

1 April 2018—Submitted to *American Mineralogist*

2 **HIGHLIGHTS AND BREAKTHROUGHS**

3 **Biosilica: Structure, function, science, technology,**
4 **inspiration**

5 **Konstantinos D. Demadis^{1,*}**

6 ¹*Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete,*
7 *Voutes Campus, Heraklion, Crete, GR-71003, Greece.*

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9 **Keywords:** biosilica; diatoms; sponges; biomineralization; biosilicification
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12 ***E-mail:** demadis@uoc.gr
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14 Biomineralization is a complex ensemble of concomitant phenomena, driving the development
15 of complex biological structures, associating highly organized organic matrices which function
16 as templates for the nucleation and organization at the nanoscale of inorganic nanostructured
17 phases (Sprio *et al.* 2014). These inorganic phases are called biominerals. They can be deposited
18 within the tissues of living organisms (or in the immediate surroundings) as a result of the
19 organism's metabolism (Skinner, 2000). These biomineral-forming organisms are known as
20 biomineralizers. Their impressive diversity, recently reviewed by Ehrlich *et al.*, (2008) boasts ~
21 128,000 mollusk species, ~ 800 coral species, 5000 sponge species (including 550 species of
22 glass sponges), 700 species of calcareous green, red and brown algae, more than 300 species of
23 deep-sea benthic foraminifera and 200 000 diatom species (Mann and Droop 1996).

24 Among the plethora of biominerals, silicon dioxide (SiO₂, silica) in its various amorphous

25 forms is undoubtedly one of the most intriguing and enigmatic, because it is the first and oldest
26 natural bio-skeleton, it possesses unique mechanical properties, and it demonstrates high specific
27 surface area and therefore, unique adsorption properties. Justifiably, these properties highlight
28 silica as the most widely-distributed biomineral. It is worth-noting that silicic acid [Si(OH)₄], the
29 “starting material” for biosilica synthesis, is found in very low concentrations in oceanic and
30 fresh waters, with its levels in the range 10 - 180 μM (Sarmiento *et al.* 2007 and Marron *et al.*
31 2013). Nevertheless, species such as diatoms are able to pre-concentrate it up to concentrations
32 of 19 - 340 mM (!) without any polycondensation (Martin-Jézéquel and Lopez 2003), whereas,
33 *in vitro* we can only form silicic acid solutions in circumneutral pH of ~ 2 mM, before
34 condensation starts (Demadis *et al.* 2014).

35 In the Review “Biosilica as Source of Inspiration in Biological Materials Science” by M.
36 Wysokowski, T. Jesionowski, and H. Ehrlich (PLEASE ADD SPECIFIC CITATION), the
37 authors set the ambitious goal to provide a thorough and comprehensive coverage of
38 biosilicification as an interdisciplinary and multifaceted topic with controversial hypotheses and
39 numerous open questions. Some of these refer to processes prior to biosilicification. Why do
40 biosilicifiers select “Si” as the element of choice (in spite of its low levels in natural water
41 systems)? Precisely, how is “Si” transported from the environment into the cell? How is it
42 possible for silicifiers, such as diatoms, to “pre-concentrate” “Si” (in the form of silicic acid) up
43 to concentrations of 340 mM (compared to a mere 8 mM in laboratory, *ex vivo* experiments), an
44 achievement that would make any inorganic chemist jealous? Other unanswered issues concern
45 the biosilicification process itself. How is biosilica formed in such a controlled manner, in
46 intricate and awesome morphologies (compared to the almost unexceptional spherical silica
47 particles that we make in the lab) and in a timely fashion? What are the biomacromolecules

48 involved, and which is their precise function? Silaffins are well-known biological catalysts
49 (Pamirsky and Golokhvast, 2013) that speed-up the biosilicification process, but what are
50 precisely the chemical moieties that are involved and why?

51 The authors elegantly present the structural diversity of biosilica in some prokaryotes,
52 and also in unicellular and multicellular eukaryotes with emphasis on biosilica of poriferan
53 origin (sponges). They also illustrate strategies and approaches to ways in which the structural
54 wealth and functions of biosilica formers can inspire new breakthroughs in artificial
55 biomineralization and biomimetic technological advances.

56 The Review starts out with a concise description of biosilica of virus, bacteria and plant
57 origin and its practical applications. Next, biosilicification in diatoms follows as source for bio-
58 inspiration in materials and related scientific disciplines. Finally, the current state-of-the-art
59 related to the unique siliceous structures in sponges is discussed, in light of recently-obtained
60 experimental results. Silicofossils are also appropriately mentioned.

61 Based on the composition, morphology and physicochemical properties of a wide range
62 of biosilicas, several bioinspired and biomimetic approaches have been launched. For example,
63 whereas industrial production of glass requires very high temperatures, Nature has mastered the
64 fabrication of extremely complex glass structures at low temperatures. As the Authors nicely put
65 it, this is “a capacity that is far beyond the reach of current human technology”.

66 The Review discusses the interplay among flexibility, strength, hierarchical
67 microstructure and unique optical properties of biosilica. Undoubtedly, these concepts already
68 are, and will continue to be a source of inspiration for future structural and functional biomimetic
69 approaches with the goal to discover the next-generation high performance composites materials.
70 Although there are still several open questions and unsolved puzzles, as mentioned above, these

71 can act as motives for further intense studies and discoveries in the scientific community of
72 chemists, materials scientists, physicists and, of course, mineralogists. In the end, is it possible to
73 mobilize a global and interdisciplinary effort to delineate biosilicification as a universal
74 phenomenon, and utilize the tools of individual scientific and technical fields to advance our
75 knowledge on why and how “Si” plays a vital role in the cycle of Life?

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ACKNOWLEDGEMENTS

78 I would like to thank several funding agencies, such as the European Commission, General
79 Secretariat of Science & Technology (Greece), Ministry of Education (Greece), University of
80 Crete (Greece), which allowed me for several years to carry out exciting research in my Group in
81 the field of (bio)silicification. Last, but not least, I thank Prof. Hermann Ehrlich for being a
82 constant source of information and inspiration, either in personal discussions, or through his
83 high-quality papers and books.

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