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MASTER THESIS

Biomimetic potential of sponge spicules

An investigation of the optical properties and growth mechanism of sponge spicules and approaches for the improvement of fibre optics and photonics applications

Submitted in partial fulfilment of the requirements of the academic degree

Master of Science in Engineering - MSc

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Keywords

biomimetics, biomimetics in energy systems, biomimicry, biomineralization, bionics, biosilica, biosintering, composite, daylight, circadian rhythm, daylight guidance systems, daylighting, earth quake proof, hierarchical architecture, rocking core, office buildings, optical fiber, optical fibre, photovoltaic, porifera, silica, solar, solar cells, solar energy, spicule, spiculogenesis, sponge, syneresis, transparent, waveguide, zeitgeber

Schlagwörter

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Abstract

Sponges (Porifera) have been living in the ocean for more than 700 million years, making them the oldest living animals. Most sponges possess a hard inner skeleton mainly made of hydrated amorphous silica (SiO_2). Skeletal elements, termed *spicules,* serve various purposes that go beyond structural support and have been found to conduct light. Moreover, the complex structure of spicules entails mechanical properties that are extraordinary for glass-based materials. High flexibility, strength and toughness as well as a mild failure mode characterize this organic/inorganic composite material. Hierarchical architecture as well as effects that emerge due to structuring at the nano-scale are decisive for these properties. The synthesis of sponge spicules differs remarkably from other mineralization processes since it is driven and controlled by an enzyme, while enzymatic control of a mineralization process is unknown in all other organisms. This unique process holds promise for sustainable low-temperature manufacture methods, e.g. of optical fibres that share remarkable similarities with sponge spicules. Other fields that can draw inspiration from the unique synthesis and material properties of spicules are material sciences, the biomedical sector and advanced optical applications like laser technology. The manifest similarity of spicules and technical light-guiding fibres suggests an application in daylight guidance systems for buildings. In times of increasing urbanization, at the end of the era of cheap energy we need novel, more sustainable building concepts. Taking furthermore into account the current reappraisal of natural light, daylight guidance systems offer great opportunities to implement biomimetic light management systems. To exemplify further possible contributions of concepts observed in sponges, an adaptive façade element and a whole-building system for seismic hazard zones are devised.

Abriss

Schwämme (Porifera) bevölkern seit mehr als 700 Millionen Jahren den Ozean und sind somit die ältesten noch lebenden Tiere. Die meisten Schwämme bilden ein Endoskelett das überwiegend aus amorphem wasserhaltigen Silikat (SiO_2) besteht. Die physiologischen Funktionen der Skelettelemente, sog. Spiculae oder Schwammnadeln, sind dabei keineswegs darauf beschränkt dem Schwamm seine Struktur zu verleihen. So können die Spiculae beispielsweise auch Licht leiten. Die komplexe Struktur dieser Elemente bedingt mechanische Eigenschaften die für ein glasbasiertes Material außergewöhnlich sind. Das organisch/anorganische Komposit zeichnet sich durch hohe Flexibilität, Festigkeit und Zähigkeit sowie durch einen „gutartigen“ Versagensmechanismus aus. Der hierarchische Aufbau und durch die Strukturierung auf Nano-Ebene bedingte Effekte sind dabei entscheidend. Die Synthese von Spiculae unterscheidet sich erheblich von anderen Mineralisierungsprozessen insofern er von einem Enzym getrieben und kontrolliert wird. Dieser

einzigartige Prozess stellt nachhaltige Produktionsverfahren in Aussicht, besipielsweise für Lichtwellenleiter die den Spiculae bemerkenswert ähneln. Daneben können auch die Materialwissenschaften, die biomedizinische Forschung und Entwickler hochentwickelter optischer Komponenten für Laser-Technologien von der Synthese und den Materialeigenschaften der Spiculae lernen. Die offenkundige Ähnlichkeit von Spiculae und technischen Lichtewellenleitern legt Anwendungen in Tageslichtsystemen für Gebäude nahe. Die fortschreitende Urbanisierung am Ende des Zeitalters der billigen Energie verlangt nach neuartigen, nachhaltigeren Konzepten im Bauwesen. Zusätzlich zeichnet sich eine Neubewertung des natürlichen Tageslichts ab, was große Chancen eröffnet Tageslichtsysteme mittels bionischer Ansätze zu verbessern. Um aufzuzeigen, wie die Bionik zu diesem Anwendungsgebiet beitragen könnte, wurden ein adaptives Fassadenelement sowie ein komplettes Gebäude für erdbebengefährdete Regionen entworfen.

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What is Biomimetics?

Inspiration derived from nature has been an invaluable source for many great scientists and engineers for centuries. The astounding features of animate nature have already been inciting the very first "technical" inventions in pre-historic times. Polymaths like Leonardo da Vinci observed birds' flight to lend wings to humanity and D'Arcy Thompson scrutinized the mechanical and physical qualities of organisms like Nautilus to bridge the gap between engineering and technology (Sánchez, 2012).

However, this transfer of knowledge from nature to technology rested in the hands of individual scholars and engineers. Only half a century ago a shift to a more systematic approach was on the horizon. Involved in this task himself, Otto H. Schmitt also was very fond of verbal play - and coined the term "biomimetics" from the Greek words for "life" and "to imitate". About the same time, Jack E. Steele came up with the closely related term "bionics", a term that is sometimes used synonymously with biomimetics for the abstraction and implementation of principles found in natural systems (Harkness, 2002) (Ehret et al., 2012). Since that time, formalization of the biomimetic approach has come a long way.

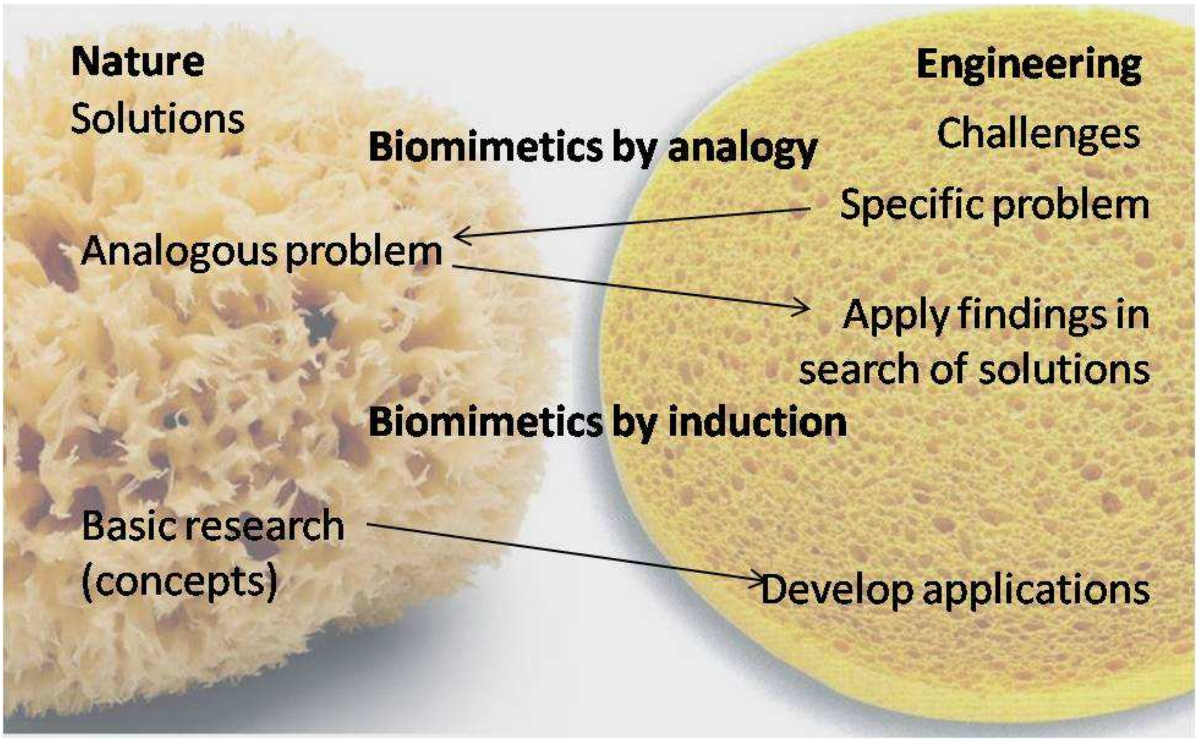


Figure 1 Methods in biomimetics. This graphics contrasts the two methods commonly distinguished within the biomimetic approach. Text reproduced from (Gebeshuber & Drack, 2008), pictures: ©by Manufactum and kitespot-ruhrgebiet.blogspot.com

Apart from this methodological dichotomy, a cornucopia of sub-fields that divides biomimetics according to the fields of application has emerged (Nachtigall, 1998).

This work seeks to elaborate on features of sponge spicules of potential interest for energy-related systems and to suggest ways to implement appealing principles. According to the aforementioned classification this constitutes a project of biomimetics by induction in the field of energy related systems, as presented by (Latzelsperger, 2012).

On a basic level, two general methods are usually distinguished by researchers and engineers that have adopted the biomimetic “point of view” (Schmitt, 1957). Either basic research leads to the recognition of basic, biological concepts that are subsequently used for technological applications, or a technological challenge triggers the search for the solution of an analogous problem that helps to surmount the initial problem. Even though the general idea seems to be widely accepted, terminology for these complementary methods differs considerably. While Gebeshuber and Drack (2008) distinguish biomimetics “by induction” vs. “by analogy” (Figure 1), researchers at the Georgia Institute of Technology use the terms “solution-based” vs. “problem-based” (Georgia Tech, n.d.), and researchers in Freiburg refer to them as “bottom up” vs. “top-down“ mechanisms (Plant Biomech, n.d.).

For a more detailed account of different methodologies in biomimetics and the current state of biomimetics in energy systems refer to (Schäfer, 2011). A successful example for biomimetics by analogy in the field of photovoltaics can be found in (Bach, 2011).

Sponges

Phylogeny

Sponges look simple. So simple that not few people can hardly believe them to be animals. Even the great taxonomist Carl von Linné (Linnæus) mistakenly assigned sponges to the kingdom of plants in his opus *Systema Naturae* back in the 18th century (von Linné, 1759). Subsequently the group sponges (Porifera) was recognized to be at the base of the kingdom Metazoa, more commonly known as animals, because unlike plants, they are heterotrophic and possess no cell walls.

More recently, taxonomists challenged the validity of the phylum (systematic group) Porifera based on genetic analyses implying that Sponges are a paraphyletic group (Borchiellini et al., 2001) (Müller et al., 2007a). Commonly, taxonomists demand that all the constituents of a taxon (systematic group) are more closely related to each other than to any organism of another taxon (Monophyly). Grouping calcareous sponges and siliceous sponges together does not meet this criterion.

Figure 2: Simplicity of a Sponge. The large photo shows the spheroid architecture of a common bath sponge in the Mediterranean Sea. The inset shows a rare hexactinellid reef off the coast of British Columbia, Australia, exhibiting a more complex shape. © by schule-bw.de and livingoceans.org

That leaves us to talk of “siliceous sponges”, a subgroup of sponges that shares the common, derived trait (synapomorphy) of a skeleton containing glass-spicules, among other features. For readability, we will nonetheless continue to use the term “sponge”, specifying the taxon when it is relevant. Commonly, researchers divide this group in Hexactinellids (Glass sponges) and Demosponges (Borchiellini et al., 2001). While none of these classifications is unchallenged, we will focus on the characteristics of sponges currently described as the classes Demospongiae (Sollas, 1885) and Hexactinellida (Schmidt, 1870) (Brien et al., 1973) (Tabachnick & Reiswig, 2002).

Demosponges include the vast majority of the 5,000-10,000 known extant sponges, among them various species known as “common bath sponges” (e.g. *Spongia officinalis* var., *Hippospongia equina*). Not so common are glass sponges, with a mere 500 described species (Tabachnick & Reiswig, 2002). Since, however, we know more about the dark side of the moon than about their preferred habitat - the deep sea - these figures might change drastically.

For (evolutionary) biologists, sponges are fascinating organisms, since they are believed to bear resemblance with the Urmetazoa, the precursor of all animals. Intriguingly, sponges have survived several evolutionary bottlenecks and changes in their environment over the course of more than 540 million years - earning them sobriquets like “living dinosaurs” and “living fossils” (Krautter et al., 2001) (Müller, 1998) (Steiner et al., 1993) (Steiner, 1994). When siliceous sponges first emerged, oceans were richer in silica than today and hence suggested Silicium to be included in the first skeletons. In fact silicatein, the enzyme driving the formation of glassy sponge spicules, has likely heralded the era of biogenic mineral deposition/ biomineralization (Li et al., 1998) (Müller et al., 2007a), a process that is essential for the formation of all hard skeletons. This view has been challenged by the discovery of fossils from Namibia representing 750 million year old, possibly calcareous sponges (with Ca-based skeletons) that were reported in July 2012 (Brain et al., 2012). Molecular data, however, still suggests that Hexactinellida are the phylogenetically oldest extant animals (Müller, 1998) (Müller et al., 1995) (Kruse et al., 1997).

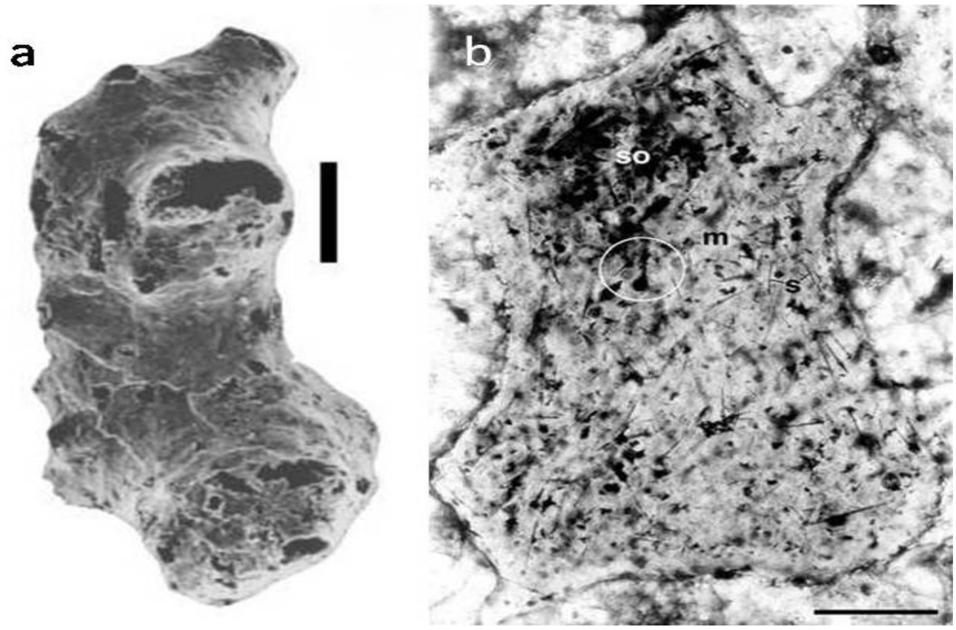


Figure 3: Early fossils of sponges. Recent additions to the fossil record of sponges have revived the discussion whether calcareous or siliceous sponges occurred first. (a) Scanning Electron Micrograph of *Otavia* in (Brain et al., 2012), a genus of possibly calcareous microscopic sponges dating from 750 million years ago (mya) (b) Cross section of a tubular demosponge from 580 mya, discovered in Doushantou, Southern China (Li et al., 1998). Scale bars are 100 µm. ©by (Brain et al., 2012) and (Li et al., 1998)

Body plan

Almost all sponges are sessile filter-feeders that constantly pump water through their bodies to extract suspended organic particles. Their body has multiple, small pores called ostia distributed all over their surface that serve as inlets for water and accordingly food as well as oxygen. This peculiar texture has inspired Grant to give sponges their scientific name *Porifera* ("pore-bearer"). Usually at the top, a single larger opening – the osculum - serves as outlet for water and waste-products dissolved therein. Water-flow through the sponges ' widely ramified system of internal channels can be explained by Bernoulli's law: The water flow at the top of the sponge tends to be faster than near the base, hence suction drives water away from the osculum and fresh water accordingly flows in through the pores. Additionally, flagella direct the stream of water through the sponge. In most sponges, a mineralized internal skeleton made of amorphous silica (siliceous sponges) or calcium carbonate ($CaCO_3$, calcareous sponges) is responsible for their shape, though in some siliceous sponges also a soft, proteinaceous skeleton of spongin and hard, armour-like exoskeletons made of $CaCO_3$ can be found (Bergquist, 1998) (Ruppert & Fox, 1994)

Tissues, the next higher level of hierarchy above cells in higher animals, are unknown in sponges; as are circulatory and digestive systems. Although it might seem far-fetched to postulate a nervous system in sponges, researchers have found evidence that sponges react to external stimuli (Meech, 2008). In this context, a light perception system and an "optical nervous system" involving the sponges' siliceous spicules have been proposed (Müller et al., 2006a) (Müller et al., 2010).

In demosponges, one layer of cells lines the mesohyl, the gelatinous matrix constituting the shape of the sponge, one the interior and another one the exterior surface. In glass sponges the mesohyl is reduced and the structure is exclusively provided by fused silica-spicules. Cells are, like in higher animals, differentiated (specialized) but can re-differentiate into other cell types and migrate to other parts of the sponge. Though various cell-types contribute to the synthesis of the mineralized skeleton (spiculogenesis) (Krasko et al., 2002) (Wang et al., 2012b), sclerocytes are of eminent importance for this process, since spiculogenesis commences in these cells (Minchin, 1909). In demosponges, this type of cells is embedded in the collagen matrix of the mesohyl, while in glass sponges sclerocytes merge into characteristic, spider-web-like agglomerations of cells called syncytia (Leys & Lauzon, 1998) (Bergquist, 1998).

Spicules

Glassy spicules have raised the interest of naturalists as early as 1780. However, it would remain enigmatic for a century what these spicules actually were, i.e. what their biological origin was. Only after the first oceanographic cruise, the Challenger-expedition 1873-76, this question could be clarified (Schulze, 1887). Between the two classes of siliceous sponges, Hexactinellida produce larger and by far more conspicuous silica structures (Figure 6). As these dwell mainly in the deep sea and near Antarctica it is not surprising that it was – and still is - a tedious endeavour to explore siliceous spicules, especially *in vivo*.

There are various physiological functions to sponge spicules (Figure 7), but it is after life, when spicules of glass sponges have a paramount ecological impact: skeletal elements of dead glass sponges are a major ecological factor in their habitats. Mats of this biomaterial line the benthos of extensive areas of the Antarctic sea and thus provide a hard substrate that other organisms can dwell on (Barthel, 1992) (Leys et al., 2007).

Since siliceous sponges are among the oldest multicellular organisms, their phylogeny is closely related to the occurrence of skeletons (Uriz et al., 2003). We can only conjecture why the first skeletal structures were built and have been preserved in evolutionary younger organisms (fixation by evolution). Rik Huiskes cut right to the chase referring to a different class of biological material: “If bone is the answer, then what is the question?” (Huiskes, 2000). Considering the manifold functions of sponge spicules, that might well be more diverse than the functions of bone, the “question”, i.e. what evolution has selected for, might be similarly complex. A striking example of unexpected evolutionary constraints that has been discussed controversially relates to the origin of calcareous skeletons. According to one theory, the first calcium carbonate based skeletons contested to the need to control intracellular Ca-levels, and only later evolved for other purposes, including structuring of the body (Kingsley & Watabe, 1982).Though this explanation (exaptation) has been refused by others (Vermeij, 1989) it shows how complex it is to fully grasp what any biological material or structure really is (Uriz, 2006).

Structure

Skeletons based on spicules have been very successful throughout more than half a billion years (Uriz, 2006). Sponges have retained the principle of using small spicules as a base for the construction of their skeletons. Interestingly, the conservation even includes the shape of spicules, for most spicule-morphologies observed in the fossil record can still be found in living organisms today, i.e. they occur in extant species (Hinde, 1887-1893) (Wiedenmayer, 1994). This clearly demonstrates that this architecture is favourable under a variety of conditions, for sponges have survived long geological times and concomitantly changing environments (Uriz, 2006) This striking adaptability makes them very competitive in regions with strong anthropogenic influences. In the western central pacific, e.g., encrusting demosponges of the genus *Terpios* have been found to overgrow (and thereby kill) coral reefs in pollution-stressed zones off the coasts of Guam, Micronesia (Bryan, 1973), and Japan (Rützler & Muzik, 1993).

Spicules are, however, not always just "needles" scattered throughout the body of sponges. On a larger scale, individual spicules can be fused together to form massive endoskeletons (cf. Figure 6h) in some hexactinellid sponges, but more frequently they occur unattached throughout the body of sponges, interlocked (Figure 7c) or joined by the protein spongin (Butler, 1961) (Uriz, 2006). Especially in sponges with rigid skeletons like Venus' Flower Basket (*Euplectella aspergillum*) individual spicules may be barely discernible (cf. Figure 6d,h, Figure 7d). In contrast loosely attached or unattached spicules of other sponges readily scatter around the site upon death and disintegration of the sponge (Butler, 1961).

The morphology of spicules has been widely used for identification of genera and species (Butler, 1961) (Dohrmann et al., 2011) (Li, 1987). However this is far from trivial, since one individual sponge usually contains spicules with differences regarding number of symmetry axes, surface, size, ornaments and extremities while similar spicules are shared among various genera. The most basic distinction has been to distinguish larger spicules (*megascleres)* from smaller *microscleres* (Lévi, 1973). Although the concept has been shown to be flawed, since calcareous spicules do not represent this dichotomy and in siliceous sponges microscleres exceeding the size of megascleres have been found (Uriz, 2006), it is still widely used (Wiens et al., 2011) (Valisano et al., 2012) (Voznesenskiy et al., 2011).

The main purpose of this classification is nowadays a functional one. Megascleres are essential for the architecture of the spongial skeleton, while the lack of microscleres, which are considered accessory skeletal elements, does not seem to involve any conceivable disadvantage for a sponge (Uriz et al., 2003). Another basic distinction regards the number of axes of symmetry (cf. Figure 4). While megascleres of demosponges either are monaxons (one axis) or tetraxons (four axes), in hexactinellids the characteristic triaxons occur instead of tetraxons (Uriz, 2006).The triaxons of glass sponges seemed so conspicuous to Schmidt that he decided to name this class after the number of actins (or arms) of spicules Hexactinellida (“six-armed”) (Schmidt, 1870). Altogether, 12 basic shapes of megascleres have been identified in Demospongiae, while in Hexactinellida 20 basic morphologies are distinguished (Boury-Esnault & Rützler, 1997) (Tabachnick & Reiswig, 2002).

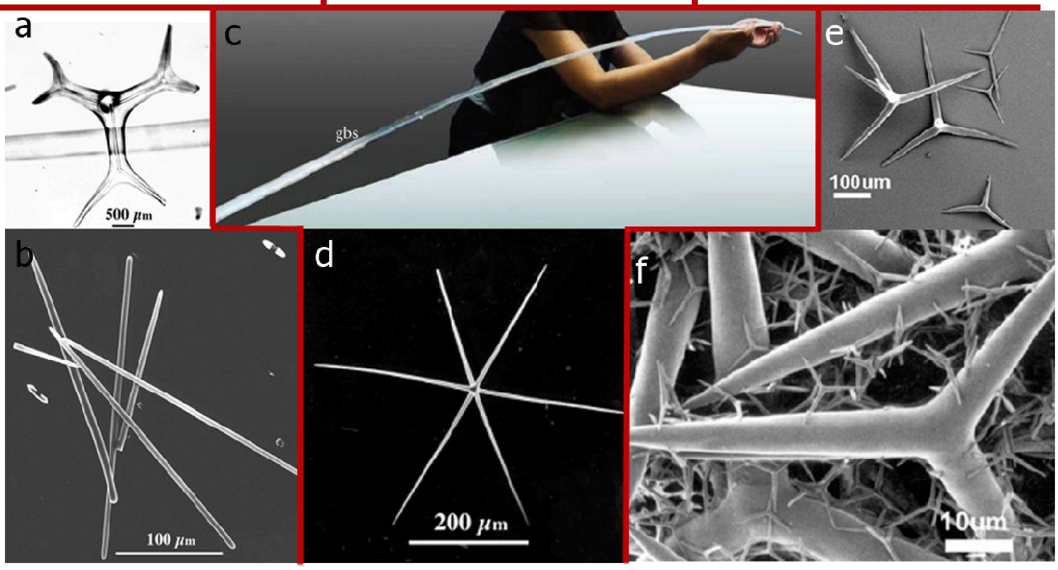
Class	Demosponges	Hexactinellids	Calcareous sponges
Mineral component of spicules	Silica (SiO_2)	Silica (SiO_2)	$CaCO_3$ (Calcite or aragonite)
Typical spicules			

Figure 4: Spicules of the three classes of sponges. One consistent difference between spicules of Demospongiae and Hexactinellida is the number of axes of symmetry (Uriz, 2006): While megascleres with triaxonal symmetry (3 axes, picture (d)) are exclusively found in Hexactinellida, tetraxonal megascleres (4 axes, picture (a)) are only found in Demosponges. Additionally, in both classes monaxonal (1 axe) spicules can be found. (b, c). Picture (c) represents the Giant Basal Spicule of *Monorhaphis chuni.* In Calcarea, (e,f) di-, tri-, and tetractinal (2-4 arms/actins) spicules are found. Size of c: length 2.7 m © (Wang et al., 2011a) for (c), (Uriz et al., 2003) for (a), (b) and (d), (Uriz, 2006) for (e) and (f).

The shape of microscleres varies considerably more. Their classification according to axes of symmetry alone yields six different basic categories (Butler, 1961), compared to only three in megascleres. Taking into account more morphological features like pointed vs. rounded extremities, straight vs. curved shape, microscleres in demosponges pertain to 25 and 24 basic types in Demospongiae and Hexactinellida, respectively (Boury-Esnault & Rützler, 1997).

Spicules are examples of the class of biogenic composites, i.e. composites that are synthesized by living organisms: In Calcarea, different polymorphs of calcium carbonate ($CaCO_3$) are arranged in a determined way to form spicules (Jones & Jenkins, 1969). They possess a core made of (crystalline) calcite embedded in a massive layer of amorphous calcium carbonate and a thin external sheath of calcite (Aizenberg et al., 2003). Calcareous skeletons are the most common biominerals, occurring in many different taxa (systematic groups of organisms)(Lowenstam & Weiner, 1989).

This work, however, is mainly concerned with siliceous spicules, made of amorphous, hydrated silica ($SiO_2 \cdot nH_2O$). Since their appearance and chemical composition are similar to the gemstone, spicules are also said to be made of biogenic opal (e.g. (Wang et al., 2009). The organic component contained in sponge spicules and the intricate hierarchical structure make their properties different from “normal” biosilica. Other silicifying organisms like diatoms share a similar structure at a very small scale (ultrastructure)(Crawford et al., 2001) but lack distinct structures at larger length scales (Weaver et al., 2007). Combining elasticity of the proteinaceous component with the inherent flexibility and durability of silica yields a type of biosilica that excels in strength, flexibility and toughness (Aizenberg et al., 2005) (Wang et al., 2011a) (Kulchin et al., 2009). This holds true for spicules of both classes of siliceous sponges, even though they exhibit differences in structure and silica-content. As seen in Figure 5, the cross-section of most hexactinellid spicules reveals a layered structure consisting of up to eight hundred silica lamellae (Wang et al., 2011a) while broken spicules of demosponges reveal a more homogeneous composition (Wang et al., 2012c). The difference in silica content relates to the respective ecological niches of demosponges and hexactinellids. The latter class is confined to the deep sea and the Antarctic Ocean since photosynthetic microorganisms (phytoplankton) deplete most silica from the photic zone, i.e. as deep as light penetrates the sea, outside the Antarctic region. (Ragueneau et al., 2000) (Uriz, 2006). Though present-day oceans are far from being saturated with silica (<1 mM as opposed to 4.5 mM required for spontaneous mineralization at natural pH and temperature) (Ehrlich et al., 2008) (Ehrlich et al., 2010) even in deep sea environments, the higher concentration there facilitates secondary bio-silification, i.e. to fuse spicules together in a silica-based matrix (Wang et al., 2012c) (cf. Figure 5b).

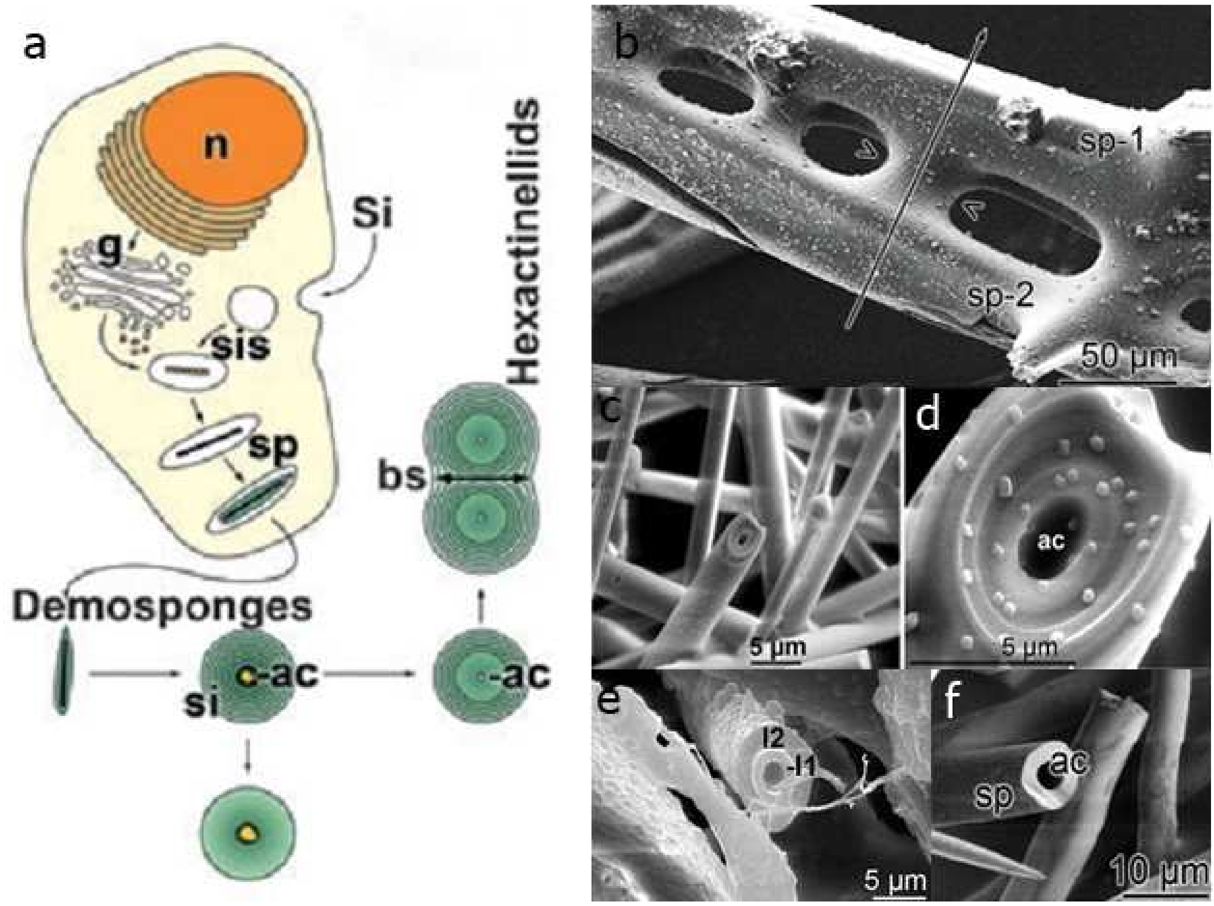


Figure 5: Contrasting biosynthesis and morphology of demosponge- and hexactinellid-spicules ((Müller et al., 2007a) (Wang et al., 2012b) (Wang et al., 2012c)) (a) Biosynthesis commences in specialized cells called sclerocytes in both classes of siliceous sponges. After the initial longitudinal growth, immature spicules are extruded to the extracellular space where appositional, and further longitudinal, growth take place. Thereafter, all lamellae of each individual spicule are fused together (biosintering) in demosponges (c-f), while in many hexactinellids a similar process cross-links adjacent spicules (b). Apart from the innermost region, the layers of most hexactinellid spicules remain distinct. © by (Wang et al., 2012b)(a), (Wang et al., 2012c) (b, f) and (Müller et al., 2007a) (c-e)

It is interesting to notice that individual spicules can largely vary in their dimension. Though the terms microsclere and megasclere admittedly give a clear hint to size differences, these terms come nowhere close to correspond to the differences that span six orders of magnitude: The limit between micro-and megascleres is usually indicated to be in the range of tens or hundreds of micrometers (microscleres < 100 µm and megascleres > 300 µm (Wang et al., 2009), 20 µm (Wang et al., 2012c)). Therefore, the size of megascleres extends over 4-5 orders of magnitude, while microscleres are much more uniform in size.

Strikingly, the largest known natural silica structure, the 3 metre long Giant Basal Spicule of the hexactinellid *Monorhaphis chuni* (Schulze, 1887) (cf. Figure 6i) is assembled by a very similar mechanism like the minute, spiny isochela (microsclere) with its finely "chiselled" ornaments (Figure 6a). The diameter of megascleres commonly varies between 3 µm and 30 µm (De Laubenfels, 1955), but can grow up to 12 mm (Levi et al., 1989) (Wang et al., 2009) in *M. chuni* – after growing for several thousand years (Wang et al., 2011d). The slow growth process has proven to be of substantial interest: Very much like ice cores from the polar regions, that are used as climatic archives since they reveal changes in atmospheric conditions like CO_2 concentration and temperature (Fischer et al., 1999), basal spicules include trace elements like magnesium and calcium in their structure that can be used to determine past temperature fluctuations in the oceans (Jochum et al., 2012). For the purpose of this work these inorganic trace elements are attractive in an entirely different way, though. In present day fibre-optics various desirable optic dopants cannot be used because their use would destroy the fibre during the fabrication at high temperature (devitrification). It has been demonstrated that the presence of these inorganic dopants in sponge spicules increases the refractive index locally and thereby enhances the waveguide properties of these natural glass fibres (cf. Figure 19Figure 20) (Aizenberg et al., 2004) (Sundar et al., 2003).

Considerable differences between the sizes of individual spicules are only one factor that makes it interesting to observe sponge skeletons at different length scales. Especially the fused skeletons of glass sponges reveal completely different structures at different scale, i.e. they show a high level of hierarchy (Currey, 2005). In the well-known Venus' Flower Basket Aizenberg and colleagues (2005) counted seven different levels of hierarchy from silica-beads at the ultra-structural level up to the full body size (cf. Figure 9, Figure 7d Figure 6d, h) This aspect will be taken up again further down.

For this work a closer look at the length scale of several tens to hundreds of micrometers is particularly rewarding, since it reveals the relative orientation of algal filaments and spicules in demosponges like *Tethya seychellensis* that host symbiotic algae (Figure 6e, f). In Figure 6 f, a radial bundle of spicules in the sponge core can be seen with entangling algal filaments, while in Figure 6 f the exact shape of a filament that had previously been removed from the spicule can be seen.

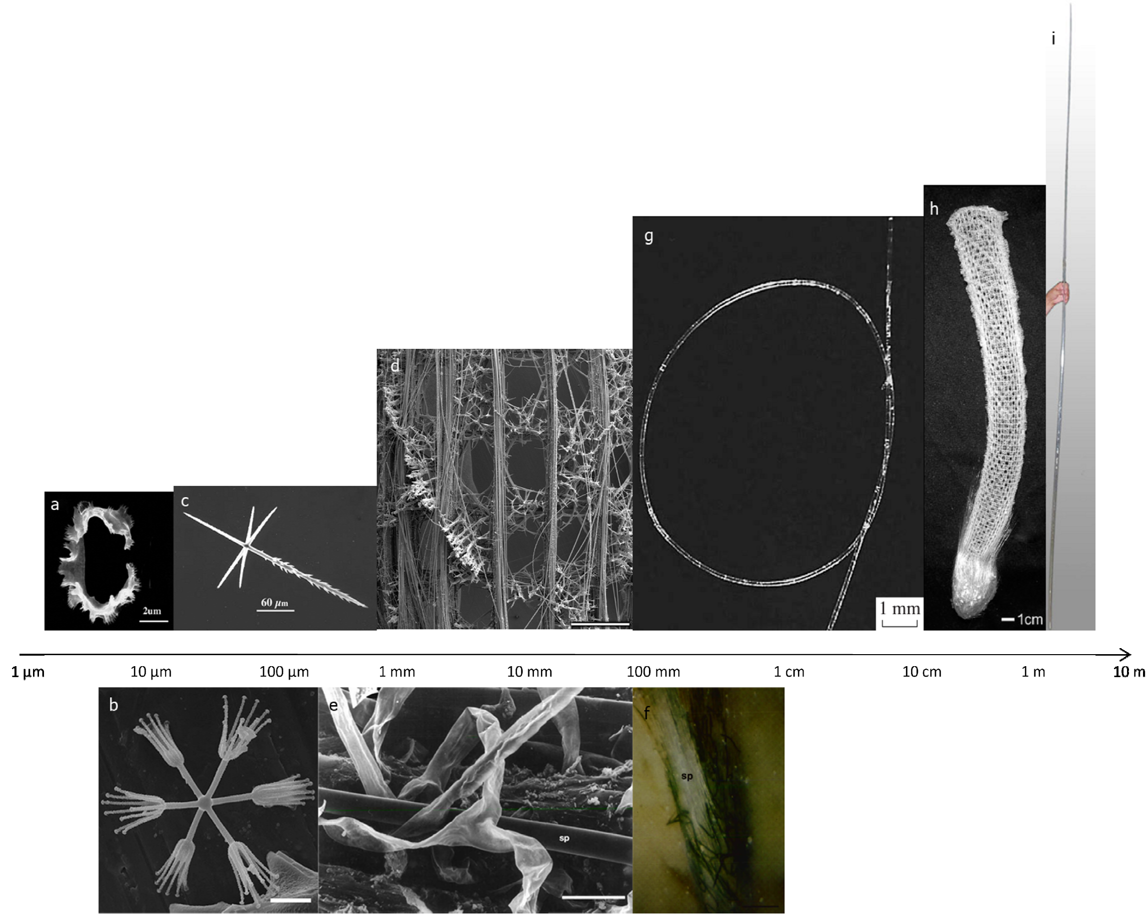


Figure 6: Scale of glass spicules. Individual spicules can be as short as a few micrometers or exceed the body height of humans at 3 metres length. (a) shows a spiny microsclere found in a demosponge of the genus *Guitarra,* while (b) is a modified triactinal spicule (lophodiscohexaster) of the glass sponge *Psilocalyx wilsoni.* (c) A hexactinellid megasclere, roughly one order of magnitude bigger than (a), is shown. (d) Interlocked and fused spicules yielding "struts" that constitute the cage-like skeleton of the hexactinellid *Euplectella aspergillum* (h). (e,f) The close proximity of spicules and algal filaments is shown on the scale of individual spicules and bundles of spicules. This pioneering observation of photosynthetic symbionts deep inside a demosponge (Gaino & Sara, 1994) was a first hint at the light-conducting properties of sponge spicules. The remarkable flexibility of this biomaterial is obvious in the (knotted) basal spicule of the glass sponge *Hyalonema sieboldi* (g). The longest natural siliceous structures known so far are Giant Basal Spicules of the glass sponge *Monorhaphis chuni* (i) measuring up to 3 metres Scale bars: (a) 2 µm, (b), 10 µm, (c) 60 µm, (d) 2.5 mm, (e) 50 µm, (f) 400 µm, (g) 1 mm, (h) 1 cm, (i) length of spicule: 2.7 m © by (Uriz, 2006) for (a), (Dohrmann *et al.*, 2011) for (b), (Uriz et al., 2003) for (c), (Weaver et al., 2007).for (d) and (h), (Gaino & Sara, 1994).for (e) and (f), (Kulchin et al., 2007) for (g), (Wang et al., 2011d) for (i)

Biological functions

Skeletal functions in sponges range from ubiquitous to unique and from evident to equivocal. It is intuitively clear that any skeleton provides structure and stabilizes the shape of an organism. Certain microscleres are reminiscent of man-made structures, e.g., the clip-like placochela microsclere found in *Guitarra sp*. demosponges (Figure 7c). Some monaxonal spicules have swellings or hook-like structure at their extremities that facilitate the attachment to other spicules or to spongin - the proteinaceous, soft part of skeletons found in many demosponges. Even though obvious functions for many spicules have been reported, the roles of many microscleres and the reason for the (unnecessary) coexistence of spicules with seemingly equivalent functions remain enigmatic (Uriz et al., 2003). In glass sponges the structural functions are even more apparent. Mechanical stability of these structures can be attributed to the level of hierarchy, i.e., the dissimilar structures at different length scales. Various structures have specifically been mentioned as enhancers of mechanical stability in *Euplectella aspergillum*. The upper, widened region of the tube-like body would be mechanically unstable, but an increased number of horizontal and diagonal external ridges prevent deformation under lateral strain (Aizenberg et al., 2005).

Plasticity of skeletons is an essential factor for the success of sponges, since it allows the sponge to grow upwards and thereby stay in contact with the water-column it relies on for food and oxygen (Jackson, 1979). Thereby, sponges can avoid being overgrown by neighbouring organisms and furthermore can reshape their body to meet all their physiological needs at minimum metabolic cost (Riisgard et al., 1993) (Riisgaard & Larsen, 1995). From a technical point of view, this is a self-optimizing system that adapts itself lifelong to environmental conditions like hydrodynamic forces, food availability and the concentration of sediment suspended in the water by means of restructuring.

Another widely used, but less obvious function of spicules is improved dispersal of larval stages and spermatocysts (seminal vesicles). Specialized spicules have been reported to affect the buoyancy of spongial stages, like the “gemmoscleres” (Figure 7g, right) that form a pneumatic layer around asexual reproduction vesicles (gemmules). These gemmules are only formed under unfavourable environmental conditions and therefore the increased buoyancy, conveyed by the pneumatic layer may increase the chance of survival for the species (Hartman, 1981). Another example are the hooked microscleres that accompany spermatocysts of *Asbestopluma hypogea* (Figure 7g,left), increasing their buoyancy and enhancing the chance of getting entangled with the long filaments of another individual of the same species (Uriz et al., 2003).

The spicules of *A. hypogea* first raised the interest of researchers for another, quite surprising reason. Different from virtually all other known sponges, these sponges cannot rely on filter-feeding because their habitat (certain caves and the deep sea) is extremely food-poor. In these environments macrophagy (feeding on macroscopic food items) is a better call (Gage & Tyler, 1992). As an adaptation to this requirement *A. hypogea* has developed filaments that bear hooked spicules to capture small crustaceans (Figure 7b) and accordingly facilitate a carnivorous lifestyle (Vacelet & Boury-Esnault, 1995).

A controversial issue is the role of spicules as deterrents of predators. Intuitively, it makes sense, for some spicules look quite menacing (cf. Figure 6c); yet keeping in mind length scales of predators like fish and turtles (cm) and the size of most spicules (µm) this effect may easily be circumvented (Wulff, 1994). Another problem for the sponge is that various organisms have developed special tools to overcome armours made of hard materials. And though spicules can be accumulated in the cortex of some sponges under attack (Hill & Hill, 2002), noxious chemicals, like triterpene glycosides (Kubanek et al., 2000) and alkylpyrrole sulfamates (Kicklighter et al., 2003) seem to be more effective at deterring predators like fishes.

A promising observation regarding a further role of skeletal elements in siliceous sponges has been made by Gaino and Sara (1994). They described for the first time the existence of photosynthetic organisms deep inside a demosponge (*Tethya seychellensis*). Close associations between sponges and many different microorganisms had been known previously (Sarà & Vacelet, 1973) (Wilkinson, 1980), but photosynthetic organisms had been thought to be confined to the outer tissues (Gaino & Sara, 1994) and the interior of sponges with very loose architecture that allow for the passage of light (Ruetzler, 1990). Therefore, the interior of compact sponges like *T. seychellensis* should have been prohibitive for photosynthetic organisms. Finding algae of the genus *Ostreobium* in this supposedly aphotic (dark) zone required an explanation. The hypothesis that “sponges could use spicules as a natural pipeline for light, a natural condition similar to modern fibre-optic systems” (Gaino & Sara, 1994) was a first milestone in our understanding of the intriguing optical properties of this biomaterial. However, this hypothesis has only recently been proven *in vivo* (Brümmer et al., 2008).

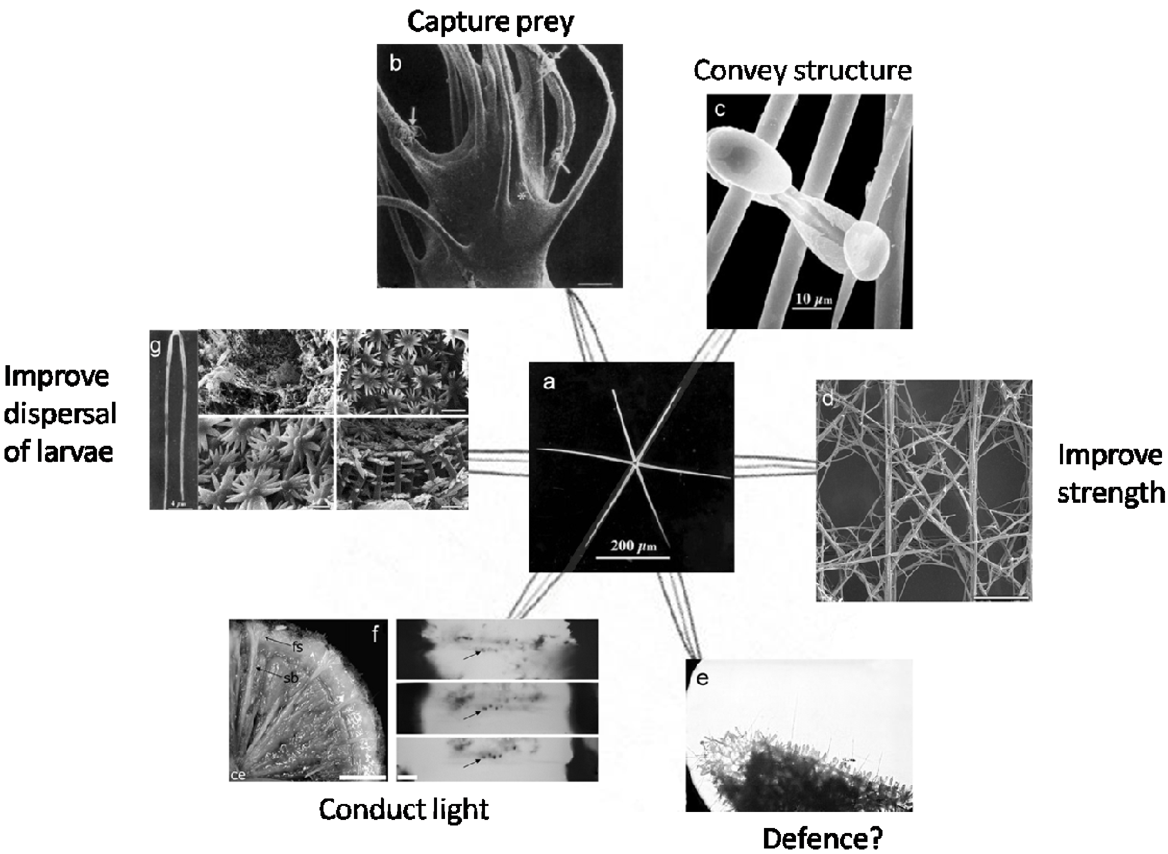


Figure 7 Spongial skeleton elements (a) are multifunctional. They serve various purposes; some are found all across the taxon of siliceous sponges, some are confined to few species. An extreme example are the hooked spicules of *Asbestopluma hypogea* (b) allowing the carnivorous sponge to passively trap shrimps ((Vacelet & Boury-Esnault, 1995). Like any hard skeleton, it allows for a programmed arrangement of cells within the body plan, provides structure and improved strength (b) and(c). Though spicules might not be appreciated by sponge-predators like sea-urchins (Ferguson & Davis, 2008), they seem to be effective only when backed by chemical defence mechanisms(Freeman & Gleason, 2011) (Pawlik et al., 1995). Light conduction via spicules is vital for demosponges that host photosynthetic symbionts (Brümmer et al., 2008), but has also been suggested to play a role in a non-ocular photosensory system (Müller et al., 2006a) (Müller et al., 2010) and in the light directed (phototactic) behaviour of sponge larvae (Leys et al., 2002). Certain larvae and spermatocysts bear spicules on their surfaces, which improve their buoyancy and allow for dispersal to distant areas (Hartman, 1981) (Trégouboff, 1942). Scale bars are 200 µm (a), 285 µm (b), 10 µm (c), 2 µm (d), 1 cm (f), 4 µm, 50 µm, 20 µm, 10µm, 20µm (g, from top left to bottom right) © by (Uriz et al., 2003) for (a), (c) and (g) (left part), (Vacelet & Boury-Esnault, 1995) (b), (Weaver et al., 2007) for (d), mareco.org for (e), (Brümmer et al., 2008) for (f), (Pisera & Sáez, 2003) for (g) (right part).

The demosponge *Tethya aurantium*, similarly to *T. seychellensis* hosts photosynthetic endosymbionts (microalgae). In a straightforward experiment, Brümmer and colleagues inserted photosensitive paper into the sponge and illuminated the sponge. Dark spots could subsequently be seen where the photosensitive paper had been in contact with the ends of spicule fascicles (Figure 7f). Thereby, strong evidence for the use of light transmitting properties by demosponges has been provided. Research on the optical properties of spicules has somewhat paradoxically been focused almost exclusively on hexactinellid sponges (Kulchin et al., 2009) (Aizenberg et al., 2004) (Sundar et al., 2003), but (cf. (Müller et al., 2009a) due to their larger size.

In demosponges, however, the light transmitting properties of spicules are allegedly involved in far more complex systems than simple guidance of light to “feed” symbionts: A photosensory system involving spicules has been proposed (Müller et al., 2010). Spicules do not transmit light with wavelengths shorter than 580 nm (Müller et al., 2010). In this context, it is interesting to observe some technical details relating to light reception. It was shown that in seawater light sources and light receivers are most efficiently coupled in a wavelength region far from the absorption- maximum of the receiver (D'Sa et al., 1999). Additionally, coupling of emitter and absorber can be tuned more sensibly and more efficiently at wavelengths far from the maxima of absorption and emission (Müller et al., 2010). Observing these principles the wavelength spectrum from 580 nm to 600 nm seems very well suited to be used for a sensitive photoreception system. Further hints to the importance of these wavelengths come from behavioural experiments: larvae of siliceous sponges react to light at 440 nm and 600 nm approx. (Leys et al., 2002). More recently, a luminescent system (luciferin/luciferase) that emits light in the range between 400 nm and 600 nm has been found in sponges (Müller et al., 2006a). Having found a cryptochrome-like protein (related to a photoreception protein in humans) in *Suberites domuncula,* Müller and colleagues (2010) felt confident to propose a sensory system based on three to four elements: Sunlight or the luminescent system as light sources, the spicular network as waveguides transmitting light, and cryptochrome as photoreceptor. It should be mentioned that this sensory systems would not be limited to sunlight as input, since luminescence can be triggered by various stimuli.

Hierarchical architecture and emerging properties

Principles

One of the highlight principles found in siliceous spicules is structural hierarchy. The benefits of hierarchical architecture have been recognized early on by engineers, although no general trend to more stratified structures in engineering seems to exist (Lakes, 1993). With respect to hierarchy, materials and structures can be classified starting with a continuum (order 0) to a simple structure (order 1). Real hierarchical architecture therefore can be considered to start at order 2, where the elements constituting a structured material show a discernible structure themselves at a smaller length scale. Accordingly, adding up the number of length-scales with a distinct structure indicates the hierarchical order of a material.

Lakes (1993) demonstrated that hierarchical architecture can yield remarkable increase in strength. Contrasting primary and secondary honeycomb structures, made of paper and glue, he found that the secondary structure (honeycombs cemented together to form a larger honeycomb) was 3.8 times more resistant to compression while the densities in both models were equal. This observation can easily be extended to other parameters related to strength and toughness. This can be exemplified by the strength-to-density ratio of a hierarchical foam that increases with hierarchical order (Figure 8b). Interestingly, one single mechanism has been proposed to be the most essential reason for hierarchical structuring in natural materials: deflect cracks that might threaten the integrity of a structure by opening up new surfaces, making it energetically unfavourable for the crack to travel (Currey, 2005). Other authors, however, see this as one among many mechanisms (Mayer, 2005) (see below).

Hierarchically structured materials in nature show many interesting properties that are related to phenomena at the nanoscale. Nano-crystalline materials (crystal size < 1 µm) are “superelastic” due to the large interface areas between individual crystals, i.e. they can deform significantly without fracturing. Furthermore, this conformation entails very short diffusion distances, making processes, like sintering, that require high temperatures in most materials possible at lower temperatures. (Lakes, 1993) In spicules of sponges, this process occurs at the temperature of the surrounding sea- or lake water (Müller et al., 2009b)(Wang et al., 2012c).

Equally due to the small length scale of the lowest hierarchical levels in biominerals, another crack-inhibiting effect arises. For most minerals, the Griffith criterion that accounts for crack-like flaws and localized stress concentration in the mineral structure governs failure (Griffith, 1921). However, below a certain mineral size, the so called Griffith length, failure is governed by the theoretical strength of a given material, i.e. the material is insensitive to pre-existing cracks or flaws. Since the theoretical failure criterion of a mineral is much higher than the Griffith criterion, it has been proposed that nano-scale of minerals in bio-composites is the result of selection for fracture strength and robustness (Gao et al., 2003).

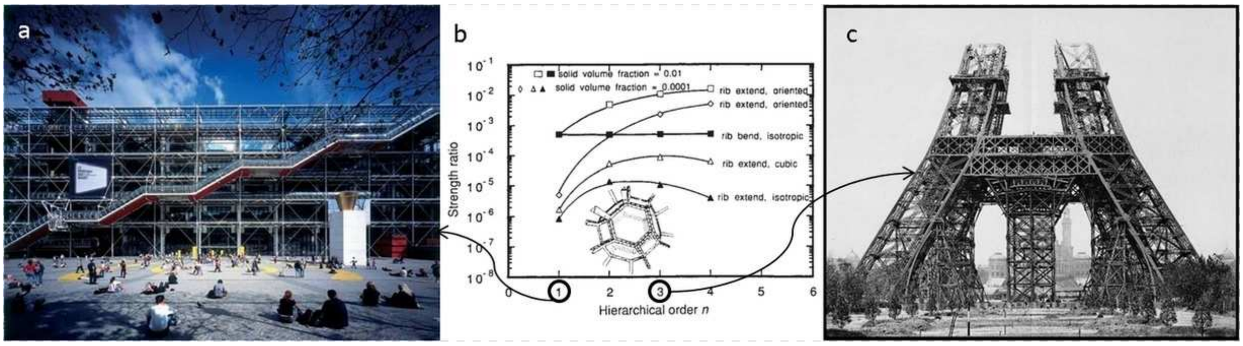


Figure 8: Hierarchical architecture. These two landmark buildings of Paris epitomize the benefits but also the practical difficulties when it comes to man-made hierarchical architecture. The Eiffel tower (c) has been erected 1887-89 and, at least according to Mandelbrot (1983), Gustave Eiffel perceived the advantage of building his most famous edifice as a third order hierarchical structure: its relative density is approximately fivefold lower than the first order hierarchical structure of far more modern buildings like the Pompidou Centre (a). Counterintuitive as this may seem, it might well be because practical reasons (cost of fabrication and maintenance) still outweigh the material savings (Lakes, 1993). (b) Strength of a structure rises with hierarchical order, explaining why nature has adopted this principle for virtually all biominerals; a trend that we might want to adopt for smarter engineering; be it in the building industry or in nanotechnology. © conservapedia.com (a) and (Lakes, 1993) (b)

Man-made vs. natural architecture

In man-made structures, hierarchical structure is not always intentional. The structure of the Eiffel Tower in Paris can be assigned hierarchy of level three (Figure 8c): the overall structure is composed of shorter diagonal and horizontal struts, which reveal their ordered inner life at a closer look.

Mandelbrot (1983) has suggested this hierarchical structure to be intended by the architect, as it conveys the same mechanical stability of a first order hierarchical structure (Figure 8a) at a mere 20% of its weight. Others, however, asserted more practical reasons why Eiffel might have opted to use short trusses, like the relative ease of construction (Harriss, 1975). Even if Eiffel had deliberately made use of the principle of hierarchy; in modern structural engineering it does not seem to find favour (Figure 8a). This is largely due to high cost of construction and maintenance (Lakes, 1993). Trivial as this reason might seem, it reflects a fundamental difference between natural and man-made construction. Vincent (2008) summarized this observation as follows:

“In materials-processing nature replaces the massive use of energy (for example high temperatures or harsh chemical reactions,) with the use of information (which equates with structure at all levels”

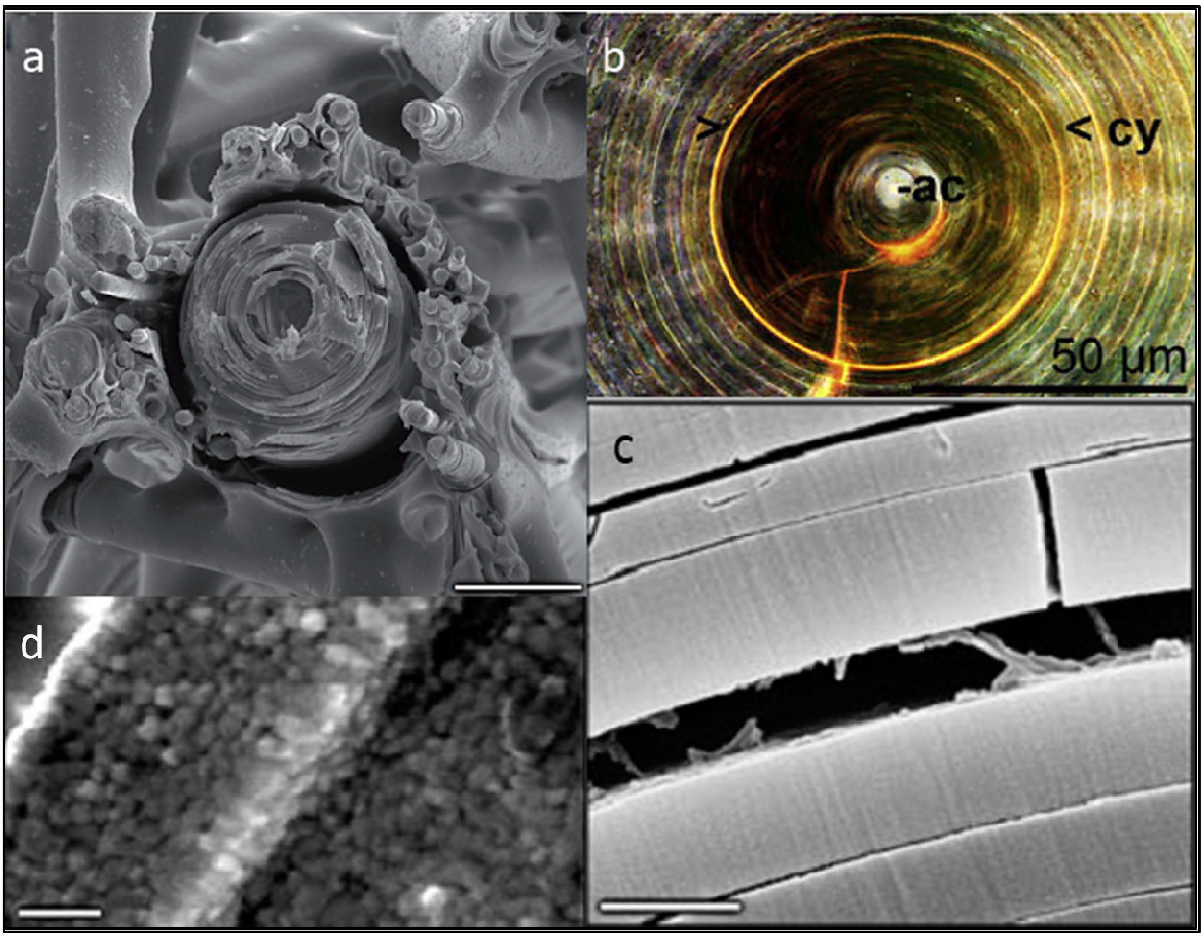


Figure 9: Levels of hierarchy in a hexactinellid sponge. (Aizenberg et al., 2005) (Müller et al., 2009b) (Weaver et al., 2007) Skeletons of siliceous sponges show high levels of hierarchy on the microscopic but frequently also on the macroscopic scale. Individual fibres are bundled in a glass matrix (a), while the individual fibres are composed of numerous concentric siphons (silica layers) (b). The individual siphons alternate with protein layers, gluing them together (c) and consist of consolidated glass nano-spheres (d). Scale bars are20 µm (a), 50 µm (b), 1 µm (c) and 500 nm (d). © by (Müller et al., 2009b) for (b),(Weaver et al., 2007) for (a), and (Aizenberg et al., 2005) for (c) and (d).

This principle accordingly is of paramount importance for technological applications where only a limited number of elements and materials are used (Gebeshuber et al., 2009). Gebeshuber and Gordon (2011) explored the relationship between structure, material and function for nano- and micro-electromechanical systems (MEMS). The properties of available materials for these systems are very limited; making the use of composite, hierarchically structured materials a promising approach for devices with more complex functionalities.

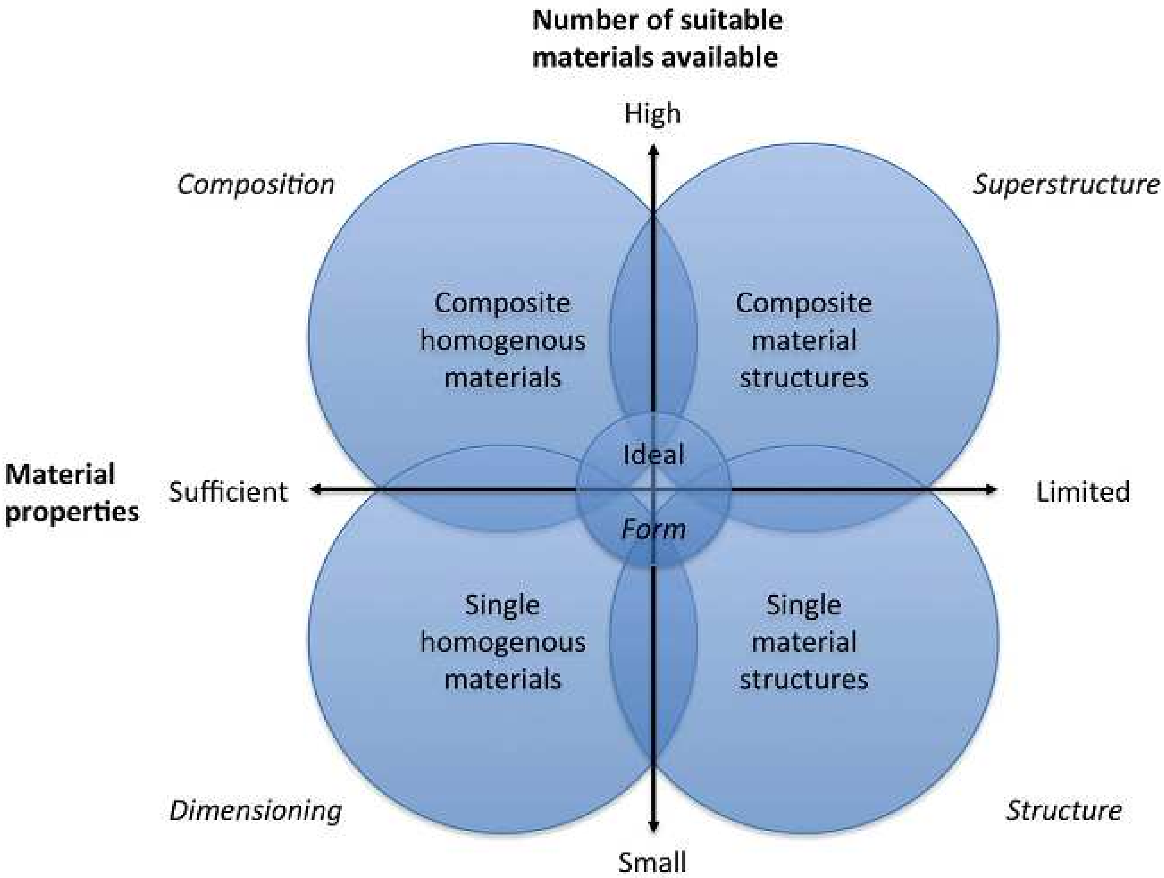


Figure 10: Structuring facilitates more complex functionalities. Current MEMS are mostly relying on the properties of single material structures. Since this approach limits the complexity of functions that MEMS, consisting of few elements, structuring the materials can replace the common technological approach of adding more, different materials to accommodate increased functionality.© by (Gebeshuber & Gordon, 2011)

It is indicative of the current state of our technology that it is cheaper to use more energy and material than to use more sophisticated and stratified structures ("information").

Hierarchical structuring clearly entails interesting mechanical consequences.

Opportunities emerge no less. Hierarchical structuring makes it possible to use very common materials that are inferior to commonly used building materials and yet yield very useful materials (Buehler & Yung, 2009). Not the high quality, not the high variety of building blocks used is the basis of functionality in natural materials. Rather, the used materials are tuned at different length scales independently (Vincent, 2008). Taken to an extreme, hierarchical structuring rescinds the importance of the constituents of functional materials and solely relies on the structuring of these almost arbitrary constituents (Buehler, 2010). Accordingly, the exceptional mechanical properties of the skeleton of *Euplectella aspergillum* would likely remain largely the same if silica were replaced by calcareous minerals like calcite, aragonite and apatite, if only the structuring remained the same (Aizenberg et al., 2005) (Currey, 2005).

Taking it to a higher level: structural hierarchy in *Euplectella aspergillum*

What exactly are the levels of hierarchy contributing to the mechanical properties of this "thick, somewhat clumsy, brown tube, perforated with irregular openings [that contains an] arrangement of support so delicate and symmetrical?" (J.E. Gray during the expedition on HMS Challenger 1872 (Thomson et al., 1887) (cf. Figure 6h). Not an easy question, considering that one single issue of *Science* already contains two differing answers (Aizenberg et al., 2005) (Currey, 2005). At the lowest level of hierarchy, consolidated SiO_2 – nanoparticles are arranged around the proteinaceous axial filament (Figure 9d). The silica-spheres constitute layers, also known as siphons or lamellae (Schröder et al., 2007) that alternate with considerably thinner organic interlayers (Figure 9b, c). On the third level, Individual spicules are bundled, yielding struts (Figure 9a).

At the fourth level, a square lattice with diagonal reinforcement elements can be distinguished with the naked eye (Figure 7d). Above that level, two (Currey, 2005) or three (Aizenberg et al., 2005) further structural have been identified. While Aizenberg and co-workers reported the siliceous matrix covering the bundles of spicules (level 4) as the next higher level of hierarchy, Currey opted in his analysis to include that feature in level 4. Level 5 according to Currey is the wrapping of this plain, 2D lattice into a curved cylinder, while the helical external ridges seen in Figure 6h represent the largest structural level. Aizenberg et al. in contrast, do not consider the wrapping of the planar sheet into a cylinder as a distinct structural level, but assign level 6 and 7 to the aforementioned helical ridges and the flexural anchoring of the entire skeleton to the sediment.

The benefits of the macroscopic structural levels are self-evident, reminding largely of man-made reinforced structures. Interesting details include the finding that the reinforcement of every other square in the lattice by a diagonal strut (level 4, Figure 7d) has been predicted as an optimum for the ratio of mass and metabolic effort (energy used) to stiffness (Deshpande et al., 2001). Strikingly, the diagonal, shear-stress reducing elements do not occur in every square but, just like expected for an optimized structure, in every other.

Diagonal struts are important factors of the skeletal stability, supporting torsional, bending and shear loads (Weaver et al., 2007).

The external helical ridges (level 6 according to Aizenberg et al.) have specifically been explained as structures avoiding the ovalization of the tube like skeleton. Deformation of the circular shape of the skeleton to an oval cross section would otherwise be a likely failure mechanism. The circular ridges prevent this, although at the cost of making failure due to torsion more likely, which is counteracted by helical ridges in opposite direction (Weaver et al., 2007). Epitomizing the benefit of differentially arranged structures at different length scales, the torsional strain can also be absorbed by the diagonal struts at level 4 (Currey, 2005) (Deshpande et al., 2001).

At the level of the individual spicules, the aforementioned crack arresting mechanism (Currey, 2005) is brought to bear. Since the organic interlayers between the silica layers are much weaker than these, any crack that might occur is arrested at the interlayers. Failure therefore is usually not due to one catastrophic event, but a series of crack nucleation, propagation over a single silica layer and arrest at the interlayer (Chai & Lawn, 2002) (Seshadri et al., 2002). Cracks are also prevented from penetrating deep inside the spicule by decreasing width of the silica-lamellae towards the periphery (Weaver et al., 2007). A revised, more detailed mechanism is presented by Johnson and co-workers (2010), see below).

At the ultrastructural level (nanoscale) individual silica spheres can be made visible by etching while usually each lamella appears as amorphous, bulk silica. Accordingly, an individual lamella is as brittle as normal glass and fractures yielding planar surfaces (Weaver et al., 2007) For the optical properties of silica spicules, Rayleigh scattering due to inhomogeneities is an important factor as it causes transmission losses. The presence of distinct nanospheres would increase the scattering, as at the boundary of every nanosphere the density fluctuates. Therefore, the high condensation to amorphous glass achieved here is probably essential for the optical qualities of spicules (Aizenberg et al., 2004).

Biomineralization

"*Biomineralization links soft organic tissues, which are compositionally akin to the atmosphere and oceans, with the hard materials of the solid Earth. It provides organism with skeletons and shells while they are alive, and when they die these are deposited as sediment*."

From the preamble of (Leadbeater & Riding, 1986)

Overview

Biomineralization shapes animate and inanimate nature alike. For a discussion of biomineralization, a short overview of mineralization in general is helpful.

The most basic mechanism is inorganic mineralization, a process that is usually endothermic and leads to the solidification of previously dissolved monomers like metals or salts of metals. Depending on the elements involved, crystalline or amorphous solids with well defined structure and chemical composition can result from inorganic mineralization.

Inorganic mineralization of silica in the ocean for example can lead to the formation of quartz crystals. As this process is endothermic, it only occurs where thermal energy is high enough (e.g. near black smokers) and commonly at high pressure. The building blocks in this case are usually monomers of orthosilicic acid that are dissolved in sea water (Müller et al., 2009c).

For biomineralization, Mann (1983) proposed a distinction between biologically induced and biologically controlled mechanisms. Even though the actual degree of control of the biomineralization process in different organisms certainly varies in much finer steps, this concept provides a first impression.

A typical process of biologically induced mineralization is the crystal growth on the surface of a cell, whose biological activity triggers the deposition of a mineral (bioseed). In this process, the organism can usually alter certain parameters of its direct environment (pH, concentration of CO_2, etc.) and thereby favour the formation of particular minerals. However, the organism has no means of directly governing the type and habit (mineral structure) of the precipitated mineral. Therefore minerals generated by processes of this class are usually quite heterogeneous, i.e. they contain different elements, and irregularly shaped. Importantly, the inorganic precursors are precipitated from a non-saturated solution into the mineral (Weiner & Dove, 2003) (Müller et al., 2009c).

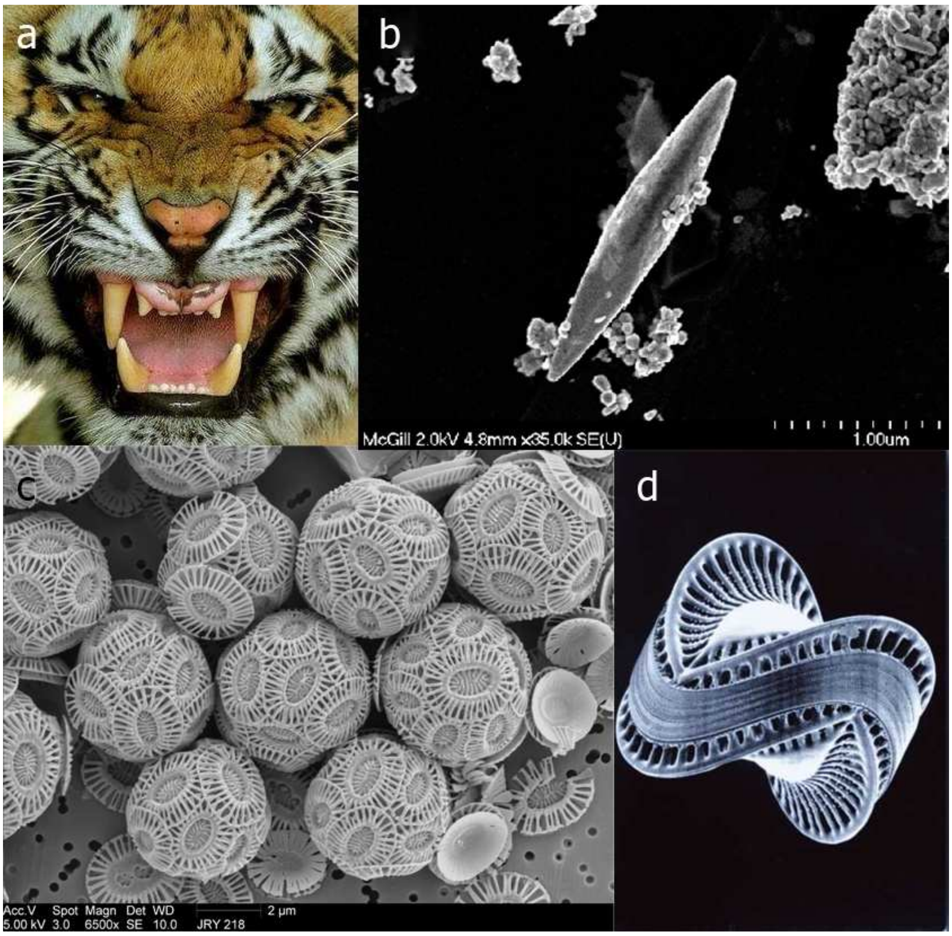


Figure 11: Biogenic minerals. Living organisms form mainly four different types of minerals: Calcium phosphate, like in bones and teeth of mammals (a), magnetite (b), calcium carbonate (c), and silica (d). (b)-(d) Representing the intricate structures of biominerals synthesized by microorganisms. Scale bars are: 100 µm (b), 2 µm (c), diameter of frustule: 15 µm approx. (d) © by thecynicaltendency.blogspot.com (a), (Schumann et al., 2008)(b), ulg.ac.be (c) alisha-smiles.blogspot.com (d)

In biologically controlled mineralization mechanisms, bioseeds and organic matrices exert a higher degree of control over the mineralization process. The formation of teeth and bones in mammals are examples of this mechanism. Organic molecules act as seeds for the initiation of mineralization, but also as scaffolds determining the morphology of the biominerals, and the velocity of the reaction. The organic scaffolding gets integrated into the biominerals, making biominerals composites with unusual combinations of mechanical properties (Lowenstam & Weiner, 1989) (Weiner & Dove, 2003) (Müller et al., 2009c). The organic fraction of these is decisive for some of the most remarkable features of biominerals, as highlighted for the toughness of nacre, e.g. in the abalone-shell (Smith et al., 1999).

Common biominerals

Biominerals are a highly diverse group of materials. More than 60 different biominerals have been identified, and together these show an astounding variety of morphologies, properties and functions (Nudelman & Sommerdijk, 2012). These have interested material scientists for many decades now, especially since their mechanical properties often are in striking contrast to geological and synthetic minerals. Mainly, these properties emerge from the unparalleled combination of high precision and adaptability that natural organisms show when lying down these complex structures (Lowenstam & Weiner, 1989).

In humans, like in all vertebrates and many more species, calcium phosphate is used as the mineral component of teeth and bones (Figure 11a). Bones consist of a nanocomposite with hydroxyapatite-crystals embedded in collagen fibres at the ultrastructural level (hydrated calcium phosphate) (Weiner & Wagner, 1998). Like sponge spicules, bones are also a highly hierarchical material with mechanical properties depending on features of the different length scales (Rho et al., 1998). Two salient features of mammalian bones are the high organic content, as compared to other mineralized skeletons, that conveys a remarkable toughness and the orientation of internal struts depending on the direction of loads in trabecular bone (Currey, 2005).

Another common class of biominerals, especially amongst microorganisms are ferrous biominerals like magnetite (Figure 11b). Certain aquatic bacteria use nanoparticulate magnetite (Fe_3O_4) for orientation, using the effect geomagnetic field lines have on magnetite (Faivre & Schüler, 2008). These magnetotactic bacteria do not travel very far usually, but since they “live at low Reynolds numbers” they cannot tell up from down in the water column and therefore rely on additional cues to dwell at the depth that suits them best (Gebeshuber et al., 2012).

Functions of magnetite and other iron biominerals include also structural roles, such as in the hardening of teeth and the stretching of tissues. Sometimes they also seem to be simply storage deposits for iron that is e.g. required in ionized form for catalytic purposes (Lowenstam & Weiner, 1989).

Calcium carbonate ($CaCO_3$) based biominerals are the most abundant exponents of this class of materials. Calcareous skeletons are ubiquitous in organisms of the oceans and fresh water bodies, including sea urchins, corals, calcareous sponges and many more. Various types of hydrated and un-hydrated calcium carbonate crystal conformations are known, including the aragonite as found in nacre (see below). As with other biominerals, functionally this group of biominerals is diverse: Sensing gravity in land animals, receiving light in marine brittlestars (Aizenberg et al., 2001) and structuring of corals are just a few examples (Lowenstam & Weiner, 1989) (Nudelman & Sommerdijk, 2012).

Biomineralization of silica is another vast field that has attracted lots of research, not least because silicon technology is essential for communications and computers. Most of the silica that is biomineralized in the ocean, but also in fresh water comes from single celled algae – diatoms and radiolarians (Lowenstam & Weiner, 1989). Interestingly, also various animals can mineralize silica, as well as higher plants. Within the kingdom of animals, the use of silica for structural support is confined to siliceous sponges (Gray, 1825).

Silica in diatoms

Diatoms, especially their intricate shells or frustules have been investigated for more than two centuries. Nowadays, potential applications in nanotechnology (Gebeshuber, 2007a), large–scale production of micro electro-mechanical systems (MEMS) (Saliterman, 2006) (Gordon et al., 2009) or about any field of structural engineering (Sterrenburg, 2005) are important incentives for research on diatoms. On the level of basic science, diatoms offer a chance to close the gap between genotype and phenotype, i.e. researchers hope to be able to show the exact correlation between the 1D structure of DNA and the (at least) 3D chemistry and physics of the appearance of the organism (Gordon et al., 2009).

In earlier days, pioneering (amateur) researchers in that field had presumably a somewhat different motivation:

Figure 12 Array of diatoms. These unicellular algae are known for their seemingly infinite variety of different frustules (shells) made of amorphous silica. Researchers hope to learn about the interdependence between of genotype and phenotype, i.e. how a one-dimensional code connects to the multiple dimensions of a phenotype (Armbrust et al., 2004) (Gordon, 1999). In this context it is interesting to determine how closely the biomineralization of the highly ordered frustules is govern*ed by g*enetic control (Brzezinski, 2008)(Sumper & Brunner, 2008). The array is 1.78 x 2.30 mm. © by (Gordon et al., 2009)

Diatoms look really nice (cf. Figure 12). It is indeed very likely that their aesthetic appearance, due to the now extensively studied phenomenon of iridescence (Parker &

Townley, 2007) (Bertheier, 2007) and their intricate structure, has spawned much of the early (and possibly, ongoing) research (Gordon et al., 2009). Frustules have attracted research for their tribological properties, namely their sub-micrometer hinges and interlocking devices as well as their "waterproof" adhesives (Gebeshuber, 2007a) (Gebeshuber & Crawford, 2006). Mechanisms that diatoms use to attach to each other offer great potential for bioinspired applications, e.g. because they allow relative movement of the algae without detachment (Ussing et al., 2005). This led Gebeshuber and Gordon (2011) to propose a variety of best practice mechanisms derived from diatoms for implementation in MEMS. Lessons can be learned for dynamic, mechanical, structure-and surface related problems, leading to MEMS with increased functionality and better durability.

Gordon and co-workers (2009) suggested a five-step mechanism that can be used for the description of silica biomineralization in diatoms:

(i) formation of silica nanospheres with Ø 30-50 nm

(ii) transport of silica spheres inside specialized membrane bound vesicles to the edges of the flat silicalemma (SL, another membrane-bound vesicle) and release into the SL

(iii) growth of a flat, one layer of silica spheres thick disc starting at a central nucleation centre

(iv) pore formation

(v) thickening and sometimes pattern formation in 3D

In an effort to synthesize artificial nacre, a step-by-step description was a key factor for the very successful biomimetic approach (Finnemore et al., 2012) (cf. Figure 21). This description should, in contrast to this suggestion, be in the "language" of technically feasible synthesis steps. The role of the silicalemma e.g. should be abstracted to invite the use of technically available tensegrity structures on this length scale.

Spiculogenesis

Overview

Spiculogenesis is a rather special case of biologically controlled biomineralization. It was largely enigmatic how the highly ordered structure of sponge spicules originated, until Cha and colleagues (1999) demonstrated *in vitro* that an enzyme directed the polymerization of silica. The organic filament in the core of sponge spicules had long been known, yet only in 1998 it was found that it contained an enzyme, that has been termed silicatein (*silica* pro*tein*) (Shimizu et al., 1998). The arising mechanism has been termed *enzymatically controlled and driven biomineralization* (Morse, 1999) (Müller et al., 2007a). During this catalytic process, the filament containing silicatein serves as a scaffold directing the formation of the polysilicate (Müller et al., 2008b).

Subsequently more proteins that are involved in spiculogenesis have been identified. Apart from identifying various sub-types of silicatein (silicatein α-γ) that are specific for different species of demosponges (Müller et al., 2007c), the first silicatein of hexactinellids has been reported (Müller et al., 2008a). This hexactinellid silicatein has a high structural similarity to demospongial silicateins, corroborating the idea that the mechanisms involved in early spiculogenesis of both classes of siliceous sponges are similar.

Another class of functional proteins has been identified in the axial filament of spicules (Wiens et al., 2009) (Wiens et al., 2011). Silicatein interacting proteins (silintaphins) have been reported to convey elasticity to the spicule during spiculogenesis and to be involved in defining the morphology of spicules (Müller et al., 2009c).

A third class of proteins in the axial filaments are the catabolic (degrading) silicases, first identified in the demosponge *Suberites domuncula* (Schröder et al., 2003). Silicases are assumed to be involved in the deposition of silica, yet their exact functions remain elusive (Wang et al., 2012b).

The underlying mechanism of the silicatein reaction has been revised since its first description by Cha and colleagues (1999) (see above) and now accounts for the roles of silintaphins, various forms of silicateins and silicases (Schröder et al., 2010) (cf. Figure 13f for a reaction mechanism with a synthetic analogue of silicic acid).

Recently, various reviews have summarized the steps involved in spiculogenesis (Wang et al., 2012c) (Wang et al., 2012b) (Müller et al., 2009c) focussing on different processes suggested for bioprospecting (Wang et al., 2011a) (Hayden, 2003), including biomimetic and biotechnological perspectives. Three major stages have been proposed by Müller and colleagues (2009c):

(i) Intracellular phase (initial growth)
(ii) Extracellular phase (consecutive appositional growth)
(iii) Extracellular phase (final morphogenesis)

It is essential to recognize that spiculogenesis, like other types of biologically controlled biomineralization, takes place at near neutral pH (6-8), ambient temperature and pressure (Cha et al., 1999).

This process is quite fast, and accordingly difficult to observe in adult sponges. At an ambient temperature of 21°C for example the synthesis of a spicule with a diameter of 6-8 µm and a length of 190 µm is completed after 40 hours (Weissenfels, 1984). Therefore, much of the evidence here has first been gained *in vitro,* as is common in molecular biology. A novel technique, however, was the introduction of a 3D cell culture, the so-called primmorphs that allow experiments in a near-natural environment. These primmorphs consist of pluripotent stem cells (cells that can differentiate to become any cell type) and the spicule forming sclerocytes of the demosponge *Suberites domuncula* (Imsiecke et al., 1995) (Custodio et al., 1998). Since these cell cultures, like the actual sponge they are derived from, mainly form monactinal, straight megascleres (Müller et al., 2005), much of the present knowledge summarized here specifically holds for this type of spicules.

Initial growth

Silicon is present in seawater at low concentrations (≤10 µM), mainly in the form of orthosilicic acid ($Si(OH)_4$) (Fröhlich & Barthel, 1997). In *Suberites domuncula,* Schröder and co-workers (2004) found a transport protein that mediates the import of $Si(OH)_4$ into specialized cells (Figure 13a). This ability to extract silica from aqueous media with very low concentrations distinguishes the biomineralization in sponges from all other silica mineralizing organisms, like diatoms, that rely on super-saturated concentrations of silica in their environment (Inagaki et al., 2003). Inside the cells (sclerocytes) silica is accumulated in membrane-bound vesicles (silicasomes) where the initial phase of spicule synthesis occurs.

In parallel, the proteins yielding the axial filament are synthesized, processed and imported into silicasomes. Within these vesicles, silicateins, silintaphins and silicases assemble into the axial filaments. For the self-assembly of the silicateins into oligomers (Figure 13b-d) a fractal mechanism has been proposed (Murr & Morse, 2005). The silicasomes are associated with filaments that likely direct them towards the cellular membrane and are crucial for the extrusion of the immature spicule into the extracellular matrix later on (Wang et al., 2011c).

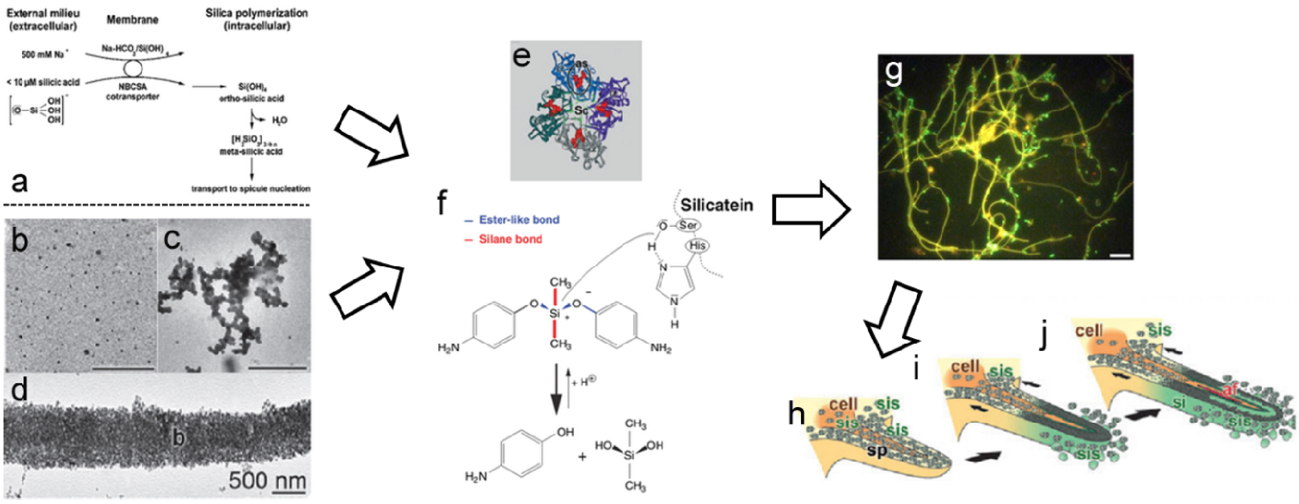


Figure 13: The first steps of spiculogenesis occur within specialized cells (sclerocytes). The intracellular portion of the biosynthesis of spicules in hexactinellids and demosponges is very similar (Müller et al., 2007a) (Wang et al., 2012b) (Wang et al., 2012c). (a) Silica is transported actively into the cell, presumably in the form of ortho-silicic acid and enriched intracellularly (Schröder et al., 2004). (b-d) At the same time the enzyme silicatein (and other proteins) self-assemble to form an organic filament within vesicles called silicasomes (Murr & Morse, 2005). The micrographs show an *in vitro* experiment of self-assembling silicatein /silintaphin solutions after incubating for 1 (b), 30 (c) and 240 (d) minutes (Müller et al., 2007b). (g,f) Silicatein catalyzes bio-mineralization of silica onto the filament cleaving the bonds of silicic acid (or an analogue, cf. f) (Müller et al., 2005) (Müller et al., 2008a). (g) Fluorescence micrograph, silica clusters (green) are deposited on (artificial) axial filaments *in vitro*. (h-j) New spicules are built in evaginations of sclerocytes, where multiple silicasomes (sis) provide building material for the deposition of mineralized silica onto the axial filament (af) (Wang et al., 2012b) Scale bars are 500 nm (b-d), 10 µm (g) © by (Müller et al., 2008a) for (a, f), (Schlossmacher et al., 2011) for (b-d), (Wang et al., 2012b) for (e, h-j), (Müller et al., 2005) for (g)

Silicatein is active as a homotetramer, i.e., in the form of four equal subunits that self-assemble in a determined way (Figure 13e). In this form, silicateins assemble silica in a three step mechanism. The first two steps catalyze the di-/ trimerization of silicic acid in a nucleophilic substitution reaction, i.e., two and later three silicic acid molecules are bonded together. The third step consists in the cyclization of the trimer. Since this reaction pathway involves hydrolysis steps, water molecules, which are cleaved off the initial building blocks (silicic acid), are released. These water molecules have to be removed during a maturation process (see below).

How the circular silica trimers synthesized in this reaction further proceed (polycondensation, linking individual trimers) is less well known, but silintaphins are believed to guide the assembly in silica into nanospheres (Schröder et al., 2010) (Wang et al., 2012b).

This mechanism allows for the deposition of silica beads onto the filament within the silicalemma of sclerocytes. Using the common precursor tetraethoxysilane (TEOS) as an analogue of the naturally used silicic acid, the deposition of silica beads onto silicatein-containing filaments could be observed (Figure 13g) (Müller et al., 2005).

Appositional and axial growth

At the beginning of the second stage, the primordial spicule is extruded to the extracellular space. Interestingly, the spicules then re-attach to a sclerocyte and remain in close association throughout axial and appositional growth (Wang et al., 2011c). In a remarkable form of contact between spicule and the sclerocytes, the cell evaginates (protrudes) into the axial canal of the becoming spicule (Figure 14a-f). As can be seen in Figure 14b and f, the evaginations of the cell do not extend all the way to the closed apex of the axial canal (Figure 14c). At the boundary between intracellular space (ics/cp) and extracellular space (ecs), the release of silicasomes (sis) from the evaginations can be observed. These provide the building blocks, silicateins and silica for the intra-spicular biosilica deposition. By this process, the innermost silica-structure surrounding the axial filament (the mantel) is synthesized and the diameter of the avail canal decreases (Wang et al., 2011c). Since the apex of the axial canal is closed, longitudinal growth can only occur at the open, basal end of the axial canal, where the evagination of the sclerocyte enters (Wang et al., 2012b). Observing the underlying mechanism of the evagination, it becomes evident that hydrodynamic forces push the cell membrane outwards into the spicular axial canal. These forces gradually displace the spicule outwards while in the growth region (gr, Figure 14a,d) at the sclerocyte cell-body more silica is laid down. In effect, the elongation of the spicule is driven by intracellular hydrodynamic forces (Wang et al., 2012b). This principle of flow-induced formation of biosilica structures has been used in a biomimetic approach (Wang et al., 2012a).

In the Giant Basal Spicules of the glass sponge *Monorhaphis chuni* that attracted a lot for interest for their remarkable optical and mechanical properties as well as their sheer dimension, several peculiarities have been found. Especially during the later stages of appositional growth, the deposition of the surface layers, deviations from the mechanism outlined above have been observed (Wang et al., 2011d) (Wang et al., 2009) (Wang et al., 2011a). During this stage, cells (or fragments of syncytia) are present in small depressions on the surface of the spicules. These cells are involved in the deposition of silica in astoundingly regular, circular ribbons on the surface of the spicule. After synthesis of these ribbons, the silification proceeds and yields a smooth surface, while the sclerocytes remain attached on the surface and are "recycled" for the next round of lamellar (ribbon-shaped) silica deposition. This mechanism lays down a type of biosilica that chemically, mechanically and optically differs from the type found more centrally. A higher concentration of mono- and divalent cations (Na^{+}, Mg^{2+}, Ca^{2+} and Mn^{2+}) is found in the surface lamellae. Mechanically a higher concentration of these ions makes glass less hard (Wiederhorn, 1969) (Wang et al., 2011d). Additionally, these ions are desirable dopants for optical fibres since they increase the refractive index and thus improve the waveguide properties (Sundar et al., 2003) (Aizenberg et al., 2004).

On the outer surface of the spicule that is exposed to the extracellular space (mesohyl) a very similar process takes place (Wang et al., 2011b). According to Schröder and colleagues (2006), extra-spicular biosilica deposition is mediated by a string composed of silicatein and galectin. Silicatein is provided by sclerocytes that closely surround the spicule and forms filaments together with the most abundant protein in the mesohyl – galectin – in a calcium-dependent process. These filaments are arranged in a proteinaceous framework around the spicule (Figure 14h, i). Collagen has been suggested to act in concert with the galectin/silicatein fibres to establish the framework. Unlike silicatein, however, collagen is not involved in the catalysis of silica deposition and does not form part of the eventual structure of the spicules (Wang et al., 2012b). The arising framework serves as catalyser and template for the biomineralization of silica on both its surfaces (centripetal and centrifugal).

On top of the newly formed silica layer on the external (centrifugal) surface a new, identical proteinaceous framework is laid down, initiating the next cycle of silica deposition (Schröder et al., 2006). The iteration of this process yields a layered structure (Figure 15a) that is characteristic for hexactinellid spicules (Schulze, 1887), but has also been found in demospongial spicules (Müller et al., 2006b).

Final morphogenesis

To achieve the mechanical qualities that are commonly recognized for silica spicules a maturation step after the termination of the silicatein driven polycondensation is needed. If this step is inhibited, spicules are not hard, smooth rods (Uriz, 2006), (Figure 15h,i) but porous and fragile rods with irregular silica-bumps on their surfaces (Figure 15d,e). The basic difference between the two types of spicules depicted here is that the porous one (Figure 15d,e) consists of hydrated silica while the smooth spicule (Figure 15h,i) has released water during a condensation reaction.

This striking difference has been shown in an experiment with primmorphs that could not express (build) the water-specific membrane channel aquaporin sufficiently (inhibition by manganese sulphate) (Müller et al., 2011). Thus aquaporins seem to be essential for the controlled removal of water, which in turn allows the hardening of the spicules. This extrusion of water is referred to as syneresis, a mechanism also commonly used in technical sol-gel processes (Brinker & Scherer, 1990).

Syneresis in spiculogenesis also depends on a proteinaceous gel, mainly consisting of galectin that surrounds the spicule (Müller et al., 1997). Water extruded from the spicule is trapped in this gel-matrix and subsequently imported into “wandering cells”. These are highly mobile thanks to the structure of the galectin matrix and can transport water away from the spicules. Thus, they maintain an electrochemical gradient that makes syneresis feasible. In their absence water would accumulate around spicules rendering the extrusion of more water unfavourable (Wang et al., 2012b) (Wang et al., 2012c).

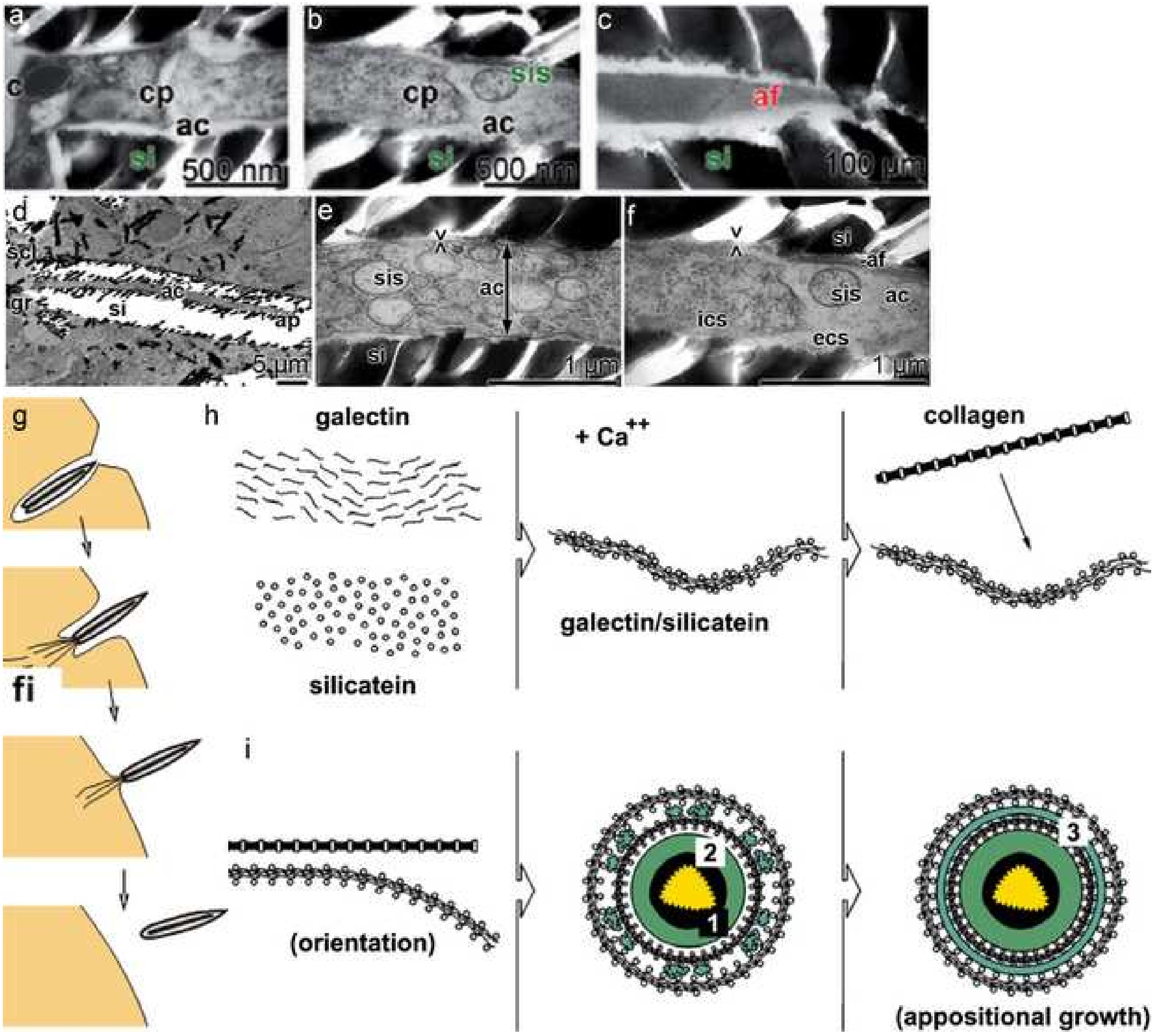


Figure 14: Axial and appositional growth of spicules.-At the verge between intra- and extracellular space, sponge spicules grow longitudinally (a-f) and, with a slight delay, they start to thicken by appositional growth (h,i) (Schröder et al., 2006). (a) Within evaginations of cells ("c") growing spicules can be found. Cellular protrusions (cp) reach into the axial canal (ac) of growing spicules (si) and contribute to the deposition of silica there by releasing silicasomes (sis) (e and f) (Wang et al., 2012b). (b and f) Inside the axial canal (ac) the boundary of pt marks the limit between intracellular (ics) and extracellular space (ecs). (c) The axial filament (af) extends from this boundary to the apex of the axial canal. (d) At the apex (ap) the axial canal is closed, while the growth region (gr) is adjacent to the sclerocyte (scl). (g) The aforementioned process takes place while the spicule is being released but still remains associated with the cell. (h) A mechanism has been proposed for the radial growth of demosponges (Schröder et al., 2006). Filaments made of the enzymes silicatein and galectin form in a Ca-dependent process, align with collagen fibres, wrap around immature spicules and serve as a scaffold and catalyser for deposition of biosilica layers. © by (Wang et al., 2012b) for (a-c), (Wang et al., 2011c) for (d-f), (Müller et al., 2005) for (g), (Schröder et al., 2006) for (h)

During this process the diameter of spicules decreases considerably. This can easily be understood using the concept of "van der Waals surfaces". These surfaces represent a physical model that indicates how densely molecules can be packed. For hydrated silica, i.e.

before syneresis, a space-filling arrangement of 30 silica monomers occupies 30% more space than a condensated arrangement of the same molecules after syneresis (cf. Figure 15c vs. g). Through the mechanism exemplified here, the diameter has been found to decrease from 10 µm in a developing spicule (Figure 15b) to only 2-3 µm in a mature, polycondensated spicule (Figure 15f) (Schröder et al., 2006) (Müller et al., 2006b). Compared to the rapid synthesis (steps i and ii) the maturation of spicules is far slower.

Interestingly this exact mechanism is also likely causing more complex shapes in spicules. It has been proposed that bending of spicules can be induced by apposition of a cell to the spicule. This would trigger the increased removal of water from that area as outlined above and thus locally reduce the volume of silica. Since the volume on the side of the spicule not attached to the cell remains constant, the spicule bends towards the direction where the cell resides (Wang et al., 2012b).

Even the rendering of complex shapes and ornaments found in many spicules may well depend on localized removal of water. Examples in hexactinellid spicules include the spikes found on some megascleres (Figure 6c). In demosponges, this might well be exemplified by the spiny, curved isochela microscleres of the genus *Guitarra* (Figure 6a). The process of forming these ornaments is not only of interest because of their biological (and aesthetical) value, but also because it has been found that light guided through a spicule is out-coupled via spines (Aizenberg et al., 2004). Thus, spines serve as illumination points and might be taken into consideration for biomimetic applications where localized release of light from a waveguide is desired.

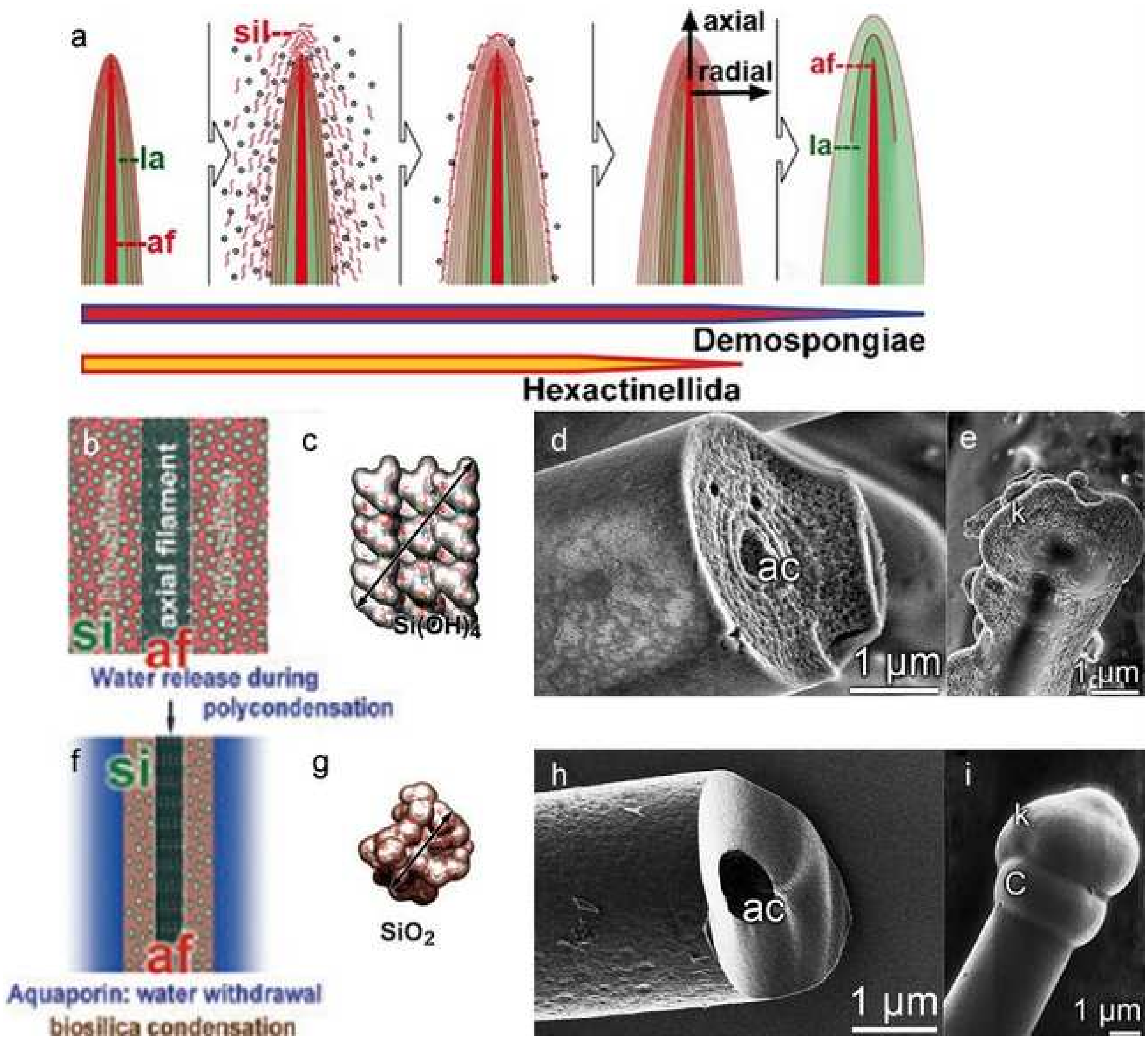


Figure 15: Extracellular phase of spicule formation with a focus on syneresis (withdrawal of water) from immature spicules. (a) After extruding spicules to the extracellular space, axial and radial growth continues as described in Figure 14. More layers (la) of silica are deposited alternately with organic sheets made of silicatein and galectin. These usually remain distinct in Hexactinellida and biosinter together in Demospongiae. After the fast process leading to the layered structure of spicules, a slower maturation-process occurs that is essential for the mechanical properties of spicules, including their surprising hardness and strength (Lakes, 1993) (Uriz, 2006) (Wang et al., 2012b). (b,f) During the condensation of spicules, that lead to decrease of the diameter by 70-80%, water is released through specific channels (aquaporins). Contrasting the van-der-Waals surface of hydrated (c) and condensed (g) silica explains the shrinking diameter during syneresis. In vitro experiments with 3D cell cultures (primmorphs) revealed that spicules are porous and less strong when syneresis is inhibited. (e,f) Spicules grown in primmorphs lacking aquaporins could not develop normally and showed irregular silica-deposits on their surfaces as well as a spongy texture. (h,i) Spicules from a control experiment, where syneresis could occur, show a smooth surface with well-defined knobs (k) and collars (c) at their apices (Müller et al., 2011). © by (Müller et al., 2009c) for (a), (Wang et al., 2012b) for (b,c,f, and g), (Müller et al., 2011) for (d,e,h and i)

Opportunities in Biomimetics

The teachings that we can derive from sponge spicules are diverse. And it does not seem to matter how close we keep to the original structure or how far we get away from it. We can in fact make use of the spicule itself as it occurs in nature, though this would of course not classify as biomimetics. Therefore, let it suffice to say that a shift to the "next higher level" above biomimetics, to bioprospecting[1] (Wang et al., 2011a) would effectively multiply the opportunities we can find in sponge spicules. Interesting hints to the direct utilization of sponge spicules abound, e.g., for the use in optical-electronic instruments that would benefit from the fluorescence properties of spicules (Kulchin et al., 2007) or earlier, in pre-Columbian South America, as well as in Neolithic and Iron Age cultures of Sub-Saharan Africa, when people used sponge spicules to reinforce pottery (Costa et al., 2004) (Mcintosh & MacDonald, 1989). Considering that sponge spicules are an abundant biomaterial that can easily be collected with the risk of biopiracy being minimal (for nobody owns the ground of the ocean) a revival of spicules in modern composites might be a way to cheap, sustainable materials.

On the other side of the spectrum, general principles alluded to in the previous chapters, like self-assembly, hierarchical architecture (Lakes, 1993) (Fratzl & Guille, 2012), or the benefits of nano-structured materials (Currey, 2005) (Buehler, 2010) can be studied in sponge spicules. One approach inherent to all biological structures is the bottom-up approach of (controlled) self-assembly, as can also be observed in spiculogenesis. This process of growing – rather than being fabricated – allows for a superb dynamic adaptability that is not usually found in man-made technology, among other benefits (Jeronimidis, 2000) (Fratzl, 2007).

Some of these concepts offer far-reaching opportunities. We might learn from nature how to use cheap, common base materials (Buehler, 2010) that limit our dependence on expensive elements. In the light of the potential for geopolitical conflicts that arise because

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[1] The term bioprospecting can loosely be defined as the translation of discoveries in biology and related fields into products or processes. According to this definition it would be a useful umbrella-term, including the biomimetic approach but also refer to the direct utilization of natural structures, materials and compounds. Unfortunately this term is widely disregarded by researchers, probably because the term also serves as a euphemism for biopiracy (Hayden, 2003).

of rare earths (Zajec, 2010) or any mineral resource (Rekacewicz, 2009), these considerations go far beyond material sciences. Apart from these implications, this approach might also help to make our technology "greener". Reducing our dependence on specific materials and focussing on structures instead opens up possibilities for better MEMS and better control of tribological properties (Gebeshuber & Gordon, 2011). These advances in nanotribology would be an important contribution to a greener technology, helping us to address energy-related global challenges (Gebeshuber, 2012a) (Gebeshuber, 2012b).

In this chapter, however, the focus will be on materials that are inspired by the sponge spicules in a more direct way, i.e. where the observed principles have been abstracted to a lesser extent prior to their implementation. These applications obviously rely nonetheless on the aforementioned general principles. Additionally the light transmitting and waveguide properties of sponge spicules are very important.

Concepts learned from spicules

Research on sponge spicules has recently been driven by expectancies for useful applications in nanotechnology. A major contributor to the knowledge about spicules and especially spiculogenesis is the German-Chinese Joint Lab Nano-Bio-Materials and the researchers at the affiliated institutions (National Research Center for Geoanalysis, Chinese Academy of Geological Sciences, Beijing, Tsinghua University Beijing, Johannes Gutenberg-Universität Mainz and others). They primarily focus on the development of intelligent nanomedical biomaterials, e.g. for bone replacement to help patients suffering from fractures or osteoporosis (Uni Mainz, 2011). In fact, nanotechnological materials for bone replacement have been proposed by the researchers (Schröder et al., 2005) (Schröder et al., 2007) (Müller et al., 2009c).

Another line of research has been pursued in Russia, where researchers took particular interest in the optical, fluorescent and photonic properties of sponge spicules (Kulchin, 2011) (Kulchin et al., 2009) (Kulchin et al., 2008). They conclude that the non-linear optical properties that arise because of the composite structure of silica and protein in spicules hold great potential for applications in photonics. Non-linear optical behaviour can be detected by using very short (~10 nanoseconds) laser pulses and observing the fluorescent response at different light pulse intensities. The strong nonlinearity in sponge spicules has specifically been attributed to the high concentration of irregularly interspersed organic compounds in the spicules (Maslov et al., 2006). A promising result here is the fabrication of artificial nanocomposites by a sol-gel process that mimics these distinct nonlinear optical features of spicules (Kulchin, 2011). In a very interesting contribution, Voznesenskii and colleagues (2010) reported the transmission spectra for spicules of three different species of glass sponges (Hexactinallida). These spectra seem to differ from the ones reported for the Giant Basal Spicule of *Monorhaphis chuni* (GBS) (Müller et al., 2009a) and the stalk spicules of *Hyalonema sieboldi* (Müller et al., 2006a) in their cut-off. While the two latter spicule-types share a similar short-wavelength limit at 600 nm approx. (between red and orange light), the spicules tested by Voznesenskii and colleagues (2010) transmitted the entire visible spectrum and near infrared (400-1400 nm approx). These transmission properties have been preserved in a biomimetic nanocomposite synthesized by Kulchin and co-workers (2011).

Unfortunately, experimental differences seem to be the main reason for the difference in observed properties. In the protocol of Voznesenskii and colleagues (2010) also scattered light was registered, while in the previous experiments only transmitted light was regarded. The authors accordingly conclude that in the 3 different species investigated, transmission spectra are in agreement with previously published results. They did, however, observe that the preferentially guided wavelength (resonance) of a spicule varied with layer thickness. Obviously, this finding is interesting for the transmission of light for illumination purposes and suggests that the transmission properties of biomimetic waveguides can be tuned to transmit only specific wavelengths by altering the exact structure of the waveguide.

Returning to the advanced optical properties of sponge spicules, various applications have been envisaged. The regularly spaced silica/organic layer structure that entails photonic bandgaps, allows to consider spicules as one dimensional photonic crystals (Kulchin et al., 2007). The aforementioned nonlinear dependence of fluorescence on the input energy opens up the possibility to devise optical-electronic devices (Kulchin et al., 2007) (Kulchin, 2011).

Optical diodes that become possible based on the Bragg light propagation regime in spicules (Kulchin et al., 2009) could become very interesting for optical computing. Optical computing relies on all optical chips (opposed to conventional computer chips with electrons in semiconductors). Photons are superior to electrons as carriers of information in a number of ways, e.g., their higher speed and lower losses during transmission. However, to really build those chips devices like optical diodes need to be available (Ozin & Hall, 2003).

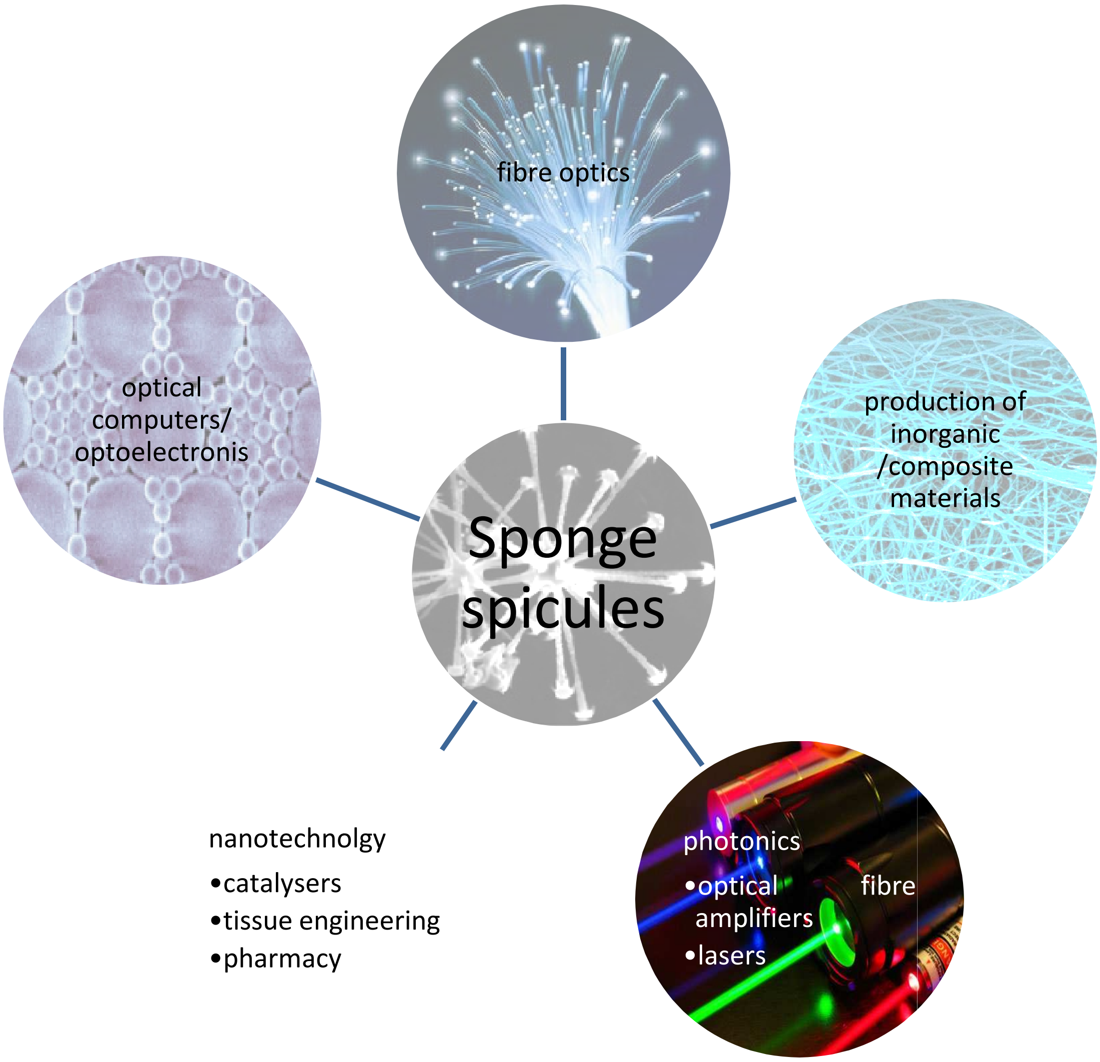

Figure 16 Sponge spicules offer inspiration for a variety of technological domains. As highlighted by (Müller and co-workers (2007a) and Kulchin and co-workers (2009), telecommunication fibres made of fused silica play an ever increasing role in our lives. Therefore, elucidating the secrets of organisms that have 700 million years more of experience in silica production might teach us valuable lessons. Nanotechnology can learn from the bottom-up synthesis of silica structures, e.g., for the production of nanoparticles (Ould-Ely et al., 2011) or nanotubes (Meegan et al., 2004). As for fields of application of these nanocompounds catalysers, materials for tissue engineering and pharmacological compounds have been suggested (Voznesenskiy et al., 2011). (Kulchin, 2011) also hints at advanced optical properties like Bragg-light propagation regimes, that might contribute to the invention of novel devices like optical diodes; which would be interesting, e.g., for optical computer chips (Ozin & Hall, 2003). Non-linear optical properties of sponge spicules make them interesting for laser technology- as a source of inspiration or as integral part of lasers or optical amplifiers (Kulchin et al., 2009). Very promising seems the prospect to learn how to improve the mechanical characteristics of structures made of very few, but readily available base materials (Fratzl, 2007)(Jeronimidis & Atkins, 1995). As an example one can mention how hierarchical structuring, as in biosilica of sponges, can make otherwise brittle SiO_2 much stronger and more flexible. © by laserfest.org, (Ozin & Hall, 2003) (Uriz, 2006), sciencedaily.com

On the subject of spicule inspired nanostructures many different approaches have been pursued. Cha and colleagues (2000) soon after their discovery of the silicatein controlled synthesis of spicules reported the successful synthesis of silica structures by a biomimetic approach. In the mineralization process, silicatein was replaced by a synthetic peptide (consisting of cysteine and lysine) that catalyzed the deposition of regular silica rods.

It has been found out that for the efficient deposition of silica two amino acids in the sequence of silicatein were crucial (Zhou et al., 1999). The identification of this essential feature of silicatein helped researchers to find simple chemical compounds that catalyze the formation of silica structures. In this line of research, Park and Choi (2010) used small simple molecules, an amino acid derivative and a surfactant, to catalyze the formation of individually separated microspheres at near-neutral pH.

A different approach in nanotechnology is the use of (recombinant) silicatein to catalyze the deposition of other metal oxides than silica. Conceptually, it is not clear whether this classifies as biomimetics because the naturally occurring enzyme is used directly, and no abstraction is being made at that level. However, as stated by André and co-workers (2012), the emulation of the chemistry behind natural mineralization processes is indispensable for the use of known biomineralization agents like silicatein in technological processes. Thus, at the scale of chemical conditions relevant for the mineralization process some degree of abstraction is recognizable.

Examples of successful attempts to use silicatein, immobilized on synthetic surfaces, for mineralization of metal oxides include the formation of layered titania (TiO_2) and zirconia (ZrO_2) (Tahir et al., 2005) and the formation of gallium oxide ($GaOH / Ga_2O_3$) nanocrystals on filaments (Kisailus et al., 2005). In the examples presented here, the absence of alkali and acid (near-neutral pH) was stressed as distinctive to previous protocols for the synthesis of similar compounds. André and colleagues (2011) went one step further by including not only silicatein, but also silintaphin (a protein interacting with silicatein *in vivo*) that enhanced the deposition of the metal oxide used. Specifically, TiO_2 nanorods were coated with silicatein and silintaphin and subsequently catalyzed the deposition of either zirconia or silica.

Irrespective of the assembled molecules, there have been identified two key features of the polycondensation reaction by silicatein or a biomimetic analogue. The hydrolysis of the precursor molecules is catalyzed and controlled by silicatein (or its analogue) while the surface coated with the enzyme (usually a filament consisting of the actual protein) serves as template (André et al., 2012).

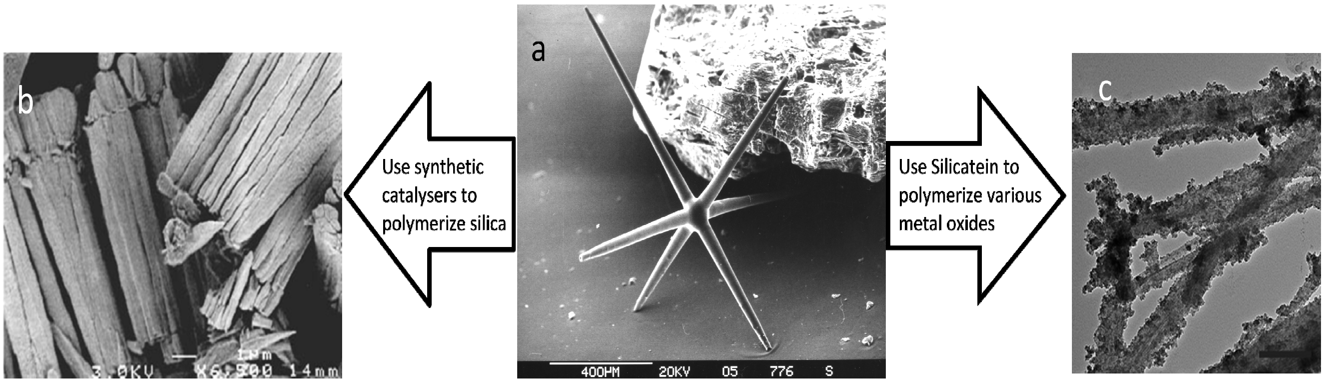

Figure 17 Different polymerization methods inspired by sponge spicules. (André et al., 2011) (Cha et al., 2000) Biomineralization of sponge spicules (a) has inspired various lines of research. One strategy has been to polymerize silica by synthetic catalysts that act as a replacement for silicatein. Here, synthetic block copolypeptides have been used to mineralize silica (b). In attempts rather pertaining to biotechnology, silicatein has been immobilized on axial filaments and inorganic metal oxides have been polymerized on it at near-neutral pH and ambient temperature (c). Scale bars are 400 µm (a), 1 µm (b) and 100 nm (c). © by Hannes Grobe/AWI (a),(Cha et al., 2000) (b), and (André et al., 2011) (c).

Mechanical properties of spicules

Turning to the mechanical properties of spicules of sponges, the distinction between basal and skeletal elements is relevant. Skeletal elements are rather rigid and convey hardness and shape to the sponge, while the, usually threadlike, basal spicules are surprisingly flexible (cf. Figure 6h) and anchor the sponge to the substrate (Kulchin et al., 2007). Values of micro-hardness and elastic (Young's) modulus of sponge spicules are comparable to that of fused silica used in glass fibres (Samsonov & others, 1978). Yet, they are for more flexible, because these values are not uniform across the radius of basal spicules and show a pronounced decrease from the centre to the periphery. This is due to the distinctive layered structure of these spicules with the periodicity of organic/silica sheaths decreasing from centre to periphery (Kulchin et al., 2008).

Very challenging for the adaption of bio-inspired materials for technology, is the decisive role of moisture. Johnson and colleagues (2010) investigated mechanical properties of basal spicules form *Euplectella aspergillum* in dependence of hydration. They compared the mechanical properties of dried spicules and specimens soaked in seawater for 1, 24 and 48 hrs (Table 1). The values for soaked spicules are considered to be representative for the mechanical properties in living sponges, while dried spicules give a good indication of values that could be expected for a biomimetic technological material useable as structural element or optical fibre. Dry spicules have a significantly higher Young's modulus (are stiffer) and an equally higher stress to failure (engineering stress) than soaked specimens. The latter finding came as a surprise, since moisture had been believed to allow for better dissipation of energy of biominerals because it makes the contained organic matrix more plastic (Mayer, 2005). The plasticization of the organic matrix and other moisture related phenomena had been shown to be beneficial for the toughness of other biominerals like nacre (Mayer et al., 2004).

Table 1: Mechanical properties of spicules in bending to determine moisture effects in seawater. Adapted from (Johnson et al., 2010)**, values ±SD**

Time soaked in seawater	dry	1h	24h	48h
Elastic modulus (GPa)	13.7 ± 2.2	9.3 ± 2.7	9.1 ± 1.0	8.9 ± 1.9
Maximum strain	0.044 ± 0.005	0.041 ± 0.008	0.044 ± 0.005	0.044 ± 0.005
Engineering fracture stress (MPa)	431 ± 87	320 ± 72	303 ± 41	300 ± 33
No. of samples	4	9	4	6

As mentioned before the fracture of spicules is not linear. It was believed that cracks become arrested in the organic interlayers after a short length and fracture occurs as a series of successive micro-fractures. Thus, the outer, thin layers are considered sacrificial, i.e. their fracture relieves the stress for the core of the spicule and therefore protects it from failure (Currey, 2005) (Chai & Lawn, 2002). Johnson and colleagues (2010), however, proposed a much more complex mechanism for failure due to bending, including seven steps.

The initiation of cracks occurs at flaws in the surface layers (1) that travel towards the core and around the spicule until they are arrested and diverted by the organic interlayers (2). The arresting of the crack entails viscoelastic deformation of the interlayer that delays crack propagation (3). Thereby the crack continues to grow circumferentially in the silica-layer until it is energetically more favourable to break the organic layer (4). Subsequently a new crack initiates at a flaw in the next layer, or packet of layers (5) that travels similarly to the first crack, but also causes delamination (6). The last step consists in the iteration of steps 2-6 until, well before getting to the core of the spicule, a critical crack length leads to fast fracture.

Thus the originally proposed mechanism is an oversimplification, especially since often individual layers of silica are observed to fracture as “packets” instead of sequentially. Still, during bending more energy is dissipated in spicules than in melt-processed glass fibres. Furthermore the authors found that spicules showed superior dampening characteristics compared to glass fibres.

In general terms, the composite arrangement here conveys improved ductility, resilience and an increased capability to dissipate energy. Comparing fracture strength, strain-to-failure and fracture energy between spicules and massive glass rods demonstrates that the natural materials are several times more stable (cf. Figure 18) (Sarikaya et al., 2001)

As most rigid biomaterials, sponge spicules possess a highly directional structure, which causes anisotropy. The dependence of mechanical properties on the direction of an applied force is therefore an important boundary condition to keep in mind.

Spicules and optical fibres

The preceding overview of the mechanical properties of basal spicules makes these spicules seem an appropriate role model for durable optical fibres. It is unlikely that basal spicules guide light *in vivo* and the waveguide properties are therefore almost certainly an accidental side-effect of a structure optimized to quite different ends (cf.Aizenberg et al., 2004). Nonetheless, the optical properties are remarkable (Voznesenskii et al., 2010) (Kulchin et al., 2011) and can compare to those of spicules whose light transmission properties serve a biological purpose (Müller et al., 2009a).

Thus, the idea of using spicules as role model for telecommunications fibres is not a linear abstraction from one biological role model. Rather, better optical fibres should draw on basal spicules as their paradigm regarding mechanical properties and on skeletal spicules of demosponges that serve a biological purpose as light guides for their optical properties.

Since the optical properties happen to be similar in many basal and skeletal spicules, this distinction might be of theoretical and conceptual nature only.

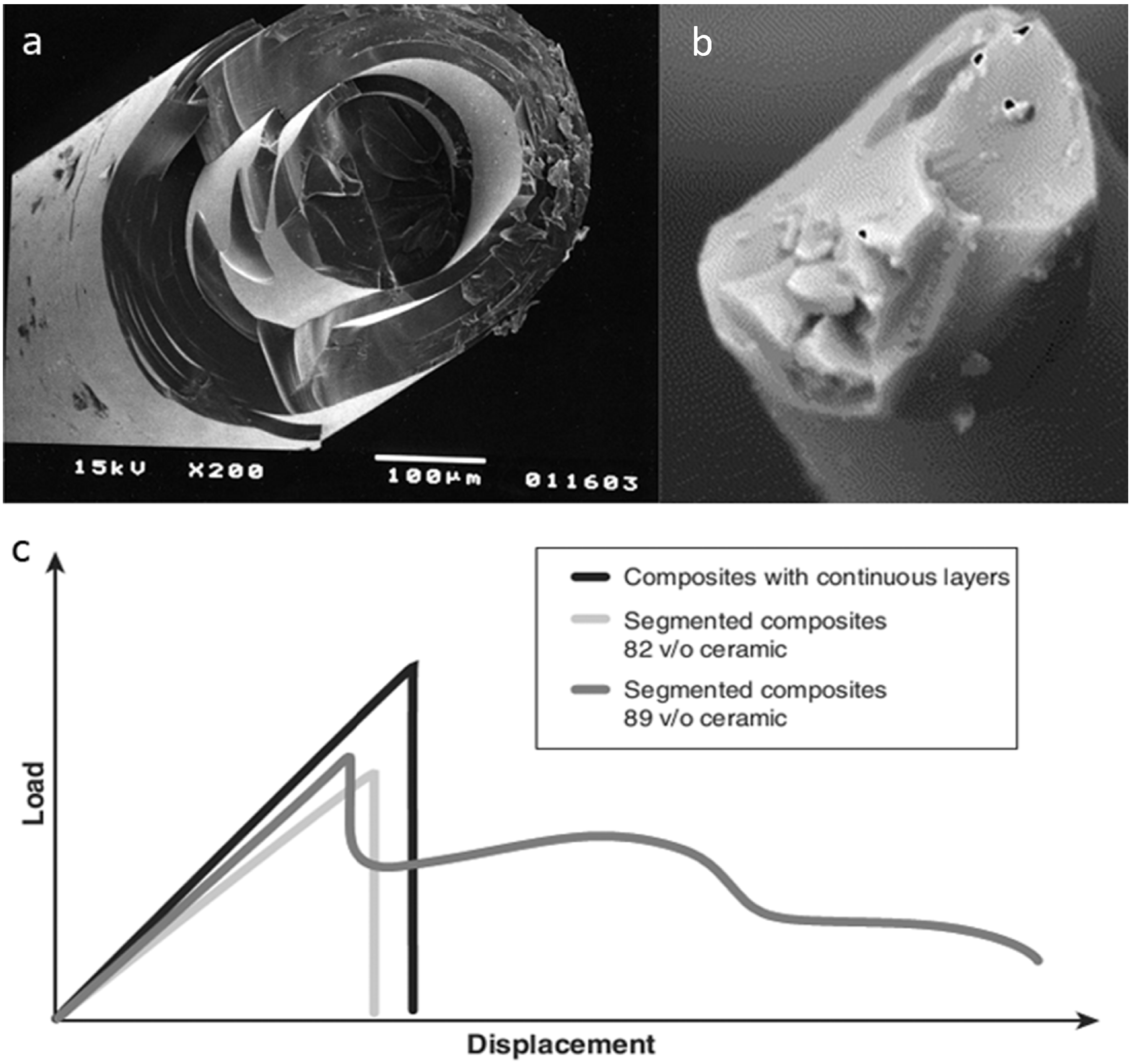

Figure 18: Differences in fracture strength between multi-layered spicules and simple glass fibres. (a) represents the untreated, fractured surface of a hexactinellid sponge spicule, while (b) shows the considerably less structured, untreated structure of a common glass fibre at ~10,000x magnification. (c) Qualitative comparison of energy dissipation during bending of different materials. The triangular curves represent the behaviour of b, while the dark grey curve demonstrates the residual strength of composites like sponge spicules. © by (Mayer, 2005) (for a and c) and (Militky et al., 2002) (for b)

Instead of the benign failure mode of spicules (see above, (Koehl, 1982)) commercial communications fibres fail due to a single, catastrophic event (cf. Figure 18c). Spicules also excel in flexibility due to their gradient in Young's modulus and hardness while these properties are homogeneous in communications fibres, making them brittle (Aizenberg et al., 2004). In commercial fibres failure is due to simple crack growth (Sundar et al., 2003). Spicules are also known for their high purity that compares to quartz grade glass (Wang et al., 2011a).

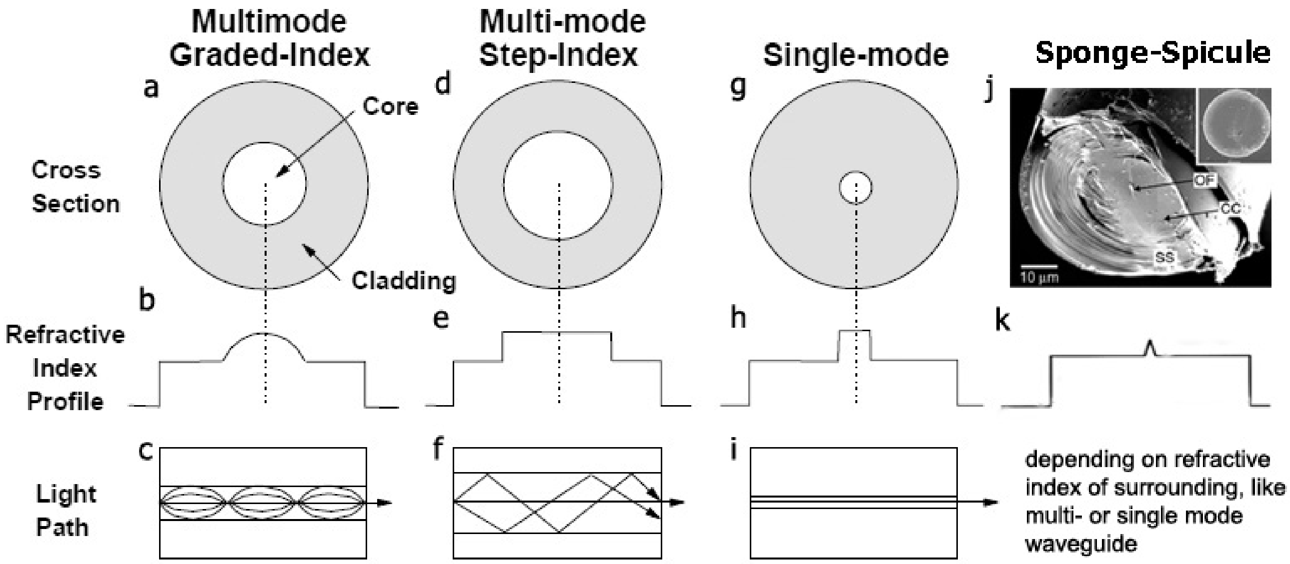

Figure 19 Sponge spicules resemble commercial optical waveguides. Apart from being made of the same material, sponge spicules can have a similar diameter like glass fibres, the most commonly used waveguides for telecommunications. Most interestingly they have a similarly graded refractive index - a high-index core and a lower index cladding ((b), (e), (h) and (k)) (Aizenberg et al., 2004). Depending on the refractive index of the surrounding medium (n_{ext}), spicules can act as a multimode waveguides (like (c) and (f)) for $n_{ext} < n_{spicule}$, or as single-mode waveguides (like (i)), if $n_{ext} > n_{spicule}$. Another important prerequisite for the spicule to operate as a multimode fibre is that the difference in n between the environment and the material of the spicule be considerably larger than the difference between core and cladding (Voznesenskiy et al., 2011) © by fiberoptics4sale.com for (a)-(i) and (Aizenberg et al., 2004) for (j) and (k)

The macroscopic scale of sponge spicules is a good precondition for the successful transfer of concepts from nature to technology. As Mayer (2005) pointed out, the adaptation of general architectural configurations and material characteristics has its limits. Very often insurmountable difficulties occur when trying to translate a natural process at the nano- or microscale to a technologically feasible structure at the macroscale; and that at a reasonable cost. Our understanding of the deep principles at the basis of properties of biomaterials is usually incomplete, which is an obstacle especially when scaling effects set in.

The adaption in commensurate applications, like 3D-MEMS, circumvent these potential problems (Gebeshuber et al., 2009) (Gebeshuber, 2012c). Thus, the similarity in scale, referring to the diameter of spicules of course, allows for a rather direct adaptation of spicules for production of optical fibres. This holds great promise for a successful implementation.

Optical properties of siliceous sponge spicules and conventional glass fibres, in contrast to their mechanical properties, are similar indeed. Not surprisingly, this observation was picked up by researchers at the renowned Bell laboratories, a leader in research on telecommunication technology.

Specifically, (Sundar et al., 2003) investigated the basal spicules of Venus' Flower Basket (*Euplectella aspergillum*) that protrude 15 cm approx. in a crown-like formation from the base of the cage-shaped skeleton. These spicules have a 40-70 µm wide cross section that appears homogeneous when breaking the spicule. When the broken surface is treated (mechanical stress or etching), though, a distinct zonation becomes visible (Figure 19j). A homogeneous core including the organic axial filament (OF) is inserted into an equally smooth central cylinder (CC) while the exterior cladding is striated (SS). The chemical composition between the three regions varies. The 2 µm central core consists of pure silica, while the central cylinder has a remarkably high organic content. In the outer shells again the organic content decreases in centrifugal direction. This distinct chemical and structural profile of the spicular cross-section is indeed reflected by a tripartite profile of the refractive index n. The central core has a high refractive index exceeding that of vitreous silica, while the central cylinder is far less refringent (lower n). In the outer cladding, the layered structure is reflected by an oscillating refractive index that is higher than in the central cylinder and furthermore increases notably towards the surface (Sundar et al., 2003). The reason for the increased refractive index of the spicule core compared to vitreous is the inclusion of sodium ions as refractive index-raising dopant (Aizenberg et al., 2004).

The profile of a high index core with a lower index cladding is found in all technical optical fibres (cf. Figure 19a,b,d,e,g,h). Depending of the diameter of the high-index core as well as the continuous *vs*. stepwise decrease of the refractive index from the core to the cladding different classes of optical waveguides can be distinguished. The distinction between these different classes of waveguides is important for communication fibres, since single-mode waveguides can transmit light encoded signals over greater lengths without distortion. Sponge spicules can adopt both modes, depending on the refractive index of the surrounding medium, but are multimode waveguides in their natural environment - sea water (Aizenberg et al., 2004) (Voznesenskiy et al., 2011).

Another feature of sponge spicules distinguishing them from commercial fibres is the absence of birefringence, i.e. the dependence of the refractive index on the polarization of a light-wave (Aizenberg et al., 2004). This phenomenon is unwanted in optical fibres for communication because it can distort the information being carried. In technologically available fibres it occurs because of residual thermal stresses that arise from the high processing temperatures (Varnham et al., 1984).

Not surprisingly, there are also difficulties to overcome when building spicule-inspired optical fibres. As mentioned earlier, Rayleigh scattering and concomitantly transmission losses increase due to inhomogeneities that are hard to overcome in a fibre that is like sponge spicules, composed of silica-nanospheres (Aizenberg et al., 2004).

Another issue to address is the differential transmission of wavelengths (Figure 20c). In general, the losses during transmission of light are quite low. Basal spicules of glass sponges 140 µm across where found to transmit light with a loss of 0.1 dB/m for red light at $\lambda = 633$ nm (Kulchin, 2011). More generally Voznesenskiy and colleagues (2011) claim that the losses between 500 nm and 900 nm are acceptable for technological applications. Commonly used telecommunication fibres attenuate light only 4-5 dB/km, however (LuxLink.com, n.d.). Additionally, the white-to-red shift in hexactinellid basal spicules (Figure 20b) (Müller et al., 2009a) is not desirable when designing fibres, e.g., for illumination purposes. As mentioned earlier, fine-tuning of the layer width can alter transmission properties of a spicule-like waveguide and possibly attain the transmission of the entire visible spectrum (Voznesenskii et al., 2010).

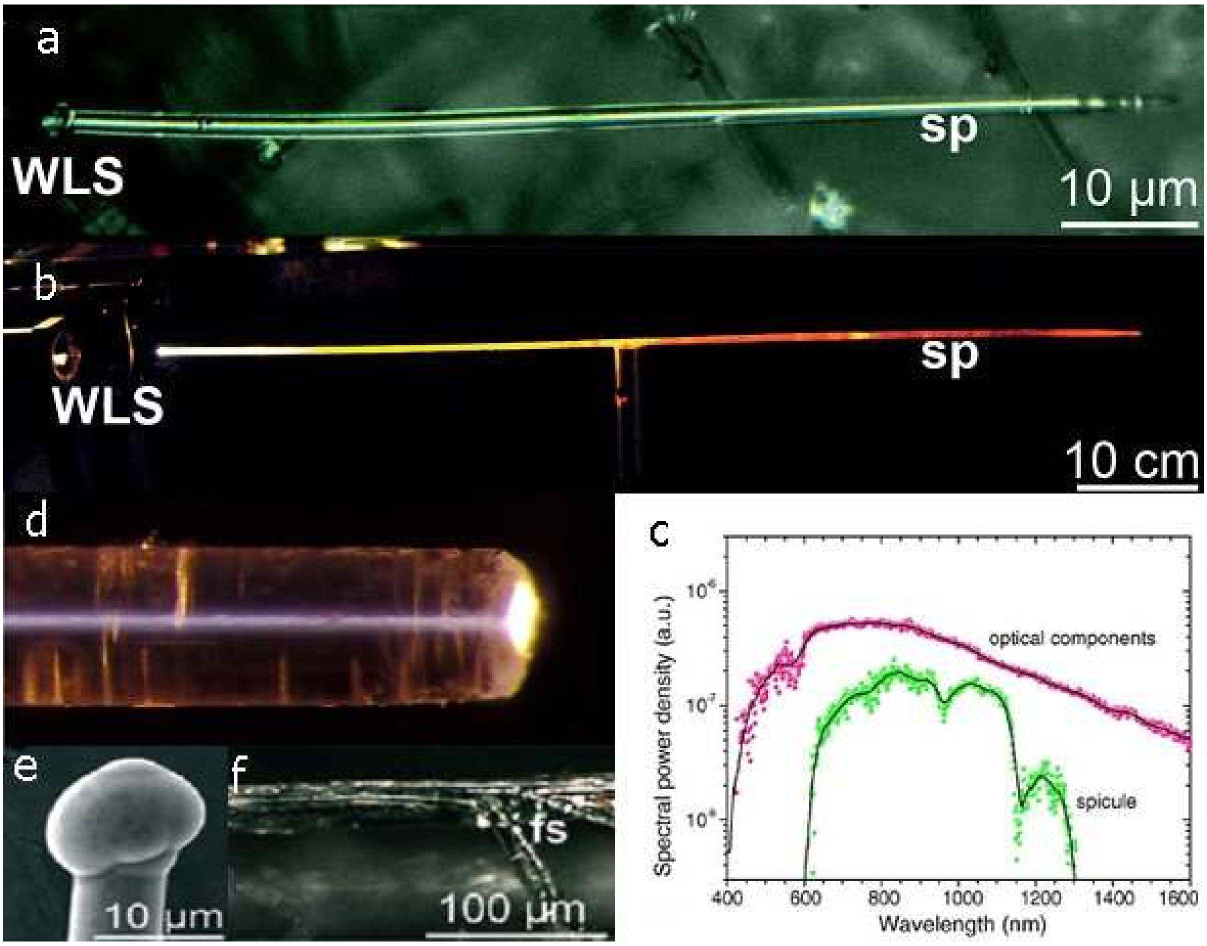

Figure 20: Light guiding properties of sponge spicules. Even though light transmission through spicules of demosponges has been demonstrated to serve a biological purpose (Brümmer et al., 2008), most research on waveguide properties has been carried out on spicules from glass sponges, where light guiding properties might be an accidental by-product of the spicular architecture (Aizenberg et al., 2004). (a) shows the first (Müller et al., 2009a) and (to the best of my knowledge) only demonstration of the waveguide properties of a demospongial spicule. Other than all known hexactinellid spicules - that act as a high- and low-pass optical filter with a cut off at 600 nm and 1300-1400 nm (c) and therefore show a characteristic shift from white to red colour (in (b)) – demospongial spicules do not alter the quality of light (Müller et al., 2009a). However, this might well be due to the low length of the spicule and not according to structural differences between glass sponges and demosponges. In (d, magnification 100 x) the axial filament of a glass sponge spicule appears brighter than the cladding due to increased scattering. (e) shows the lens-shaped distal end of a demospongial spicule that couples more light into the "waveguide". (f) Highlighting that light guided in fascicles of glass sponge spicules is split at fusion sites (fs). © by (Müller et al., 2009a) for (a) and (b), (Müller et al., 2006a) for (c) and (d), (Müller et al., 2010) for (e) and (f)

In (Figure 20c) two minima of transmittance through the spicule are apparent. These are due to the presence of bound water in spicules (Galkina et al., 2009) (Wang et al., 2009). The minima closely correspond to the three absorption lines of water at 970 nm, 1150 nm and 1190 nm (Braun & Smirnov, 1993) whereat the latter two absorption lines cannot be resolved in the graphic.

Biomimetic potential of different bio-mineralization pathways: Nacre

An interesting biomineral only recently has been copied successfully: Nacre, or mother-of pearl. Finnemore and colleagues (2012) synthesized artificial nacre in a completely synthetic way without the use of any biological molecules but like its natural role model, on the basis of cheap and abundant calcium carbonate. Like spongial biosilica, nacre attracted research because of remarkable mechanical properties and an optical effect.

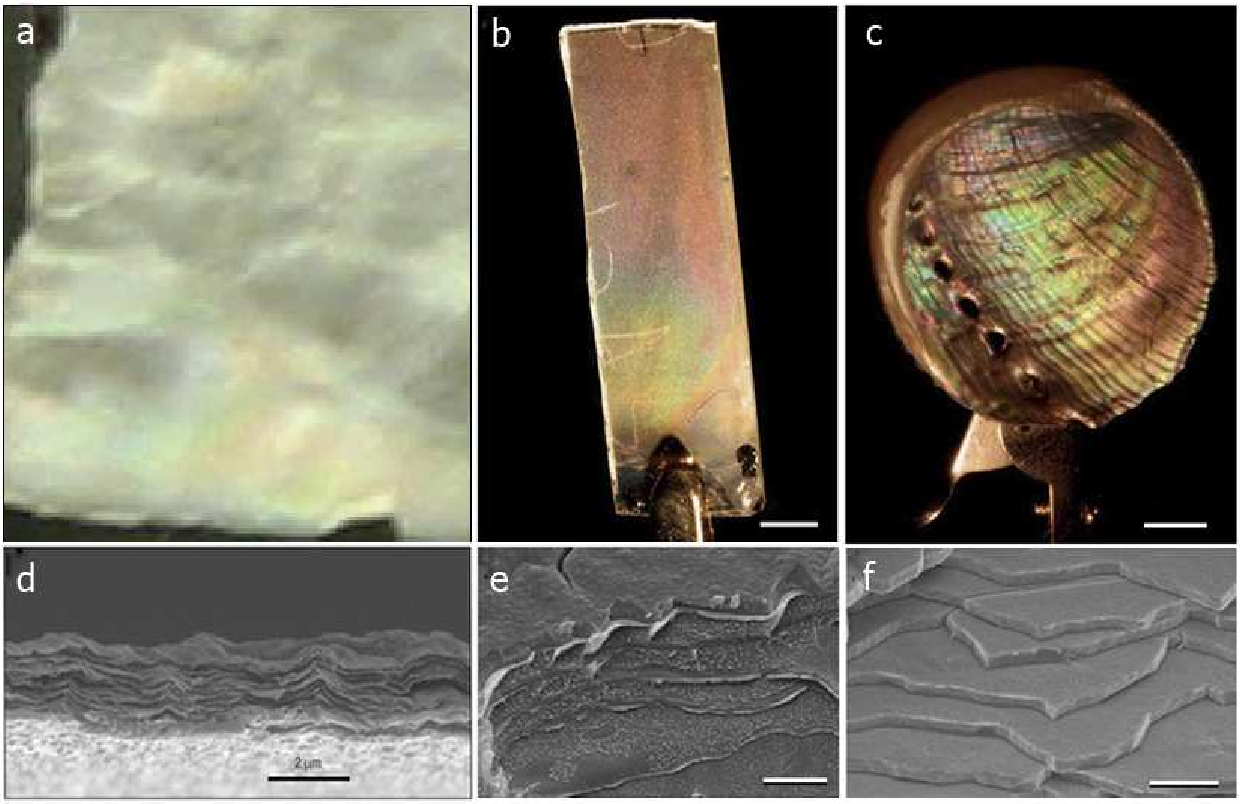

Figure 21: Progress in synthesis of artificial nacre. Mimicking the intricate structure of this hard, tough biological composite has proved as an instructive effort for scientists. Careful step-by-step synthesis of bio-inspired composites has helped to understand biological mechanisms at work during the growth of nacre. An early attempt to mimic nacre, using montmorillonite clay platelets by (Tang et al., 2003) (a, size of film: 2 x 4 cm), the first $CaCO_3$–based artificial nacre from (Finnemore et al., 2012) (b) and a shell of oreille de mer (*Haliotis tuberculata*) (c). (d-f) SEM images of fractured surfaces of (a-c). Scale bars are 5 mm (b), 5 mm (c), 2 µm (d), 1 µm (e), 2 µm (f). © by (Tang et al., 2003) (a and d) and (Finnemore et al., 2012) (b,c,e and f)

This section is included in this work otherwise focussed on silica because it seems a very convincing example how to copy a biogenic mineral. As mentioned before, the idea of mimicking specific biomaterials instead of transferring only general principles makes the implementation easier and bypasses scaling issues (Mayer, 2005). The exact, mechanistic description of the steps involved in the synthesis of biogenic nacre and the control for all relevant parameters in the macroscopic biomimetic replica seem to be on an advanced level compared to efforts regarding siliceous spicules (Wang et al., 2012c) (Wang et al., 2012b) (André et al., 2012) (Voznesenskii et al., 2010).

Synthesis of artificial nacre has long been envisaged (Sellinger et al., 1998) (Tang et al., 2003). Hallmark properties of this biomineral are its remarkable strength and toughness as well as its iridescence (Figure 21c) (Smith et al., 1999). Nacre is a layered structure with alternating layers of aragonite ($CaCO_3$) and thin organic membranes in a brick-and-mortar fashion. As reviewed by (Mayer, 2005) there are at least ten different mechanisms contributing to energy dissipation, and hence toughness, of nacre. Among these are mechanisms also found in sponge spicules, like crack diversion at organic interlayers and the creation of new surfaces by cracking and delamination (Kamat et al., 2000), as well as various nacre-specific mechanisms.

Earlier attempts to copy the "structure-function harmony of nacre" (Tang et al., 2003) include a nanostructured nacre presented be these authors. Various mechanical properties of the artificial thin film, like tensile strength, were similar to that of nacre. However, like other attempts in the last decade (Bonderer et al., 2008), base materials far less abundant than $CaCO_3$ (e.g., montmorillonite clay) were used. More decisive however was the lack of a complete implementation of the structural features that make the mechanical properties of nacre so remarkable. In the aforementioned, clay-based artificial nacres as well as in attempts with $CaCO_3$(e.g., (Wei et al., 2007) the horizontal connection between mineral layers was not implemented. These connections are essential to establish a nacre-typical microstructure and accordingly the typical mechanical properties (Finnemore et al., 2012).

In the publication of the most recent attempt (Finnemore et al., 2012) a surprisingly short list of steps, which are essential to mimic the synthesis of nacre was included:

(i) stabilize amorphous $CaCO_3$ precursor in solution

(ii) specifically aggregate these and form a continuous film on an organic surface

(iii) deposit a porous, functionalized thin organic layer on the continuous mineral film

(iv) crystallize the previously deposited mineral films

(v) repeat steps (i)-(iv)

The resultant artificial nacre visually resembles its natural role model on all different scales. Scanning electron micrographs (SEM, Figure 21e *vs*. f) reveal that the characteristic tablet structure of aragonite in nacre is similarly maintained in the calcareous tablets of the artificial nacre. With the naked eye a feature related to the same, small scale can be detected: iridescence (change of colour with the viewing angle). This optical phenomenon arises due to the regular periodicity of nacre (Figure 21c), and is quite similarly observed in the artificial nacre plate (Figure 21b), confirming the good control over layer thickness in this artificial organic-inorganic composite. Indentation of artificial and natural nacre revealed that the toughness of both materials is similar, with differences due to the used crystal from of $CaCO_3$ (cal_{org} in artificial nacre *vs.* aragonite in biogenic nacre).

The approach reported in that publication importantly is quite similar to the biomineralization of nacre in the living organism, e.g., abalone (Lin et al., 2008). Importantly, the methods used during synthesis (e.g. dip-coating, etching with NaOH) should easily be up-scaled. This stands in contrast to many attempts to mimic the formation of sponge spicules, since often biomolecules (like silicatein) are involved in proposed and experimented pathways (Tahir et al., 2005) (Müller et al., 2009c) (André et al., 2011).

Daylight guidance systems (DGS)

Benefits

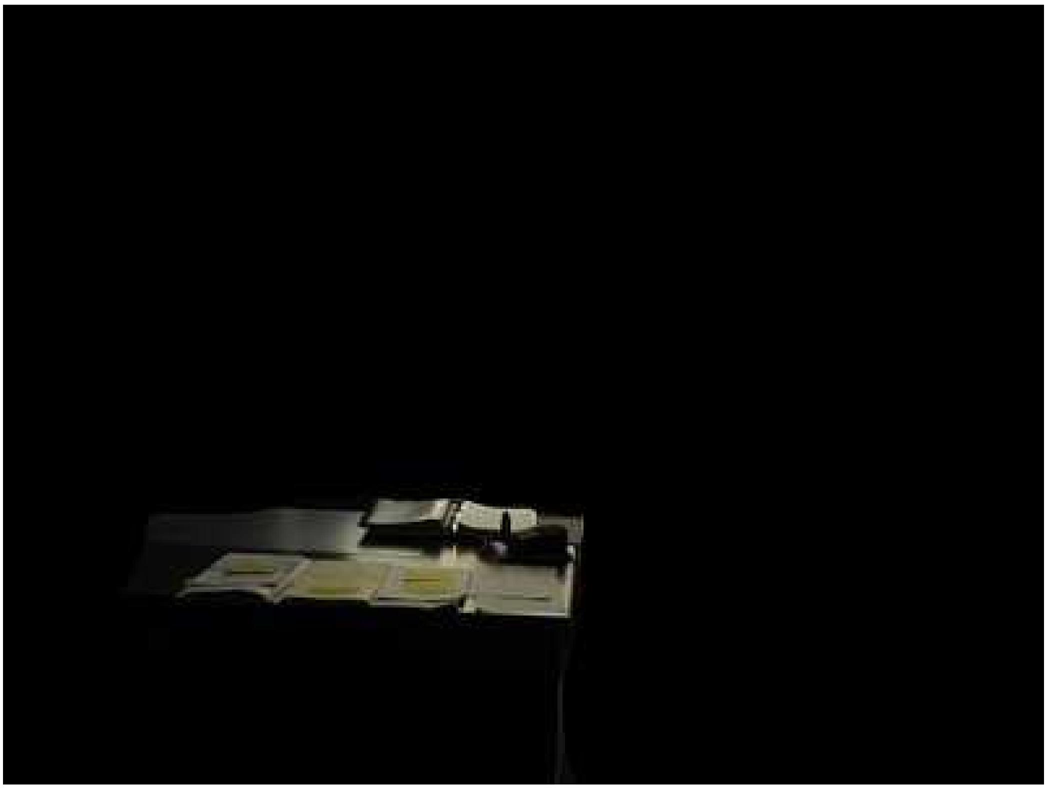

Figure 22: A darksome desk. An ever increasing number of people work in deep-plan office buildings where daylight that can be delivered by conventional windows or atria is insufficient. Most people, however, prefer natural light for illumination for a variety of reasons, including well-being and improved performance. © strangelycutlemon.com

We live in an urbanized world. As of 2008, more than half of the world's population lives in cities (UN news, 2008). This increasing urbanization is not confined to any specific region of the world, though there are hot spots like Lagos (10.4 million inhabitants, growth rate: 4.44 % p.a.) and Kinshasa (9 m, 3.89 %) in Africa, Lahore (7.7 m, 3.12 %), Karachi (20.7 m, 3.19 %) and Dhaka (15.4 m, 3.79 %) in Pakistan and Bangladesh (population from (Demographia, 2012), growth rates from (citymayors.com)).

A lot of living- and working space is being created and will have to be created in the future to accommodate this urban populace. The importance of creating this environment according to the principle of ecologic sustainability can hardly be overstated (Costanza, 1991). Sustainable development, according to the widely accepted definition of the

Brundtland Report, is “development that meets the needs of the present without compromising the ability of the future generations to meet their own needs” (WCED, 1987).

It might not be obvious how this relates to dark (Figure 22) or well-lit offices.

A closer look at the demands that sustainability makes, in this case on the construction industry should shed light on this issue. In 2005, heads of states of the United Nations declared their intention to foster sustainable development considering three factors: “economic development, social development and environmental protection as interdependent and mutually reinforcing pillars” (UN, 2005). While environmental protection is intuitively understood to be essential for ecological sustainability, the social aspect (Gebeshuber, 2007b) (Gebeshuber et al., 2011) has got less attention (Smith & Pitt, 2011).

Not to consider this aspect would be negligence, though, since by building we provide the environment for society. As stated by Dickie and Howard (2000): “what we build today will provide the built environment of the future and will influence the ability of future generations to meet their needs”. This holds, of course, especially in a modern, urban world, where people’s lives are closely connected to buildings. We eat in buildings, we work in buildings, we sleep in buildings.

In this context, it is interesting to find out what makes for a good, sustainable workplace.

This question will be addressed here with a focus on light and more specifically, with the potential roles of natural daylight in mind.

An obvious demand regarding a workspace is that there be sufficient light to perform visual tasks like reading well. With natural daylight colours are rendered very well, better than with many artificial light sources that give colours an unwanted hue. In general, daylight matches our visual response closely (Li & Tsang, 2008), as is to be expected considering that our eyes evolved to make use of this light source. During the last century, new building designs, especially deep-plan buildings that cannot only be lit by daylight through windows became possible thanks to artificial light. Yet, the era of cheap energy has passed, leading to a reappraisal of our oldest and cheapest light source (Mayhoub & Carter, 2012). The expectation of energy savings, raised from common sense and early publications on the matter (Hunt, 1977) (Crisp, 1977) have stimulated research towards daylighting design. While the goal, a (subjectively) well-lit workspace, has been clear and has got a lot of attention, we cannot satisfactorily describe such a space in objective terms. In other words, we lack parameters that quantify our requirements. This makes the design of lighting a task that relies rather on the intuition and experience of designer than on a systematic approach (Mardaljevic et al., 2009). Advances in that field include more sophisticated *in silico* experiments that now precede most constructions (Mayhoub & Carter, 2012). Importantly, these most recent simulations do not only provide more reliable results by using a better temporal resolution, but also by including more realistic input parameters than the most commonly used “Daylight Factor” (Mardaljevic et al., 2009).

Figure 23 Planning of appropriate lighting of work-spaces involves manifold considerations. Apart from obvious demands like the provision of sufficient light for visual tasks, increasingly complex requirements related to general well-being are taken into account when designing the illumination of offices. Many companies wish to epitomize certain premium aspirations and hence design the ambiance of their offices accordingly. Light is also known as the most important cue (zeitgeber) calibrating our internal clock (circadian rhythm) (Aschoff, 1951) (Roenneberg et al., 2007) (Salazar-Juarez et al., 2006). Recent epidemiological evidence suggests a correlation between reduced exposure to the natural 24 hours light-dark cycle and prevailing medical conditions like obesity and diabetes (Roenneberg et al., 2012) (Scheer et al., 2009), making the adequate illumination of work-spaces a more pressing issue© (top left to bottom right) by Arun Kulshreshtha, progressivepioneer.com, cokeonline.ch, wdr.de, plusmood.com, (none), mz-web.de

Notwithstanding the problems involved in planning, and the uncertainty whether daylighting is really effective to reduce energy consumption of buildings (Bordass et al., 2001) (Mardaljevic et al., 2009) efforts keep being made, for most people clearly prefer natural light over electric light (Roche et al., 2000). Individual preferences of people are hard to describe. As observed in an empirical study by Roche and colleagues (2000) satisfaction with daylight is very complex. Almost 75 % of the participants of their study in office buildings across the UK asserted their clear preference for a workplace near a window. At the same time, problems related to glare and reflections lead to a greater acceptance for low levels than high levels of daylight, even though this study was carried out in the UK where the daylight levels (especially within buildings) are rarely above the “about-right “ level (Roche et al., 2000) (cf. Figure 23). Windows therefore are a controversial asset in office buildings. Appreciated by employees for the natural light and potentially nice view they provide, the lack of which even can cause claustrophobic and depressing feelings, windows do not always add to the quality of a workspace. Direct sunlight and even scattered natural light (skylight) can contribute to eye-fatigue, visual discomfort and large windows contribute to undesirable heat gain or loss (Kim & Wineman, 2005).

In the last years several works have been published that stress the wellbeing of employees in the context of more sustainable workplaces. Pech and Slade (2006) observed an increasing disengagement of employees, i.e. they do not identify with their work, and have no positive, energetic connection with their work (Bakker et al., 2008). This development is very likely a loss for the company, since productivity decreases, while absences and complaints increase if employees have a negative perception of their workplace (Roelofsen, 2002).

With regards to lighting of buildings it might therefore be hard to ascertain the “right” light conditions as the perceptions of people seem to be highly complex and idiosyncratic (cf. (Kim & Wineman, 2005) (Roche et al., 2000)). Therefore considering another factor contributing to a better, more sustainable workspace might be worth considering. Lee and Brand (2005) found that employees have a better impression of their workspace and are therefore more satisfied with their job if they feel in control over their physical environment. This want could partially be complied with if a lighting system offers the possibility to personally modify it.

Not only on the level of individuals and companies, however, lighting of office spaces entails noteworthy consequences. A large scale epidemiologic survey (65,000 valid entries) revealed that people in central Europe over the last decades get to bed at increasingly late hours (later "chronotype") (Roenneberg et al., 2012). Since at the same time working hours remained largely the same, an increasing portion of the working population experiences chronic sleep loss (Wittmann et al., 2006). According to one theory, this phenomenon is due to a misalignment of our internal clock (circadian clock) and "social clocks", i.e. when our job requires us to be awake. Comparing the times people get up on work days vs. free days this phenomenon, termed social jetlag, is quantifiable and has been found in the region the study has covered (mainly central Europe) and is likely to prevail in other industrialized nations, too (Roenneberg et al., 2012).

Since the sequels of chronic sleep loss are known to include higher risks for overweight and metabolic diseases like diabetes mellitus, thanks to vast evidence from epidemiological studies e.g.(Bjorvatn et al., 2007) (Scheer et al., 2009) and it is simply unpleasant to go to work sleep-deprived (*pers.obs.*) the question remains, why people go to bed later now than few decades ago. The sleeping duration per night, during working days has shortened by an impressive 40 minutes, based on the aforementioned survey (Roenneberg et al., 2012) (Foster, 2012)

Although, there are a few obvious answers to that question- like late night TV, computer games, the internet (Foster, 2012)– an alternative, or maybe complementary explanation seems convincing. It has been observed early on, that humans possess an intrinsic feeling for time that can collide with external, social timekeeping (Plautus, c.200 B.C.). Much later this intrinsic clock, termed circadian rhythm (Aschoff, 1951), has been recognized to be endogenous, i.e. it exists without external input. The basic rhythm that, via hormones, governs our sleep pattern and other metabolic functions in a cycle lasting roughly 24 hrs can however be *entrained* (modified) by external cues termed zeitgeber (German for "giver of time"). The strongest zeitgeber is, not surprisingly, the 24 hour dark-light cycle e.g.(Salazar-Juarez et al., 2006). According to Roenneberg and colleagues (2012), the shift in our sleeping habits (social jetlag) is due to greatly reduced zeitgeber-strength, because we are less exposed to strong (natural) daylight and additionally exposed to artificial light at night.

Importantly, social jetlag is closely correlated with obesity and likely other metabolic phenomena according to the wide database of Roenneberg and colleagues (2012). From 1980 to 2008, obesity has doubled worldwide and 65% percent of the world population (of more than seven billion people) live in countries where more people die because of obesity and overweight than because of underweight (www.who.int/topics/obesity/en/)(Foster, 2012). Hence, if the social jetlag theory is further corroborated, better *entrainement* or other measures to realign social and circadian clocks seem an imperative. In this context it is relevant to state that the photoreceptors likely involved in the *entrainment* of the circadian rhythm absorb blue light (446-488 nm) (Brainard & Hanafin, 2004) (Bellia et al., 2011).

This factor relates specifically to workplaces, because working hours usually are during daylight time, which accordingly makes natural light a good option for lighting. There have been reported numerous other health related concerns with regards to illumination of workspaces (reviewed in (Wilkins, 1993)). These include problems with low-frequency magnetic fields and rapid variation in luminous intensity (including flicker), both examples that are not a concern in daylighting.

A very different concern is the ambiance of an office. As has been discussed by Kaplen (1975) the design of an office space is often used to convey a message about the identity and aspirations of a company. Light and lighting systems can help to improve the perceived value of such a space. Since novel systems for lighting, like most innovative systems, require higher investment from the client, it is desirable to offer the client not only functionality and aesthetic design, but also the possibility to express their identity or philosophy.

Obviously, there are great local differences in the incidence of sunlight and other factors influencing the availability of daylight for lighting. For planning and simulation purposes different fraction of external illuminance (availability of light) are commonly distinguished, e.g. direct normal (DN) (Figure 24) and global horizontal (GH) illuminance. GH illuminance in this case accounts for all scattered and reflected light. Numerical values for these parameters, as well as other data for illuminance and solar radiation, can be obtained with good temporal and regional (20 km steps) from (free) websites (soda-is.com). Distinguishing different types of light (illuminance) is essential in this context, because some daylight guidance systems can only make use of direct normal irradiation, making these inappropriate for places like London. The same system might however outperform other daylighting systems that can additionally use indirect light in very “sunny” places (high DN illuminance) like Tarifa, Spain (Mayhoub & Carter, 2011).

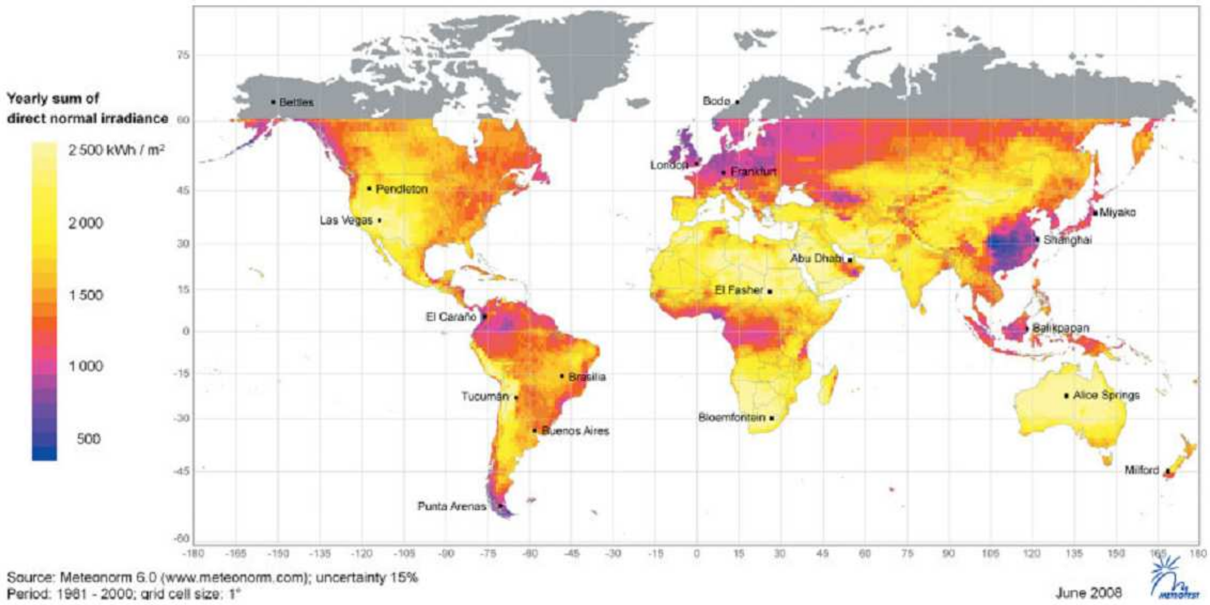

Figure 24: World map of sunshine (direct normal irradiance). The performance of daylight guidance systems (DGS) depends on geographic latitude, the ratio of direct normal irradiance to indirect and horizontal irradiance, among other factors. Careful assessment of local conditions and *in silico* experiments are needed to fully exploit the ene*rgy sav*ing potential and other benefits of DGS (Mayhoub & Carter, 2011) (Zhang et al., 2002). Conversely, façades should prevent glare by direct sunlight and overheating of the interior due to excess sunlight (Kaase et al., 2012).

Various ideas have been developed how to guide daylight deeper into buildings. Edmonds (2005) described the improvement of useful daylight in high rise buildings by reflecting panels. These laser-cut reflectors could, when arranged adequately, convey up to three times more daylight to office buildings in Hong Kong before glare became a problem. This method is however still limited by the presence of windows in close proximity and is accordingly not useful for the lighting of the core of deep-plan buildings.

Light shelves, light distribution systems that distribute incident daylight in buildings are another daylighting system, especially useful in regions with high incidence of sunlight. Usually, plane elements are placed horizontally or at an angle above eye-level behind windows to prevent glare from direct sunlight and to redistribute it deeper into the building (Soler & Oteiza, 1997).

For tropical and temperate regions, another type of daylight guidance system is attractive: Anidolic light guides. Courret and colleagues (1998) proposed to introduce an additional ceiling that is connected to a tilted façade element that collects light for redistribution in the office space. The protruding façade element contains a collector that diverts the incident sunlight by non-imaging (anidolic) optics deeper into the building where another anidolic element releases the light into the room. The authors suggest that under overcast conditions, and in a typical urban, obstructed landscape this system provides 2-3 times better lighting deep inside buildings than conventional windows. Additionally, the provided light reportedly makes for high visual comfort, and the system could be installed when retrofitting office buildings.

Commercially available systems

Most common light guidance systems on the market, though, rely on a quite straightforward approach. Daylight is conducted from the rooftop or façade and conducted by optical fibres or tubular light ducts deep into the building (Figure 25). Some more recent products aim at intertwining artificial and natural light to provide reliable lighting through a single integrated system. Commercially available hybrid systems currently include Himawari (himawari-net.co.jp), Parans (parans.com), Hybrid Solar Lighting (HSL) ((sunlight-direct.com) and the SCIS Solar Canopy Illuminance System (lightinglab.fi).

Some of these systems employ active collectors that track the sun (Himawari, HSL) while other rely on stationary light collectors. A further difference is the mounting location of the different systems. While Himawari and Parans can be mounted both on rooftops and façades, the other lighting systems are restricted to either roof (HSL) or façade (SCIS).

Commonly these systems can conduct light over distances not exceeding 20 metres (parans.com) (himawari-net.co.jp). Thus a combination of both mounting locations (roof and wall) would be desirable for implementation in high rise office buildings.

Mayhoub and Carter (2011) simulated the use of three commercially available hybrid lighting systems (HSL, Parans and SCIS) under a variety of conditions relevant for all climatic regions ranging from cold, fully humid over temperate and sub-tropic to arid and tropical regions. They discovered great potential for improvement of these systems, as all systems were outperformed by simple tubular daylight guidance systems (TGDS) in all climatic regions, especially close to the equator.

Additionally, they compared the demands that the different systems made to the geometry of buildings where they can be installed. Here, the greater flexibility of fibre based systems compared to TGDS became apparent, although SCIS seems to be difficult to integrate into existing building. Also, once installed, fibre-based systems can better be adapted to modifications that might become necessary, e.g. when the building use changes.

Thus, fibre based systems hold great promise and the challenges regarding efficiency should be addressed. Two problems have been discussed in the abovementioned article. First, guidance technology should be improved. This might become possible with novel materials that allow for fewer transmission losses and accordingly the guidance of light to deeper regions of the building. Secondly, collection efficiency needs to be addressed. All the hybrid lighting systems presented here concentrate light before guiding it to the interior of the building. This prevents them from using diffuse daylight efficiently, making a close tracking of the sun important. Only SCIS can make use of scattered light to some extent, because it has a lower concentration ratio (Mayhoub & Carter, 2011) (Rosemann et al., 2008). Thus, the presented hybrid systems rely on expensive sun-tracking mechanisms. An interesting way around this problem was suggested by Schäfer (2011). Inspired by desert-dwelling Window plants, he suggested dome-shaped anidolic collectors that have a wide reception angle and can concentrate light. This would accordingly minimize, or even abolish, the need to track the sun. The lower concentration ratio (Stine & Geyer, 2001) as compared to the collectors of HSL, Parans etc. could be balanced by coupling light from various anidolic collectors into one light-guide.

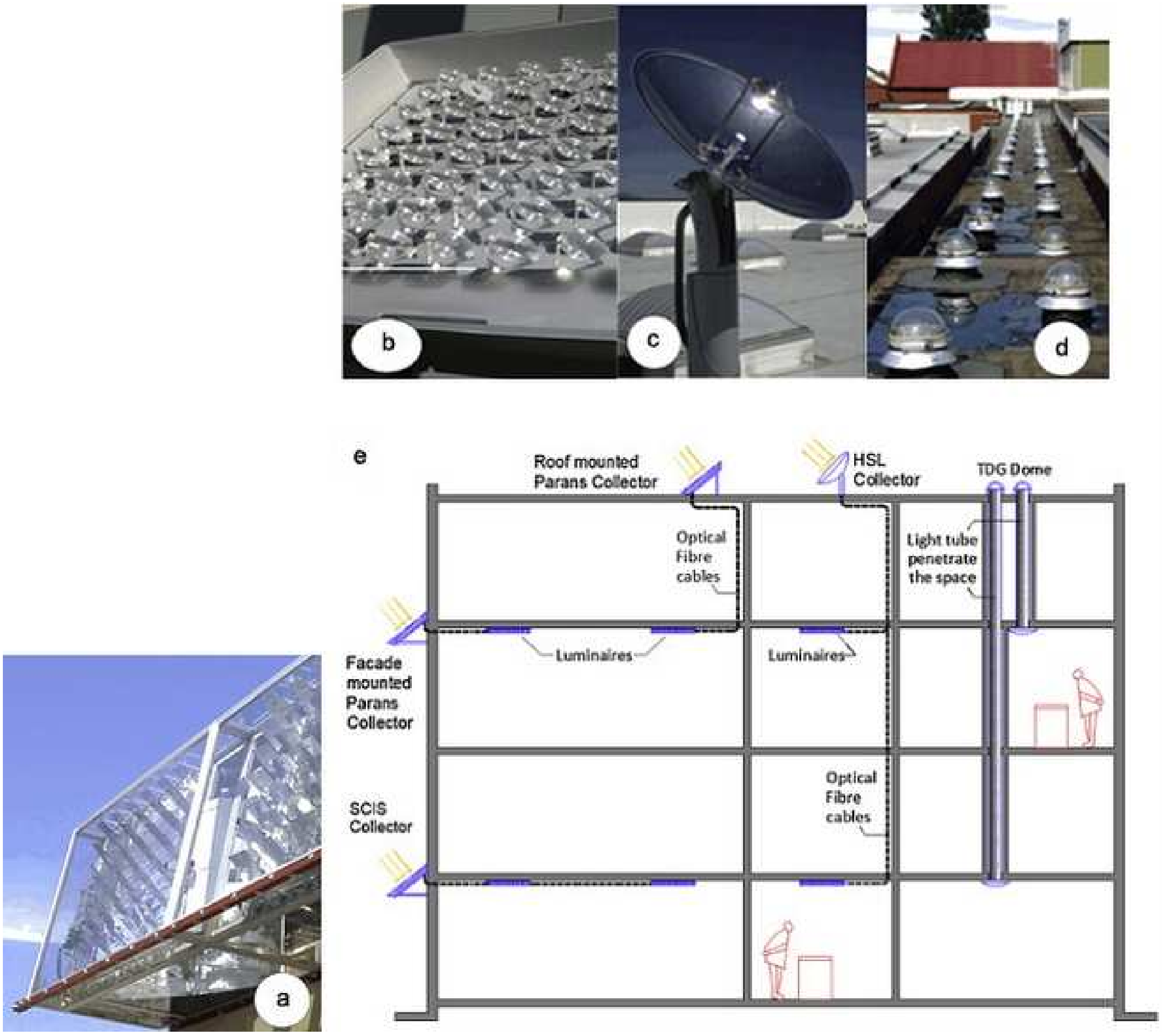

Figure 25: Daylight Guidance Systems. (a)-(d) show collectors of different commercially available systems, mainly hybrid systems that integrate lighting by natural and artificial sources. Solar Canopy Illuminance System (SCIS) (a) is a sun-tracking system with a dual function (artificial and natural) light duct mounted on façades. Parans system (b) and Hybrid Solar Lighting HSL (c) are both hybrid daylight guidance systems with roof-mounted collectors, but whereas HSL tracks the sun, Parans obtains more sunlight by additional, façade-mounted elements. These two systems rely on optical fibres for the transmission of light to the interior of the building. The Tubular Daylight Guidance System TDGS (d) relies on dome-shaped collectors and light tubes that transmit the light from the rooftop. Interestingly, the relatively simple TDGS allows larger energy savings than modern hybrid systems (in most scenarios calculated by Mayhoub and Carter (2011)). (e) provides an overview of the aforementioned systems. © by (Mayhoub & Carter, 2011)

Earthquake proof buildings

Some of the fast growing megalopoleis lie within areas regularly affected by earthquakes (e.g. Karachi and Dhaka) (Salzgitter AG, 2008). New buildings, especially high-rise buildings should of course correspond to this latent danger to save lives and prevent destruction.

Figure 26: Severely damaged office building in Concepción, Chile after the 2010 earthquake. The O'Higgins building (right) had only been inaugurated months before the earthquake; a consternating example indicating that earth-quake proof construction is still widely disregarded[2] even in high risk areas like the "Pacific Ring of Fire". Possibly, integrating other functions, like lighting, into earthquake-proofing structures would increase their acceptance. Strong, bio-inspired optical fibres might pave the way for multifunctional "rocking cores" (Calugaru & Panagiotou, 2011) in high rise buildings. © by imageshack.us

In the aftermath of the Great Japan Earthquake 2011 various approaches used in earthquake proofing of high-rise buildings have been evaluated (Takewaki et al., 2011). Especially viscoelastic dampers (e.g. made of hard rubber) that decouple the building from

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i[2] The owners of the property, however, allege that a tenant has removed columns inappropriately and thereby compromised the stability of the building (e-construcción, 2010).

the ground have been reported to be highly effective in protection high rise buildings. The idea of isolating and dampening large buildings by mounting isolation elements might seem surprising but can be scaled up seemingly *ad libitum.* The largest seismically isolated building is currently the Sabiha Gökçen International Airport terminal building in Istanbul (Sesigur et al., 2008).

There are however various other factors that can contribute to lower damages due to earthquakes. Especially high ductility frames are now widely used for high-rise buildings in seismic prone regions (Paganoni & D'Ayala, 2010). As summarized by Calugaru and Panagiotou (2011), the two presented mechanisms have three basic functions: (i) reduce floor accelerations and forces (ii) control deformations due to robustness in one or two planes (iii) reduce post-seismic damage and make building adaptable.

Usually these ductile frame or “rocking core” occupies a lot of space that is accordingly not available for other uses. Therefore it might interest architects to add functionality to these otherwise dead spaces that only become important during earthquakes.

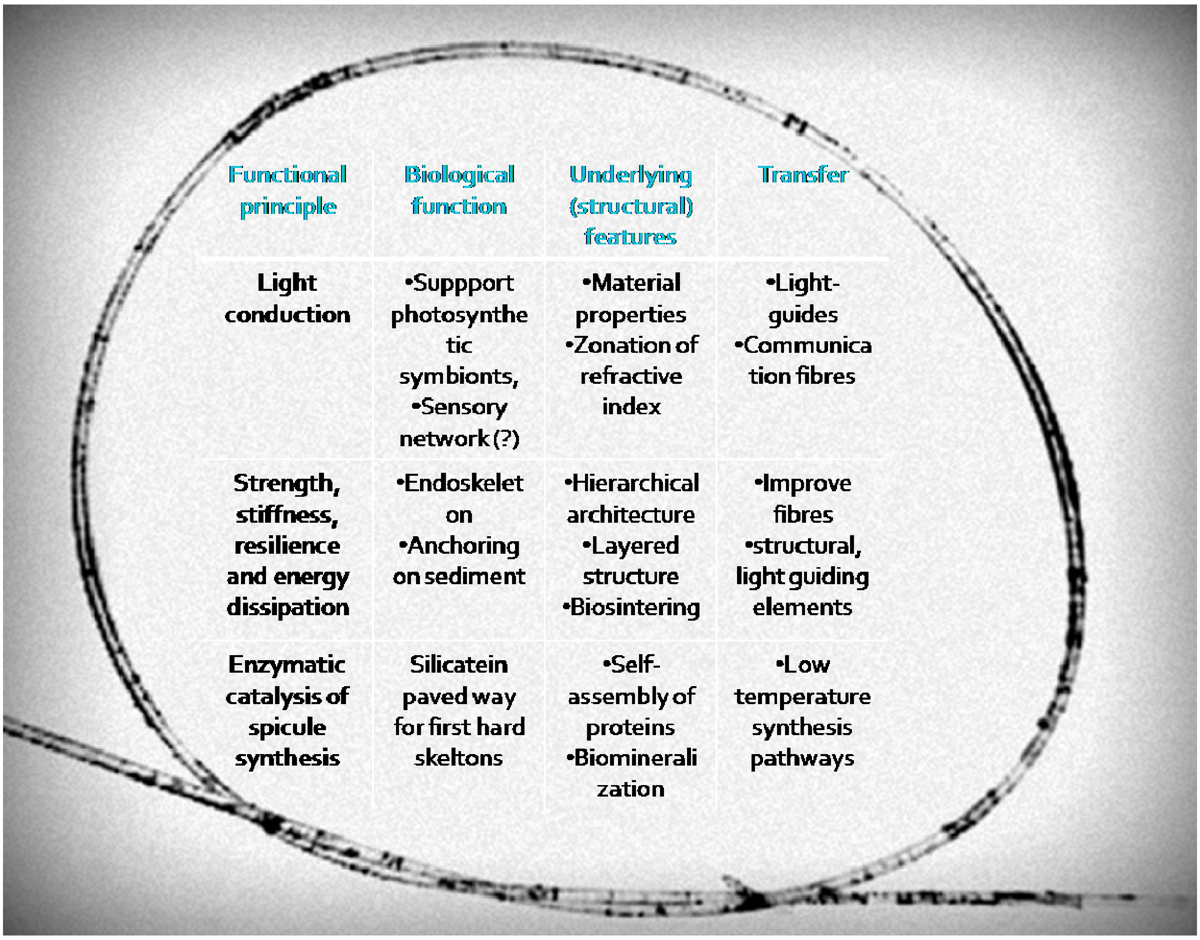
Biomimetics: Sponges and buildings

Sponge spicules conjoin a variety of interesting properties, ranging from mechanical stability and flexibility over transparency and other optical features to a sustainable, low temperature synthesis (Figure 27). Though there have been reports on unexpected optical behaviour, like the white-to-red shift of light transmitted light through spicules (Figure 20b), sponge spicules hold promise as stable and flexible light guides. At the same time our increasingly urbanized environment requires us to design more carefully than ever how we use light and how we expose ourselves to non-visual effects of light. Spongial skeletons epitomize a smart way to integrate additional functions into structural elements. Though siliceous spicules are (if we interpret the evolutionary history of hard skeletons right (cf. (Huiskes, 2000) (Uriz, 2006)) primarily structural elements, they integrate other functionalities and physiologically relevant properties (Figure 7). We could learn from this evolutionary "learning process" regarding integrating structural support and conducting light. After all, nature has maintained and improved this arrangement throughout more than 500 million years. In fact the symbiosis with microorganisms and the presence of a hard skeleton were probably the most important factors for the evolutionary success of sponges (Müller et al., 2007a) Since the symbiosis frequently involves photosynthetic organisms (Rützler & Muzik, 1993)(Usher et al., 2004), light management is essential for a successful mutualistic relationship.

In conclusion, sponges exemplify how to successfully integrate structural and light conducting properties. Their long history and the resulting exposure to changing environmental conditions they survived maintaining a siliceous skeleton (Müller et al., 2009c) suggest that this arrangement is very robust and sustainable.

Considering the scale of sponges and the frameworks supporting high rise buildings, scaling effects and associated problems come to mind immediately. Undeniably the scale of sponge spicules (3 m long at most in *Monorhaphis chuni*) and skyscrapers (up to 829 m, Burj Khalifa) make the suggestion of simple copies sound naïve, and obviously this is not proposed here. This work suggests the incorporation of principles observed in spongial skeletons on two different levels.

On a small scale, the structure of sponge spicules is regarded a good role model for robust glass fibres as desirable for lighting in buildings (Figure 25). Structure as well as synthesis of these elements could imitate spicules closely. Promising approaches have been reported for the imitation of the synthesis of this biomaterial (e.g. (Park & Choi, 2010) (Wang et al., 2012a) (Müller et al., 2009c)). Yet, most attempts have been limited to the nanoscale so far. Therefore, it might be worthwhile to learn from successful attempts to mimic other biominerals at the macroscale. Especially the conceptual clarity leading to successful fabrication of artificial nacre and the apparent possibility to produce the biomaterial at industrial scale with few changes to the pathway of synthesis (Finnemore et al., 2012) hopefully will inspire progress in "artificial spiculogenesis".



Functional principle	Biological function	Underlying (structural) features	Transfer
Light conduction	•Suppport photosynthe tic symbionts, •Sensory network (?)	•Material properties •Zonation of refractive index	•Light-guides •Communica tion fibres
Strength, stiffness, resilience and energy dissipation	•Endoskelet on •Anchoring on sediment	•Hierarchical architecture •Layered structure •Biosintering	•Improve fibres •structural, light guiding elements
Enzymatic catalysis of spicule synthesis	Silicatein paved way for first hard skeltons	•Self-assembly of proteins •Biominerali zation	•Low temperature synthesis pathways

Figure 27: Features of sponge spicules. As discussed earlier, sponge spicules possess an intriguing combination of mechanical and optical properties. Furthermore, their enzyme enzymatically controlled and driven biomineralization serves as an example for technological low-temperature synthesis of hard materials. © background picture adapted from Hermann Ehrlich.

On a larger scale, bio-inspired glass rods, albeit with better fracture toughness, stiffness, resilience and energy dissipation than “normal” glass rods will not replace steel in the cores of high rise buildings. General concepts, such as structural hierarchy, multifunctional structural elements and the general trend to use cheap, abundant base materials in a smart way (information vs. energy, (cf. Vincent, 2008)) can, however, well contribute to better buildings in the future.

Thus, not a clear dichotomy between principles that may be imitated at the two different scales is proposed, but rather a higher degree of abstraction for the large scale than for the small scale.

Table 2: Principles implemented in the proposed light guidance systems. At the level of fibres the natural epitome, spicules, could be imitated by manufacturing in a biomimetic way. Desirable material properties, like flexibility and toughness should be retained in biomimetic fibres. On a higher level, the benefits of hierarchical architecture as well as aspects of sponges with photosynthetic endosymbionts are transferred.

System	Façade element	Complex solution
Level of fibres	• Flexibility, toughness • Lightguide properties • Manufacturing method	• Flexibility, toughness • Lightguide properties • Manufacturing method • Dampening characteristics
Level of system	• Transmission of light to the interior • Protection of internal elements (e.g. solar cells)	• Transmission of light to the interior • Inclusion of fibres for higher level of hierarchy in structural elements

Based on these proposed criteria for abstracting features of spicules, two different ideas for better use of light in office buildings will be presented. First, a façade element for adaptive shading/ lighting of workspaces will be presented. Secondly, a complex solution for the integration of lighting elements into earthquake-proof buildings is outlined. Additionally, the availability of spicule-inspired, robust optical fibres would certainly be of interest for integration into common daylight guidance systems.

Façade elements

A structural element containing spicule like glass fibres could be installed in façades of non-residential buildings for adaptable lighting. The fibres should span from the outside of the façade to the interior allowing for the passage of light. On the interior face of the building they would protrude from the solid matrix they are contained in which allows to bend them. The interior face of this element would be covered a perforated layer of dye solar cells. In the default state, spicules are straight, providing lighting for the interior through the orifices of the perforated solar cell. Under excess sunlight conditions, or when desired, the spicules can be bent to provide light for the solar cells.

This bending could be governed by an external controlling mechanism or triggered by the incidence of solar light in an autonomous response mechanism. As a tentative mechanism to induce bending it is suggested to intercalate expandable elements between the free ends of the fibres. Thus, when excess light irradiates onto the façade, the elements would be expanded, leading to a diversion of sunlight onto the organic solar cells.

Sponge spicules of some demosponges possess lens-shaped extremities pointing towards the exterior (Figure 20e). These were found to be effective at coupling more light into the spicule (Müller et al., 2010). Thus following the pathway of spiculogenesis closely, it should be possible to achieve similar structures to increase the amount of light coupled into the building.

Specifically dye solar cells are suggested here, because they are increasingly cheap to produce but in most cases degrade quickly due to UV radiation, temperature changes and other environmental factors (Ke et al., 2010) (Yoo et al., 2011). These could clearly be minimized inside buildings, for temperature changes are minimal inside buildings and the transmission spectrum for all investigated sponge spicules cut off the entire UV spectrum; a characteristic that should be easily retained in biomimetic fibres.

Following the natural example of symbiotic sponges, the building would thus provide protection for these elements and yet let light of the needed wavelength pass for energy conversion (and here: lighting) in the interior. These panels could therefore provide glare-free lighting for office spaces using natural light. Considering other relevant aspects of workspace design, at least two more features adding to the value of such a panel can be mentioned.

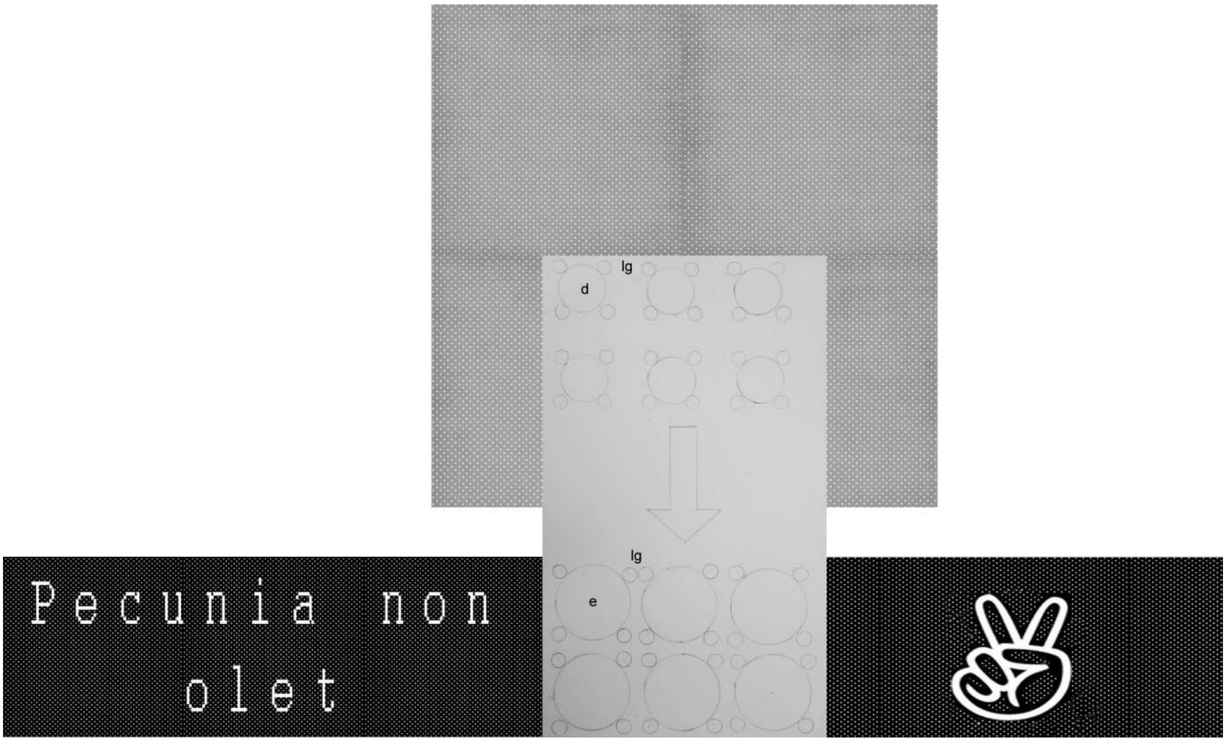


Figure 28: Spicule-panel in open state and differentially shaded state. In the upper part the expandable elements are in their default state (d). Light is transmitted to the interior space for lighting purposes. Upon extension of the elements that are interspersed between the light-guides (lg), the light guides are bent and transmit light to the dye solar cells that line the interior face of the panel, The area where spicules are bent accordingly is dark; no or little light is conveyed to the interior. When only selected glass fibres are bent, messages, patterns, or a corporate logo can be displayed.© background picture by pixelscrapper.com

Control over these panels could be assigned to the person working in that specific part of the office which allows this person to change the light conditions in his/her workspace. As mentioned before, the control over physical conditions at the workplace usually benefits the engagement and motivation of employees (Lee & Brand, 2005). Of course simple sun-blinds can also (usually) be operated by the employees, but these panels could integrate more variable parameters. Specifically they can be operated locally and let light pass differentially at a very small scale.

This flexibility certainly would also add to the design-appeal of such elements, another relevant factor for companies and employees alike. Since the control mechanism could potentially actuate the transmission of light at a small scale, shapes formed by bright and dark areas could be displayed. Depending on the exact location within the office building, anything from the corporate logo alternating with the companies mission statement, or patterns to the liking of employees working in the adjacent space.

These façade elements would hence make use of the mechanical flexibility and good light transmission of bio-inspired glass fibres. Additionally, an analogy between photosynthetic endosymbionts of sponges and the solar cells used can be drawn.

For façades with high incident radiation these elements could thus provide adaptive lighting while preventing solar (heat) gain that is mostly undesired and counteracted by energy-intensive air-conditioning (Li & Tsang, 2008) (J Mardaljevic et al., 2009).

Complex solutions

Earthquake proof buildings usually contain steel structures that help preventing global failure. Of paramount importance to dissipate energy during earthquakes is the ductility and flexibility of this material (ArcelorMittal, 1996). This material property can come into effect in steel-concrete structures like composite walls or mixed design systems including concrete walls and steel or composite beams. During an earthquake the steel structures yield and the concrete elements remain elastic, preserving the overall structure.

Since in many cases the concrete structures occupy large spaces (Figure 29) it would be desirable to add functionality to these portions. In the depicted case below, the massive concrete core in the centre of the building seems to be inviting the integration of a fibre based daylighting system. Light could be conveyed from collectors placed on the protruding core and conveyed to parts of the building that are too deep inside the building to get direct daylight. The mechanical properties of spicules that we might be able to achieve in biomimetic glass fibres are better suited to such design than conventional glass fibres that would fail at lower seismic activity.

Figure 29 The Qube, Vancouver. Architects in Canada agreed on it being one of the most earthquake-proof buildings there (Vancouver Sun, 2004), though unfortunately no analysis has been published. The impressive concrete core is decisive for seismic proofing, and could likely be combined with illumination elements in future buildings with a similar building plan. Taken form Abirkill, Wikimedia Commons.

In most commercially available daylighting systems, light is released to the interior via *luminaires,* structures that remind of conventional light spots but integrate natural and artificial light. This solution could obviously be used here, too. An interesting alternative would be to lay the fibres openly below the ceiling. As has been observed in sponge spicules, light is out-coupled at spines on the surface (Aizenberg et al., 2004) (Uriz, 2006). Researchers explained such modifications by localized syneresis (extrusion of water) due to apposition of a cell to the spicule (Wang et al., 2012b). Syneresis is a process already commonly used in sol-gel synthesis processes (Brinker & Scherer, 1990) and could be adapted to induce similar changes in bio-inspired light guides. The spines should be localized on the surface facing downwards to provide daylight for lighting.

Another application to increase the quality of a workspace within such buildings is the use of green solar architecture, pioneered by Schempp (1997). His approach of using plants and even trees for a healthier indoor climate could be assisted by providing natural light in deep spaces of a building. When selecting plants according to the light available through the fibre daylighting system, this green solar architecture would contribute to a more sustainable building with no energy expenditure after installation.

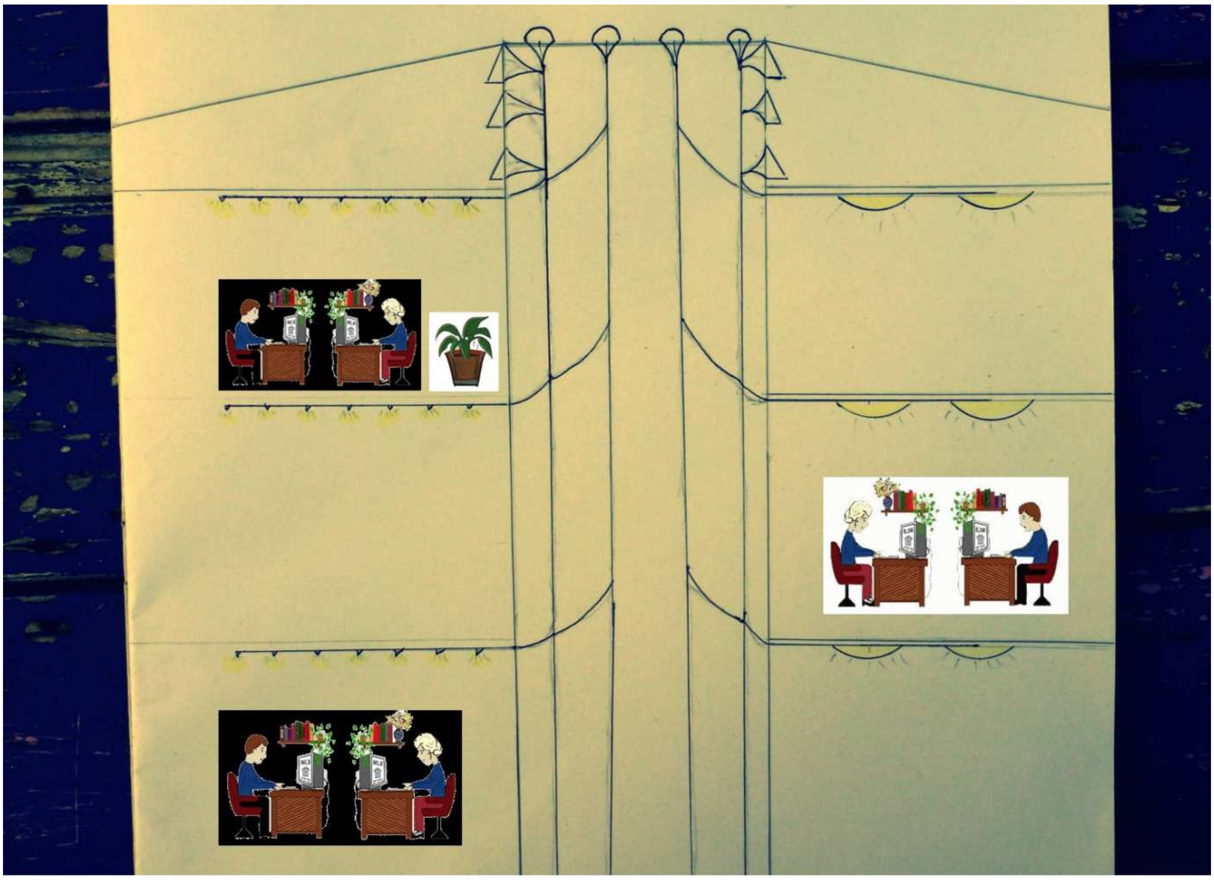


Figure 30: Daylight system integrated into the core of an earthquake-proof building. Dome-shaped light collectors are installed on top of the concrete core, whereas tilted panels line the lateral surface. Glass fibres, potentially in fascicles, guide light to the inside of the building. Light can be diffused by *luminaires* that integrate natural and artificial light sources (right side) or at spines on the lower surface of the light-guide. Spines have been reported to out-couple light from spicules (Aizenberg et al., 2004) and could be introduced by localized syneresis (Wang et al., 2012b). © for inset cartoons by serradinho.com

Summary

Investigation of siliceous sponges and their endoskeleton allows inferring multiple useful concepts for biomimetic innovations. A wealth of research has been published regarding the unique synthesis mechanism as well as structural, mechanical and optical properties of this astounding biomaterial.

Hierarchical architecture and nanostructuring are the two main factors yielding a strong, tough and yet flexible SiO_2-based composite. This has been stressed by contrasting engineered structures and the highly hierarchical skeleton of the glass sponge Venus' Flower Basket.

The low temperature synthesis of spicules can be subdivided into three basic steps, all of which occur within or in close association with specialized cells. Depending on the class of sponges and the type of spicule within a sponge, spicules can become solid in the last step (most demosponges) or retain a distinct, layered structure (most hexactinellids). To appreciate the peculiarities of spiculogenesis, the pathway of synthesis has been contrasted to other mineralization processes.

It became apparent that the enzymatic control of this process is a useful role-model for sustainable low-temperature fabrication methods in nanotechnology, bone replacement materials and for other metal-oxide materials. In a short digression, the synthesis of artificial nacre is highlighted. This calcareous biomaterial has been copied in even more convincing ways than spicules and provides hints for successful biomimetic fabrication of hard materials. Especially the optical properties of this transparent material raised the interest of researchers in communication engineering and laser physics. For the latter field nonlinear-optical properties of sponge spicules including Bragg reflection and a variable fluorescence decay time are interesting. For communication technologies resemblance between spicules and waveguides has triggered research revealing that sponge spicules can conduct light in single- and multimode regimes. The effective guidance of light through spicules, that has been shown to serve a biological purpose in some sponges, suggested an application in daylighting systems.

Buildings have adopted geometries that became only possible thanks to the availability of artificial light in the last century. However, currently we are re-discovering the importance

and comfort of natural light, especially since energy has become less cheap. This trend coincides with an increased awareness of the effect of sustainable workplaces. Medical studies have furthermore pointed out the importance of non-visual effects of light and natural light. In this context various daylighting systems with a focus on commercially available, fibre-based hybrid systems are presented. Another requirement for buildings, namely in earthquake hazard regions, is the presence of seismic proofing structures which are described shortly.

The evolutionary stable strategy to add functionalities to structural elements serves as guidance for the idea to integrate novel lighting concepts into buildings. Mechanically stable spicule-inspired light-guides might be useful for the improvement of current daylighting systems, and additionally pave the way for different innovative daylight guidance systems. Two concepts for the incorporation of these fibres into office buildings are presented. An adaptive element for façades exposed to strong solar irradiation and a whole building solution for a daylight guidance system that aims at adding functionality to seismic proofing structures.

We should raise the wealth of opportunities slumbering in sponges and their spicules in the depth of the ocean to learn more sustainable manufacturing methods, to imitate their astonishing multifunctionality and to create an urban environment that matches our needs.

Glossary

Birefringence: dependence of the refractive index of a material on the polarization and the direction of light passing through the material.

Endoskeleton: internal skeleton, sometimes with elements protruding the surface, antonym of *exoskeleton*.

Endosymbiont: Partner in a symbiotic life-form that lives within its counterpart.

Evolutionary bottleneck: Event that drastically decreases the number of species or individuals.

Extant: describes organisms that are currently living on earth, antonym of extinct

Heterotroph: organisms that cannot fix carbon and thus rely on organic carbon. All animals are heterotrophic, while, e.g., plants are *autotrophs.*

*Hierarchy: (*structural hierarchy) at different length scales different structures are used for construction.

Mesohyl: gelatinous, matrix that occupies the space between inner and outer layer of cells (mainly in demosponges)

Ostium: small pore in the outer surface of sponges, allowing water to flow into the sponge.

Osculum: larger orifice, usually on the superior side of a sponge. Serves as outlet for water and waste products dissolved therein.

Phylum: Systematic unit in the tree of life. Valid phyla include all descendants of a given ancestor (monophyletic group). If the constituents of a group of organisms include not all of these organisms, or additionally include organisms that have closer relatives in another systematic unit, the group is paraphyletic.

Sintering: Diffusion-based process that creates solid materials from powders, usually at high temperatures.

Superelastic: material that can deform drastically without failing.

Syncytium: agglomeration of cells that is delimited by only one external membrane layer, can behave like one cell with multiple nuclei or like many cells with one membrane. Common in glass sponges.

Syneresis: Extrusion or extraction of water or another liquid from a solidifying gel.

Taxonomy: biological discipline concerned with designating and naming biological groups based on shared characteristics.

Tensegrity: structural principle using tensile elements and compressed members to define a space. The compressed elements do not touch each other and are held in place by the continuous tension throughout the structure.

Tribology: science investigating surfaces in relative motion, including adhesion, lubrication and friction.

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