

NOTE ON EARLY DIAGENESIS OF SOME SCLERACTINIAN CORALS FROM THE GULF OF EILAT, ISRAEL

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Debris of *Favia* sp. and *Favites* sp. from the dry beach of the Gulf of Eilat was found to be partly recrystallised. Microprobe analysis showed development of high Sr-Mg calcite. The process of calcite formation involves three steps: dissolution of aragonite preferably where organic material has been concentrated, preferred loss of Ca during short-distance transportation of the solution, and precipitation of high Sr-Mg calcite.

Corals and debris of corals constitute an important part of many deposits. Since many scleractinian corals are aragonitic they are subject to recrystallisation. The process of alteration is of interest from both the palaeontological and sedimentological points of view.

The recrystallisation process implies structural as well as chemical aspects. The present work deals with some ultrastructural and chemical changes connected with early recrystallisation as exemplified by specimens collected in the Gulf of Eilat, Israel.

Friedman (1968) published the results of chemical analysis of reef material collected from the same area as that from which the material for the present study originates. Harris & Matthews (1968) dealt with the Sr/Ca ratios in a reef complex on the island of Barbados, W.I. Recently Sorauf (1969), Pingitore (1969) and Wise (1969) published abstracts on some observations on coral structures and recrystallisation.

Material and methods

The material was collected from the shore of the Gulf of Eilat. The sampling locality is situated about 20 km south of the town of Eilat. The samples were taken from approximately 1.5 m above high tide level and consisted of loose coral debris ranging in weight from 0.5 to 10 kg.

As specimens belonging to the genera *Favia* and *Favites* showed particularly uncomplicated microstructure, they were used for the present investigation. For X-ray fluorescence analysis submarine specimens of *Acropora* sp. were used.

The specimens studied with the electron microscope were prepared according to the technique described by Hansen (1967, 1969).

Microstructure

Specimens of scleractinian corals belonging to the genera *Favia* and *Favites* studied in thin sections under the light microscope between crossed nicols demonstrated that the skeletal elements consist of needles with a spherulitic arrangement. In most cases a series of closely spaced spherules were seen to be fused together, so that the growth of the single spherule in the direction parallel to the surface has been inhibited; this has led to an almost palisade-like arrangement of the needles (pl. 1, fig. 1). The spherules have a maximum diameter of about 500–600 μ and are subdivided into concentric rings marked by dark circular figures.

In both thicker and thinner skeletal elements dark bands were observed. These bands have diffuse boundaries and high light-absorption, indicating a high content of organic material. These bands do not reach the surface of the elements.

In some of the thinner skeletal elements consisting of a single row of closely packed spherules, the dark band is composed of the closely spaced spherule centres. The distance between the centres varies somewhat, ranging from 20 to 100 μ .

In thin sections of exposed surfaces of subaerial specimens areas of different textures from that described above were observed. Two types of areas with different shapes could be distinguished.

The one showed the primary structure with disseminated single grains or clusters of grains, which showed random optical orientation.

The other had the shape of continuous stripes situated at the margins of the skeletal elements with no remains of the primary textural features. The boundary between the stripes and the primary structure had the appearance of a stylolite, as known from limestones (pl. 1, fig. 2).

The "stylolites" run parallel or subparallel to the surface and to the dark bands mentioned earlier.

The grains in both types of area had a diameter of up to 25 μ .

Uncovered thin sections of specimens with the two different textures were run in an X-ray diffractometer where the "stylolite-bearing" areas were found to be composed of both aragonite and calcite.

Ultrastructure

In the scanning electron microscope partly dissolved spherules were observed where the concentric structure as well as the radial arrangement of the aragonite needles was still recognisable (a so-called ghost structure) (pl. 1, fig. 3). The dissolution had taken place preferably along the concentric rings where concentrations of organic material had been present, as indicated by replicas of etched sections of submarine specimens studied in the transmission electron microscope (pl. 1, fig. 4).

In other areas, minute euhedral calcite crystals were seen lying in the "stylolite" zone between the primary aragonite needles and the areas with larger euhedral calcite crystals (pl. 2, fig. 1).

Besides pure euhedral calcite crystals, others containing aragonite needles from the original coral skeleton, were found (pl. 2, fig. 3).

Larger crystals of calcite are often concentrated in the centres of the spherules, while smaller ones are disseminated throughout the radiating structure. The difference in size indicates that precipitation of calcite in this structure started in the centres, provided that the rate of crystal growth was identical in all areas.

Calcite with a smooth surface showing no crystal faces was found predominantly in cavities within the skeletal elements (pl. 2, fig. 2). This smooth-faced calcite also locally contained needles of aragonite. Although the smooth calcite was found to envelop the euhedral crystals, the age-relationship between them is not clear. On fracture surfaces the smooth calcite showed the rhombohedral cleavage characteristic of calcite. However, the calcite lining the cavities showed different cleavage directions in different parts of the same filling and must therefore be regarded as an aggregate.

The concentration of organic material found in the centres of the spherules, in the concentric rings and between the aragonite needles of the original coral skeleton was not found in the recrystallised areas.

The majority of specimens shows dense and complex systems of borings presumably caused by algae. The diameter of the borings is about 2μ . No correlation between the borings and the ghost structure and/or the presence of calcite crystals and smooth-faced calcite could be found.

Chemical analysis

Microprobe scan-profiles were run across recrystallisation "stylolites" for Ca, Sr, and Mg. The profiles showed no evident change in the amounts of any of these three elements.

In order to obtain more precise data on the amounts of Ca and Sr, about

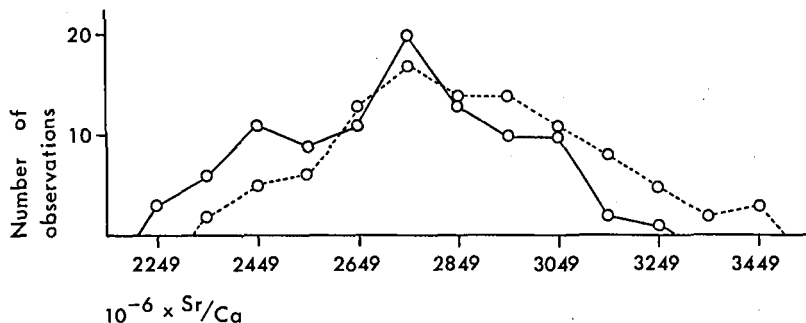


Fig. 1. Size-frequency distribution of the Sr/Ca ratio recorded with the microprobe in counts /10 seconds for aragonite (full line : $n = 97$, $\bar{X} = 2695 \times 10^{-6}$, $s = 232 \times 10^{-6}$) and for calcite (broken line: $n = 100$, $\bar{X} = 2866$, $s = 250 \times 10^{-6}$) in the septum of *Favia* sp. from the Gulf of Eilat.

100 points were measured in counts/10 seconds in each of the two types of area, i.e. primary and recrystallised. The amount of Sr in the aragonite was 0.71 % and in the calcite 0.73 %. The Sr/Ca ratio changes from one area to the other as demonstrated in fig. 1. The Sr/Ca weight-ratio in aragonite was 0.0125 while it was 0.0131 in calcite.

The two distributions of the Sr/Ca ratios of the two different areas have been tested statistically by the t-test. The F-test gave a P_F value higher than 10 %. The t-test gave a value of 4.972 corresponding to a P_t value of less than 0.1 %. There is thus significant difference between the Sr/Ca ratio in the aragonite and in the recrystallised calcite.

Scanning pictures of the Sr distribution in the calcite areas made with the microprobe, demonstrated that the Sr is neither concentrated along grain boundaries nor in the form of strontianite grains, but is evenly distributed throughout the area.

The amounts of Mg found with the aid of the microprobe were roughly identical in both areas (0.19 %) with slightly lower values in the calcite.

X-ray fluorescence analysis of submarine specimens of *Acropora* sp. showed that Mn was concentrated only on the outer surfaces of the corals, while the interior of the skeletons showed no traceable amounts.

Discussion and conclusions

In eight samples of corals from the Gulf of Eilat Friedman (1968) found an average Sr-content of 0.83 % and an average Mg-content of 0.20 %, which corresponds well to the values obtained by the present authors, and which are also in good agreement with values found by Harris & Matthews (1968).

It appears puzzling that the Sr/Ca ratio is higher in the recrystallised calcite than in the aragonite, as there is usually a smaller amount of Sr in calcite than in aragonite (see e. g. Dodd, 1967).

The almost identical amounts of Sr in the primary and in the recrystallised areas, together with the difference in Sr/Ca ratios, point to a preferred loss of Ca during recrystallisation.

The nearly identical amounts of Mg in the aragonite and in the calcite make it probable that there was no supply of ions from outside the coral skeleton.

Pingitore (1969) suggested a "volume for volume" solution of aragonite and local reprecipitation of calcite in recrystallised specimens of *Acropora palmata* from Barbados. The excess of material was said to be precipitated as filling-in calcite in the cavities of the coral reef. The excess material is caused by a density difference of about 10 % between aragonite and calcite.

The recrystallisation process cannot be considered a direct substitution of aragonite by calcite, as indicated by the dissolution ghost structures as well as by the random optical and morphological orientation of the precipitated calcite.

The recrystallisation process, as envisaged by the present authors, changes the microstructure as well as the ultrastructure throughout and only the shape of the skeletal elements remains.

In view of the experiments by Bishoff (1968) on Mg-ion inhibition of calcite nucleation, the finding of specimens undergoing recrystallisation under purely subaerial conditions, is readily understood.

If the relatively small size of the samples, their surface position and the atmospheric conditions to which they were subjected (Friedman, 1968) are considered, together with the evidence from the laboratory investigations presented here, an order of events leading from the unrecrystallised to the partly recrystallised coral can be outlined.

Coral debris which is brought to the shore is dried out, which causes shrinkage of the organic material. Atmospheric conditions of high temperature, intense evaporation and low precipitation of moisture, prevail. Moisture originating from rain and dew attack the skeleton both from the surface and in the interior cavities left after the drying-up or decay of the organic material, resulting in the formation of ghost structures. A part of the solution enriched in Ca leaves the local system causing the Sr/Ca ratio to change. Under these conditions a high amount of Sr is incorporated in the calcite lattice. This is, accordingly, unstable and is subject to recrystallisation in later stages of diagenesis. This later recrystallisation is accompanied by a loss of Sr as shown by Harris and Matthews (1968).

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Dansk sammendrag

Stykker af koral kolonier af slægterne *Favia* og *Favites* fra stranden ved Eilat, Israel, er blevet undersøgt i lysmikroskop, transmissions elektronmikroskop og i scanning elektronmikroskop. Koralskeletterne, der oprindeligt var opbygget af aragonit, kan strukturelt vises at være under rekrySTALLISATION.

Røntgen-diffraktions undersøgelser viser at aragoniten omdannes til calcit.

I elektron mikrosonden er den kemiske sammensætning af omdannelsesproduktet bestemt til at være CaCO_3 med et ret højt indhold af strontium og magnesium.

RekrySTALLISATIONSprocessen forløber gennem tre trin: Opløsning af primær aragonit – transport af det opløste materiale – ensidigt tab af calcium i forbindelse med udfældning af calcit med højt indhold af strontium og magnesium.

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Plate 1

Fig. 1. *Favia* sp. Thin skeletal element showing closely packed spherules with closely spaced centres. SEM.

Fig. 2. *Favites* sp. Recrystallisation "stylolite" between aragonite (left) and calcite (right). Photomicrograph.

Fig. 3. *Favia* sp. Dissolution ghost structure in aragonite spherule with euhedral calcite crystals in the centre. SEM.

Fig. 4. *Acorpora* sp. (submarine). First carbon-shadowed replica of etched section showing organic concentrations in a spherule. TEM.

Plate 2

Fig. 1. *Favia* sp. Stylolite with small calcite crystals between aragonite (upper part) and larger euhedral calcite crystals (lower part). SEM.

Fig. 2. *Favia* sp. Smooth-face calcite in spherule centre with enclosed aragonite needles. SEM.

Fig. 3. *Favia* sp. Euhedral calcite crystal enveloped by smooth-face calcite. Note the enclosed aragonite needles in the crystal. SEM.

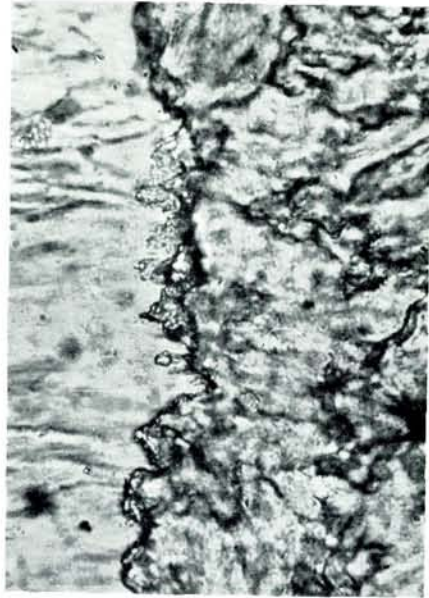
SEM; Scanning electron microscope

TEM: Transmission electron microscope.



1

50 μ



2

20 μ



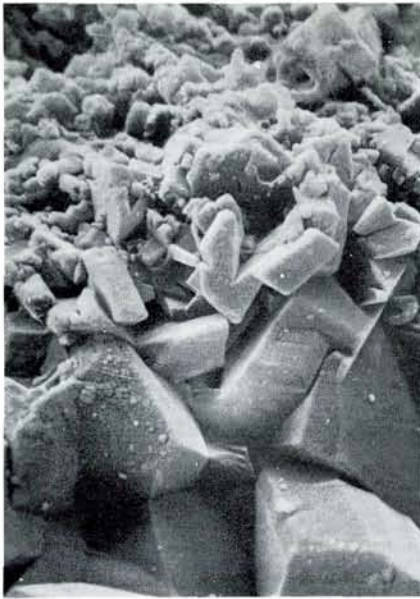
3

10 μ



4

4 μ



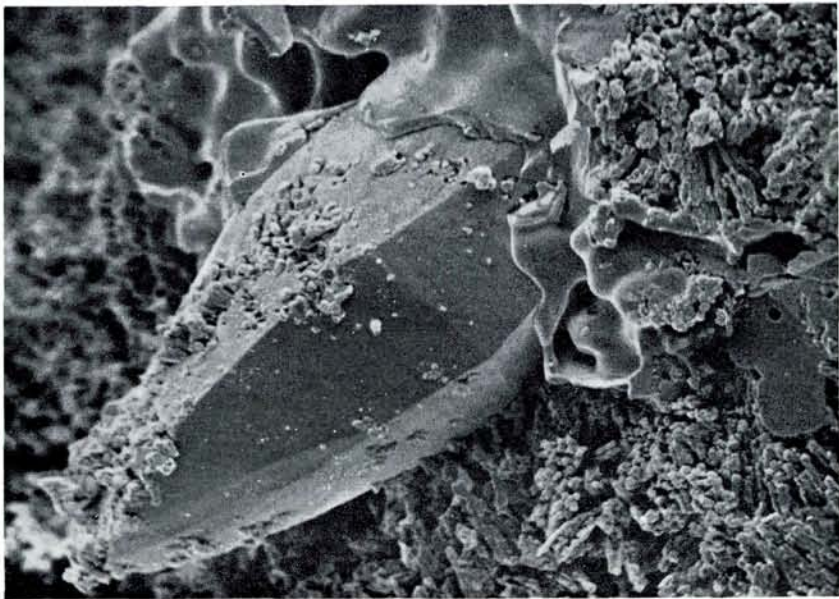
1

5 μ



2

2 μ



3

10 μ