

INTERNATIONAL WORKSHOP IAS - ASF - IGCP 380

MICROBIAL MEDIATION IN CARBONATE DIAGENESIS

ABSTRACT BOOK

ASSOCIATION SEDIMENTOLOGISTES FRANÇAIS

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INTERNATIONAL ASSOCIATION OF SEDIMENTOLOGISTS





International Workshop

^{on} Microbial Mediation in Carbonate Diagenesis



Chichilianne (France)

September 22-24 1997

Convenors : ····

Gilbert CAMOIN INRS, CEREGE, Aix-en- Provence mail : camoin@cerege.fr Annie ARNAUD-VANNEAU CNRS, Université J.Fourier, Grenoble email : aarnaud@ujf-grenoble.fr



PROGRAM



9:00 am: « Microbial mediation in carbonate diagenesis: introduction » (speaker: G. Camoin)

Theme I - « Microbial mediation in carbonate diagenesis: processes »

Keynote: NANNOBACTERIAL MEDIATION IN CARBONATE DIAGENESIS R. L. FOLK

THE POSSIBLE ROLE OF BACTERIA IN THE FORMATION OF COLD SEEPS CARBONATES S. CAVAGNA, C. PIERANGELO & MARTIRE LUCA

EVIDENCE FOR NANNOBACTERIALLY PRECIPITATED DOLOMITE IN PENNSYLVANIAN CARBONATES J. GOURNAY, R. L. FOLK & B. L. KIRKLAND

- 10:30 am: coffee break
- 11:00 am: CRYSTAL ORGANISATION IN SPARRY MAGNESITE OF BACTERIAN ORIGIN J.J.GUILLOU, F. WESTALL & C. VAZ PARENTE

LIMESTONE DIAGENESIS COMPARED FROM THE MICROBIOGEOLOGIST POINT OF VIEW S. CASTANIER, G. LE METAYER-LEVEL & J.P. PERTHUISOT

FROM CARBONATOGENESIS CONCEPTS TO BACTERIAL REGENERATION OF LIMESTONES (MICROBIAL LIFTING) G. LE METAYER-LEVEL, S. CASTANIER, G. ORIAL, J.F. LOUBIERE & J.P. PERTHUISOT

FIRST BACTERIAL PRODUCTION OF MAGNESITE IN ANAEROBIC STRICTLY CONTROLLED CONDITIONS. P. PONTOIZEAU, S. CASTANIER & J.P. PERTHUISOT

-----LUNCH-----

2:00 pm: CALCIFYING CYANOBACTERIA AND CYANOBACTERIAL MICRITE PRODUCTION: ENVIRONMENTAL INTERPRETATIONS M. MERZ-PREIß EXPERIMENTAL MODELING OF MICROBIAL ACTIVITY IN BEACHROCK DIAGENESIS U. NEUMEIER

THE NATURE OF SPONGE-ASSOCIATED BACTERIA G. SCHUMANN-KINDEL, M. BERGBAUER, W. MANZ, J. REITNER, & U. SZEWZYK

CARBONATE AND SILICA PRECIPITATION ASSOCIATED WITH MICROBES IN HOT SPRINGS (>73°C) IN KENYA AND NEW ZEALAND B. JONES & R.W. RENAUT

4:00 pm: coffee break

4:30 pm: Technical workshop on processes in microbial diagenesis

Tuesday September 23

Theme II: « Microbial diagenesis in continental environments »

9:00 am: Keynote: MICROBIAL INDUCED PRECIPITATION IN CONTINENTAL ENVIRONMENTS : TRAVERTINES H.S. CHAFETZ

> INITIAL STAGES OF LAMINAR CALCRETE FORMATION WITHIN DETRITAL SEDIMENTS. EXAMPLES FROM THE TERTIARY OF CENTRAL SPAIN. A.M. ALONSO-ZARZA

CARBONATE PRECIPITATION BY FUNGI IN TERRESTRIAL SEDIMENTS AND SOILS E.P. VERRECCHIA & C. LOISY

- 10:20 am: coffee break
- 10:50 am: DOLOMITE FORMATION IN DISTAL EPHEMERAL LAKES OF THE COORONG REGION, SOUTH AUSTRALIA D. T. WRIGHT

FROM BACTERIA TO CRYSTALS IN KARSTIC WATERS. THE ROLE OF NUTRITIONAL CONDITIONS. J.P. PERTHUISOT, S. CASTANIER, G. LE METAYER-LEVEL & J.F. LOUBIERE

11:40 am: **Poster session**

-----LUNCH-----

Theme III: « Microbial mediation in mud mound development »

2:00 pm: Keynote: MICROBIAL CONTRIBUTION TO REEFAL MUD-MOUNDS IN ANCIENT DEEP-WATER SETTINGS B. R. PRATT

> THE ORIGIN OF THE EARLY DEVONIAN KESS-KESS MUD MOUNDS OF THE EASTERN ANTI-ATLAS (MOROCCO): EVIDENCE FOR SUBMARINE VENTING OF METHANE-RICH FLUIDS Z. BELKA

THE CONTRIBUTION OF MICRITES TO THE STABILIZATION OF CARBONATE MUD MOUNDS H. ZANKL

- 3:20 pm: coffee break
- 4:00 pm: Technical workshop on mud mounds: applications, observations
- 5:30 pm: News from IGCP 380 « Microbialites Processes and products ». (speakers: F. Neuweiler and J. Reitner)

Wednesday September 24

Theme IV: « Stromatolites: development and preservation »

9:00 am: Keynote: STROMATOLITES: DEVELOPMENT AND PRESERVATION R. RIDING

CYANOBACTERIAL MATS IN THE MIOCENE FALUN FORMATION OF TOURAINE J.-G. BREHERET

PARAGENESIS OF HOLOCENE CRYPTIC REEFAL MICROBIALITES, HERON REEF, GREAT BARRIER REEF, AUSTRALIA G. E. WEBB, J. C. BAKER & J. S. JELL

BRYOSTROMATOLITES: AN EVOLUTIONARY MODIFICATION OF STROMATOLITES IN MODERN TIMES J. SCHOLZ 10:45 am: coffee break

11:15 am: Poster session

-----LUNCH-----

- 2:00 pm: Technical workshop on stromatolites: applications, observations
 3:30 pm: coffee break
- 4:00 pm: Technical workshop on continental microbialites

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ENVIRONMENTAL SIGNIFICANCE OF MICROBIALITES IN QUATERNARY REEFS: THE TAHITI PARADOX G. F. CAMOIN, L.F. MONTAGGIONI & G. CABIOCH

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A FERRIC IRON-ENCRUSTED BIOFILM ON A MARINE BIVALVE SHELL: A LIVING MODEL FOR ANCIENT FERRIC-IRON MICROBIAL ECOSYSTEMS? D. GILLAN & C. DE RIDDER

FRESHWATER STROMATOLITES : EXUBERANCE OF THE BIOLOGICAL FELT COMPOSITION, SCARCITY OF PRIMARY SHAPE OF CRYSTALS, AND VARIETY OF DIAGENETIC FORMS OF RECRYSTALLIZATION P. FREYTET & E.P. VERRECCHIA

AN ULTRAMODERN (POST-1947) STROMATOLITIC SYSTEM DEVELOPED IN A SMALL POOL, UPPER GUADIANA RIVER VALLEY (CENTRAL SPAIN). GARCÍA DEL CURA, M.A., GONZÁLEZ, J.A., FERNÁNDEZ, A. & ORDÓÑEZ, S.

BIOLOGICAL INFLUENCE AND DIAGENETIC MODIFICATION WITHIN TRAVERTINE DEPOSITS IN BELGIUM. A. JANSSEN & R. SWENNEN

MICROBIAL MEDIATION IN SECONDARY PRECIPITATION OF PEDOGENIC MICRITE C. LOISY, A. PASCAL & E.P. VERRECCHIA

TUFA DEPOSITION: INORGANIC PRECIPITATION AND ORGANIC TEMPLATES M. MERZ-PREIß

BIOGENIC MUD MOUNDS AND COLD SEEP CARBONATES COMPARED F. NEUWEILER, J. PECKMANN, J. REITNER, C. GAILLARD, P. GAUTRET, V. THIEL & W. MICHAELIS ROLE OF MICROBIAL ORGANISMS IN THE FORMATION OF RED MATRICES, DEVONIAN, MONTAGNE NOIRE A. PREAT, B. MAMET, A. BERNARD & D. GILLAN

THE LOWER PERMIAN ROTLIEGEND STROMATOLITES FROM THE SAAR-NAHE BASIN (SW-GERMANY) ARE UNDOUBTEDLY BIOGENIC BUILDUPS K. R.G. STAPF

ABSTRACTS

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It can be observed that in sediments successions deposed in such "lagunomarine" or "laguno-lacustrine" environments, surfaces of discontinuities with fossilized microbial mats are indicating inversion of paleogeographical and sedimentological trends (*R. AINARDI*, 1992, Intern.Symp.Seq.Stratigr.,Eur.Bas., Dijon).

Inside such microbial mats and evaporites crusts, the development of cyanobacteria and other microorganisms like sulfate-reducing and sulfuroxidizing bacteria, induces chemical transformations during early diagenesis. Gypsum crystals were changed into carbonates ; this transformation of sulfates gave from a part calcium-carbonates and liberated sulfur. A simultaneous presence of metals contained would produce the appearance of sulfides (R... AINARDI, 25ème Annivers.SGA, Nancy., Proceedings in : "Source, Transport and Deposition of Metals", Pagel & Leroy (eds), 1991, Balkema, Rotterdam).

INITIAL STAGES OF LAMINAR CALCRETE FORMATION WITHIN DETRITAL SEDIMENTS. EXAMPLES FROM THE TERTIARY OF CENTRAL SPAIN.

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INTRODUCTION. - Laminar calcretes have been the aim of many studies during the last 30 years, however discussion on their origin still goes on. Thick laminar calcretes profiles have recently been interpreted as multiple phases of erosion, deposition and soil formation occurring at the top of the soil. The aim of this paper is to discuss the origin of thin carbonate laminae whose morphology and texture indicate that they are the initial stages of formation of thick laminar calcretes. For this study we have selected three different paleosol profiles developed on clay to coarse sand substrates. The profiles are Miocene in age and were developed on distal alluvial fan deposits from the Madrid Basin (Paracuellos de Jarama profile) and Duero Basin (Villacadima and Viñegra profiles). In all cases the degree of development of the laminar calcrete is very low so we can isolate the different laminae.

VILLACADIMA PROFILE. It consists on several horizontal carbonate laminae intercalated on the detrital substrate (red sandy clays). The base and top of the profile are gradual. Maximum thickness is 50 cm. The carbonate laminae are from several to 10 cm in thickness, they are very indurated and mostly consists thinner individual laminae of about 3 mm formed by alveolar septal structure, peloids and micritic coated grains and etched detrital grains within an equigranular mosaic of calcite crystals. In some cases a network of micritic filaments can be observed within the calcite crystals as well as on the detrital grains. Under the SEM the micrite laminae consist on a porous mosaic of subehedral to anhedral calcite crystals of about 0.3 μ m wide arranged on mucus or organic films that show spherical and tubular voids of about 1.5 μ m in width. Larger and more euhedral calcite crystals occur irregularly distributed within the micrite.

PARACUELLOS PROFILE. In the Paracuellos de Jarama area the profiles, developed on sandy clays, consist on three different horizons: bioturbated clays, prismatic and platy horizons. Mean thickness of the profile is 1.5 m, being the base very gradual and the top very sharp. The carbonate laminae occur within the bioturbated clays as well as in the platy horizon. They are horizontal and its length of several dm, width averages 5 mm. The carbonate laminae and/or veins consist of calcite and/or dolomite crystals up to 20 μ m across. In some cases the arrangement of the crystals follow a concentric pattern so in the innermost part of the laminae the crystals are isodiametric and do not show intracrystalline porosity. This zone is coated by a micritic ring. In the outermost area the crystals are elongated and do not show intercrystalline porosity.

VIÑEGRA PROFILE. The paleosol profiles developed on coarse arkoses and are up to 2 m thick. The carbonate laminae are mostly horizontal although some vertical ones connect different levels of horizontal ones. The laminae ranges 3 to 30 mm in width and their lateral extent reach a few metres. The laminar horizon is overlain by a fine and irregular network of calcified roots that form the uppermost horizon of the profile.

The carbonate laminae/veins are formed by very porous and soft micrite. The pores are spherical in transverse section and tubular in longitudinal ones. SEM images show that the detrital grains and clay are coated by mucus or organic films. Messes of needle fibre calcite lies on the organic films. The arrangement of the messes follows a "tissue-like" pattern as they do not coat homogeneously all the film but only areas surrounding circular zones of about 5 μ m across. The messes of needles are connected among them and sometimes may form balls of needles up to 1 μ m in diameter. The needles are of 1-2 μ m in length and 0.1 μ m in diameter. Longer filaments up to 100 μ m occur associated with the organic films and coating the detrital grains.

DISCUSSION. - The three studied profiles are very similar as the distribution of carbonate is concerned. In Villacadima the texture of the carbonate laminae indicate calcification around small root structures. The common occurrence of alveolar septal structures and the recognition of micritic filaments may indicate associations between roots and fungi (Mycorrhizae type). In Paracuellos the size and arrangements of the crystals indicate calcification of cell-walls of roots (Alonso-Zarza *et al.*, in press). In the third study case the interpretation is more difficult as only the porosity of the root is preserved, however the occurrence of mucus, filaments and needle fibre crystals indicate an important microbial activity related with the radicular systems.

In all the study profiles the occurrence of carbonate laminae seems to be related with root activity and the associated microorganisms. The arrangement of the laminae within the profiles indicates that their formation occurred in relation with the buried part of the plant and not in direct contact with the atmosphere. The low pegodenic weathering of the host indicates poorly developed soils in which pedogenesis is mostly reflected in the formation of the laminae. These laminae formed when sedimentation rate was relatively low and episodic so that the radicular system may progressively occupy higher topographic positions, giving place to the formation of different carbonate veins separated by clastic sediments. If the sedimentation rate is very low different laminae will tend to occupy similar positions allowing the development of thicker and harder laminar crusts, sometimes called rhizogenic calcretes (Wright *et al.*, 1995) or rootcretes (Jones, 1992). However, our study has not considered other laminar crust formed by spherulites (Verrecchia *et al.*, 1995) on the uppermost part of the soil.

REFERENCES

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Wright, V.P., Platt, N.H., Marriott, S.B. y Beck, V.H. (1995). Sediment. Geol., 100, 143-158.

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THE ORIGIN OF THE EARLY DEVONIAN KESS-KESS MUD MOUNDS OF THE EASTERN ANTI-ATLAS (MOROCCO): EVIDENCE FOR SUBMARINE VENTING OF METHANE-RICH FLUIDS

Z. BELKA

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Spectacular conical Early Devonian mud mounds up to 55 m high outcrop in the eastern Anti-Atlas of southern Morocco. The mounds constitute massive structures which in the field appear to be composed of a single lithology. There is no differentiation into a core facies and flank strata. Coarse detrital deposits or slumping phenomena are absent on the flanks. The mound facies is predominantly composed of skeletal wackestones and mudstones riddled by common small-sized stromatactis cavities. Small tabulate corals (auloporids, thamnoporids, and favositids) are the most abundant organisms, displaying an exceptionally high diversity.

A total absence of stromatoporoids and calcareous algae is a feature of the Kess-Kess mounds. Conodonts, trilobites, and dacryoconarids prove the Emsian age (*inversus* Zone) of the buildups, which are essentially microbially mediated mud mounds developed in a deep-water environment on the Hamar Laghdad elevation created by a submarine eruption.

During the Lochkovian, basaltic glassy lava was issued on the sea floor and amalgamated with wet sediments to form up to a 100 m thick peperite complex. Its deposition created obviously a flat submarine rise which subsequently became a site of extensive crinoid colonization. At the moment, it is not clear whether the crinoid colonization had profited at that time from volcanic emanations, or whether the crinoids and other benthic organisms only used enhanced water circulation at this place. The isotopic data point to the marine character of the early cements in these carbonates. The mud mounds occurrence coincides well with the greatest thickness of the crinoidal limestones. In addition, they show a distinct trend in their spatial distribution, following a network of radial and tangential faults which were formed during Emsian times as a result of the doming caused by the underlying subvolcanic laccolithic intrusion. Geochemical results (REE data) although only at a preliminary stage document that the mound carbonates and the calcite cements in the neptunian dykes were precipitated from brines constituting a mixture of hydrothermal fluids and sea-water. The radial and tangential faults served as conduits for ascending hydrothermal fluids, the origin of which was the magmatic centre beneath the Hamar Laghdad. The springs were dynamic and episodically active until the Famennian but only during the Emsian were the vents sites of extensive carbonate production.

The carbon isotopic signals recorded in the mound carbonates have a complex origin resulting from the mixing between different carbon reservoires. Typical is a strong depletion in ¹³C (between -4 and -18 ‰ PDB) which suggests a contribution from thermogenic methane derived from the underlying basaltic intrusives. Aerobic bacterial oxidation of methane is favoured as a main process driving the carbonate precipitation and the rapid lithification of the mounds. The bacterial "infection" of the vent sites, stimulated and controlled by fluids entering the carbonate system on the sea floor, possibly played the crucial role in the origin of the Kess-Kess mounds.

TOURAINE (FRANCE)

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During Miocene, shelly sands have been deposited in a large gulf opened in the western part of the Bassin de Paris. Their accumulation gave a formation known as the Faluns de Touraine. Coastal facies have been evidenced on the edges of this gulf, particularly in the areas of Blois (East) and Savigné-sur-Lathan (North).

Several sections exposed in the Blésois quarries (eastern part) display sands filling tidal channels. The neritic environment is otherwise evidenced by the fauna, mainly oysters. Rip up clasts are very numerous in certain channels, and microslumps are frequent. They originate from erosion and reworking of the superficial mats of tidal flats. They are composed of a chalky material, more or less pulverulent. Microscopical and XRD investigations reveal low-Mg calcite rhombs of several microns size.

In a quarry of Saint-Laurent-de-Lin located in the north-western area, close to Savigné-sur-Lathan undisturbated tidal rhythmites are recorded ; they are characterized by a regular lamination. It is composed of millimeter sized alternating layers which are made of terrigenous detrital silts on the one hand, and of homogeneous carbonate silts on the other. These carbonate silts are composed of small low-Mg calcite rhombs quite comparable to the material observed in the Blésois quarries. No evidence of mud cracks or root imprints have been found ; bioturbations are very rare. In the lower part of the section, cross-bedded sands are preserved corresponding to small fillings of tidal channels. They display abundant carbonate rip up clasts. Thanks to microscopic investigations, some of these clasts show obvious microbial remnants which can be reported to filamentous cyanobacteria.

The lamination expressed by the alternation of terrigenous and carbonate layers is intepreted as the result of both physical and biogenic processes. The carbonate layers may be the by-product of a algal or microbial activity to say the calcite precipitation occuring on an organic substrate provided by cyanobacterial sheaths (or diatomophyceae ?) as it may be suggested by the obvious remnants of filamentous cyanobacteria discovered in some cases. As calcified cyanobacteria are essentially absent from marine environments from the beginning of the Cenozoic, the occurences reported here suggest a strong supply of fresh water in the coastal environment evidenced.



SIGNIFICANCE OF THE STROMATOLITES ENCOUNTERED IN THE UPLIFTED TASMALOUM FRINGING REEF (SW ESPIRITU SANTO, SW PACIFIC).

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In the tropical zone of the South-West Pacific Ocean, at the convergent boundary of the Australian and Pacific Plates, the subduction of the d'Entrecasteaux ridge system has caused rapid uplift of the central New Hebrides island arc. A maximum uplift rate of 6 mm.yr⁻¹ occurs along the southwest coast of Espiritu Santo Island (15°S), near the plate boundary. Along this coast, at Tasmaloum, an emerged Holocene reef shows a series of narrow and broad terraces, which suggests a continuous process of uplift with only brief intervening pauses. We drilled this emerged Holocene reef to depths as great as 40-45 m, in order to recover the past 20 ka of reef growth.

Colonization of the Tasmaloum fringing reef occurred by 24 ka, upon a pre-reef substrate composed of a huge bioclastic sand formation accumulated during a part of the last glacial period. During the post glacial sea level rise, the vertical succession of reef assemblages reflects environmental and bathymetric variations with time. Bathymetric variations suggest that the uplift rate may have not been constant during the last 24 ka. Changes of reef growth pattern, particularly clear from 15 to 12-10 ka, imply an increase of uplift rate.

Stromatolites are found in abundance from 16 to 12-10 ka, a period of very fast sea-level rise (Fairbanks, 1989), during which sea surface temperatures varied significantly (Beck *et al.*, 1997). After 6 ka, which corresponds to the time of sea level stabilization, stromatolites disappear within the assemblages. This period constituted a generally more favorable period for reef growth. This is particularly well explained by changes in sea surface temperatures recorded through isotopic methods in a number of *Porites* (Beck *et al.*, 1997) : sea surface temperatures are very close to present in the youngest corals, but several degrees lower than Present in the oldest corals (from 5 to 10.3 ka).

Nevertheless, other parameters may occur. Relationships have been established between the abundance of stromatolites and terrigeneous inputs in the Tahiti barrier reef (Camoin *et al.*, submitted) and in the Great Barrier Reef (Reitner, 1993). In the Tahiti reef, the highest abundance of stromatolites is linked with an enrichment of interstitial waters in nutrients by meteoric groundwater, that provides an increase of the carbonate alkalinity by intense weathering of basalts and soils. In Vanuatu, this scenario seems to be slightly different. Because Espiritu Santo is intermittently uplifted, the fringing reef may emerge at times, so that freshwater and terrigeneous inputs may have been abundant. Although these uplift movements continued after 6 ka, stromatolites disappear within the assemblages. One explanation may be related to nutrient input changes : 1through the establishment of a new hydrologic and oceanographic regime during the stabilization of sea level, accompanied by, in particular, warming of tropical waters (see above) or 2- through the increase of the uplift movements yielding a rapid alternation between meteoric groundwater and marine environments and preventing stromatolites to grow favorably in cryptic niches.

ENVIRONMENTAL SIGNIFICANCE OF MICROBIALITES IN QUATERNARY REEFS: THE TAHITI PARADOX

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Drill cores from the barrier reef-edge of Tahiti exhibit 85 to 93 m thick coralgal sequences recording at least 13,500 years of continuous reef growth. The cored reef sequences form an overall shallowing-upward succession with assemblages of gracile or domal colonies of Porites at the base overlain by a robust-branching community (Acropora danai /A. robusta assemblage) thickly encrusted by coralline algae, sessile vermetid gastropods and arborescent usually composed of laminated foraminifers. Microbialites, crusts (« stromatolites ») and clotted micritic masses (« thrombolites »), form mm to cm-thick locally up to 20 cm coatings over coral branches, or more commonly, over related encrusting organisms, thus appearing as a major structural component of the reef framework (average volume of 40% and up to 80%). The dominance of stromatolites in large pores in robust acroporid frameworks indicates that they were more light-(and possibly energy-) dependent than the thrombolites. These formed in reduced light and energy conditions, in association with deeper coralgal associations and in residual pores of shallower coralgal assemblages where they overgrow stromatolite crusts. However, both types of microbial coatings are commonly associated, forming compound crusts where thrombolites are usually the last stage of encrustation.

The crusts are characterized by planar or wavy laminae that may have little lateral persistence, and surfaces usually display bulbous or domal accretions. Their distribution shows that crusts have grown upwards or centripetally from the margins of the pores. Their internal structure consists of clotted to dense micrite that may include the remains of cyanobacterial filaments; clots and peloids range in size from 5 to 50 μ m.

The relative scarcity of extraneous particles and the abundance of microbial remains in the micritic crusts suggest that trapping and binding processes were less important than calcification of microbial mucilaginous material and in-place, microbially-mediated, precipitation of micrite. Rapid lithification may be deduced from the occurrence of borings in the crusts.

X-ray diffraction analyses indicate that the major carbonate mineral in the micritic crusts is a high-magnesium calcite, containing 7 to 16 mole percent MgCO₃. The micritic crusts exhibit a narrow range of carbon and oxygen isotope values, ranging from +2.05 to + 3.92‰ δ^{13} C PDB (average: +3.37‰; n=41) with a standard deviation of 0.03‰ PDB and -0.86 to +0.86‰ δ^{18} O PDB (average: 0‰; n=41) with a standard deviation of 0.04‰ PDB.

The nature of the biological communities, stable isotope data and high $CaCO_3$ accumulation rates indicate that environmental conditions have been optimal for reef growth for the last 13,500 years. The widespread development of microbialites in the reef framework may be related to periodic runoff and terrestrial groundwater seepage which induced an increase in nutrient availability and alkalinity in interstitial waters during reef growth from 13,500 to about 5,500 yrs B.P. The sharp decrease in microbialite abundance at 7 m.b.r.s. is dated at 5770±100 ¹⁴C yr B.P. and predates slightly the stabilization of sea level to its present position.

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LIMESTONE GENESIS CONSIDERED FROM THE MICROBIOGEOLOGIST POINT OF VIEW.

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In nature carbonate precipitation may theoretically occur following several known processes : i. abiotic chemical precipitation from saturated solutions by evaporation, temperature increase and/or pressure decrease; ii. lowering of CO_2 pressure under effect of autotrophic processes (photosynthesis, methanogenesis...); iii. passive and active heterotrophic bacterial production; iv. external or internal skeleton production by eucaryots. Both former processes are limited by the amount of carbonate and bicarbonate ions in the medium, which is generally very low apart in a few continental environments. Furthermore, photosynthesis of eucaryots is balanced by respiration so that only cyanobacteria and other photosynthetic bacteria may play a geological role through this process. Thus, apart from stromatolitic formations, such processes hardly account for extent limestones sedimentation or diagenetic carbonate cements formation.

Several series of experiments in the laboratory as well as in natural conditions teach that the production of carbonate particles by heterotrophic bacteria follows different ways. The "**passive**" carbonatogenesis is generated by modifications of the medium that lead to the precipitation of solid particles. It is induced by several metabolic pathways which are : i. the ammonification of amino-acids or urea in aerobiosis; ii. the dissimilatory reduction of nitrates in microaerophily or in anaerobiosis; iii. the dissimilatory reduction of sulphates in anaerobiosis. The "**active**" carbonatogenesis is independent of the mentioned metabolic pathways. The carbonate particles are produced by ionic exchanges through the cell membrane following still poorly known mechanisms such as the activation of calcium pumps (Castanier, 1987; Castanier *et al.* 1997)

Carbonatogenesis appears to be the response of heterotrophic bacterial communities to an enrichment of the milieu in organic matter. After a phase of latency, there is an exponential increase of bacterial strengths together with the accumulation of metabolic end-products. These induce an accumulation of carbonate and hydrogenocarbonate ions in the medium and, by different ways, a pH increase that favours carbonate precipitation. This phase ends into a steady state when most part of the initial enrichment is consumed. Particulate carbonatogenesis occurs during the exponential phase and ends more or less after the beginning of the steady state. The active carbonatogenesis seems to start first. It is followed by the passive one which induces the growth of initially produced particles.

Quantitatively, the production of solid carbonate depends essentially upon the strain or the used bacterial population, the environmental conditions (temperature, saltiness, etc.), the quality and quantity of available nutrients, and time. To date, among number of experiments undertaken in the Microbiogeology Service of the Laboratory of Biogeology of the University of Nantes, the record of production has been obtained with a strain of Bacillus sp. cultivated on a medium of Castanier (1984). With a nutritive input of 4 grams of organic matter, 2.4 grams of solid carbonate (calcite) were obtained per litre and per day (Le Métayer-Levrel, 1996), that is to say an output around 60% (weight of produced calcium carbonate / weight of provided organic matter). Such a production would correspond to approximately 880 kg of calcite per m³ and per year i.e., given the density of calcite (2.7), the deposition of a compact limestone layer ca. 32 cm thick (on 1 m²). This represents the totality of the calcium carbonate dissolved in a column of present normal sea water, 1 m² in section, 3700 m in depth. The precipitation of 32 cm of limestone in a year under effect of evaporation would imply that 70% i.e. 2600 m of the initial water column should evaporate in a year. The experimentally obtained solid productions with carbonatogenic strains were always found higher than 0.8 grams for the same 4g organic matter input that is an output of 20%.

When considering only marine and paralic environments, organic matter sedimentation is comprised between 20 and 10,000 g m⁻² y⁻¹ (Basson *et al.*, 1977; Allen *et al.*, 1979). Given mentioned extreme outputs, this should lead to a solid carbonate sedimentation comprised

between 4 and 6,000 g m⁻² y⁻¹ i.e. a yearly limestone layer between 1.5 μ m and 2.20 mm thick. Mentioned numbers concern experiments with monospecific strains. In nature, carbonatogenesis is generally carried out by plurispecific populations so that sedimented organic matter may be totally mineralised into carbonates.

The yield of heterotrophic bacterial carbonatogenesis and the amounts of solid carbonates production by bacteria are potentially very high as compared to autotrophic or chemical sedimentation from marine, paralic or continental waters. Furthermore, bacterial heterotrophic carbonatogenesis is neither restricted to particular taxonomic groups of bacteria nor to specific environments so that it has been an ubiquitous phenomenon since Precambrian times : it just requires organic matter enrichment. Thus, heterotrophic bacterial carbonatogenesis much more likely accounts for azoic (or apparently abiotic) limestones deposition and for carbonate cementation than any other process. As far as biodetrital particles are concerned, one must observe that the carbonate shells and tests of organisms are built from their mitochondria (or chloroplasts) activity. Other organites may be involved such as Golgi apparatus (Hemleben *et al.*, 1986). These cellular organites are nowadays considered by number of biologists as endosymbiotic bacteria (Margulis & Sagan, 1986).

Thus, apart from (probably mythical) purely evaporitic and autotrophic ones, all Ca and/or Mg carbonates must be considered as from heterotrophic bacterial origin. By the way, the carbon of carbonates comes from primary organic matter, which asks questions about interpretations from isotopic data on carbonates.

Such considerations may also provide renewed conceptions over genesis of azoic limestones, their deposition rates, their initial consistency and stability (slumping), and their diagenesis. Finally, bacterial heterotrophic carbonatogenesis appears as a fundamental phase in the relationships between atmosphere and lithosphere and in the geobiological evolution of Earth.

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THE POSSIBLE ROLE OF BACTERIA IN THE FORMATION OF COLD SEEPS CARBONATES

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In the last twenty years the explorations on the ocean floor have played a key role in the discovery of many examples of hydrocarbon seeps and vents in different geological settings. Many mussels, clam bivalves, tube worms have been observed in these hydrocarbon venting sites. Active deposition of carbonates (characterized by δ^{13} C strongly negative values), sulphides and sulphates have been reported from these sites, too. Microbial mats were collected in the hydrothermal vent areas in the Pacific Ocean (Jannasch *et al.*, 1989) and in the Gulf of Mexico (Larkin *et al.*, 1994). The predominant microorganism in these mats is the giant bacterium *Beggiatoa* that builds mats at the water-sediment interface and seems to act as a borderline between the anoxic sediments beneath it and the oxic water column above. Because of its ability to oxidize sulphide and fix CO₂, *Beggiatoa* plays an important role in sulphur and carbon cycles near hydrocarbons vents (Larkin *et al.*, 1994). These recent cold-vent studies have contributed to the interpretation of some anomalous carbonate-rich rocks as the fossil record of this process.

Some outcrops of unusual carbonate rocks have been recognized in the terrigenous Tertiary sequence of the western Monferrato hills (NW Italy). In this area two different types of carbonates occur. The *Lucina* limestones (Clari *et al.*, 1988) are cream-light brown marly limestones packed with large bivalve remains. The Marmorito limestones (Clari *et al.*, 1988) are grey calcite- and dolomite-cemented mudstones and sandstones crosscut by calcite veins and barren of fossils. The geochemical analyses, the comparison between the organic communities living by the actual venting sites and the mussels present in the *Lucina* limestones led to interprete these rocks as the geological result of a process related to cold vents of methane-rich fluids. The dense communities of clams observed on the ocean floor are quite similar to the blocks packed with large bivalves remains found in the Monferrato region.

Ancient cold-seeps communities have been reported from different places and several names have been proposed to call these rocks: pseudobioherms (Gaillard *et al.*, 1992), chemoherms (Aharon, 1994). What is clear is that chemosynthetic life occurs in the vicinity of seeps where early diagenetic carbonates precipitate and that bacterial mediation in hydrocarbon oxidation and sulphate reduction is an important link in the anomalous food chain of cold-seep communities. The aerobic and anaerobic CH_4 oxidation led both to the dissolution of skeletal carbonates and to the precipitation of sulphide and carbonate cements in pore spaces and veins at different depths in the sediment column (Fig. 1). Also the model proposed for the interpretation of Marmorito limestones implies an important role of hydrocarbon venting because of strongly depleted δ^{13} C values of the carbonate phases. In this case the carbonate precipitation took place at very shallow burial depths: these rocks are barren of fossils and show no trace of surface exposure (burrowing, boring); therefore the carbonate precipitation must have occur at a certain distance from the watersediment interface, but not too deep because the porosity of the sandstone was still high. Do bacteria play an important role in this case, too or not? Are they responsible for the different carbonate phases that can be distingushed in both pore-filling and cavity-filling cements (dolomite, calcite, aragonite)?

Some direct evidence of bacterial activity are provided by several structures and fabrics of carbonate cements that are similar to those described in environments where the role of bacteria on carbonate precipitation is well documented:

• the abundant pyrite fraction present in the groundmass of these carbonates is an important evidence of the presence of sulphate-reducing bacteria. The samples collected from present ocean floors show pyrite tubules that may represent fossilized *Beggiatoa* (Larkin *et al.*, 1994);

• laminated sediments evidenced by textural changes and by interposition of thin cement layers between two laminae;

• presence of peloids of microcrystalline aggregates and of small ehuedral to subhedral dolomite crystals;

• presence of dolomite sphaerulites consisting of: large aggregates with a fibrousraggiate structure;

• ongoing studies by epifluorescence-microscopy show that cloudy and filamentous calcite structures found in Marmorito limestones contain high concentrations of organic matter; combined gas chromatography and mass spectrometry revealed the presence of biomarkers in the organic extracts of these limestones (J. Peckmann, personal communication).

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BACTERIAL PROCESSES			SEDIMENTARY DIAGENETIC EFFECTS	
9		sea water O2 SO4		
DIFFUSE FLOW	Aerobic → CH₄ oxidation		Carbonate precipitation?	0
		- $ -$	Skeletal carbonate dissolution	Ň
	Anaerobic → CH₄ oxidation →	HCO3	Intergranular carbonate precipitation	SULPH.
	Sulphate	H ₂ S	Sulphide precipitation	ANOX
CHANNELLIZED FLOW	Aerobic and anaerobic → CH₄ oxidation in veins and cavities		Peloidal internal sediments	ROENV.
		HCO3	Complex carbonate cement precipitation	OX. MIC
			Aragonite cement partial dissolution	OX./AN

Fig. 1



MICROBIAL INDUCED PRECIPITATION IN CONTINENTAL ENVIRONMENTS: TRAVERTINES

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Bacterially induced precipitates have been recognized from samples which come from a wide variety of non-marine environments and deposits, including pedogenic, lacustrine, caliches, freshwater stromatolites, etc. The best documented occurrences are from hot water travertine systems.

Bacterially induced precipitates within hot water travertines (~20°C and above) range from individual dumbbell-shaped forms, generally less than 10 μ m long, to equi-dimensional silt-sized grains, to shrubs that most commonly are 1 to 4 cm in height. These precipitates have been reported from many hot water travertine systems, and bacterially induced precipitates are also likely present, though not as abundant and/or conspicuous, in cold (ambient temperature) water systems. Normal, submicron-sized, bacteria, as well as nanobacteria, have been recognized as integral components within these travertines. Interesting aspects of these deposits include: the relationship between micron-sized aragonitic aggregates and coarse calcitic spar crystals, the gradational relationship between shrubs and ray crystal deposits, and the origin of Mn-rich black shrubs.

Small crystal aggregates (e.g., dumbbells, spherulites) are commonly formed in hot water travertines and are essentially identical to aggregates formed by bacteria under controlled laboratory conditions. The aggregates, in both cases, are generally 5 to 10 μ m long, have clumps of bacteria at their centers, and are composed of aragonite. Coarser calcite crystals are intermittently associated with the bacterially induced aragonitic aggregates. Cylindrical holes pierce many of the calcite crystals and indicate that these crystals formed diatom stalks. It is believed that the vital activity of the bacterial clumps changed the microenvironment in their immediate surroundings to a higher state of supersaturation. As a result, the aragonite aggregates precipitated, enveloping the bacterial clumps, whereas immediately adjacent to them, the coarse calcite crystals formed around the stalks of the diatoms.

The most conspicuous bacterially induced precipitates within hot water travertines are the shrubs, bush-like forms which have a gross morphological similarity with the common garden variety woody plant. The shrubs are morphologically similar to the clotted and dendritic forms of *Epiphyton* and *Renalcis* (this similarity is believed to be due to a similar bacterially induced origin). The bacterially induced calcitic shrubs grade into dominantly abiotic (physico-chemical) calcitic ray crystal deposits; the two end members display similar megascopic morphologies. Hybrid forms exist between the dominantly biotic shrubs, at one end, and the dominantly abiotic ray crystal precipitates, at the other. The abiotic ray crystal deposits attain maximum heights in excess of a meter. The ray crystal growth, such as vent orifices and the edges of rimstone pools. These are sites of rapid CO₂ degassing, and thus, high saturation states, which lead to high abiotic rates of precipitation. Petrographic examination of ray

crystal accumulations show that, although they are predominantly an abiotic precipitate, they contain microscopic shrubs co-incident with the crystal growth lamina that cross the long axes of the ray crystal fabrics. Evidence for the micro-shrubs is not readily apparent in the megascopic morphology of these dominantly abiotic ray crystal structures. Thus, even though these are abiotically dominated precipitates, bacterially induced precipitation plays a role in their formation.

Black Mn- and Fe-rich shrubs, similar in essentially all other aspects to the shrubs described above, occur in Moroccan travertines. The shrubs are dominantly composed of a variety of Mn minerals, including pyrolusite, cryptomelane, and goethite. SEM analyses show that bacterial bodies are densely packed within the Mn-rich black travertine shrubs, whereas no bacterial bodies are evident within the enclosing aragonite and calcite laminae. The bacterial bodies range in shape and size from rods (commonly 0.8 μ m long by 0.1 μ m in diameter), to spherical forms (commonly 0.3 μ m in diameter) which comprise rods up to 1 μ m long, to nanobacterial spheres (150 to 200 nm in diameter) which make up densely packed chains commonly 15 μ m in length. The black Mn-rich shrubs are believed to be genetically related to features such as desert varnish, deep sea Mn-nodules, and *Frutexites*, i.e., all are the result of bacterially induced precipitation.

These precipitates indicate the variety of deposits that are induced by the vital activity of bacteria within travertines.

TRANSITIONAL FACIES ANALYSIS AND PETROGRAPHIC OBSERVATIONS IN HOLOCENE TRAVERTINE CHALKS FROM SOUTHEASTERN FRANCE

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Fluvial quaternary travertine sedimentary sequences and their paleoenvironmental setting have been studied (Magnin *et al.* 1991). In these sedimentary sequences, the vertical succession is, from bottom to top : gravels, silts, chalks, travertines s.s. (moss to algal laminated facies), travertinous sands and finally, silts. The study of malacofaunas (Magnin, 1991) demonstrated that maximum qualitative development of travertines (stromatolitic encrustations) corresponds to maximum extension of forest cover. Travertines developments seem to be connected with warm and wet climatic phases (Hennig *et al.* 1983 ; Viles & Goudie, 1990). For the Holocene, the optimum of travertine formation took place during Atlantic period. The decline of travertines, which started during the mid-Holocene, may be explained by anthropogenic pressure on the environment (Goudie *et al.*, 1993).

The "canal EDF" section at Meyrargues (Bouches-du-Rhône, France), where the typical sedimentary sequence has been described, represents the lower half of the sequence. Travertine chalks are particularly well represented in this section and show a fine and complex macroscopic stratification.

According to the fact that chalks precede the optimum facies of the travertine sequence (travertine s.s.), a sedimentological study revealed the existence of a gradual evolution in the deposit environment. The results, including textural, granulometric, densimetric, geochemical, mineralogical and petrographic analyses, show the existence of gradients. From bottom to top, sediments become more sandy, carbonates rates of the sand fraction increase from 92% to 100% and the silt/clay fraction from 84% to 98% with a minimum of 74%. The organic matter rate falls from 2.3% to 1%. Mineralogical and petrographic analyses reveal the increase of the calcitic encrustations (bed veneers, oncoids, cementations around plants or vegetal fragments) and the coevaldecrease of clastic elements.

A transitional facies analysis involving macroscopic field observations and laboratory results was carried out. An example of the application of a transitional facies analysis for the study of lake deposits was published by Blanc (1991). I applied the same analysis with travertine chalks. Transitions observed on the section were noted and integrated in a data matrix, and calculations were realised according to the Selley's method (1969). A residual matrix was calculated, which allowed to express significant predictable relations, certain, for the series (Gingerich, 1969). Quantitative sequential analysis gives prominence to foreseeable transitions between some facies. Two main successions have been found. The first one, with a very high probability, is represented by the succession of travertinous sands to grey silts. The second one, with a high probability, is represented by the transition of grey silts associated with travertinous sands to light silts associated with travertinous sands and then to travertinous sands only. The results show the existence of a predictable evolution interrupted by uncertain transitions. This semimarkovian model of evolution, proves that the sequence must be determined by paleoclimatic conditions.

Microscopic observations have been realised to confirm results mentioned above. The silt/clay fraction contents is mainly composed of microcrystalline calcite. Biologic calcite crystals are represented by numerous acicular crystals (fungi products) and, in small proportions, a few cellular pseudomorphs after calcium oxalate crystals (ashes from Angiosperms). A lot of spherical particles (20- $25 \mu m$) formed with calcite crystals seem to be carbonate encrustations related to bacterial biocrystallogenesis (Adolphe, 1986).

A few clastic particles such as coccoliths, quartz and charcoals also occur.

The transitional facies analysis shows that the formation of travertine chalks, marked by successive transitions from detrital facies to pure biogenic carbonates, is environmentally and climatically- controlled.

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NANNOBACTERIAL MEDIATION IN CARBONATE DIAGENESIS

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Nannobacteria are dwarf forms in the 0.03- to 0.25-µm range, intermediate between "normal" bacteria (about 1 mm) and virus particles (usually 0.01 to 0.02 µm). They were first discovered on the sulfurous hot springs of Viterbo, Lazio, Italy, and have since been found in a great many rocks and minerals worldwide, including all the carbonates, sulfur, chert, metallic sulfides, and even clay minerals. Shapes are most commonly spherical, but they can range up to bean, caterpillar, and beaded filament forms. In carbonate rocks some can be seen without any treatment, but in most rocks they are made much more obvious by brief etching (1% HCl for 1 minute). It is of the utmost importance to gold-coat the specimen for 30 seconds or less; otherwise many "nannobacteria-looking" artifacts can be produced. Magnification of 35,000-100,000X is usually required to adequately resolve the small bodies and confirm their biological shapes. Nannobacterial cells minutes old (e.g., in hot springs) look exactly like cells more than 2 billion years old; so they are easily fossilized. Because of the negative charge of their cell walls, they collect cations and cause local supersaturation on a submicrometer scale, initiating the formation of carbonate minerals of all types.

Nannobacteria are abundant in subaerial environments such as travertines, streams, lakes, and soil calcretes. In Bahaman oolites and other oolitic sediments the nannobacteria precipitate aragonite needles of cylindrical shape, 0.1 mm in diameter, with bodies of matching size at their tips. Some Bahaman needles and hardground cements are made of regular rows of minute particles of about 0.02 mm, in the size range of viruses. The fact that viruses, because of their electrical charges, can arrange themselves in regular geometrical arrays makes it not too far-fetched to suppose that they can precipitate minerals as well.

Carbonate cements in limestones, whether aragonite, calcite, or magnesium calcite, are commonly precipitated wholly by or at least initiated by nannobacteria. Some cements are solidly nannobacterial bodies; in others they are sparse or occur only at the bases of the crystals. Some micrites and pellet rocks contain abundant bodies; others contain few. Microbial mats are sometimes full of bodies; others are sparse. The reason for the sporadic occurrence is unknown; in some microenvironments there may be a tendency for the bodies to be eaten instead of preserved.

Many dolomites, both early (aphanitic) and late replacement, are found to be rich in nannobacteria when etched with 10% HCl for 10 minutes. Nannobacteria are vastly more abundant than "normal" bacteria in carbonate rocks, and their biomass is probably an order of magnitude greater. Investigations concerned with the earliest origins of life, and the problem of whether stromatolites are organic or inorganic, should concentrate on the search for nannobacterial fossils. The putative nannobacteria found in Martian carbonate globules exactly match those found on earthly rocks, and nannobacteria may well be widespread in outer space.



FRESHWATER STROMATOLITES : EXUBERANCE OF THE BIOLOGICAL FELT COMPOSITION, SCARCITY OF PRIMARY SHAPE OF CRYSTALS, AND VARIETY OF DIAGENETIC FORMS OF RECRYSTALLIZATION

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Freshwater stromatolites (travertines) result from the calcification of a « biological felt » (Forel, 1901), including bacteria, fungi, cyanobacteria, eucaryotic algae of various groups, and animals. Cyanobacteria constitute between 0% (absence) to more than 50% of the felt. The stromatolite shape can be related only to the algae growth (homogeneous stromatolites) or to the encrusted substratum form such as mosses, bullrushes, and tubes of chironomid larvae (heterogeneous stromatolites).

The aim of this study is to present recent observations and petrographic investigations at various scales on (1) present day travertines (Freytet and Plet, 1996; 1996) and their associated facies and minerals (Freytet and Verrecchia, 1993, 1995, 1997), and (2) fossil algae and stromatolites (Bertrand-Sarfati et al., 1994; Freytet, 1997).

I. Exuberance of the organic composition the biological felt

Lists of genera and species obtained after decalcification of the biological felt can be found in the literature for lacustrine and river travertines as well as for rivers and lakes with waters of various hardnesses. In a recent synopsis, Freytet and Verrecchia (1997) have reported the presence of 46 Coccogonophycea, 123 Hormogonophycea, 2 Chrysophycea, 33 Chlorophycea, 3 Xanthophycea species, 2 diatoms, and 4 Rhodophycea species. These figures are less than what we can expect in nature because algae are often sterile and cannot be specifically identified : we estimate that the number of encrusted Chlorophycea species can be more than 50, and 10 to 15 for Xanthophycea. The 2 kinds of diatoms reported here are the only ones that are fixed by a mucous stalk, which is enclosed in big sparitic crystals. Nevertheless, mobile diatoms are numerous in travertines (more than 100 species) but their role is not clearly understood. On average, a biological felt is composed, after decalcification, by 1 to 3 dominant species (50 to 90% of the pro- and eukaryotic algal population), 10 accompanying species (frequent) and 1 to 3 rare species (among a possible 200 to 300), as well as bacteria and fungi, which were not studied in this paper.
II. Scarcity of primary crystallizations

Approximately, 0.(...)1% of the crystals are formed by Ca-oxalates (Freytet and Verrecchia, 1995), 99% are formed by micritic tubes around filaments (cell walls of sheaths), and < 1% are formed by sparitic crystals with spectacular shapes, whose importance is often exaggerated (Freytet and Verrecchia, 1997). The mineral origin is related to a double scalar process: (1) in the sedimentary environment, the conditions for mineral precipitation are attained (favorable temperature, gas loss, photosynthesis), (2) in the microenvironment around the sheath or the cell walls, the algae and their epiphytes excrete substances which can be used as crystal seeds (polysaccharides) and influence their mineralogy (oxalates, carbonates) and shapes (micrite, needles or dendrites, large rhombohedra, layered crystals, etc.). It seems that oxalates are only related to fungal activity.

III. Variety of diagenetic recrystallizations

Oxalates are metastable and quickly transformed into calcite, as was suspected by Emig (1917) and demonstrated by Verrecchia et al. (1993, 1996). In *Phormidium inscrustatum / Gongrosira incrustans* felts, the micritic tubes harden and only rarely recrystallize into microsparite or sparitic fans (Monty and Mas, 1981). In *Schizothrix spp*. felts, the micritic tubes easily recrystallize into sparite as clusters of isodiametric or radial palisadic crystals (the former being frequently confused in the literature with sinters, which are purely physicochemical in origin).

Other algae associated with sparitic crystals are difficult to identify because diagenesis results in the disappearence of the organic matter. Nevertheless, a few examples can be cited : calcite druses associated with *Hydrurus*, complex branching crystals associated with *Oocardium*, clusters of isodiametric crystals associated with *Rivularia*, *Diochothrix* or *Scytonema*, wide prismatic crystals associated with diatom stalks. All of these shapes are periodically confused in the literature with *Microcodium* or sinters.

Terrestrial stromatolites record a lot of information on the variation of the (Mg)-CaCO₃- CO₂-H₂O-oxalate system by the various shapes of crystals, which result from crystallization / recrystallization occurring during travertine formation and diagenesis. But first of all, it is necessary to complete the inventory of hard water encrusting algae before studying the mecanisms of differentiation and shape variation of crystals associated with travertines.

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AN ULTRAMODERN (POST-1947) STROMATOLITIC SYSTEM DEVELOPED IN A SMALL POOL, UPPER GUADIANA RIVER VALLEY (CENTRAL SPAIN).

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In Central Spain has been found and described by the authors active tufas in the Dulce river, Upper Tajo river, and Jucar river. In the Upper Guadiana river is located the Ruidera Pools National Park, figure 1, developed around a serie of tufa barriers. The small pool wich is described in this paper is situated in an erosional channel trenching the tufa barrier located between Tomilla pool and Tinaja pool, figure 2. The erosional channel has been generated in 1947, as a consequence of a spillover related with a flooding, and from there has been active until 1990, after this year the small pool was non active, as a consequence of the long dry period and probably ground water level fall from water extraction for irrigation. The dimension and distribution of stromatolites in the pool is represented in the figures 3 and 4.

The spill waters of Tomilla Pool that feed the stromatolitic system are close to saturation with respect to calcite and dolomite, as well in the winter as in summer, the saturation index is 1,56 for calcite and 2,00 for dolomite. The δ ¹⁸O isotopic composition of waters in the Tomilla pool varies strongly, thus in the period 1991-1995 δ ¹⁸O values increase from -5,20 to 0.00, whereas the δ ¹⁸O average values of ground waters was -6,68 in the same period.

The stromatolite types found may be described as follow: A) Bottom inlet channel stromatolites, wave ($\Delta = 20$ cm) planar stromatolites, commonly consist of alternating ligth - dark brown couplets of laminae. The light lamina may be described as a fan like fibrous calcite macrocrystals (1,6 to 2,2 mm), with bluegreen algae trichoma in intracrystalline position, thickness of the individual light laminae may up to 10 mm; the most compact laminae, the dark laminae, consist in a simple row of teeth like crystals, the length of monocrystals is up to 1 mm, and the maximun widenes is 0.2 mm. B) Cascade stromatolites, the main facies of this type is moss tufa, that consist of thin fringe cements developed into the once living plants surfaces and micritic microfacies with clotted and peloidal textures, this moss tufa alternating with thinner light laminae; C) Hemispheroidal domes located in the lower part of the cascade, consist mainly of thin light laminae alternating with thinner micritic laminae. D) Isolated spheroidal columnar domes (h = 60 cm, r = 40 cm), located into the pool, and occupie both lateral sides of the lower part of cascade, are deposited in subcritical laminar flow zone of the pool; the microstructures consist of polyciclic laminae with a predominance of spogiostromata facies. E) Pinnaded domes (h=20 cm), located in the subcritical turbulent flow and in the deepest part of the pool, consist of light lamina of fibrous

calcite macrocrystals. F) Bottom outlet channel hemispheroidal stromatolites, similar to described in the A), light lamina are formed by ray crystals 0,7 - 2 mm long, and in dark lamina the sheats of cyanobacterial filaments show bacterially induced spherical precipitates of calcite (0,2-1:m).

The DRX (d_{104}) and FRX data of carbonates display a wide variation of crystal chemistry of calcite in spite of the lower dimensions and near similar environmental conditions within the stromatolitic system described.

The δ ⁸O and δ ¹³C data of different laminae for the same stromatolitic buildup display a strong covariance, and may be correlated with the regional climatic data for the 1947-90 interval.

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A FERRIC IRON-ENCRUSTED BIOFILM ON A MARINE BIVALVE SHELL: A LIVING MODEL FOR ANCIENT FERRIC-IRON MICROBIAL ECOSYSTEMS?

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The shell of the marine bivalve *Montacuta ferruginosa* is usually covered with a rust-coloured iron-encrusted biofilm. The latter is a structured microbial mat with three separate layers. The outer layer is essentially microbial (filamentous bacteria and protozoa). The intermediary layer is both microbial and mineralized (heavily iron-encrusted filamentous bacteria and protozoa). The inner layer is essentially mineralized (amorphous hydrated ferric phosphate determined by infrared analyses and SEM examination) and generally devoid of living microorganisms.

The biofilm is a diverse microbial community composed mainly of filamentous bacteria. Such living mineral-microbial community, present at an active ferric iron deposition site, could bring important informations to sedimentologists and geochemists studying ancient iron-incrusted microbial ecosystems. For instance, bacteria associated to such deposits are not necessarily iron-oxidizing and chemolithoautotrophic, as frequently thought. Indeed, on *M. ferruginosa*, iron-oxidizing bacteria are probably not quantitatively important (as shown by molecular studies) and the community appears dominated by heterotrophic and aerobic microorganisms.

The genesis of this mineralized microbial mat could is explained by a sequence of processes :

(1) ferric iron deposition within bacterial sheaths in the outer layer;

(2) release and accumulation of heavily ferric iron-encrusted sheaths after lysis of the bacteria in the intermediary layer;

(3) degradation of bacterial sheaths and accumulation of ferric iron minerals in the inner layer

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EVIDENCE FOR NANNOBACTERIALLY PRECIPITATED DOLOMITE IN PENNSYLVANIAN CARBONATES

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SEM investigations suggest that nannobacteria are responsible for early dolomite precipitation in Pennsylvanian micrite within the phylloid algal bioherms in the Anasazi-1 core from the Aneth field of southeastern Utah. The first sample was etched in a one percent HCl acid solution for one minute, and the second etched for ten minutes in a ten percent HCl acid solution. Both samples were gold sputter-coated for 30 sec. to minimize artifacts. The JEOL TSM-330A SEM was set at 30kV, a low spot size (9-11 on our machine), and images were taken at 30,000 – 100,000X.

At magnifications greater than 35,000X, nannobacterial bodies were readily found within many of the small dolomite rhombs. The bodies ranged in form from spherical to ovate (0.08 - 0.2 microns), elongate (0.4 microns long), and chains of balls (1 micron in length). Additionally, the entire surface of each dolomite crystal had textures that often take the form of lineations which trend perpendicular to the c-axis of the crystals.

This discovery provides corroborating evidence for bacterially mediated dolomites. Furthermore it adds evidence that bacterially mediated modern dolomite is not a new process.



CRYSTAL ORGANISATION IN SPARRY MAGNESITE OF BACTERIAN ORIGIN

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Introduction : Sparry magnesites are distributed from the early Proterozoic to the Permo-Carboniferous (1). They occur in lagoonal environments as lenses of rather coarse crystallinity which grade laterally into paralic carbonate horizons, forming lenses in the central or marginal parts of the lagoon. Despite their sparry crystallinity (crystals up to 20cm) they contain very thin rythmic organic laminae and finely preserved microflora. Some of these fossils are the walls of cells belonging to soft bodied organisms (fungi imperfecti, incertae sedis...). The perfect conservation of the micro-organisms, showing details of a few tens of nanometers, implies the existence of an early colloidal deposit (2), possibly of bacterian origin (3).

Structure : The high resolution SEM (JEOL JSM 6400F) and TEM studies of the Cambrian magnesites from Pacios (Lugo, Spain) documented the remains of micro-organisms in these rocks. They also demonstrated the relationship of the latter with certain parallel and originally horizontal intra-crystalline organic laminae : the overall structure could be interpreted as a tabular stromatolite (3). By comparison, the very lightly metamorphosed Namurian deposit of Eugui (Navarra, Spain) is formed of more regular crystal layers, exhibiting a doublefence structure separated by interbeds of sometimes fossiliferous pelite.

Ultrastructure : The magnesite samples were polished to optical grade and etched with normal HCl or HF, then observed with a high resolution SEM. The studied samples from Eugui and Pacios (grey fine bedded facies) are formed by individual optically perfect crystals (200µm to 2-3cm), which can be recognised by the light microscope. However these crystals are, themselves, formed by associated globules ranging in size from some 100 to more than 200nm. These associations of globules have different size and shape in Eugui and Pacios:

- (a) irregular masses of different sizes, up to a few μ m,
- (b) rounded masses of about 2µm (Eugui).
- (c) rhomboidal associations of some µm (Eugui).
- (d) lineations formed in section of a number of globules, giving rise to diameters of more than 200-300nm (Pacios). These lineations are parallel.
- (e) coarser lineations formed by the association of the (b) rounded masses (Eugui).

Interpretation : The globular, rounded morphology of the magnesite surface in (b) and (e) is very similar to that of modern biofilms coated particles (7). In fact minerals can precipitate within as onto the surface of biofim as well as onto bacteria (8). With respect to the globules, the S.E.M. studies of the samples show three to four levels of organisation: in the first place the globules form. Then they coalesce giving rise (a) to © associations. In the case of Eugui, the rounded masses (b) associate to form lineation (d). Finally all kinds of associations form the perfect crystal. These levels of organisation seem to succeed each other temporally, starting from the elementary globules and resulting in the perfect type crystal by :

- 1) spatial arrangement and,
- 2) auto-oriention of the globules and of their associations, followed by
 - smoothing which gives these structures the optical aspect of a perfect crystal.

This process permits an exceptional phenomenon to take place: the conservation of fragile organic structures such as the walls of vegetable cells or bacteria and their details, al least in the form of a "ghost" (3). Bacterian influence : The structuring of the magnesite is different in the two ores, Pacios {with (d) associations} and Eugui {with (b, c ,e) associations}. The case of large, perfect crystals, which are formed by the association of globules (crystallites), is well documented in some mineral, such as sulfides, quartz, sulfates, carbonates..., either of organic or inorganic origin, formed in different conditions (4,5,6). The ultrastructures of the samples studied of sparry magnesites are not an isolated phenomena. Thus, once the colloidal mineral has formed in a microbial environment, dehydratation and cristallite orientation will follow normal thermodynamic laws.

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BIOLOGICAL INFLUENCE AND DIAGENETIC MODIFICATION WITHIN TRAVERTINE DEPOSITS IN BELGIUM.

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Several recent and paleo-travertine deposits in Belgium are studied with respect to their building components and diagenetic modification. Evidence is provided by both petrographical and geochemical techniques especially with regard to the biological influence on travertine precipitation.

Biological influence

Organisms, such as mosses, algae and diatoms are abundant in the recent precipitates, where they occur in close association with carbonate precipitates. The latter formed on and between organic structures. They may possess characteristic crystal morphologies related to specific organisms such as for example hexagonal calcite crystals on mosses, dodecahedral crystals on algae and fibre calcite crystals formed by fungi. These observations point to an important organic influence on travertine formation, but based on these data alone, it is not possible to determine the exact influence of organisms on carbonate precipitation.

Stable carbon isotopes can provide additional information about biological interference in travertine precipitation. Most values of δ^{13} C for the Belgian deposits vary around -10.8 ‰ PDB for the recent precipitates and around -9 ‰ PDB for the fossil deposits. These values point to a mixture of at least two sources of CO₂ that is incorporated in the CaCO₃. The first source is atmospherical or recycled marine CO₂, both with values of around 0 ‰ PDB, while the second source, namely biological or soil CO₂, possesses values of around -25 ‰ PDB. From these values, a biological contribution is obvious.

Diagenetic modification

Diagenetic modification within travertines is studied by the comparison of both recent and paleo-deposits. Several characteristic crystal morphologies in the pores of the paleo-precipitates were differentiated, such as euhedral crystals, gothic-arch calcite crystals, needle crystals and fibre calcite crystals. These crystals are formed during either meteoric phreatic or vadose diagenesis. Further evidence of diagenesis is provided also by stable oxygen and carbon isotope analysis, that shows evolution towards more positive values and a smaller variation in the paleo-deposits. This feature is probably due to addition of diagenetic phases from saturated ground-waters.

CARBONATE AND SILICA PRECIPITATION ASSOCIATED WITH MICROBES IN HOT SPRINGS (>73°C) IN KENYA AND NEW ZEALAND

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Hot-springs and geysers, which eject water at temperatures of greater than 73°C, are common in many parts of the Kenyan Rift Valley, Africa and in the Taupo Volcanic Zone on the North Island of New Zealand. In the Kenyan hot-spring systems, calcite and aragonite are common precipitates whereas opaline-A silica is usually only found along the margins of the outflow channels from those springs. In contrast, most of the hot-springs in the Taupo Volcanic Zone are characterized by opaline-A silica precipitates and calcite is only found at scattered localities.

Microbial communities are common throughout the hot-spring systems of Kenya and New Zealand. There is, however, a significant contrast between the role of microbes in the carbonate-producing systems and the silica-producing systems. Carbonate deposits associated with the Kenyan hot-springs are characterized by complex arrays of non-crystallographic dendritic calcite crystals and skeletal aragonitic crystals. Similarly, calcite found around some of the New Zealand hot springs are typically in the form of composite pseudodendritic crystals or skeletal crystals. Microbes appear to play little or no active role in the formation of these crystals. In the Kenyan calcite and aragonite crystals, for example, there is no evidence that microbes directly influenced the formation of these crystals. Many of these crystals, however, are covered with a reticulate coating that has a high content of Si along with lesser amounts of Mn, and locally Al. In some areas, thermophilic bacteria are associated with these coatings. The origin of these coatings is, however, open to debate. Although they may represent mineralized extracellular polymeric substances that are associated with the bacteria, there is some evidence that indicates an abiogenic origin for these coatings. Irrespective of the origin of this coating, its formation is independent of the calcite and aragonite precipitation and appears to represent a different stage in the evolution of the spring waters.

In New Zealand, opaline-A silica deposits are found in and around the vents of hot-springs and geysers that commonly issue boiling water. Although these deposits bear the attributes of geyserite, they are not abiogenic. Indeed, many of these silica deposits contain a diverse array of microbes that clearly played a critical role in the precipitation of the silica and associated elements. Filamentous microbes, which are commonly less than 1µm in diameter, acted as templates for silica precipitation and stromatolitic structures are common in many areas. The preservation of microbes in these settings is commonly spectacular with many of the original morphological attributes of the microbes still being apparent. Thus, evidence of original sheaths, cell walls, septae, and sulphur globules are

preserved in some of these microbes. In general, microbes appear to have little influence on the formation of dendritic calcite crystals and skeletal aragonite crystals in the hot springs of Kenya and New Zealand. In contrast, microbes appear to play an important role in the formation of opaline-A silica precipitates of the Kenyan and New Zealand hot-springs. In the latter case, the microbes provide a template for silica precipitation.

FROM CARBONATOGENESIS CONCEPTS TO BACTERIAL REGENERATION OF LIMESTONES (MICROBIAL LIFTING)

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The capacity of carbonate production by bacteria (Castanier, 1987; Castanier *et al.*, 1996) may be used for biotechnological purposes notably for the protection and restoration of limestone monuments and statuary (Orial *et al.*, 1993). These techniques are described in two patents the licenses of which are the property of CALCITE S.A..

Several sorts of limestones are used for building and sculpture. Two great categories may be distinguished according to the size of their constitutive elements and their porosity. The first category includes fine-grained limestones the porosity of which may be rather high but is formed of small size pores (less than 10 μ m wide). This is the case of the famous so-called tuffeau which is largely used in western France historic monuments. The second category is composed of limestones of variable porosity formed of both larger grains and larger pores (more than 10 μ m wide) such as the Saint-Maximin limestone (Le Métayer-Levrel, 1993).

The process of biomineralisation first consists in spraying over the whole surface to be protected a suitable bacterial suspension culture. Afterward, the deposited culture is fed daily or every two days with the suitable medium. Industrial and financial constraints restrict the number of feeding applications to five. The nutritional medium is conceived to stimulate the bacterial active and passive production of carbonate.

The process has been simulated in the laboratory on miniature walls composed of both kinds of limestones. Several carbonatogenic bacterial strains have been tested as well as two feeding frequencies (once by 24 hours and once by 48 hours). The daily frequency is more suitable for fine grained limestones the other one for coarse grained ones. The best operating strains are also different depending on the type of limestone. In mentioned conditions, carbonate producing bacteria colonise the whole surface of the stone (even including the cristoballite spheres in the case of the Tuffeau) which is rapidly coated by a "biocalcin". This is a smooth blanket, several micrometers thick, composed mainly of encrusted bacterial bodies mixed with carbonate excreta. It partially fills the voids of surficial porosity and is thus rooted in the structure of the stone. The biocalcin insures the protection of limestones, by restricting the exchanges between the rock inside and atmosphere and, by the way, by limiting the penetration of degradation agents into the stone.

The first life-size experimentation was realised in Thouars (Deux Sévres) on the tower of St Médard church. This church was built during the 12th century with Tuffeau limestone and, since that date, has been restored several times. The tower was entirely restored in 1988 so that the surface of the tuffeau processed by biomineralisation was but little damaged. The processing treatment was applied in June 1993 on an area of 50 m². The evolution of the bacterially produced biocalcin exposed to weather variations has been surveyed during the course of two measurements campaigns respectively 6 months and 1 year later. Five tests were performed in 20 points over the treated surface : macroscopic observation, SEM imagery, measure of surficial permeability (by measuring the time of water absorption), numeration of bacterial populations, evaluation of surface roughness by imprints moulding. The last measurements set (June 1994) confirmed the good quality and steadiness of the biocalcin. To date, three years after treatment, the external aspect of the tower has not changed.

The same surficial biomineralisation process was also tentatively applied to limestone statuary (Le Métayer-Levrel, 1996). Twenty prototype statues comprising all usual sculptural features have been manufactured for a test program aiming at studying the ageing of biomineralisation protection coating on statues placed in different climatic environments. Both above mentioned types of limestones and five types of environmental ageing were studied. Three sites of ageing were chosen outdoors, in rural (Loire Atlantique), urban (Paris) and littoral (Vendée) environments. The other statues were placed in an ageing accelerating climatic station. The biomineralisation process was applied to statues in January 1994. Couples of treated and untreated statues were installed after one year maturation in the laboratory. Three series of controls have been performed, the last one after 15 months exposure. They revealed the biocalcin has undergone a similar evolution in all outdoor sites. As compared to untreated statues, treated ones displayed but little degradation and only in parts where rainwater tends to accumulate. The accelerated ageing gave remarkable results. Non processed prototype statues have been heavily degraded whereas processed ones remained intact. Surficial biomineralisation by carbonatogenic bacteria thus also appears as a good protecting process for limestone statuary.

Furthermore, it is possible to create a surficial patina on limestones when applying the biomineralisation process by adding natural pigments into the nutritional medium. The pigments are integrated into the biocalcin and thus give a persistent light colouring to the stone. Of course, before processing, experiments are needed for choosing the suitable pigment and its concentration in order to obtain a given tone. Such a technique may be used, for example, to conceal the replacement of some stones on a monument.

Another application of bacterial carbonatogenesis is the conception of biological mortars or cements (Castanier *et al.*, 1995). They are obtained from a mixture of bacteria, finely ground limestone and nutritional medium in variable proportions. They can be used to paste small pieces broken out of statues or to fill small cavities of limestone surfaces. It is equally possible to include pigments into the mixture in order to obtain coloured biological mortars. This is a new concept that may be very useful in limestone monument restoration.

All mentioned applications tend to recreate a naturally produced material as similar as possible to the limestone substrate following the same metabolic ways the latter was born in nature.

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MICROBIAL MEDIATION IN SECONDARY PRECIPITATION OF PEDOGENIC MICRITE

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Many needle microcrystal shapes have been described in carbonate accumulations (see synthesis and typology in Verrecchia and Verrecchia 1994). The present investigation is part of a comprehensive study of the micro-rod group (width = $0.5 \mu m$ and length = $2 \mu m$) using scanning electron microscopy coupled with a microprobe, UV-epifluorescence microscopy, and transmission electron microscopy. Micro-rods have been observed in a variety of environments affected by pedogenic processes, including calcareous soils (Bruand 1980; Verges et al. 1982; Ould Mohamed and Bruand 1994), « calcretes » (Pouget et al. 1980; Riche et al. 1982; Phillips and Self 1987; Verrecchia and Verrecchia 1994) and terraces and alluvial fans (Ducloux et al. 1984; Monger et al. 1991; Reheis et al. 1992).

Micro-rods have been observed at the top of indurated carbonate horizons composed of cryoclastic chalky sands and gravels coated with cemented limeyclayey silts. These horizons overly a periglacial cryoturbated chalk formation, in contact with the present day soil, which developed during the Holocene. Induration of these horizons is the result of physico-chemical (carbonate reprecipitations) and biological processes (precipitations of fungal needle-fiber calcite - NFC - and micro-rods).

Micromorphologically, two kinds of organic micro-rods have been identified. The first kind is composed by smooth micro-rods with bulbous terminations. They are from 2 to 3 μ m in length and 0.15 μ m in width. This type is identified as bacilliform bacteria (Fig. [1]). A second kind of micro-rods is composed by smooth, single, and flexible threadlike rods forming bundles and trabecula between chalk matrix grains. Their length is approximately 2 to $6 \mu m$, and their average width is 0.08 µm. This type is identified as threadlike bacteria. Micro-rods show several morphologies and spatial arrangements. Variations in morphologies are related to the progressive biomineralization of the organic rods. Progressive centripetal mineralization results in a decrease in the length of the organic micro-rods and the disappearance of their bulbous terminations. The two kinds of bacteria can combine to form random calcified mesh fabric. Micro-rods coat micro- and mesopores in the weathered chalk, the NFC, and infill the space between the MA needle-fibers. Therefore, there is no genetic relationship between fungal hyphae and micro-rods. During diagenesis, the arrangement of mineralized rods evolves from a random mesh to recrystallized micritic platelets (Fig. [2]). In a later step, micro-rods become nearly invisible and fuse together. Microsparitic grains formed by stacked platelets characterise the final step, i.e. the reprecipitation of an authigenic and microbial micritic matrix. Recrystallization of

microbial micrite into microsparite is a common process and plays a major role in the hardening of the indurated layer.

It is not clear if the microorganism calcifies during its life or after its death. When micro-rods are coalescent and begin to fuse, they are entirely composed by calcium carbonate. Nevertheless, microdiffractometry analysis confirmed that they are low magnesium calcite (LMC) and monocrystalline in nature.

In conclusion, the microbial activity results in the precipitation of micrite, which evolves diagenetically to microsparite and partly hardens the paleosol layer. Therefore, the primary matrix of the paleosol is greatly enriched in $CaCO_3$ by the bacterial micro-rods, i.-e. an *in situ* biogenic process rather than calcium carbonate leaching.



Figure : [1] Scanning electron micrographs of purely organic micro-rods in a Quaternary indurated layer from Champagne. Cluster of organic bacilliform micro-rods rooted in an elementary grain of the chalk matrix. Some of the terminations are curved without any bulges. [2] Mineralized micro-rods after undergoing diagenesis. The coalescence of micro-rods leads to smooth micritic platelets. The random mesh shows a differential recrystallization that can depend on the bacterial maturity.

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CALCIFYING CYANOBACTERIA AND CYANOBACTERIAL MICRITE PRODUCTION: ENVIRONMENTAL INTERPRETATIONS

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Calcifying cyanobacteria can contribute to the accumulation of mud mounds. They are relatively easily recognized when occuring in the sediment as micritic tubes but might also have contributed significantly to the mud fraction. Calcification of cyanobacteria is extracellular and influenced by environmental factors. Calcification of fossil cyanobacteria therefore also reflects these environmental factors. In this way the occurence of calcifying cyanobacteria in mud mounds might help to interpret their environment of formation.

In the Recent, calcification of cyanobacteria is restricted to non marine environments and environmental influences on calcification can only be studied there. The phosphate concentration of the water and its saturation state with respect to carbonate turn out to be key factors influencing calcification. The same factors should be important for the calcification of marine cyanobacteria, even if the absolute values need not to be the same.

Calcifying cyanobacteria are restricted to oligotrophic environments and can best be cultured in artificial media with especially low phosphate concentrations. Their occurrence in mud mounds should therefore be restricted to times of oligotrophic oceans.

Calcification of modern cyanobacteria either results in the formation of solid micrite tubes or of carbonate mud. Micrite tubes are formed when high degrees of supersaturation with respect to carbonate in the ambient water lead to an encrustation of the filaments. Observations in tufa of fresh water streams and other non-marine environments suggest that this form of calcification occurs at saturation indices around 0.8 and higher (KEMPE & KAZMIERCZAK, 1990; MERZ-PREIß & RIDING, 1995). The value could, however, differ in seawater.

In waters of lower saturation state another form of cyanobacteria calcification can occur. When low CO_2 concentrations induce active bicarbonate uptake for photosynthesis, pH and subsequently carbonate saturation is raising locally within the sheath (MERZ, 1992). This photosynthesis driven calcification results in an impregnation of the sheaths with micritic carbonate. Upon death of the cyanobacteria the calcified sheaths disintegrate and a carbonate mud is formed. Low CO_2 concentrations are generally due to high rates of photosynthesis in dense cyanobacteria or algal populations. If the cyanobacterial origin of a mud can be established, it therefore might indicate the growth of dense cyanobacteria mats in only slightly carbonate supersaturated water.

If cyanobacterial carbonate production was relevant for the accumulation of mud mounds, than mud mound development throughout Earth history has been influenced by all the above mentioned environmental factors. Occurence of cyanobacteria tubes should reflect times of high carbonate saturation of the oceans. In times of lower carbonate saturation of the sea water cyanobacteria might have contributed to the mud fraction of mud mounds. Both forms of cyanobacteria calcification, however, should be restricted times of low phosphate concentrations.

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TUFA DEPOSITION: INORGANIC PRECIPITATION AND ORGANIC TEMPLATES

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Glas and copper substrates were exposed for several hours up to three months in a tufa depositing fresh water stream. Macroscopically, glas is soon covered by carbonate while copper remains uncalcifed even after exposure for several months. Microscopically, however, on all substrates, even copper, crystals can be found after a few hours. Precipitation seems to proceed in two stages.

In a first step, acidic mucopolysaccharides cover the surfaces. Especially during the summer these macromolecules adhere to the surfaces within several hours. The mucopolysaccharides can also be found free floating in the water Staining experiments with Alcian Blue suggest that the column. mucopolysaccharides are extruded by various microorganisms such as cyanobacteria and algae. Within the polysaccharides, single crystals can be found on glas as well as copper substrates. With increasing exposure time crystal aggregates form around the seed crystals. This first step can be found on glas as well as copper substrates. A macroscopic carbonate crust, however, is only developed in a second step when microorganisms settle on the substrates exposed for several weeks. Cyanobacteria filaments and fungi hyphen can be found, encrusted by solid micrite tubes. Bacteria occur as well, but do not show indications of preferential calcification. This step of calcification is lacking on the copper, which is toxic to microorganisms.

The development of a macroscopic carbonate crust sets in at about the same saturation values which lead to inorganic calcite precipitation (SI= 0.8, SVENSSON, 1992; KEMPE & KAZMIERCZAK, 1990; MERZ-PREIß & RIDING, 1995). The localisation of precipitation, however, seems to depend on extracellular organic macromolecules extruded by various microorganisms. Substrates which cannot be overgrown by microorganisms remain macroscopically uncalcified, although no indication was found that the physiologic acitivity of the organisms is crucial for calcifcation.

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EXPERIMENTAL MODELING OF MICROBIAL ACTIVITY IN BEACHROCK DIAGENESIS

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Beachrocks are formed in the intertidal zone by a rapid cementation of sandy beach sediments in approximately tens of years. Diagenesis is limited to intertidal zone, sediments below and above stay unlithified. Cements consist of aragonite or high-magnesian calcite (HMC). Coastal areas with this early lithification resist much better to coastal erosion and to consequences of sea-level rise. Their reservoir characteristics are also interesting. Numerous hypotheses have been proposed to explain early diagenesis in this particular environment. The quoted processes may be summarised in two groups (Scoffin and Stoddart, 1983): 1) physico-chemical processes (precipitation from evaporating sea-water, CO2 degassing at the phreatic/vadose limit from continental CO2-rich water, precipitation from brackish water in the mixing zone of marine and meteoric water), 2) biological processes (precipitation within micro-environments created by microbial metabolism, directly microbial controlled precipitation, sediment immobilisation by micro-organisms; Krumbein, 1979). So far, none of the different hypotheses have been unquestionably and universally proven, and probably several processes intervene during beachrock formation.

During this study numerous recent beachrocks from Crete, continental Greece, the Red Sea and French Polynesia have been studied in a large variety of geological contexts. Generally, several diagenesis phases follow one another producing different cements of various habitus and mineralogy. The most general pattern is alternation of micritic and prismatic cement, either in HMC or in aragonite. Usually diagenesis starts with micritic cement. This first cement seems to control and initiate beachrock diagenesis. Potential microbial morphologies are visible, particularly in HMC micrite: micrite fringes with irregular undulations (Bernier and Dalongeville, 1988), and, on micron scale, globular bodies resembling bacteria (Folk, 1993). Additionally, sea and interstitial water was analysed to determine salinity and calcite/aragonite saturation.

As investigations of beachrock cement with traditional techniques give no conclusive differentiation of biological or physico-chemical induced cements, a laboratory experiment was developed. A model was built, which simulates the conditions of beachrock formation, i.e., intertidal zone of sandy beaches. The model reproduces porosity of beach sand, tidal movements (alternation of phreatic conditions with sea-water saturation and vadose conditions with aeration according to tidal cycle), temperature, evaporation and water composition (sea-water, with control of following parameters: salinity, Ca, Mg, ΣCO_2 , pH, calcite/aragonite saturation). Artificial sunshine imitating daily cycles is possible but was not used. All components could be sterilised and the model is protected against microbiological contaminations during the experiment. Two parallel experiments, with and without microbial activity, allow comparison of

biological and physico-chemical products. Particular care was taken to reproduce natural CaCO₃ saturation and nutriment concentration.

During the initial experiments, physico-chemical conditions measured in a Red Sea beachrock were simulated, and activity of micro-organism population (undetermined) sampled in the same beachrock was observed. First results show the development after 2-3 months of microbial-mediated calcium carbonate crystals presenting various habitus. Their size ranges from micrite to 20 μ . The largest were identified as calcite. These crystals could correspond to first micrite cement of natural beachrocks. The sterile control experiment did not produce equivalent crystals.

These results support the interpretation that microbial activity controls formation of the micrite cement which start beachrock diagenesis. The prismatic cement, that usually follows, was formed in different conditions and could result from abiotic diagenesis. This could mean that although physico-chemical mechanisms intervene in beachrock formation, microbial activity is the main controlling factor.

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BIOGENIC MUD MOUNDS AND COLD SEEP CARBONATES COMPARED

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Biogenic mud mounds (BMM) and cold seep carbonates (CSC) are mainly composed of authigenic micrite presumably produced via different modes of microbial (mainly bacterial) processes. The purpose of this paper is to identify and compare these processes which are crucial for the formation of these structures. Examples come from the Lower Cretaceous (Albian, N Spain) in the case of BMM and the Upper Jurassic (Oxfordian, S France) in the case of the CSC. BMM were formed at marginal platform settings ranging in hight from several cm to 70 m with primary slopes of around 25°. CSC form lenses up to 25 m in hight embedded within stratified marlstones. Their geometry suggests that main accretion occurred within the sediment (pseudobiohermal sensu GAILLARD *et al.* 1992).

Benthic community: : Lower Cretaceous BMM are dominated by sponges and Upper Jurassic CSC also contain sponges which may be locally abundant. BMM bear a diverse association of lithistid and non-lithistid demosponges, hexactinellid and coralline sponges associated (depth related) with encrusting foraminifera, thecidean brachiopods, bryozoans and minor scleractinian corals, calcareous algae and rudists. CSC exhibit a dominance of hexactinellid sponges over demosponges and are associated with chemosynthetic lucinid bivalves (locally dominant), echinoids, ammonites and gastropods as well as decapod crustaceans. In both cases in situ calcified microorganisms are extremely rare.

<u>Micrite production in place</u>: By quantity and function in-situ formed micrites are crucial for the formation of BMM and CSC. Within BMM there is a spectrum of automicrites ranging from container automicrites (bacterial soft tissue degradation of sponges, pocket fillings, interstitial spaces) to accretionary automicrites (biofilms) lining former sediment/water interfaces. These accretionary automicrites form massive, thrombolitic and stromatolitic structures. Both types of automicrites can be regarded to act as a primary and secondary frame deposit. CSC are characterized by a nodular fabric with carbonate concretions often formed around body fossils (ammonites, bivalves) or trace fossils (burrows). A microbial origin of this fabric is suspected. Within CSC micrite production in place partly corresponds to bacterial degradation of sponge soft tissue resulting in spiculitic, clotted micrites. Commonly these sponge remains are covered by an outer rim of pyrite. The delineation of former sponge bodies by automicrites contributes to the nodular fabric of CSC.

<u>Primary Mineralogy</u>: In both cases the primary mineralogy of automicrites was a high Mg-calcite. BMM automicrites reveal residual MgCO₃ concentrations going along with early marine rim cements (2.0 to 3.5 mole-%). Lower Oxfordian CSC bear aragonitic botryoids growing upon calcitic cement and represent the final cement reducing residual pore space. Despite the fact that minor portions of these botryoids were micritized and calcitized most botryoids reveal their primary aragonitic mineralogy.

Stable isotopes: Stable isotopes measured as δ^{13} C and δ^{18} O permil vs PDB provide a distinct separation of BMM and CSC micrites (Fig.1). The comparative analyses of various depositional and diagenetic phases of BMM limestones provide evidence that automicrite formation is equilibrated with marine waters thus coinciding with early marine cements (δ^{13} C=2.9 to 3.6) and well separated from rudistid limestone and associated biomicritic phases (δ^{13} C=2.3 to 2.5). Consequently automicrites can be used as a diagenetic indicator along freshwater-phreatic/vadose overprints. δ^{13} C-values of CSC show an extremely wide variation from light (-25) to heavy values up to +15. This bidirectional excursion of δ^{13} C is related to both the oxydation of methane or longer chained n-alkanes and methanogenesis (heavy values), the latter related to Archaea.

Biomarker analyses: Gaschromatograms of the hydrocarbon fraction of BMM core sediments are dominated by short-chained n-alkanes and show a distinct predominance of phytane over pristane (indicating local anoxic conditions) as well as a distinct hump of the unresolved complex mixture. This organofacies is autochthonous and points to strong effects of microbial biodegradation in connection with the formation of automicritic core sediments. Analyses of intracrystalline organic compounds provide a spectrum of amino acids with relative high amounts of the acidic fraction Asp and Glu, typical for calcifying organic substrates. Chromatograms of CSC provide a smooth n-alkane distribution indicating aquatic sources and typical for samples of medium and high thermal maturity and crude oils. Hopanoids represent the input of bacterial organic matter, whereas specific acyclic isoprenoids are derived from archaebacteria. The high contents of n-alkanes presumably reflect the primary energy source of the chemosynthetic community.

Fig.1: Stable istopes (δ^{13} C, δ^{18} O permil vs PDB) of Biogenic Mud Mounds and Cold Seep Carbonates. Oxfordian data from GAILLARD *et al.*

<u>Processes:</u> Lower Cretaceous biogenic mud mounds and Upper Jurassic cold seep carbonates were generated via reactive states of organic matter triggering matrix-mediated micrite production in place (organomineralisation). In the case of biogenic mud mounds the organic matter was derived from a benthic microbial/metazoan community dominated by heterotrophic bacteria and siliceous, bacteria hosting sponges. In the case of cold seep carbonates energy flux is initiated via seepage of reduced fluids from deeper sources, probably petroleum. Degradation of organic matter via chemoorganotrophic bacteria and sponge soft tissue degradation is crucial. Sponges of cold seep carbonates presumably contain chemoorganotrophic symbionts.

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FROM BACTERIA TO CRYSTALS IN KARSTIC WATERS. THE ROLE OF NUTRITIONAL CONDITIONS.

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The solid products of bacterial carbonatogenesis were first studied in eutrophicated karstic originated waters from a natural pool situated at Les Cugnes near Les Eyzies (Castanier, 1987). They were collected on glass plates suspended directly in the natural environment and in jars containing natural water. Both were amended in order to intensify the several metabolic pathways of bacterial carbonatogenesis. In such experiments it is difficult to part the active production from the passive one. However, several considerations tend to indicate that the former, which corresponds to membrane processes, occurs first. It should be followed by the later which is due to the accumulation in the medium of carbonate and bicarbonate ions together with metabolic end-products.

The first solid products are probably amorphous and perhaps hydrated at the beginning (Castanier *et al.*, 1988). They appear on the surface of the bacterial bodies as patches or stripes that extend and coalesce until forming a rigid coating (cocoon). In other cases, solid particles formed inside the cellular body, are excreted from the cell (excreta). All these tiny particles, including more or less calcified bacterial cells, assemble into biomineral aggregates which often display "precrystalline" or rather "procrystalline" structures. Sometimes the bacterial bodies themselves present an angular crystalline shape as if they would contain a growing single crystal. Such a feature could be compared with the cubic shaped bacteria that are found in hypersaline environments (Gerdes *et al.*, 1985). At this stage of evolution and in numerous cases, the calcified bacterial cells tend to arrange themselves into nearly crystalline structures and sometimes into dendritic or fibroradial fabrics the latter being considered as possibly prefiguring ooïds (Castanier *et al.*, 1989). The angles of such structures are generally close to but neither exactly those of the rhomboedral system nor those of the orthorhombic one as if bacteria were disliking the crystallographic physical rules.

The primary aggregates grow and form secondary biocrystalline assemblages or buildups which progressively display more crystalline structures with growth. Tetrahedral assemblages and pentagonal faces are often observed. This phase should correspond to the passive carbonatogenesis. There seems to be different types of crystallogenetic sequences following the different metabolic pathways (Castanier, 1987). This has to be explored further but if it reveals to be a reality, it could lead to the reconstitution of palaeomicrobiotopes from the examination of carbonate particles as long as they are not disturbed or changed by diagenesis.

Bacterial calcite from an helicitie (Collett, 1878) of Clamouse Cave, formed in an oligotrophic environment was also investigated (Le Métayer-Levrel, 1996). Two microorganisms are present. The first one is constituted by chains of budding spheres or ellipsoids ca. 0.5 to 1 μ m in diameter. Cells are usually covered by a thick carbonate cocoon. From its morphological characters, this form should be attributed to the genus "Isosphaera" which is the only budding, non photosynthetic bacterium forming chains of spherical cells (Giovannoni and Castenholz, 1989). It is a gliding bacterium. Here however, it could be another species than the only known species "Isosphaera pallida" Giovannoni, Schabtach and Castenholz, which lives naturally in hot springs and in the laboratory within a temperature range of 40-55°C.

The second organism is constituted by more or less anastomosed ribbons 1 μ m wide, wearing very numerous finger shaped refringent, strongly calcified excrescences 0.1 to 0.3 μ m wide. This organism is probably the mobile gliding species *Vitreoscilla filiformis* Strohl which grows better in nutrients-poor than in nutrients-rich milieus (Strohl, 1989). Such a species is undoubtedly well adapted to the nutritional environment of caves.

Collected images show remarkable relationships between these two organisms and carbonate crystals the outer shapes of which are generally non rhomboedral.

The "Isosphaera" chains, when they are short and constituted of probably young ellipsoidal cells, point out perpendicularly to the crystal faces and are often situated parallel to a crystalline plan. They seem either to spring out of automorphous cavities of the crystalline structure or to rise directly from the crystalline mass. In this case, a pad ringing round the basis of the filament is often observed at the surface of the crystal. This ring is usually irregular but sometimes forms a well rounded areola that connects regularly with the crystalline surface. This suggests that this pad is a carbonate deposit, perhaps amorphous, due to bacterial activity, which is progressively but rapidly incorporated into the carbonate crystal.

The *Vitreoscilla* filaments flatten against crystals faces and are gradually incorporated into the crystal masses. Their constitutive equipment and notably the calcified excrescences are then rapidly smoothed in the very thread of the crystalline structure. Images show that the quasitotality of the mass of crystals is from bacterial origin.

Surfaces of carbonate crystals do not show clear relationships between the crystalline structures and the orientation of the filaments; that is why we have operated a. After a partial dissolution of crystals with EDTA, SEM imagery clearly shows that the filaments act as axes of nucleation to series of piled calcite rhomboedra. When the crystalline equipment has almost totally been removed by dissolution, there remains a network of more or less calcified filaments.

These observations and experiments show that in both nutritional conditions bacteria play a major role over crystallisation both in supplying carbonate matter and in its structuration. After eutrophication, bacterial activity is very high at the beginning and early solid products as well as biomineral aggregates hardly follow the crystalline structurations which are overwhelmed by biological luxuriant processes. On the contrary, in oligotrophic conditions, bacterial production rate is low so that the crystallographic rules soon overcome the biological primary disorder. Thus, observations of recently formed or unmodified carbonate bacterial grains could give informations on their original nutritional microenvironment.

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FIRST BACTERIAL PRODUCTION OF MAGNESITE (MgCO₃) IN ANAEROBIC STRICTLY CONTROLLED CONDITIONS.

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Until recently, one of the most puzzling problems in carbonates sedimentology was the experimental production in the surface conditions of high-Mg carbonate, notably magnesite. Lippman (1973) defined "the magnesite problem" as the incapacity for searchers to synthesise magnesite (MgCO₃) in temperature and pressure conditions compatible with the field observations. Indeed, many occurrences of magnesite have been demonstrated as being of sedimentary origin. Meanwhile, the hypothesis of a microbial mediation in the genesis of high-Mg carbonates was proposed to solve the problem of the origin of these carbonates. For instance, Perthuisot (1975) proposed an intervention of sulphate-reducing bacteria in the genesis of huntite (CaMg₃(CO₃)₄) and magnesite (MgCO₃) in Sabkhat el Melah (Tunisia). Indeed, the usual relationship between high-Mg carbonates and the development of sulphate-reducing bacteria has been often noticed (Hardie, 1987; Lasemi *et al.*, 1989; Perthuisot *et al.*, 1990; Middelburg *et al.*, 1990).

Sulphate-reducing bacteria are able to oxidise organic matter by using the oxygen of sulphates as final electron acceptor. They produce therefore their energy by consuming sulphate. As heterotrophic organisms, sulphate-reducing bacteria oxidise the carbon of the organic matter and produce HCO_3^- and CO_3^- ions that may combine with the magnesium in high Mg^{++}/Ca^{++} brines to form magnesite.

Bacterial sulphate-reduction may be summarised following the reaction proposed by Kempe and Kazmierczak (1994):

$\mathrm{C_{106}H_{263}O_{110}N_{16}P_{1}} \ + \ 53\ \mathrm{SO_{4}^{2-}} \ + \ 14\ \mathrm{H_{2}O} \ \rightarrow \ 53\ \mathrm{H_{2}S} \ + \ 106\ \mathrm{HCO_{3}^{-}} \ + \ \mathrm{HPO_{4}^{2-}} \ + \ 16\ \mathrm{NH_{4}^{+}} \ + \ 14\ \mathrm{OH^{-}}$

In addition to the accumulation of bicarbonate ions, such a reaction increases the alkalinity of the medium which favours carbonates precipitation.

In sediments, if iron is present, the produced S⁻ would be fixed in iron sulphide (FeS) which may evolve into pyrite (Fe₂S). If the medium contains no iron, the H₂S, which is highly volatile, would escape to the atmosphere. Both processes induce the increasing of pH which favours the precipitation of carbonates the composition of which also depend on the Mg⁺⁺/Ca⁺⁺ ratio. Therefore the precipitation of high-Mg carbonates in sediments will be favoured by i. anoxic conditions allowing the development of heterotrophic sulphate-reducing bacteria; ii. the presence of consumable organic matter; iii. the presence of sulphate; iv. a high Mg⁺⁺/Ca⁺⁺ ratio.

Such conditions are found notably in continental salt lakes and paralic sabkhas which are producers of organic matter, massively during the early stages of their sedimentary evolution and even during the final evaporitic stages. Besides, in the course of sedimentation, calcium is trapped in carbonates (calcite, aragonite) and sulphates (gypsum, anhydrite) leading to generally highly magnesian residual brines. Dissolved and deposited sulphates constitute the source of energy necessary for the development of sulphate-reducing bacterial populations.

All these environmental conditions are found in salt lakes situated in the vicinity of Los Monegros (Spain) in the present sediments of which Pueyo-Mur *et al.* (1987) demonstrated the presence of magnesite. During the course of a field mission (July 1995) sediments and waters were aseptically sampled within the sulphate-reduction zone.

Collected natural bacterial populations were incubated in an anaerobic hood, in a medium which favours the development of sulphate-reducing strains, with a salinity of 10 % and an initial Mg⁺⁺/Ca⁺⁺ ratio of 7,75. After 6 months incubation at a temperature of 36° C, solid products were observed through SEM imagery and analysed through X-ray microprobe. Most produced particles, some of them reaching ca. 50 µm in length, display a typically rhomboedric crystalline outer shape. Besides, microprobe analyses indicate these particles are composed of nothing else than Mg, C and O. Semi-quantitative X-ray estimations give a Mg/O atomic ratio of approximately 1/2,5 which is close to the magnesite (MgCO₃) composition but higher than the

theoretical one (1/3). The measured lesser proportion of oxygen may be explained by interference due to the proximity of the K α peaks of oxygen and magnesium. Such a ratio anyhow excludes this mineral from being hydrated. Thus, the obtained mineral is an anhydrous, rhomboedric Mg-carbonate, in a word, magnesite.

As far as we know, here is the first time this mineral is experimentally produced, through bacterial activity, in the conditions of Earth's surface. The Lippman's "magnesite problem" seems, at least partly, to be solved. As a matter of fact, observations of present nature and experimentation show that magnesite formation occurs rather rapidly, in the surface condition, in highly magnesian waters under effect of sulphate-reducing bacterial activity.

Other experiments aiming at producing high-Mg carbonates in aerobiosis and/or microaerophily, were performed using the nitrogen cycle (ammonification of aminoacids, dissimilatory reduction of nitrate), with an acetate substrate in order to avoid phosphates precipitation which were previously obtained with phosphorated substrate (Pontoizeau *et al.*, 1996). After a few days experiment, obtained solid carbonates have always been hydromagnesite (monoclinic). The reason of such a difference with the sulphate-reducing way are still unknown but one may call for nucleation and crystallisation rates, ionic strength, water activity. Further studies are needed.

Anyhow, if bacterial sulphate-reduction is considered as being one of the most efficient way of magnesite formation it could then explain the antagonism sulphate-magnesite noticed by Guillou (1980) in Ancient series and also the temporal distribution of magnesites.

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MICROBIAL CONTRIBUTION TO REEFAL MUD-MOUNDS IN ANCIENT DEEP-WATER SETTINGS

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Deep-water mud-mounds are reefs whose micrite-dominated frameworks owe themselves to the activities of microbes, presumably primarily cyanobacteria and bacteria. Lagoonal mud-banks in Florida Bay therefore are not direct analogues; 'lithoherms' in the Straits of Florida are not well enough known for close comparison. Deep-water mud-mounds are not really a distinct class of carbonate buildup, for their framework composition intergrades with that of shallow-water reefs.

Several types of microbial structures can be recognized, relating to calcification of organic material and sediment binding. The relative importance of each of these processes depended in large part upon the associated sedimentproducing benthic community which, in turn, was governed by its evolutionary history and specific environmental factors. Composition of the microbial community must have been complex and variable, but is impossible to determine in most cases. Bathymetry is an indirect control because light penetration and turbulence hinge upon it.

Clotted micrite and crusts of micritic filaments and other microfossils arose through calcification of near-pristine to degraded biofilms. This micrite is typically denser than lime mudstone, and is laced with small fenestral pores. By contrast, biomicrite, commonly with unoriented bioclasts and sheltering laminoid fenestrae and growth-framework cavities (stromatactis), was from sediment held in place by variably flocculent mats until stabilized by synsedimentary cementation. Stromatactis developed mainly from winnowing of loose sediment adjacent to and under bound material; dilation cracking (perhaps from synsedimentary earthquake-induced ground motion) formed some laminar stromatactis.

Proterozoic mud-mounds are stromatolites consisting of precipitated micrite as stromatoids commonly conforming to *Conophyton* or *Baicalia*; thrombolites developed in rare cases, and unlaminated fabrics exist locally within stromatolite buildups. The underlying cause of the lamination-and the episodicity it implies-is uncertain. The Cambrian heralded the loss of this propensity for lamination, and this may have been a response to both microbial evolution and the appearance of new mechanisms-presumably biotic-of lime mud production.

Calcified filaments assigned to Girvanella formed tufa-like frameworks at current-swept platform margins during the Middle Cambrian to Early Ordovician. This was a biotically depauperate interval after mass extinction of Lower Cambrian reef-building and reef-dwelling elements. Once the reefal community recovered by the Middle Ordovician, such frameworks no longer developed. These settings instead became the sites of biomicrite-dominated mud mounds for the remainder of the Paleozoic. The end-Permian mass extinction

affected the crinozoans and fenestrate bryozoans and meant that similar biomicrites never again developed. Lower energy areas, such as intrashelf basins, were dominated by thromboids and clotted micrite crusts throughout the Paleozoic and Mesozoic. The Cenozoic saw the displacement of microbial elements by crustose coralline algae.

Dunham limestone classification predates modern understanding of mudmound fabrics. Obviously, identifiable stromatoids, thromboids and Girvanella crusts are frameworks and therefore constitute boundstones. Mud-mound biomicrite has a wackestone or packstone texture, but if originally bound by microbial biofilms or mats then it is boundstone also. Other terms for biolithites, such as bindstone, framestone and bafflestone, are superfluous; bafflestone is misleading when macrofossils are not in growth position because it holds that they were responsible for trapping their own matrix.

MICROBIAL MAT

Cambrian-Lower Ordovician

DEGRADATION & CALCIFICATION

DEGRADATION & CALCIFICATION

Proterozolc-Triassic?

SEDIMENTATION

biomicrite Middle Ordovician-Cretaceous?

ROLE OF MICROBIAL ORGANISMS IN THE FORMATION OF RED MATRICES, DEVONIAN, MONTAGNE NOIRE

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Two Devonian sections are studied at Coumiac (Frasnian/Famennian) and at the Pic de Bissous (Eifelian/Givetian). The sediments are an outer ramp-type grey-red mudstones and wackestones rich in benthic and pelagic fossils.

The Coumiac sequence is strongly condensed with numerous hardgrounds that indicate the presence of hiatuses. The Pic de Bissous succession is more complete and of shallower sedimentary origin. In both cases, the origin of the red coloration of the micritic matrix is the same and linked to bacterial activity. The latter is responsible of submicronic hematite and manganese oxides production. The iron concentration is low (average 0,2 % Fe2O3) and is the equivalent to that of the manganese.

In thin-section the existence of these bacteria is indicated by the presence of microstromatolites, blisters, microtufts, "hedgehogs" filling sponge perforations in trilobites and mollusks, and thin, continuous mineralized films (of probable biofilm origin) covering the shells. All these bioconstructions are mainly ferruginous. Hardgrounds developed in the mudstones and wackestones are also underlined by microstromatolitic constructions.

The origin of the matrix color is related to the destruction of all these constructions, the submicronic hematite covering the crystal faces of the calcitic mosaic. During lithification, early microfissures appear and these are still invaded by bacterial colonies. Indeed scanning microscope shows that they are composed of bacilliform rosary beads. This proves the continuity of the ferruginous processes during early diagenesis. Moreover these early fissures are cut off by burrows. Subsequently a secondary fissure network will transect all the previously described sedimentary structures. This late fissure network is underlined by remobilised hematite and/or calcite. The latest processes are stylolitisation and an ultimate tectonic fracturation.


MICROBIALLY-MEDIATED LITHIFICATION IN BAHAMIAN STROMATOLITES

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Modern stromatolites, forming in open marine environments in Exuma Cays, Bahamas, are characterized by millimeter-scale lamination. This lamination is caused by the periodic formation of lithified laminae with a distinct microstructure: lithified layers consist of micritic crusts, 10-50 µm thick, overlying micritized sediment grains truncated at the suface by microboring (Reid and Browne, 1991; Reid et al. 1995; Macintyre et al., 1996). These layers form within microbial mats at the surface of the stromatolites. Closely co-ordinated analyses of biogeochemical gradients, biological communities and microbial physiology of shallow subtidal stromatolites at Highborne Cay, at the north end of the Exuma chain, are being conducted to investigate geomicrobiological processes responsible for the formation of these lithified layers.

Photopigment analyses indicate that microbial mats on the surfaces of the stromatolites are composed predominantly of the filamentous cyanobacteria, *Schizothrix*, with a minor contribution of diatoms (Pinckney and Reid, 1997, Pinckney et al., 1995). Initial measurements of respiration, sulfate reduction, nitrogen fixation and chemical gradients within these mats indicate the presence of a diverse heterotrophic community that is tightly coupled with biogeochemical gradients. Microautoradiography shows that the highest microbial activities are associated with epiphytic bacteria on cyanobacterial sheaths. Relatively high ratios of O₂ production relative to consumption in the mats suggests that fixed carbon, in the form of biomass and extracellular polymeric substances (EPS), accumulates within the mats. The calcium-binding properties of EPS may prevent CaCO₃ precipitation on living cyanobacterial sheaths. Heterotrophic consumption of EPS appears to facilitate CaCO₃ precipitation and formation of micritic crusts preserved within the stromatolites.

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STROMATOLITES: DEVELOPMENT AND PRESERVATION

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The key controls on benthic microbial carbonates are microbial growth and environmentally influenced calcification. Microbes do not fully control the precipitation processes that are essential for stromatolite accretion and preservation. As a result, formation of stromatolites and related microbial deposits depends on an intimate combination of organic and inorganic factors. These not only determine the sedimentary characters of microbial carbonates, but also are the principal influences on their distribution in time and space.

Microbes through time

Although cyanobacteria appear, overall, to have been the principal builders of microbial carbonates, modern marine stromatolite communities such as those at Shark Bay and Lee Stocking Island contain a significant component of diatoms and other algae. It can be expected that community composition will have changed as microbes evolved, and there may have been a progressive shift from bacterial- towards cyanobacterial-, and then algal-dominated deposits through time. But it is still difficult to assess these possibilities.

Precipitation

depend on Because they both organic and inorganic factors (mixomineralization), microbial carbonates can be regarded as mixocarbonates (from Gk mixo-, mixed). Cyanobacterial calcification, for example, does not proceed unless the saturation state of ambient water favours CaCO₃ precipitation. Other process-related categories of sedimentary carbonates are abiocarbonates, reflecting inorganic controls (abiomineralization), e.g. spring carbonates; and biocarbonates, reflecting organic controls (biomineralization), e.g. most shells. The status of some non-skeletal carbonates, such as ooids, early marine cements, and peloids is still debated; some workers regard them as abiocarbonates, others as mixocarbonates. In microbial carbonates, environmental facilitation raises overall supersaturation levels and biological activity provides local stimulus to precipitation through metabolic processes that increase alkalinity, such as photosynthesis, methanogenesis, sulphate reduction, and ammonification.

Products

Microbial carbonates consist of (i) precipitated micrite, (ii) allochthonous grains, and (iii) early fibrous and equant spar cement crusts on organic tissue and grain and mineral surfaces. Subordinate attached calcified eukaryotes may also be present. Microbial micrite is usually a principal component and results from calcification of extracellular polymeric substances (EPS) present as biofilm or sheath mucilage. This produces both clotted (spongiostrome) fabrics and calcified (porostromate) fossils that form crusts and masses ranging from dense deposits with few primary voids, to frameworks with sizeable cavities. The various patterns of accretion and calcification, together with the relative importance of agglutinated and precipitated material, result in distinctive macrofabrics: layered/laminated (stromatolite), clotted (thrombolite), dendritic (dendrolite), structureless (leiolite).

Shape

The external form of subaqueous microbial carbonates ranges from digitate to domal. Shape depends mainly on vertical relief, which in turn reflects accretion rate relative to adjacent sedimentation. High accretion rate results in high relief which limits lateral interference from adjacent sediment and results in simple shapes, such as the classic microbial dome. Low accretion rate results in low relief which allows growth to be interrupted and deflected, and results in complex digitate morphologies.

Microbial carbonates through time

At the present day, supersaturation with respect to carbonate minerals varies spatially and directly affects microbial carbonate sedimentation. This can be seen by comparing tufa stromatolite formation in freshwater, at one extreme, with the absence of stromatolites from cold marine waters at the other. Through time, in marine environments, microbial calcification has been common during episodes termed Cyanobacterial Calcification Episodes (CCEs), marked by relative abundance not only of microbial carbonates, but also of non-skeletal carbonates. CCEs are believed to represent periods of elevated carbonate saturation. They may correspond with one or more of the following: high global temperature (which enhances precipitation rate), low sea-level and low skeletal abundance (which increase availability of calcium and bicarbonate), and development of alkalinity pumps from stratified basins.

Decline models

Synsedimentary lithification is not only the key to the formation, maintenance, preservation and abundance of microbial carbonates, but is probably more important than metazoan interference in determining success through time. Interpretations of stromatolite decline, from Precambrian to Recent, have commonly invoked the effects of grazing invertebrates or algal competition. Recognition of the importance of synsedimentary calcification and lithification directs attention away from this emphasis on ecological interactions, and supports the view that declining carbonate precipitation may have been responsible for stromatolite decline. Following this view, the success of present-day stromatolites at Shark Bay and Lee Stocking, and also much more widely on carbonate tidal flats, is not because these environments are hostile to most metazoans, but because these are habitats where precipitation is enhanced. Shark Bay and Lee Stocking, respectively, are wave and current swept environments where water movement will promote marine cementation, and intertidal carbonate flats are sites of evaporation which has a similar effect. These are not refuges from metazoan interference, but environments of rapid early lithification. The same reasoning can be applied to heavily calcified stromatolites that form in freshwater lakes and pools.

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BRYOSTROMATOLITES: AN EVOLUTIONARY MODIFICATION OF STROMATOLITES IN MODERN TIMES

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Laminated crusts composed of bryozoan sheets are frequently found. There is some evidence that this peculiar structure is stimulated by confrontational processes with benthic microorganisms (microbial mats).

Self-overgrowth is a regular bryozoan defense mechanism against mat overgrowth (SCHOLZ & KRUMBEIN 1996). In most cases, the mats do not lithify ("potential stromatolites") and induce a considerable carbonate production by bryozoans. Sponge mats, cyanobacteria, diatoms, and pathogenic fungi have similar effects. If the epizoic mats agglutinate sediment, processes can also be recognized in the fossil record (LEE et al., in press).

If the overgrowth interactions between bryozoans and (epizoic) microbial mats show a reversibel pattern, cyclic competitive intergrowth can result in the formation of **high-frequency bryo(-zoan)stromatolites**. This type has been described from Recent aphotic zones (submarine caves and upper bathyal) from the Philippines and the Gulf of Aqaba, and from shallow marine habitats of New Zealand region (SCHOLZ 1996; STERFLINGER & SCHOLZ, in press). The potential for the evolution of bryostromatolites, and the radiation of Upper Cretaceous bryozoans in general (see VOIGT 1979) may have been enhanced by the radiation of slime-producing benthic diatoms in the mid-Cretaceous (see RIDING 1994).

Nodular, reef-like structures produced by microbial mats (stromatolites), self-overgrowing bryozoan sheets and microorganisms (bryostromatolites), and frontally budding bryozoan colonies (Bryolites).

Aside from high-frequency structures, low frequency



bryostromatolites are formed by postmortal and microbially induced lithification inside bryozoan zooecial cavities. Seasonal fluctuations of environmental parameters control a phase displacement of bryozoan and microbial mat / stromatoid growth. One of these undulating factors is salinity. While bryozoan crusts (and serpulids) grow at euhaline conditions, the microbiota - for example the coccoid cyanobacterium *Pleurocapsa* - precipitate carbonate during yearly periodes of hypersalinity and low sealevel stands. The interplay can result in the construction of meter-wide reef structures such as present in the Coorong lagoon and Lake Clifton (Southern Australia) (see SPRIGG & BONE 1993; SCHOLZ 1996). It is assumed that several modern stromatolites are in fact bryostromatolites.

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THE NATURE OF SPONGE-ASSOCIATED BACTERIA

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Sponges are evolutionarily ancient organisms, which fundamently shaped, together with other reef-building organisms, the topology of our contemporary world by the formation of huge CaCO3 structures. Although the geological and pharmacological relevance of these metazoa has been elucidated, the relevance of associated bacterial populations for the sponges and specific processes as biomineralization and production of secondary metabolites is almost completely unknown. The presence of bacteria in living sponges is well documented, mostly by microscopic (REITNER 1993, VACELET & DONADEY 1977) and culture techniques (SANTAVY *et al.* 1990, WILKINSON 1978a). Since only a small portion of the bacteria could be selected and partly characterized from few sponges, the function of the majority of the sponge-associated microorganisms is still unknown.

One of the sponges investigated to clarify the bacteria-sponge interactions is the mediterranean species *Chondrosia reniformis*. Bacteria associated with this sponge were examined by aerobic and anaerobic cultivation and cultureindependent methods as whole cell *in situ* hybridization, PCR-assisted rDNA sequence retrieval and comparative sequence analysis. *In situ* probing was performed using fluorescently labeled 16S and 23S rRNA-targeted oligonucleotide probes specific for the domains *Archaea* (probe ARCH915, STAHL & AMANN, 1991) and *Bacteria* (probe EUB338, AMANN *et al.* 1990) as well as the alpha-, beta-, gamma-, and delta-subclasses of *Proteobacteria* (probes ALF1b, BET42a, and GAM42a, respectively; MANZ *et al.*, 1992) and species-specific probes for sulfatereducing bacteria (MANZ et al., unpublished data).

Hybridization of bacteria within the sponge tissue showed that the majority of them are members of the *Proteobacteria* (SCHUMANN-KINDEL *et al.*, 1997). Computer-aided sequence analysis of pure cultures isolated from *Chondrosia reniformis* indicated close relationships to the family *Vibrionaceae*.

Using highly specific oligonucleotide probes for detecting sulfate-reducing bacteria, distinct signals could be found scattered in native sponge tissue.

Anaerobic cultivation of sponge-associated bacteria resulted in the enrichment of various gram-negative sulfate-reducing bacteria, assigned to different phylogenetic taxa within the *Desulfovibrionaceae* and *Desulfobacteriaceae*.

Further studies of culturable sponge-associated microorganisms are in progress to investigate the ecology of sponge-associated microorganisms. This survey will elucidate the physiological properties and, by molecular analysis, the phylogenetical affiliation of these organisms. Occurrence and spatial distribution of even uncultured bacteria in sponge tissue will be analyzed by *in situ* hybridization with specifically designed rRNA-targeted oligonucleotides.

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THE LOWER PERMIAN ROTLIEGEND STROMATOLITES FROM THE SAAR-NAHE BASIN (SW-GERMANY) ARE UNDOUBTEDLY BIOGENIC BUILDUPS

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Stromatolites are laminated, accretionary structures, which are commonly regarded to have formed by the sediment-binding or precipitating activities of ancient microbial mats or biofilms (composed mainly of cyanobacteria). But as stromatolites only rarely contain fossil microbes, their biogenicity is tacitly assumed on the basis of morphological comparisons with modern, demonstrably biological structures (GROTZINGER & ROTHMAN 1996). According to RIDING (in NEUWEILER et al. (Ed., 1997) stromatolites and other associated microbial carbonates (e. g. thrombolites) are the most common and conspicuous fossils in the Precambrian, but are comparatively scarce at the present day. Synsedimentary lithification and calcification is central to microbial carbonate accretion and preservation. Thus, stromatolites develop at times and in locations where environmental factors are favourable. In these conditions, microbial carbonates can co-exist with or even displace metazoans.

In agreement with supplementary sedimentogical and palaeontological data the Lower Permian Rotliegend stromatolites appear in the Saar-Nahe Basin (SW-Germany) both as lacustrine and as fluvial forms.

Amongst the lacustrine forms in littoral but quiet water zones of ancient lakes subspherical, domed and tabular bioherms are developed as well as tabular and domed biostromes. The branching types of the Rotliegend columnar stromatolites are multifurcate, bifurcate, lateral, dendroid, parallel, moderately divergent and markedly divergent but there are also non-branching Rotliegend columnar stromatolites of turbinate, bulbous, nodular and hemispherical type (GREY 1989, WALTER et al. 1992). Additionally non-columnar Rotliegend stromatolites are developed which are flat-laminated, undulatory, pseudocolumnar, columnar-layered and/or cumulate.

The fluvial forms of the Rotliegend stromatolites are mostly noncolumnar.Sometimes they encrusted floating stems of woody plant and produced several m long objects with 20 cm in diameter (SCHÄFER & STAPF 1978, FREYTET et al. 1996).

Really cyanobacterial or algal structures are mostly not preserved in the Rotliegend stromatolites. For the first time STAPF (1992) found in lacustrine stromatolites of the youngest carbonate-producing Rotliegend lake well preserved but silicified blue-green algae such as *Schizothrix*, *Dichothrix* and *Rivularia*. The reason for the good preservation of these fossils is an early diagenetic silicification of the gentle algal structures caused by volcanic ash fall and the following saturation of the top of the algal-bearing stromatolites by diagenetically mobilized SiO₂.

Particularly these true fossils prove undoubtedly the biogenic character of the Rotliegend stromatolites of the Saar-Nahe Basin and this is in sharp contrast to the recently proposed abiotic model for stromatolite morphogenesis (GROTZINGER & ROTHMAN 1996).

Besides the columnar and non-columnar Rotliegend stromatolites oncolitic forms of littoral agitated water zones of ancient lakes are also developed.

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CARBONATE PRECIPITATION BY FUNGI IN TERRESTRIAL SEDIMENTS AND SOILS

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Fungi are common biota in terrestrial sediments and soils. They are very resistant as single hyphae as well as in symbiosis with algae with which they form Lichens. This aptitude to survive allows them to colonize all kinds of environments, including the most extreme. Surprisingly, their role in sedimentary processes has not been studied in detail. A few papers emphasize their potential role in carbonate precipitation and diagenesis in surficial environments (Kahle 1977; Klappa 1979a,b; Phillips et al. 1987; Phillips and Self 1987; Jones 1988; Verrecchia 1990). The aim of this paper is to propose an overview of fungal contribution to limestone diagenesis in surficial environments and to introduce new data on the process of calcite precipitation by fungi in carbonate indurated layers of paleosols and sediments.

Two main kinds of features are related to fungal activity in carbonate soils and sediments : calcified filaments and needle-fiber calcite.

A calcified filament has been defined as "one wherein $CaCO_3$ has replaced the filament or has been precipitated on or within the filament" (Kahle 1977, p. 415). Although some of these calcified filaments are obviously root hairs (Coniglio and Harrison 1983) or algae (Kahle 1977), most of them have the size and shape of fungal filaments. Another argument that can be used to attribute filaments to fungal hypha is their association with Ca-oxalates (Verrecchia et al. 1993).

The Ca-oxalate cycle in sediments and soils, and its role in early diagenesis are complex: during the fungi's life, the hydrolysis of oxalo-acetate produces oxalic acid, which is released in free form into the medium through the hyphal wall. The availability of Ca²⁺ in the environment leads to weddellite precipitation. The uptake of calcium for weddellite formation releases carbonate anions into the pore solution, which can contribute to secondary precipitation of calcite outside the pore (Verrecchia and Dumont 1996). The metastable weddellite can easily transform into whewellite (by water loss - Frey-Wyssling 1981; Verrecchia et al. 1993), which in turn can be transformed into calcite after oxidation by bacteria. Therefore, the presence of fungi in the porosity allows a redistribution of calcium carbonate and impregnation of the pore walls, hardening the micritic matrix around pores. This secondary cementation can be very strong and forms indurated layers in paleosols. In addition, certain fungi are also able to directly precipitate calcite as needle fibers (NFC).

Needle-fiber calcite is a common feature of carbonate soils and sediments. The ability of fungi to precipitate NFC has been demonstrated by Callot et al. (1985) in the laboratory. Three types of NFC have been described (see synthesis on NFC in Verrecchia and Verrecchia 1994): long and smooth monocrystalline (MA), long and serrated-edged monocrystalline (MB), and polycrystalline (P) crystals. Fungi form the long, smooth MA rods. The serrated-edged needles result from reprecipitation of calcite on MA rods after their release from the hypha. The origin of the P form is unclear and probably related to supersaturation of soil solutions with calcite. Our observation of present-day carbonate soils show that NFC is precipitated inside the mycelium strand and released into the medium either by lateral / apex percing during fungi life or after its death by the decay of organic matter.

A crystallographic study of the MA needles with a TEM coupled to a microdiffractometer confirmed their calcitic (LMC) and monocrystalline nature as observed by Phillips and Self (1987). But their isotopic signature remains unclear : measurements on microscopically, and virtually, identical NFC resulted in differences in δ^{13} C‰ PDB content greater than 10. Can this property be explained solely by diagenesis ?

The production of NFC does not increase the hardening of the sediment but notably increases the porosity (specific surface) and the $CaCO_3$ content of the layers where they form. These characteristics can explain the *in situ* enrichment in calcite inside calcic layers without using *per descensum* or leaching processes.

In conclusion, fungi transform the carbonate rocks, concomitantly increasing their porosity, strength, and calcite content. They seem to play a major role in the diagenesis of surficial carbonate as calcretes through complex reactions involving organic acid excretion, calcium oxalate precipitation, and calcium carbonate biocrystallization.

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PARAGENESIS OF HOLOCENE CRYPTIC REEFAL MICROBIALITES, HERON REEF, GREAT BARRIER REEF, AUSTRALIA

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Cryptic, Mg-calcite microbialites have been described from many Holocene coral reefs (Reitner, 1993; Zankl, 1993; Camoin & Montaggioni, 1994; Webb & Jell, 1997) and may account for many previously described Mg-calcite reef cements (e.g., Macintyre & Marshall, 1988). The biotic or abiotic origin of fine-grained carbonates has been a source of continuing controversy in the sedimentology of both modern and ancient carbonates. Although Reitner (1993) observed the biofilm community responsible for microbialite formation in reef caves at Lizard Island, the origin of most reefal microbialite has been inferred from gross morphology (e.g., Camoin & Montaggioni, 1994; Webb & Jell, 1997). We present microstructural evidence supporting the organic origin of cryptic microbialite from Heron Reef, southern Great Barrier Reef, Australia, and document the early sequential development of biologically induced microstructure. The early transformation of Heron microbialite accretionary fabric is considered "paragenetic," because it occurs contemporaneously with microbialite accretion, in much the same way as aragonite needles in Halimeda alter to anhedral micrite during the life of the alga (Macintyre & Reid, 1995). The paragenetic masking of the biological origin of Heron microbialite suggests that great care must be taken in using microstructure, such as crystal morphology, when assessing the biotic versus abiotic origin of fine Mg-calcites.

Heron microbialites occur as crusts of individual, finger-like microcolumns or branching dendrolites, rarely more than one centimeter long (Webb & Jell, 1997). Observation of the tips of individual microcolumns, which are interpreted as the most recently growing surfaces, using scanning electron microscopy reveals sub-0.5 µm, rounded Mg-calcite crystallites coalesced into smooth, thin crusts that drape over underlying topography. These crusts are interpreted as the calcified basal layer of a biofilm. No calcified bacterial remains or filaments have been positively identified on the surface. Crystallite morphology progressively changes along the microbialite surface away from the tip towards the base of the microcolumn. Crystallites become larger and more euhedral, although they remain, for the most part, randomly oriented. Sharp, euhedral 1.0 µm scalenohedrons commonly occur in low areas of the surface near the bases of microcolumns. The microstructure also changes progressively from the tip surface towards the interior, and base, of the microcolumn. Within 15-20 µm of the outer surface the smooth crusts have been replaced by euhedral crystals with dimensions up to 1.0 µm. These crystals are generally more, or less, randomly oriented, except where they grow into abundant pore spaces. Deeper within the microbialite interior, crystal size increases, yielding, at the bases of microcolumns,

fringes of well-formed, oriented, >3 µm scalenohedra that are indistinguishable from previously described Mg-calcite cements (e.g., Macintyre, 1977, Fig. 4C).

The progressive transformation of sub- μ m, anhedral crystallites into euhedral, oriented fringes of scalenohedra that reach dimensions over 3.0 μ m is interpreted as having occurred concomitantly with accretion of new carbonate at the growing tip. We infer little if any additional alteration to the fabrics since the disappearance of the biofilm. If the alteration occurred, after removal of the active biofilm, it would be expected to have equally affected the crystallites over the entire surface, and all crystallites would be expected to be similar. Additionally, Mg-calcite fringe cements do not lithify porous sediments associated with some of the microbialites; anhedral Mg-calcite scalenohedra are confined to the interiors and bases of microbialites. Finally, etching experiments were not able to reproduce surficial morphologies on freshly broken surfaces of the microbialite interiors. Hence, the observed distribution of microstructures represents a "snapshot" of the processes occurring prior to the disappearance of the biofilm, and the scalenohedra were precipitated only within waters affected by the biofilm.

The paragenetic alteration of calcified biofilms into oriented fringes of scalenohedra identical to "abiotic" cements has important implications for interpretations of the origin of cryptocrystalline carbonates and cements. If the gross morphology and surficial microstructure of Heron microbialites were not preserved, microstructural evidence alone would suggest an abiotic origin for the deposits. This brings into question the origin of other apparently abiotic Mg-calcite cements in reefal and other shallow marine environments. With the ubiquity of biofilms in the shallow marine environment, we might ask how much Mg-calcite cement is biologically induced. Perhaps all of it is.

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DOLOMITE FORMATION IN DISTAL EPHEMERAL LAKES OF THE COORONG REGION, SOUTH AUSTRALIA

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A number of lakes in the Coorong region of South Australia contain a sedimentary infill of modern dolomite, a relatively rare mineral in Recent sediments whose mode of formation is uncertain. Previous evaporative and other models proposed for the origin of Coorong dolomite are unconvincing, because they fail to explain how the kinetic inhibitors to dolomite formation in saline waters are overcome, and because the proposed mechanisms conflict with empirical data. Important inhibitors include the strength of the Mg²⁺_H₂O bond, the extremely low activity of $CO_3^{2^2}$ anions, and the presence of sulphate.

In early summer, lakewaters from dolomitic lakes are characterised by high pH (8 - >9), elevated concentrations of carbonate and magnesium, and compared with other lakes, relatively low levels of sulphate. Lake macrobiotas are unable to survive increased salinity as desiccation ensues. Microprofiles of sediment porewaters show high pH values in the uppermost levels, promoting high carbonate ion concentrations and activities. Ultimately all the lakewater sulphate is removed during evaporation, with no precipitation of gypsum, leaving a crust of halite overlying the dolomitic mud. The presence of hydrogen sulphide indicates that intense bacterial sulphate reduction occurs in the anoxic lake sediments, and is responsible for the absence of gypsum, confirmed by XRD analysis of the dolomite. Sulphate reduction may also lead to increased alkalinity during organic degradation, and thus has the potential to remove all kinetic inhibtors to dolomite formation, providing a mechanism for dolomite precipitation in the shallow subsurface sediments.

In contrast, waters in the non-dolomitic Stromatolite lakes are characterised by extremely high sulphate and magnesium concentrations coupled with relatively low carbonate concentrations and pH levels. Again, gypsum is absent, though halite crusts overlie the sediment. Hydrogen sulphide in the lake sediment indicates microbial sulphate reduction, but the activities of a burrowing infauna may aerate the sediment so that low concentrations of sulphate are maintained, thus favouring aragonite precipitation rather than dolomite.



THE CONTRIBUTION OF MICRITES TO THE STABILIZATION OF CARBONATE MUD MOUNDS

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The famous "Steinplatte Reef" of Upper Rhaetian age in the Northern Calcareous Alps has been interpreted by STANTON and FLÜGEL, 1995, as a mound forming an accretionary distally steepened ramp. The question rises: how can a mound with a thickness of 170 m in its final stage and with a slope dipping 35° towards the Kössen basin be stabilized?

There is only a minor amount of framework preserved, formed by corals, sponges, and tabulozoans. The major part of the mound is made up of bioclastic packstones and grainstones.

A key to the problem how this sediment pile was stabilized is found in the origin of micrites. They occur in micritic rims, peloidal cements or small scale microbolitic encrustations on hard substrates. These micrites act as stabilizing cements. Their fabric cannot be resolved by light microscope. The microfabric is better seen under high resolution SEM: micritic rims, peloidal cements, and microbolites differ in crystal shape, size and crystal boundaries. The micrite fabric is the product of recrystallization of earlier cryptocrystalline carbonates (< 1 μ), possibly precipitated in different organic matrices. An environment suitable for the nucleation of carbonate can be created either by the decay of organic molecules, or other physiological activities of microorganisms.

The final result in geological record are micrites with a characteristic microfabric.

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