Project: Mi 157/10 „Biogeochemie moderner Porifera und Mikrobialithe der Lizard-Inselgruppe und fossile Vergleiche", Project Leader: W. Michaelis (Hamburg)

Biogeochemistry of Modern Porifera and Microbialites from Lizard Island (Great Barrier Reef, Australia) and Fossil Analogues

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Area of Study: Various localities, emphasis on Great Barrier Reef samples (e.g. Lizard Island reef caves)
Environment: Various settings, marine to limnic
Stratigraphy: Mesozoic (Upper Jurassic) to Recent
Organisms: Sponge-microbiota communities, cyanobacteria and others
Depositional Setting: Various settings of carbonate buildup formation, marine (carbonate shelves) to lacustrine (terrestrial sedimentation)
Constructive Processes: Different modes of microbialite formation, carbonate precipitation by reef sponges
Destructive Processes: Boring organisms, microbial corrosion
Preservation: Variable, ranging from well (recent) to poorly preserved (some heavily recrystallized fossil materials)
Research Topic: Application of organic geochemical techniques as a tool for the characterization of recent and fossil biocommunities in carbonate deposits

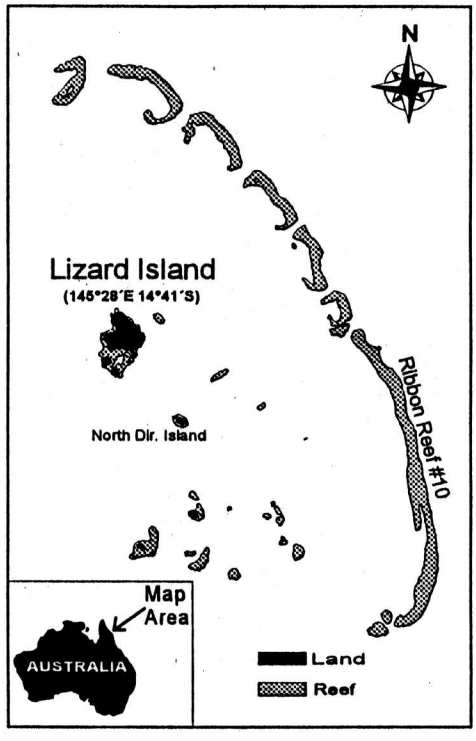

Fig. 1: Location of the Lizard Island Group (after WÖRHEIDE et al. in press).

Abstract

Organic geochemical techniques were applied to study the lipid content of living reef organisms and rock samples from different carbonate facies. The characterization of individual organic compounds ("biomarkers") yields information on the biology and paleontology of microbially derived carbonate rocks, sponges and sponge-microbiota communities on a molecular level.

1 Aims and Methods

Aims

Characterization of/information on:
- organic compounds (biomarkers) produced by reef organisms in various carbonate facies
- early diagenetic alterations of these components
- bacterial biomass and host-symbiont interactions in recent sponge-microbial communities
- sponge chemotaxonomy
- molecular fossils in ancient carbonates

Methods

Carbonate was removed by treatment with diluted hydrochloric acid. The samples were extracted with organic solvents. The resulting extracts were fractionated by chromatographical methods. The obtained, purified fractions (hydrocarbons, alcohols, ketones, carboxylic acids) were analyzed by gas chromatography and combined gas chromatography/mass spectrometry.

Samples

- cyanobacteria (pure cultures)
- cyanobacterial mats
- recent "phototrophic" microbialites
- soft demosponges
- sclerosponges
- lithistid sponge
- hexactinellid sponge
- recent non-phototrophic microbialites
- coral framestone
- red algae crusts
- fossil sponges and sponge-microbial crusts
- fossil microbialites

REITNER, J., NEUWEILER, F. & GUNKEL, F. (eds., 1996): Global and Regional Controls on Biogenic Sedimentation. I. Reef Evolution. Research Reports. – Göttinger Arb. Geol. Paläont., **Sb2**, 129-132, Göttingen

2 Results

2.1 Biological Markers Produced by Reef Organisms in Different Recent Carbonate Facies

Carbonate rocks from different recent and subrecent facies types can be classified by organic compounds left by their main component organisms. In extension, associations of different groups of organisms contributing organic matter into the forming carbonate rocks can be distinguished by the occurrence of the respective marker molecules. For example, a mixed population of (predominantly) cyanobacteria, demosponges, diatoms, green algae and anoxygenic bacteria is documented in the active layers of the Lee Stocking Island stromatolite. A semiquantitative classification of the studied materials with respect to the occurrence and relative abundances of some molecular markers is given in Tab. 1. A high source specificity for a given biomarker or biomarker pattern implies its limitation to a defined organism or facies type (e.g. VOLKMAN 1986, PETERS & MOLDOWAN 1993). For example, individual mid-chain branched monomethyl alkanes are characteristic for structures with a contribution of cyanobacteria. Other compounds, like the linear short-chain alkanoic acids, show a broad distribution in organisms and thus exhibit a comparably low marker quality (e.g. THIEL et al. subm. a).

2.2 Early Diagenetic Alterations of Biological Markers

The diagenetic fate of a given organic compound is the key for the application of the biomarker concept on fossil carbonates.

- An incorporation of cyanobacterial hydrocarbon markers into carbonate rocks is evident from their presence in inactive microbialites ranging back in age to the Late Pleistocene (Mono Lake, Pyramid Lake, Searles Lake). However, our data revealed that their extent of preservation is strongly affected by microbial degradation processes at a very early stage and is apparently favored by an early incorporation into massive rock structures.
- A good preservation potential of fatty acid marker patterns was observed in all samples for which surface and mature portions were compared.
- Alcohols, namely sterol markers derived from eukaryotic organisms, show a broad variability in their fossilization behavior. Their distribution may be completely retained (e.g. in a coral framestone, a red algae crust and the basal skeleton of the sclerosponge *Spirastrella wellsi*), or severely altered (like in the basal skeleton of the stromatoporoid *Astrosclera willeyana*). Poor retainment of sterols was generally observed within microbialite structures which may show even a complete lack of these compounds in their mature compartments. It is suggested that the extent and the quality of sterol degradation is bacterially driven.

In microbial carbonates, all compound classes exhibit a preferential preservation of saturated vs. unsaturated components, long-chain vs. short-chain homologues, branched and cyclic vs. linear compounds.

2.3 Bacterial Biomass and Host-Symbiont Interactions in Recent Sponge-Microbial Communities

It is known that the presence of bacteria in sponges can be traced by the occurrence and the relative abundance of unique prokaryotic fatty acid markers (GILLAN et al. 1988). These compounds comprise branched acids typically found in pure cultured prokaryotes. In this study, unique isomer mixtures of symbiont derived mid-chain methylated homologues were characterized for the first time (THIEL et al. subm. b). Demosponge membrane fatty acids (="demospongic acids") can be clearly distinguished from the symbiont derived components by the presence of characteristic molecular properties, i.e. high carbon chain lengths (C_{24}-C_{30}) and distinct unsaturation patterns (LITCHFIELD et al. 1976). The analysis of total sponge fatty acids therefore reveals a sensitive tool to determine the portion of symbiont vs. host derived cell biomass. As an example, low percentages for branched fatty acids were found in the nearly symbiont free sclerosponge *Spirastrella (Acantochaetetes) wellsi* (4.3 %). In contrast, particularly high abundances of these compounds in the lithistid demosponge *Coralistes typus* (64.2 %) and the demosponge *Agelas oroides* (59.0 %) reflect the presence of very high amounts of heterotrophic bacterial symbionts within these organisms.

The analysis of fatty acid characteristics also reveals useful information about host-symbiont interactions. This is highlighted by the discovery of terminally branched demospongic acids in *Coralistes typus* and the sphinctozoan-type sclerosponge *Vaceletia* nov. sp. These sponges evidently utilize bacterially derived short-chain homologues as building blocks for the synthesis of their respective demospongic acids.

2.4 Sponge Chemotaxonomy

The chemical composition of reef sponges may reflect their taxonomical position within the Porifera (e.g. BERGQUIST et al. 1986). In a case study, we investigated the lipid characteristics of the recent stromatoporoid *Astrosclera willeyana* (WÖRHEIDE et al. in press) in comparison to various other sponges to characterize its taxonomical position. Comparative analyses revealed that *A. willeyana* matches the patterns found in demosponges belonging to the taxon Agelasidae. The agelasid "fingerprint" which is clearly recognized in *A. willeyana* includes

- the pronounced presence of the isoprenoid 3,7,11,15-methylhexadecanoic (phytanic) acid;
- the presence of the consecutive C_{24}, C_{25}, and C_{26} $D^{5,9}$ dienoic acids as the principal demospongic acids (e.g., CARBALLEIRA & EMILIANO 1993);
- the absence of Δ^5-unsaturated sterols combined with the prominent abundance of saturated as well as "primitive" steroid compounds tentatively identified as Δ^7 and Δ^8-sterols
- the presence of unique brominated antibiotics typical for agelasid demosponges.

2.5 Molecular Fossil Origins in Ancient Carbonates

Four principle processes determine the composition of organic matter found in ancient carbonates:

1) Input of organic matter from the water column (phyto- and zooplankton, higher plants),

2) Input of organic matter from benthic organisms (e.g. algae, sponges, microbial mats),

3) Early postsedimentary microbial and chemical alteration (degradation of primary lipids, additional input of bacterial lipids),

4) Late diagenetical and catagenetical maturation (temperature, pressure).

The postsedimentary processes (3, 4) generally account for a loss of primary information. Depending on their degra

Tab. 1: Distributions of selected biological markers in reef carbonates and associated organisms.

Table 1 Distributions of selected biological markers in reef carbonates and associated organisms

COMPOUND	STRUCTURE	FEATURE	ORIGIN	SAMPLES																													
				'Cyanobacterial facies'										Reef carbonates (marine)										Sponges											
				Cultures		Carbonates (recent)				Carbonates (mature				Microbialites					Others					Agelasids			Others							
n-Heptadecane		high relative abundance	Cyanobacteria			xx	xx	xx	xx	x	x	x	xx																				
n-Heptadecenes		high relative abundance	Cyanobacteria	xx	xx	xx	xx	xx	xx			tr	xx																				
n-Octadecenes		high relative abundance	Green algae (?)			x	x	xx	x		xx		xx																				
Mid-chain br. alkanes		discrete isomers	Cyanobacteria			xx	xx	xx	xx	tr	xx	x	x																				
Dimethyl-alkanes		presence	Cyanobacteria				x					xx																				
Diploptene		high relative abundance	Cyanobacteria		x	x	x	xx	x	xx	xx	x	x																				
Short-chain *n*-alkanes		modal distributions	Metabolites?											xx	xx	xx	xx	x	xx	xx				x							x	
Mid-chain br. alkanes		complex mixtures	Metabolites?											tr	xx	xx	xx	x	x	x				x							tr	
Linear fatty acids <C25	COOH	high relative abundance	widespread	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	xx	x	xx	xx	xx	xx	xx	x	xx	xx						
Terminally br. fatty acids	COOH	presence	Anoxygen. bacteria			x	x	x	tr	o	x	x	x	tr	xx	xx	x	xx	x	x	xx	xx	xx	xx	xx	tr					
Mid-chain br. fatty acids	COOH	presence	Heterotr. bacteria				tr	x	x	o	tr	x	tr		xx	xx	tr	xx	tr		xx	xx	xx	xx	xx	tr					
Demospongic acids	COOH	presence	Demosponges						x	o					xx	xx		xx			xx	xx	xx	xx	xx	xx					
Highly br. isoprenoids		presence	Diatoms						xx																						
Cholesterol	HO	presence	Animals, algae			xx	o		tr				o		xx	xx		tr	xx	xx				xx		xx	xx					
Δ7-Sterols	HO	presence	Animals, sponges				o						o					tr			xx	xx	xx			x					
Halogenated compounds	Br, Br, N, COOH	presence	Sponges										o		xx	xx		tr			xx	xx	tr	x	tr						
n-alkanes >C25 (odd)		high relative abundance	Higher plants			x	xx	xx	tr	xx	xx	xx	x	x	tr	tr	xx	x	tr	tr					x						x
				Oscillatoria sp.	*Chroococcus* sp.	Everglades cyanobacterial mats, surface	Pyramid Lake stromatolite, surface	Walker Lake stromatolite, surface	Lee Stocking Island stromatolite, surface	Everglades cyanobacterial mats, 12-14cm	Searles Lake stromatolite, Pleistocene	Pyramid Lake stromatolite, Pleistocene	Mono Lake stromatolite, subrecent	Cebu Island, reef caves	Lizard Island, thrombolitic microbialite	Lizard Island, laminated microbialite	St. Croix, Salt River Canyon, Carribean	Lizard Island, mature laminated microbialit	Lizard Island, reef caves, red algae crust	Lizard Island, reef caves, coral framestone	*Astrosclera willeyana*, Great Barrier Reef	*Agelas oroides*, Mediterranean	*Agelas axifera*, Great Barrier Reef	*Vaceletia* nov. sp., Osprey Reef	*Coralistes typus* (lithistid), Bahamas	*Strongylophora* sp., Great Barrier Reef	*Spirastrella wellsi*, Lizard Island reef caves	Deep-water hexactinellid, Darwin Bay	

Explanations

XX = main compound / pronounced feature
X = minor relative abundance / subordinate feature
tr = trace compound
o = compound fraction not analyzed
no entry: compound / feature absent or below detection limit
br. = branched

dation resistance, individual lipid markers may be retained, severely altered or may even disappear during their burial history. Further problems include the sample quality (maturity, recrystallization, weathering, contamination), the lack of known biological precursors and, vice versa, multiple possible origins of several organic compounds found in the studied samples. These ambiguities clearly require further investigation. Nevertheless, diagenetic changes often follow rules which may enable the attribution of a given fossil molecule to its original source organism (TISSOT & WELTE 1984, PETERS & MOLDOWAN 1993). Some of the features observed in the studied fossil Mesozoic microbialites and sponge-microbially derived structures are given in the following:

- Best results were obtained from samples of low thermal maturity and low degree of recrystallization. Particularly high yields of extractable organic matter were obtained from small carbonate buildups embedded in clay-rich sediments (e.g. Upper Jurassic-Thüste; Upper Triassic-Cassian).
- In most cases, significant variation in hydrocarbon compositions was found between different horizons of the same locality (no diagenetical "homogenization")
- A lack or very low concentrations of steroids (derived from eukaryotic precursors), but major relative amounts of hopanoids (bacterial precursors) were observed in all fossil samples.
- The abundance of odd-numbered, long-chain n-alkanes signifies allochthonous organic matter contributions (terrestrial plants).
- Hopane isomerization ratios are often used in the oil industry to determine the stage of thermal maturity (PETERS & MOLDOWAN 1993). Our results from 14 samples of the Upper Jurassic spongiolites (Swabian Alb) indicate that this parameter must be applied with caution, since a striking positive correlation of this parameter with the carbonate content was observed in samples >90 % $CaCO_3$.
- Varying patterns of mid-chain and terminally branched alkanes are found in all fossil samples except the Thüste stromatolite (Upper Jurassic). There is evidence that they derive from corresponding classes of bacterial fatty acids by diagenetical alteration.
- The distributions of hydrocarbons, in particular branched alkanes, in the Upper Jurassic spongiolites exhibit a strong coherence with corresponding compounds found in living sponges and in the recent sponge-microbial crusts from the reef caves of Lizard Island.
- High abundances of isoprenoic hydrocarbons and -carboxylic acids in the Thüste material are most likely due to a prominent contribution from archaebacterial sources. Moreover, organic sulfur compounds found in the Thüste stromatolite are suggested to characterize a highly anoxic environment of deposition.
- Jurassic spongiolite materials typically exhibit the cooccurence of the isoprenoic hydrocarbons squalane and lycopane (HEFTER et al. 1993). These compounds may be derived from archaebacterial sources but we have also detected them in the recent lithistid demosponge *Coralistes typus*.

Acknowledgements

We acknowledge financial support from the Deutsche Forschungsgemeinschaft (Mi 157/10-5, Mi 157/10-6).

The application of organic geochemical techniques on paleontological problems promoted an intense interaction between scientists from different disciplines. Particular emphasis is placed on the initiation and future continuation of a very fruitful cooperation with the group of J. Reitner (Göttingen).

We thank our colleagues, who contributed significantly to the development and completion of this project. Jens Hefter, Hans-Hermann Richnow and Richard Seifert (Hamburg) provided results from other projects supporting our ideas. They are also acknowledged for technical support and many helpful discussions. The Jurassic spongiolite samples from the Swabian Alb were prepared and analyzed by Angela Jenisch and Ursula Galling. The analytical workup of the sclerosponges was done by Antje Löwenberg. We are thankful to Helmut Keupp (Berlin) and Stephan Kempe (Darmstadt) for their initiation of the preceding project Ke 322/10, for providing sample material and for their stimulating discussions in the early stages of the geochemical investigations. Gert Wörheide (Göttingen) has collected the sample materials from the Lizard Island reef caves and from the Osprey Reef. Both, Gert Wörheide and Fritz Neuweiler (Göttingen) are also acknowledged for many critical comments and for providing useful information on the biological and paleontological background of the studied samples.

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