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Cathodoluminescence of Recent biogenic carbonates: an environmental and ontogenetic fingerprint

V. BARBIN,*† K. RAMSEYER,† J. P. DEBENAY,‡ E. SCHEIN,§ M. ROUX§ & D. DECROUEZ*

* Muséum d'Histoire naturelle, 1 route de Malagnou, C.P. 434, CH-1211 Genève 6, Switzerland
† Geologisches Institut, Universität Bern, Baltzerstrasse 1, CH-3012 Bern, Switzerland
‡ Laboratoire de Géologie, Université du Maine, route de Laval, F-72017 Le Mans cédex, France
§ Laboratoire des Sciences de la Terre, Université de Reims, B.P., 347, F-51062 Reims cédex, France

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Abstract – Cathodoluminescence (CL) examination of Recent biogenic carbonates shows that they are often luminescent regardless of their mineralogical composition (calcite v. aragonite), habitat (marine v. fresh water), way of life (sessile v. vagile) or environment (hyper- v. hyposaline water). Thus, the presence of luminescence in biogenic particles is not a reliable indicator of diagenetic alteration as some authors have suggested. In addition, CL can reveal variations in the mineralogy of shell material (e.g. regenerated calcitic v. primary aragonitic) and can highlight growth-related structures. Manganese (Mn^{2+}) is the most likely activator of this luminescence, and its content in the shells of benthic organisms seems to be linked to growth rate, ontogeny, open sea conditions, bathymetry and salinity. In neritic environments the Mn^{2+} content and the CL of molluscs and foraminifera appear to increase with decreasing salinity. This study indicates that CL may be an important tool for the determination of environmental and ontogenetic parameters in biogenic carbonates in addition to its current use in diagenetic studies.

1. Introduction

Since 1965, cathodoluminescence (CL) has become of increasing interest to geologists (e.g. Smith & Stenstrom, 1965; Long & Agrell, 1965). Although this method is now an important tool in sedimentary petrology (e.g. Meyers, 1974; Dorobeck, 1987; Marshall, 1988) its palaeontological applications have not been examined in detail. CL, however, often reveals outlines and the internal structure of fossils that are invisible in transmitted light (Smith & Stenstrom, 1965; Long & Agrell, 1965; Martin & Zeegers, 1969; Miller & Clarkson, 1980; Martini *et al.* 1987; Amieux, 1987; Barbin *et al.* 1988; Barbin, Ramseyer & Decrouez, 1989; Barbin *et al.* 1989*a*); and differences in CL colour have been used to detect mixing of fossils from different environments (Richter & Zinkernagel, 1981; Barbin *et al.* 1989*b*). Nevertheless, most authors still consider Recent primary biogenic carbonates to be non-luminescent (e.g. Czerniakowski, Lohmann & Wilson, 1984; Popp *et al.* 1986; Adlis *et al.* 1988; Saelen & Karstang, 1989; Saelen, 1989).

Little is known about the precise original chemical composition (e.g. trace element content) of fossil mollusc shells, alga thalli and foraminiferan tests. Thus, it is difficult to evaluate the degree of diagenetic alterations in fossils. There are no adequate criteria for distinguishing diagenetic alterations from variations in shell chemistry related to an organism's response to the environment or ontogenetic variation (Rosenberg, 1980). A crucial point is that incorporation of trace elements (including Mn^{2+}, the main activator for CL) in a mollusc shell is a metabolic process which takes place within the extrapallial fluid of the mollusc (e.g. Wilbur, 1964). This fluid is situated between the mantle and the inner surface of the shell and is therefore not in direct contact with the surrounding water. This implies that changes in the trace element content of the sea water (or fresh water) have to be transferred through the living aqueous system (the extrapallial fluid) before the trace elements are incorporated in the calcareous shell.

The aim of this paper is to show variations in the chemical composition (mainly Mn) of biogenic carbonates, and the links between Mn variation and changes in environment (e.g. bathymetry, salinity), growth rate and ontogeny.

2. Sampling

CL studies where carried out on modern foraminifera, molluscs, and coralline algae. The hyaline foraminiferan *Ammonia beccari* and the related species *A. tepida* were chosen due to their worldwide distribution and their euryhaline nature. Porcelaneous foraminifera (Miliolidae) were also studied. Samples were collected in Casamance (Senegal), St-Vincent Bay (New Caledonia), Bourgneuf Bay (France), and were complemented by samples from Cap Timiris (Mauritania), Marseille Bay (France) and Banyuls (France). The specimens from Casamance were removed from the topmost 5 mm of sediment of a grab sample, and

kept in neutralized formaline. The microfauna was then washed on a 50 μm sieve, stained with 2% rose Bengal solution and separated on carbon tetrachloride (Debenay, Pages & Diouf, 1989). Foraminifera from Casamance and Cap Timiris were alive less than two weeks prior to sampling (older specimens show evidence of extensive dissolution). Foraminifera from Banyuls were collected alive on *Posidonia* thalli. Specimens from Bourgneuf Bay were picked from a sediment sample, but they were in perfect state of preservation and were alive no more than 2 or 3 months prior to sampling. The Peneroplidae from St-Vincent Bay were also very well preserved and parts of organic material were inside the tests; we therefore are certain that the animals had been dead less than one year. The specimens from Marseille Bay were also picked up in a sample from the topmost sediment layers. We have no more detailed information on their freshness but no visible alteration was observed.

For our investigations on mollusc shells we chose: *Pecten maximus* (Brest Harbour, France) whose growth history is precisely known; *Mytilus edulis* and *Ostrea edulis* from Leucate Pond (Port Barcares, France) which is open to the sea; and *Anadara senilis* from the lagoon of Mbodiène (Senegal). These marine bivalves were supplemented by an *Anodonta* shell from the fresh water pond of La Neuville en Hez (Oise, France) to compare marine with fresh water biogenic aragonite. All marine bivalves were collected alive *in situ* and the *Anodonta* was 'recently dead' as the soft parts were not totally disaggregated.

The last group that we studied is *Neogoniolithon* sp. (coralline algae) from the lagoon of Bahiret el Biban (Tunisia). This lagoon is slightly hypersaline, with salinities ranging from 41 to 51‰, but after heavy rainfall it may temporarily become brackish (F. R. Keer, unpub. M.S. thesis, Duke University, 1976; Thornton, Pilkey & Lynts, 1978). Thalli were sampled in the living part of an algal ridge but we have no evidence that they were alive when collected.

In summary, the samples are from various environments, all molluscs are unequivocally freshly-killed, most of the Foraminifera show evidence that they were very recently dead if they were not killed when they were collected, and though it is difficult to demonstrate that all the algae thalli were alive at the time of sampling, they appear to be unaltered.

3. Methods

A high sensitivity (hot cathode) CL-microscope which allows the observation of low-intensity luminescence was used for this study (instrument described in Ramseyer *et al.* 1989). The operating conditions were: an accelerating potential of 30 keV and a beam current density of 0.4 μA/mm^2. Photomicrographs were taken using Ektachrome 400 transparency film, developed at 800 ASA. Mollusc shells were air dried, embedded in epoxy resin, and section from umbo to ventral margin along a plane perpendicular to the shell surface. All tests were prepared carefully to avoid altering the microstructure, and no preparation-induced artefacts were detected under high magnification SEM examination of the polished surfaces. Foraminifera were randomly fixed on epoxy resin and polished. After observation under CL, the staining method of Warne (1962) was used to distinguish aragonite from calcite.

4. CL detection limit

Richter & Zinkernagel (1981) consider that biogenic calcite requires 20–40 ppm Mn^{2+} (aragonite less) to show CL. However, spectral analyses of luminescence in calcite white marbles indicate that less than 5 ppm manganese still produces weak but visible luminescence (Barbin & Ramseyer, unpub. data). This is 5 to 10 times lower than the concentration published by Richter & Zinkernagel (1981), Marshall (1988), and Hemming, Meyers & Grams (1989).

For biogenic carbonates we have observed an orange luminescence of medium intensity in a *Pecten maximus* shell where the Mn^{2+} content is below the 50 ppm detection limit of the electron microprobe (Fig. 2, parts 4 and 5). Our material CL detection limit of Mn^{2+} in biogenic carbonate is thus below 50 ppm if we refer to literature data on Mn content of biogenic carbonates (Milliman, 1974).

5. Previous CL observations on Recent organisms

Following Milliman (1974), Glover (E. D. Glover, unpub. Ph.D. thesis, Univ. Wisconsin, 1977) considered that with few exceptions the Mn level in calcareous marine organisms is considerably below 100 ppm and concluded that 'a variety of carbonate exoskeletons showed none or very little of the characteristic orange–red luminescence that many carbonate rocks show: exceptions are barnacles (calcite containing less than 0.30% Mg, bright luminescence), oysters (mostly calcite), sand dollars (Mg calcite) and some corals (mostly aragonite with some octocorallia in Mg calcite, weakly luminescent)'. Richter & Zinkernagel (1980) observed luminescence zoning in 16 of 18 Recent echinoid tests examined from several offshore locations. The zonation was interpreted to reflect physiological changes that resulted in cycles of skeletal growth (Richter & Zinkernagel, 1981).

Sommer (1972) used CL to identify original regenerative calcite and vaterite in aragonite *Amblema* shells (bivalve) and areas with large variations in Mn concentration. Although Sommer observed a yellow–green luminescence of aragonite in the inner nacreous surface of a marine gastropod (*Architectonica*), he nevertheless considered this colour to be characteristic

of fresh water molluscs. Richter & Zinkernagel (1981) indicated that the role of Mn^{2+} as an activator of luminescence in biogenic aragonite is not clear and that the role of Sr as quencher is not yet established for the concentrations observed (up to 2.5%). They described bright yellow–green luminescence in a marine aragonitic gastropod (*Bittium*).

6. New results from Recent biogenic carbonates

6.a. Foraminifera

CL observations (Table 1) on recently living benthic species *Ammonia* (Fig. 1, part 3) and Miliolidae (Fig. 1, parts 4 and 5) reveal that many individuals are luminescent. For a given location luminescence intensity is rather comparable; however, there is a variation among samples from different regions. The high-Mg calcite tests of Miliolidae (porcelaneous foraminifera) were generally more luminescent than Rotaliidae (*Ammonia*) which have a hyaline structure and apparently consist of calcite to low-Mg-calcite regardless of species (*A. beccarii* is reported to contain up to 6 mole% $MgCO_3$ though no Mg was detected in this species by microprobe analysis; Ausseil-Badie, Favillier & Giresse, 1985). Our preliminary data from a variety of environmental settings indicate no clear link between salinity and CL intensity. In general, however, a higher luminescence intensity is observed in normal and low salinity environments. Unfortunately the specimens that were indisputably alive at the time of collection are all from hypersaline environments, and thus are principally non-luminescent. Nethertheless, luminescent foraminifera from Banyuls which were freshly-killed show luminescence comparable with the specimens illustrated in Figure 1.

Data on the trace element content of foraminifera are mostly for planktonic foraminifera. Krinsley (1960) states that 'the manganese concentrations in planktonic foraminiferal tests are related to location and probably time'. The range in Mn content of some benthic foraminifera lies between 2 ppm (*Calcarina* and *Heterostegina*, both hyaline foraminifera composed of high-Mg calcite) and 80 ppm (*Archaias*, also high-Mg calcite but porcelaneous; Milliman, 1974). This is in accordance with our observations of a higher luminescence intensity for Miliolidae compared to that of *Ammonia*. Therefore, the wall microstructure seems to be an important parameter in determining luminescence intensity. Another possibility is the influence of the life habits. *Ammonia beccarii* and Miliolidae could be both epiphytic or endofaunal foraminifera and so an influence of the sediment by pore water interaction is possible. Further study is planned on foraminifera from many localities and diverse environments that are unequivocally freshly killed.

6.b. Mollusc shells

6.b.1. Pecten maximus

Larvae of *Pecten maximus* were collected in the Saint Brieuc Bay in July 1976 and transferred to Brest Harbour in March 1977 where they remained until September 1981 (Buestel, Gerard & Guenole, 1987, Roux *et al.* 1990). *P. maximus* has a calcitic shell except for the myostracum which is aragonitic. With CL, hair-like orange luminescing bands that parallel the annual growth increments are visible in the calcitic part of the shell (Fig. 2, part 5b); consequently, it is easy to follow growth layers throughout the inner layer, where the most internal part is more brightly luminescent (probably due to its slower growth rate). These stripes can be correlated to several periods of

Table 1. Cathodoluminescence characteristics of Recent biogenic carbonates

Organism	Mineralogy	Habitat	Main CL colour	CL intensity
Ammonia spp.	Calcite and low Mg calcite?	Marine shelf	Orange Non-luminescent	Dull to medium
Miliolidae	High Mg calcite	Marine shelf	Orange Non-luminescent	Dull to bright
P. maximus		Marine shelf		
Outer and inner layers	Calcite		Orange	Dull to medium
Myostracum	Aragonite		Non-luminescent	
Ostrea edulis		Saline pond		
Prismatic and foliated layers	Calcite		Orange	Bright
Chalky structure	Calcite		Orange	Medium to dull
Myostracum	Aragonite		Non-luminescent with greenish bands	Medium to dull
Mytilus edulis		Saline pond		
Outer layer	Calcite		Orange	Dull to bright
Inner layer	Aragonite		Non-luminescent	
Anodonta sp.	Aragonite	Fresh water pond	Green and yellow	Bright
Anadara senilis		Lagoon		
Initial shell	Aragonite		Blue-green	Dull
Regenerated	Calcite		Orange	Medium to bright
Red algae	Mg calcite	Lagoon	Orange	Dull to bright

slow growth, but not directly with major breaks in growth. No other imaging technique is able to detect this growth zonation. In addition, bioeroded (e.g. bacteria, microboring organisms) zones are characterized by bright orange luminescence with a palisade aspect (Fig. 2, part 4b). The aragonitic myostracum is non-luminescent (Fig. 2, parts 4a, b). It is evident that the luminescence of bioeroded surfaces is due to external factors and was not produced by the mollusc biomineralization process.

According to Segar, Collins & Riley (1971), analysis of *P. maximus* revealed a Mn content of 4.9 to 12 ppm (Milliman, 1974, reports values as high as 130 ppm for a *Pecten* sp.) for the shell, whereas the soft parts average 140 ppm and a value of 410 ppm was recorded for the gut and digestive gland (Segar, Collins & Riley, 1971). Bryan (1973) found 15300 ppm Mn (90% of the total Mn of the animal) in the kidneys of *P. maximus*. He considers that changes in the Mn concentration of the kidneys are 'almost equivalent to changes in the whole animal' and observed that seasonal variations in the Mn content of kidneys occur, with highest values during autumn and winter and lowest values in spring and early summer. Masuda (1981) came to a similar conclusion regarding the importance of seasonal influence in the Mn content after analysing the outer calcitic layer of *Mizuhopecten yessoenis*. He noted high concentrations of Mn, Fe, Mg and Ba associated with annual rings and seasonal variations versus a lower amount of Li and Na at the same intervals. These observations fit well with variations in CL intensity in *P. maximus*, in which bright-orange stripes contrast with weakly-luminescing blueish areas. These zones of bright luminescence correlate with growth events during winter and environmental perturbations of unknown origin in summer and also correlate with variations in the stable isotope ratios (Roux *et al.* 1990 and Barbin *et al.* in press).

The presence of bacteria and/or microalgae on the outer surface of the shell may be important in controlling the concentration of Mn on the shell surface (e.g. Allen, 1960; Rosenberg, 1980). This hypothesis could explain the palisade aspect of biocorroded areas in the shell we examined (Fig. 2, part 4).

6.b.2. *Ostrea edulis*

Ostrea edulis from the Leucate Pond shows a bright orange luminescence in the thin prismatic outer layer and in the main foliated parts of the calcitic shell (Fig. 2, part 3). The 'chalky structure' exhibits a diffuse orange luminescence with bright orange luminescing ridges (Fig. 2, part 6), whereas the aragonitic myostracum is, as in the case of *P maximus*, non-luminescent except for three fine greenish lines (Fig. 2, part 3b). These greenish luminescing bands are not visible in transmitted or polarized light (Fig. 2, part 3a).

In *Crassostrea virginica*, Rucker & Valentine (1961) have shown correlations between Mn ($r = -0.45$) and Na ($r = +0.36$) concentrations and salinity. Elements that correlate negatively with salinity are those that are presumably diadochic with calcium in the calcite structure. It is possible that the lower concentration of the preferred calcium ions increases the incorporation of less desirable ions during shell construction (Rucker & Valentine, 1961). Proton microprobe analyses performed by Carriker, Swann & Ewart (1982) on shells of living oysters (grown under relatively constant environmental conditions in a fibreglass tank) revealed that the relative concentrations of Na Cl, S, Mn, Fe and Zn increased slightly with the age of the oyster and that other elements stayed relatively constant. This phenomenon is comparable to the observations made on *P. maximus* (Carriker, Swann & Ewart, 1982). These authors also indicated that a 'continuous enrichment of seawater by addition on the metals Fe, Cu, Zn and Mn in the algal nutriment medium probably accelerated uptake of most of these elements in the shell and could explain why Mn, Fe and Zn (though not Cu) increased in concentration in the shell of live *oysters* over time'.

6.b.3. *Mytilus edulis*

The shell of *Mytilus edulis* has two layers: a calcitic outer layer that consists of prismatic fibres which, as with *P. maximus*, show orange stripes under CL (Fig. 1, part 6b) and an aragonitic nacreous inner layer with no detectable luminescence.

Electron paramagnetic resonance (EPR) analyses performed by Blanchard & Chasteen (1976) on *M. edulis* shells revealed that the prismatic region typically contains 10 ppm of Mn^{2+} and from 20 to 50 ppm Fe, most likely coordinated to the matrix protein of the shell. Their EPR data were consistent with Mn^{2+} substituted for Ca^{2+} in the calcite lattice of the prismatic region. No Mn^{2+} was observed in EPR in the nacreous layer although atomic absorption spectroscopy (AAS) detected about 8 ppm. The nacre exhibited a Fe^{3+} signal and a very weak but anisotropic Mn^{2+} signal of unknown origin. There was no relationship between 'total Mn' by AAS and the position of the animal in the intertidal zone, but there was a 'strong positive correlation (coeff 0.916), albeit on a limited number of samples (5), between the Mn^{2+} substituted for Ca^{2+} in calcite and the position above low tide' (Blanchard & Chasteen, 1976).

It is still unclear why specimens living above the mean low water level have a 'higher Mn^{2+}/Mn_{total} ratio than those growing below this level' (Rosenberg, 1980). Rosenberg (1980) suggested that the duration of the organism's exposure to either the atmosphere or well-oxygenated intertidal waters might be an

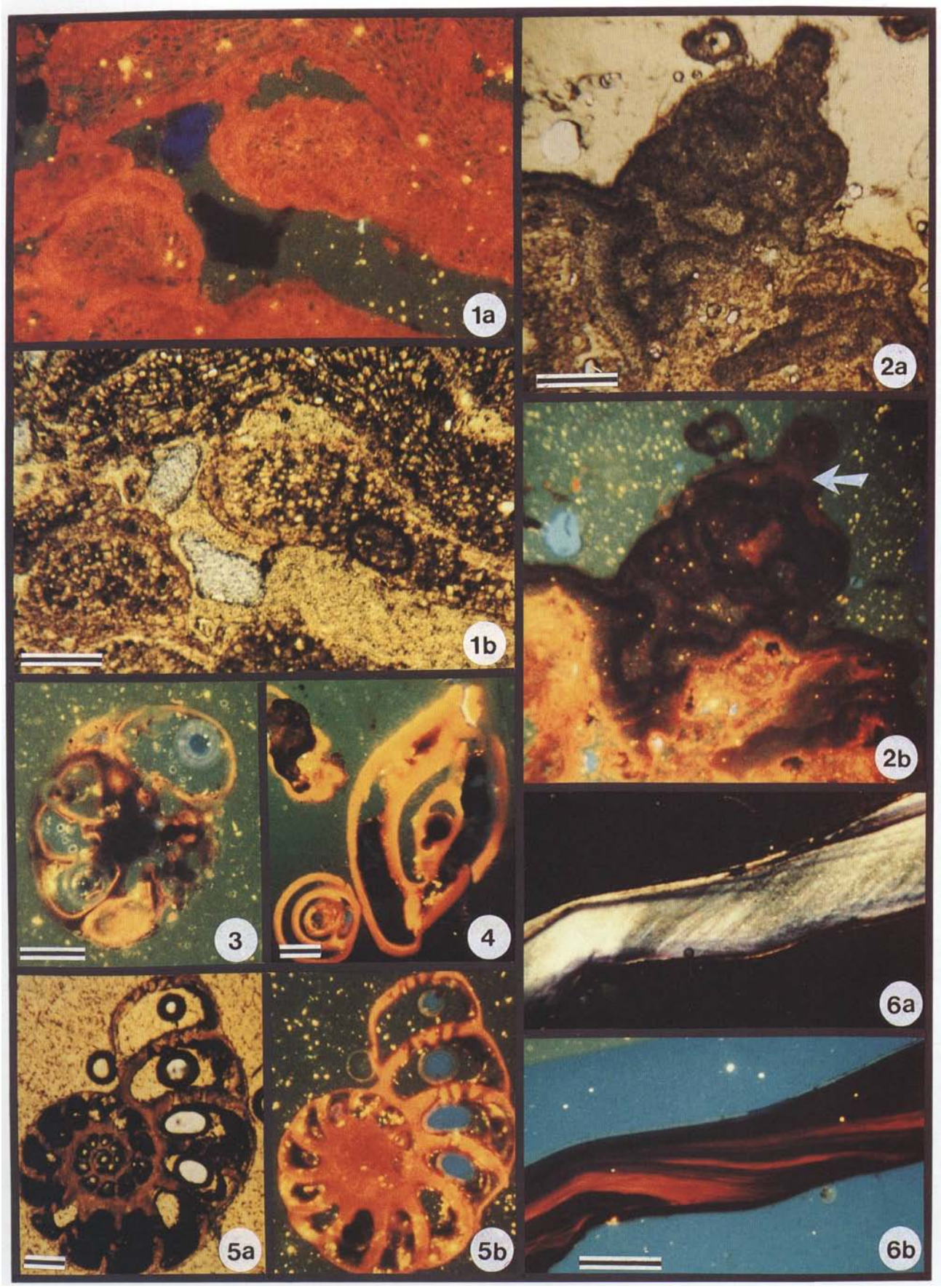

Figure 1. (1) *Neogoniolithon* sp., Bahiret el Biban Lagoon, X 30: (a) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.); (b) transmitted light photomicrograph. (2) *Neogoniolithon* sp., Bahiret el Biban Lagoon, X 30: (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.). (3) *Ammonia beccari*, Bourgneuf Bay, *S* (salinity) = 35‰; X 120; cathodoluminescence photomicrograph (objective 10, 30 sec. exp.). (4) Miliolidae, Marseille Bay, cathodoluminescence photomicrograph (objective 6.3, 30 sec. exp.), X 75. (5) Porcelaneous foraminifera, Saint-Vincent Bay, depth between 10 and 20 m, $35<S<35.5$‰, X 75: (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 6.3, 15 sec. exp.). (6) *Mytilus edulis*, Leucate Pond (May, 1989), X 30: (a) crossed nicols light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.). Scale bars: (1), (2), and (6) = 500 μm; (3), (4) and (5) = 100 μm.

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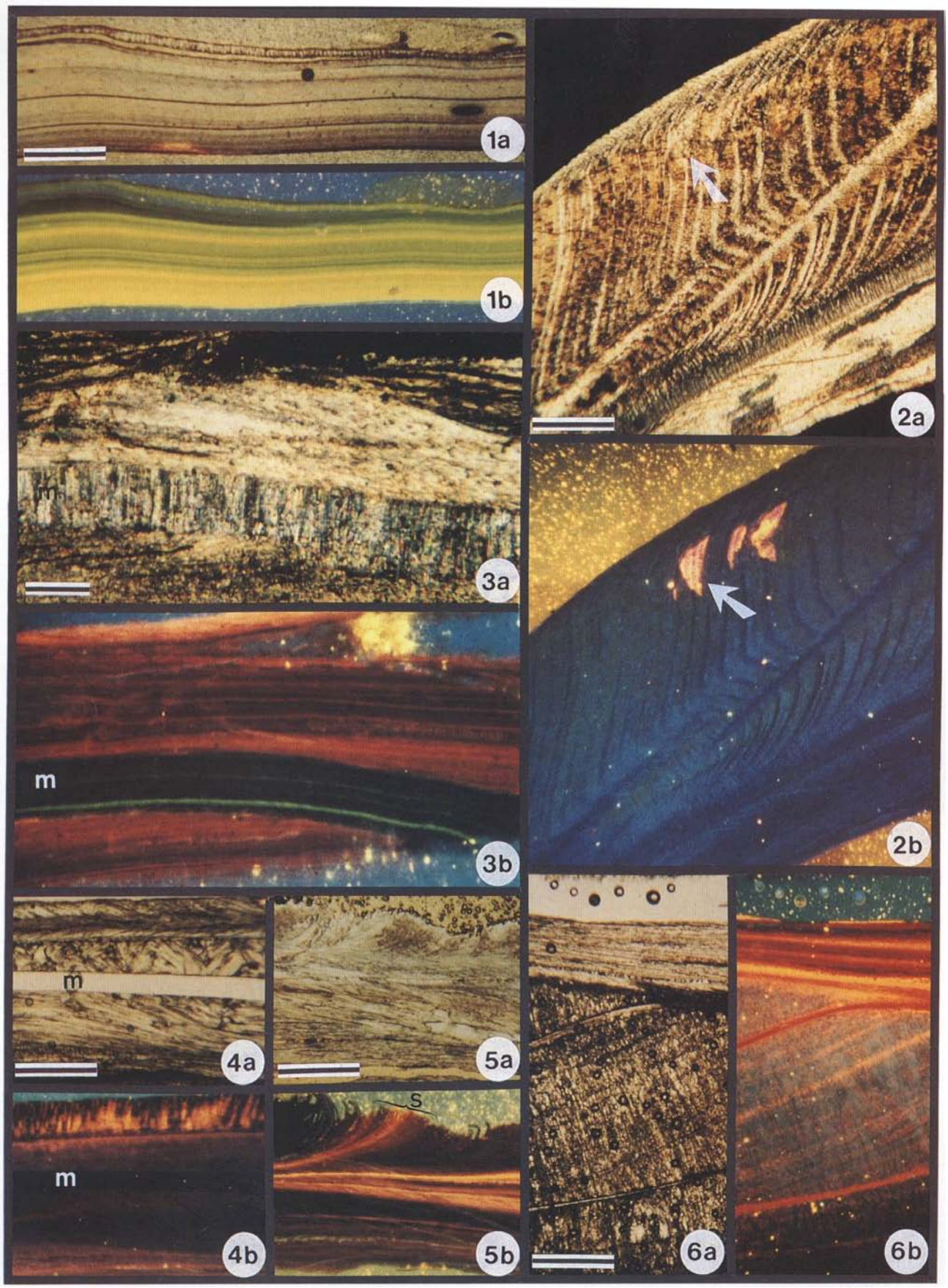

Figure 2. (1) *Anodonta* sp., La Neuville en Hez fresh water pond, X 30: (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 8 sec. exp.). (2) *Anadara senilis,* Mbodiène Lagoon; X 30. Arrows show regenerated parts; observe the bright orange luminescence in (b); (a) crossed nicols light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 2 min. 30 sec. exp.). (3) *Ostrea edulis,* Leucate Pond (May 1989), X 120: (a) crossed nicols light photomicrograph; (b) cathodoluminescence photomicrograph (objective 10, 1 min. exp.). (4) *Pecten maximus,* Brest Harbour, m = myostracum, X 30: (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.). (5) *Pecten maximus,* Brest Harbour, X 30. S = growth decrease during late summer; (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.). (6) *Ostrea edulis,* Leucate Pond (May, 1989), X 30: (a) transmitted light photomicrograph; (b) cathodoluminescence photomicrograph (objective 2.5, 30 sec. exp.). Scale bars: (1), (2), (4), (5) and (6) = 500 μm; (3) = 100 μm.

important factor. During exposure the molluscs react by closing their shell and this could modify the composition of the extrapallial fluid. Direct influence of well-oxygenated intertidal waters is problematic, as higher concentrations of Mn^{2+} are generally found in oxygen-free waters.

6.b.4. Anodonta sp.

The *Anodonta* shell is aragonitic and is characterized by alternating bright green and yellow luminescing bands (Fig. 2, part 1). This type of luminescence is thought to be characteristic of non-marine bivalvia (Sommer, 1972) and marine gastropods (Sommer, 1972; Richter & Zinkernagel, 1981). The green colour is very similar to that in the myostracum of *Ostrea*.

Anodonta as a fresh water genus, generally contains much more Mn in the shell carbonates than related marine molluscs (Boycott, 1921; Gordon, Carr & Larson, 1970). In shells of *Unio* from Lake Maggiore, Mn appears to be distributed inhomogeneously and increases in concentration with age and size (Merlini *et al.* 1965). Thus, as we have shown for *P. maximus* and after the literature data from *Ostrea*, the Mn content seems to increase with age.

6.b.5. Anadara senilis

A homogeneous population of *Anadara senilis* in the Mbodiène lagoon was continuously monitored for one year (Debenay, Bellion & Hebrad, 1987). Shells from this population, generally considered to be aragonitic, give a weak blue-green luminescence where the growth lines are visible in both CL and transmitted light. In one of the shells three small areas with an orange luminescence were visible (Fig. 2, part 2b). Staining shows that the three small orange luminescent areas are calcitic and confirm that the shell is largely composed of aragonite. These areas probably result from bioerosion of the shell and subsequent precipitation of compositionally distinct fresh shell material. Wilbur & Watabe (1963) induced shell regeneration in five species of molluscs, and observed that the mineralogy of regenerated parts frequently differs from the existing shell material. These experiments are consistent with our interpretation of the three orange luminescent areas.

Ausseil-Badie Favillier & Giresse (1985) noted the presence of calcite (5–7%) in XRD patterns of Recent *Anadara senilis* from a population very similar to those we sampled. They proposed a number of possible origins for the calcite, such as early diagenetic alteration, contamination by a crust, intergranular cementation, or mixed initial mineralogy. Considering our results, it seems that the *Anadara* forms calcite and not aragonite under certain stress situations and thus the calcite observed in XRD patterns may be regenerated shell material.

6.c. Red algae

Encrusting coraline algae *Melobesia* (*Neogoniolithon*), which forms microridges in the shallow lagoon of Bahiret el Biban, were collected for this study. The location of the microridge that was sampled may be related to less restricted conditions in this part of the lagoon or to a higher concentration of Ca^{2+} due to infiltration of rain water (Denizot *et al.* 1981). There is no proof of a direct correlation between the higher concentration of carbonates and a particular growth of *Melobesia* (Denizot *et al.* 1981).

In some samples, *Melobesia* shows an orange luminescence. The thick, indistinctly layered perithallium gives a higher intensity of luminescence than the multilayered hypothallium (Fig. 1, part 1). In other samples the internal part of the colonies shows similar characteristics to those previously described, but is surrounded by a weaker luminescent or non-luminescent thallus. The outermost parts of the thallus are weakly luminescent (Fig. 1, part 2, arrow). The cause of these variations is most likely heavy rainfall which temporarily transforms the physicochemical conditions by lowering lagoon salinity and temperature. We have not observed evidence of cementation in the algal cells.

7. Cause of variable Mn^{2+} content of biogenic carbonates

Numerous studies have examined the relationship between the trace-element content of mollusc shells and environmental conditions. Salinity, water temperature, mineralogy, nutrition and organic processes have all been shown to affect the distribution of trace metals during biomineralization of invertebrate skeletal carbonate material. Harris (1965) considered that in molluscs, 'crystal growth and/or metabolic processes are primary controls on the distribution of manganese, iron and strontium'. Because crystallization takes place in the extrapallial fluid, 'the partitioning of minor elements between skeletal material and sea water does not adhere to criteria for equilibrium' (Harris, 1965); thus factors other than sea water composition may be important.

The Mn content of mollusc shells was initially considered to be principally a function of diet (Bradley, 1910), but in recent years, efforts have been made to correlate Mn content with other parameters. From the literature it appears that salinity is the dominant environmental control on the concentration of both Na and Mn in invertebrate shells (e.g. Rucker & Valentine, 1961; Pilkey & Goodell, 1963, 1964, or Gordon, Carr & Larson, 1970). The Mn content seems to increase inversely with salinity, but the relationship is by no means clear (Rosenberg, 1980).

There are three possible ways to increase the Mn content of the water: evaporation, an influx of fresh

water, or a decrease in Eh. In general the Mn^{2+} concentration of sea water (0.3 ppb) is lower than that of river water (8 ppb, Broecker & Peng, 1982). In comparison, the Mn content of shell material lies between 2 ppm and several hundred ppm, and in soft parts it can be as high as 15000 ppm. Thus a metabolic concentration process must control the Mn content of carbonate shells, as calcite directly precipitated from sea water would contain only 1–2 ppm Mn (Veizer, 1983). Two possibilities arise: (1) the flux of Mn is constant and it is only the growth rate that controls the Mn content of the shells; or (2) the Mn content of extrapallial fluid is variable and stress conditions release the Mn in order to produce more shell material. Under stress conditions molluscs close their valves and therefore have less or no contact with the surrounding sea water. As shown for Pecten shells (Barbin *et al.* in press), growth rate and ontogeny can strongly influence CL intensity.

It is difficult to compare the luminescence of molluscs and foraminifera because they do not have the same metabolism. Our preliminary data from numerous observations on a variety of *Ammonia* and Miliolidae from different locations indicate that, in benthic foraminiferal tests, open sea conditions and very shallow water depths favour higher luminescence intensity.

8. Conclusions

Despite the difficulties of understanding the effect of metabolism on the Mn^{2+} content of mollusc shell and foraminiferal test material, and the fact that biomineralization takes place within the extrapallial fluid in molluscs (i.e. not in equilibrium with the surrounding water) the following points are evident:

(1) Unaltered biogenic calcareous particles are frequently luminescent. This is very important as geologists require unaltered shell material to establish baselines for geochemical studies representative of ancient marine conditions, and luminescence has been used as a criterion in determining alterations. Thus, presence or absence of CL in skeletons does not provide evidence for or against diagenetic alteration of biogenic carbonate.

(2) Using only non-luminescent biogenic carbonate to investigate the past history of sea water may provide a device with which to estimate initial chemical composition, because such material forms under specific environmental and ecological conditions or metabolic processes.

(3) Manganese concentration in the shells of neritic benthic organisms seems to correlate positively with slow growth, open sea conditions and ontogeny, and, but less strongly, negatively correlates with salinity and water depth.

(4) Cathodoluminescence microscopy is useful in detecting minor changes in Mn content which can mimic environmental variations, growth lines, and regenerative areas in calcareous skeletal material.

(5) Much more work needs to be done particularly on Recent ostracoda, brachiopods, crinoids and *Nautilus* which have diverse mineralogical compositions, way of life, and are also important as fossils.

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References

Adlis, S., Grossman, E. L., Yancey, T. E. & McLerran, R. D. 1988. Isotope stratigraphy and paleodepth changes of Pennsylvanian cyclical sedimentary deposits. *Palaios* **3**, 487–506.

Allen, J. A. 1960. Manganese deposition on the shells of living molluscs. *Nature* **185**, 336–7.

Amieux, P. 1987. Description pétrographique de foraminifères par combinaison d'images en lumière naturelle et en cathodoluminescence. *Comptes Rendus de l'Académie des Sciences. Paris* (II) **304**, 741–4.

Ausseil-Badie, J., Favillier, Th. & Giresse, P. 1985. Significations écologique ou diagénétique des variations minéralogiques et chimiques de tests calcaires de milieux marginaux-littoraux ouest africains et méditerranéens: premier bilans. *110ème Congrès National des Sociétés Savantes*, Montpellier, sciences VI, 359–71.

Barbin, V., Ramseyer, K., Decrouez, D. & Herb, R. 1988. Cathodoluminescence des parois de rhodophytes et de foraminifères actuels et fossiles. *12ème Réunion des Sciences de la Terre*, Lille, Société Géologique de France (édit.), Paris, 9.

Barbin, V., Ramseyer, K. & Decrouez, D. 1989. Cathodoluminescence microscopy: a tool for paleoenvironmental investigation. EUG V, Strasbourg. *Terra Cognita* **1** (1), 419–20.

Barbin, V., Decrouez, D., Ramseyer, K., Maier, J. L. & Herb, R. 1989a. Cathodoluminescence applications aux problèmes paléontologiques et archéologiques. *Cristallier Suisse* **4**, 376–86.

Barbin, V., Ramseyer, K., Decrouez, D. & Herb, R. 1989b. Remaniement synsedimentaires de microorganismes: mise en évidence en cathodoluminescence. *Geobios* **22** (2), 253–9.

Barbin, V., Schein, E., Roux, M., Decrouez, D. & Ramseyer, K. in press. Stries de croissance révélées par cathodoluminescence dans la coquille de *Pecten maximus* récent de la rade de Brest (Pectinidae, Bivalvia). *Geobios*.

Blanchard, S. C. & Chasteen, N. D. 1976. Electron paramagnetic resonance spectrum of a sea shell. *Mytilus edulis*. *Journal of Physical Chemistry* **80** (12), 1362–7.

BROECKER, W. S. & PENG, T. H. 1982. *Tracers in the Sea*. Eldigio Press, 690 pp.

BUESTEL, D., GERARD, A. & GUENOLE, A. 1987. Croissance de différents lots de coquille Saint-Jacques *Pecten maximus* en culture sur le fond dans la rade de Brest. *Haliothis* **16**, 463–77.

BOYCOTT, A. E. 1921. Further observations on the occurrence of manganese in land and fresh-water Mollusca. *The Naturalist* June 1, London, 209–211.

BRADLEY, H. C. 1910. Manganese in the tissues of lower animals. *Journal of Biological Chemistry* **8**, 237–49.

BRYAN, G. W. 1973. The occurrence and seasonal variation of trace metals in the scallops *Pecten maximus* (L.) and *Chlamys opercularis* (L.). *Journal of the Marine Biological Association of the United Kingdom* **53**, 145–66.

CARRIKER, M. R., SWANN, C. P. & EWART, J. W. 1982. An exploratory study with the proton microprobe of the ontogenetic distribution of 16 elements in the shell of living oysters. *Marine Biology* **69**, 235–46.

CZERNIAKOWSKI, L. A., LOHMANN, K. & WILSON, J. L. 1984. Closed-system marine burial diagenesis: isotopic data from the Austin Chalk and its components. *Sedimentology* **31**, 863–877.

DEBENAY, J. P., BELLION, Y. & HEBRAD, L. 1987. La biologie d'un mollusque actuel (*Anadara senilis*) appliquée à la paléontologie du Quaternaire récent du bassin sénégalo-mauritanien. *Comptes Rendus de l'Académie des Sciences, Paris* (II) **305**, 807–10.

DEBENAY, J. P., PAGES, J. & DIOUF, P. S. 1989. Ecological zonation of the hyperhaline estuary of the Casamance River (Senegal): Foraminifera, zooplankton and abiotic variables. *Hydrobiologia* **174**, 161–76.

DENIZOT, M., GUELORGET, O., MASSIEUX, M. & PERTHUISOT, J. P. 1981. Une remarquable construction récifale à mélobésiée dans une lagune sursalée du sud-est Tunisien (la Bahiret el Biban). *Cryptogamie: Algologie* (II) **4**, 253–66.

DOROBECK, S. L. 1987. Petrography, geochemistry, and origin of burial diagenetic facies, Siluro-Devonian Hedelberg group, central Appalachians. *American Association of Petroleum Geologists Bulletin* **71**, 492–584.

GORDON, C. M., CARR, R. A. & LARSON, R. E. 1970. The influence of environmental factors on the sodium and manganese content of barnacle shells. *Limnology and Oceanography* **15**, 461–6.

HARRIS, R. C. 1965. Trace element distribution in molluscan skeletal material I. Magnesium, Iron, Manganese and Strontium. *Bulletin of Marine Science* **15** (2), 265–73.

HEMMING, N. G., MEYERS, W. J. & GRAMS, J. C. 1989. Cathodoluminescence in diagenetic calcites: the roles of Fe and Mn as deduced from electron probe and spectrophotometric measurements. *Journal of Sedimentary Petrology* **59** (3), 404–11.

KRINSLEY, D. 1960. Trace elements in the tests of planktonic foraminifera. *Micropaleontology* **6** (3), 297–300.

LONG, J. V. P. & AGRELL, S. O. 1965. The cathodoluminescence of minerals in thin section. *Mineralogical Magazine* **34**, 318–26.

MARSHALL, D. J. 1988. *Cathodoluminescence of Geological Materials*. Boston: Unwin Hyman. 146 pp.

MARTIN, H. & ZEEGERS, H. 1969. Cathodo-luminescence et distribution du manganese dans les calcaires et les dolomie du Tournaisien supérieur au Sud de Dinant (Belgique). *Comptes Rendus de l'Académie des Sciences, Paris* (II) **269**, 922–4.

MARTINI, R., AMIEUX, P., GANDIN, A. & ZANINETTI, L. 1987. Triassic foraminifers from Punta Tonnara (SW Sardinia) observed in cathodoluminescence. *Revue de Paléobiologie, Genève* **6** (1), 23–27.

MASUDA, F. 1981. Chemical composition in marine carbonates as an indicator of paleoenvironment. *Report, Grant-in-Aid, Sciences Research* (C), project N 454262, pp. 1–44.

MERLINI, M., GIRARDI, F., PIERTRA, R. & BRAZZELLI, A. 1965. The stable manganese content of molluscs from Lake Maggiore determined by activation analysis. *Limnology and Oceanography* **10**, 371–8.

MEYERS, W. J. 1974. Carbonates cement stratigraphy of the Lake Valley formation (Mississippian), Sacramento Mountains, New Mexico. *Journal of Sedimentary Petrology* **44**, 837–61.

MILLER, J. & CLARKSON, E. N. K. 1980. The post-ecdysial development of the cuticle and eye of the Devonian trilobite *Phacops rana milleri* Steward 1927. *Philosophical Transactions of the Royal Society* **288**, 461–80.

MILLIMAN, J. D. 1974. *Marine carbonates*. Berlin: Springer-Verlag, 375 pp.

PILKEY, O. H. & GOODELL, H. G. 1963. Trace elements in recent mollusk shells. *Limnology and Oceanography* **8** (2), 137–48.

PILKEY, O. H. & GOODELL, H. G. 1964. Comparison of the composition of fossil and recent Mollusk shells. *Geological Society of America Bulletin* **75**, 217–28.

POPP, B. N., PODOSEK, F. A., BRANNON, J. C., ANDERSON, T. F. & PIER, J. 1986. $^{87}Sr/^{86}Sr$ ratios in Permo-Carboniferous sea water from the analyses of well-preserved brachiopod shells. *Geochimica et Cosmochimica Acta* **50**, 1321–8.

RAMSEYER, K., FISCHER, J., MATTER, A., EBERHARDT, P. & GEISS, J. 1989. A cathodoluminescence microscope for low intensity luminescence. *Journal of Sedimentary Petrology* **59** (4), 619–22.

RICHTER, D. K. & ZINKERNAGEL, U. 1980. Mn-activated cathodoluminescence in Echinoid tests. *International Association of Sedimentologists, 1st European Regional Meeting 1980, Bochum, Abstracts*, 172–6.

RICHTER, D. K. & ZINKERNAGEL, U. 1981. Zur Anwendung der Kathodolumineszenz in der Karbonatpetrographie. *Geologische Rundschau* **70** (1), 276–302.

ROSENBERG, G. D. 1980. An ontogenetic approach to the environmental significance of bivalve shell chemistry. In *Skeletal growth of aquatic organisms* (eds. D. C. Rhoads and R. Lutz), pp. 133–168. New York: Plenum.

ROUX, M., SCHEIN, E., RIO, M., DAVANZO, F. & FILLY, A. 1990. Enregistrement des parametres du milieu et des phases de croissance par les rapports $^{18}O/^{16}O$ et $^{13}C/^{12}C$ dans la coquille de *Pecten maximus* (Pectinidae, Bivalvia). *Comptes Rendus de l'Académie des Sciences, Paris* (II) **310**, 385–90.

RUCKER, J. B. & VALENTINE, J. W. 1961. Salinity response of trace element concentration in *Crassostrea virginica*. *Nature* **190**, 1099–1100.

SAELEN, G. 1989. Diagenesis and construction of the Belemnite rostrum. *Palaeontology* **32** (4), 765–98.

SAELEN, G. & KARSTANG, T. V. 1989. Chemical signatures of Belemnites. *Neues Jahrbuch für Geologie und Paläontologie Abhandlungen* **177** (3), 333–46.

SEGAR, D. A., COLLINS, J. D. & RILEY, J. P. 1971. The distribution of the major and some minor elements in marine animals, part: II Molluscs. *Journal of the Marine Biological Association of the United Kingdom* **51**, 131–6.

SMITH, J. V. & STENSTROM, R. C. 1965. Electron-excited luminescence as a petrologic tool. *Journal of Geology* **73**, 627–35.

SOMMER, S. E. 1972. Cathodoluminescence of carbonates, 2. Geological applications. *Chemical Geology* **9**, 275–84.

THORNTON, S. E., PILKEY, O. H. & LYNTS, G. W. 1978. A lagoonal crustose coralline algal micro-ridge: Bahiret el Bibane, Tunisia. *Journal of Sedimentary Petrology* **48** (3), 743–50.

VEIZER, J. 1983. Chemical diagenesis of carbonates: theory and application of trace element technique. In *Stable isotopes in sedimentary geology* (eds M. A. Arthur, T. F. Anderson, I. R. Kaplan, J. Veizer and L. S. Land), pp. 3–100. Dallas: SEPM short course no. 10.

WARNE, S. ST. J. 1962. A quick field or laboratory staining scheme for the differentiation of the major carbonate minerals. *Journal of Sedimentary Petrology* **32** (1), 29–38.

WILBUR, K. M. 1964. Shell formation and regeneration. In *Physiology of Mollusca* (eds K. M. Wilbur and C. M. Yonge), pp. 243–82. London, New York: Academic Press.

WILBUR, K. M. & WATABE, N. 1963. Experimental studies of calcification in molluscs and the alga *Coccolithus huxleyi*. *Annals, New York Academy of Sciences*, 82–112.