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*Research Article*

# Structural Arrangement and Properties of Spicules in Glass Sponges

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The morphology, chemical composition, and optical properties of long monoaxonic spicules were studied in several species of marine deep-sea hexactinellid sponges of different orders and families: *Asconema setubalense* (Hexasterophora, Lyssacinosida) and *Monorhaphis chuni* Schulze (Monorhaphiidae). Their macrostructural organization is a system of thin layers laid around the central cylinder containing a square canal filled with organic matter. A significant role in spicule organization is played by the organic matrix. The macrostructural of organization of the spicule in *Monorhaphis chuni* is a system of the "cylinder-within-a-cylinder" type. However the spicule surface is covered with ridges. They penetrate a few layers into the spicule. Analysis of the elemental composition of the basalia spicule of *Monorhaphis chuni* demonstrates a heterogeneous allocation of C, O, Si on the spicule surface, subsurface layers, and on ridges. All studied spicules have the properties of anisotropic crystals and they demonstrate a capability to the birefrigence. On the other hand we discovered unique property of spicules—their capacity for triboluminescence. The discovery of triboluminescence in composite organosilicon materials of which the spicules of hexactinellid sponges are built may contribute to the creation of biomimetic materials capable of generating light emission.

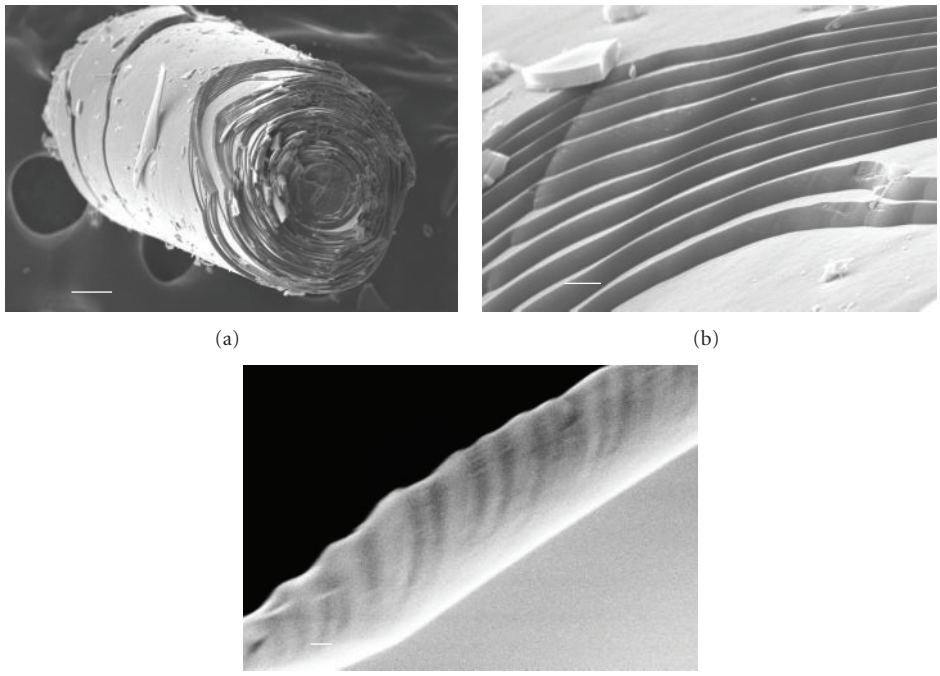
## 1. Introduction

There are 5,000 species of sponges and around 600 of them belong to the classes of so named glass (Hyalospongia) or six radial (Hexactinellid) sponges. Not much more than a dozen years ago a small note by Italian authors [1] drew attention to the spicules of Hexactinellids, because they are similar to artificial optical fibers. For the last ten years the Hexactinellids spicules have been intensively studied by very different investigators: physicists, chemists, and biologists of different specialties (zoologists, cytologists, molecular biologists, biotechnologists, etc. [2–8]). Glass sponges are exclusively marine animals; they occur at depths from 10 to 6,770 m in all oceans. They have skeletons of siliceous (glass) spicules with a distinctive triaxonic (cubic three rayed) symmetry [9]. Furthermore, glass sponges are highly unusual in that their major tissue component is a giant "syncytium" that ramifies throughout the entire body. They have amazing diversity of spicules. Only for their morphological description more than 400 terms have been suggested, which are used in taxonomy of Hexactinellids [10].

Study of basalia spicules of *Euplectella aspergillum* shows that the spicules of glass sponges can function as single-mode, few-mode, or multimode fibers. They have spines serving as illumination points along the spicule shaft. The presence of a lens-like structure at the end of the fiber increases its light-collecting efficiency. These spicules are similar to commercial optical fibers [11, 12].

At the same time, the organization of corporeal spicules of skeletons of glass sponges is extremely diverse. Principal studies of the physical and chemical properties of spicules of hexactinellid sponges are carried out on basal monoaxonic megascleres, which are diactine or pentactine spicules with a hypertrophied proximal ray and reduced other rays.

The principal function of the spicules of hexactinellids is certainly a skeletal one. Still, their organizational traits imply the presence of other functions. In particular, a hypothesis was suggested that these spicules perform the function analogous to that of nervous system. The spicules



(a) (b)

(c)

Figure 1: The morphology of a long ray of a pentactine spicule of *Monorhaphis chuni*. The cross-section shows the central cylinder with a canal surrounded with concentric layers. Scale (a) 100 $\mu$m, (b) 5 $\mu$m, and (c) 100 nm.

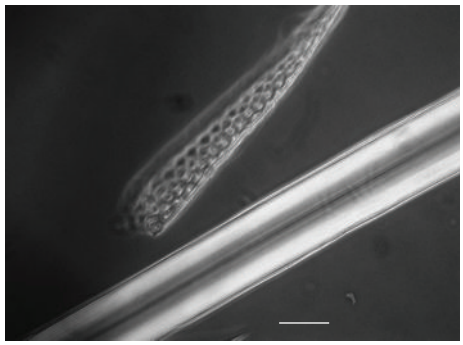


Figure 2: A view of spicules of *Asconema setubalense* after treatment with 1 M NaOH. The lower spicule is intact similar but untreated one, and the upper one shows the honeycomb structure of the organic matrix. Scale: 60 $\mu$m.

may serve as waveguides transmitting optical, electric, or chemical signals and carry information on the state of the environment to cells within a sponge [6, 7].

Previously, it was shown on the basis of investigation of the morphology of spicules, of absorption spectra, and fluorescence, as well as of the composition of fatty acids, that the glass hexactinellid sponge *Pheronema raphanus* possesses photosynthesizing cyanobacteria [13]. This fact implies that the spicules of these sponges may have unusual optical properties providing the function of photosynthesizing systems in complete darkness.

This study deals with investigation of the structural organization of corporeal and basalia spicules and their characteristics with special traits of birefringence and their luminescence in the normal state and upon destruction.

## 2. Material and Methods

The morphology, chemical composition, and optical properties of long monoaxonic spicules were studied in several species of marine deep-sea hexactinellid sponges of different orders and families: *Asconema setubalense* (Hexasterophora, Lyssacinosida, Rossellidae Schulze, 1885) and *Monorhaphis chuni* Schulze (Monorhaphiidae). The material was taken from the collection of the Institute of Oceanology of the Russian Academy of Sciences (Moscow, Russia) or collected during the voyage of research ship *Akademik Oparin* in the South China Sea. The spicules were sputtered with platinum and examined under a LEO 430 scanning electron microscope (SEM).

Elemental composition was then obtained by using an energy-dispersive X-ray (EDX) module attached to the SEM. Platinum-coated specimens were analyzed for the presence of carbon, and carbon-coated specimens were analyzed for the presence of C, O, Na, Si, cu.

For destruction, the middle part of a spicule was heated. The heated part exploded. The explosion was accompanied by a popping sound and luminescence. Linear heating of a sample was provided by a miniature ceramic heater. The basis of the luminometer was an R928 photoelectric amplifier in configuration E717-22 (Hamamatsu Photonics, Japan) loaded at the input resistance of an ASK 3107 digital four-channel oscillograph (ASK, Russia). Acoustic emission

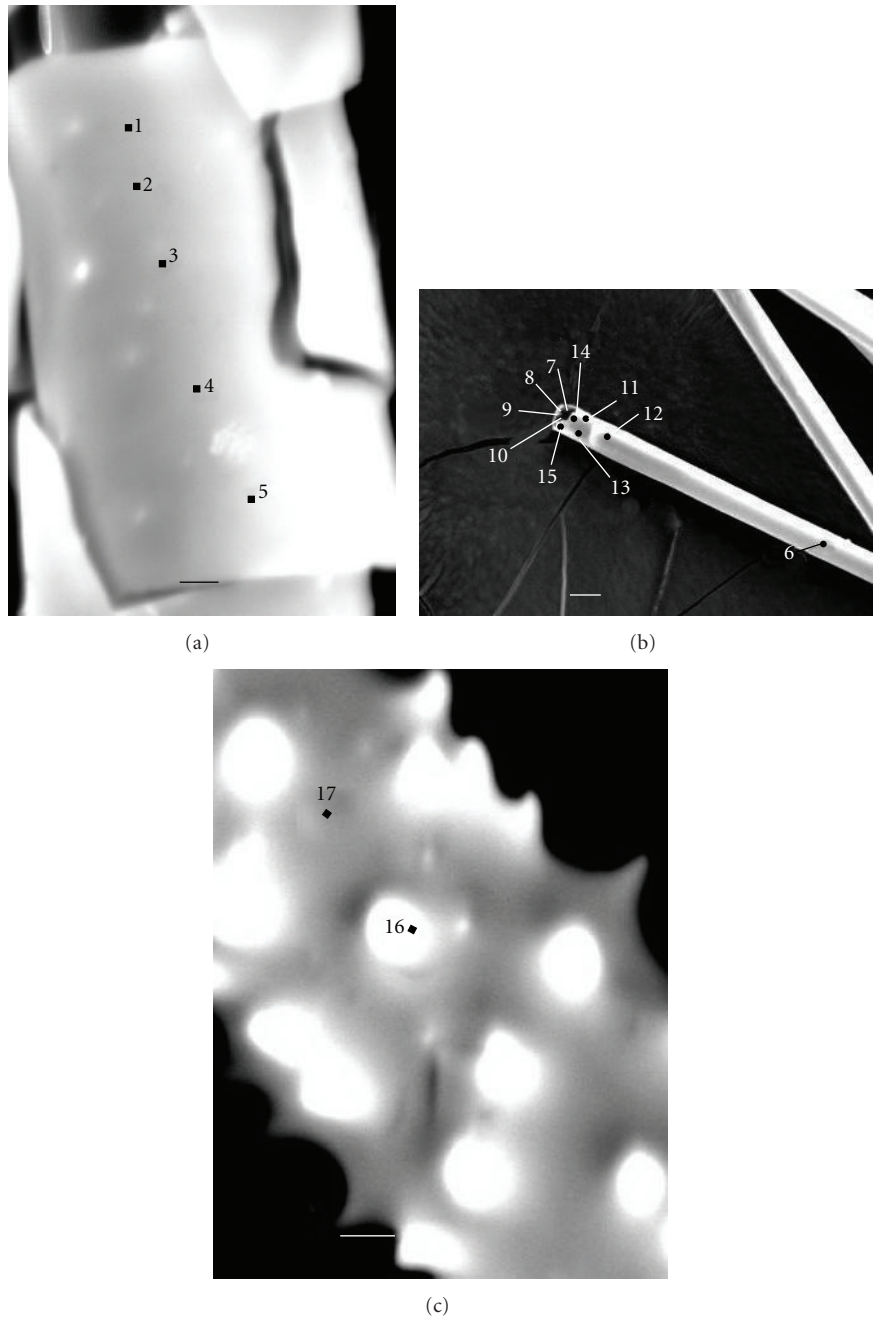



Figure 3: Localization of probes for the analysis of the elemental composition in spicules *Asconema setubalense*: (a) intact spicule surface, (b) in cross-section, (c) after etching with NaOH. Scale: (a, c) 1 $\mu$m, (b) 130 $\mu$m.

was taken directly in the working chamber of the triboluminometer with a built-in electret microphone. Selection, synchronization, amplification, and processing of signals were provided by the working program of an ASK-3107-PO1 oscillograph.

We studied the birefringence, or double refraction, with an optical microscope, rotating the table with specimens, through which the polarized light passed.

## 3. Results

*3.1. Organization of Spicules.* The spicules of the investigated species of glass sponges from different orders and families are similar in structure. Their macrostructural organization is a system of thin layers laid around the central cylinder containing a square canal filled with organic matter (Figures 1(a) and 1(b)). The diameter of the central cylinder is ca 50 $\mu$m and the thickness of layers laid around it is ca.

Table 1: The elemental composition of C, O, Si, Na, Cu in percentages by weight in the corporal monoaxonic spicule of *A. setubalense*: on the surface of the spicule (1–5), on spading cross-section of the spicule (6–15), and after etching with NaOH (16, 17) (Figure 3).

| Spectrum number | C | O | Si | Na | Cu | Total |
|---|---|---|---|---|---|---|
| Spectrum (1) | 29.39 | 54.39 | 34.60 | 1.08 | | 119.47 |
| Spectrum (2) | 27.09 | 56.02 | 36.28 | 0.87 | 0.53 | 120.78 |
| Spectrum (3) | 25.68 | 56.47 | 36.78 | 0.90 | 0.58 | 120.39 |
| Spectrum (4) | 27.87 | 52.66 | 35.15 | 0.90 | | 116.58 |
| Spectrum (5) | 26.36 | 47.96 | 34.04 | 0.85 | 0.54 | 109.75 |
| Spectrum (6) | 52.25 | 46.95 | 30.31 | 0.31 | 0.71 | 130.53 |
| Spectrum (7) | 82.77 | 18.04 | 1.64 | | | 102.83 |
| Spectrum (8) | 68.89 | 23.59 | 1.90 | | | 94.37 |
| Spectrum (9) | 69.55 | 22.69 | 1.77 | | | 94.01 |
| Spectrum (10) | 96.61 | 31.72 | 3.93 | 0.47 | 0.52 | 133.25 |
| Spectrum (11) | 97.44 | 65.20 | 26.47 | 0.93 | 0.53 | 190.57 |
| Spectrum (12) | 96.66 | 50.88 | 20.82 | 0.53 | 0.84 | 169.72 |
| Spectrum (13) | 89.15 | 32.15 | 4.57 | 0.42 | 0.67 | 129.96 |
| Spectrum (14) | 70.45 | 24.80 | 1.84 | | | 97.09 |
| Spectrum (15) | 20.93 | 61.69 | 35.71 | 1.13 | 0.55 | 120.01 |
| Spectrum (16) | 12.72 | 35.79 | 35.36 | 0.40 | 0.66 | 84.94 |
| Spectrum (17) | 100.38 | 67.53 | 24.12 | 1.03 | 0.63 | 193.69 |
| Max. | 100.38 | 67.53 | 36.78 | 1.13 | 0.84 | |
| Min. | 12.72 | 18.04 | 1.64 | 0 | 0 | |

Table 2: Elemental composition of C, O, Si. Cl, K in percentages by weight in basal spicule *M. chuni* (15–20) (Figure 5).

| Spectrum number | C | O | Si | Cl | K | Total |
|---|---|---|---|---|---|---|
| Spectrum (15) | 10.52 | 30.51 | 33.11 | | 0.22 | 74.36 |
| Spectrum (16) | 6.02 | 24.64 | 31.60 | | 0.27 | 62.52 |
| Spectrum (17) | 6.11 | 45.26 | 39.02 | | 0.31 | 90.70 |
| Spectrum (18) | 12.20 | 25.90 | 29.63 | 0.27 | 0.22 | 68.23 |
| Spectrum (19) | 16.48 | 27.49 | 30.24 | 0.22 | 0.25 | 74.69 |
| Spectrum (20) | 24.79 | 35.13 | 31.85 | 0.39 | 0.27 | 92.43 |

40 nm. The layers are penetrated by channels, usually in pairs (Figure 1(c)).

A significant role in spicule organization is played by the organic matrix. It may be revealed after delicate extraction of silicon oxide during long time, around two months, in 1 M NaOH. After such procedure the spicules assume a honeycomb structure, composed by the organic component (Figure 2).

The interconfiguration of the organic matrix and the silicon oxide is very intricate, which is revealed by microsound analysis of elemental composition in spicules (Figure 3, Table 1).

Analysis of the elemental composition of C, O, Na, Si, Cu in percentages by weight of the corporal monoaxonic spicule of *A. setubalense* (Figure 3, Table 1) shows that the spatial organization of spicules is complicated and elements are disposed on the spicule incoherently. On the spicule surface in points 1–5 the composition of elements C, O, Na, Si, Cu is approximately equal. Silicon content is 34–36%, carbon: 25–29%, sodium: about 1% and trace amounts of copper: not more than 0.58%. Oxygen is the most variable: 47.96–54.47%. Highly variable amounts of carbon (68.89–97.44%), oxygen (18.04–65.2%), and silicon (1.64–26.47%) are found on the cross-section.

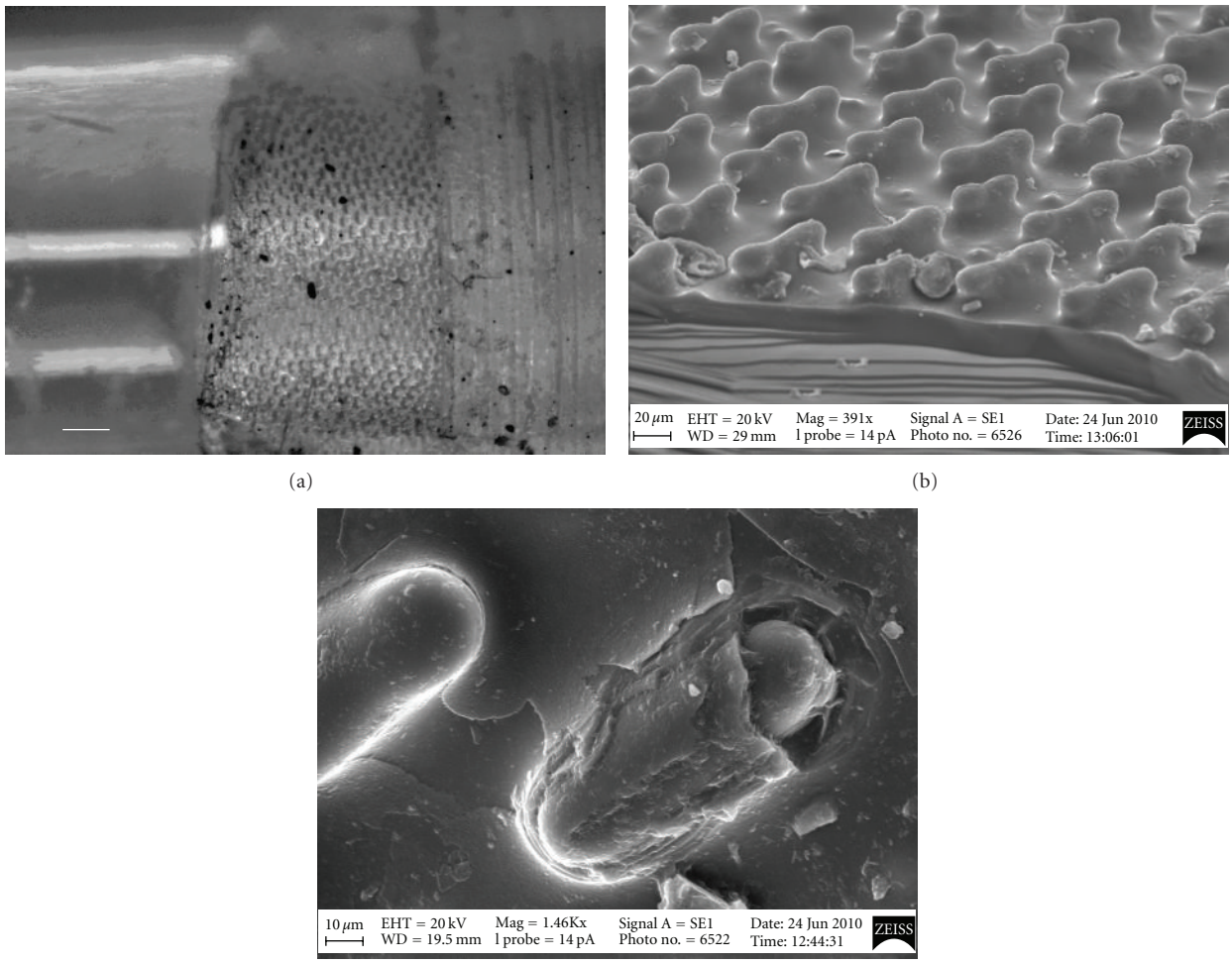
*3.1.1. The Ultrastructure of the Basalia Spicule of Monorhaphis chuni.* This glass sponge has a single basalia spicule. It may be very long (up to 3 m) and thick (up to 30 mm in diameter) [14]. The central part of such spicule has the classic structure. There is a well-defined organic axial filament, located in the central channel. Around the filament are silica layers alternating with layers of the organic matrix. As a result, the macrostructural organization of the spicule is a system of the "cylinder-within-a-cylinder" type.

However the surface layers of this spicule have different structure (Figure 4). The spicule surface is covered with ridges having a length of approximately 50 $\mu$m and height of approximately 10 $\mu$m. They penetrate a few layers into the spicule.

Analysis of the elemental composition of the basalia spicule of *M. chuni* (Figure 5, Table 2) demonstrates a heterogeneous allocation of C, O, Si, Cl, K on the spicule surface, subsurface layers, and on ridges. This is evidence of a very complicated structure of this basalia spicule.

### 3.2. Spicule Properties

*3.2.1. Birefringence.* The intensity of the passed polarized light transforms during rotation of corporeal spicule (Figures 6(a)–6(d)). When passing polarized light through a cross-section of the basalia spicule, a characteristic conoscopic figure in the form of an obscure cross is observed, located exactly in the center of picture (Figure 6(e)).




(a) (b)

(c)

Figure 4: Morphology of the surface layers of basal spicule of *Monorhaphis chuni*. Scale: (a) 100 $\mu$m; (b) 20 $\mu$m; and (c) 5 $\mu$m.

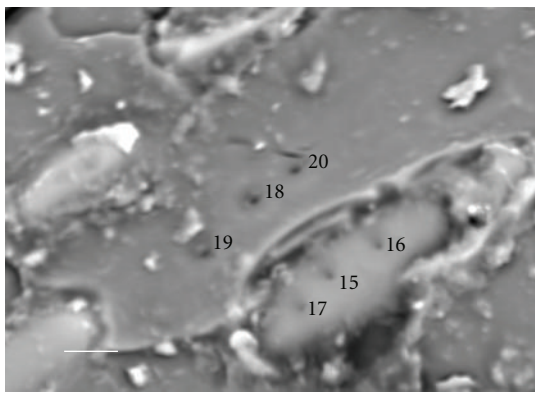



Figure 5: Location of probes of elemental composition in basal spicules of *Monorhaphis chuni*. Scale: 5 $\mu$m.

*3.2.2. Triboluminescence of Spicules.* The spicules may be destroyed by various methods. Local heating of a spicule was used in the present case. When spicules are heated, they keep their optical transparency to 120°C. The spicule begins to be destroyed at approximately 150°C. Swellings appear on the spicules. Above 320°C, the spicules are destroyed. In some cases, when a spicule was destroyed, the integrity of outer concentric layers was explosively disrupted, but the central cylinder is not destroyed and retains its integrity (Figure 7).

The process of destruction of the peripheral layers of spicules is accompanied by a popping sound and a luminescent flash (Figure 8).

## 4. Discussion

In spite of a lot of studies devoted to the structure and physicochemical properties of spicules in Hexactinellids, (e.g., [3–8, 11, 12, 15–17], etc.), their biogenesis, organization, function, and biological meaning are far from being perfectly understood.

Furthermore in the last dozen years certain mythology related to spicules has taken root in the scientific community, which has been repeated and practically not called into question. It concerns both the spicule organization as well as spicule properties and function. Macrostructural spicule organization was interpreted as an intercalation of silica

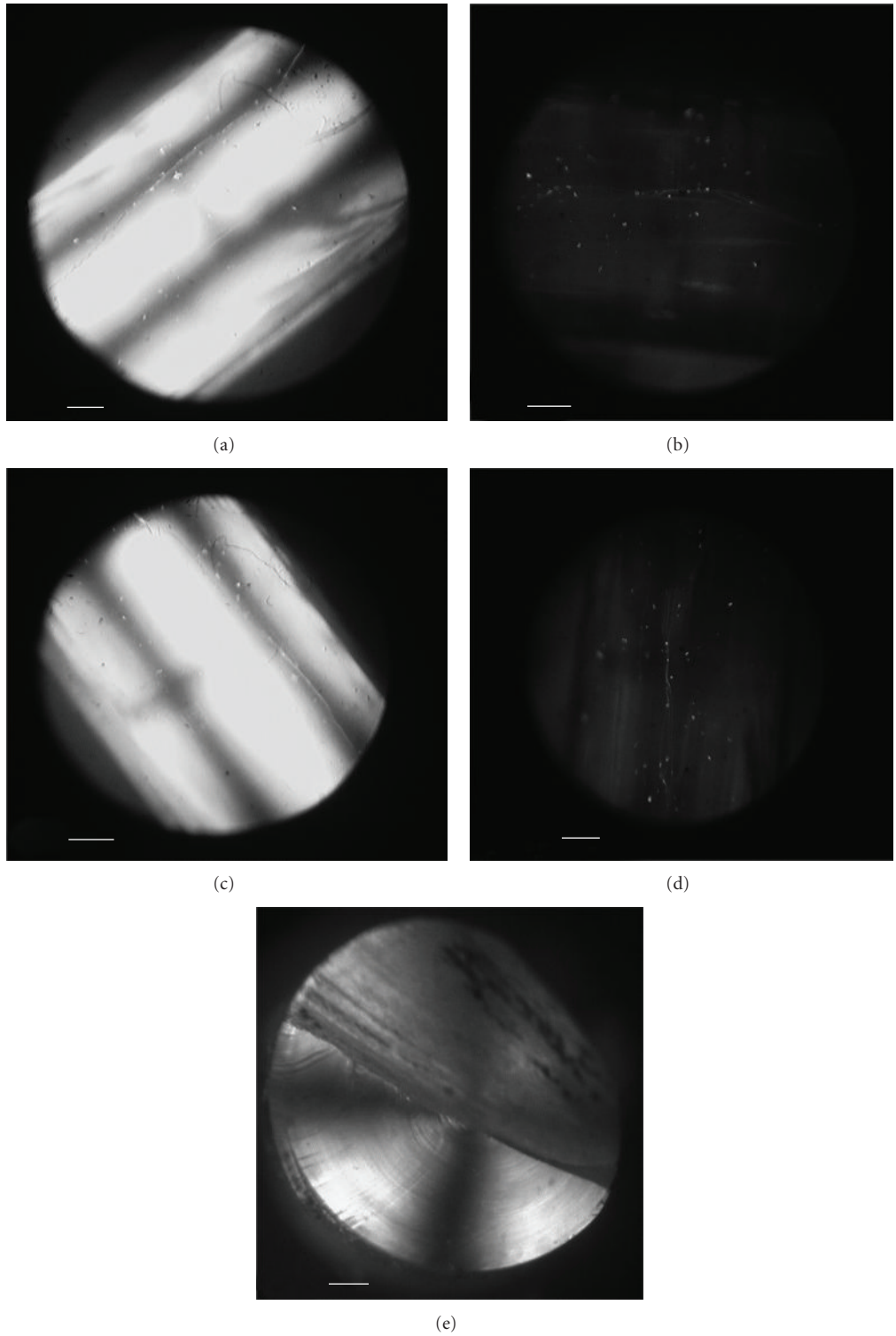
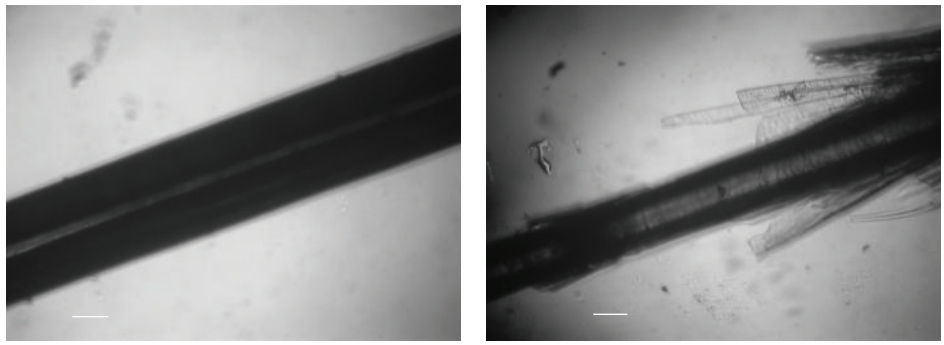



Figure 6: The 360° rotation of specimen of corporeal spicule of *M. chuni* in crossed polarizers. (a)–(d) Photos at each 45° of rotation. (e) Polishing section of the basalia spicule of *M. chuni* in crossed polarizers. Scale: (a)–(d) 20 $\mu$m; (e) 300 $\mu$m.

layers and organic matrix of a "cylinder-within-a-cylinder" type [3–5, 8]. Spicule biogenesis was represented as a result of absorption of silica from marine water around proteins silicateins [15, 17–20]. This process was suggested to be repeated and resulted in a multilayer structure with alternating mineral and organic layers.

Our data on spicule ultrastructure and elemental composition indicate a very complicated spicule organization.



(a) (b)

Figure 7: Triboluminescence of the spicules of hexactinellid sponges: (a) an intact spicule of *Monorhaphis chuni*; (b) its appearance after local thermal impact. Concentric layers are destroyed, but the central cylinder remains intact. Scale: 50 $\mu$m.

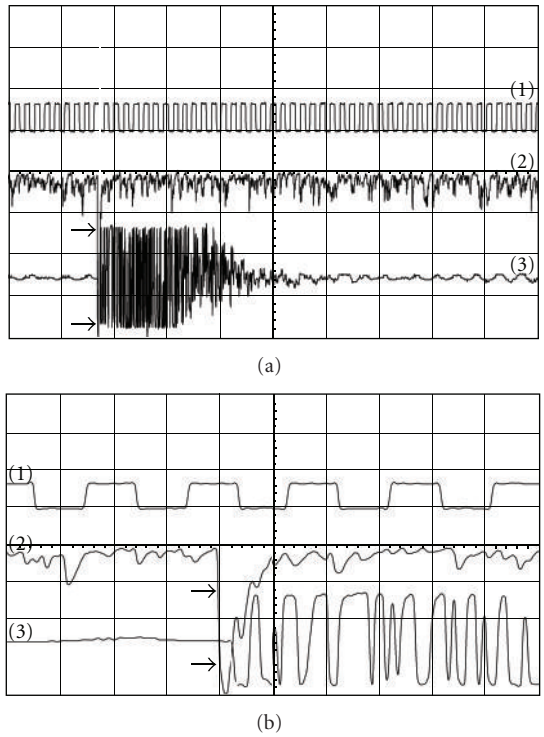



Figure 8: Triboluminescence of a corporeal spicule of a glass sponge *Asconema setubalense* upon thermal destruction (scales in (a, b) are different). (1) A 1 ms time mark; (2) the outcome of the luminescence signal. Deviation of the recording line corresponds to accretion of the optic signal. (3) The acoustic signal. The flash on the recording is the acoustic emission upon the explosive destruction of a spicule. The arrow indicates the anterior front of the luminescence signal.

The organic matrix has a three-dimensional arrangement. It is located not only in the central spicule channel but also in the intermediate layers between silica layers. It also permeates these layers with radial rays. In other words, the organic spicule components form the volumetrical three-dimensional skeleton of the whole of spicule, which organizes the silica mineral component of a spicule. Both these constituents form a composite material possessing anisotropic crystal characteristics.

Glass sponge spicules are able to bifurcate polarized light rays, that is, they have birefringence. At this point our data contradict the prevailing opinion that birefringence in glass sponge spicules is absent [11].

Another unique property of spicules, that we suggest now, is their capacity for triboluminescence. Triboluminescence (mechanoluminescence), the emission of light at destruction of materials, has been known for more than four hundred years. Triboluminophores are a rather wide class of organic and inorganic substances in a crystalline form. The nature of this physical phenomenon is not quite clear [21]. As a rule, the spectrum of triboluminescence nearly or completely coincides with the spectrum of photoluminescence [22].

There are no available published studies on triboluminophores among composite materials. Triboluminescence occurring upon destruction of the composite organosilicon material composing a part of sponge spicules has been described here for the first time. Destruction may be attained in various ways. In our experiments, the thermal blasting of spicules was used. Due to local heating of a spicule, it explodes, which is accompanied by a popping sound and a subsequent photoemission.

Triboluminescence of organosilicon spicules seems to be due to their complex multilayered organization. In different parts of spicules, there is mechanical tension between layers that is removed upon destruction of the spicule. The discovery of triboluminescence in spicules of deep-sea hexactinellid sponges suggests that the spicules may provide photons to the photosynthesizing symbionts living in them. It is likely that, under certain conditions, the sponge itself may provide its own symbionts with light energy [13].

Recently, the interest in new materials capable of triboluminescence has increased due to the creation of light-emitting sensors of destruction [21, 22]. The discovery of triboluminescence in composite organosilicon materials of which the spicules of hexactinellid sponges are built may contribute to the creation of biomimetic materials capable of generating light emission. This, in turn, may be used in

various technical constructions for the transformation of energy.

Additional investigations are required for understanding of biological meaning of complicated and unique properties of hexactinellids spicules.

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## References

[1] R. Cattaneo-Vietti, G. Bavastrello, C. Cerrano et al., "Optical fibers in an Antarctic sponge," *Nature*, vol. 383, pp. 397–398, 1996.

[2] A. L. Drozdov, *Biology for Physicists and Chemists*, Far Eastern University Press, Vladivostok, Russian, 2005.

[3] H. Ehrlich, A. V. Ereskovskii, A. L. Drozdov et al., "A modern approach to demineralization of spicules in glass sponges (Porifera: Hexactinellida) for the purpose of extraction and examination of the protein matrix," *Russian Journal of Marine Biology*, vol. 32, no. 3, pp. 186–193, 2006.

[4] H. Ehrlich and H. Worch, "Sponges as natural composites: from biomimetic potential to development of new biomaterials," in *Porifera Research: Biodiversity, Innovation and Sustainability*, M. R. Custodio, G. Lobo-Hajdu, E. Hajdu, and G. Muricy, Eds., pp. 303–312, Museu Nacional, Rio de Janeiro, Brasil, 2007.

[5] H. Ehrlich, *Biological materials. Invertebrates*, Springer, Dordrecht, Netherlands, 2010.

[6] X.-H. Wang, J.-H. Li, L. Qiao et al., "Structure and characteristics of giant spicules of the deep sea hexactinellid sponges of the genus *Monorhaphis* (Hexactinellida: Amphidiscosida: Monorhaphididae)," *Acta Zoologica Sinica*, vol. 53, no. 3, pp. 557–569, 2007.

[7] X. Wang, S. Hu, L. Gan, M. Wiens, and W. E. G. Müller, "Sponges (Porifera) as living metazoan witnesses from the Neoproterozoic: biomineralization and the concept of their evolutionary success," *Terra Nova*, vol. 22, no. 1, pp. 1–11, 2010.

[8] Y. N. Kul'chin, A. V. Bezverbny, O. A. Bukin et al., "Optical and nonlinear optical properties of sea glass sponge spicules," in *Biosilica in Evolution, Morphogenesis, and Nanobiology, Progress in Molecular and Subcellular Biology, Marine Molecular Biotechnology*, W. E. G. Müller and M. A. Grachev, Eds., vol. 47, pp. 315–340, Springer, Berlin, Germany, 2009.

[9] H. M. Reiswig, "Classification and phytogeny of Hexactinellida (Porifera)," *Canadian Journal of Zoology*, vol. 84, no. 2, pp. 195–204, 2006.

[10] K. R. Tabachnick and H. M. Reiswig, "Dictionary of Hexactinellida," in *Systema Porifera: A Guide to the Classification of Sponges*, J. N. A. Hooper and R. W. M. van Soest, Eds., pp. 1224–1229, Kluwer Academic/Plenum Publishers, New York, NY, USA, 2002.

[11] J. Aizenberg, V. C. Sundar, A. D. Yablon, J. C. Weaver, and G. Chen, "Biological glass fibers: correlation between optical and structural properties," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 101, no. 10, pp. 3358–3363, 2004.

[12] J. Aizenberg, J. C. Weaver, M. S. Thanawala, V. C. Sundar, D. E. Morse, and P. Fratzl, "Materials science: skeleton of *Euplectella* sp.: structural hierarchy from the nanoscale to the macroscale," *Science*, vol. 309, no. 5732, pp. 275–278, 2005.

[13] A. L. Drozdov, O. A. Bukin, S. S. Voznesensky et al., "Symbiotic cyanobacteria in Hexactinellids," *Doklady Biological Sciences*, vol. 420, no. 4, pp. 192–194, 2008.

[14] K. R. Tabachnick, "Adaptation of the Hexactinnelid sponges to deep-sea life," in *Fossil and Recent Sponges*, J. Reitner and H. Keupp, Eds., pp. 378–386, Berlin, 1991.

[15] W. E. G. Müller, A. Krasko, G. Le Pennec et al., "Molecular mechanism of spicule formation in the demosponge *Suberites domuncula*: silicatein—collagen—myotrophin," *Progress in Molecular & Subcellular Biology* , vol. 33, pp. 195–222, 2003.

[16] W. E. G. Müller, C. Eckert, K. Kropf et al., "Formation of giant spicules in the deep-sea hexactinellid *Monorhaphis chuni* (Schulze 1904): electron-microscopic and biochemical studies," *Cell and Tissue Research*, vol. 329, no. 2, pp. 363–378, 2007.

[17] W. E. G. Müller, J. Li, H. C. Schröder, L. Qiao, and X. Wang, "The unique skeleton of siliceous sponges (Porifera; Hexactinellida and Demospongiae) that evolved first from the Urmetazoa during the Proterozoic: a review," *Biogeosciences*, vol. 4, no. 2, pp. 219–232, 2007.

[18] K. Shimizu, J. Cha, G. D. Stucky, and D. E. Morse, "Silicatein $\alpha$: cathepsin L-like protein in sponge biosilica," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 95, no. 11, pp. 6234–6238, 1998.

[19] J. N. Cha, K. Shimizu, Y. Zhou et al., "Silicatein filaments and subunits from a marine sponge direct the polymerization of silica and silicones in vitro," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 96, no. 2, pp. 361–365, 1999.

[20] H. C. Schröder, A. Boreiko, M. Korzhev et al., "Co-expression and functional interaction of silicatein with galectin: matrix-guided formation of siliceous spicules in the marine demosponge *Suberites domuncula*," *Journal of Biological Chemistry*, vol. 281, no. 17, pp. 12001–12009, 2006.

[21] G. Bourhill, L. O. Pålsson, I. D. W. Samuel, I. C. Sage, I. D. H. Oswald, and J. P. Duignan, "The solid-state photoluminescent quantum yield of triboluminescent materials," *Chemical Physics Letters*, vol. 336, no. 3-4, pp. 234–241, 2001.

[22] I. Sage and G. Bourhill, "Triboluminescent materials for structural damage monitoring," *Journal of Materials Chemistry*, vol. 11, no. 2, pp. 231–245, 2001.