

# Complex materials from simple chemistry: biomorphs and biomaterials

Stephen T. Hyde and Juan Manuel García-Ruiz

La conférence du professeur Stephen Hyde à la réunion de l'ECIS (voir *L'Act. Chim.* de janvier 2004, page 19) a été, à notre avis, un moment fort de la réunion de Florence. A notre demande, il a rédigé, spécialement pour *L'Actualité Chimique* et en dépit des nombreuses sollicitations, un résumé qui devrait intéresser beaucoup de nos lecteurs par son originalité. Ils apprécieront certainement aussi la qualité des photos qui l'illustrent. Nous remercions de tout cœur les auteurs de cet article d'avoir fourni à notre revue une version à la portée de tout chimiste.

Nos remerciements vont également au professeur Jacques Livage. Il a relu rapidement le document et nous a confirmé l'intérêt et l'originalité des expériences qui y sont décrites.

Gilbert Schorsch

<b>Résumé</b>	<b>Des matériaux complexes issus d'une chimie simple : biomorphes et biomatériaux</b> Une variété de « biomorphes », semblables à ce que l'on retrouve dans le monde vivant, se forment par co-précipitation de silice et de carbonates alcalino-terreux à pH élevé. Des formes variées, des filaments torsadés et des feuillets ressemblant aux inclusions microscopiques des roches anciennes, communément identifiées comme d'anciens microfossiles, ont été obtenues. Ces « biomorphes » sont des exemples représentatifs de colloïdes minéraux auto-organisés, formant des composites à base de bâtonnets nanométriques de nanocristaux de carbonates et de sphères de silice amorphe colloïdale. La complexité structurale de ces matériaux, avec des ordres/désordres à diverses échelles de taille, rappelle celle de beaucoup de biomatériaux durs, tels que les os.
<b>Mots-clés</b>	<b>Auto-assemblage, colloïdes inorganiques, origine de la vie, croissance cristalline, biomorphes, biomatériaux.</b>
<b>Abstract</b>	A variety of life-like « biomorphs » can be grown by co-precipitation of silica and alkaline-earth carbonates at high pH. Forms include twisted filaments and sheets, that are indistinguishable from microscopic inclusions in ancient rocks, commonly identified as ancient microfossils. Biomorphs are spectacular examples of self-assembled inorganic colloids, forming composites of nm-sized rod-shaped carbonate nanocrystals and colloidal amorphous silica spheres. The structural complexity of these materials, with orientational and translational order/disorder at distinct length scales, is reminiscent of many hard biomaterials, such as bone.
<b>Keywords</b>	<b>Self-assembly, inorganic colloids, origins of life, crystal growth, biomorphs, biomaterials.</b>

The most exciting area of modern materials chemistry at present overlaps significantly with biology: there is no doubt that materials synthesized *in vivo* remain far more advanced than the most lauded « advanced materials » humans can synthesize in the lab. It has been pointed out years ago, and remains true today, that a humble blade of grass far exceeds any synthetic material in its resistance to fracture and ability to withstand extreme stresses without failure. Even the simplest biominerals reveal traits characteristic of structural biological materials, from eggshells to skeletons:

1. composite chemical nature (e.g. proteins and calcite; collagen and hydroxyapatite...);
2. hierarchical and complex structural features, with distinct structure over many orders of magnitude, from the atomic scale, to the mesoscale and micron ultrastructural scale.

The ability of *in vivo* (bio)chemical systems to engineer even modestly complex biomaterials under the (generally)

benign chemical conditions required to sustain life is evidently worth emulating in designing and constructing novel materials. Our work, started many years ago, shares these characteristics with biological matter, yet is *remarkably simple* in chemical terms. The ramifications of the work reach in many directions beyond materials chemistry, both organic and inorganic, including paleontology, liquid crystal and membrane physics. Here we can only describe in general terms the work and curious readers should consult the primary literature for more details.

The syntheses are very simple, requiring only a source of carbonate ions (e.g. atmospheric CO<sub>2</sub>), strongly alkaline aqueous solutions, silica and alkaline earth cations (Ba and Sr, Ca at high T (see references in « Further reading », plus references therein) (see example in *figure 1*). The preparation is as follows. Equal volumes of a solution (typically 10 mM) of the alkaline earth salt (typically the chloride) is added to a silica sol or gel, prepared by aqueous dilution of standard

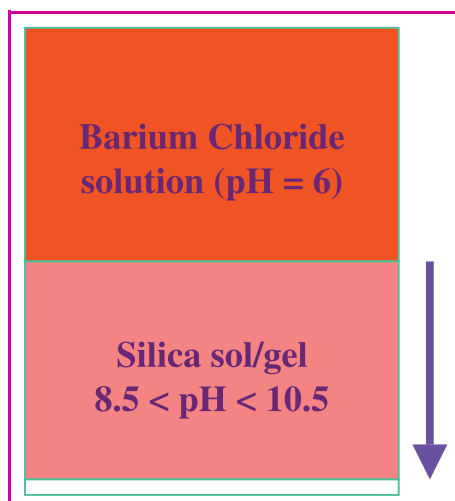


Figure 1 - Schematic diagram of the reaction chamber for production of  $\text{BaCO}_3$ -silica biomorphs.

$\text{BaCl}_2$  solution is introduced to alkaline silica sol or gel. Carbonate species are present, due to dissolution of atmospheric  $\text{CO}_2$  into the solutions. Diffusion provokes precipitation of the composite biomorphs.

water glass ( $\text{Na}_2\text{Si}_2\text{O}_5$ ) solutions (not less than about 1:500 silica:water by volume) to give greater than 300 ppm silica. The experiments have been conducted at a range of pH values; a typical value of ca. 10.5 is used, achieved by addition of small amount of 1 M NaOH solution. The mixture is left open to the atmosphere (with loose-fitting covers to avoid biological contamination), allowing dissolution of appreciable atmospheric  $\text{CO}_2$  in the form of bicarbonate and carbonate species in the alkaline mixture. Diffusion of the cationic alkaline earth species leads to gradual precipitation of carbonate crystallites, intimately intergrown with silica.

The resulting carbonate-silica « biomorphs » exhibit very complex structures, reminiscent of biominerals, with hierarchical structural ordering and composite nature. There is no doubt that the complexity is due to the presence of silica in the system; if the silica content is lower than ca. 300 ppm, conventional carbonate precipitates, including spherulites and standard twinned crystals form. For higher silica contents (irrespective of whether the growth occurs in a sol or a gel) complex morphologies, strikingly dissimilar to conventional precipitates, are found, whose form is dependent on pH of the medium. Most interesting forms result between pH values of 9-11. Around pH values of 10.5, structurally complex « seeds » are visible in the optical microscope within hours. Further growth, results in more regular, larger forms, consisting of sheets and helical filaments (within a day), whose dimensions vary from a few  $\mu\text{m}$  up to hundreds of  $\mu\text{m}$  (typically largest in gels). The helical filaments display morphologies ranging from (racemates of) double helical « ropes » with S-shaped cross-section to fatter, loosely scrolled « worms ».

Their self-organisation at the sub-micron scale and lower is remarkable. Higher magnification images reveal the presence of an external (silica-rich) « skin », sheathing the biomorphs. The skin consists of aggregates of reasonably monodisperse silica spheres, typically 100 nm in diameter. Immersion of the biomorphs in mild acid (dissolving all carbonate material) leaves only this skin, with its complex morphology intact. Within the as-prepared biomorph, aggregates of rod-shaped colloids are seen, coated within a

continuous silica matrix. These rods are typically 400 nm long and 40 nm across. Dissolution of the siliceous component of the biomorphs (in mild base) retains the carbonate material, consisting of packed arrays of rods, with quasi-hexagonal cross-sections, consistent with twinned single crystals of aragonite-type carbonates (witherite, strontianite), consistent with X-ray and electron diffraction patterns (with the long axis of the rod parallel to the c-axis of the orthorhombic crystal). The orientation of the rods varies smoothly throughout the biomorphs, so that they are arranged with a mutual twist between neighbouring rods, reminiscent of the orientational field in blue and TGB mesophases of chiral liquid crystals. Evidently, three distinct structural scales can be found in these materials: complex curved ultrastructures (multi- $\mu\text{m}$  scale), orientationally-ordered mesostructure (100 nm scale) and crystalline atomic ordering in the carbonate crystallites ( $\text{\AA}$  scale).

We are still investigating the physical origins of these extraordinary forms. Related forms can be found in dissipative systems, and the filaments resemble myelin figures formed at the interface between under-swollen lamellar mesophases of lyotropic lamellar liquid crystals and excess solvent. Nevertheless, we believe that our biomorphs assemble due to colloidal interactions between silica and carbonate constituents. A number of scenarios are feasible, though unproven. Possibly, the biomorphs are templated by a preformed silica skin that is grown in the presence of cationic counter-ions. Alternatively, they are the result of (twisted) self-assembly of the carbonate rods. Indeed, they may grow by a combination of both silica and carbonate cooperative assembly.

The implications of these findings reverberate wider than the confines of colloid science. Their resemblance to

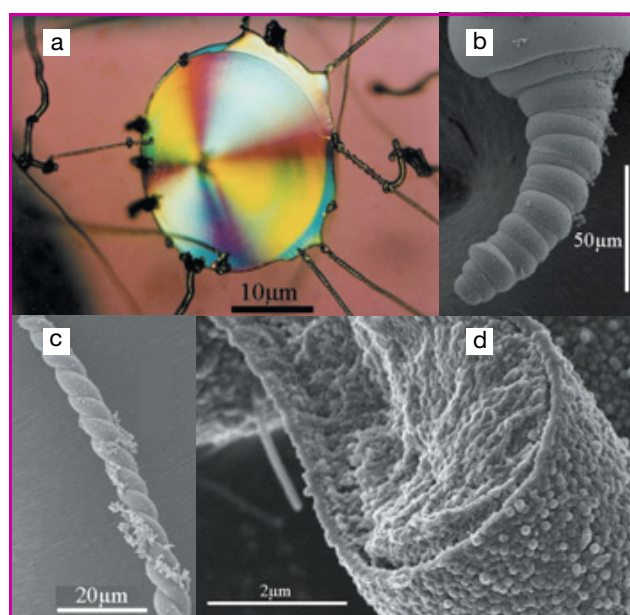


Figure 2 - (a) Optical micrograph showing a silica-carbonate biomorph containing a central (rather flat) sheet and radiating twisted filaments. (b) Field-emission scanning electron micrograph (FESEM) image of a biomorph « worm », (c) FESEM image of a double-helical « rope ». (d) FESEM image showing the composite nature of the biomorphs: an outer silica-rich skin, composed of spherical colloids and the inner carbonate (and silica coated) nanorods.

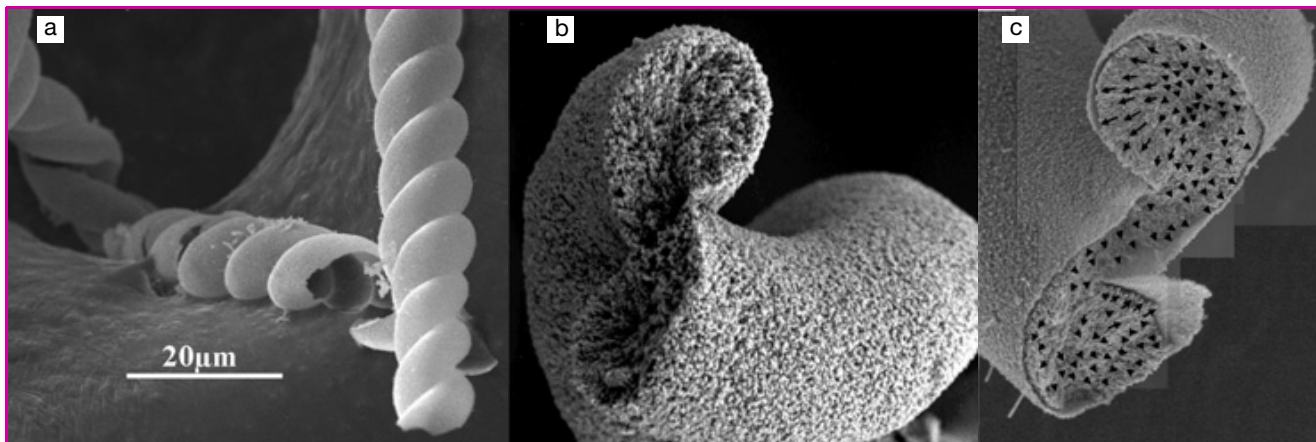


Figure 3 - (a) FESEM images of hollow silica skin left after immersion of the biomorphs in dilute acid. (b) Removal of silica by immersion in weak base, leaving the aggregated carbonate nanorods. (c) As-prepared biomorph, with the orientational ordering of silica-coated carbonate nanorods indicated by the arrows.

biological materials may offer clues to understanding the growth mechanisms of biominerals; a long-held goal of modern materials science. Indeed, the filaments resemble in form and dimension bacteria and supposed bacterial microfossils. Their synthesis *in geo* is entirely plausible in the primitive earth, with its CO<sub>2</sub>-rich atmosphere and abundant hydrothermal sources of water, silica and alkaline earth salts. Further geochemically plausible alteration of these biomorphs can produce organic coatings, whose precursors are *inorganic*! These latter findings challenge current understanding of the genesis of Life on Earth, dated largely by the discovery of « bacterial microfossils » to 3.5 G years. Alternatively, the formation of intact membranes – inorganic or organic – and complex curved forms from purely inorganic precursors offers tantalizing routes to formation of very primitive proto-biological aggregates. Biomorphs are thus candidate substrates for later development of biological Life, alternative to clays or sulphurous precursors discussed to date. Such speculations are exciting, though very difficult to substantiate further without much deep thought and experimentation.

Fashionable though these speculations concerning origins of Life are, perhaps the most important relevance of this work currently is to materials science. The controlled design and synthesis of polymer-crystal composites with complex ordering over various length scales is currently impossible, though our work, and advances of others, suggests that we may be inching closer to the simpler efforts of Mother Nature, who – thanks to many millions of years of trial and error experiments – remains the Supreme Engineer of structurally sound, energetically cheap materials. Perhaps one day soon we too will be able to harness Nature's techniques that allow manufacture of materials whose features surpass even the multifold functionality and resilience of the humble blade of grass!

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### Further reading

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