

# SHELL STRUCTURE OF FOSSIL FORAMINIFERA STUDIED BY CATHODOLUMINESCENCE

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## Biography

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*Fig. 1. Equatorial section of a Miocene *Amphistegina* sp. (Sample CM 394, Quebrada Ganado, Herradura Promontory, Costa Rica). Seen in normal transmitted light (a) and cathodoluminescence (b,c). Note the gain in information on the morphology of the test in CL. Note red/orange colour banding in the test wall and fine pores revealed by digital imaging in c. a. and b. are taken on Ektachrome P800-1600 slide film exposed at 1600 ISO, Horizontal Field Width (HFW) 930  $\mu\text{m}$ . c. is a digital recording with the Kodak DCS 200 Digital camera. The raw image was treated for colour, contrast, and sharpness, and then printed on a Sony 5000 UP video printer. Scale bar = 100  $\mu\text{m}$ , illustrated area about 500 $\times$ 500 pixels.*

## Introduction

Larger Foraminifera are benthic marine rhizopod protists that are from 1 mm to over 100  $\mu\text{m}$  in size. Their calcareous shells are found both in modern shallow marine environments and as fossils and have been widely used in geology to determine the biostratigraphic age and the palaeoenvironment of marine sediments, particularly those of Late Paleozoic, Cretaceous and Tertiary age. Modern larger Foraminifera have been found very interesting by biologists and have been studied in great detail both for their soft parts (1) and their tests (2). The observation of the complex shell structures, critical to the systematic description of this highly diverse group is hampered in most fossil material by diagenetic transformation, i.e. the precipitation of carbonate cements that fill the complex porosity of the tests. Fossil material is generally studied by transmitted light microscopy (TL) of thin sections (30-40  $\mu\text{m}$  thick) of rock or isolated specimens. Cathodoluminescence (CL) has been used for a number of years in geological sciences to trace processes of crystallisation (3) but has only recently been found useful for the observation of microfossils in thin sections (4). During our biostratigraphic work dealing with larger Foraminifera from the Caribbean region, we have systematically used CL, in order to obtain detailed observations of test microstructures. The objectives of this article are: 1. To discuss both conventional CL photography, video, and digital imaging techniques applied to polished rock thin sections. 2. To show the gain in information by CL observation as compared to transmitted light. 3. To discuss a variety of preservational stages of foraminiferal tests and to debate their biogenic and/or diagenetic origin. The colour banding observed in some tests is related to biomineralisation processes and

reveals fluctuations in the palaeoenvironment as well as vital effects.

## Method and equipment

Cathodoluminescence in carbonate minerals depends on the presence of activators which are stimulated to emit light when bombarded with energetic electrons (3) (5). In carbonates the best known activator is bivalent manganese ( $\text{Mn}^{2+}$ ). Bivalent iron ( $\text{Fe}^{2+}$ ) is the most important quencher ion (5).

The relationship between CL emission intensities and trace-element concentration has been controversial, principally because results were reported as qualitative (visual) estimates of CL intensity and colour. In addition,  $\text{Mn}^{2+}$  concentrations of luminescing calcites are near or below the practical detection limit of the electron microprobe. In recent work both on natural and synthetic calcites, it has become clear that for low  $\text{Fe}^{2+}$  contents the lower detection limit of CL activation is around 10-20 ppm Mn (6). Moderate CL intensities were reported from calcites containing 200 to 700 ppm and bright intensities from calcites with more than 700 ppm  $\text{Mn}^{2+}$ . A linear relationship between  $\text{Mn}^{2+}$  concentration and photometrically measured CL intensity can be observed at low concentrations (7). Above 400-600 ppm, the increase of CL intensity is less than the linear trend, perhaps due to the beginning of concentration quenching (8). Data on the effect of  $\text{Fe}^{2+}$  quenching are still controversial. However, CL intensity of calcite seems to be more sensitive to  $\text{Mn}^{2+}$  activation than  $\text{Fe}^{2+}$  quenching (7). Increased Fe/Mn ratios result in steeper slopes of the Mn/luminescence linear trend. However, no extinction, even for low Mn values, was observed up to 3000 ppm of Fe. In general, more than 10,000 ppm (1 wt.%) of  $\text{Fe}^{2+}$  are needed to extinguish Mn-activated CL (5).

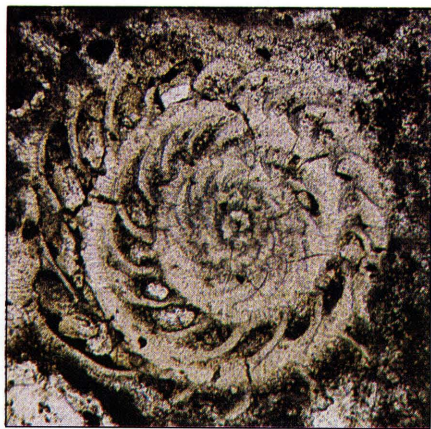


Fig 1a



Fig 1b

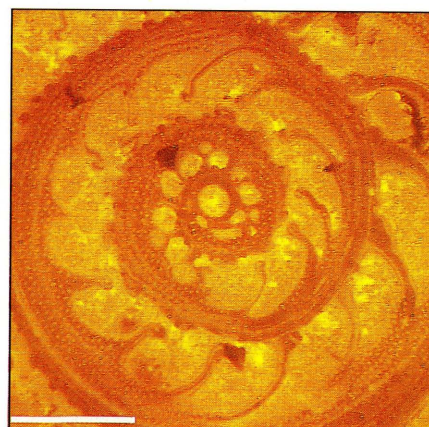


Fig 1c

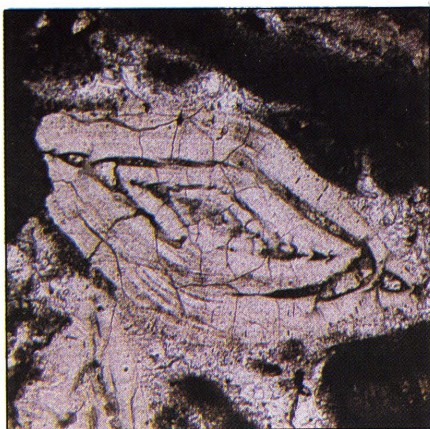


Fig 2a



Fig 2b

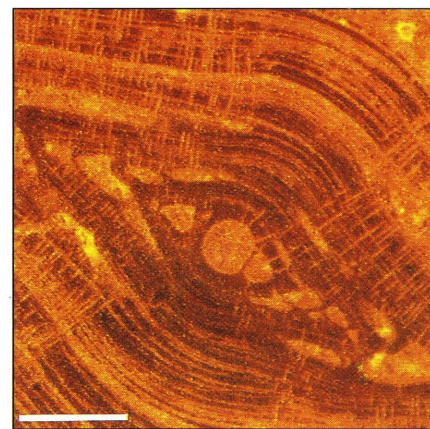


Fig 2c

Fig. 2. Axial section of a Miocene *Amphistegina* sp. same sample and same imaging as Fig. 1. a. Normal transmitted light, HFW 930  $\mu\text{m}$ . b. CL, same scale. c. CL digital image, scale bar = 100  $\mu\text{m}$ , 1012 $\times$ 1012 pixels. Note continuous pores (revealed by infilling cements with brighter CL) cutting through the lamellar structure of the test wall.

The growing interest to geologists in CL of carbonates is principally founded in its potential for the interpretation of diagenetic environments. However, little work has been done to assess the original chemical composition and CL response of biomineralized carbonate, the source material of most carbonate rocks. Recent biogenic carbonates show a wide range of CL intensities (9). Both metabolic processes and changes in the environment can be invoked to explain Mn variations during growth of calcareous shells.

The amount of trace elements incorporated in inorganically precipitated calcite is dependent of their availability, the physical chemical conditions of the precipitating fluid and the partitioning behaviour of the elements. For the aragonite/calcite and calcite/calcite recrystallization an enrichment in  $\text{Mn}^{2+}$ , and hence brighter CL, of later calcites should be the general case. However, depletion may occur in open marine systems with a high flow rate of Ca-supersaturated and Mn-poor waters, resulting in low CL intensities.

Standard geological thin sections were prepared oriented parallel and perpendicular to the bedding of all samples and were studied in transmitted light. For cathodoluminescence 40  $\mu\text{m}$  thick thin sections were highly polished with diamond paste. A good polish is essential to achieve high resolution and well focused images.

CL images were obtained in a Technosyn 8200 MkII which was operated at 15-20 kV and 0.4-0.5 mA with an unfocused cold cathode electron beam under a He atmosphere at 0.2 torr. The Technosyn was mounted on an Olympus BH-2 microscope.

The CL intensity of natural limestones varies greatly and weakly luminescent objects are at the limit of colour photography. We have investigated ways of recording CL images by means of highly sensitive CCD-video cameras and more recently by a CCD-photographic camera with digital output.

Photographs were made on Ektachrome P800-1600 film exposed at 1600 ISO, using SPlan Apo 4x and 10x objectives and the Olympus automatic exposure camera system. Exposures typically ranged between 2 and 20 s. The advantage of conventional photography is the high saturation of colours which results in good contrast (Figs 1b, 2b). The resolution is limited by the grain of the highly sensitive film. In addition, colour shifts (due to the Schwartzschild effect of the film) are unavoidable. Therefore, colours and intensities shown on CL photos are not comparable between different objects, because they are affected by the highly variable exposure time. Longer exposure

times tend to produce more reddish colours. We therefore measured CL intensities of small areas with the digital photometer of the Olympus photomicrographic system. Measurements were made at constant CL conditions of 15 kV acceleration voltage and 0.5 mA beam current. An objective 20x and spot measuring mode was used, which resulted in measurements of an area about 50  $\mu\text{m}$  in diameter. The photometer was set at 2000 ISO and reciprocity factor = 0, which resulted in displayed exposure times in seconds inversely proportional to CL intensity. The measured values varied between 60 s for non-luminescent and 2.1 s for brightly luminescent material.

Video images were obtained by means of a Panasonic colour video camera (WV-CL700/G). Combined with its control unit (WV-CU 204) the electronic shutter speed could be adjusted from 1/30 s down to 1 s, which allowed video observation and printing of even the weakest CL intensities. Working copies were printed on a Sony UP-5000P colour or a UP-811 black and white video printer. The advantage of video imaging is the direct observation of the result and the possibility of searches on the screen rather than the microscope. Low intensity CL is, however, at the limit of video detection and the images become very noisy.

Digital images were obtained by means of the Kodak DCS 200 Digital Camera. The acquired images were transferred via the SCSI interface to a Macintosh Quadra 840 AV and treated with Adobe Photoshop. Printing was done both on a Tektronix colour printer and on the video colour printer Sony UP-500P, which was connected to the video output of the Macintosh. Some of the Figures in this report were produced that way (Figs. 1 c, 2c, 3-4). The Kodak DCS 200 digital camera is a charge coupled device (CCD) with a frame resolution of 1524 x 1012 pixels resulting in images that consist of 1.5 megapixels of 24 bit colour depth (4.5 MBytes of data). Best exposures were obtained by setting the camera in the automatic mode, at one stop overexposure at 100 ISO. Exposure times are comparable to conventional photography between 2 and 50 seconds.

The digital images enhance the resolution of optical CL down to a few  $\mu\text{m}$  (Fig. 4b), which is twice the resolution of conventional photography. The advantages are the possibilities of digital treatment of the images, the easy control of the results on the computer screen and the option of digital image analysis. We are currently studying the ways to digitally measure colour and intensity. Low intensity CL, however, is again at the

detection limit of this CCD-equipped camera. If exposure time is manually prolonged, more saturated but very noisy images result. The best option is to take several shots and digitally sum them on the computer. The illustrations presented herein are, however, all single shots which were digitally enhanced for colour, contrast, saturation and sharpness.

#### Test morphology and growth structures of larger foraminifers observed in Cathodoluminescence

Larger foraminifers have a complex shell structure, known mostly from studies of recent material (2) (10). A complex internal porosity was revealed by impregnation with synthetic resins and subsequent dissolution of the tests (11). In fossil material, this ultrastructure usually became obliterated due to diagenesis: The fine perforations of the test (pores 4-5  $\mu\text{m}$  in size, Fig. 4b) became plugged by the growth of syntaxial cement during initial diagenesis that intervened after death of the organism in an open marine environment. The foraminiferal chambers also became partially cemented by the growth of syntaxial fibrous calcite during early diagenesis, making detailed morphologic studies difficult, especially for the nummulitids. In the following, we briefly discuss some phenomena that are invisible in transmitted light, but have been identified for the first time in fossil specimens using CL.

Growth structures and detailed foraminiferal ultrastructures are revealed by primary variations in luminescence of the lamellar structure of the tests and by contrasts between the shell material and the earliest cements which fill the microporosity. Fossil specimens with preserved growth structures have so far been observed only in rocks that underwent a transport into deeper water after their formation in a shallow bank environment. Even in this displaced material, the majority of Larger Foraminifera shows a completely recrystallized test. Only some specimens show preservation of growth structures. We also exam-

ined shallow water limestones of Costa Rica, Panama and Florida, but did not find specimens with well preserved growth structures. We therefore suspect that the preservation of growth structures is the result of displacement of tests that underwent only the earliest phase of diagenesis in shallow water. Displacement into a deeper marine environment would have interrupted major diagenetic alteration of tests.

Well preserved nummulitids show test walls with alternating dark and light bands (Fig. 1-7). The *Amphistegina* sp. illustrated in Figs 1-4 have tests with dominantly low CL intensity alternating with fine orange bands. There are forms with broad yellow bands (Fig. 5), and others which are dominantly orange and have fine yellow bands (Fig. 6). The lamellar structure is normally invisible in transmitted light because it is oriented perpendicular to the radial calcite fibres of the test.

Nummulitids grow spirally by adding new chambers to the distal end of the planispiral coil. With the addition of each new chamber, a layer of calcite is deposited over the whole of the last whorl. These layers become visible under CL probably due to primary variations of  $Mn^{2+}$  incorporated in calcite during growth. Our observations in equatorial sections (Fig. 1) suggest that with each new chamber, an orange/yellow couplet is formed. In addition, there are periods, where the yellow part of the couplet is dominant, making a thick yellow and a very thin orange band. The thickness of layers and the amount of incorporated  $Mn^{2+}$  may depend on a variety of environmental factors. The thickness of the outer lamellae seems to be related to water depth and/or water energy. The highest thickness/diameter ratios can be expected in shallow, high light, relatively high energy environments (12).

In Recent mollusc and foraminifer shells  $Mn^{2+}$  concentrations correlate positively with slow growth and open sea conditions, and correlate negatively with salinity and water depth (9). In our case of nummulitids, an orange/yellow couplet is formed during each growth step. This implies a vital effect governing the distribution of  $Mn^{2+}$  incorporated in each new lamella. In addition,

broad yellow bands alternate with thin yellow bands (Fig. 1b,c.) which implies variable uptake of  $Mn^{2+}$  during the ontogeny of the organism, perhaps due to changing environmental conditions.

The test wall of nummulitids is perforated by numerous micropores (Figs 1 c, 2b,c, 3, 4) which become apparent due to their plugging with earliest cements with contrasting CL. These pores are continuous through the lamellar system (Figs 2b, c, 3).

Pillars are the non-perforate structures of nummulitids which appear by their solid nature (Figs. 3, 7). Successive lamellae thicken in the area of pillars and form an outwards thickening bulge. It appears that the formation of pillars is established during juvenile growth stages and that they steadily increase during growth of the organism. This observation could confirm a functional importance of pillars such as focusing of light.

#### Diagenesis of foraminiferal tests

The first "free growing" cement is a thin lining of the chamber walls and sometimes the outer surface of Larger Foraminifera. It is formed by small stubby, apparently skalenocentric crystals of weakly luminescent (brownish-red), probably high-Mg calcite (Fig. 6) This stubby cement has the same characteristics as the pore filling cements and may be either synchronous with or slightly later than the latter.

As noted above, most of the foraminiferal tests show in CL a partially or totally homogenized texture, leaving traces or nothing at all of the growth structures. We consider this homogenization to be an early process that occurred synchronously or soon after the formation of pore filling and lining stubby cements. It certainly occurred prior to displacement into deep water. The actual process of homogenization is yet unclear. In some specimens, a distinct granular CL fabric is produced by slight variations in CL intensity. We believe that this texture is the result of ongoing precipitation of calcite that originated from the pore filling cements and continued, gradually replacing the entire test material. It should be noted that this recrystallization is only seen in CL. It leaves no

trace in transmitted light (Figs 1a, 2a.). It therefore must have been syntaxial, i.e. it preserved the optical properties of the original fibrous calcite of the tests.

The early diagenetic environment in an unstable sediment was certainly well oxygenated and characterized by high fluxes of normal sea water through the porosity. Although Mn-concentrations of sea water are probably sufficient to precipitate Mn-bearing, luminescent calcite (6), the

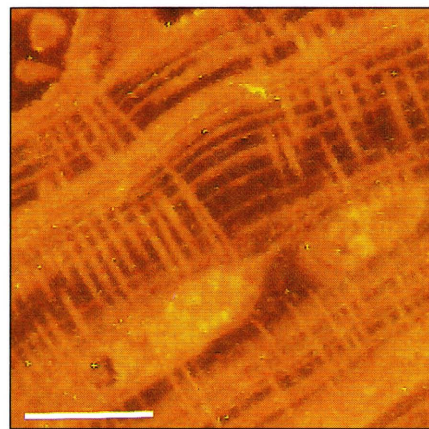


Fig 3

Fig. 3. Detail of axial section of *Amphistegina* sp., same sample and imaging as Fig. 1 c., digital image, scale bar 50  $\mu$ m, approx. 260 $\times$ 260 pixels. Note imperforate pillar structure in centre.

Fig. 4. CL photomicrograph of detail of a tangential section of *Amphistegina* sp., showing red/orange colour banding, fine perforations of the shell and imperforate zones (pillars). Same sample and imaging as Fig. 1c, Digital image, scale bar 200  $\mu$ m, 1012 $\times$ 1012 pixels, no sharpening applied. b. detail of a, showing pixel structure of digital image. Pores are about 5  $\mu$ m in width. Scale bar 10  $\mu$ m, about 54 $\times$ 54 pixels.

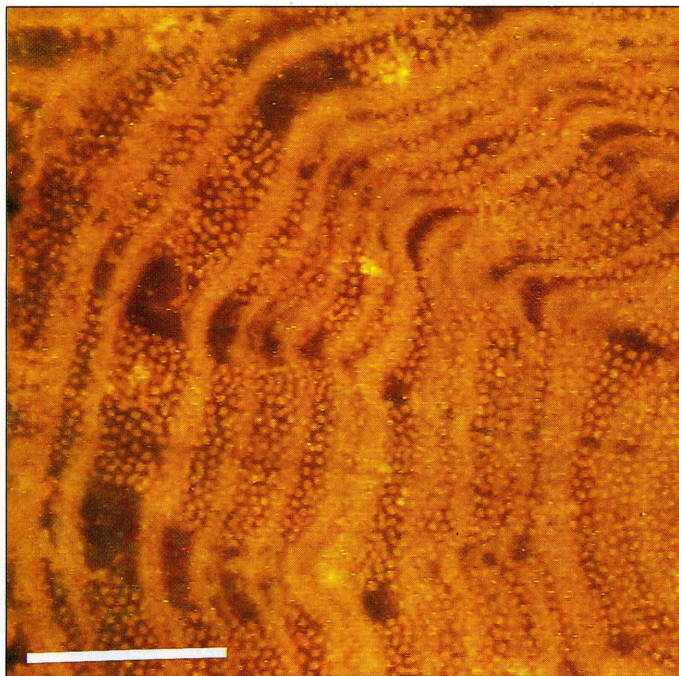


Fig 4a

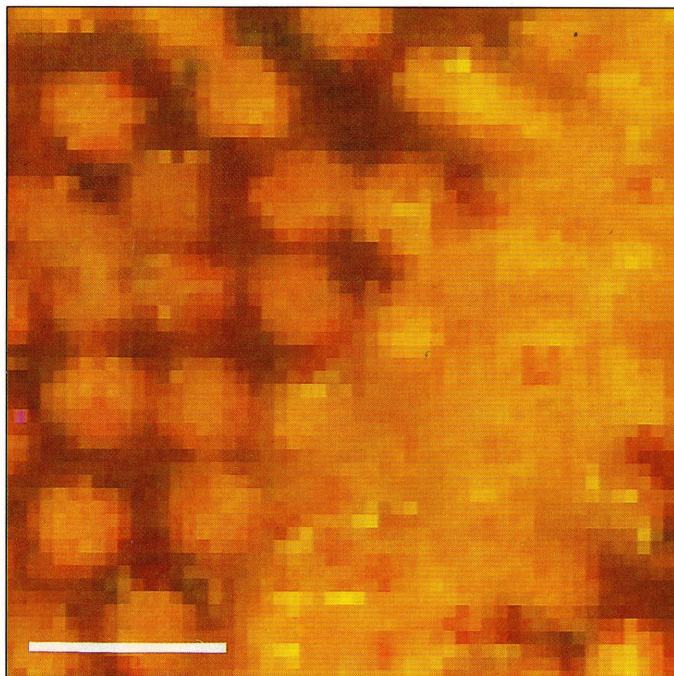


Fig 4b

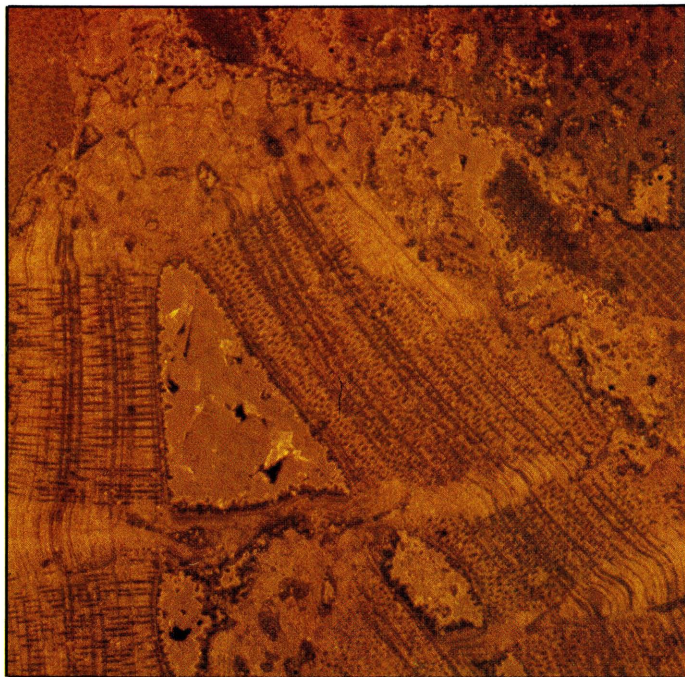


Fig. 5

positive Eh must have prevented its availability as  $Mn^{2+}$ , to be incorporated in significant amounts into calcite. The same reasoning applies even more to  $Fe^{2+}$ . The early cements that precipitated in skeletal porosity or partially/totally replaced the tests are weakly luminescent and show dull brown-orange colors. These cements are interpreted as poor in  $Mn^{2+}$  and  $Fe^{2+}$ .

#### Summary and Conclusions

Cathodoluminescence is an excellent method to analyze the original microscopic structure of Larger Foraminifera, since original, biomineralized material can be distinguished from diagenetic cements. CL permits safe systematic description of benthic and planktonic Foraminifera even in highly recrystallized rocks. Systematic definitions of larger foraminifer species may need revision as a result of the gain in morphologic resolution.

The dark/bright CL banding parallel to the lamellar structure observed in some nummulitids is interpreted as a primary growth structure. It resulted from variable incorporation of  $Mn^{2+}$  during phases of biomineralisation, due to changing environmental and/or metabolic conditions.

Preservation of fine growth structures in larger foraminifers seems to be restricted to carbonate material penecontemporaneously displaced into deeper water environments. Even under this condition, the majority of larger foraminifers show a completely recrystallized test. We have been unable to find any growth structures in shallow water limestones, in material that underwent lithification in the shallow environment.

We conclude that the preservation of growth structures is the result of displacement of tests into deeper water. In the open marine, carbonate bank environment, recent tests that had undergone the earliest diagenetic plugging of microporosity only, must have coexisted with already transformed material. The resedimentation process sampled such a mixture and displaced it into a deep water environment, which preserved the earliest stages of diagenesis. In contrast, high fluxes of seawater through consolidated sediment

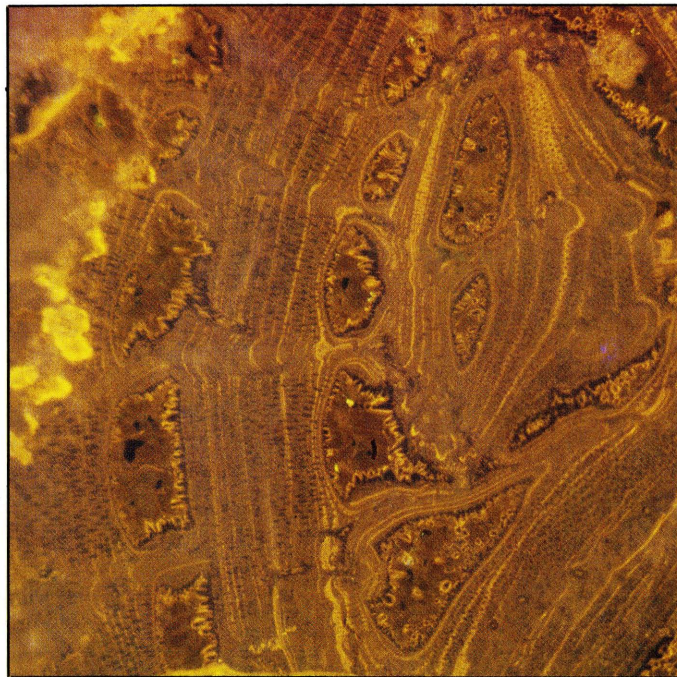


Fig. 6

in shallow bank environments led to total recrystallization of all tests and to rapid early lithification under homogeneous Eh/pH conditions resulting in undifferentiated CL.

We conclude that further high resolution morphologic work on benthic foraminifers should preferably be carried out by using CL in resedimented material, rather than platform limestones.

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Fig. 5. CL photomicrograph of axial section of *Ranikothalia* sp. with well preserved growth structures. CL of test material is brighter than pore filling cements. Test is mainly yellow, with narrow orange bands. Sample CM 324.1, Playa Mangle, Burica Peninsula, Costa Rica. HFW 930  $\mu m$ .

Fig. 6. CL photomicrograph of axial section of a *Ranikothalia* sp. with well preserved growth structures. CL of test material is barely brighter than pore filling (red) cements. Test is mainly orange with narrow yellow bands. Sample CM 806, Playa Espadilla, Quepos, Costa Rica. HFW 930  $\mu m$ .

Fig. 7. Tangential section of *Discocyclina* sp. Concentric rings (like tree rings) reveal growth of pillars under fluctuating environmental conditions. Same sample as Fig. 6.

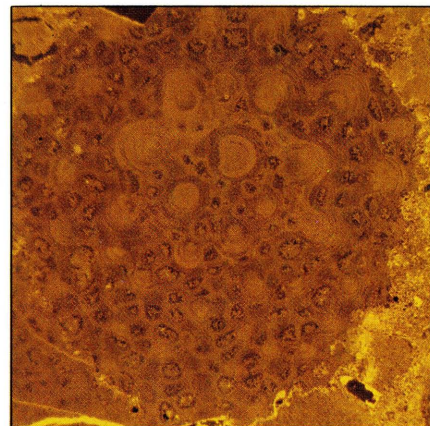


Fig 7

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