening of crossed lamellar relicts was seen when a crossed lamellar layer in a bivalve shell was followed for some distance. Here the original relict structure with needles of 3rd order well preserved (pl. 2, fig. 6), grades into a shell where only the rods of the first order are still seen, while needles have disappeared (pl. 3, fig. 1). Further on two to several neighbouring rods fuse into larger units (pl. 3, fig. 2). Even further, more coarsened rod relicts grade into a gypsum crystal with only traces of rods and finally no relicts of the former shell structure is preserved. While in some portions of the shells only the relicts of the originally aragonitic shell show up as morphological features (pl. 3, fig. 2), in others, the crystal faces of the larger gypsum units are clearly seen in addition to the former structures like crossed lamellar pattern and growth lines (pl. 2, figs. 3, 4; pl. 3, fig. 3). These pictures document, without further need of analysis, that the original shell has turned into something else and new, that is, that aragonite has been replaced by gypsum. Other sections (pl. 2, figs. 5, 6) can very easily lead to the impression that nothing has happened at all until polarized light brings out the bright coloration of the gypsum. Here the original structures are preserved in such detail that only X-ray analysis removes doubts.

In the case of the primary HMC stereom of the sea-urchin, observations are basically the same (pl. 3, figs. 6, 7). SEM and light section show that the original skeletal pattern is preserved well in places, and has totally disappeared in others. The originally HMC shell material has been transformed into gypsum in those places where the structure is still seen while in places nearby, the structure has not survived diagenetic alterations.

IV. Reconstruction of diagenesis

When the transformation of aragonite and calcite of the molluscan and echinoderm shells began, these shells had been unaltered by diagenesis. After death of the organisms, the tissue was decomposed and only calcareous shell remained. Shells became settled by various organisms which drilled or etched themselves into them for shelter or to feed on organic shell substance. But we can observe no alteration of the shells due to this boring, which effected only parts of the shells anyhow.

The shells buried in loose, coarse, calcareous, detrital sediment afterwards became affected by pore water that must have been saline. No earlier calcareous cement formed in shell, lumina or bore holes. Thus we have to take into consideration a change in the environment from normal marine, warm, shallow water to saline brines, probably connected with the Messinian phase during which the whole Mediterranean Sea was transformed into a saline lake (HSÜ & CITA, 1973). Brines brought about the changes that we have observed here. Similar features have been observed from modern Abu Dhabi coastal flats by BÜTLER et al (1982). They noted a pseudomorph change of gastropod shells into gypsum but did not study the microstructure of the shell. DULLO & BANDEL (1986) reviewed the course of changes leading from the original molluscan (cephalopod) shell structure to that seen in the fossil. These authors noted that usually the originally aragonitic structure is lost when recrystallized into calcite, but when transformed into phosphates, silica and pyrite may preserve its original pattern. Due to the present study, it becomes evident that the same may be the case when aragonitic or calcitic biocrystallite structures are transformed into gypsum.

The diagenetic environment in our case from the Sahabi locality is clearly that of saline ground water. It seems likely that transformation occurred within the sediments underlying saline lagoons and sabkhas which have left gypsiferous evaporites (Formation P). It seems as if at first a molecule-by-molecule transformation into $CaSO_4$ occurred that preserved parts of the microstructure. With increasing change of the diagenetic environment towards more saline conditions the transformation from $CaCO_3$ into $CaSO_4$ is characterized by a coarser pattern of the gypsum crystals which still exhibit some relics. In the last stage gypsum crystals are formed that preserve no trace of the original structure, not even remnants, since they are transparent and clean. It is interesting to note that during the transformation into gypsum no difference is found between aragonitic or calcitic primary structure. In other cases of diagenesis, aragonite usually behaves quite different from calcite (DULLO & BANDEL 1986).

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Plate 1

Fig. 1: SEM picture of crossed lamellar structure preserved in the gypsum of the shell of a *Vasum* (Neogastropoda). Scale 0.1 mm.

Fig. 2: SEM picture of the *Vasum* shell fractured to show the well preserved original structure as well as areas of coarse calcium sulphate. Scale 1 mm.

Fig. 3: SEM picture with relict crossed lamellar structure and large places with total disappearance of structure. All shell is now gypsum *(Vasum)*. Scale 0.3 mm.

Fig. 4: SEM picture with lamellae of first order of the original crossed lamellar structure well visible. Scale 0.1 mm.

Fig. 5: SEM picture of *Vasum* shell with well preserved needle-like lamellae of third order. The bore holes excavated by cyanobacteria or fungi are still unfilled. All now gypsum. Scale 0.01 mm.

Fig. 6: SEM-detail of Fig. 6 with coarsening of lamellae of third order of the original aragonitic structure from 0.2 micron up to several micron. Scale 3 micron (0.003 mm).

Plate 1

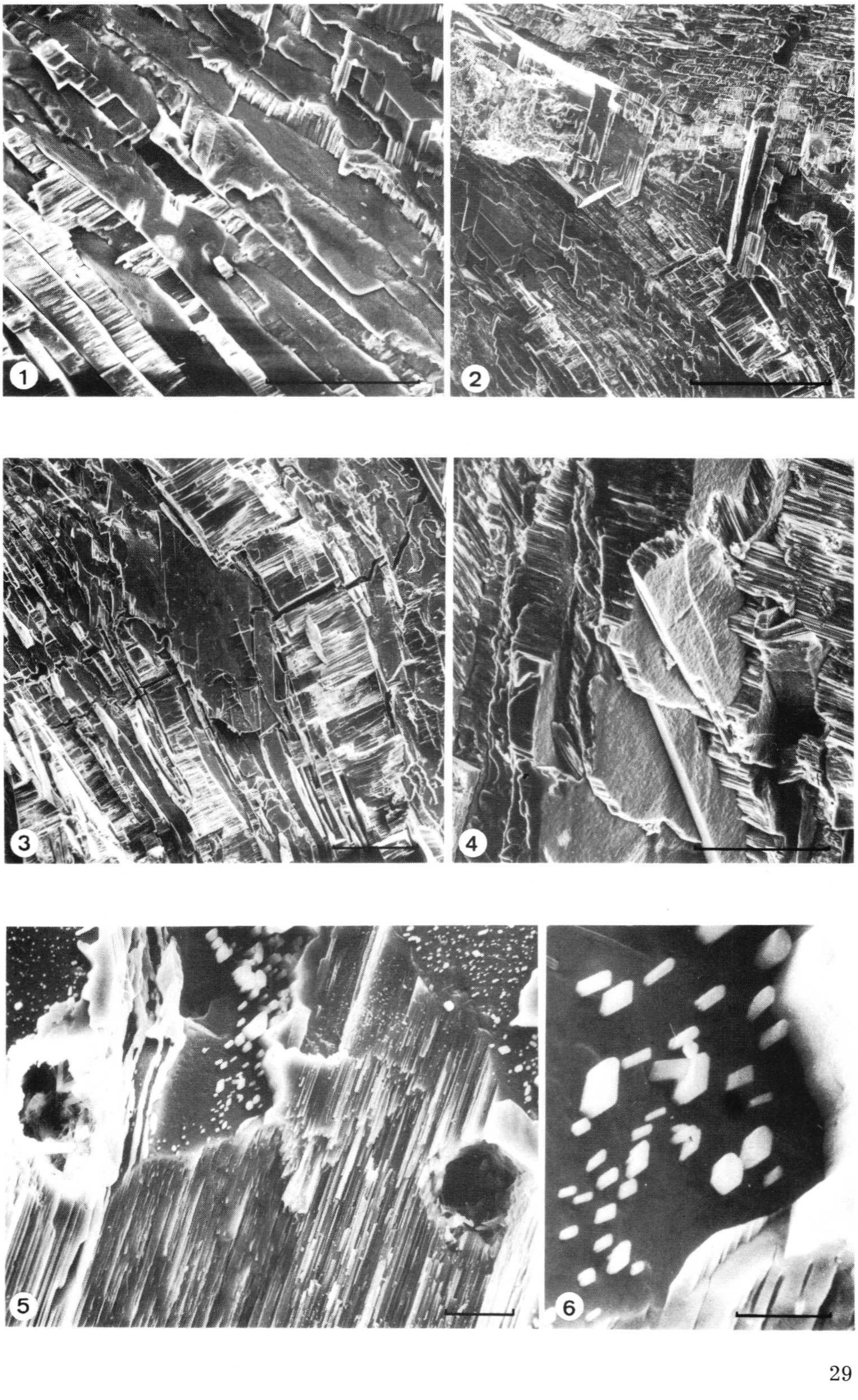

Plate 2

Fig. 1: SEM-detail of *Vasum* shell with crossed lamellar structure preserved in the upper part, and totally destroyed in the lower part. Scale 0.1 mm.

Fig. 2: Detail of Fig. 1 shows lamellae of first order, one fractured parallel to needle axis of lamellae of third order the other one fractured vertically to it. Needles of the third-order-lamellae have become fused to larger units when calcium carbonate was transformed into calcium sulphate. Scale 0.03 mm (30 micron).

Fig. 3: Optical view of thin section through crossed lamellar structure vertically to lamellae of first order. The inclined lines in the pillars of the lamellae of first order represent growth zones in the gypsum crystal. Scale x80

Fig. 4: Optical view similar to that of Fig. 1 with crossed lamellar structure well preserved in one layer, and totally destroyed in the next one. Scale x80.

Fig. 5: Thin section through calcium sulphate fossil shell, showing well preserved traces of lamellae of first and third order of the originally aragonitic crossed lamellar structure. Scale x240.

Fig. 6: Bivalve shell now totally gypsiferous shows the zebra-like pattern of the original crossed lamellar structure. Scale x50.

Plate 2

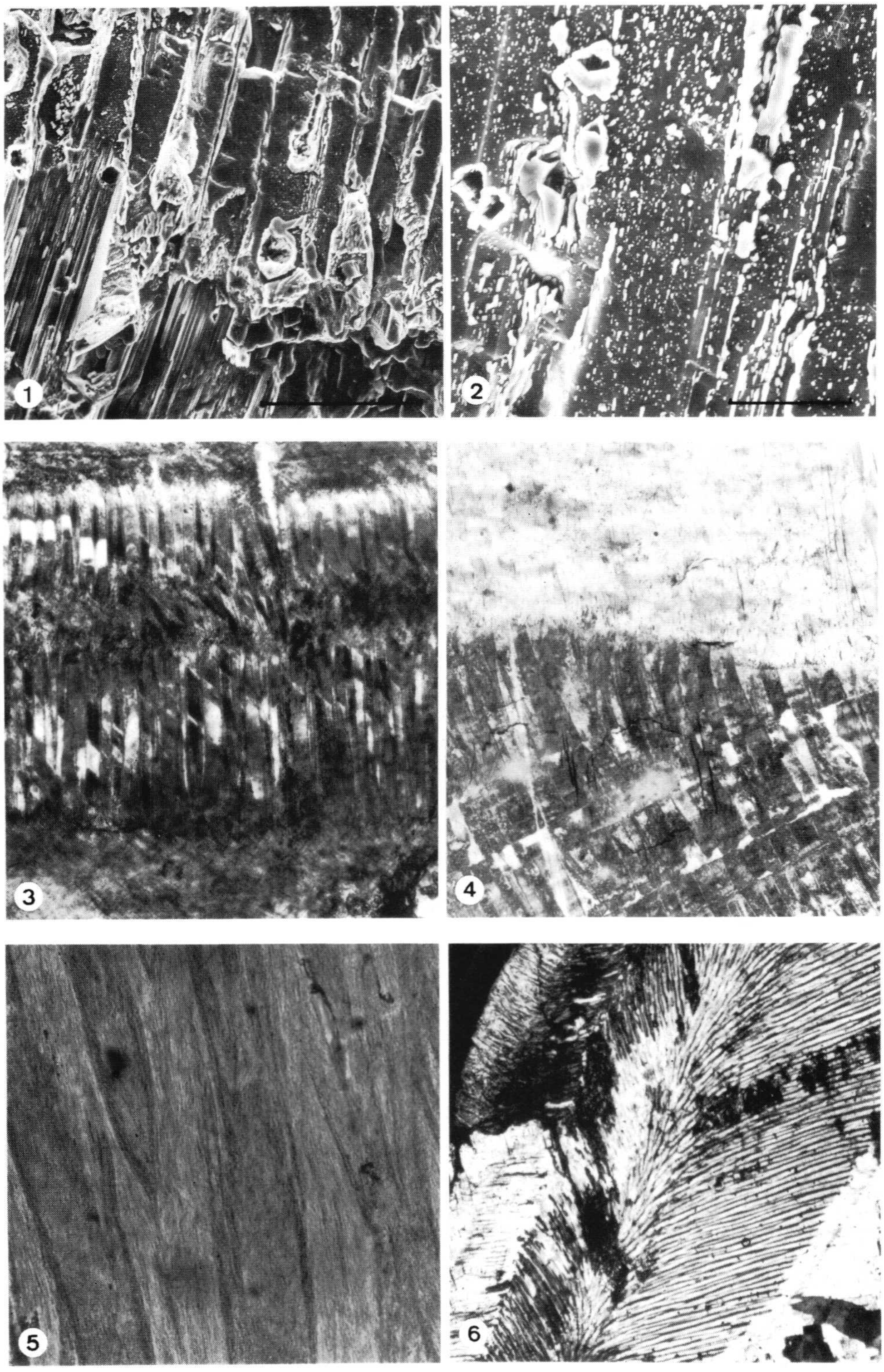

Plate 3

Fig. 1: Same shell as that shown in Pl. 2, Fig. 6, with same layers, but two lamellae of first order fused. Scale x50.

Fig. 2: Same shell as in Pl. 2, Fig. 6, and Pl. 3, Fig. 1, but with several lamellae of first order fused and increased structures of gypsum crystals visible. Scale x50.

Fig. 3: Alternating prismatic and crossed lamellar structure transferred into gypsum. The new crystal growth faces cross original shell structures as inclined, straight lines. Scale x80.

Fig. 4: Shell fragment with several layers of crossed lamellar structure well preserved, even though now totally gypsiferous. Scale x80.

Fig. 5: Thin-sectioned bivalve shell shows relicts of the crossed lamellar structure as well as cleavage lines of a large gypsum crystal now composing the former aragonitic shell. Scale x50.

Fig. 6: Relict of stereom structure of the corona of a seaurchin within a gypsum crystal. Scale x80.

Fig. 7: As Fig. 6 seen in fractured fossil corona with the SEM. Scale 0.1 mm.

Plate 3