

DIAGENESIS OF SOME SCLERACTINIAN CORALS FROM THE GULF OF ELAT, ISRAEL

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Skeletal material of Pleistocene and Holocene scleractinian corals of the families Poritidae and Pocilloporidae, from the Gulf of Elat, Israel, is shown to have undergone diagenesis under submarine and subaerial conditions. The diagenetic processes affecting the submerged part of a reef complex are recrystallisation to, and void filling by, aragonite crystals. The morphological and optical orientation of these crystals correspond to that of the primary aragonite needles building the coral skeleton. The secondary crystals are composed of high strontium aragonite. Void filling by, and recrystallisation to high magnesium calcite occurs as well.

Subsequent diagenesis under subaerial conditions involves recrystallisation to low magnesium calcite of both the remaining primary skeletal aragonite and the products of its submarine diagenesis.

Direct diagenesis of coral debris on a beach poor in carbonate matter leads to high magnesium high strontium calcite.

Diagenesis does not affect morphology, while the ultrastructure preserved during the submarine diagenetic stage is thoroughly altered during subaerial diagenesis; the primary spherulitic structure is replaced by clusters of rhombohedral crystals.

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Coral diagenesis has been investigated by many authors (Siegel, 1960; Stehli & Hower, 1961; Matthews, 1967; Harris & Matthews, 1968; Purdy, 1968; Pingitore, 1970, and others). These investigations dealt mainly with the chemical aspects of the aragonite-calcite recrystallisation under subaerial conditions. Spiro & Hansen (1970) discussed also the ultrastructural aspects of recrystallisation under the same conditions.

The ultrastructural, mineralogical and chemical alterations affecting scleractinian corals under submarine conditions as well as the subsequent subaerial diagenetic changes are the subjects of the present study.

Material and methods

Samples of corals belonging to the Poritidae and Pocilloporidae for the study of submarine diagenesis originate from Ras el Burqa, a reef complex situated on the western shore of the Gulf of Elat, Red Sea, about 40 km south of the town of Elat. A summary of the climatic, physiographic, and marine data recorded near the sampling locality are given by Friedman (1968).

Below the living bioherm a massive reef-wall drops almost vertically about 20 m down to the talus slope. The wall has an abraded appearance and bears almost no living corals. Samples were collected by aid of a hammer, from the base of the wall up to the reef flat. Branching forms were very scarce in the wall in contrast to their abundance in the bioherm. The reef material is intensively bored by pelecypods, (e.g. *Lithophaga*) and in general heavily encrusted by coralline algae.

Samples from uplifted reefs were collected at Sharm esh Sheikh at the southern end of the Gulf of Elat.

Thin sections were studied under the petrographic microscope. Ultrastructures were investigated by means of scanning and transmission electron microscopes, following preparation techniques described by Hansen (1969).

Chemical analyses were made with an electron microprobe using standards analysed by atomic absorption.

Mineralogical determinations were made in an X-ray diffractometer and a Guinier camera.

Ultrastructure alteration

The exact taxonomic determination of the submarine specimens examined, from the reef wall at Ras el Burqa was precluded by strong abrasion and by rich encrustation by coralline algae, masking the morphological features. Nevertheless the specimens examined can be attributed to the Poritidae and Pocilloporidae.

Thin sections of all specimens studied under the petrographic microscope show the skeleton to be composed of closely spaced spherules, apparently identical to the structure known from living corals (Spiro & Hansen, 1970).

In the scanning and transmission electron microscopes the spherules composing the skeleton of living corals are seen to be built of radiating needles, which are anhedral, with a diameter of 0.5 – 1.5 μ , a length of up to 300 μ , and to be divided into segments by concentric organic membranes.

The needles form bundles with irregular cross sections up to 30 μ in diameter.

In submarine dead specimens, however, crystals with developed faces occur at the surface of the skeletal elements or inside them, generally in bands according to the primary segmentation (pl. 1, fig. 1) although irregular patches are common as well (pl. 1, fig. 2). These individual crystals correspond generally to a whole needle bundle in living corals and like the latter form a spherulitic structure. An X-ray investigation showed the presence of aragonite only. It would appear that the larger aragonite crystals are a product of recrystallisation of the skeletal aragonite. As recrystallisation proceeds, the concentric ring pattern disappears and the whole skeleton is finally built of the large aragonite crystals. It is noteworthy that while in living specimens spaces filled by organic membranes are present along and between the aragonite needles, few or no such spaces are present between the secondary crystals, the skeleton becoming massive and devoid of organic membranes. The alteration affects neither the spherulitic structure nor the morphology of the elements formed by their arrangement; moreover, in some cases the surface of the skeletal element may remain unaltered (pl. 1, fig. 3).

Samples collected from a depth of 2 m under the reef flat were found to be highly recrystallised. Below, the degree of additional recrystallisation (i.e. ratio recrystallised:original skeletal material) increases only gradually with depth.

The strontium content of corals altered under submarine conditions is nearly the same as that of living corals, while their magnesium content is lower than that measured in samples of living corals. Skeletal aragonite of living corals has a strontium content of 0.75–1.2 % wt. (0.9–1.5 mol %) and a magnesium content of 0.08–0.16 % wt. (0.3–0.6 mol %).

Void filling by aragonite

Thin sections of dead submarine specimens studied under the petrographic microscope show clear crystals projecting from void walls and with the same optical orientation as the needles building the skeleton. Similar crystals were observed in voids of *Acropora palmata* from Barbados by Pingitore (1970).

In the scanning electron microscope these crystals can be seen to be euhedral, pinacoidal, or prismatic up to 100 μ long and 10 μ wide (pl. 1, fig. 4). Some of these crystals seem to grow in continuation of one bundle of skeletal needles. Some of the void filling crystals possess a pseudohexago-

nal cross section suggestive of aragonite. X-ray investigation of the void filling crystals in a Guinier camera confirmed this assumption.

In places the euhedral crystals penetrate into the coral and a diffuse boundary between the void filling and the skeletal aragonite is produced (pl. 2, fig. 1). Furthermore, remains of original coral needles within the euhedral aragonite crystals indicate that a process of recrystallisation to aragonite, initiated at the surface of the skeletal element, is taking place concurrently with the void filling.

Chemical analysis of the void filling aragonite made with the electron microprobe shows it to be composed of high strontium aragonite. The strontium content of about 0.9% wt. (1.1% mol.) is slightly higher than that measured in specimens of living corals. There is no detectable amount of magnesium present in the void filling aragonite.

Void filling by and recrystallisation to high magnesium calcite

Voids in specimens collected near the abraded surface of the reef wall at Ras el Burqa are seen in the scanning electron microscope to be lined with a layer of euhedral crystals having a rhombohedral and scalenohedral habit, rough faces, and a size up to 50 μ (pl. 2, fig. 2). On fracture surfaces where the contact between these crystals and the coral skeleton can be seen, remains of original skeletal aragonite needles are seen within the euhedral crystals (pl. 2, fig. 3).

Guinier camera analysis of powdered parts of thin sections containing this microcrystalline void filling showed in addition to aragonite reflexes of the coral itself, also reflexes indicative of calcite though with a shift, that of the $10\bar{1}4$ reflex, with $\Delta d = 0.032$ Å (after correction of the internal quartz standard reflex in respect to the ASTM data). This shift indicates a high magnesium calcite.

Microprobe analysis showed a content of about 4.2% wt. (16 % mol.) magnesium, and a strontium content of about 0.01 % wt. The roughness of the crystal faces might be a consequence of numerous lattice defects caused by the high magnesium content.

It seems therefore that a process of growth of high magnesium calcite at the expense of skeletal aragonite is taking place during submarine diagenesis. There is no indication that void filling aragonite and high magnesium calcite are mutually exclusive, nor is it possible to demonstrate an order of growth (pl. 2, fig. 4; pl. 3, fig. 1). Therefore it is assumed that both kinds of void filling grow at the same time, viz. under the same conditions.

Subaerial diagenesis

As explained above, the products of submarine diagenesis of corals are high strontium low magnesium recrystallised and void filling aragonite, and high magnesium calcite. Under subaerial conditions low rhombohedral and smooth faced crystals (pl. 3, fig. 2) appear in place of the high magnesium calcite crystals which are seen in the scanning electron microscope to be high rhombohedral and rough faced. The amount of the low rhombohedral crystals in the samples studied is too small for an X-ray diffraction determination, but it is probable that they are low magnesium calcite.

Dissolution under subaerial conditions affects progressively the original and secondary aragonite: the original needles of the coral disappear more readily, while the void filling aragonite crystals preserve their euhedral faces for some time (pl. 3, fig. 3). In samples from older uplifted reefs (Sharm esh Sheikh) rhombohedral crystals of low magnesium calcite with random optical and morphological orientation are found to replace both the skeleton and the void filling aragonite. (pl. 3, fig. 4) Nevertheless the morphology of the coral is still preserved. The lower stability of the skeletal aragonite compared to the that filling voids might be due to the latter's lower magnesium content.

Discussion

The present study tends to show that the diagenesis of scleractinian corals under submarine conditions involves mainly recrystallisation of high strontium high magnesium aragonite to high strontium low magnesium aragonite, together with void filling by both high strontium low magnesium aragonite and high magnesium calcite. Subaerial diagenesis, on the other hand, leads to replacement by low magnesium calcite of the remaining skeletal material and of the submarine diagenetic products. Organic membranes disappear during submarine diagenesis, but the general morphology of corals is preserved despite far reaching alterations in composition and texture.

Aragonite as a diagenetic product presents a problem of environmental and geochemical interest, particularly since most previous studies dealt mainly with aragonite as a cementing agent. Cementation by aragonite of carbonate sediments at the Yellow Bank, Bahamas, was described by Taft (1968). Hathaway & Degens (1969) described sandstones cemented by aragonite and high magnesium calcite, dredged from depths of 320–440 m from the continental margin off the northeastern United States. Cryptocrystalline and fibrous aragonite cementing sandstone at the depth of 79 m off Delaware Bay were described by Allen et al. (1969). These latter

authors in agreement with Hathaway & Degens, believe that cementation took place on the sea floor near submerged tidal marshes. Aragonite cemented materials of cores from the floor of the Red Sea near pools of hot brines were studied by Gevirtz & Friedman (1966). Aragonite precipitated during "whitening" of the Dead Sea, when the temperature ranged between 33–36°C and the salinity was 28.8‰, was recorded by Neev (1964), and Neev & Emery (1967). Beachrock cemented by fibrous and cryptocrystalline aragonite from the Mediterranean shore of Israel was described by Gavish & Friedman (1969). All the authors mentioned attribute the occurrence of aragonite needles to high temperature and/or high salinity, or to other special marine conditions. Lately Pingitore (1970) reported void filling aragonite needles believed to be of marine origin, in samples of *Acropora palmata* from a Pleistocene uplifted reef complex on Barbados W. I.

The sampling locality of submarine specimens examined during the present study is a fore-reef where slightly hypersaline conditions prevail (Friedman, 1968). The subaerial specimens originate from an uplifted reef complex near the southern end of the Gulf of Elat. In both groups of specimens originating from localities 200 km apart and from formations quite different in age, the products of submarine diagenesis are present. Thus it seems that void filling and recrystallisation to aragonite occur over a wider range of marine conditions than assumed earlier. Purdy (1963, 1968) observed recrystallisation of corals and other skeletal, as well as non-skeletal carbonate to cryptocrystalline carbonate without apparent change in mineralogy. With respect to coral fragments see also Friedman (1968).

Since recrystallised and unaltered portions of the skeleton are undistinguishable in the visual display of the microprobe, measurements of magnesium are obviously averages of both kinds of skeletal material. Nevertheless, the general trend towards low magnesium values in specimens evidently recrystallised at least in part, indicates that the recrystallisation process is associated with loss of magnesium. The loss of magnesium in the recrystallisation (high strontium aragonite) of the skeleton and the near absence of magnesium in the (equally high strontium) void filling aragonite may point to a similar formation in both cases.

Under the petrographic microscope, thin sections of submarine coral material show a dark line separating the coral skeleton from the bigger crystals partly or totally filling a void. This line was therefore thought to mark the periphery of the primary void, and the bigger crystals within this line, to be a product of precipitation with no genetic relation to the coral skeleton. Such a dark line may be no more than an optical phenomenon or on the contrary, due to the presence of an organic envelope. In the transmission

electron microscope no indication for the presence of an organic membrane between the coral skeleton and the void filling crystals could be found.

The recrystallisation of high magnesium aragonite coral needles to aragonite poor in magnesium and to high magnesium calcite, is a stabilisation process leading from the biogenic mineral unstable in the surrounding aqueous medium, to minerals stable in this respect. The presence of both minerals in the same place, formed apparently during the same time interval and therefore, presumably under the same chemical and physical conditions, demonstrates that coprecipitation of aragonite and high magnesium calcite is possible. Winland (1969) observed recrystallisation of magnesian calcite skeletal elements to aragonite, in recent marine sediments, and proposed an explanation based on the distribution coefficient for partitioning strontium between aragonite and the aqueous phase on the one hand, and magnesium between calcite and the aqueous phase on the other. The calculated free energy of formation for magnesian calcite is higher than that calculated for aragonite. Recrystallisation of high magnesium calcite to aragonite might thus be explained. Thermodynamic data on high magnesium high strontium skeletal aragonite is lacking, but the present work suggests that this kind of aragonite is less stable than high magnesium calcite into which it recrystallises.

The organic membranes seem to play important, though different roles in diagenetic processes. The preservation of the concentric ring-pattern after the organic membranes during early stages of submarine diagenesis shows that they exist until recrystallisation occurs. Furthermore, preservation of surface features of skeletal elements while the interior is already altered, might point to difference in thickness or constitution of the organic membranes. By contrast, under subaerial conditions, the formation of "ghost structures" points to preferred dissolution where organic matter had been concentrated (Spiro & Hansen, 1970) which suggests the destruction of organic matrix prior to dissolution of the coral skeleton.

Subaerial diagenesis in different environments leads to different products. Coral debris from a sandy silicious beach in the Gulf of Elat where conditions of intense evaporation and low precipitation prevail, were found to be recrystallised to high magnesium high strontium calcite (Spiro & Hansen, 1970). This observation agrees with the model of recrystallisation under conditions of low fluid:solid ratio and low primary concentration of calcium in the fluid (Sass 1970, personal comm.). Subaerial diagenesis, as observed in an uplifted reef complex, under similar climatic conditions leads to low magnesium low strontium calcite. Purdy (1968) envisaged subaerial diagenesis of corals to be volume per volume replacement of aragonite by low-magnesium calcite preserving the coral architecture. Matthews (1968) discussed mechanisms of solution-reprecipitation occurring in uplifted reefs

on Barbados island, W. I. There, loss of strontium in the reef material is reflected by the progressive increase of strontium concentration in ground-water in deeper parts of the reef aquifer (Harris & Matthews, 1968). As indicated above, the ratio recrystallised:original skeletal material increases within 2 metres below the reef flat at Ras el Burqa, while the rate of recrystallisation and void filling process at greater depth seems to decrease. This may point to the fact that a relatively high degree of recrystallisation is attained rather rapidly. Gradual sealing of the coral skeleton by the growing massive aragonite crystals eliminates the spaces between and along skeletal needles, and the cover of void filling aragonite crystals inhibits percolation within the coral skeleton and seals it off from the surrounding medium. It seems that the contribution of sea-water precipitated aragonite in later stages of submarine diagenesis is rather small. The sealing off process may have also an effect on the composition of the pore fluid. Loss of magnesium during recrystallisation of high magnesium skeletal aragonite may lead to a higher concentration in magnesium of the pore fluid; this may play a role in the precipitation of high magnesium calcite. On the other hand, a progressive increase in magnesium concentration in the precipitant is believed to inhibit calcite precipitation (Fyfe & Bischoff, 1965, Bischoff 1968).

After the manuscript was submitted for publication the abstract of Friedman et al. (1970) came to hand. With the exception of the higher magnesium content of the void filling aragonite crystals reported their results largely corroborate the findings of the present study.

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Dansk sammendrag

Skelettet i pleistocæne og holocæne scleractinie-koraller fra Gulf of Elat, Israel, har været udsat for diagenese under submarine og subaeriske forhold. I havdækkede dele af et revkompleks sker en rekrystallisation til aragonit med et højt strontiumindhold. Den sekundære aragonit har samme morfologiske og optiske orientering som den primære aragonit i koralskeletterne. Der foregår også en rekrystallisation til calcit med et højt indhold af magnesium.

Den efterfølgende subaeriske diagenese involverer rekrystallisation af den tilbageværende primære aragonit samt de sekundære produkter af den submarine diagenese til calcit med et lavt magnesiumindhold.

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Plate 1

Figs. 1, 2, 4. *Porites* sp.

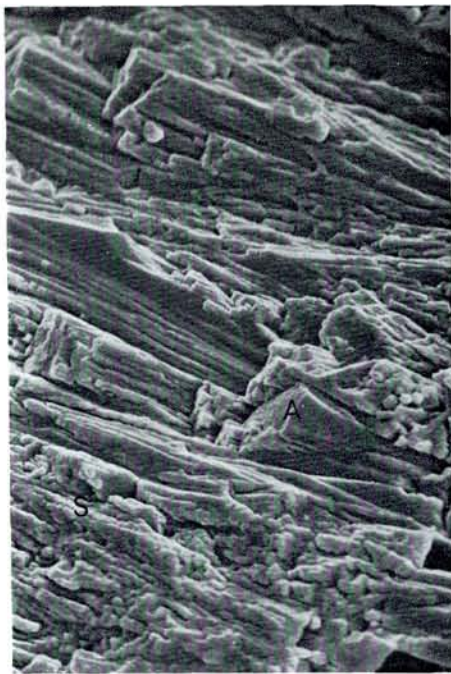
- 1: A band of larger recrystallised aragonite crystals between bands of original coral needles. The banding runs according to the primary structure of the spherule.
- 2: Recrystallised larger aragonite crystal (A) developed in patches among original skeletal aragonite needles (S).
- 3: *Pocillopora* sp. Interior of a partly recrystallised skeletal element, its surface apparently unaltered.
- 4: *Porites* sp. Void filling aragonite in big euhedral crystals (A). Coral skeleton (S).

The figured specimens originate from the submerged part of the reef complex at Ras el Burqa, Gulf of Eilat. All figures are scanning electron micrographs of fractured specimens.



1

2 μ



2

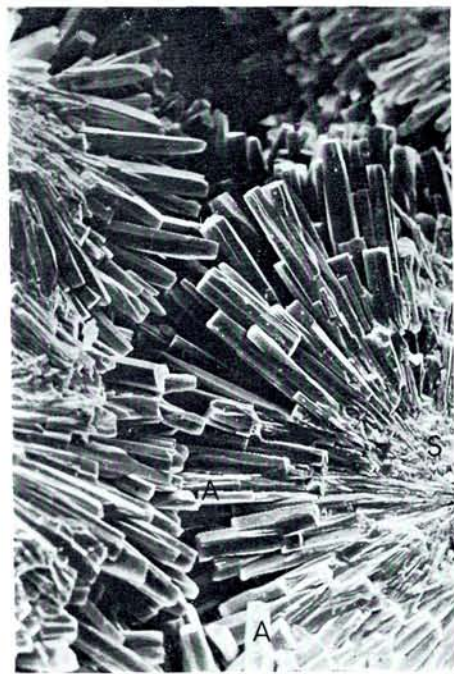
5 μ



3

10 μ

2*



4

40 μ

Plate 2

Figs. 1–4. *Porites* sp. from the submerged part of the reef complex at Ras el Burqa, Gulf of Elat.

- 1: Diffuse boundary between euhedral void filling aragonite crystals (A) and skeletal aragonite (S). Note that traces of needles are recognisable in the void filling crystals.
- 2: Void filling rhombohedral high magnesium calcite crystals.
- 3: Remain of coral needles (S) in high magnesium calcite crystals (C) indicating a recrystallisation proces.
- 4: Euhedral rhombohedral high magnesium calcite crystals (C) in a void lined with aragonite crystals (A).

All figures are scanning electron micrographs of fractured specimens.



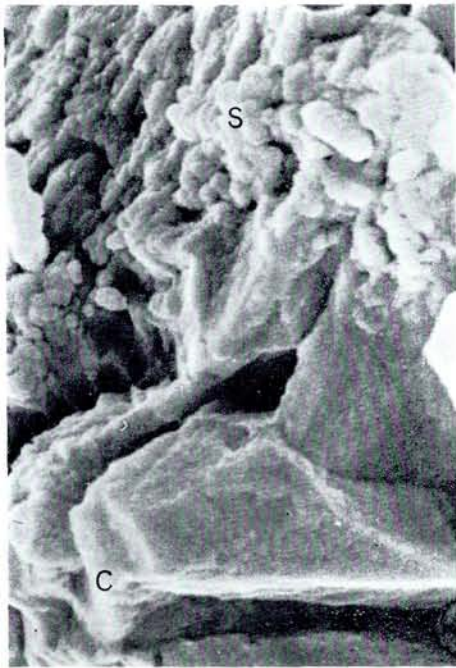
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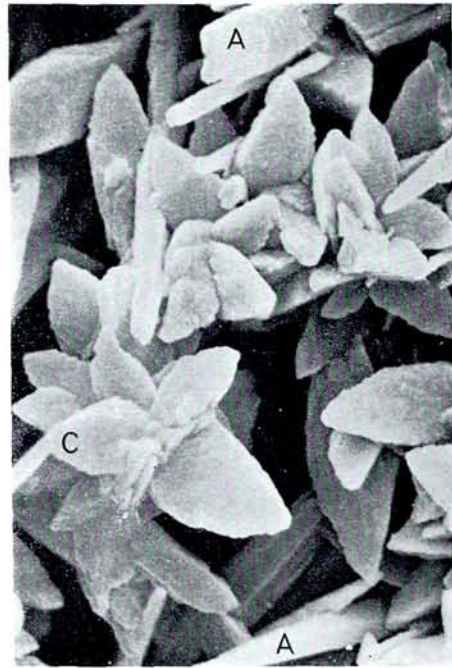
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1 μ



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2 μ

Plate 3

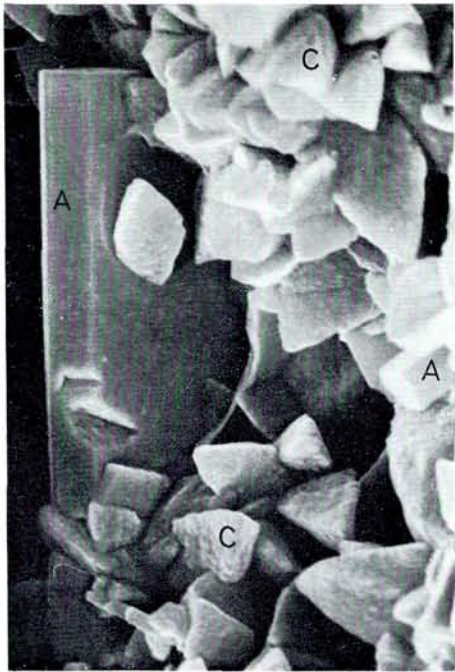
Fig. 1. *Porites* sp. from the submerged reef at Ras el Burqa. Intergrowth of aragonite (A) and high magnesium calcite (C) in a void lined with high magnesium calcite crystals.

Fig. 2. Indeterminable coral from a raised Quaternary terrace 2 m above sea level at Sharm esh Sheikh. It shows smooth faced, rhombohedral crystals, presumably low magnesium calcite, in a subaerially altered specimen. (A) void filling aragonite.

Fig. 3. Indeterminable coral from a raised Quaternary terrace 2 m above sea level at Sharm esh Sheikh. The coral skeleton has been subjected to subaerial diagenesis; the original skeleton (S) is less resistant than the void filling aragonite (A).

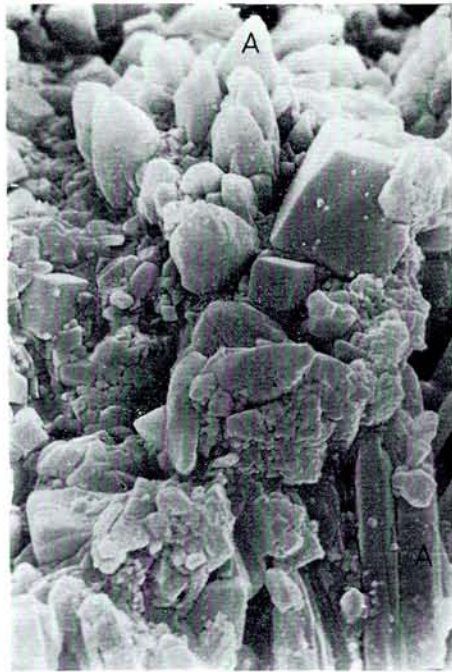
Fig. 4. Indeterminable coral from a raised Quaternary terrace 20 m above sea level at Sharm esh Sheikh. The coral skeleton has been subjected to subaerial diagenesis. Note that the skeleton is built of rhombohedral calcite crystals with no traces of a primary spherulitic structure.

All figures are scanning electron micrographs of fractured specimens.



1

2 μ



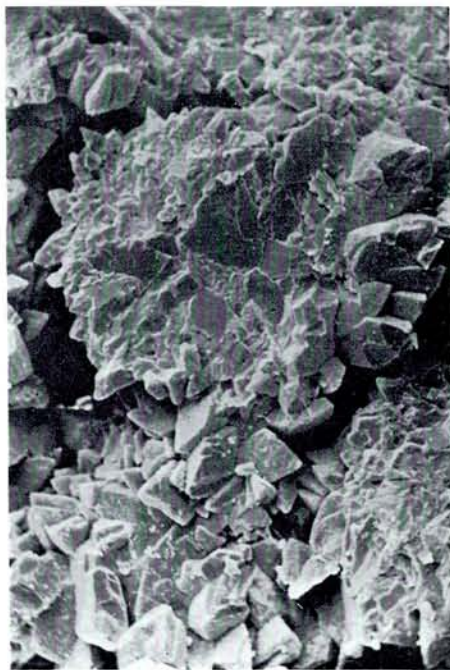
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