

MICRITIZATION OF CARBONATE PARTICLES:  
PROCESSES OF PRECIPITATION AND DISSOLUTION IN MODERN  
SHALLOW-MARINE SEDIMENTS

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ABSTRACT

Carbonate grains in sublittoral marine sands are pitted and bored by micro-organisms, predominantly algae, fungi, and sponges. In inshore zones with incessant sediment movement, there are few opportunities for the organisms to colonize the particles, and the grains have rounded, glossy surfaces, formed by mechanical abrasion. In warm seawater, highly supersaturated with calcium carbonate, the borings become filled with secondary carbonate, either acicular aragonite, or rhombohedral Mg-calcite with about 15 mole %  $MgCO_3$  in solid solution. The process is well known, and leads to the formation of micrite envelopes. In the studied material, which comes from eight areas in the West Indies and the Mediterranean, the mineralogy of the secondary carbonate is usually host-controlled; in the absence of host-control, the mineral form is aragonite. No organisms take a direct part in the precipitation of the carbonate, and the process is regarded as a form of marine carbonate cementation. In waters where the level of carbonate saturation is low, the borings remain empty.

In the cold waters along the Swedish coasts in Skagerrak, Kattegat, and the Baltic Sea, skeletal carbonates are selectively dissolved. Affected grains have etched surfaces, leached rims, and a micro-porous fabric. The dissolution process causes the lustre and the translucency of the shells to fade and disappear; in petrographic thin sections, the shells appear opaque and cryptocrystalline. Such *shell-residue micrite* consists of the isolated, remaining lamellae of the original fabric. The mineralogy is not affected. The selective removal of material from within skeletal particles is attributed to intraskeletal variations in solubility. A diagnostic criterion on shell-residue micrite, as contrasted to micrite envelopes, is its dependence on internal particle structures. The effects of submarine and subaerial leaching of aragonite shells are similar.

RÉSUMÉ

Dans les sables marins sublittoraux, les grains de carbonate sont cariés et perforés par des micro-organismes, surtout des algues, des filaments mycéliens et des éponges. Dans les zones entre les brisants et la laisse de basse mer, où les sédiments sont en mouvement incessant, ces organismes n'ont guère le temps de coloniser les particules; les grains, à cause de l'abrasion mécanique, ont des surfaces polies et brillantes. Dans l'eau de mer chaude, saturée de carbonate de calcium, les trous sont remplis par de l'aragonite cristallisée en aiguilles ou de la Mg-calcite rhombohédrique avec environ 15 mole % de  $MgCO_3$  en solution solide. Le processus est bien connu; il résulte en la formation d'enveloppes de micrite. Les échantillons examinés viennent de huit régions différentes de la mer des Antilles et de la Méditerranée; la minéralogie du carbonate secondaire y suit en général celle de son hôte; sinon, elle suit celle de l'aragonite. Les organismes ne prennent pas part directement à la précipitation du carbonate; le processus est considéré comme une forme de cimentation marine de carbonate. Dans les eaux peu saturées de carbonate, les trous restent vides.

Dans les eaux froides au long des côtes de la Suède au Skagerrak, au Kattegat et en la Baltique, les carbonates squelettiques se dissolvent en partie. Les surfaces et les bords des grains sont affectés par le lessivage; leur consistance est poreuse. A cause de la dissolution, les tests perdent leur brillant et leur transparence; dans les lames minces, ils paraissent opaques et de structure crypto-cristalline. Cette micrite composée de fragments de tests consiste de lamelles isolées du tissu original. Leur minéralogie n'est pas changée. La dissolution très partielle des particules squelettiques est attribuée par l'auteur à des variations intérieures de la solubilité des tissus. Ce qui, dans une micrite faite du résidu de tests, permet de la séparer avec certitude d'une micrite d'enve-

loppe, est sa dépendance des structures intérieures des particules. Dans la zone submarine comme dans la zone subaérienne, les effets du lessivage sur les coquilles d'aragonite sont les mêmes.

## INTRODUCTION

An important process in marine shallow-water diagenesis of carbonates is the obliteration of original internal organization in skeletal fragments and oöoliths, and the gradual alteration of such particles to grains of cryptocrystalline calcium carbonate, *micrite*. More than one mechanism has been reported to take part in the micritization process; for example, recrystallization (Purdy, 1968), dissolution-reprecipitation within an organic mucilaginous sheath (Kendall & Skipwith, 1969), and repeated boring by endolithic algae, followed by precipitation of micrite in the vacated borings (Bathurst, 1964, 1966, 1971; Winland, 1968; Friedman, Gebelein & Sanders, 1971). The boring-precipitation mechanism is, in particular, associated with the feature called the *micrite envelope*, a clearly defined isopachous rind of micrite which encloses a core of unaltered material (Bathurst, 1966).

Micrite envelopes are common in biosparites, where they are of particular importance for the preservation of the original outline of skeletal grains (Bathurst, 1966; Winland, 1968; Buchbinder & Friedman, 1970). However, as long as their genesis is poorly understood, the envelopes *per se* are of little use as indicators of depth, light, temperature, or other environmental parameters (cf. Friedman, Gebelein & Sanders, 1971). Intragranular precipitation of aragonite and Mg-calcite takes place in various hollow sediment particles in the warm, carbonate-supersaturated regions of modern seas (Purdy, 1968; Glover & Pray, 1971; Alexandersson, in press *b*), and it is possible that the growth of micrite in the borings is a variant of the same process. In that case, micrite envelopes should form only in supersaturated seawater, while skeletal fragments in cold, barely saturated waters should have borings without any micrite infillings. On the other hand, if the growth of micritic carbonate depends on the activities of organisms in the cavities, the relations to the carbonate satu-

ration level in the surrounding seawater become less evident, and micrite envelopes should be considered from a more biological point of view.

In this paper, the boring-infilling processes are studied with emphasis on the origin of the cryptocrystalline carbonate in the borings. The processes of recrystallization, and of dissolution-reprecipitation within mucilaginous sheaths, are not included. The restriction of scope should be noted, since observations made in the course of this study support the opinion that the processes leading to a secondary cryptocrystalline fabric may involve several complex mechanisms.

There are at least three basically different alternatives for the genesis of micrite infillings, namely, (i) they are produced by the primary boring organisms; (ii) they are produced by secondary organisms, for example, by bacteria which break down the dead excavating organisms, or by other microorganisms which simply nestle in the vacated borings; and (iii) they are the product of inorganic precipitation from the surrounding seawater. Here, a number of modern calcareous sediments from warm and cold shallow-marine environments are described from the following aspects: (i) general characteristics of bored particles and borings; (ii) relations between microorganisms, borings, and micrite infillings; and (iii) mineralogy, fabric and ultrastructure of the micrite.

In a special section, some early diagenetic alterations of skeletal carbonates in cold, shallow marine and brackish waters are given further consideration. The purpose is to point out that the course of events in cold waters differs characteristically from the more studied diagenesis in warm seas. The divergencies are ultimately related to the differences in the state of carbonate saturation in cold, respectively, in warm shallow seawater. A particular form of micritization of aragonite shells, previously known from subaerial diagenesis, is described from cold, shallow-marine conditions.

## MATERIAL, METHODS, AND TERMINOLOGY

*MATERIAL.* Most of the warm-sea material was selected from a series of near-shore calcareous sands

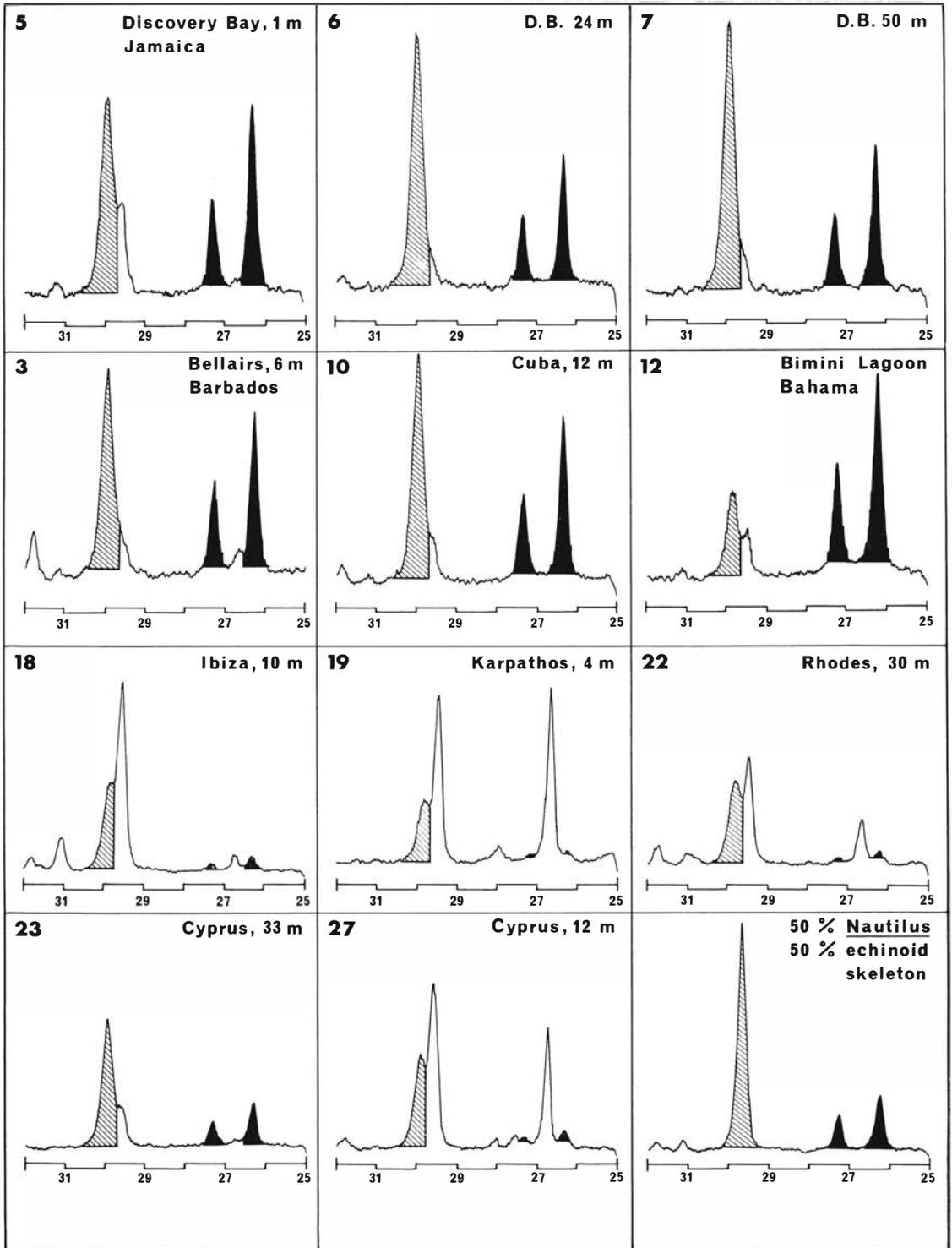
Table I. *Sediment sample locations. Dr. Robin Bathurst, Liverpool, provided the material from the Bahamas; Dr. Erwin Suess, Kiel, provided the material from Bermuda; sample No. 29 from Kristineberg is a dredge sample. The rest of the material was collected by the author in connexion with diving operations. X-ray diffraction patterns of the samples Nos. 3, 5, 6, 7, 10, 12, 18, 19, 22, 23, and 27 are given in Fig. 1.*

Location	Water depth (m)
(The West Indies, and Bermuda)	
Barbados:	
1 Buccaneer Point, inshore zone	1
2 Freshwater Bay, inshore zone	2
3 Bellairs, rippled sand	6
4 First Ridge, outer reef slope	30
Jamaica:	
5 Discovery Bay, inshore zone	1
6 " " , NW of bay mouth	24
7 " " , outer reef slope	50
Cuba:	
8 Varadero Beach, inshore zone	2
9 W of Matanzas, reef front	6
10 E of Cayo Piedras, rippled sand	12
Bahamas:	
11 Bimini Lagoon, B-220, skeletal sand	
12 " " , B-247, skeletal sand	
13 Browns Cay, oölite	
14 Joulter's Cays, oölite	
Bermuda:	
15 Marley Beach, skeletal sand	1
(Mediterranean)	
Ibiza:	
16 Cala Conta, littoral sand	
17 " " , sublittoral slope	5
18 " " , sublittoral slope	10
Karthos:	
19 Diaphani, offshore	4
20 Vurgunda, near amphora mound	6
Rhodes:	
21 Ladhiko, bay sediment	5
22 " " , base of fault scarp	30
Cyprus:	
23 W of Kyrenia, offshore	33

24 Famagusta Beach, inshore zone	3
25 Cape Greco, algal mound	18
26 " " , open rippled sand	19
27 Cape Andreas, open rippled sand	12
(Skagerrak)	
28 Grebbestad, rippled sand	7
29 Kristineberg, offshore	45
(Kattegat)	
30 W of Båstad, sublittoral slope	4
31 " " " " "	9
32 " " " " "	18
(Baltic Sea)	
33 N Öland, coarse rippled sand	8
34 Nielsen's Shoal, shell debris	16
35 " " , submarine slope	21

from islands in the Mediterranean and the West Indies, collected by the author during various periods of field work in 1966—1971. These sediments were sampled on the sediment surface by scooping material into plastic bags, as a rule in connexion with free- or SCUBA-diving, and the general sedimentary environment of each sample is therefore known from personal observations. The material represents a variety of near-shore marine environments where calcareous sands are being deposited, for example: the open coast, and back-reef positions on the west coast of Barbados; the small, protected bay, and off-reef positions at Discovery Bay on the north coast of Jamaica; open positions around Matanzas on the north coast of Cuba; and open positions on the coasts of Ibiza, Karpathos, Rhodes, and Cyprus in the Mediterranean. In addition, Dr. Robin Bathurst, Liverpool, generously provided samples of micritized skeletal and oölitic sands from Bimini, Browns Cay, and Joulter's Cays, Bahamas; Dr. Erwin Suess, Kiel, kindly supplied material from Marley Beach, Bermuda.

In general, the sediments studied were unstable sands, sparsely covered by vegetation; the West Indian material belongs to the corallgal, and to the oölite lithofacies (Bathurst, 1971, p. 103), while the skeletal material in the Mediterranean sediments mainly derives from coralline algae, porcellaneous benthic foraminifers, and mollusks. The West Indian samples are practically 100 %



carbonate, dominated by aragonite; the carbonate content in the Mediterranean material varies between 50 % and almost 100 %, and the dominating carbonate minerals are Mg-calcite, and detrital low-Mg calcite (representative X-ray diffractograms, Fig. 1).

As a crude generalization, the salinity in the Mediterranean is 37–39 ‰, and the summer water temperature is 21–26°C at the surface, and 16–20°C at diving depths below 15–20 m. The ocean water salinity in the West Indies is about 36 ‰, and the water temperature in open positions is 22–26°C at most of the depths within reach of SCUBA-diving. Both parameters vary considerably according to local conditions (cf. Bathurst, 1971).

The cold-sea material consists of modern, skeletal carbonates, collected from the Swedish west coast along Skagerrak (salinity 30–34 ‰), and Kattegat (salinity 15–20 ‰); a few samples are from the brackish Baltic Sea (salinity 7–10 ‰). At a water depth of 10–15 m, the summer temperature range is 12–15°C; the winter temperature is 4–8°C. With exception for one dredge sample from a depth of 45 m off Kristineberg, Skagerrak, the cold-water samples were also collected by means of SCUBA-diving. These sediments are dominated by terrigenous minerals, and the carbonate content is usually less than 10 %. All samples are listed in Table I.

**METHODS.** The samples were rinsed, first in distilled water under vacuum, and then in alcohol, and

dried overnight at 70°C. Sample splits were embedded in plastic epoxide, and thin-sectioned for reference studies with a petrographic microscope. Splits of all samples were also ground for 15 minutes in a Fritsch Pulverisette O laboratory mill, and analysed by means of X-ray powder diffraction, using nickel-filtered copper radiation.

The details of micritization are far beyond the powers of light microscopy, and the major part of the study was made with the aid of scanning electron microscopy (SEM). The instrument was a JEOL JSM-U3 microscope, equipped with two X-ray spectrometers; one a Nuclear Diodes EDAX energy dispersive analyzer, and the other a JEOL SMU-3 single dispersive spectrometer.

The SMU-3 spectrometer works like the ordinary electron microprobe, and the analyses are made element for element, preferably on polished surfaces. The EDAX spectrometer analyses the total elemental composition of the area under the electron beam, including Na and heavier elements; it has a lower sensitivity than the SMU-3 but works well on uneven, fractured surfaces. Element distribution scans can be made with both instruments.

To the petrographer this means, among other things: (i) that morphological elements, such as crystals down to a size of 0.2–0.5  $\mu\text{m}$ , can be identified and studied in three dimensions; (ii) that major differences in composition, for example, between aragonite and Mg-calcite, can be related to morphological characteristics on a scale of a few  $\mu\text{m}$ ; and (iii) that the distribution of elements can be studied with a spatial resolution of less than 1  $\mu\text{m}$ , preferably on ordinary petrographic thin sections without cover glasses. For accurate routine analyses, however, the electron microprobe is still the superior instrument.

For the SEM work, grains were selected under a binocular microscope and mounted, complete or fractured, in Araldit on specimen holders. As a rule they were coated, first with carbon, and then with gold-palladium, in an evaporation chamber.

**TERMINOLOGY.** In the field of carbonate sedimentology, the micro-organisms which penetrate into calcareous substrates are commonly referred to

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*Fig. 1.* Bulk powder X-ray diffraction patterns of marine calcareous sands. The numbers refer to the sediment sample numbers in Table I. The runs were made on a Philips PW 1009/80 instrument, using Ni-filtered Cu-radiation. 38 kV, 18 mA, attenuation 4, time constant 8, 0 zero suppression. Scanning speed  $0.5^\circ 2\theta$  per minute, paper speed 1 cm per minute. Rate for the upper eight patterns  $4 \times 10^2$ , for the lower eight patterns  $1 \times 10^3$ . In order to facilitate general comparisons, the aragonite peaks 111 and 021 are black; the part of the calcite peak 104 which represents Mg-calcite is grey. The relative intensities of the aragonite and calcite peaks in a 1/1 mixture are shown in the lower right square (aragonite from a Pacific *Nautilus* shell, Mg-calcite from an echinoid skeleton from Gran Canaria).

as *boring organisms* while *burrowing* implies excavation into unconsolidated deposits (cf. for example: Shinn, 1968; Perkins & Halsey, 1971). An outcome of the Symposium on Penetration of Calcium Carbonate Substrates by Lower Plants and Invertebrates, held at the AAAS meeting in Dallas, Texas, 28—30 December 1968, was an attempt at standardizing the terminology, and to give specific, clearly defined meanings to terms such as bore, drill, burrow, etc. (Carriker & Smith, 1969). A consequence of these recommendations is that "boring algae" would become "burrowing algae", in itself maybe a minor change. However, there has been no sign of a general acceptance of the standardized terminology, and, after some hesitation, I decided to retain the familiar sedimentological usage of the words "bore" and "burrow" in this paper.

The term *micrite*, originally introduced as a contraction of "microcrystalline calcite" (Folk, 1959), is here used in a wide sense, meaning a fabric of coherent crystals which are less than a few  $\mu\text{m}$  in size, and poorly resolved in the petrographic microscope. The word applies to carbonate minerals only, but otherwise it no longer has any mineralogical implications. From a linguistic point of view, "aragonite micrite" is an unfortunate construction, but it is nevertheless recognized by the sedimentologist (cf. Friedman, 1968; Bathurst, 1971). The typical micrite is opaque and structureless in thin sections, with yellow or brown colour in transmitted light. The term micrite is here only used for a coherent fabric; a loose deposit of micrite-sized crystals is called ooze or mud.

*Micritization* means the alteration of a pre-existing fabric to micrite. The term is not associated with any genetic implications. As commonly described, shallow-marine micritization may involve a decrease in crystal size (for example, the alteration of an echinoderm fragment), an increase in crystal size (for example, the alteration of a miliolid foraminifer), or mainly the destruction of an ordered arrangement (for example, the alteration of a mollusk fragment). The process may, or may not involve changes in mineralogy.

Accretionary growth of micrite, for example, as cement in the interstices of beachrock, or as fillings in the voids of hollow particles, is not regarded as micritization. However, it may in the end prove difficult to uphold a distinction between precipitation in an original cavity, such as a foraminiferal chamber, and precipitation in a secondary cavity, such as an algal boring, in particular where the two kinds of fillings occur together in the same grain (cf. Alexandersson, 1969, in press *b*; Ginsburg, Marszalek & Schneidermann, 1971; Schroeder, 1972).

*Precipitation*, unless specified, means the general process of crystal growth from supersaturated fluids under non-metabolic conditions. The triggering may be purely physicochemical, for instance, evaporation, as well as biochemical, for instance, photosynthesis. The important condition is the supersaturated environment.

#### MICRITIZATION BY THE BORING-INFILLING MECHANISM

##### *General characteristics of bored particles and borings*

*Particles.* Calcareous sediments from turbulent environments in warm seas are characterized by well-rounded grains with glossy surfaces. As a rule, there are no borings in the polished grains, and their form is a product of mechanical abrasion (Fig. 2). Evidently, the boring micro-organisms do not readily attack sand-sized grains under the conditions which characterize the turbulent near-shore environment. Protection is the most obvious benefit of an endolithic mode of life, and it seems an anomaly that practically no organisms seek that protection in the extreme near-shore environment, where shelter is most needed. The apparent explanation is that where the sediment is in almost constant movement, there are no opportunities for the organisms to settle, and to escape beneath the grain surface. It is known that the larvae of the boring sponge *Cliona* need 2—3 days for the excavation of a cavity that will barely accommodate the organism (Nassonow,

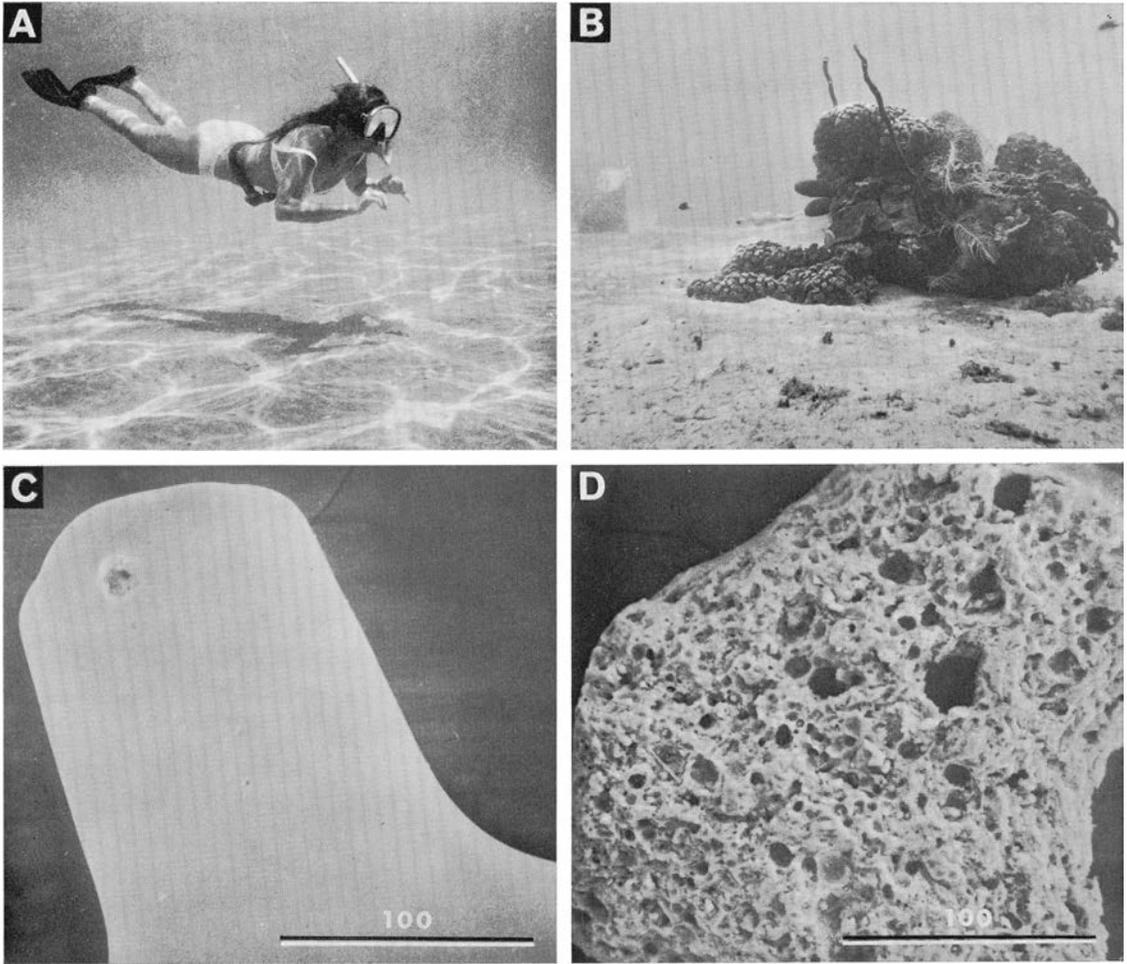


Fig. 2. Sublittoral environments and the activity of microborers.

(A) The sedimentary environment of sample No. 24, inshore zone, Famagusta Beach, Cyprus. Depth 3 m. The sediment particles are frequently kept in motion, and there is little colonization by microborers. The environment is characterized by smooth, beautifully rounded forms.

(B) The sedimentary environment of sample No. 6, Discovery Bay, Jamaica. Depth 24 m. Height of the coral knob 0.5 m. The sediment particles are at rest for long periods of time, and the activity of microborers

is high. Calcareous particles are deeply pitted and bored.

(C) Calcareous spicule with glossy surface from the environment shown in A. The particle has been broken and polished by mechanical abrasion, but there is little evidence of the activity of boring organisms. Scale bar 100  $\mu\text{m}$ .

(D) Similar calcareous spicule from the environment shown in B. The surface morphology of the particle is characterized by biochemical destruction. Note the absence of any mucilaginous sheath. Scale bar 100  $\mu\text{m}$ .

1883). The settling time needed by algae and fungi is not known, but it is clear that conditions of frequent turbulence are unfavourable to the boring-infilling mechanism of micritization.

The relations between mechanical abrasion, and

boring activity, change gradually along traverses from shallow waters with incessant sediment movement, towards deeper waters where the sediment grains are at rest for long periods of time. The micro-morphology of the particles shows how

the effect of mechanical abrasion decreases, and how the activity of micro-borers increases, although the pattern is complicated by sediment transport and mixing. On gently shoaling beaches in open positions in the Mediterranean, the percentage of polished grains drops off rapidly at a water depth of 2—5 m, and at 10—12 m depth almost all calcareous particles, with the exception of fresh skeletal material, have a sub-angular form and dull external surfaces.

*Surface morphology of bored particles.* The dull surfaces seen on shallow-marine calcareous particles under a binocular microscope are complex records of repeated attack by organisms, mainly by borers, but also by scavengers and sediment ingestors. There are striking differences in micro-morphology between a polished skeletal fragment from a turbulent inshore position, and a corresponding bored particle from quiet water (Fig. 2).

Many plants and lower invertebrates penetrate calcareous substrates (cf. the symposium volumes on penetrating organisms: Sognaes, 1963; Carrier, Smith & Wilce, 1969; also the annotated bibliography on marine borers by Clapp & Kenk, 1963). Only the microscopic organisms are likely to attack sand-sized grains, and for the development of micrite envelopes, the blue-green and other photosynthesing algae seem to be the most important (Bathurst, 1966, 1971; Golubic, 1969; Kendall & Skipwith, 1969; Swinchatt, 1969). Other possible contributors are bacteria (DiSalvo, 1969), fungi (Kohlmeyer, 1969; Perkins & Halsey, 1971), sponges (Cobb, 1969; Evans, 1969), and polychaete worms (Evans, 1969). Identifiable traces of specific microborers are found on the surfaces of sediment particles in the early stages of biological destruction, while the grain-surface morphology of severely affected particles gives little information about the destructive organisms involved. This is partly a result of the gradual breakdown of the grains, a process that exposes former internal cavities at the particle surface.

The most common traces of boring found on the external surfaces of particles are: (i) shallow *pits*, 30—50  $\mu\text{m}$  in diameter; and (ii) long, narrow *grooves*, 1—2  $\mu\text{m}$  in width (Fig. 3). The

grooves are usually the first evidence of organic destruction on an exposed surface, and isolated, winding grooves are occasionally found even on highly polished grains from turbulent environments. The grooves are clearly an effect of biochemical dissolution of the substrate; commonly they can be traced over the surface of a particle to a point where they disappear beneath the surface. Single, winding forms without branches, and straighter, bifurcating forms, both single and paired occur (Fig. 3 A, B, E). The grooves are widely distributed, and similar forms occur in both warm-sea and cold-sea sediments. It is well known that many forms of filamentous boring algae are differentiated into endolithic parts which penetrate into the substrate, and epilithic parts which spread over the surface (Golubic, 1969). A certain proportion of the grooves are probably the traces of epilithic algal filaments. In view of the observations of Perkins & Halsey (1971) that fungi are among the earliest organisms that infest calcareous particles, it seems probable that the epilithic grooves in part are of fungal origin.

Shallow, superficial pits are commonly made by sponges of the genus *Cliona*. Nassonow (1883), Warburton (1958), and Cobb (1969) have shown how the boring is achieved through the etching out of small chips which are discarded through the excurrent water canals. Abortive borings, consisting of a few pits around a central column, are very common in the material described here (Fig. 3 C, D). The *Cliona* borings proper leave only entrance and exit openings for the incurrent and excurrent papillae on the external surfaces, while there may be entire galleries of interconnected cavities within the substrate (Goreau & Hartman, 1963).

*Borings.* A fracture through a calcareous particle shows a variety of borings, of which few can be related with certainty to a particular organism. The most common types of borings exposed by fracturing are: (i) marginal *pits*, 30—50  $\mu\text{m}$  across, and 50—100  $\mu\text{m}$  in depth; (ii) *simple tunnels*, 2—8  $\mu\text{m}$  in diameter, which are straight or gently winding and penetrate deep into the particles; and (iii) *convolute marginal tunnels*, a clearly defined

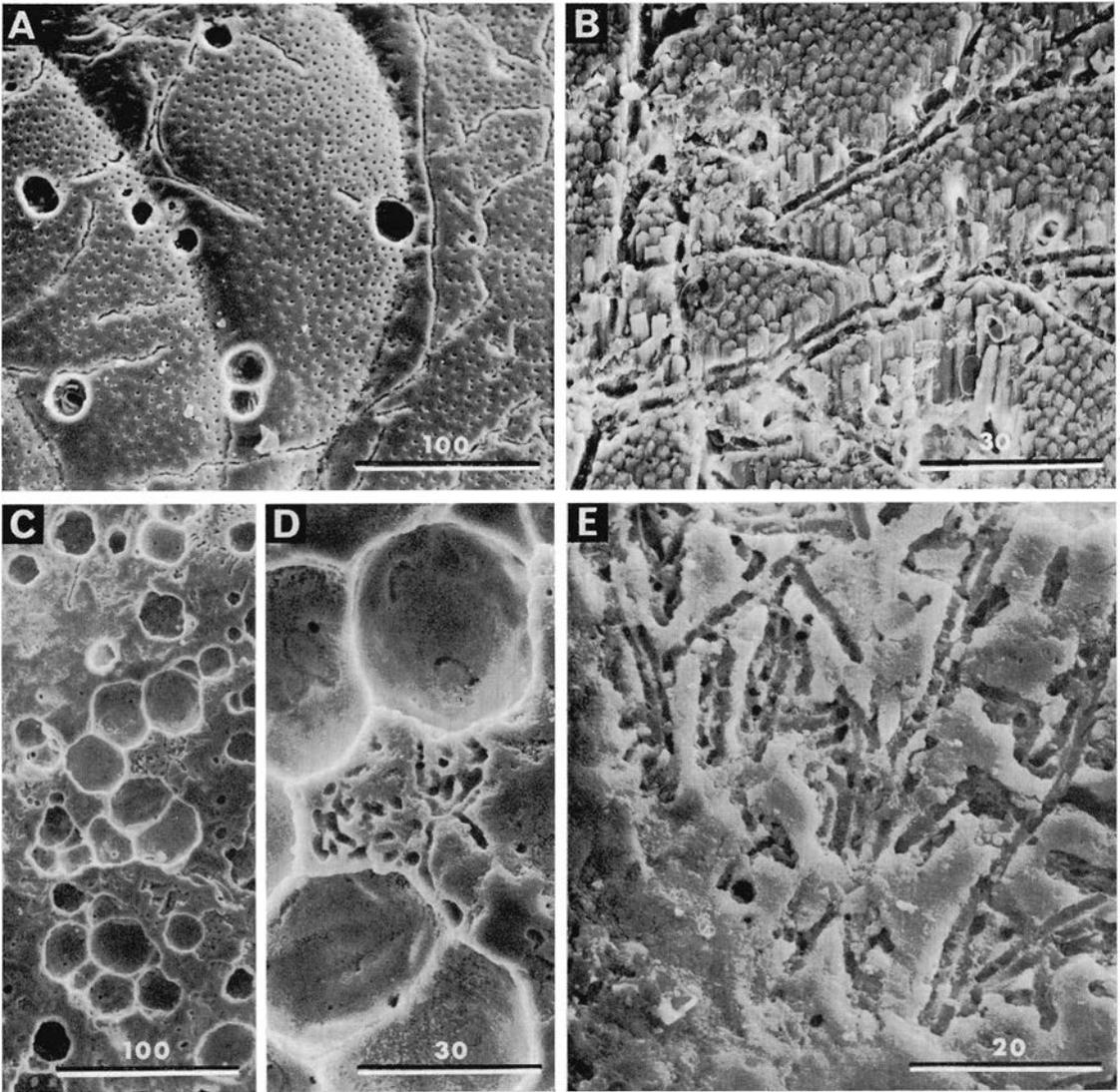


Fig. 3. Surface morphology of bored particles.

(A) External surface of a porcellaneous Mg-calcite foraminifer of the genus *Archaias*. Sample No. 8, Varadero, Cuba. An early stage of biochemical destruction, with pits and grooves on an almost intact surface. The microporosity is part of the original test structure. Scale bar 100  $\mu\text{m}$ .

(B) External surface of *Mytilus* fragment, prismatic calcite part. Sample No. 31, west of Båstad, Kattegat. The particle surface is riddled with shallow grooves, and

slightly etched by syngedimentary dissolution. Compare with E. Scale bar 30  $\mu\text{m}$ .

(C—D) External surface of unidentified calcareous particle, sample No. 18, Cala Conta, Ibiza. Abortive borings of the sponge *Cliona*. Scale bars 100, respectively 30  $\mu\text{m}$ .

(E) External surface of mollusk shell fragment, sample No. 10, east of Cayo Piedras, Cuba. Shallow grooves with endolithic continuations. Note the absence of signs of etching. Compare with B. Scale bar 20  $\mu\text{m}$ .

zone of densely spaced, intertwining borings just beneath the external surface of the particle.

The pits are frequently *Cliona* borings, in places

continuing as a chain of pits into the substrate, in accordance with the boring habits previously referred to. The simple tunnels within the particles

are often similar to the superficial grooves, and some are obviously the endolithic continuations of such grooves. Others branch out from a common opening on the surface, and are not related to any pattern of grooves. Simple tunnels are obviously produced by algae, as well as by fungi (Perkins & Halsey, 1971). Both simple tunnels, and convolute marginal tunnels have been found as taxonomically specific patterns in endolithic bluegreen algae. In an exposure experiment in the upper tidal zone at La Parguera on the south coast of Puerto Rico, *Hormatonema paulocellulare* Ercegovic produced a marginal zone of convolute borings, 30–50  $\mu\text{m}$  in depth in Iceland spar in three years, while *Hyella caespitosa* Bornet & Flahault penetrated 120–300  $\mu\text{m}$  in the form of branching tunnels in the same experiment (Golubic, 1969; Golubic, Brent & LeCampion, 1970).

*Interparticle variations.* The activity of microborers is a prerequisite condition for the progress of the boring-infilling mechanism of micritization, and biological patterns of reaction will therefore govern this particular form of diagenesis. Particularly important are any reactions of borers in relation to the choice of substrate, since selection at this stage would lead to preferential attack of certain substrates, and selective removal, alternatively micritization of these. Marine boring fungi have been reported to attack mollusk shells preferentially, although they occur also in foraminifers, ostracods, and calcareous sponge spicules (Kohlmeyer, 1969). In their study of microborers in the present-day sediments on the Carolina shelf, Perkins & Halsey (1971) found that mollusk shells were preferentially attacked, both by algae and by fungi, and therefore selectively removed from the sediments. In contrast to sponges and algae, fungi apparently bore for food, and Perkins & Halsey found no fungal borings in limestone clasts.

Schroeder (1972) noted that the endolithic alga *Ostreobium* in Bermuda cup reefs selectively infested shells of the gastropod *Dendropomum irregulare*, while the tests of the foraminifer *Homotrema rubrum* were hardly bored at all. On the Dutch coast, Boeschoten (1966) found the

most diverse assemblage of boring organisms in mollusk shells.

The results of this study also suggest that mollusk material is preferentially attacked by the boring organisms, although borings have been found in all kinds of carbonate particles, including detrital limestone grains. Perfect micrite envelopes observed here were almost invariably developed on mollusk fragments, and a cursory survey of the available literature on Recent micrite envelopes reveals that there is a great predominance for mollusk-based micrite envelopes in the accompanying illustrations (Bathurst, 1966, 1971; Winland, 1968, 1971; Lloyd, 1971). It is interesting to note that this top ranking of mollusks as most susceptible to boring organisms is not matched by the same high ranking on a list showing susceptibility of various skeletal constituents to submarine "recrystallization" (Purdy, 1968, p. 191).

#### *Relations between micro-organisms, borings, and micrite infillings*

*Organisms in borings.* Only few organisms are found in the intraparticle cavities, and the great majority of borings contain no trace of organic tissues. This is assumed to represent natural conditions, since the treatment of the samples involved no intentional removal of organic substances, and, furthermore, the organisms that do occur are well preserved. Most common are thin filaments, 2–6  $\mu\text{m}$  in diameter, in straight or gently winding tunnels; some filaments branch into root-like features (Fig. 4B). The filaments are probably endolithic algal thalli, and fungal hyphae, but no attempt has been made to have them identified. In addition to the filaments, various unidentified organisms, and organic parts occur in cavities in the grains, but they are rare and must be of very limited importance as cavity producers for a micritization process (Fig. 4C, D). A small constituent is formed by various foraminifers, and ostracods, which settled in the borings by accident, and became trapped during growth. Their skeletal parts show remarkable adjustments to the confining cavity walls, but there are no traces of any excavating ability in these animals.

The behaviour of the penetrating organisms is

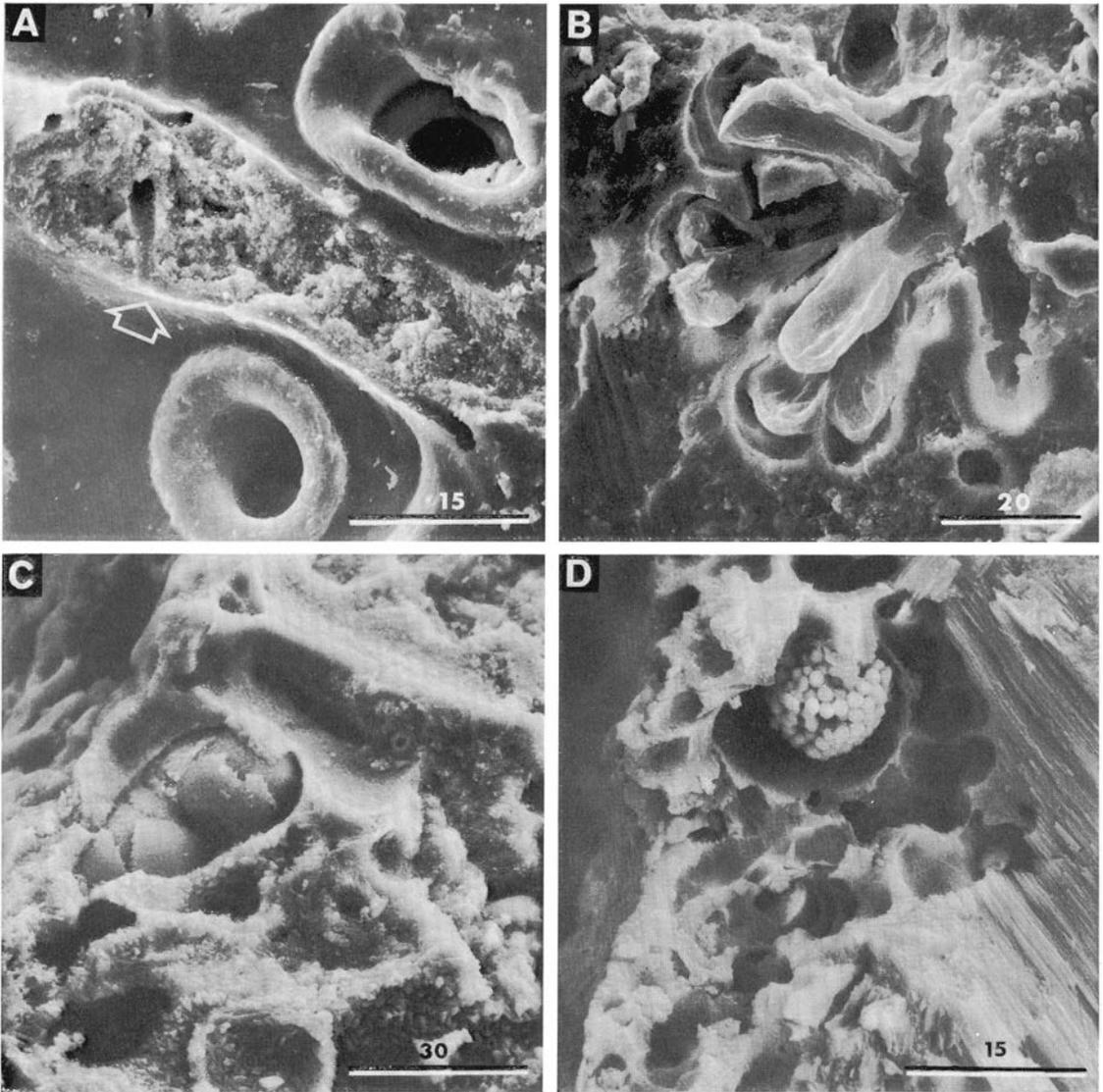


Fig. 4. Organisms in borings.

(A) Internal chamber walls of a fractured specimen of *Archaia* sp. Sample No. 8, Varadero, Cuba. A bored tunnel runs vertically from the upper left in the picture; the arrow points to a sudden change of direction. Typically, the boring organisms react negatively against the act of emerging from the calcareous substrate. Thus they avoid contact with other borings, and with pre-existing internal cavities. Scale bar 15  $\mu\text{m}$ .

(B) Fractured mollusk shell, sample No. 11, Bimini Lagoon. Root-like branching filaments, probably of algal origin. Scale bar 20  $\mu\text{m}$ .

(C) Margin of fractured foraminifer, sample No. 9, west of Matanzas, Cuba. External surface to the left in picture. Unidentified spheric bodies, filling borings, and (not visible in picture) primary chamber cavities. Scale bar 30  $\mu\text{m}$ .

(D) Margin of fractured mollusk shell, sample No. 22, Ladhiko, Rhodes. External surface to the left. Unidentified botryoidal body in cavity. Note the residual particle fabric between different borings, and the absence of micrite infillings. Scale bar 15  $\mu\text{m}$ .

such that they will not grow out of the calcareous substratum. Instead of growing into another tunnel, or into the chamber space of a foraminifer, the organism changes the direction of growth and remains within the crystalline substance (Fig. 4 A). In the scanning electron microscope, relatively few electrons are emitted from an extremely thin part of a specimen, and voids immediately beneath a surface therefore show up as dark areas. Because of this effect, it can be seen how organism filaments have penetrated into skeletal fragments, a fraction of a micron beneath a void surface, and yet without emerging from the mineral substance.

A reaction pattern like that leads to the preservation of a residual frame-work of original particle fabric between borings in highly bored grains. Thus even heavy attack by microborers will leave behind a spongy, cavernous ghost of original particle substance, which may act as a nucleation substrate for a possible secondary lining of calcium carbonate. As a consequence of the same reaction pattern, each excavating organism will also create its own system of tunnels, and avoid contact with the various kinds of pre-existing voids in a bored particle.

*Organic linings in borings.* Many burrowing and boring macro-organisms line their cavities with an organic mucus. The observations by Kendall & Skipwith (1969) suggest that also the assemblage of microscopic organism within, and on, calcareous grains may produce mucilaginous sheaths that surround the grains completely. In the material studied here, some sediment grains seem to be coated by very thin organic films of the kind described by Chave & Suess (1967, 1970), and Suess (1970), but there are no real mucilaginous envelopes. The possibility remains that the boring organisms produce organic linings of extra-cellular matter on the walls of their borings; linings which might affect the solubility of calcium carbonate in the intraparticle solutions, and influence the processes of crystal nucleation and growth during precipitation in the tunnels.

Processes of a similar effect have been described. Gebelein & Hoffman (1971) demonstrated that the mucilaginous sheaths of the stromatolite-

forming bluegreen alga *Schizotrix calcicola* concentrate Mg relative to Ca, and thus serve as a Mg-source and may affect mineralogy and growth of a carbonate precipitate. Schroder (1972) found that the filaments of the endolithic green alga *Ostreobium* exerted microenvironmental control on the fabric and mineralogy of cement in Bermuda cup reefs.

The possible presence of organic linings in microscopic borings was investigated in the following manner: Skeletal particles with borings were fractured and mounted on 5 × 5 mm glass plates by means of Araldit. After polymerization of the glue, the mounts were immersed in EDTA solution buffered to pH 7 for variously 2, 5, and 10 minutes, gently rinsed in distilled water, dried at 70°C, and placed on SEM specimen holders for study in the scanning electron microscope. The buffered EDTA solution removes calcium carbonate very gently and without effervescence, while any soft organic tissues, and other water-insoluble compounds, are left in relief above the etched mineral surface. Water-soluble compounds go into solution. Similar methods are commonly used in the study of shell ultrastructure.

The organic matter found in the borings was invariably in the form of organism tissue, mostly bifurcating algal and fungal filaments with a diameter of 2–6 μm. The filaments were well preserved, without signs of shrinkage, collapse, or dissolution, and with a close fit into the cavities. It is concluded that secreted organic linings in microscopic borings are rare, alternatively, that any extra-cellular mucus in the tunnels consists of water-soluble substances. In either case, mucilaginous organic linings should at best have a limited influence in the genesis of micrite infillings.

*Vacated borings.* The number of vacated borings greatly exceeds the number still inhabited. It is difficult to determine the proportions of inhabited to vacated borings, for this varies from particle to particle, and from sediment to sediment. As a subjective estimate, based on about 80 instrument hours of SEM work, less than 5% of the borings in the present warm-sea material contain any

organisms. The "lifetime" of a sediment particle is certainly very long in comparison with the lifetime of a given excavating organism, and the great amount of vacated borings is supposed to be a slowly accumulated record of repeated boring, representing several generations of endolithic organisms.

Perkins & Halsey (1971) point out that fungal colonies are capable of indefinite growth, and are known to have grown continuously for 400 years or more. Conditions for continuous growth must be rare in shallow marine calcareous sands, and the boring of skeletal grains is most likely a series of short attacks, interrupted by shallow burial, passage of the particle through the alimentary tract of a sediment ingester, etcetera. There is no invasion by nestlers or other secondary organisms into the empty borings. The boring organisms are rarely found in a state of decay, and any presence of tissue-decomposing bacteria must be temporary. There is practically no sediment fill in vacated borings, although material of that kind is common in larger open voids, such as the slits in echinoid spines.

In conclusion, the general microenvironment in borings is not an environment with a particularly high concentration of organic matter, such being present only during the lifetime of the boring organism, and during a relatively short, postmortal period of organism decay. It is stressed that the sediments studied here, in general are clean, aerated calcareous sands from sedimentary environments with low organic productivity. In sheltered areas with mud deposits, high organic content, and periodically stagnant conditions, the consequences of organism activity should be more important (Oppenheimer, 1960, 1961; Cloud, 1962).

*Micrite infillings.* Secondary calcium carbonate is not invariably found in the borings, and consequently, there can be no direct relationship between the penetrating organisms and the formation of micrite infillings. As originally pointed out by Bathurst (1964, 1966), this kind of micritization must be a two-stage process, and the boring activity alone is not equivalent to micritization. The amount of micrite in the borings varies

according to two basically different patterns: (i) *gradational intraparticle variations*, between the different borings in a given particle, and (ii) *environmental variations*, between sediments from different environments.

*Gradational intraparticle variations.* In bored grains with micrite infillings, the amount of secondary carbonate varies from boring to boring. Micrite has not been found in cavities which still contain the excavating organism, or the remains of such an organism. Vacated borings occur in all stages of infilling; some are empty, others contain small crystals in the earliest stages of growth, and a great number of borings are completely occluded by secondary carbonate. Where the fillings consist of aragonite needles, the size of the crystals increases with increasing infilling of the void (Fig. 5 A, B). In an incipient stage of infilling, the walls are lined with extremely small crystals (lower detection limit for the microscope is about  $0.1 \mu\text{m}$ ), while in a densely occluded tunnel, the needles are intergrown and as large as the space will permit.

Precipitation of micrite is probably not related to the processes of excavation. In filamentous algae, the boring is performed by the terminal cell of each filament which dissolves a small volume of the substrate, and is pushed further into the excavated space by the growth of the filament (Golubic, 1969). How the dissolved material is transported from the point of dissolution, whether by intra-cellular or by extra-cellular transport, is still uncertain. The condition that excavation takes place in the distal part of tunnels which are occluded by organism filaments, suggests intracellular transport. No observations indicate that the boring algae and fungi secrete aragonite or Mg-calcite at a possible final stage of metabolic calcium carbonate turnover. In the case of boring sponges, the removed material is mainly transported as particulate matter (Goreau & Hartman, 1963; Cobb, 1969), and there is no question of an organic formation of calcium carbonate.

Several workers have noted a connexion between boring micro- and macro-organisms, and the precipitation of cement close to the borings (Otter, 1937; Emery, Tracey & Ladd, 1954; Macintyre,

Mountjoy & d'Anglejan, 1968, 1971; Schroder, 1972, in press). Such a relationship might be an effect of extra-cellular transport of the dissolved calcium carbonate over short distances in the pore solutions, that is, re-distribution of calcium carbonate within an almost closed system. As described earlier in this paper, the borings in a calcareous particle are not an integrated communicating system of voids; rather, each boring organism creates an individual system, and avoids connecting with pre-existing tunnels and other voids. Consequently, the grains lack a void system suitable for extra-cellular distribution of organically dissolved calcium carbonate within the particles. The conclusion is that intraparticle re-distribution of the dissolved calcium carbonate is not the mechanism behind the growth of micrite.

*Environmental variations in micrite content.* Typical end-members in a series of environmental variations are, on the one hand, shallow-water carbonate sands from the Bahama Bank, where micrite infillings are ubiquitous, and on the other hand, cold-sea sediments from the Swedish west-coast in Skagerrak, where calcareous grains are seriously attacked by microborers, but without all trace of any secondary calcium carbonate in the borings. In the majority of the West Indian samples, and in most Mediterranean samples from depths down to about 10 m, secondary carbonate can be found in practically every investigated grain, and heavily bored particles contain distinct infillings of micrite (Figs. 5, 6). This is taken as evidence of crystal growth in progress under present-day conditions. Other samples contain a minor proportion of micritized grains together with heavily bored grains with no micrite infillings at all. Such is the case, for example, with sample No. 23 from a water depth of 33 m west of Kyrenia, Cyprus, and with sample No. 26 from 19 m at Cape Greco, Cyprus (Table I).

Both samples were taken in late summer, beneath sharp thermoclines, in water temperatures of respectively 16°C and 18°C. The temperatures are probably close to the yearly maxima. The bored grains with empty cavities are assumed to represent the present-day conditions of low tempera-

tures, and low levels of carbonate saturation; the micritized constituent is regarded as transported material from more shallow depths.

In the cold-sea carbonate grains from the Swedish coasts, there are no micrite infillings whatsoever in the borings. On the contrary, the grains show evidence of dissolution, a process that will be given more attention in a later section of this paper. It is interesting to note that Perkins & Halsey (1971) do not mention any occurrences of carbonate infillings in the calcareous grains on the Carolina shelf.

*Growth of micrite and relationships to the state of carbonate saturation in seawater.* The pattern of carbonate saturation in the oceans is known only in very general outline, with high supersaturation in the upper part of tropical and subtropical seas, and lateral, regional transitions to lower levels of saturation in cold seas (Hoods, Berkshire, Adams & Supernaw, 1963; Heath & Culberson, 1970). Analytical determinations of the degree of carbonate saturation in seawater, and saturation measurements with the carbonate saturo-meter (Weyl, 1961, 1967), are not without ambiguity; for example, it is subject to discussion whether open ocean waters are saturated with respect to calcite down to 500—1,000 m (Li, Takahashi & Broecker, 1969), or down to about 100 m only (Pytkowicz, 1965; Pytkowicz & Fowler, 1967). It is generally agreed that warm, shallow seawater is highly supersaturated with calcium carbonate. Typical values for low-latitude surface waters are 300—500% supersaturation relative to calcite (Cloud, 1962; Sass, 1965; Broecker & Takahashi, 1966; Pytkowicz, 1971; Schmalz, 1971).

Several factors contribute to make the carbonate saturation conditions in shallow, near-shore areas particularly varied. The effects of photosynthesis and respiration may cause diurnal variations of the saturation level (Schmalz, 1967; Schmalz & Swanson, 1969; Weber & Woodhead, 1971), and the state of saturation is also affected by evaporation, and by the mixing of different water masses (Runnels, 1969; Schmalz, 1971). The conditions certainly vary on a vertical scale, even within the depths accessible for SCUBA divers, and

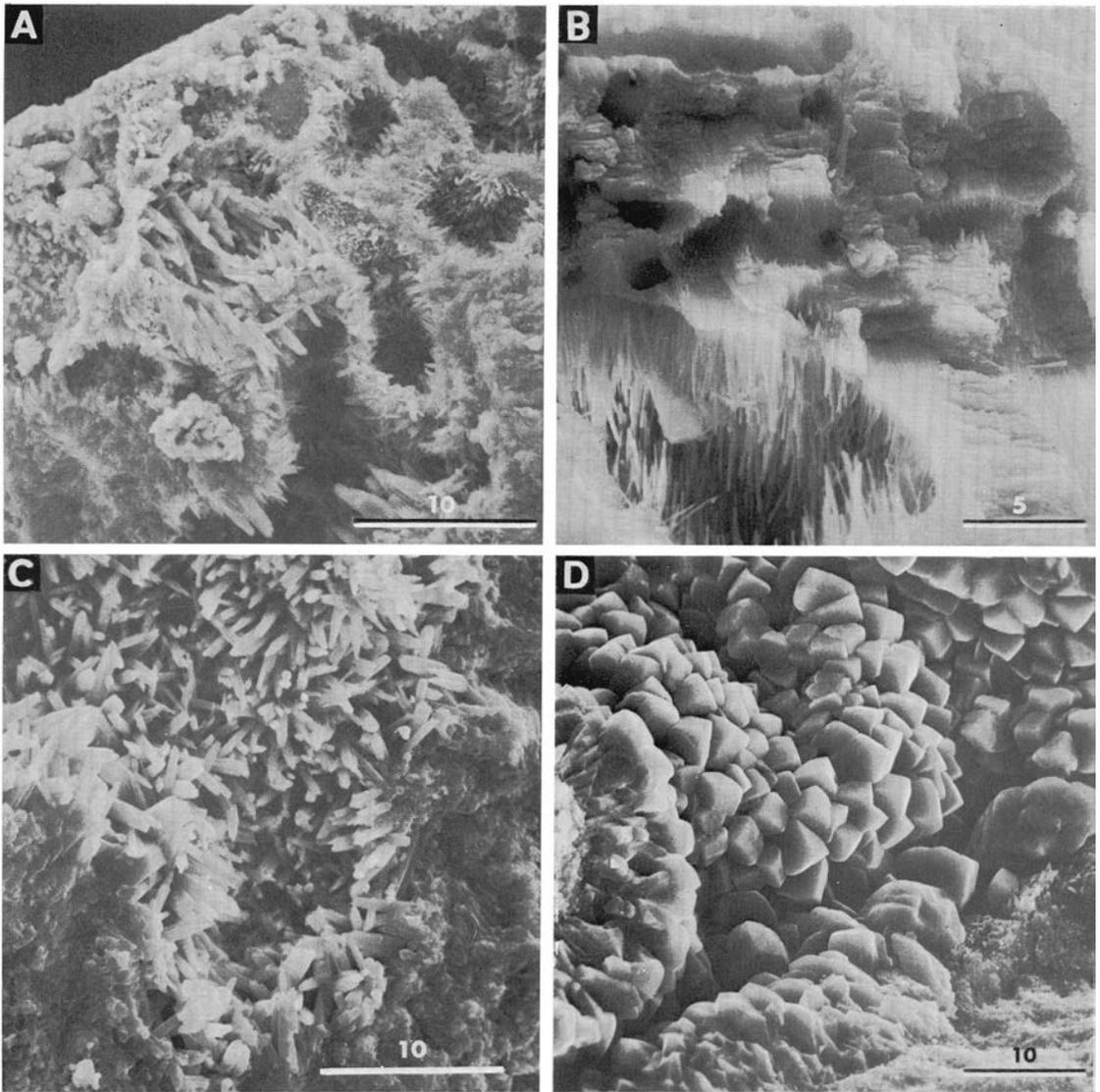


Fig. 5. Secondary aragonite and Mg-calcite in borings.

(A) Margin of fractured mollusk shell, sample No. 12, Bimini Lagoon, Bahama. Several generations of aragonite needles in convolute marginal tunnels. Scale bar 10  $\mu\text{m}$ .

(B) Fractured mollusk fragment, sample No. 4, First Ridge, Barbados. Syntaxial overgrowth of aragonite needles on the biogenic aragonite fabric. The borings occur in various stages of infilling; the same orientation of the precipitate is found in all stages. Scale bar 5  $\mu\text{m}$ .

(C) Boring with a lining of aragonite needles of fairly

uniform size. Unidentified fragment, sample No. 12, Bimini Lagoon, Bahama. Apparently the growth of the aragonite started simultaneously at a number of nucleation sites in the cavity. The conditions suggest heterogeneous nucleation from a supersaturated solution. Scale bar 10  $\mu\text{m}$ .

(D) Secondary Mg-calcite in a foraminifer of the genus *Archaias*, sample No. 12, Bimini Lagoon, Bahamas. The mode of growth, with successive nucleation leading to a rigid fabric of uniform crystals, is typical for void-filling Mg-calcite. Scale bar 10  $\mu\text{m}$ .

furthermore, in areas with marked differences between summer and winter temperatures there is probably a seasonal variation. As a conclusion, there are significant variations of the synoptic saturation pattern over horizontal and vertical distances of a few meters in the shallow marine environment. Over a given period, the conditions at a certain locality may vary between high supersaturation and slight undersaturation, even in the tropics.

The observed environmental variations in formation of micrite in borings are in good agreement with the generalized saturation pattern. There is, however, no question of making a rigorous correlation between the carbonate saturation conditions, and the intraparticle precipitation. No record of the diurnal and seasonal variations of saturation at a given locality is available, least of all from a sediment surface in a submarine position. In addition, a number of the samples studied here were collected on near-shore submarine slopes, and some certainly contain material from up-slope positions, but the effects of sediment transport and mixing cannot be evaluated.

*Time needed for precipitation.* Available data on saturation conditions, and on crystal nucleation and growth rates in natural marine waters, do not allow meaningful calculations of the time needed for precipitation. Radiocarbon datings of the complex mixtures, which constitute most carbonate sediments, give very general information, difficult to interpret; at best, only the order of magnitude of the time spans involved can be estimated.

A few figures, indicating the minimum time spans involved in appreciable marine precipitation, are here quoted from the literature: The outer 10% of the volume of ooliths from nine scattered localities on the Bahama Bank gave a general age of less than 160 years (Martin & Ginsburg, 1965; reference quoted from Bathurst, 1971, p. 135). Heavily micritized skeletal sand from British Honduras was approximately 400 years old (Purdy, 1968, p. 192). Corals with a radiocarbon age of about 130 years were found cemented by Mg-calcite at a depth of 26 m off Discovery Bay, Jamaica (Land & Goreau, 1970; Land, 1971);

cemented corals from a depth of 15–20 m on the west coast of Barbados were about 500 years (Macintyre, Mountjoy & d'Anglejan, 1968, 1971). Weakly cemented layers in Hussain Lagoon, Persian Gulf, were about 120 years, and mollusk shells from submarine cemented layers at 18 m depth west of Dukhan, Persian Gulf, were less than 240 years (Shinn, 1969). Obviously, interparticle cementation can take place in the sublittoral marine environment in less than 100 years. Cementation of beachrock in intertidal positions may occur in less than 10 years (Schmalz, 1971).

In view of such data, it seems probable that the growth of crystals in micron-sized borings of the kind studied here is a process that requires years, rather than hundreds of years, given favourable conditions.

#### *Mineralogy, ultrastructure, and fabric of micrite*

*Mineralogy.* The minerals previously reported from micritized grains are aragonite (Bathurst, 1966, 1971; Purdy, 1968), and Mg-calcite with 14–17 mole %  $\text{MgCO}_3$  in solid solution (Winland, 1968, 1971; Purdy, 1968). The same mineral polymorphs are known as intragranular fillings in hollow calcareous particles from shallow marine sediments (Glover & Pray, 1971; Winland, 1971; Alexandersson, in press *b*), an occurrence which apparently is genetically related to the precipitation in borings.

As a consequence of the small size of the crystals in the borings, and of their intimate association with other carbonates in the host grains, it is virtually impossible to make direct determinations of the mineralogy in micrite envelopes. This is determined by indirect methods, such as bulk powder X-ray diffraction (Bathurst, 1966; Purdy, 1968; Winland, 1968), staining methods (Winland, 1971), and electron microprobe analysis (Glover & Pray, 1971). The staining and electron microprobe methods are based on the assumptions that the presence of Mg indicates calcite, while the absence of Mg, and, preferably, the presence of Sr, indicates aragonite.

In cases where the individual crystals can be observed, the mineralogy can be inferred from the crystal habit. Marine non-skeletal aragonite

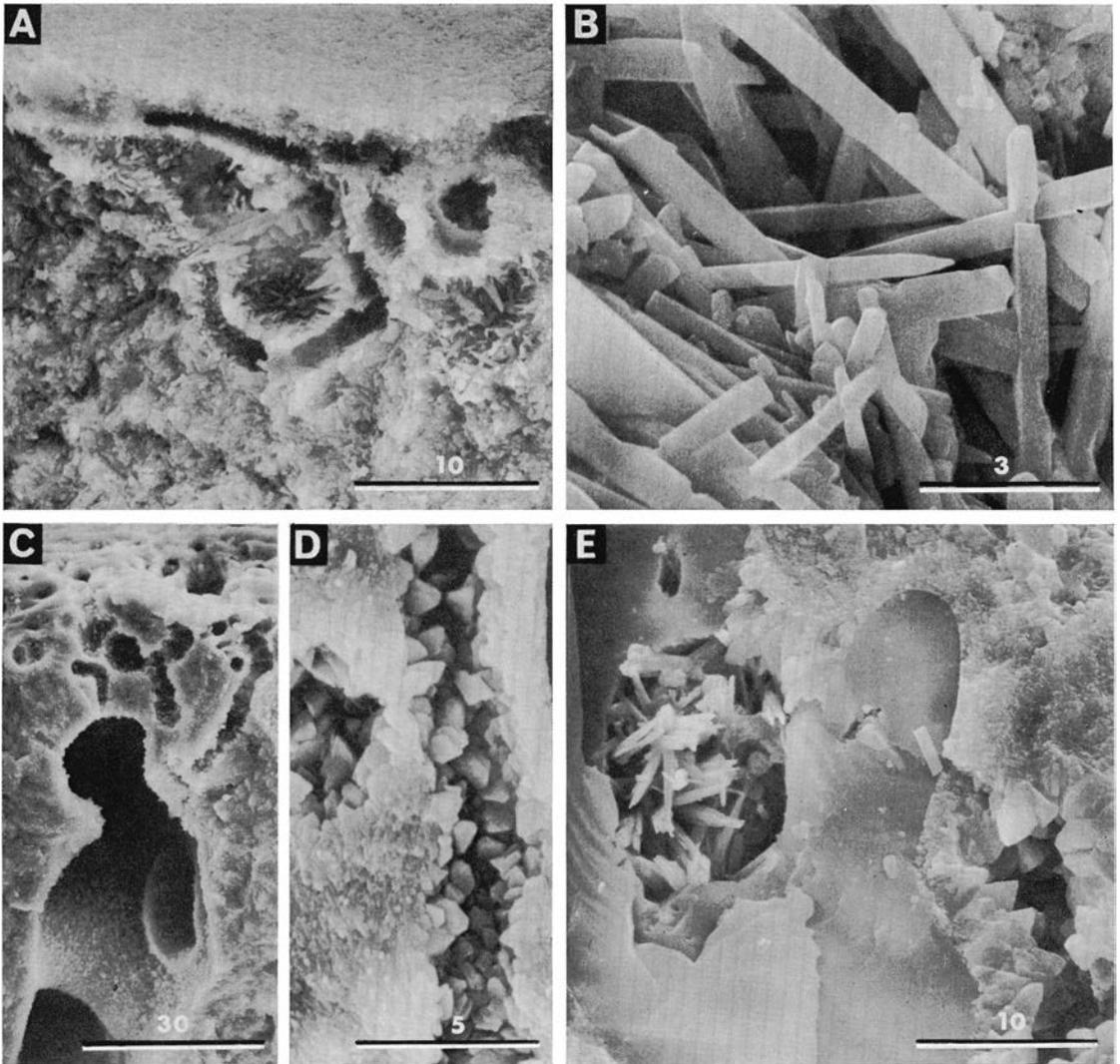


Fig. 6. Secondary aragonite and Mg-calcite in borings.

(A) Fractured oöolith, sample No. 13, Browns Cay, Bahamas. Several generations of borings and secondary aragonite, immediately beneath the external particle surface. Secondary Mg-calcite has not been observed in oöoliths. Scale bar 10  $\mu\text{m}$ .

(B) Aragonite needles, growing centripetally in boring. Fractured oöolith, same sample as in A. Note the clean faces of the aragonite crystals, and the absence of organic mucus. Scale bar 3  $\mu\text{m}$ .

(C) Fractured foraminifer of the genus *Archaias*, sample No. 8, Varadero, Cuba. External surface up. Incipient growth of secondary Mg-calcite in borings, and on

internal chamber walls. There is no secondary carbonate on the external surfaces of the particle. Scale bar 30  $\mu\text{m}$ .

(D) The same foraminifer as in C. Detail, showing rhombohedral precipitate in the borings. Note the much smaller size of the crystallites in the biogenic fabric. Scale bar 5  $\mu\text{m}$ .

(E) Fractured echinoid spine, sample No. 21, Ladhiko, Rhodes. Voids in the biogenic Mg-calcite have fillings of acicular aragonite (left centre), and of rhombohedral Mg-calcite (lower right). Mg was not found in the acicular precipitate by means of the energy dispersive X-ray spectrometer. Scale bar 10  $\mu\text{m}$ .

which grows in protected spaces, such as the interstices of sediments, and the interior of hollow particles, normally occurs in the form of needles. This is true both for the intertidal zone (Taylor & Illing, 1969), and for the sublittoral and deep marine environment (McFarlin, 1967; Taft, Arrington, Haimovitz, MacDonald & Woolheater, 1968; Shinn, 1969). The acicular habit is not found in aragonite which grows on exposed, external surfaces, for example, in oöoliths (Loreau, 1970), and in supratidal aragonite scales (Alexandersson, in prep.). The observations by Perkins, McKenzie & Blackwelder (1972) suggest that also aragonite crystals of calcifying green algae have specific forms, and may be distinguished from a straightforward precipitate on morphological grounds.

The well-known whittings present an interesting problem. They are dense suspensions of microscopic aragonite crystals which suddenly occur in warm, shallow seawater, for example, on the Bahama Bank (Broecker & Takahashi, 1966), in the Persian Gulf (Wells & Illing, 1964), in Pacific lagoons (Revelle & Fairbridge, 1957), and in the hypersaline waters of the Dead Sea (Neev & Emery, 1967). Should they represent rapid precipitation in suspension, the crystal habit of the aragonite formed is of great interest.

Small, rhombohedral crystals, equidimensional or slightly elongated, and frequently with curved faces, are a diagnostically reliable habit of non-skeletal marine Mg-calcite (Land & Goreau, 1970; Ginsburg, Marszalek & Schneidermann, 1971; Alexandersson, in press *a, b*). Schroeder (in press) has described several modifications of the rhombohedral habit in Mg-calcite cement from cup reefs in Bermuda.

In this study, the micrite was classified as aragonite where it consisted of acicular crystals (Figs. 5 A—C, 6 A, B), while rhombohedral crystals were assumed to be Mg-calcite (Figs. 5 D, 6 C—E). These assumptions were repeatedly tested by means of an energy dispersive X-ray spectrometer, attached to the scanning electron microscope. A Mg-content of 14—17 mole %  $\text{MgCO}_3$ , which is common in marine calcites, is readily detected with this instrument; the Sr-content in aragonite

is not detectable. At least 200 points were analysed for Mg in the course of this investigation; the acicular precipitate was consistently found to be Mg-free, while Mg could be identified in all occurrences of rhombohedral secondary carbonate. It is concluded that morphological criteria as a rule are sufficient for the correct distinction between aragonite and Mg-calcite of non-skeletal marine origin.

In the material studied here, the most common precipitate in borings is aragonite. It is the only polymorph so far found in aragonite host grains, for example, in gastropod and pelecypod fragments, coral fragments, and oöoliths; frequently, aragonite also occurs in Mg-calcite hosts, such as miliolid and peneroplid foraminifers, echinoid fragments, and coralline algal fragments. Secondary Mg-calcite has been observed in calcite hosts only (Figs. 5, 6). In other words, the mineralogy of the precipitate is to a great extent controlled by the mineralogy of the host, and aragonite is the polymorph that occurs in the absence of host-control.

These conditions are in agreement with the data reported by Glover & Pray (1971), but they are at variance with the observations of Winland (1968, 1971), who found Mg-calcite micrite in the aragonite shells of the pelecypod *Chione cancellata* from Florida Bay.

The factors that control the polymorphic form of precipitating calcium carbonate in seawater are imperfectly known, but the major physicochemical characteristics of seawater are obviously not decisive. The mineralogy of a precipitate is affected by various organic substances in the solution (Kitano & Hood, 1965), and by the surface properties of the seed particles which act as growth substrates (for example: Walton, 1967). Possible active surfaces are the mineral surfaces of sediment grains, although it seems probable that these are, to a great extent, blocked by adsorbed organic coatings (Chave & Suess, 1967, 1970; Suess, 1970). During biologic calcification, the mineralogy and the organization of crystals is governed in detail by organic matrices which remain in the skeletal carbonates (Wilbur & Watabe, 1963; Travis, 1968; Travis & Gonsalves,

1969). Such organic matrices retain some ability to induce a particular carbonate polymorph, even during inorganic precipitation (Wilbur & Watabe, 1963), and they are probably an important factor behind host-control of a secondary precipitate.

Consequently, the complex assemblage which constitutes a modern carbonate sediment contains a variety of microenvironments with different conditions for crystal nucleation and growth. Almost any warm, shallow marine environment contains both non-skeletal aragonite, and non-skeletal Mg-calcite (Glover & Pray, 1971; Winland, 1971; Alexandersson, in press *b*). It is apparent that a mineralogical uniformity of a marine precipitate is found only in restricted environments where, for some reason, there exists a supreme controlling factor. Such is the case, for example, within certain cemented reef and algal frameworks, which are dominated by Mg-calcite (Alexandersson, 1969; Land & Goreau, 1970; Ginsburg, Marszalek & Schneidermann, 1971; Schroeder, 1972); and similarly, in many cemented intertidal and shallow-marine sediments, where commonly either aragonite or Mg-calcite has been the preferred polymorph throughout the deposit (Taft, Arrington, Haimovitz, MacDonald & Woolheater, 1968; Alexandersson, in press *a*). However, even in cemented deposits, variations in the mineralogy of the cement may be more common than was previously suspected (Shinn, 1969; Taylor & Illing, 1969).

The dubious whittings excluded, oöolith growth is a rare example of monomineralic deposition of non-skeletal calcium carbonate in the open marine environment. It is interesting to note that a proteinaceous matrix of ultimately organic origin is involved in that particular form of precipitation (Mitterer, 1971).

The development of monomineralic micrite envelopes on the various particles in a composite carbonate sediment would require far more uniform conditions than those found today at the average sediment surface. The characteristics of such an environment remain a field for speculation; they are not represented at any of the localities studied here.

**FABRIC AND ULTRASTRUCTURE OF FIL-LINGS.** The secondary carbonate crystals in the borings are consistently based on the walls of the cavities, and it is clear that their growth started from these walls (Figs. 5, 6). This mode of growth does not indicate precipitation on, or within, gelatinous algal sheaths, in similarity with the process described by Gebelein & Hoffman (1971); nor is it in accordance with dissolution-precipitation of carbonate material within an organic mucilage, as described by Kendall & Skipwith (1969). It is also quite different from the formation of fibrous overgrowths of Mg-calcite on *Ostreobium* filaments, occurring in Bermudan cup reefs (Schroeder, 1972). The relationships between substrate and crystals suggest that the crystals were formed by heterogeneous nucleation from supersaturated solutions onto the walls in otherwise empty cavities.

**Aragonite.** Most commonly the aragonite occurs as single needles, and as radiating clusters of needles. Their preferred orientation is normal to the surface on which they grow. The size of the crystals is limited mainly by the size of the cavity, and it is clearly related to the amount of filling in the cavity (Fig. 5 A, B). This shows that, once nucleated, the aragonite crystals continue to grow as long as space is available. Nucleation is rarely repeated in voids where aragonite growth is in progress. The common fabric is an irregular mass of intersecting needles (Fig. 6 B). In places the secondary needles have grown in syntaxial continuity with the aragonite in the skeletal fabric (Fig. 5 B), a form of growth which is quite common during cementation (cf. Bathurst, 1971, pp. 352—354, 429).

**Mg-calcite.** In borings, Mg-calcite has only been found in the form of rhombohedral crystals with a modal size of about 4  $\mu\text{m}$ . In large cavities, the crystal size does not increase with the amount of secondary carbonate in the voids; instead, new crystals are nucleated on the faces of the pre-existing ones, and the Mg-calcite micrite extends into the void as a rigid fabric of randomly oriented small crystals (Fig. 5 D). The same mode of growth for Mg-calcite has been described from Mediterranean beachrock, and from intragranular

precipitation of calcium carbonate in hollow calcareous grains (Alexandersson, in press *a, b*). Uniform linings of oriented calcite crystals (drusy calcite, palisade cement, calcite fringes) have not been observed in borings.

*GROWTH OF A MICRITE ENVELOPE.* The described conditions are interpreted in the following way: (i) the borings represent a long series of age groups, the most recent ones with organisms still in position, a few in a transitory stage of organic decay, and the greater number vacated for increasingly longer periods of time; (ii) crystal growth starts on the walls of a boring after the disappearance of the organism, and may proceed until the cavity is practically filled; (iii) the dominating part of the precipitate, if not all, is formed after the decay of the original excavating organism; (iv) neither the excavating organism, nor secondary organisms in the borings, are responsible for the growth of the fillings; (v) the precipitation depends on supersaturation in the surrounding seawater.

The explanation is, essentially, the same as that originally given by Bathurst (1966).

Note added in proof: The processes of boring and infilling in Bahamian ooliths were recently studied with the aid of SEM by Margolis & Rex (1971). They found that an abundance of borings were empty of organisms as well as of carbonate infillings, whereas other borings occurred in various stages of being filled with acicular aragonite. They arrived at the conclusion that the processes of aragonite growth in the algal tunnels were influenced either by algal metabolism, boring activities, or by bacterial action on decomposing algae.

#### SYNSEDIMENTARY CHANGES IN COLD-SEA CARBONATE GRAINS

*General characteristics of skeletal grains.* The studied carbonates represent the cold marine waters of Skagerrak (latitude about 58°N), and the more brackish waters of Kattegat and the Baltic Sea. The sediments are as a rule coarse, shallow sands from areas with Precambrian bedrock;

northern Öland is an Ordovician limestone area, but the sample sediment is predominantly a moraine-derived, non-calcareous sand. The Nielsen Shoal is an isolated peak in the Baltic Sea, almost 40 km from the nearest land. It reaches up to a water depth of 15 m in an area where the common depth is 140 m. Sand-sized carbonate grains from the studied localities along the Swedish coast are fragments of modern, carbonate-secreting organisms, and they can usually be directly related to the living organism assemblage at each station. Dominating constituents are mollusk shell fragments, frequently from the blue mussel *Mytilus edulis* Linné, echinoid and asteroid fragments, and fragments of barnacles. The breakdown of calcareous particles seems to be very rapid, and skeletal fragments in the size range 1–0.25 mm commonly retain their original colours.

*Borings and micrite.* Skeletal particles are commonly bored, and the borings are similar to those found in the warm-sea material. Clionid borings, simple tunnels, and convolute marginal tunnels have been observed. Several boring organisms are known to have a very wide, if not cosmopolitan distribution; for example, sponges of the genus *Cliona* (Nassonow, 1883; Warburton, 1958), and various endolithic green, and bluegreen algae (Golubic, 1969; Schroeder, 1972). The processes of excavation are certainly similar, and probably identical, both in warm-sea and cold-sea carbonate grains. Infillings of micrite in the borings have not been observed, and there is nothing to indicate that they once existed, and were removed by dissolution. It is therefore concluded that micritization of calcareous particles by the boring-infilling mechanism does not take place in waters where the level of carbonate saturation is low.

The studied cold-sea carbonate grains consistently show evidence of slow leaching, and it is clear that the waters in question are undersaturated for long periods with respect to the skeletal carbonates. The dissolving processes are remarkably selective, and the ultrastructural relationships of the particle fabric are exposed in great detail (Fig. 7). In an initial stage, the particles have etched surfaces which, on continued exposure,

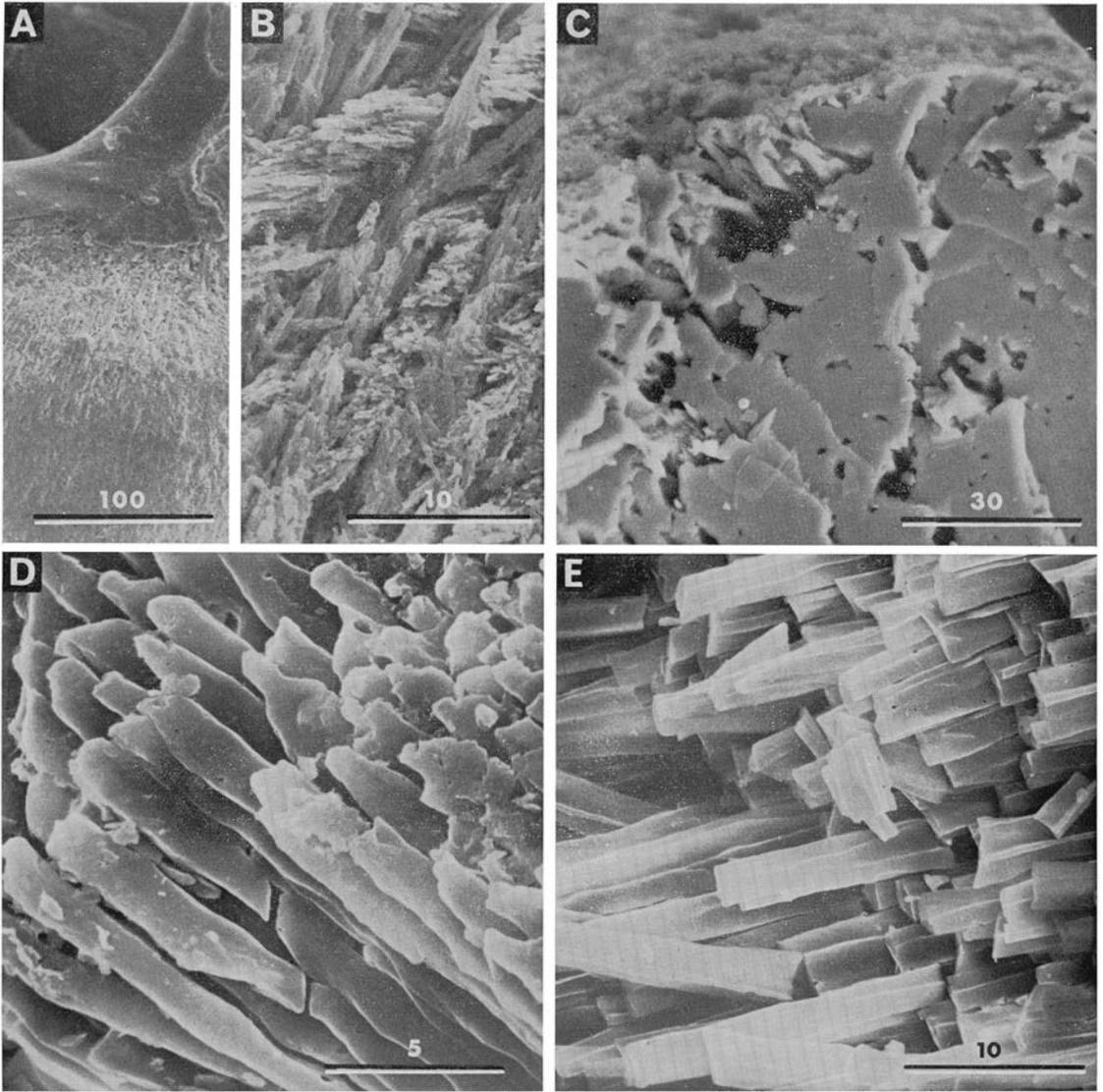


Fig. 7. Selective dissolution in cold-sea carbonate particles.

(A) External surface of gastropod protoconch, showing part of the aperture. Sample No. 29, Kristineberg, Skagerrak. Scale bar 100  $\mu\text{m}$ .

(B) Detail of A. The dull particle surface is an effect of differential dissolution of lamellae from the aragonite fabric. Scale bar 10  $\mu\text{m}$ .

(C) Fractured particle, probably barnacle fragment. Sample No. 31, east of Båstad, Kattegat. Surface etching, and leaching of voids. Scale bar 30  $\mu\text{m}$ .

(D) Partly fractured *Mytilus* fragment, sample No. 28, Grebbestad, Skagerrak. A few fibres have been removed during the sample preparation in the lower part of the picture. The calcite fibres show evidence of leaching, and the fabric is beginning to open up. Scale bar 5  $\mu\text{m}$ .

(E) Oblique fracture through *Mytilus* fragment from the same sediment sample as D. The fibres are almost disconnected, and the particle was more like a soft brush than a calcareous skeletal fragment. Scale bar 10  $\mu\text{m}$ .

develop into leached rims. In many shells, the leaching proceeds deep into a seemingly intact fabric along growth lamellae.

*Selective leaching and micritization.* In the discussions on the origin of a cryptocrystalline fabric, micrite, in skeletal particles, it is generally assumed that the micritization processes involve an alteration of the original carbonate matter in the particle, alternatively, a complete removal of the original substance, followed by formation of new material. The change may be called neomorphism (Folk, 1965), or recrystallization (Purdy, 1968), both terms, according to the quoted authors, being "comprehensive terms of ignorance"; or the process may be one of dissolution-reprecipitation (Kendall & Skipwith, 1969), or the one which initiated this study, boring-infilling (Bathurst, 1966). Common to all these mechanisms is that the resulting micrite substance is something different from the original carbonate substance.

Micrite, in the sense of an opaque cryptocrystalline fabric, can also be the unaltered, remaining part of an otherwise removed fabric. During subaerial diagenesis mollusk shells commonly lose their lustre and translucency, and become brittle and friable. In thin sections and transmitted light, thus affected shells appear dark brown or almost black, while in incident light they are chalky white. The process frequently proceeds along growth lamellae in the shell, and reproduces the cross-lamellar structure of the fabric (Fig. 8). Irregular patches can be completely altered, while the rest of a fragment is unaffected.

The dark colour in transmitted light, and the white colour in incident light, suggest the presence of small voids in a thus altered fabric. SEM pictures of affected parts of thin-sectioned shells reveal that discrete lamellae, and sheafs of lamellae, are missing, while the surrounding fabric remains seemingly unaffected (Fig. 8). According to X-ray diffraction analyses, changes in mineralogy are not involved. The process is one of highly selective removal of aragonite, and the micrite thus formed consists of the remaining lamellae of the original shell fabric. Particularly in its early stages, this kind of micritization is readily recognized because

of its dependence on internal shell structure, but in late stages this criterion is largely absent.

This form of selective leaching is common during early subaerial diagenesis. See, for example, the comment by Land (1967, p. 923). The material shown in Figure 8 is a thin-bedded biosparite from the shoreline at Freshwater Bay, Barbados; according to X-ray diffractometry, this particular sample contains aragonite, and possibly trace of Mg-calcite, in a coarse mosaic of low-Mg calcite cement. Almost all of the original Mg-calcite is now low-Mg calcite. The age of the layers around Freshwater Bay is probably less than 80,000 years (Matthews, 1967, 1968; Mesolella, Matthews, Broecker & Thurber, 1969). Features which indicate selective leaching of shells have also been observed in Silurian oösparites and biosparites from Gotland in the course of this study.

A particular form of replacement in Tertiary aragonite shells from northern Iceland depends on the same mechanism (Alexandersson, 1972). Well-preserved shells with original mineralogy are there gradually replaced by a black, X-ray amorphous siliceous substance, and the replacement proceeds into the shell, governed by selective dissolution of discrete lamellae.

*Selective leaching and micritization in cold seawater.* Cold-sea carbonate grains from the Swedish coasts show evidence of selective leaching, not readily distinguished from the subaerial leaching just described. As mentioned, skeletal grains are heavily attacked by microborers, but there is no secondary micrite in the cavities. Yet mollusk shells are frequently altered to cryptocrystalline carbonate, dark in transmitted light, and white in incident light. The alteration commonly proceeds along growth lamellae, and the cross-lamellar organization in the shell may be clearly visible (Fig. 9). The process does not lead to the formation of micrite envelopes on grains in early and intermediate stages of alteration; rather, the core seems to be more susceptible to changes than the margins. A skeletal fragment in a late stage of alteration is opaque and uniformly cryptocrystalline, showing no internal structures in the petrographic microscope.

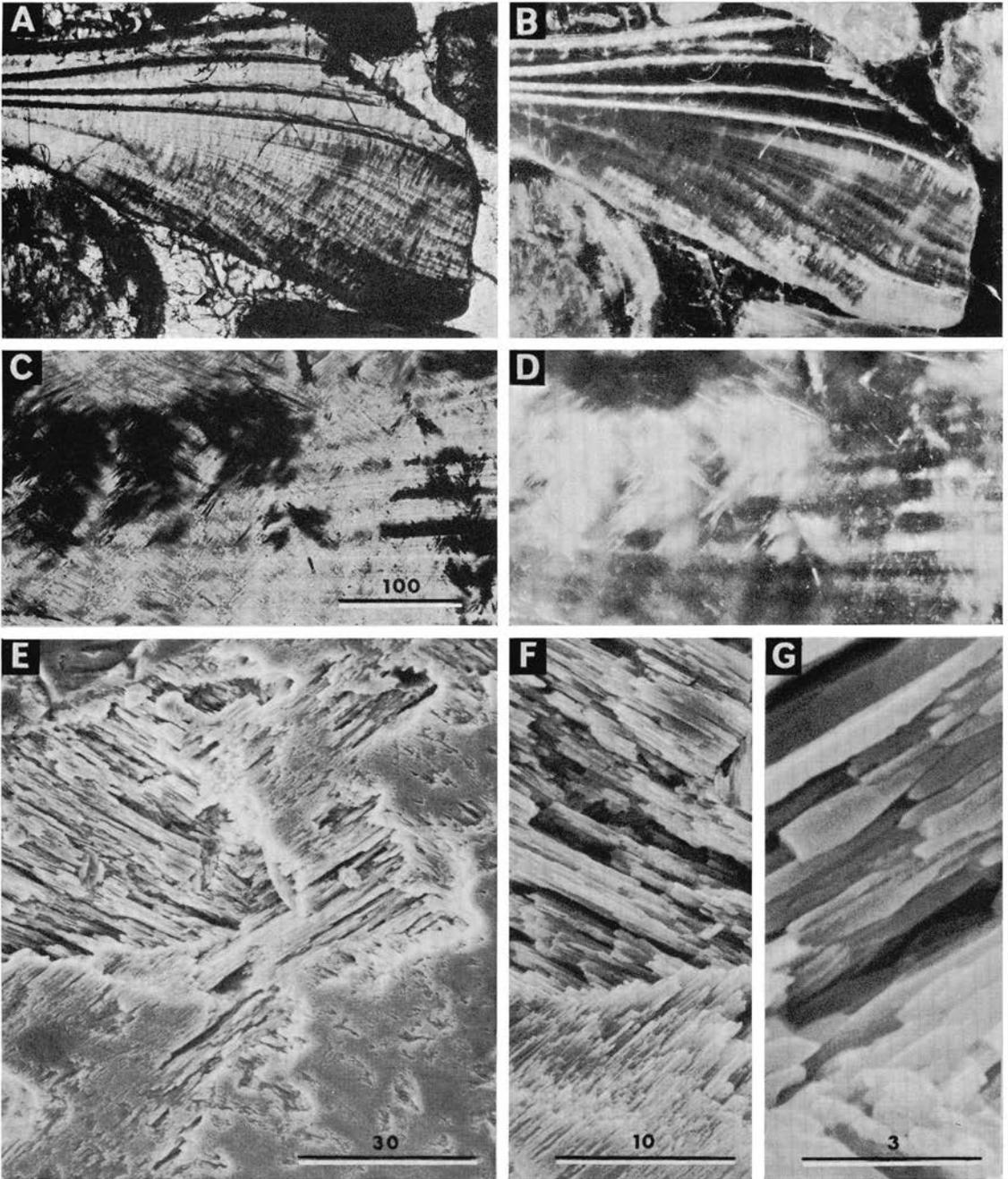
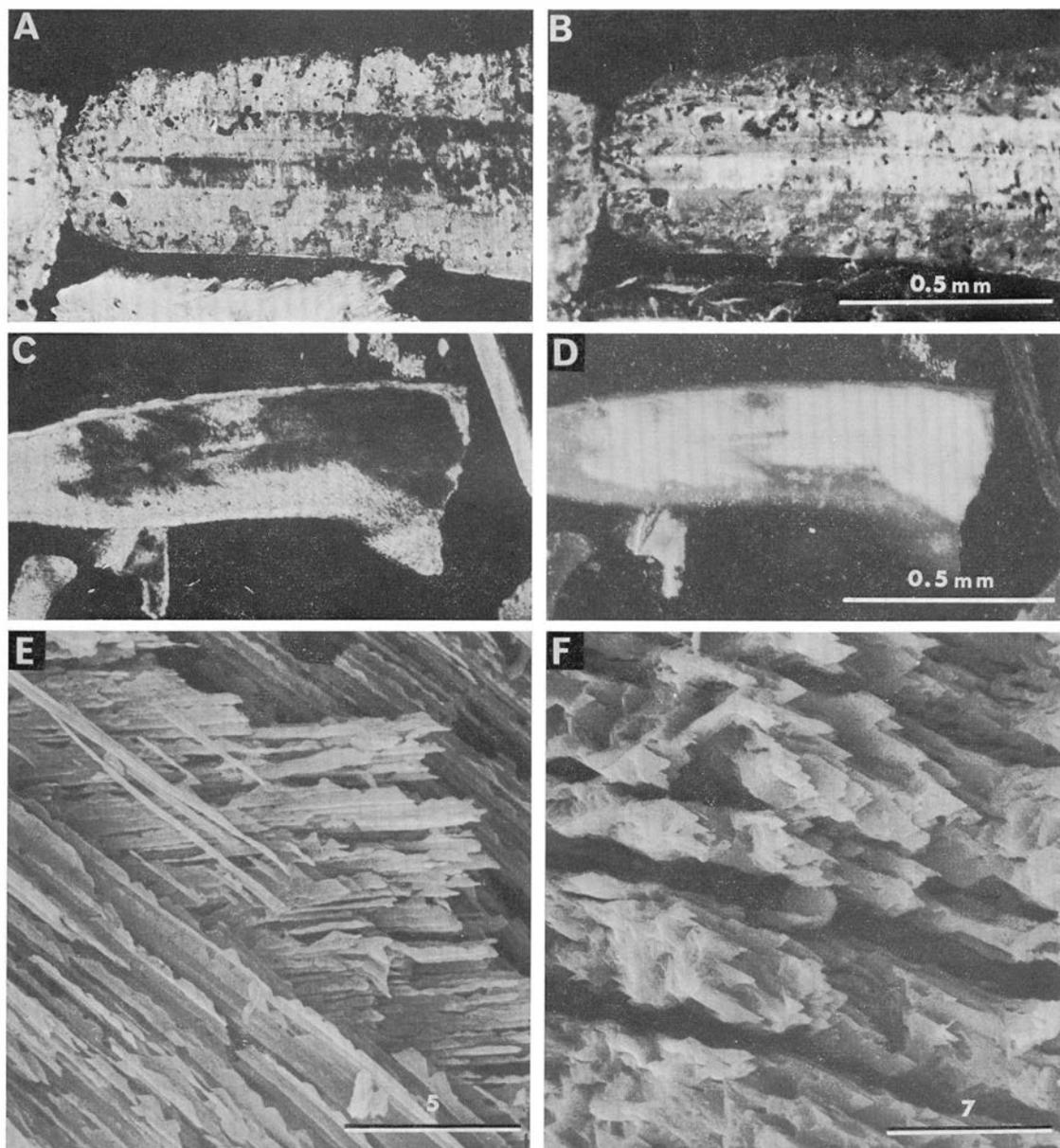


Fig. 8. Selective leaching of aragonite shells in Pleistocene biosparite, Freshwater Bay, Barbados. In thin sections, the shells are more or less opaque, dark brown in transmitted light (A, C), and white in incident light (B, D). The processes of alteration proceed along growth lamellae, and reveal the cross-lamellar structure in the fabric. The field in A—B is 1 mm in width; the scale bar in C represents 100  $\mu\text{m}$ .

(E—F—G) SEM pictures of the same petrographic thin section without cover glass. The specimen was cleaned three minutes in ultra-sound after the final polish. Discrete aragonite lamellae, and sheafs of lamellae, are missing from the fabric. The opaque, cryptocrystalline areas of the shell consist of the micro-porous residue of the original fabric. The scale bars represent 30, 10, and 3  $\mu\text{m}$ .



*Fig. 9.* Selective leaching of cold-sea carbonate grains. (A—B) Mollusk shell from sample No. 29, Kristineberg, Skagerrak. Thin section, transmitted light with crossed polarizers, respectively incident light. Rows of aragonite lamellae are missing from the core of the shell. The particles are heavily bored, but there is no micrite in the cavities. The grain in the lower part of the picture has a leached margin with high surface relief.

(C—D) Mollusk shell from sample No. 28, Grebbestad, Skagerrak. Thin section, transmitted light with crossed polarizers, respectively incident light. The shell core is cryptocrystalline, while the marginal parts retain

their lustre and translucency. The alteration follows the internal lamellar structure.

(E) Leached aragonite lamellae, mollusk shell from sample No. 31, east of Båstad, Kattegat. Fracture, SEM micrograph. An estimated 20—40 volume % of the shell material has been removed by the leaching process. There is no increased leaching in the vicinity of the boring, partly visible in the upper part of the picture. Scale bar 5  $\mu\text{m}$ .

(F) Leached fabric in mollusk shell, sample No. 32, east of Båstad, Kattegat. Fracture, SEM micrograph. The entire fabric has been thinned out, and some layers have been preferentially removed. Scale bar 7  $\mu\text{m}$ .

SEM pictures of transverse fractures, and of thin-sectioned shells, show that the crystalline material has been partly removed by a process, governed by the internal organization of the skeletal particle. The cryptocrystalline material, in other words, the micrite, consists of the porous, residual shell fabric. Lamellae, prisms, or other skeletal elements, retain their original spatial arrangements, and there is no evidence of re-crystallization, or other mineralogical transformations of the skeletal carbonate (Figs. 7, 9). This is clearly seen in *Mytilus* fragments. The outer, prismatic layer in such shells is organized as calcite fibres, 2–4  $\mu\text{m}$  in thickness, and millimetres in length; these fibres in turn are built of small prisms, held together by inter- and intra-prismatic organic layers (Travis, 1968; Travis & Gonsalves, 1969; Wise, 1969). Discrete fibres are leached from the fabric, while others remain in position, and sand-sized *Mytilus* fragments, still with a blue or reddish tinge, are commonly an open fabric of almost disconnected fibres (Fig. 7 D, E). Such particles disaggregate to isolated fibres from the very gentle pressure with a needle.

The process, which leads to differentiated removal of skeletal carbonate, is assumed to be slow, ultra-selective leaching in a marine environment which is undersaturated with calcium carbonate. The studied sediments are supposed to represent present-day conditions at, or near, the sediment surface.

*Mechanisms of selective leaching.* Selective leaching is evidently a consequence of variations in solubility in the dissolved phase. The well-known fact that the various faces of a given crystal have slightly different solubilities may account for a great deal of particle surface relief, and for partial dissolution in leached rims under conditions of slight undersaturation. A different explanation is needed for the removal of discrete lamellae deep within a fabric of similar, but unaffected, lamellae (Fig. 9 A, B). Although the distances for intra-particle transport are short (less than 1 mm), initially undersaturated fluids which move from the particle surface through the submicroscopic pores of the fabric must be close to saturation relative to the particle mineral when approaching

the core (cf. Weyl, 1958). In order for sheafs or rows of lamellae in the interior of such a core to be preferentially removed, these must be of a higher solubility than the rest of the fabric.

That the constituent crystalline material in a shell, or in any other skeletal particle, should include phases of different solubilities is not a new observation. The fact that some shells consist partly of aragonite, partly of calcite, indicates that differences in solubility may occur. Furthermore, the ratio calcite/aragonite in a marine organism is apparently dependent on environmental conditions, and should be expected to show variations (Lowenstam, 1954). The dissolution behaviour of echinoid skeletons indicates that phases of different solubilities are present (Schroeder, 1969). The Mg-content in the jaw apparatus of echinoids may vary between 3 and 43 mole %  $\text{MgCO}_3$  in solid solution, that is, the mineral varies between low-Mg calcite and protodolomite (Schroeder, Dwornik & Papike, 1969). Such great compositional variations must obviously be reflected in solubility variations.

Travis (1968) described impurity crystals of strontianite ( $\text{SrCO}_3$ ), witherite ( $\text{BaCO}_3$ ), celestine ( $\text{SrSO}_4$ ), and barite ( $\text{BaSO}_4$ ) from the calcite fabric of *Mytilus edulis*. The submarine leaching of *Mytilus* fragments exposes a pattern of skeletal micro-elements in the calcite fibres of the prismatic part of the shell (Fig. 10). Evidently, the normal metabolic processes of calcification include a range of variations; among others, compositional variations which result in mineral phases of different solubilities.

*Shell-residue micrite.* The observations made on the cold-sea carbonate grains, and on aragonite shells from subaerial positions, lead to the following conclusions: (i) a cryptocrystalline fabric is formed as a consequence of selective leaching of ultra-structural elements, such as aragonite lamellae; (ii) the effects of subaerial leaching, and of leaching in a cold marine environment, are similar, if not identical; (iii) the processes are governed in detail by the internal organization of the shell; (iv) the structural control depends on solubility variations on a micro-scale; (v) the residual cryptocrystalline

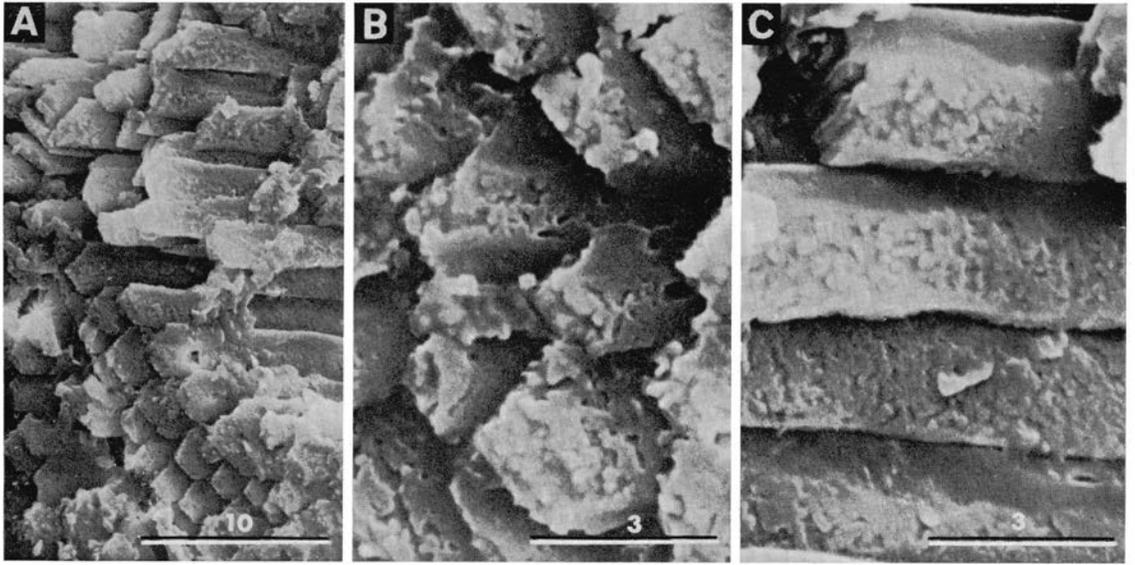


Fig. 10. Selective submarine leaching in *Mytilus* fragment. The fragment is from sample No. 28, Grebbestad, Skagerrak. It derives from the outer, prismatic calcite part of a shell.

(A) External surface morphology, showing a general thinning-out of the fabric. The fragment was still coherent, but it could be easily crushed with the point of a needle. Scale bar 10  $\mu\text{m}$ .

(B) External ends of dissolving fibres. Each fibre is composed of granules, about 0.2  $\mu\text{m}$  in size. Scale bar 3  $\mu\text{m}$ .

(C) Surfaces of dissolving fibres. The etching pattern is related to the arrangement of granules in the fibres. Note the apparent stacking of granules in the fractured fibre, close to the letter C. Scale bar 3  $\mu\text{m}$ .

fabric, shell-residue micrite, consists of original shell material.

## DISCUSSION

### *Micritization by the boring-infilling mechanism*

*Activity of microborers.* Calcareous grains are attacked by boring organisms under all the marine conditions studied here, with the only exception of turbulent environments, where the sediment grains are kept in motion most of the time. A high percentage of grains with glossy surfaces indicates that the activity of borers is low. A typical example of a locality of that kind is a gently shoaling beach with long periods of surf. Strong turbulence is not necessary for the inhibition of boring activity, since mechanical wear is a subordinate inhibitory agent; the critical factor is the limited opportunity for the boring organisms to settle

and excavate a protective cavity. The minimum time needed by a *Cliona* larva to create a cavity that will give some protection is 2–3 days (Nassonow, 1883). The amount of time necessary for penetrative algae and fungi is not known.

The warm-sea and the cold-sea carbonate grains are bored to about the same extent. The important groups of excavating organisms acting on sand-sized grains are sponges, algae, and fungi (cf. Perkins & Halsey, 1971). Sponge borings on sediment grains are mostly abortive larval borings (cf. Warburton, 1958; Cobb, 1969). The sediments studied in this investigation all belong to the photic zone, and algae are responsible for the greatest volume of intraparticle cavity. Also Bathurst (1966), and Kendall & Skipwith (1969) found filamentous algae to be the most important organisms in connexion with shallow-marine alteration of carbonates. Fungi, and heterotrophic algae, are the dominating borers at greater depths

(Friedman, Gebelein & Sanders, 1971; Perkins & Halsey, 1971).

*Growth of micrite in the borings.* The activity of microborers does not in itself lead to the formation of micrite. Tunnels with organisms in position do not contain any secondary carbonate, and no observations indicate that the boring algae and fungi secrete carbonate as part of their metabolic activity. Boring sponges remove small chips of the excavated substrate in solid form and leave no micrite in their voids.

The biochemical mechanisms of boring are inadequately understood, and it is not known how the dissolved carbonate is transported from the point of dissolution at the distal end of a tunnel. The alternatives are: (i) extracellular transport by diffusion and/or circulation in the pore fluids; and (ii) intracellular transport in the algal/fungal filaments. As each excavating organism creates its own system of tunnels, and avoids contact with other systems, the dissolved material must pass through the submicroscopic pores of the particle fabric, or back through the tunnel that is being formed. The tunnel contains the organic filament, and the possibilities of extracellular transport of solutions out through the tunnel must be limited. Evacuation of the dissolved material through the filaments is judged to be the probable mechanism. There is no increase in the amount of secondary carbonate in the voids close to a fresh boring; nor is the relative amount of infilling in a particle related to the number of borings. It is concluded that intraparticle redistribution of the dissolved material is of little or no importance for the growth of micrite.

Borings without organisms, and yet empty of fillings, are common even in the heavily micritized material from the Bahama Bank, and consequently the boring organisms may die and decay without the triggering of precipitation. The microbial breakdown of the organic substances of dead filaments can at best have a limited influence on the growth of micrite.

It is known that mucilaginous algal sheaths concentrate metal ions, and thus may influence precipitation (Gebelein & Hoffman, 1971). The

filaments of boring algae may also act directly as substrates for crystal growth, and under such conditions they control the mineralogy and fabric of the calcium carbonate (Schroeder, 1972). The manner in which crystals grow in borings is not consistent with growth within mucilaginous sheaths which later disappeared, nor with growth on organic filaments. Quite clearly, the crystals nucleated on the walls of the then empty cavities, and continued to grow centripetally. The mode of growth is the same as that found in cemented sands, and in hollow skeletal grains. The conclusion is that the micrite crystals nucleated on the walls of the borings after the disappearance of the excavating organisms, and that their growth represents slow precipitation from supersaturated seawater in the borings. With few exceptions, the space must have been empty of solid obstructions, such as sediment infill, and secondary organisms.

*Mineralogy of micrite envelopes.* It is well established that both aragonite and Mg-calcite occur in micrite envelopes (Bathurst, 1966, 1971; Purdy, 1968; Winland, 1968, 1971; Lloyd, 1971), and this is confirmed by the results of this study. It is becoming apparent that aragonite, and Mg-calcite with about 15 mole %  $MgCO_3$  in solid solution, are the two carbonate polymorphs that commonly precipitate from shallow seawater under natural conditions. There seems to be a slight increase in Mg-content in the calcite with increasing ambient temperature; about 15 mole % is common in the Mediterranean, and in Bermuda (Alexandersson, 1969, in press a; Ginsburg, Marszalek & Schneidermann, 1971; Schoeder, 1972), while 17–19 mole % is reported from the Gulf of Mexico, and the Caribbean (Purdy, 1968; Land & Goreau, 1970; Land, 1971). The highest Mg-content so far reported from a marine calcite cement is probably that of 22 mole %  $MgCO_3$ ; in Red Sea reefs (Amiel, Friedman & Miller, 1971). A positive correlation between Mg-content and temperature is in accordance with the laboratory results of Glover & Sippel (1967).

In most cases observed here, the mineralogy of the micrite corresponds to the mineralogy of the host grain. Host control is to a great extent

an effect of substrate influence on the processes of crystal nucleation, and, once nucleated, aragonite and Mg-calcite may grow together in the same micron-sized cavity. For example, porcellaneous Mg-calcite foraminifers trapped in marginal borings in aragonite shells have overgrowths of rhombohedral Mg-calcite crystals, while the adjacent cavity walls in the aragonite shells have coatings of acicular aragonite. Similarly, Schroeder (in press) describes a great variety of micro-environmental control of the mineralogy of cements in the various micro-niches in Bermuda cup reefs.

At first sight it may appear as if the mechanism of substrate control cannot be combined with the formation of monomineralic micrite envelopes, of the kind that are inferred from the study of fossil sediments (for example: Buchbinder & Friedman, 1970). However, at least one mechanism for the formation of monomineralic micrite envelopes can be suggested here, namely, local dominance of secondary organic coatings. This model is in fair agreement with observations from the modern marine environment.

*Mineralogical influence by secondary coatings.*

Theoretically, the mechanism of substrate control may act by means of secondary coatings, foreign to the host grain. Organic substances, originally derived from organisms, occur in solution and in colloidal form in natural seawater. These compounds interact with mineral surfaces, and may form thin coatings on carbonate particles; coatings which may inhibit or otherwise influence the reactions between the particles and the surrounding seawater (Chave & Suess, 1967, 1970). According to Suess (1970), 10–14% of the dissolved organic carbon in seawater associates with calcite when the mineral is added in the form of a fine powder. It has been shown experimentally that organic substances affect the polymorphic form of calcium carbonate precipitated from seawater (Kitano & Hood, 1965). Recent oöliths contain an adsorbed proteinaceous matrix which is thought to be active during the growth of the oölith (Mitterer, 1971; Suess & Fütterer, 1971).

Consequently, it appears probable that second-

ary organic coatings may occur on particles which are subject to micritization. Under certain conditions the grains may also be surrounded by mucilaginous algal sheaths (Kendall & Skipwith, 1969), and the possibility of organic linings in borings remains, although linings of that sort were not found in the material described here. To this must be added the mechanism described by Schroeder (1972) of calcification on, and within, the filaments of endolithic algae. To conclude, a variety of processes occur in the sea by which foreign organic coatings may develop on the external and internal surfaces of sediment grains. There are also indications that such an organic coating may influence the nucleation and mineralogy of a subsequent carbonate precipitate.

The field is open to speculation. Should the 0.06 weight % of proteinaceous matrix in oöliths prove to be the governing factor during oölith growth (Mitterer, 1971; Suess & Fütterer, 1971), it is equally possible that an organic coating, a few hundred Å or so in thickness, surrounds the various grains in a beach sand, and induces a particular polymorph during beachrock cementation. The presence of a uniform coating of that sort would explain the apparent absence of substrate dependence in beachrock cement (Alexandersson, in press *a, b*). Indeed, the observations by Pytkowicz (1971) suggest that a coating exists, albeit with unknown properties as a crystal substrate. The local dominance of a particular kind of secondary coating in a shallow marine environment might well explain the formation of monomineralic micrite envelopes of the kind visualized by Winland (1968, 1971), and Buchbinder & Friedman (1970).

However, the conditions observed in this reconnaissance study are different. In the micrite envelopes studied here, the mineralogy of the precipitate is, in general, host-controlled, and in the absence of host-control, the mineral form of micrite is aragonite. In other words, a given sediment contains both aragonite and Mg-calcite micrite, and the most common form is aragonite.

*Marine cementation.* As described and interpreted here, precipitation of aragonite and Mg-calcite in

vacated microborings is but another example of marine calcium carbonate precipitation within calcareous frames. The term *frame* is used in the widest possible sense, including reefs (Land & Goreau, 1970; Ginsburg, Marszalek & Schneidermann, 1971; Amiel, Friedman & Miller, 1971; Schroeder, in press), algal frameworks (Alexandersson, 1969), hollow calcareous grains (Purdy, 1968; Glover & Pray, 1971; Alexandersson, in press *b*), and probably various aggregates of grapestone character (Roberts & Moore, 1971; Bathurst, 1971, pp. 363—364).

Included are also the frames constituted by grains being cemented, as undoubtedly the grains provide a stable framework during cementation (Taft, Arrington, Haimovitz, MacDonald & Woolheater, 1968; Macintyre, Mountjoy & d'Anglejan, 1968, 1971; Shinn, 1969). On account of the characteristics of the cement, beachrock cementation should probably be considered as an example of the same kind (Schmalz, 1971; Moore & Billings, 1971; Alexandersson, in press *a*). The point here is to stress the difference between crystal growth in calcareous niches, large or small, and crystal growth on external surfaces where the crystals are exposed to the open seawater. Possible examples of the latter kind of growth in the present seas are oöoliths, aragonite muds, and whittings, but the true nature of their formation is not understood. It is, however, interesting to note that the only polymorph so far described from such occurrences is aragonite. A comprehensive term for the processes of calcium carbonate precipitation within frames is *cementation* in the sense of Murray & Pray (1965), and Bathurst (1971, p. VIII).

A rapidly increasing number of reports on marine cementation indicate that precipitation within calcareous niches is a common process in the shallow marine environment. In contrast, external growth of crystals in open seawater (open, as opposed to seawater as a pore fluid) seems to be rare, and to require special conditions. Factors of importance for this apparent anomaly are, for example: (i) an external precipitate is the first constituent to be affected by mechanical, physicochemical, and biochemical destruction; (ii) in

open, shallow waters diurnal variations in carbonate saturation are common (Schmalz, 1967; Schmalz & Swanson, 1969), and such variations are likely to affect the slow kinetics of crystal growth in seawater; (iii) during short periods of low saturation or undersaturation, the internal fluids within a calcareous frame will remain at a minimum saturation level, determined by the solubility of the most soluble mineral in the cavity walls; and (iv) during periods of supersaturation in the surrounding seawater, the fluids in small cavities, such as borings and hollow grains, will adjust to supersaturation by diffusion. These considerations refer mainly to the conditions in mm- to cm-sized cavities; obviously the problems are more complex within large frames, such as reefs and algal frameworks.

It remains to be proved that slow precipitation of calcium carbonate indeed is absent in the average, open, supersaturated seawater. No doubt, the process must be quantitatively unimportant in the normal, shallow-marine environment, but it may, nevertheless, take place. Evidence of non-skeletal growth of calcium carbonate from open, natural seawater would reduce the enigma of marine cementation in borings, hollow grains, reefs, and sediments, to matters of time, crystal survival, and fluid transport. Selective sampling by means of SCUBA, followed by SEM investigations, might help in resolving the problem.

The relations between the processes of carbonate alteration studied here, and the corresponding conditions in the shallow marine environment, are shown in a generalized form in Figure 11.

#### *Synsedimentary changes in cold-sea carbonate grains*

*Carbonate undersaturation in the sea.* Since the work of Murray & Renard (1891), interest in the state of carbonate saturation in the seas has been biased towards the determination of vertical saturation gradients. There is now ample evidence that the present seas are undersaturated with calcium carbonate at depth (Hood, Berkshire, Adams & Supernaw, 1963; Pytkowicz, 1965; Pytkowicz & Fowler, 1967; Li, Takahashi & Broecker, 1969; Heath & Culberson, 1970), although the pattern

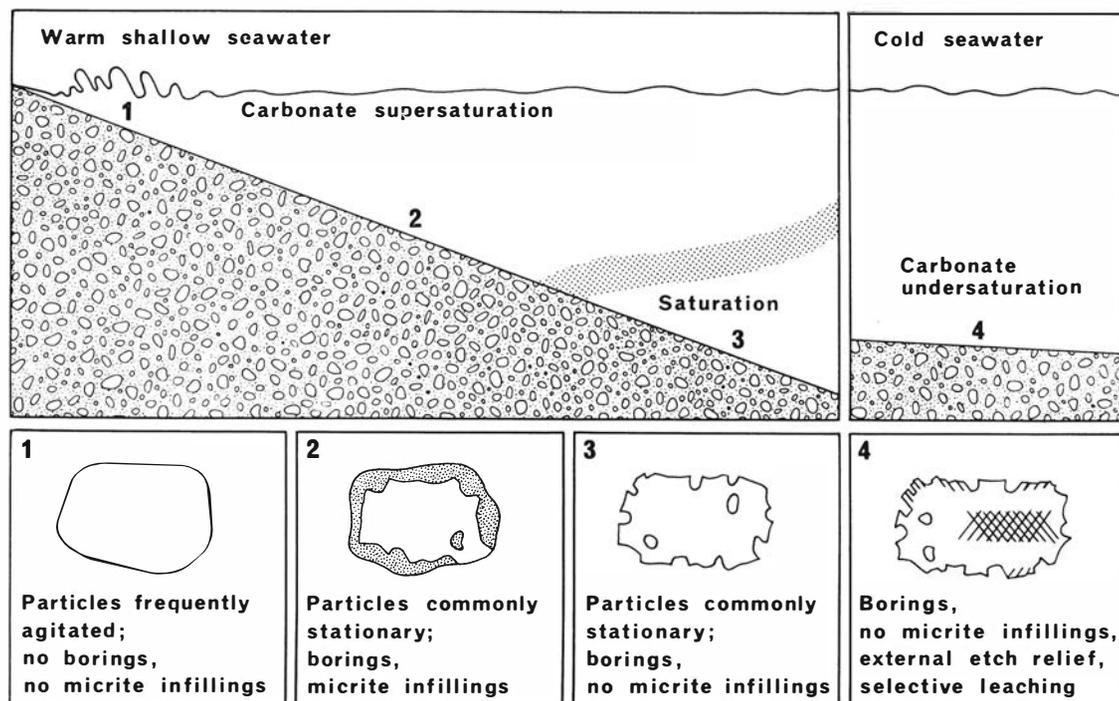


Fig. 11. A generalized representation of the relationships between shallow marine environment, and some syndepositional changes in skeletal carbonates.

is complicated by finds of cemented deep-sea sediments (Milliman, 1966; Fischer & Garrison, 1967; Bartlett & Greggs, 1969), and by a poor general correlation between water depth and carbonate content in the sediments (Smith, Dygas & Chave, 1968). Peterson (1966), and Berger (1967, 1968, 1970) have described an experimental study of the dissolving ability of deep-sea waters. Their material consisted of calcite spheres, and the tests of planktonic foraminifers, which were suspended at various depths on the wire of a moored buoy at  $18^{\circ} 49' N$ ,  $168^{\circ} 31' W$  in the central Pacific. The exposure lasted four months; Berner (1970) described the dissolution processes as selective, although he related the selectivity to the various species of foraminifers, not to mineralogy or shell fabric.

A decreasing percentage of metastable carbonate phases with decreasing particle size in sediments has been explained as a consequence of selective

leaching in relatively shallow waters (Chave, 1962; Pilkey, 1964; Neumann, 1965). The results are not quite conclusive, partly because of the presence of codiacean algae which contribute small aragonite crystals directly to the fine fractions of a sediment when decomposing (cf. Perkins, McKenzie & Blackwelder, 1972). A recent report on differential dissolution of metastable carbonate minerals in the deep sea is provided by the paper by Huang & Pierce (1971).

*Shallow-marine dissolution of carbonates.* Little attention has previously been given to the processes of carbonate dissolution in shallow marine environments. Driscoll (1967, 1970) noted some dissolution of shell material during a test period of three years in a field study of pelecypod shell destruction on the coast of Massachusetts (latitude about  $42^{\circ} N$ ). The quantitatively most important destructive forces at his test stations were mechani-

cal abrasion, and the activity of boring organisms. This seems also to be the case in the present material from the Swedish coasts, but the mechanical and biochemical processes of destruction are accelerated by the selective leaching which renders the particles porous and brittle.

The submarine dissolution is selective in microscopic detail. The external surfaces of a calcareous fragment show the ultrastructural organization of the fabric, and fractures through leached particles expose a microporous framework of biogenic shell constituents, still with their original spatial relationships. The exact mechanism of leaching is far from clear; for example, the relations between the disappearance of the organic matrix, and the dissolution of the crystals are not known. No organic ghosts remain after dissolved crystals in the naturally leached grains, yet even the most brittle fragment contains an organic matrix which is preserved as a mould after the dissolution of the particle in EDTA, or in chromium sulphate (decalcification method after Sundström, 1968). The effects of submarine dissolution on detrital limestone grains have not yet been studied.

The preferential dissolution of crystalline material from intraparticle positions in shells is clearly related to the internal organization deriving from the biogenic processes of calcification. It is assumed that the selectivity depends on small variations in solubility in the constituent biogenic carbonate. Such solubility variations are attributed to normal irregularities in the metabolic processes of calcification. The same interpretation is applicable to selective leaching under submarine conditions, and to leaching of aragonite shells under various subaerial conditions.

On basis of the available material, the relative susceptibility of various skeletal constituents to dissolution cannot be evaluated. It is clear, however, that both aragonite and calcite fragments are affected. To what extent the gross carbonate mineralogy of a leached sediment changes with decreasing grain size also remains unknown.

*The boring-infilling micritization mechanism in cold seas.* The investigation of the cold-sea carbonates was intended as a rapid and simple

comparative study of the conditions in microborings in undersaturated *versus* supersaturated seawater. On the whole, the attempt has produced more questions than answers, but at least the initial question can be given a conclusive answer: the boring-infilling micritization mechanism is not active in undersaturated waters. Microboring organisms are as common in cold as in warm seas, but they leave only empty borings behind them. The implications of this result for paleoecological reconstructions of calcareous environments are clear.

*Micrite envelopes, selective leaching, and continued diagenesis*

As described here, the characteristics of the secondary micrite in borings provide no apparent clue to the problem of why micrite envelopes frequently are preserved during the leaching and cementation of a sediment into a biosparite. The solubility-contrast model suggested by Winland (1968, 1971) is difficult to apply; that model requires Mg-calcite micrite on aragonite hosts, the only combination which was absent in the studied material.

It is felt that the important difference between the crystals of the micrite, and the fabric of a shell may be their different basic organization. The mineral building blocks of shells consist of crystallites in the size range 200—1,000 Å, enveloped in organic sheaths (Travis, 1968; Travis & Gonsalves, 1969). Should the individual crystals of micrite behave anything like single crystals (see *the single crystal concept* in Towe & Cifelli, 1967, pp. 744—745), their size is 10—100 times the size of the elementary crystallites in many shells. Individual carbonate particles smaller than about 1,000 Å are supersoluble (Chave & Schmalz, 1965), and it remains an open question how the spatial arrangement of organic matrix and crystallites in a skeletal particle will interact during slow leaching extending over hundreds and thousands of years. The organic framework may, for example, act as pathways for ionic transport. The leaching behaviour of mollusk shells, as described here, certainly indicates that calcium carbonate

is removed from the interior of an apparently intact fabric.

The problems related to the preservation of micrite envelopes in cemented limestones can be answered only partly by a study of micrite genesis on the sea floor. Equally important is a detailed study of the behaviour of various carbonates during the processes of slow leaching.

### SUMMARY AND CONCLUSIONS

*Microborers and micritization.* A variety of organisms bore into calcareous substrates (Sognaes, 1963; Carriker, Smith & Wilce, 1969). The most important microborers in marine sediment grains are algae and fungi (Perkins & Halsey, 1971), and to some extent sponges. At depths beneath the photic zone, heterotrophic algae and fungi dominate. Boring organisms have a wide, if not cosmopolitan distribution, and they occur in warm seas which are highly supersaturated with calcium carbonate, and likewise in cold seas with lower levels of carbonate saturation. Microborers do not settle on grains subjected to frequent agitation. The boring processes depend on the biochemical dissolution of calcium carbonate; the organisms do not secrete linings or infillings of calcium carbonate in their cavities. There is no apparent connexion between the decay of organic filaments, and the growth of secondary carbonate in the tunnels; recently vacated borings are empty of fillings, both in supersaturated, and in undersaturated waters. In marine environments which are known to be highly supersaturated with carbonate, for example, in the surface waters in the West Indies, and in the Mediterranean, secondary calcium carbonate grows as centripetal fillings in vacated borings. It has not been possible to relate the growth of fillings to the activity of any particular organism; it is here interpreted as precipitation, ultimately dependent on the carbonate supersaturation in the seawater. The secondary calcium carbonate consists of acicular aragonite, and of rhombic Mg-calcite with about 15 mole %  $\text{MgCO}_3$  in solid solution. As a rule, the mineralogy of the precipitate corresponds to the mineralogy of the growth substrate, substrate control, or host control.

In the absence of host control, the preferred mineral form is aragonite.

The precipitation of micrite in borings is regarded as an equivalent of marine cementation; cement with similar characteristics is found in beachrock, in cemented shallow-marine sands, in hollow skeletal grains, in algal frameworks, and in reefs. No micrite is precipitated in bored grains in waters, barely saturated or undersaturated with calcium carbonate.

*Shell-residue micrite.* In environments which are slightly undersaturated with respect to a particular carbonate polymorph, slow dissolution of this polymorph will take place. Such leaching is highly selective and reveals subtle intraskeletal differences in solubility. The selective leaching leads to differential removal of skeletal micro-elements within the fabric of biogenic particles, and renders these porous and brittle. The cryptocrystalline residue consists of the remaining elements of the original skeletal fabric, but these are not resolved in the petrographic microscope. In thin sections, affected grains appear to be partly or completely micritized; brown in transmitted light, and white in incident light. A diagnostic criterion for such shell-residue micrite is its dependence on internal shell structure. The process is previously described from the early stages of subaerial diagenesis; it is here reported from shallow-marine carbonate diagenesis in the Skagerrak.

The studied processes of shallow-marine carbonate diagenesis can be related to the generalized pattern of carbonate saturation in the sea. In warm, shallow waters known to be highly supersaturated, a variety of cementation processes occur; in cold, shallow seawater where the saturation is low, carbonate particles are subject to slow, selective dissolution. The precise mechanisms remain obscure, both in the case of marine cementation, and in the case of marine selective leaching.

*Micrite envelopes, and the preservation of texture in biosparites.* The problem as to why micrite envelopes as a rule resist dissolution during diagenesis still remains. The mineralogy of the secondary micrite corresponds commonly to the mineralogy of the host grain, and the differences

in solubility should be small. On the other hand, the leaching behaviour of skeletal grains shows that slow dissolution is selective even at the intra-skeletal level. It is believed that the basic organization of skeletal carbonates as a tissue of organic and inorganic constituents favours the differential removal of structural elements at a microscopic level. A corresponding micro-architecture is probably not present in the micrite, which is genetically a cement.

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