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DEGRADATIVE CALCIFICATION OF A MODERN SILICEOUS SPONGE FROM THE GREAT BAHAMA BANK, THE BAHAMAS: A GUIDE FOR INTERPRETATION OF ANCIENT SPONGE-BEARING LIMESTONES

FRITZ NEUWEILER,[1] ISABELLE DAOUST,[1] PIERRE-ANDRÉ BOURQUE,[1]* AND DAVID J. BURDIGE[2]
[1]*Département de Géologie et Génie géologique, Université Laval, Québec, G1K 7P4 Canada*
[2]*Department of Ocean, Earth and Atmospheric Sciences, Old Dominion University, Norfolk, Virginia 23529, U.S.A.*
e-mail: fritz.neuweiler@ggl.ulaval.ca

ABSTRACT: **Organic colloids are involved in the early calcification of the modern siliceous sponge *Spheciospongia vesparium* (Lamarck, 1815) from the Great Bahama Bank. Electron microscopy and *in situ* fluorescence microspectometry studies indicate that colloids attached within or onto a collagen network promote the precipitation of aragonite crystals in these sponges. Calcification occurs within those portions of the sponge that are buried in the sediment, preferentially in regions of agglutinated sediment particles, with sponge connective tissue being subjected to necrosis and significant degradation of the extracellular collagen matrix. The dismantling of collagen bundles leads to collagen scaffolds, which act as a sorbent and have significant adhesive effects for ions and/or organic colloids. Bacteria and other microorganisms support tissue degradation, but neither act as a substrate for aragonite precipitation or are present in significant numbers at calcification sites. This process of early calcification may explain the origin of fossil calcified siliceous sponges ("sponge mummies" and "tuberoids") as well as the occurrence of patchy calcified sponge materials, thereby calling into question the commonly accepted idea that pelletoidal texture associated with these fossil sponges indicates that bacteria are directly responsible for the calcification.**

INTRODUCTION

Calcification of siliceous sponges is a frequently described diagenetic phenomenon in Phanerozoic shelf and littoral carbonate depositional environments (Fritz 1958; Geyer 1962; Rigby 1967; Gwinner 1976; Flügel and Steiger 1981; Bourque and Gignac 1983; Keupp et al. 1990; Brachert 1992; Leinfelder et al. 1993; Reitner et al. 1995; Neuweiler et al. 1999; Kauffman et al. 2000; Neuweiler et al. 2001a; Neuweiler et al. 2001b; Duarte et al. 2001; Oloriz et al. 2003; Neuweiler and Bernoulli 2005; Choh and Kirkland 2006). The calcification process must have occurred *syn-vivo* to early *post-mortem* in order to result in lithified sponge body fossils or sponge mummies that preserve fine skeletal details (Fig. 1A, C). Even if calcification is less effective or nonpervasive, it is sufficient to produce centimeter-size fragments of calcified sponge material. Such fragments or particles were labeled tuberoids by Fritz (1958; illustrated and discussed in much detail by Flügel and Steiger 1981), thereby upgraded to an important carbonate sedimentary particle, e.g., ooids or oncoids. Indeed, calcified siliceous sponges and tuberoids can accumulate in the sedimentary environment in large enough quantities to form entire rock units, as for example the spongiolithic limestones of the European Upper Jurassic (Gwinner 1976; Flügel and Steiger 1981; Keupp et al. 1990; Leinfelder 2001). Within a broader perspective, the calcification of siliceous sponges, or siliceous sponge diagenesis in general, has constantly been invoked to explain accretionary and diagenetic processes of ancient sponge-rich carbonate mounds and/or spiculiferous stromatactis mudmounds (see footnote in Lees 1964; Wiedenmayer 1980; Bourque and Gignac 1983; Bourque and Boulvain 1993; Neuweiler et al. 1999; Leinfelder 2001; Neuweiler et al. 2001a; Neuweiler and Bernoulli 2005; Desrochers et al. 2007).

Because many living marine sponges host microbial symbionts (Lee et al. 2001; Steindler et al. 2002), and because microcrystalline to pelletoidal carbonate microtextures are commonly present in ancient calcified sponges (Fig. 1B, D; Bourque and Gignac 1983 for stromatactis mounds; Macintyre 1985; Macintyre and Aronson 2006 for discussion on peloidal textures; Neuweiler and Reitner 1993; Reitner et al. 1995; Neuweiler et al. 1999 for sponge carbonate mounds and automicrite terminology), it is tempting to consider that the calcification processes ensue from sponge-related microbial activity, with credit often given to anaerobic, heterotrophic microbial processes (Berner 1968, 1969) such as ammonification or sulfate reduction (Fritz 1958; Schumann-Kindel et al. 1997; Reitner and Schumann-Kindel 1997; discussion in Hoffmann et al. 2005). However, a generalized "sponge-microbial view" to explain siliceous sponge calcification is not consistent with a number of biological and geological facts. First, calcification of siliceous sponges occurs within two poriferan groups, the demosponges and the hexactinellids. The latter has relatively low amounts of soft tissue, and microbial symbionts are scarce (Leys 1999). Second, there are no geochemical signatures in ancient calcified sponges that could account for microbial sulfate reduction, and the carbon stable-isotope ratios do not deviate from expected marine values (see Hendry 1993, e.g., Reitner et al. 1995; Neuweiler et al. 1999; Neuweiler and Bernoulli 2005). In addition, although ferrous iron is commonly present in the newly formed carbonate minerals, pyrite, if present, forms after calcification is complete, indicating the absence of net sulfide

* The revised paper had to be submitted with deep sadness in memory of our dear colleague Pierre-André Bourque. Pierre-André passed away September 9th, 2006 during a field campaign in Morocco.

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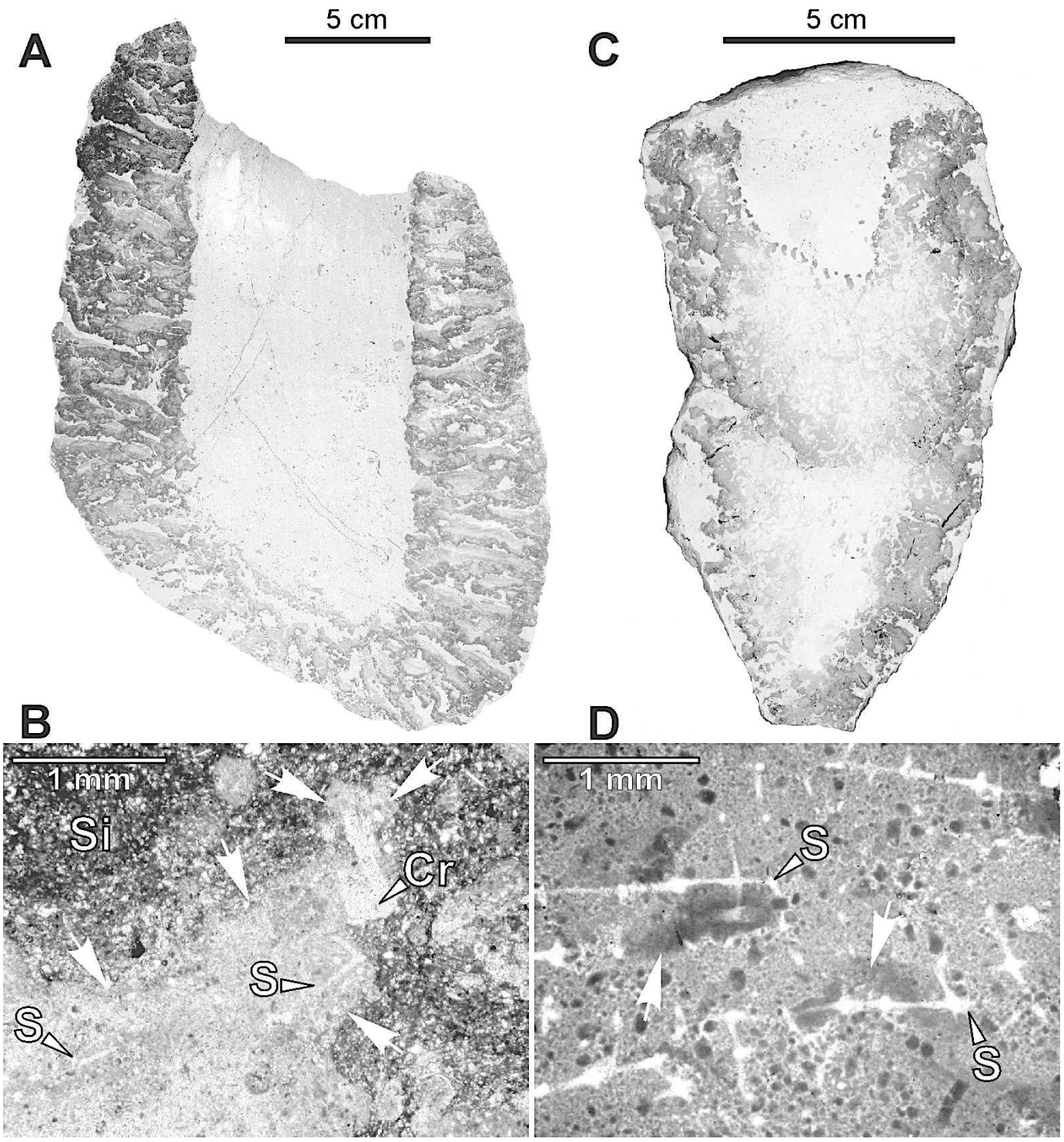

FIG. 1.— Phanerozoic calcified siliceous sponges (sponge mummies). **A)** *Malumispongium* Rigby 1967, a Paleozoic calcified hexactinellid sponge from the Lower Silurian of Gaspé, Québec, Canada (see Bourque and Gignac 1983 for early discussion). **B)** Thin section of *Malumispongium* calcified sponge tissue (sponge automicrite, white arrows) carrying autochthonous sponge spicules (= S) and incorporated bioclasts (crinoidal ossicles = Cr). The ambient sedimentary facies is an argillaceous siltstone (= Si). **C)** Two superposed specimens of a Mesozoic calcified hexactinellid sponge from the Upper Jurassic of the Swabian Alb, Baden-Württemberg, Germany. **D)** Thin section of an Upper Jurassic calcified hexactinellid sponge displaying sponge automicrite (white arrow) around sponge spicule tracts (S).

production during carbonate mineral authigenesis. Third, the geologic record displays time intervals and/or local communities in which calcification of siliceous sponges was very efficient, a situation that is in sharp contrast with the modern marine sponge community, where calcified siliceous sponges are a curiosity. Fourth, a number of marine invertebrates host a variety of microbial symbionts in abundance (Haygood et al. 1999), and there are a number of invertebrate communities that are deposited or buried under oxygen-deficient

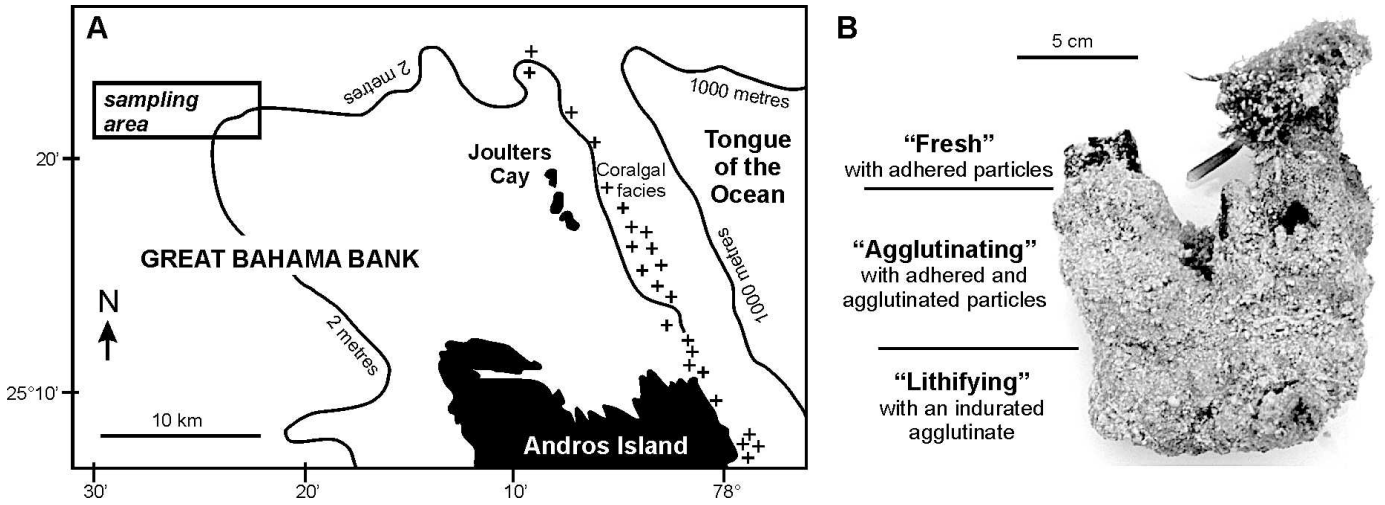

FIG. 2.—The lithifying siliceous sponge *Spheciospongia vesparium* from the Great Bahama Bank. **A)** Locality map with sampling area. The sampled specimens are from the strip of abundant sponge bioherms, as illustrated by Wiedenmayer (1978; his fig. 2). **B)** *Spheciospongia vesparium* from photo taken directly on board ship. The specimen displays the common three-part vertical zonation into fresh, agglutinating, and lithifying portions to which histological and geochemical analyses refer (Figs. 3–5, 8; see also Neuweiler and Burdige 2005).

conditions (Briggs 2003), but the geological phenomenon of invertebrate mummification via pervasive soft-tissue calcification appears to be specific to certain members of both the demosponges and the hexactinellid sponges.

The observations discussed above suggest that in order to achieve a more consistent view of the process of calcification of siliceous sponges, characteristics of the primordial soft tissue that are specific to sponges should be considered more thoroughly. During the Phanerozoic, characteristics of this tissue could have evolved with specifications and in recurring abundances throughout the history of calcifying siliceous sponges. The scientific question remains very basic: how do siliceous sponges calcify?

APPROACH

This paper deals with an example of a modern lithifying siliceous sponge, principally the species *Spheciospongia vesparium* (Lamarck, 1815) from modern sponge bioherms on the Great Bahama Bank as initially described and identified by Wiedenmayer (1978) (Fig. 2A). The original observations by Wiedenmayer (1978) are of particular interest because they imply that lithification is due to calcification that begins during the interstitial degradation of a siliceous sponge. Along with the initial lithification, Wiedenmayer (1978) reported a change in pigmentation and a general decline in sponge body stability, but he did not mention any specific odor arising from either ammonia or hydrogen sulfide. The lithifying siliceous sponges of *Spheciospongia* occur in a habitat that is associated with important seafloor lithification (Hillgärtner et al. 2001; Neuweiler and Burdige 2005).

Recently, Neuweiler and Burdige (2005) reexamined this problem and tracked *Spheciospongia* lithification, along with tissue degradation, by means of fluorescence spectroscopy, examining fluorescent dissolved organic matter (FDOM) in aqueous tissue extracts. Their results indicate that with the onset of lithification there is a significant loss of proteinaceous compounds, a shift of UV-fluorescence peaks, and a net gain of freshly formed FDOM as low-molecular-weight humic material. These authors also concluded that the (purported) authigenic $CaCO_3$ represents an effective sink for the freshly formed FDOM. This finding in turn corroborates the geological material, with significance attributed to synsedimentary fluorescence textures that occur sporadially in ancient sponge carbonate mounds as well as in spiculiferous stromatactis mudmounds (Neuweiler et al. 2000; Neuweiler et al. 2003; Desrochers et al. 2007).

At present, there are three important issues to resolve in the case of lithifying *Spheciospongia*. First, the newly formed minerals need to be examined, with particular reference to their loci, size, morphology, and mineralogy. Second, the suggested chemical changes during soft-tissue decay need to be correlated with direct observations of the degrading tissue itself. Finally, one has to decipher the detailed relationships between tissue degradation (kind of tissue, degree of degradation, role as substrate) and the authigenic mineral formation. The aim of this paper is to establish these issues in order to gain further insight into the potential of *Spheciospongia* biodiagenesis to explain calcification in ancient sponge material.

MATERIAL AND METHODS

The *Spheciospongia* material was collected from the Great Bahama Bank, northwest off the northern tip of Andros Island (Fig. 2). Sampling details are described in Neuweiler and Burdige (2005). The sponge material used herein was fixed on board ship in a mixture of glutaraldehyde, sodium cacodylate, and seawater (24–36 hours), rinsed with seawater, and stored refrigerated at 4 to 6°C. In the laboratory, the material was dehydrated and stored in 70% ethanol. Prior to further treatment, we cut out samples that represent fresh, agglutinating, and lithifying parts of *Spheciospongia* (Fig. 2B), and completed the dehydration process in 99% ethanol. For scanning electron microscopy (SEM, JEOL 840-A equipped with a NORAN light-elements energy-dispersive analysis and low vacuum SEM, JEOL JSM6360LV), samples underwent critical-point drying (CDP) and were kept in an oven at 40 °C. For light microscopy, the dehydrated samples were optionally stained in block portions with methylene blue and azur-II/methylene blue and embedded in LR White™ resin. The samples were then cut into slices, 20 µm to 50 µm thick, using a Leica saw microtome. Fluorescence microspectrometry was performed directly on unstained microtomed sections. The fluorescence microspectrometry method was used to qualify the degradation of the sponge soft tissue (pigments, collagen, FDOM, particles as sorbents) in its quasi-natural context and at high resolution (down to 20 µm). We used a ZEISS Axioplan II incident-light microscope equipped with a J&M photometer-monochromator device. The excitation

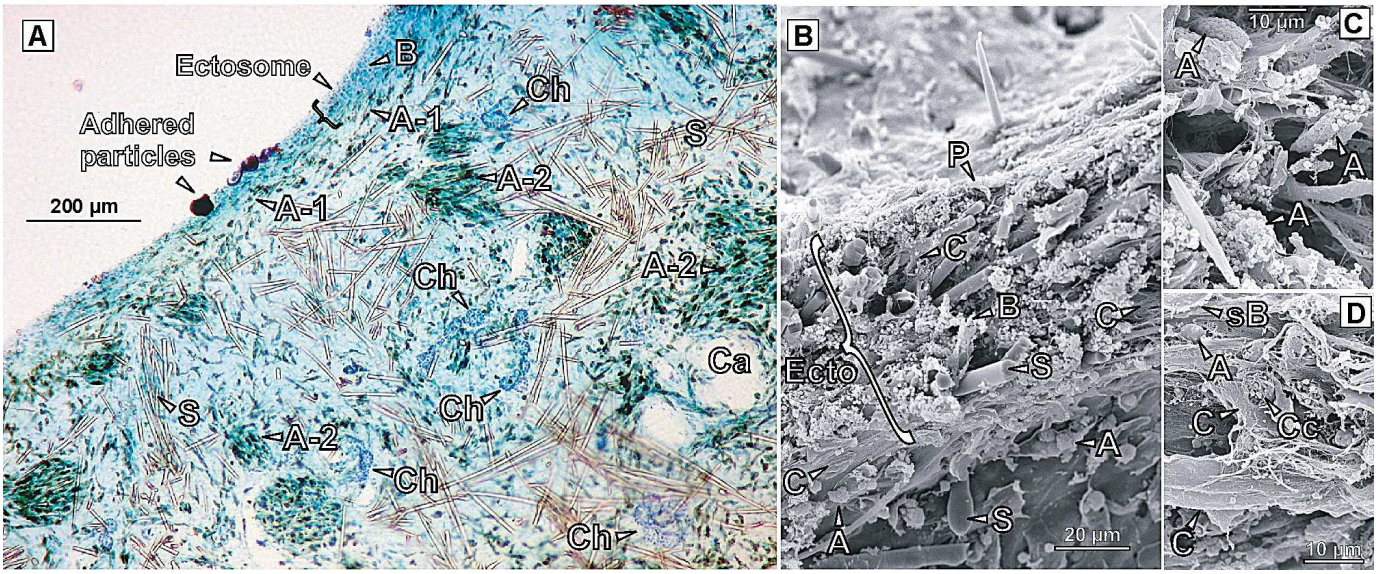

FIG. 3.—*Spheciospongia vesparium* from the sponge–water interface (sample "fresh"). **A)** Microtomed section of *Spheciospongia* stained in a mixture of methylene blue and azure II. At the surface, there are some adhered particles. The outer tissue layer (ectosome) displays numerous unicellular cyanobacteria (= B, putatively ascribed to *Synechococcus*) and some colonial cyanobacteria that are common farther below towards the subdermal cavity system (= A-1, putatively ascribed to *Aphanocapsa*). Other accumulations of *Aphanocapsa* (= A-2) relate to illuminated portions next to sponge canals (= Ca) and plumose tracts of siliceous sponge spicules (= S); choanocyte chambers (= Ch). **B)** SEM micrograph of the ectosome (= ecto) of *Spheciospongia*: External cell layer with pinacocytes (P); ectosome with unicellular cyanobacteria (= B), siliceous sponge spicules (= S), and abundant collagen tissue (= C). In the lower part of the micrograph, the subdermal cavity system is visible hosting colonial cyanobacteria (= A, putative *Aphanocapsa*). **C)** Details of putative *Aphanocapsa* (= A) embedded within collagen tissue (bundles and networks); some *Aphanocapsa* display a broken encapsulation due to shrinkage during sample preparation to display the individual bacteria. **D)** Pristine collagen tissue (= C) typically displays smooth surfaces. Note small remnant of a bacterial surface film (= sB) that is locally present lining the sponge–water interface (see also Fig. 8). Choanocyte chambers (= Cc) and some *Aphanocapsa* (= A) are visible.

wavelength was set fixed at 365 nm, beam splitting at 395 nm, with emission recorded from 420 nm to 650 nm at increments of 2.5 nm. This method was adopted from studies on hydrocarbon inclusions (Khavari-Khorasani 1987; Stasiuk and Snowdon 1997; Stasiuk et al. 2000).

RESULTS

Tissue Organization of Spheciospongia vesparium (Lamarck, 1815)

Spheciospongia vesparium is a siliceous, clionaid sponge (Demospongiae, Hadromerida) that is able to excavate limestone substrates during its early growth stages (Rützler 2002). It is dark mauve and generally lives within the sediment with ostia and oscula-bearing protrusions in the overlying water column (growth habit b of Wiedenmayer 1978).

Protrusions in contact with open water ("fresh" portion of the sponge, Fig. 2B) show an outer tissue layer (ectosome) that is composed of a dense network of preferentially tangential-oriented spicules, strings of collagen bundles, and bacteria of mainly unicellular and subordinately colonial Chroococales (Fig. 3A–C). The sponge collagen tissue is recognized by its organization in bundles or networks that display a fibrous or fibrillar structure (Garonne 1985; Garonne et al. 1985, for review); its birefringence allows its identification under the microscope. The *Spheciospongia*-related cyanobacteria are commensals or photosymbionts, whose morphology is putatively ascribed to unicellular *Synechococcus* and colonial *Aphanocapsa* (Fig. 3B, C). These cyanobacteria contain a mixture of pigments, namely chloropyll a, phycocyanin, and phycoerythrin, which give *Spheciospongia* its dark-mauve color (see Figs. 4A, 5A for natural colors, and results of fluorescence microspectrometry in Fig. 8 further below). Unicellular cyanobacteria (type *Synechococcus*) appear restricted to the ectosomal tissue, whereas colonial cyanobacteria (type *Aphanocapsa*) are also present in the subectosomal cavity system and near to the sponge canal system (Fig. 3A, B). Intriguingly, well-pigmented *Aphanocapsa* may occur several centimeters inside the sponge body, where it clusters around major sponge-spicule tracts (Fig. 3A). This pattern attributes an optical capacity to the spicule tracts, much in the manner of a natural light-conducting system or glass fiber lamp (Gaino and Sara 1994; Sundar et al. 2003; Aizenberg et al. 2004). Deeper into the sponge tissue and apart from spicule tracts, *Aphanocapsa* tends to lose its pigmentation, but the outlines of individual cells remain remarkably intact. A few bleached *Aphanocapsa* are found dispersed within the sponge mesohyl, indicating consumption by the host. The observed patterns, from ectosomal illumination towards internal consumption, corroborate more general results obtained from shading experiments on photosymbiont-hosting sponges, e.g., by Thacker (2005). Loosely adhered sedimentary particles may stick to the ectosomal tissue of "fresh" *Spheciospongia* (Fig. 3A), and a thin bacterial surface film is locally developed on the sponge surface (Fig. 3D; see also Fig. 8A further below). The ectosomal tissue is relatively rich in collagen; the pristine collagen tissue displays smooth surfaces and tightly packed fibers organized in networks and bundles (Fig. 3B, D).

Once portions of the sponge are buried by sediment, which is composed dominantly of ooids, pellets, and grapestones, the adhered particles tend to become agglutinated into marginal parts of the sponge body ("agglutinating" portion in Figure 2B, microtomed section in Fig. 4A). At first glance, agglutination appears to occur as a simple consequence of growth within a sandy carbonate sediment. However, with agglutination, the ectosome turns into a highly cohesive material that is rich in freshly produced collagen (Fig. 4B–E). We assume that mobile archaeocytes (sponge-specific stem cells) must have invaded these particle-agglutination sites to give rise to an accumulation of collagen-producing cells (Fig. 4E). Therefore, the agglutination process is actually a grow-around process with significant enrichment of ectosomal sponge tissue, specifically collagen, in direct proximity to the agglutinated particles (Fig. 4C, D). Presumably, the overall mechanism of agglutination is based on dermal irritation, inflammation, or even an immunoresponse (Müller and

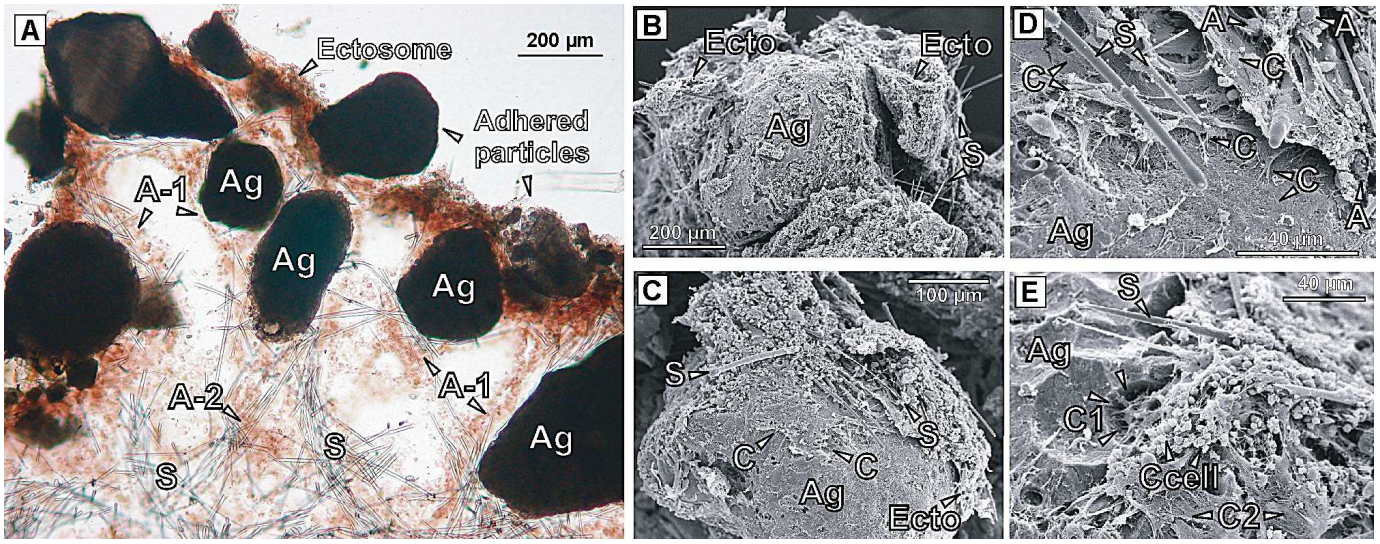

FIG. 4.—*Spheciospongia vesparium* from around the sediment–water interface (sample "agglutinating"). **A)** Microtomed section of unstained *Spheciospongia* showing coloration that closely matches the natural pigmentation. At the sponge–sediment interface, there are abundant adhered particles. The outer tissue layer (ectosome) displays a distinct pigmentation that is due to abundant unicellular cyanobacteria. Agglutinated particles (= Ag) reach entirely into the sponge and are enclosed in former ectosomal tissue. Colonial cyanobacteria (*Aphanocapsa*) are present around the agglutinated particles in association with the former ectosomal tissue (= A-1) but could also cluster deeper inside the sponge (= A-2) around sponge-spicule tracts (= S). This phenomenon expresses the capability of the siliceous spicules to conduct light. **B**, **C)** SEM micrographs displaying the situation of a newly agglutinated particle. The particle (= Ag) is encapsulated by ectosomal tissue (= Ecto) that is rich in collagen (= C) and tangentially oriented spicules (= S). **D)** Detail of part C to demonstrate the abundance of freshly formed collagen tissue (= C) that literally glues around the agglutinated particles (= Ag). The tissue around the agglutinated particles is also rich in *Aphanocapsa* (= A) and sponge spicules (compare with A-1 in microtomed section of part A). **E)** Assumed front of agglutination, displaying the direct contact between collagen (= C1) and a sediment particle (= Ag). Abundant sponge spicules (= S) and collagen tissue (= C2) indicate the ectosomal character of this portion of the sponge tissue. Individual cells that secrete collagen (= Ccell) are present near sites of agglutination. Scalloped surface of the sediment particle is due to etching during excavation by *Spheciospongia*.

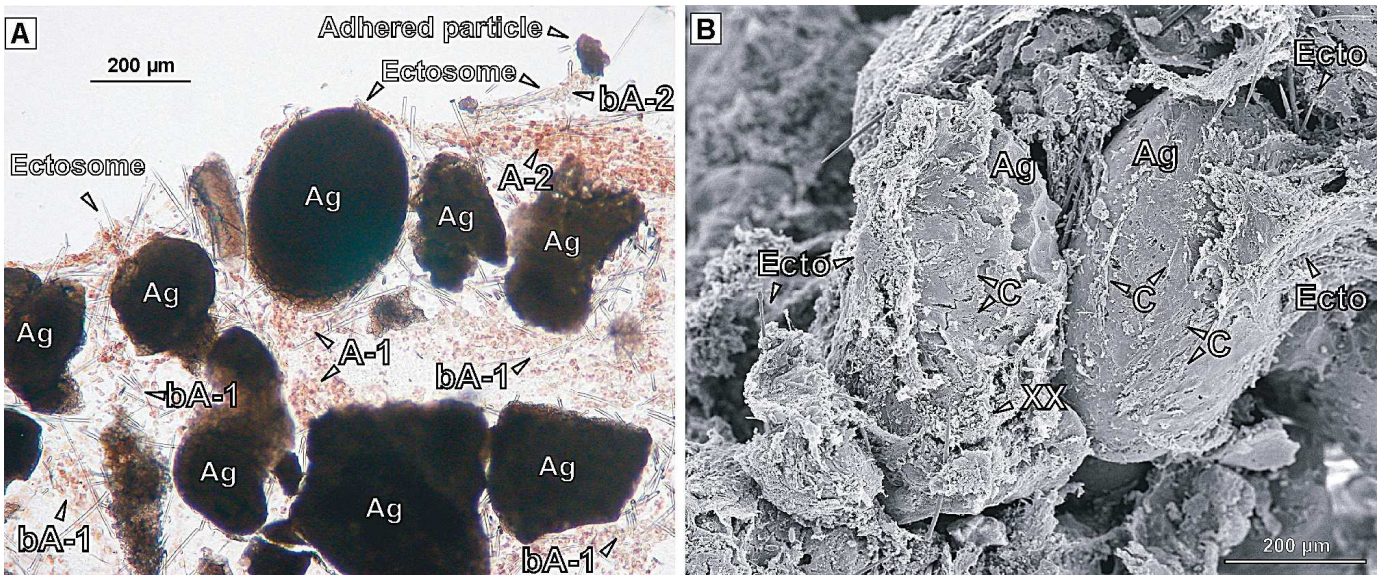

FIG. 5.—*Spheciospongia vesparium* from deeper parts of the sediment (sample "lithifying"). **A)** Microtomed section of *Spheciospongia* (unstained for direct comparison with Fig. 4A). The outer tissue layer (ectosome) is severely bleached due to the loss of unicellular photosymbionts. At the surface, only some adhered particles are present, but the agglutinated particles (Ag) are completely enclosed with tissue and reach well into the sponge. At this site the agglutination process seems to have stopped. Some pigmented *Aphanocapsa* occurs around the agglutinated particles (= A-1) and along sponge-spicule tracts (= A-2), but most of them are bleached (= bA-1; bA-2) and more randomly distributed (necrosis). **B)** SEM micrograph displaying a situation similar to that in part **A** with agglutinated particles (= Ag) that are totally enclosed in ectosomal tissue (= ecto) and abundant collagen (= C). This general context of *Spheciospongia* soft-tissue alteration correlates with the occurrence of authigenic aragonite crystals (= XX, and Figs. 6, 7 below).

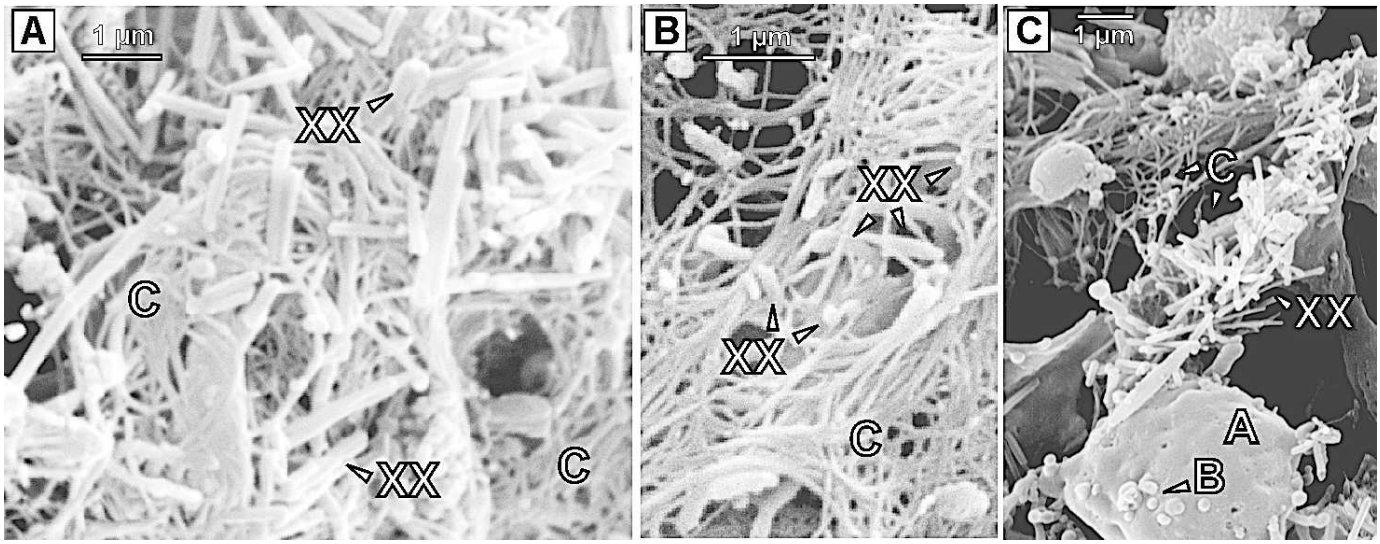

FIG. 6.—Authigenic aragonite from degraded collagen tissue, SEM micrographs, C = collagen, XX = aragonite crystals, A = *Aphanocapsa*, B = heterotrophic(?) bacteria. **A)** Aragonite crystals that grow out from dismantled collagen. The degraded collagen tissue is a relatively open meshwork of entangling fibers. **B)** Aragonite crystals that precipitated from within a degraded bundle of collagen tissue. Note nanocrystals that stick onto individual collagen fibers. **C)** Clusters of authigenic aragonite aligned along a degraded bundle (or string) of collagen tissue.

Müller 2003), as has been assumed by Hoffmann et al. (2004) for a similar case of sponge sedimentary inclusions. Independently of the specific physiological details, the reaction of the sponge is clearly a response to persisting confrontation with foreign substrates, finally leading to encapsulation and complete isolation of the agglutinated sedimentary particles from the sponge organism itself. Over the course of agglutination, the ectosomal tissue intrudes into the marginal parts of *Spheciospongia* together with some associated *Aphanocapsa*. At the surface, the ectosomal pigmentation remains distinct due to abundant bacteria of the *Synechococcus* type (Fig. 4A).

The lithifying part of *Spheciospongia* is 5 cm to 10 cm within the sediment (Fig. 2B). It shows evidence for particle adhesion, agglutination, and authigenic mineral precipitation with various signs of partial tissue degradation (Fig. 5, 6). *Synechococcus* cyanobacteria are notably absent, and the ectosomal tissue appears severely bleached (Fig. 5A). Instead, a few clusters of pigmented *Aphanocapsa* and abundant bleached *Aphanocapsa* are the main feature. Some parts of the sponge tissue literally turn into a slurry that is rich in *Aphanocapsa* cellular remains, most of them now detached from spicular tracts or spicular rims, around the agglutinated particles (necrosis; Fig. 5A). The agglutinated particles now reach farther, up to around 1 cm, into the sponge body. For these particles, indications of the former encapsulation by ectosomal tissue, i.e., a rim of dense collagen and tangentially oriented spicules, are still clearly displayed (Fig. 5A, B). The ectosomal tissue initially formed from agglutination at the sediment–water interface, but now deeper in the sediment and deeper within the sponge body, is subjected to necrosis and significant collagen tissue alteration, and at this stage displays first evidence of abundant mineral authigenesis (Figs. 6, 7).

Authigenic Aragonite

Volumetrically important amounts of authigenic precipitates correlate well with the macroscopically identified lithifying portion of *Spheciospongia* from 5 to 10 cm deep within the sediment. Based on its habitus and light-element peak pattern the authigenic mineral appears to be aragonite (Ca > Sr ≫ Mg; + distinct peak of C due to organic tissue). The aragonite crystals are rod-shaped, 200 to 400 nm in length, and less then 100 nm across, with blunt tips and smooth to subhedral faces (Fig. 6). These crystals seemingly emerge outwards from the nanometric confinements of degraded collagen (Fig. 6A, B). Collagen degradation itself is evident from the dismantling of collagen bundles into fibers and the opening of collagen fiber networks, with loss of their smooth cover substance. The growth of individual aragonite crystals out of a three-dimensional network of collagen fibers results in crystals that are randomly oriented and well separated (Fig. 6A, B). Aggregates of authigenic aragonite also form meshworks or strands supported by a degrading collagen network or by a degraded bundle of collagen, respectively (Fig. 6C). Relatively fresh, noncalcified collagen tissue and degraded, calcified collagen tissue may occur in close vicinity at the micrometer scale. Some tiny bacteria occur, mainly upon *Aphanocapsa*, indicating a certain degree of bacterial biodegradation acting within the necrolytic sponge soft tissue (Fig. 6C).

Meshworks of authigenic aragonite form minipelletoids that range from 2 µm to 5 µm in diameter. The minipelletoids may organize into lumps 10 µm to 30 µm in diameter (Fig. 7). There is, however, no unequivocal evidence of a general mechanism of mineral aggregation for these pelletoids, i.e., whether the aggregation occurs from within the collagen network (which could later retreat or dissolve) or whether it is more a surface-related phenomenon, for instance from mineralizing fluids that interact with the surface of the degrading collagen. Some of the meshwork or pelletoids are relatively planar on one side, making a surface-related origin from a sorbed fluid more likely (Fig. 7B, C). Other examples show evidence of internal precipitation due to some residual collagen fibers entangling the crystal aggregates (Fig. 6C), as a remnant of a former embedding within a collagen network.

A number of other substrates occur in close association with degraded collagen and associated aragonite (Fig. 7A). These include relatively fresh (smooth) collagen tissue, a variety of bacteria cells, various sponge cells, opaline spicules, and large surfaces of the agglutinated particles. However, none of these surfaces show direct or indirect evidence linking them to aragonite precipitation, and this observation applies even at the micrometer scale. Therefore, strong support for the degrading collagen network being crucial for aragonite precipitation derives from the strict exclusion of these other substrates as playing a role in aragonite precipitation.

Authigenic aragonite is not the only kind of carbonate deposit associated with *Spheciospongia*. For example, some of the agglutinated pellet, ooid,

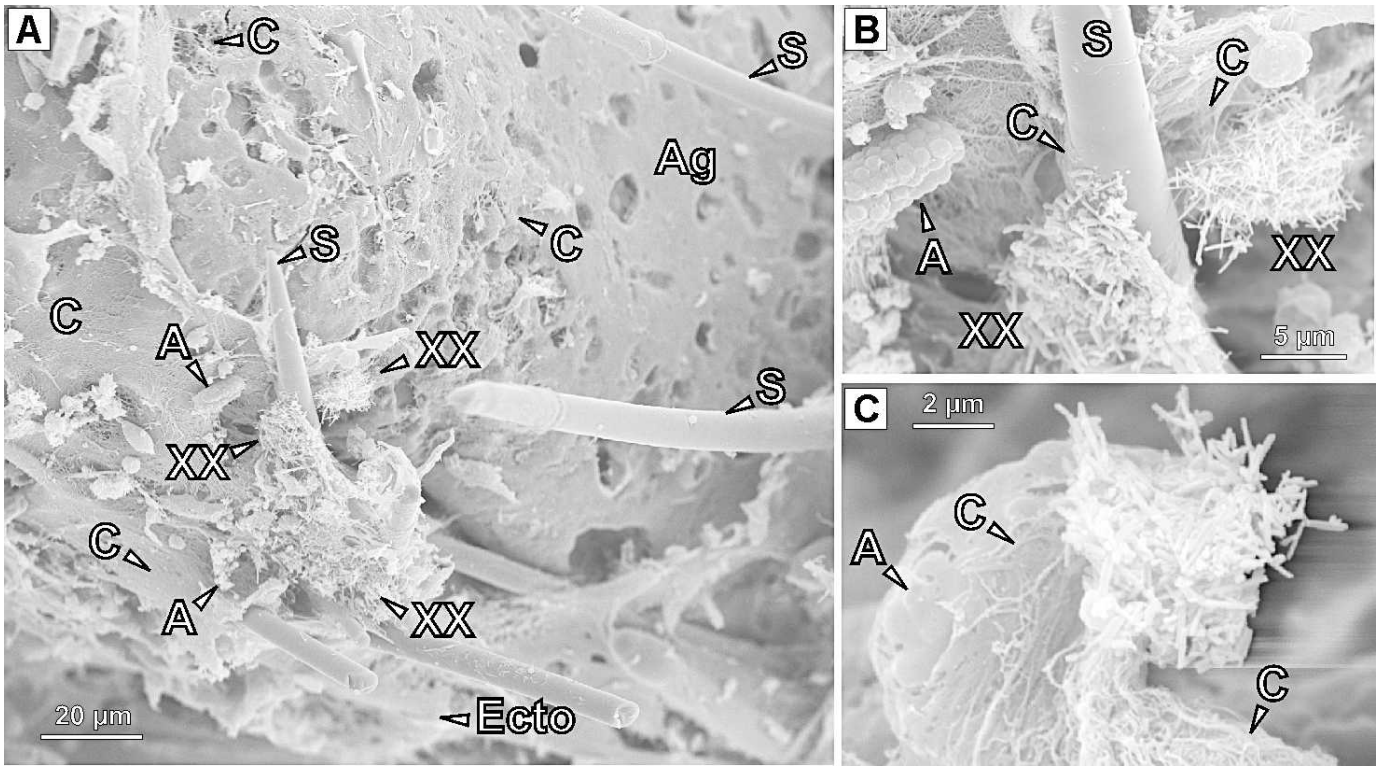

FIG. 7.—Pelletoidal meshworks of authigenic aragonite, SEM micrographs. **A)** Ectosomal layer (= Ecto) enclosing an agglutinated particle (= Ag with abundant microborings). There is relatively pristine tissue with sponge spicules (= S), smooth collagen (= C) and several *Aphanocapsa* (= A) next to local spots of degrading collagen supporting pelletoidal aragonite (= XX). **B)** Detail of part A showing pelletoidal meshworks of authigenic aragonite (= XX) supported by degraded collagen (= C) and at the same time excluding other substrates such as sponge spicule (= S), surfaces of *Aphanocapsa* (= A), or relatively smooth collagen tissue. **C)** Aragonite meshwork (minipelletoid) supported by a dismantling collagen bundle (= C); *Aphanocapsa* (= A).

and grapestone particles are riddled with etching pits from excavation by *Spheciospongia*, and some sponge chips accumulate within the sponge. In addition, a few remains of calcareous and siliceous phytoplankton do occur in the canal system. Along with its degradation in the shallow burial, *Spheciospongia* accumulates some internal sediment such as aggregates of sedimentary aragonite needle mud, loose aragonite needles, and particles with irregular outlines that show a dense mixture or amalgamation of aragonite and calcite (probably deriving from the lithifed subsurface).

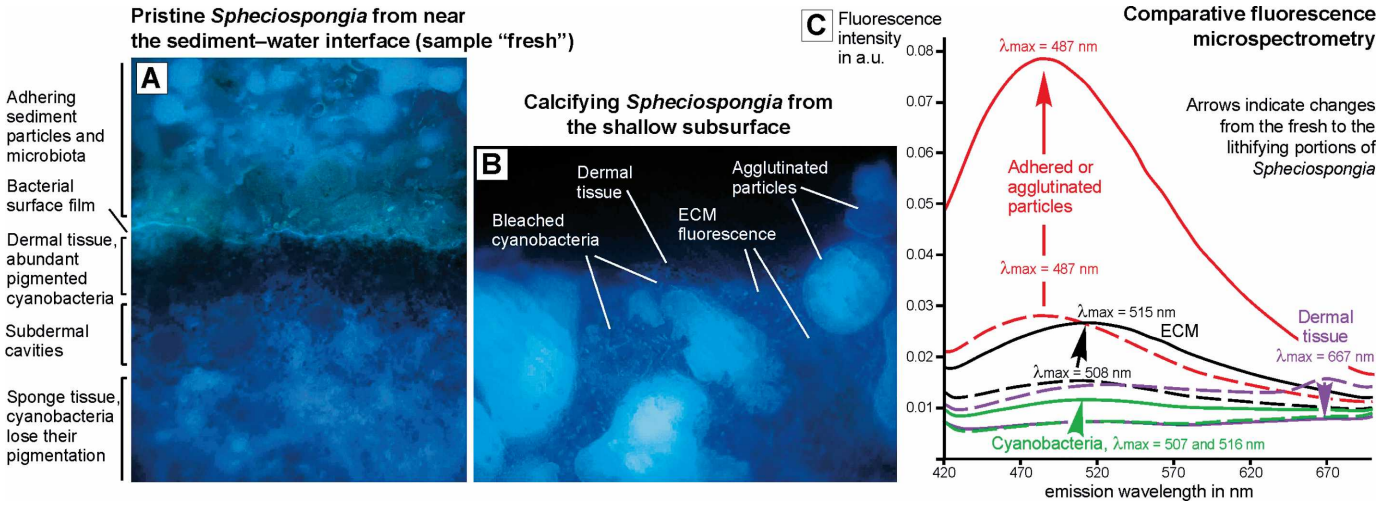

FIG. 8.—Comparative fluorescence microspectrometry between "fresh" *Spheciospongia* and "lithifying" *Spheciospongia*. **A**, **B)** Fluorescence micrographs from microtomed sections of marginal parts of *Spheciospongia*. Note the cloudy fluorescence that arises from the connective tissue of degrading *Spheciospongia*. **C)** Fluorescence emission spectra of various tissue elements and particles with arrows indicating changes between "fresh" (dashed curves) and "lithifying" (solid curves) portions of the sponge.

Fluorescence Microspectrometry

Results from *in situ* fluorescence microspectrometry (Fig. 8) on microtomed sections of *Spheciospongia* reveal a number of distinguishing features that differentiate fresh/noncalcified and degrading/calcifying parts of the sponge. Moving from the fresh to the calcifying material, the only tissue component that shows a decrease in fluorescence intensity is the ectosomal layer, with its abundant photosymbiotic unicellular bacteria. In the fresh material, in the portion of the sponge exposed to seawater (see Figs. 3A, 8A), photosymbiotic pigmentation is evident from a fluorescence peak of 667 nm (which represents chlorophyll) and, less clearly, from a broad fluorescence signature between 530 and 580 nm (which could correspond to a mixture of fluorescence from phycoerythrin and phycocyanin).

All other sponge components show a significant increase in fluorescence intensity with tissue degradation and the onset of lithification (Fig. 8B, C). In the lithifying portions of the sponge tissue, the agglutinated particles show a fluorescence maximum at 487 nm, with a threefold increase relative to their "fresh" counterparts that are loosely adhered to the surface of the sponge. The extracellular collagen matrix (ECM) shows a fluorescence maximum at 515 nm with a twofold increase in fluorescence intensity and a small red shift from an original fluorescence maximum located at 508 nm (all relative to ECM of fresh portions of the sponge). The bleached cyanobacteria (type *Aphanocapsa*) show a broad fluorescence peak between 507 and 516 nm. For these bacteria, the changes with tissue maturation are relatively indistinct, and it is unclear whether the increased fluorescence intensity of the dead bacterial cells is due to intrinsic chemical changes or is related to the more general increase in fluorescence from the background connective tissue.

DISCUSSION

Constraints on Calcification in Degrading Spheciospongia

Soft-tissue calcification of *Spheciospongia vesparium* proceeds via aragonite precipitation that is supported by degrading collagen bundles and degrading collagen networks. Our observations indicate that the degrading collagen is the only substrate for authigenic aragonite precipitation, exclusive of any other substrate. Individual aragonite crystals grow out from nanometric confinements of collagen tissue (Fig. 6). These confinements represent the space between individual collagen fibers that was created via the dismantling of the collagen bundles and strings. The phenomenon indicates that the earliest stages of decay of the extracellular collagen matrix (ECM) co-occur with an increase of collagen surface area onto which reactive fluids likewise have been sorbed. Meshworks and pelletoidal aggregates of authigenic aragonite adhere selectively within and onto the degrading collagen. Calcification is established *syn-vivo* at local spots of tissue die-off or necrosis. Initially the calcification process may well have been stimulated by enhanced production of collagen (in this respect, health sciences care about a similar phenomenon known in this field as the disease scleroderma and related calcinosis). Indeed, the enhanced production of collagen could be due to a kind of immunoresponse that develops as soon as *Spheciospongia* comes into contact with sediment particles and begins their agglutination. At the cellular level, this response involves the migration of archaeocytes, their conversion into collagen-producing cells, and encapsulation of sediment particles within newly formed ectosomal tissue. Microorganisms support the general degradation process (cell lysis, some suggested heterotrophs), but bacterial cells do not serve as the substrate for aragonite precipitation nor are microorganisms specifically present or abundant at calcification sites.

The stage of sponge soft-tissue degradation is delineated by the dismantling of collagen bundles with a loss of smooth surfaces and the opening of fiber networks in an entangled manner (see Garonne et al. 1973). In addition, bulk fluorescence of the ECM displays a doubling in its fluorescence intensity in combination with a small red shift of its fluorescence maximum. In fact, collagen is autofluorescent (Gareau et al. 2004), and medical studies show that collagen autofluorescence increases with its degradation due to, for instance, cross-linking (Sokolov et al. 2002). Our microscale to nanoscale observation of progressive degradation of the ECM corroborates well with macrosopic observations by Wiedenmayer (1978), who noted the loss of *Spheciospongia* body-shape stability with increasing burial in the sediment.

The loss of smooth surfaces in collagen bundles and collagen networks suggests an exudation and transformation of biopolymeric substances that originated in the extracellular collagen matrix. Such an alteration likely corresponds to chemical transformations, as deduced from changes in the fluorescence characteristics of aqueous tissue extracts of *Spheciospongia* (Neuweiler and Burdige 2005). These authors consider the authigenic minerals as a sink for a mixture of early geopolymers, such as humic substances, i.e., a geochemical snapshot of organogenic lithification that, within certain limits of maximum burial depth, could be detected in geological material from the Mesozoic and the Palaeozoic (Neuweiler et al. 2000; Neuweiler et al. 2003; Desrochers et al. 2007).

$CaCO_3$ Saturation States of Platform Pore Waters

Surface waters on the Bahama Bank are, in general and near our site, supersaturated with respect to major Ca-carbonate phases, including aragonite (Broecker et al. 2001; Morse et al. 2003). A variety of factors appear to inhibit precipitation, such that the process is kinetically rather than thermodynamically controlled (Morse and Mackenzie 1990; Morse 2003). In such tropical carbonate sediments, organic-matter remineralization plays a major role in mediating both precipitation and dissolution (Hu and Burdige 2007). The most important of these processes are aerobic respiration, sulfate reduction, and sulfide oxidation, because the low levels of nitrate, iron, and manganese in these sediments minimize the importance of suboxic remineralization processes (Morse et al. 1985; Walter and Burton 1990; Rude and Aller 1991; Walter et al. 1993).

Aerobic respiration generally leads to net carbonate dissolution due to the metabolic CO_2 that is produced, which lowers the saturation state and provides an acid source for dissolution (Ku et al. 1999; Hover et al. 2001; Burdige and Zimmerman 2002). Under some conditions, though, this dissolution is also accompanied by reprecipitation, with dissolution $>$ reprecipitation, resulting in net dissolution. Here, dissolution of a more soluble carbonate phase occurs under conditions that are undersaturated with respect to this phase, yet are still supersaturated with respect to a less soluble carbonate phase (Hu and Burdige 2007).

In contrast to aerobic respiration, sulfate reduction generally results in carbonate precipitation because of the alkalinity production that accompanies this process (Berner 1968, 1969; Morse and Mackenzie 1990; Boudreau and Canfield 1993; Morse 2003). However, here the $\delta^{13}C$ of the authigenic carbonate is expected to be isotopically light, given that the source of the carbonate is isotopically light sediment organic matter. In sediments of the inner Great Bahama Bank, the anoxic zone occurs from only a few centimeters to $\geq$ 10 cm below the sediment surface. Therefore, if fluxes of organic matter to such sediment are high, then one must assume that there are localized hot spots of sulfate reduction (Jahnke 1985; Rude and Aller 1991). Measurements of pore-water sulfide concentrations at sites nearby our study site (Burdige and Hu, unpublished data) indicate a high degree of variability, related largely to sediment type. In aragonite muds sulfide concentrations increase to around 1 mM within only a few centimeters of sediment depth. In coarser-grained sediments such as those inhabited by *Spheciospongia*, low sulfide concentrations are generally observed ($<$ 0.1 mM) at depths of

10 cm or greater. Much like the case for seagrasses (Burdige and Zimmermann 2002), it appears that pumping of O_2 from seawater into the sediment by *Spheciospongia* and/or production of O_2 by sponge-associated photoautotrophic bacteria may greatly complicate the chemical environment around the sponge.

Potential Processes that Lead to Aragonite Authigenesis

A classical diagenetic pathway for aragonite authigenesis involves heterogeneous nucleation from pore waters that are supersaturated due to the high carbonate alkalinity associated with anoxic decay of organic tissue (i.e., ammonification and microbial sulfate reduction; see discussions in the previous section). Such a precipitation mechanism is similar to that invoked for more common early diagenetic carbonate concretions (Berner 1968, 1969; Coleman and Raiswell 1981, 1995; Mozley 1996; Raiswell and Fisher 2004; Hendry et al. 2006). This type of precipitation could take place in two modes. One could argue that microbially induced mineral precipitation either forms cement crusts on surfaces of proximate substrates that could also include bacterial cell walls (Pentecost and Bauld 1988), or generates an internal precipitate with minerals settling out geopetally from the interstitial fluid. In the case of *Spheciospongia*, no cement-like crusts or overgrowths by newly formed aragonite are present. However, an internal precipitate from an interstitial fluid cannot be fully excluded. Such a mechanism could supply the minor amounts of individual aragonite crystals that are widely distributed in association with various types of surfaces. Interestingly, along with the progressive degradation of sponge tissue, such material could become part of an internal, geopetal sediment, or soft automicrite as described by Leinfelder and Keupp (1995). This mechanism cannot, however, account for the phenomenon of mummification of siliceous sponges, because this product requires an efficient impregnation process of the connective tissue itself. Thus, the pathway of heterogeneous nucleation of aragonite controlled solely by the degree of supersaturation does not provide a satisfactory explanation. Instead, one must argue for a more specific role of collagen to support the heterogeneous nucleation of aragonite.

An organic-template-assisted nucleation mechanism that involves surface catalysis on degrading collagen could be such a process to explain calcification in *Spheciospongia*. Such a mechanism of matrix-mediated mineralization is based on the assistance of organic macromolecules that are stereochemically arranged to match the crystal structure of the inorganic precipitate (Addadi and Weiner 1985, 1992; Lowenstam and Weiner 1989; Mann 2001; Cölfen and Mann 2003). Such highly ordered organic–inorganic interfaces are considered a typical feature of these biominerals (see Nassif et al. 2005 for another view). Commonly, matrix-mediated minerals grow from an oriented nucleation along a favored crystal face: for the case of Ca-carbonates this generally occurs along the high-energy 001 face (Heywood and Mann 1994; Mann 2001). Although collagen could be involved in the template-assisted growth of Ca-carbonates (Ajikumar et al. 2005), and such a model was indeed postulated to explain sponge-related as well as microbial Ca-carbonate authigenesis (Reitner 1993; Reitner et al. 1995), the authigenic aragonites of *Spheciospongia* neither show a preferred orientation relative to the collagen fiber substrate nor display any direct blunt contact between the collagen and a single aragonite crystal. It is therefore unlikely that template-assisted nucleation of aragonite is at work during the calcification of *Spheciospongia vesparium*.

A nucleation mechanism upon a collagen scaffold that acts as a sorbent developed largely from research on vertebrate biomineralization, including relatively recent attempts for applications in tissue engineering (Schincke et al. 1999; Veis 2003; Manjubala et al. 2005). Here, collagen tissue is considered to be the structural framework for adhering macromolecules, ions of calcium and magnesium, inorganic and organic colloids, or mineral-secreting cells themselves to stimulate crystal nucleation and oriented growth as biominerals. For the case of *Spheciospongia*, however, it is a degrading ECM with its dismantling collagen tissue that acts as a scaffold to support aragonite precipitation. Indeed, neither specific sponge cells nor sponge-related bacteria or any other microorganisms were observed to have migrated into the dismantling collagen.

Degradative calcification supported by dead sponge connective tissue points to both organomineralization (*sensu* Trichet and Défarge 1995; Défarge and Trichet 1995; Défarge et al. 1996) and the pathological case of vertebrate calcification that is due to ECM maturation and defunctionalization (Schinke et al. 1999). More specifically, here with *Spheciospongia,* the degradative collagen scaffold most likely serves to enhance fluid–colloid adhesion in confinements with subsequent mineral precipitation (Loste et al. 2004). Precipitation might initially involve an amorphous phase, not necessarily as a pure amorphous calcium carbonate (ACC) that requires extreme supersaturation (Loste et al. 2004; Politi et al. 2004), but as a hybrid mineral of calcium carbonate, water, and geopolymers or polymer gels (Cölfen and Mann 2003). Mineral nucleation from calcifying organic colloids or polymer gels (Chin et al. 1998; see also Orellana and Verdugo 2003) was proposed for the formation of carbonate-mound automicrites by Neuweiler et al. (2000) and Neuweiler et al. (2003). Sorption of such polyanionic organic material within and upon a collagen scaffold is a mechanism that could explain the strong preference of the authigenic aragonite for collagen, the random orientation of aragonite crystals, and the selective occurrence of aragonite meshworks and pelletoidal aggregates to derive from a collagen-adsorbed polymer gel.

Calcified Spheciospongia*, a Key to the Past?*

Spheciospongia vesparium is one of the very few examples of modern calcifying siliceous sponges (see Neuweiler and Burdige 2005 for short review), and to our knowledge, the only one that displays aragonite rather than calcite mineralogy. Aragonite mineralogy most likely reflects the common precipitate on the Bahama Banks, with calcite being more common towards platform flanks and deeper basin settings (Morse et al. 2003). Much more provoking is the absolute scarcity of calcification of modern siliceous sponges. What *Spheciospongia* shows is not a simply diagenetic phenomenon or a template-assisted biomineralization process, nor does it have much in common with bioskeletal growth next to or guided by fibrillar networks as discussed, for instance, in Clode and Marshall (2003). The main conclusion here is that a diagenetically altered sponge extracellular collagen matrix, and not the sponge organism, favors calcification through the exposure of collagen scaffolds. Further specifications of *Spheciospongia* ECM such as amino-acid composition, wettability, and surface charges remain to be explored. The collagen scaffolds involved here are characterized by submicrometer confinements, which indeed may have strong adhesive effects on ions and colloids, and which may also show aragonite supersaturation due to dysoxia, necrosis, and humification conditions (defunctionalization, pathological case, Schinke et al. 1999). Understanding calcification in *Spheciospongia* as a sort of impregnation of the less soluble parts of the ECM, which itself is a primordial character of multicellular animals, it becomes intriguing to realize that sponge collagens with their organization into superposed structures could be fairly specific (Garonne et al. 1973; Garronne 1985, 1999; Har-El and Tanzer 1993; Boute et al. 1996; Exposito et al. 2002).

Viewed as such, one might consider the very details of the adhesive and sorptive attributes of degraded *Spheciospongia* connective tissue as one of today's exceptions, which, however, could episodically have been the rule during the geological past. The case of *Spheciospongia vesparium* may well prove to be an analogue for ancient calcified siliceous sponges, inasmuch as it is easily conceivable that more pervasive calcification within the

collagen scaffold (Fig. 6) could result in a style of sponge body preservation, namely mummification via calcification of a degrading connective tissue, as it is displayed by ancient calcified siliceous sponges (Fig. 1). This accounts in particular for the timing and effectivness of calcification to preserve the basic organization of the siliceous sponge connective tissue, e.g., with its canal system or its dermal spicular layers. However, more or less complete body fossils of calcified siliceous sponges (Fig. 1) certainly require a primary skeletal support to sustain their shape and tissue architecture during early diagenesis, e.g., due to a rigid or semirigid nature of the spicular skeleton or due to a tight cohesion of the collagenous tissue. The mechanisms described here might also help to explain synsedimentary fragmentation of siliceous sponges, namely along preferentially calcified parts of their connective tissue to produce tuberoids in the sense of Flügel and Steiger (1981). Finally, a more patchy tissue calcification that occurs within the sediment might leave behind a record of early indurated, spicule-bearing sediment material. In turn such patches of indurated spiculiferous sediment material have repeatedly been reported (or implied) from the petrography of stromatactis-rich carbonate mud-mounds (Bourque and Gignac 1983; Neuweiler et al. 2001a; Neuweiler and Bernoulli 2005; Desrochers et al. 2007).

CONCLUSIONS

Spheciospongia vesparium is a siliceous, clionaid sponge (Demospongiae, Hadromerida) of the Great Bahama Bank that lithifies within the sediment during its degradation (Wiedenmayer 1978; Neuweiler and Burdige 2005). It might therefore serve as a modern analogue for the abundant calcified siliceous sponge material recorded in Phanerozoic sediments. In *Spheciospongia*, lithification is effective in sediment depths of 5 to 10 cm. The newly precipitated mineral is rod-shaped aragonite, 200 to 400 nm in length and less then 100 nm across, with blunt tips and smooth to subhedral faces. Individual aragonite crystals grow out from nanometric confinements that formed during the dismantling of the collagen tissue. Dismantling occurs along with an increase of collagen surface area onto which precipitating fluids likewise had been sorbed. There are also aggregates of authigenic aragonite that form meshworks in the form of minipelletoids (2 to 5 µm in diameter) that in turn may organize into lumps 10 to 30 µm in diameter. Minipelletoids and lumps stick with their flat lower surface onto the dismantled collagen tissue, supporting the importance of sorption mechanisms. Intriguingly, the authigenic aragonite precipitated highly selectively from a degrading extracellular collagen matrix (ECM); bacteria and other microorganisms indeed support tissue degradation, but neither act as a substrate for aragonite precipitation or are present in significant numbers at calcification sites.

Comparative histology and fluorescence microspectrometry corroborate the progressive degradation process along with calcification. The results of fluorescence microspectrometry implicate an effective exudation and transformation of biopolymeric substances into a local pool of freshly produced fluorescent dissolved organic matter (FDOM). Selective sorption of such polyanionic organic material onto collagen material and subsequent mineral nucleation from organic colloids provide the best explanation for calcification in *Spheciospongia*. The timing, effectivness, and style of the calcification process in *Spheciospongia* might explain a number of features of the abundant Phanerozoic calcified siliceous sponge material, e.g., the reproduction of details such as the sponge canal system, the need for *syn-vivo* to early *post-mortem* calcification, concurrent patchy sediment lithification, and sponge automicrite fluorescence. In particular, a patchy calcification within the sediment matches the descriptive and geochemical attributes of stromatactis-rich carbonate mud-mounds (Bourque and Gignac 1983; Neuweiler and Bernoulli 2005; Desrochers et al. 2007).

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