The modern calcifying sponge *Spheciospongia vesparium* (Lamarck, 1815), Great Bahama Bank: Implications for ancient sponge mud-mounds

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Abstract

Modern calcified siliceous sponges from the Great Bahama Bank, living at water depth ranges of 2 to 5 m, have been proposed as likely analogues for calcified sponges in Upper Jurassic sponge "reefs" (e.g., southern Germany), or Lower Jurassic bioherms that consist of reddish, spiculiferous limestones (e.g., Broccatello Formation of the Southern Alps). Indeed, sponge-related calcification or siliceous sponge diagenesis, in general, is widely considered a key feature for the mechanisms of accretion and textural maturation in Phanerozoic sponge mounds or spiculiferous carbonate mud-mounds. Based on a revisit of the original sites on the Great Bahama Bank (NW of Andros Island) the biostratonomy of the calcifying sponge *Spheciospongia vesparium* (Lamarck, 1815) was explored using the patterns of fluorescent dissolved organic matter (FDOM) as revealed by the application of three-dimensional excitation–emission matrix (EEM) fluorescence spectroscopy. Geochemical sampling distinguished between FDOM that was extracted from sponge tissue and FDOM that was intimately associated with CaCO\textsubscript{3} (from particles due to sediment agglutination and authigenic CaCO\textsubscript{3}), both obtained from the living sponge at the sediment surface and from the calcified sponge at the shallow subsurface (from 5 to 10 cm of depth). As expected, the sponge tissue shows highest intensities for protein-like fluorescence. However, from the surface to the subsurface, there is a loss of such relatively pristine fluorescent material in the range of 70%. Humic-like fluorescence that occurs associated with sponge tissue is relatively mature or aged, thus it most probably represents seawater FDOM taken up through active filter feeding. Relative to the sponge tissue material, the FDOM patterns associated with Ca-carbonates show much lower total fluorescence intensities, by up to two orders of magnitude. The agglutinated sedimentary carbonate particles from the surface (pellets, ooids, grapestones) exclusively show a relatively mature, humic-like fluorescence. The deeper, calcified parts of *Spheciospongia*, which represent a mixture of particles and authigenic CaCO\textsubscript{3}, provided a FDOM pattern that obviously combines the mature FDOM pattern of particles with diagenetically fresh, protein-like and fulvic acid-like fluorescence. We conclude that shallow subsurface calcification of *S. vesparium* correlates with the...
initial stage of sponge biomass humification. Such a mechanism of biomass transformation, i.e., from biopolymers to geopolymers via degradation and condensation, has also been suggested for the large-scale development of carbonate (sponge) mud-mounds. Therefore, we consider the modern calcifying siliceous sponge *S. vesparium* (Lamarck, 1815) a potential paradigm to decipher in more detail the geologically important process of biomass-induced calcification or organomineralisation with its subsequent effect of pore water FDOM preservation and sediment lithification.

Keywords: Sponges; *Spheciospongia vesparium*; Lithification; Fluorescence spectroscopy; Fluorescent dissolved organic matter (FDOM); Great Bahama Bank

1. Introduction

Modern bioherms displaying a community that is essentially composed of siliceous sponges (Hexactinellida, Demospongiae) have been reported from a wide range of oceanographic and bathymetric settings: from polar, subphotic continental margins (e.g., along the Canadian and Russian polar margin), to shallow-water tropical carbonate platforms of the Caribbean (Zenkevitch, 1963; Wiedenmayer, 1978; Van Wagoner et al., 1989; Henrich et al., 1992; Conway et al., 1991, 2001; Krautter et al., 2001). In most studies the authors emphasize the importance of their individual case for the understanding of ancient siliceous sponge mounds. Indeed, Wiedenmayer (1978, 1980) regarded modern Bahamian sponge bioherms as likely analogues to the Upper Jurassic sponge “reefs” of southern Germany (Flügel and Steiger, 1981) or to the Lower Jurassic Hierlatz or Broccatello facies of the Alps (Wiedenmayer, 1963, 1980; Neuweiler and Bernoulli, 2005). Van Wagoner et al. (1989) made reference to late Palaeozoic demosponge bioherms, in particular to Silurian lithistid sponge reefs as described by Narbonne and Dixon (1984). Conway et al. (1991, 2001) and Krautter et al. (2001) considered the modern communities they studied an analogue of Upper Jurassic hexactinellid mounds or carbonate sponge mud-mounds on a whole.

However, with the exception of Wiedenmayer (1978, 1980), all other studies missed the key geological feature of ancient sponge mounds or spiculiferous carbonate mud-mounds, namely their “carbonate island” character that requires in-place production of fine-grained calcium carbonate within a commonly carbonate-depleted surrounding facies (cf. Bourque, 2003). Reports on such calcifying siliceous sponge communities, including Wiedenmayer’s papers, only exist in small number, e.g., by Froget (1976) from the Mediterranean Sea and by Reitner (1993) and Reitner et al. (1995) from cryptic sponges of the Great Barrier Reef (Australia).

The aim of this paper is to re-examine Wiedenmayer’s descriptions and observations in order to reassess the potential of Bahamian calcifying siliceous sponges to further our understanding of ancient sponge mounds. We revisited Wiedenmayer’s original sites and made several dives to collect fresh sampling material for fluorescence studies similar to those we have carried out with samples collected from Cretaceous sponge mounds of Spain (Neuweiler et al., 2000, 2003) and Quaternary lithoherms of the Florida Straits (Neuweiler et al., in preparation). The approach we have taken here is process-oriented on a hand specimen scale. It argues for some type of correlation between sponge soft tissue degradation and calcification, irrespective of the regional setting, bathymetry, local community structure and the scale of the resulting geological feature (cf. footnote in Lees, 1964 or Bourque and Gignac, 1983 for early suggestions on the role of sponges to explain some key features of Palaeozoic spiculiferous carbonate mud-mounds).

2. Materials and methods

The sampling sites are located NW of Joulters Cay, about 15 km off the northern tip of Andros Island, Bahamas (Fig. 1). We sampled at two stations with water depths of 3.2 m and 2.0 m, salinity of 36.9‰, and water temperature of 23°C and 24°C, respectively. The sampling sites are well within the strip of “sponge bioherms” indicated in Wiedenmayer...
The sponge *Spheciospongia vesparium* (Lamarck, 1815) was collected by SCUBA diver from the sediment surface to the shallow subsurface, and specimens were immediately frozen on board of the ship. The lapse of time between sampling and geochemical analysis was within four weeks.

In the lab, samples were taken from frozen specimens from the fresh, uncalcified top of the sponge and the lower, calcified parts of the sponge. The initial sample weight varied between 0.2 and 0.6 g, values that were later used to normalize spectroscopic results to unit (initial) weight. Extraction of fluorescent dissolved organic matter (FDOM) was done in three steps using: (a) 0.5 M NaOH, (b) 1 N HCl (decalcification), and (c) again 0.5 M NaOH. Before decalcification the solid residue was intensively bleached using NaOCl (cf. Sykes et al., 1995). A procedural blank of 0.5 g commercial CaCO₃ was carried through the extraction procedure. Prior to measurements (3 ml in quartz cuvette) aqueous solutions were filtered through syringe filters of 0.45 μm pore size. Thus, our results refer to the spectroscopic properties of fluorescent dissolved organic matter (FDOM).

Excitation–emission matrix (EEM) fluorescence spectra display a three-dimensional record of fluorescence intensity as a function of excitation and emission wavelengths. Numerous studies of EEM spectra of fluorescent dissolved organic matter
(FDOM) from natural waters integrate for a common pattern of fluorescence peaks (Burdige et al., 2004; Neuweiler et al., in preparation, with references therein). For the purpose of this paper, the increased understanding of the fluorescence pattern in natural waters (Coble et al., 1990, 1998; Coble, 1996; Mayer et al., 1999; Parlanti et al., 2000; Burdige et al., 2004) serves as a base to decipher the biostratigraphic pathway of *S. vesparium*. Fluorescence spectroscopy was performed on a Spex Industries FluoroMax-2 spectrofluorometer with a DataMax software station. Data acquisition was performed in the signal over reference mode for direct subtraction of background signals (noise reduction). Mathematical processing of measured spectra includes subtraction of the procedural blank (commercial CaCO₃), the application of excitation and emission correction factors (see Burdige et al., 2004, for details), and normalization of spectra per initial weight. Quantification of fluorescence intensities was achieved from standard calibration using quinine sulfate dihydrate (QS) solution (in 0.05 M H₂SO₄). Fluorescence intensity is reported in quinine sulfate units (qsu) within the linear ppb range. Fluorescence peaks are reported according to the terminology of Coble (1996) and Burdige et al. (2004).

3. Results

3.1. Calcifying sponges

Wiedenmayer (1978) reported two species of calcifying sponges of the Great Bahama Bank, the very common *S. vesparium* and *Anthosigmella varians* which, by frequency of occurrence, is of subordinate importance. According to this author, *S. vesparium* represents by far the most important species that appears to be connected to the phenomenon of submarine lithification. *Spheciospongia* is a hadromerid demosponge (Clionaidae) that excavates limestone substrate during its early stages of life (review in Vicente et al., 1991; see also Rützler and Hooper, 2000).

*Spheciospongia* is recognized at the sediment surface by its dark colour and a number of small oscular chimneys that are arranged in a fairly open pattern with their tips standing only a few centimeters above the sediment surface (Fig. 2). In some cases *Spheciospongia* appears whitish and knobby, but in such cases it has been exhumed out of the sediment by winnowing of sediment. Lithification of *Spheciospongia* occurs in the shallow subsurface within depths of a few centimeters (Figs. 2 and 3). The immediate sediment surface is a veneer of loose

![Fig. 2](image-url)
particles, consisting essentially of carbonate pellets, ooids and grapestones. Below this sediment cover the sediment becomes a lithified patch or slab, in most cases hardened enough to form a carbonate rock that requires a hammer to be broken off. Such shallow subsurface, patchy hardgrounds reach sizes in the square meter range (cf. Fig. 2A). If locally exposed, these hardgrounds provide substrates for encrusting organisms such as serpulids, calcareous algae, bryozoans, scleractinian corals to combine for the development of small bioherms (details in Wiedenmayer, 1978). The occurrence of such eye-catching carbonate structures is, however, subsequent to sponge calcification and exhumation. Once properly identified, Spheciospongia appears to be very common within the widespread area of sparse to dense sea-grass beds on the Great Bahama Bank (R. Zimmermann personal communication, 2004).

3.2. Fluorescence spectroscopy

Sampling for fluorescence spectroscopy distinguished fresh-uncalcified and mature-calcified parts of Spheciospongia (Fig. 3). Each sample was further differentiated into FDOM patterns of “sponge tissue” (i.e., after the initial NaOH extraction) versus the pattern obtained after bleaching and decalcification, i.e., the FDOM intimately associated with mineralic CaCO₃, e.g., sediment particles and authigenic CaCO₃. For the purpose of this paper it is convenient to first present results from the sponge tissue (biological source), and to then compare these results with those obtained from mineralic FDOM (diagenetic alteration).

3.2.1. FDOM patterns of sponge tissue

Irrespective of the surface or subsurface case, the FDOM obtained from Spheciospongia tissue illustrates a fairly simple pattern of fluorescence peaks (Fig. 4A,B). The most prominent peaks occur along an emission (em.) band at emission maxima around 346 nm and excitation (ex.) maxima at 226 nm and 278 nm, respectively. This emission band (connecting so-called peaks R and T in Fig. 4A,B) likely originates from the fluorescence of the amino acid tryptophan (Mayer et al., 1999), and is often referred to as tryptophan-like, protein-like or phenol-like fluorescence. It generally reflects biological material that has undergone minimal (if any) alteration (Parlanti et al., 2000).

From peak T towards higher excitation wavelengths two minor fluorescence peaks occur (Fig. 4A,B). The more proximal peak at an excitation wavelength of 319 nm (316 nm for the subsurface case) and an emission at 395 nm (387 nm) is the so-called peak M; the more distal peak at ex. 330 nm/em.
454 nm is the so-called peak C (Coble, 1996 for terminology). Both peaks originate from humic substances, with peak M essentially representing fulvic acid-like fluorescence and peak C representing the more condensed (red-shifted) humic acid-like fluorescence (cf. Christl et al., 2000). The maturation state of humic substances can be inferred from the M/C peak ratio (Burdige et al., 2004; Neuweiler et al., in preparation). For surface *Spheciospongia* tissue the M/C peak ratio is about 2, indicating relatively mature humic substance FDOM. For subsurface *Spheciospongia* tissue this ratio is around 9, indicating relatively fresh humic substance FDOM. Another significant difference between both sponge tissue spectra is the absolute loss of total FDOM fluorescence intensity from the surface to the subsurface, on the order of around 70%.

### 3.2.2. FDOM pattern intimately linked to CaCO₃

By both quantity and quality the FDOM patterns obtained after decarbonatization significantly deviate from those obtained from sponge tissue samples (Fig. 4C,D). First, FDOM concentrations, based on total fluorescence intensities, are much lower, by up to two orders of magnitude, and second, total humic substance fluorescence (integrating peaks M, C, and A) is
much more important in this mineral-associated FDOM.

The FDOM pattern obtained from CaCO₃ particles agglutinated to *Spheciospongia* at surface exclusively shows humic substance-related fluorescence with peak A>peak M>peak C (Fig. 4C). Peak A refers to the UV humic-like fluorescence of Coble (1996), and typically shows a broad fluorescence emission signal most likely to represent a mixture of refractory, low- to high-molecular-weight humic compounds ("longer-term aging", cf. Coble et al., 1998). However, it may also include the UV-portions of fluorescence emission bands associated with peaks M and C (cf. Stedmon et al., 2003; Burdige et al., 2004). The M/C ratio of this material is relatively low at ~1.3, and protein-like fluorescence is absent. All these features are suggestive of a mature or aged FDOM pool that is bound to sediment particles such as carbonate pellets, ooids, and grapestone. Indeed, this pattern is similar to that seen in samples of ooid and grapestone sediments collected at other sites on the Bahamas (Neuweiler and Burdige, unpublished data).

The CaCO₃ associated with lithified, subsurface *Spheciospongia* includes sedimentary particles (as above) and, in addition, contains some amount of authigenic CaCO₃. The FDOM spectrum of the material extracted from the carbonate (Fig. 4D) is similar to that of the non-lithified subsurface sample of *Spheciospongia* in that it shows a distinct humic substance fluorescence with peak A>peak M>peak C. However, here the general signature of a mature FDOM pattern combines with unequivocal peaks in the region of peaks R and T, i.e., a fluorescence signal that is generally associated with minimally altered, "fresh" organic material. At the same time though, there are two other aspects of the fluorescence signature of this material which appear to be important. First, compared to the fresh sponge tissue materials, the protein-like fluorescence peaks are shifted towards a lower emission wavelength, i.e., from em. at around 345 nm to em. at around 320 nm (so-called peaks BT and SR according to Burdige et al., 2004). Second, peak M appears to be a composite peak with the more common peak (M1) at ex./em. of 328/419 nm and a second peak (M2) at 295/400 nm. The M<sub>total</sub>/C ratio of 2.6 integrates both peaks of fulvic acid-like fluorescence.

The blue-shifted proteinaceous fluorescence points to either the occurrence of some amount of a tyrosine-like fluorescence in addition to the tryptophan-like fluorescence (cf. Mayer et al., 1999), and/or an alteration of the macromolecular host, i.e., dissolved protein/peptides being altered to low-molecular-weight humic materials (Mopper et al., 1996; Mayer et al., 1999). The composite peak M requires an additional source of fulvic acid-like fluorescence with a lower excitation and emission wavelength maximum. This could be the result of newly formed fulvic acid-like compounds with a relatively low degree of conjugation and polycondensation (Senesi, 1990), i.e., characteristics of humic substances in *statu nascendi*.

4. Discussion

FDOM patterns and inferred benthic FDOM fluxes deduced from various parts of the Bahamian calcifying sponge *Spheciospongia* (Fig. 5) allow to discuss the quality of correlation between sponge soft tissue degradation and calcification, and, the implications of the obtained results for the understanding of ancient, spiculiferous carbonate mud-mounds.

4.1. Correlation between calcification and early humification

Successive degradation of sponge soft tissue material is evident from the significant loss of proteinaceous fluorescence (on the order of ~70%) from the sediment surface to the shallow subsurface. This decrease of fresh proteinaceous substances occurs along with an increase in the importance of fulvic acid-like fluorescence relative to humic acid-like fluorescence (M/C peak ratio increases from 2 to 9). The relatively mature humic substance fluorescence (M/C peak ratio=2) from the surface sponge tissue most probably originates from seawater FDOM, especially given the fact that sponges are active filter feeders (bacteria, dissolved organic matter) and the lack of independent evidence for ongoing sponge tissue degradation. At the same time, the changing fluorescence patterns also demonstrate that biopolymer degradation and early stages of humification (condensation reactions of degradation products, cf. Ziechmann, 1994) occur within the
shallow subsurface parts of *Spheciospongia*. Thus, calcification seemingly correlates with sponge tissue that has undergone degradation and is going through the stages of early humification.

The FDOM pattern intimately linked to sedimentary carbonate particles (pellets, ooids, grapestones) is the most mature of all the illustrated patterns. It exclusively shows humic substance-related fluorescence, a low M/C peak ratio and a significant signature of (refractory) UV humic-like fluorescence of peak A. For the case of the calcifying sponge *Spheciospongia* this mature sediment pattern then combines with the relatively fresh FDOM signature connected to active mineral authigenesis (calcification). Obviously the newly formed minerals record the stage of sponge soft tissue alteration through successive macromolecule–mineral interaction (Neuweiler et al., 2000). More specifically, the newly formed minerals incorporate and preserve fulvic acid-like fluorescence as a mirror of pore water FDOM during the time of their formation.

4.2. Implications for ancient carbonate mud-mounds

Carbonate mud-mounds commonly have abundant spiculiferous lime mud at variable abundance, together with calcified siliceous sponges and an early diagenetic cavity network, e.g., stromatactis (Lees, 1964; Flügel and Steiger, 1981; Bourque and Gignac, 1983; Bourque and Boulvain, 1993; Neuweiler et al., 1999, 2001; Neuweiler and Bernoulli, 2005). These carbonate mud-mounds represent a self-supported Ca-carbonate production site (Lees and Miller, 1995; Monty, 1995; Neuweiler et al., 1999, 2000; Schlager, 2003; Bourque, 2003), and as such, it appears tempting to consider them as a scaled-up and long-term geological end-product of processes similar to those occurring in modern, calcifying siliceous sponges (e.g., Fritz, 1958; Lees, 1964; Bourque and Gignac, 1983; Reitner et al., 1995 for a range of geological suggestions). So far, FDOM patterns of ancient carbonate mounds have been reported from the Cretaceous and, most recently, from Quaternary lithoherms of the Florida Straits (Neuweiler et al., 2000, 2003, in preparation). These works, combined with the results and interpretations presented herein, provide consistent evidence that fulvic acid-like substances are connected in a systematic manner to authigenic calcites (automicrite). Although the very details (e.g., nanomineral seeding, mineral growth, loci of intra-crystalline macromolecules, effects of recrystallisation) still remain to be explored, we consider sponge calcification and carbonate mud-mound formation as prominent examples of a diagenetic phenomenon generally referred to as geological calcification or organomineralisation (Mitterer, 1989; Trichet and Défarge, 1995).
5. Conclusions

(a) The demosponge *S. vesparium* (Lamarck, 1815) living on the Great Bahama Bank at a few metres of water depth displays particle agglutination and shallow subsurface calcification in association with hardgrounds.

(b) The pattern of fluorescent dissolved organic matter (FDOM) extracted from the sponge tissue essentially shows the expected peaks for unaltered biological material (protein-like fluorescence).

(c) FDOM from surface sponge tissue contains some additional amount of humic-like fluorescence that is in accord with the uptake of mature or aged seawater FDOM by active filter feeding.

(d) From the surface to the shallow subsurface, the sponge tissue lost about 70% of protein-like fluorescence but gained a significant amount of fulvic acid-like fluorescence, obviously indicating the initial stages of active humification processes.

(e) The FDOM patterns obtained from Ca-carbonate mineral material (particles and authigenic) versus sponge tissue are lower in fluorescence intensity by two orders of magnitude. At the same time, humic-like fluorescence (rather than protein-like fluorescence) dominates in these spectra.

(f) The FDOM pattern of sedimentary particles (pellets, ooids, grapestones from the surface part of *Spheciospongia*) indicates mature, humic-like fluorescence. For the FDOM pattern obtained from the calcifying subsurface (particles and authigenic CaCO₃) the mature sediment pattern of particles combines with relatively fresh FDOM (fulvic acid-like fluorescence) from newly formed authigenic CaCO₃. Thus, sponge soft tissue calcification correlates with the initial stages of organic matter humification.

(g) Fluorescence spectroscopic data and petrographic evidence reviewed from the literature suggests, with caution, that Phanerozoic sponge carbonate mud-mounds are an upscaled geological site of organomineralisation processes. Likewise they also occur during siliceous sponge biodiagenesis of *S. vesparium*.

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