

# Mineral self-assembly under extreme geochemical conditions and its relevance to primitive life detection

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## 1. Introduction

The detection of primitive life remnants in the older terrestrial rocks is an important research subject to set the timing of life on our planet (*Schopf, 1983*). As space technology advances, it will also be an essential research to know if our sister planet Mars is or not devoid of life, i.e. to know if life is or not a single unique event in the Universe (*McKay et al., 1996*). Unfortunately, identification of actual remnants of living forms from purely inorganic mineral microstructures sharing morphological and chemical properties is a formidable challenge (*van Zuilen 2002; Grotzinger & Knoll, 1999*). Nowadays, the identification of oldest remnants of life in Archean rocks mostly relies on morphology. Certainly, there are other analytical techniques such as isotopic analysis, high resolution electron microscopies to reveal the intimate structure of carbonaceous materials, and chemical identification of molecules unequivocally linked to life (molecular fossils), but all they have problems of consistency. Thus, morphological studies are critical for life detection. However, as we have claimed in 2002, morphology itself is not a reliable tool for the unambiguous identification of primitive life remnants (*García-Ruiz et al., 2002*). More precisely, the claim is that morphology does not contain definitive information on morphogenesis. This assertion could come as a shock to biologists who used to identify fossils by their morphologies, so different that the morphology of minerals and rocks. However, it should be remembered that what we use to identify fossils of ammonites, trilobites or dinosaurs as remnants of life is not morphology but comparative anatomy introduced by Cuvier in XIX century. The problem when looking for oldest remnants of life is that they are tiny and simple pieces of rocks. In this case, we are dealing with simple shapes, poor or no compartmentalization at all, namely microspheres, microrods, tubules, septated tubular shapes, simple helicoids, discoid shapes, and a few other simple shapes. Therefore it is impossible to apply comparative anatomy to these putative fossils. Thus, when identifying the physical structures of possible oldest remnants of life in this planet or primitive life in extraterrestrial bodies, we have nothing else than morphology. This made the unambiguous differentiation of actual life remnants from inorganic biomimetic counterparts a task that must be performed with caution.

The ability of inorganic precipitation processes to produce the characteristic shapes of life i.e. shapes described by fractal branching and continuous curvature, cannot be today considered an astonishing property of matter (*Fig. 1*). Structures with non-crystallographic morphologies mimicking primitive living organisms can be readily obtained under conditions mimicking the plausible geochemistry of a lifeless planet. There are different chemical reactions and physical precipitation/dissolution phenomena leading to micro- and macro-patterning strongly resembling biological organisms in both, shape

and scale. As said above, the community of micropaleontologists accepts nowadays that morphology alone does not inform on biogenicity. The same must be also accepted for those colleagues flattened by laboratory structures made in the laboratory strongly mimicking the shape of primitive life forms. Therefore, any comparison between microfossils or putative microfossils with abiotic biomimetic mineral structures must focus on detailed textures and decoration beyond morphology, as well as on inorganic morphogenesis. Any relevant study to life detection must consider and offer, at least, the following information:

- 1) A demonstration that the geochemical scenario of the rocks embedding the microfossils or putative microfossils is compatible with the chemical reactions invoked to explain the formation of the proposed abiotic structures.
- 2) A comparative study not only of the shape but also of the "decoration" of both abiotic model and putative microfossils.
- 3) A statistical study of the size and size distribution of the community of microstructures.
- 4) A morphogenetic explanation of the mechanism of formation of the complex abiotic structures.

## The symmetry of natural shapes

(classical thought)

### The realm of the crystal

Inorganic symmetry

Polyhedral, faceted shapes

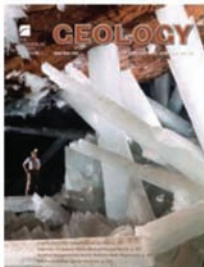
Deterministic angles

Forbidden symmetry operators

$$35 G^3_0 \subset K$$

$$A_{\gamma\gamma} = \text{minimum}$$

Shapes controlled by intimate ordered structures



### The realm of life

Organic symmetry

Sinuuous shapes

Continuous curvature

Unrestricted symmetry

$$\infty G^3_0 \not\subset K$$

$$A_{\gamma\gamma} > \text{minimum}$$

Shapes uncontrolled by intimate internal structure



Fig. 1. The existence of a sharp boundary dividing biology the realm of biology and sensuality and the realm of minerals and cold rationality has pervaded the landscape of science, arts, and philosophy for centuries. Crystals and crystallographic theories have played a major role in the intellectual construction of that false boundary.

Unfortunately, while there are hundreds of studies to analyze the morphology of fossil microstructures from the point view of biology, there are very few studies devoted to exploring the formation of complex biomimetic morphologies by inorganic mineral precipitation (*García-Ruiz, 1999; Brasier et al., 2006; Carnerup et al., 2006; Nakouzi & Steinbock, 2016*). The morphological behavior of inorganic precipitation systems can be classified into three major groups (see Fig. 2). The first one includes all mineral objects in which pattern formation is controlled by the crystal structure of the precipitating mineral phase. This group is the classical domain of mineral morphology (see for instance the view offered by the Dana System of Mineralogy or the book of *Sunagawa, 2005*). It comprises single faceted crystals, twins, ordered dendrites and dendrites were forming when mass transport governs the formation of the pattern. For many years, this group has

been identified with the inorganic world, and it is usually assumed that those natural precipitates displaying well-defined geometry with non-crystallographic symmetry are generated under biological control. In addition to this standard type of mineral patterns, there are two other types, which do not fulfill that "rule." In the first one, the morphology of the precipitates is mainly controlled by the properties of a matrix (in some cases, ordered at the mesoscopic scale) and by osmotic forces working as the driving force for morphogenesis. The most classical organic but abiotic example is provided by the bilayers made of electrically neutral lipids, which exhibit phase transitions and instabilities leading from spherical and ellipsoidal shapes to more complicated patterns. Inorganic examples of this type of materials can be found, but the one I consider most geochemically plausible is obtained when carbonate precipitates at basic pH in silica-rich environ-

## Inorganic biomimetic mineral patterns

### Shape controlled by 3D crystal structure

- Additives adhering preferentially on crystalline faces
- Mesocrystals
- Spherulites
- Competitive crystal growth

### Shape controlled by 2D crystal structure (The template way, top-down approach)

- Liquid crystals
- Crystallization on preexisting 2D surfaces
- Functionalized self-assembled monolayers
- Micelles, by-layers and colloidal structured surfaces

### Shape controlled by transport and chemical reactions

#### Self-Organized bottom-up approach

- Diffusion–reaction patterns, such as Liesegang's precipitation.
- Dissipative structures
- Silica biomorphs
- Chaotic mixing of fluids,
- Fractal viscous fingering
- Diffusion limited aggregation
- Chemical gardens
- Self-propagating particles

*Fig. 2.* The morphological behavior of mineral-base structures is much richer than currently thought. Beyond classical point symmetry groups, there are three different classes of phenomena leading to self-organized and self-assembled materials mimicking the geometry and symmetry of life.

ments. The third group includes all the inorganic aggregates (composed of crystals, molecules, atoms or their clusters) in which the morphogenetic process is mainly controlled by the fluid structures in their growth environment. They are in fact the mineral decoration of these fluid structures, which turn out to be triggered by physical and chemical instabilities. The requirement for the material record of such non-equilibrium ordered patterns is that the kinetics of the precipitation must be faster than the kinetics of pattern formation in the fluid. In consequence, it is expected that this third kind of pattern will form at a very high supersaturation in a precipitating system working far from equilibrium pattern. There are two examples that illustrate very beautifully this kind of pattern. One is the case of manganese and iron oxide dendrites formed by the decoration of Saffman-Taylor interfaces, which display shapes with symmetry properties that are unconstrained by crystallographic restrictions. A second example is the case of chemical gardens, which are tubular precipitates forming by a complex interplay of osmosis, buoyancy and chemical reaction far from equilibrium (Glaab *et al.*, 2012).

## **2. Minerals Under Extreme Geochemical Conditions**

I will discuss in detail in my lecture the above classification of complex mineral self-assembled patterns forming under extreme geochemical conditions compatible with life and prebiotic chemistry. Within this review, I will pay special attention to the following geochemical mineral structures that are relevant to life detection studies:

### ***The chemical coupling of silica with carbonate at high pH that yields complex self-organized biomimetic shapes.***

It has been shown that the chemical coupling of silica - an ubiquitous mineral in the Earth crust- with carbonates creates abiotic, purely inorganic, self-assembled

structures made of millions of nanocrystals building textures of high complexity and showing morphologies with continuous non-crystallographic curvature (García-Ruiz *et al.*, (2002 and 2003). I will review recent studies on the biomimetic effect of silica on carbonate precipitation under alkaline conditions and the geochemical plausibility of these self-organized mineral processes.

### ***The co-precipitation of silica and metal oxides in the form tubular structures***

The reaction between a soluble metal salt and soluble alkaline silicate is known to provoke a chemical precipitate with unusual morphological properties known as silica gardens (Kellermeier *et al.*, 2013). According to the membrane osmotic model, tubules in silicate gardens are produced by the injection of a jet of metal solution into the silicate solution when the membrane cracks as an effect of the internal osmotic pressure at the interface between the two fluids, a fast kinetic precipitation of a metal silicate hydrate occurs and the growth front and the interface becomes materially recorded. In the called silica gardens, the sodium silicate solution is a viscous fluid in which mass convection transport exists and therefore turbulent patterns are created and sometimes destroyed by gravity. It has been shown that these structures can be made under geochemical conditions (García-Ruiz *et al.*, 2017) and it is worth to discuss to which extent this claim can be extrapolated to Hadean and Archean times. I will also discuss how relevant these structures have been in the catalysis of prebiotic chemical reactions (Barge *et al.*, 2015; Saladino *et al.*, 2016).

### ***The formation of stromatolite-like structures (Altermann 2004)***

Stromatolites are very interesting for two different reasons. The first one is that they are the oldest putative signatures of life on the Earth, and the second that they are a good example of the difficulty encountered in decoding the genetic mechanism of natural structures through the study of their morphological features.

Stromatolites are banded mineral structures made up of calcium carbonates that show a certain degree of corrugation. It is clear that contemporarily, they are the results of life activity, as demonstrated by the examples found in Shark Bay in Australia and many other examples elsewhere. Similar structures have been found in very old Archean rocks and they have been considered proof of bacterial activity at those early times (*Allwood et al., 2006*). However, serious doubts have arisen regarding such a straightforward interpretation (*Grotzinger & Knoll 1999*). Stromatolites, like other corrugate patterns, can be considered (at least within a certain range of scale) fractal structures and they can be characterized by a given fractal dimension.

The stromatolitic structure is paradigmatic case for the misuse of fractal geometry in natural morphogenesis studies. The recent introduction of fractal geometry to measure biological and geological patterns up to now described as just complicated or intricate patterns is a new and powerful tool in modern Natural History studies. Unfortunately, in many cases the meaning of these fractal studies has been extrapolated beyond reasonable limits for a geometrical tool. Considering Euclidean shapes, Could one infer a tree-type genetic mechanism for a tennis ball because they scale with a power of 3 like the shape of an orange does?. The answer is obviously no because geometry does not contain in itself genetic information Exactly the same occurs when comparing fractal shapes, with the tenuous (but important) difference that the power is usually a fractional number. Even in those serendipitous cases where the geometrical study yields a fractal dimension characteristic of a well-known physical mechanism such as diffusion limited aggregation (DLA), the problem can only be considered closed by a physicist, who arrives at the conclusion that a Laplacian-type mechanism must be involved in the generation of the structure. However, for scientists of Natural History it then starts to be a real pro-

blem, because Saffman-Taylor instability, diffusion controlled accretion phenomena and electrical conduction all share the same Laplacian mechanism. It is of the utmost importance to select among these when explaining the origin of biological or geological structures.

### **The formation of fractal dendrites of iron and manganese.**

This group the well-known manganese and iron oxide dendrites (usually called pyrolusite dendrites) are unique in the emulation or fossil superior plants. They are non-crystallographic dendrites reminiscent of fern leaves, which exhibit fractal properties, as do fern leaves. These amazing forms, with a fractal dimension close to the golden number ( $D_f = 1,70$ ) or diffusion limited aggregation can be observed in most Natural History museums and many mineral stores. However, when observed in the field, these amorphous oxides and oxyhydroxides exhibit many other form -always non-crystallographic ones- within a wide range of fractal dimensions. The formation of all these shapes can be explained as the result of a viscous fingering process. This process is triggered by Saffman-Taylor instabilities, which form when a low viscosity fluid pushes another one of higher viscosity. When slurries of dissolved manganese and/or iron II entrapped in rocks (particularly inside cracks and sedimentary laminations) is invaded and pushed by an oxygen-rich fluid. All these fractal forms are easily obtained, as has been experimentally demonstrated (*Fig. 3*). An alternative explanation based on a DLA-type mechanism has been also proposed.

### **Pyrite trails.**

*Tyler & Barghoorn, (1963)* first reported these bizarre but rather common microstructures in Precambrian rocks made of pyrite grains with appendages. *Knoll & Barghoorn, (1974)* and other groups later studied them in detail. At least, four different types of pyrite trails in cherts in Precambrian and also in Archean rocks have been described. The

formation of these pyrite trails is still unknown. Revealing their origin could yield very interesting and novel information about the physicochemical conditions in the primitive Earth, and for the Proterozoic samples, also precious information either on the ecosystem or the taphonomy of primitive living organisms.

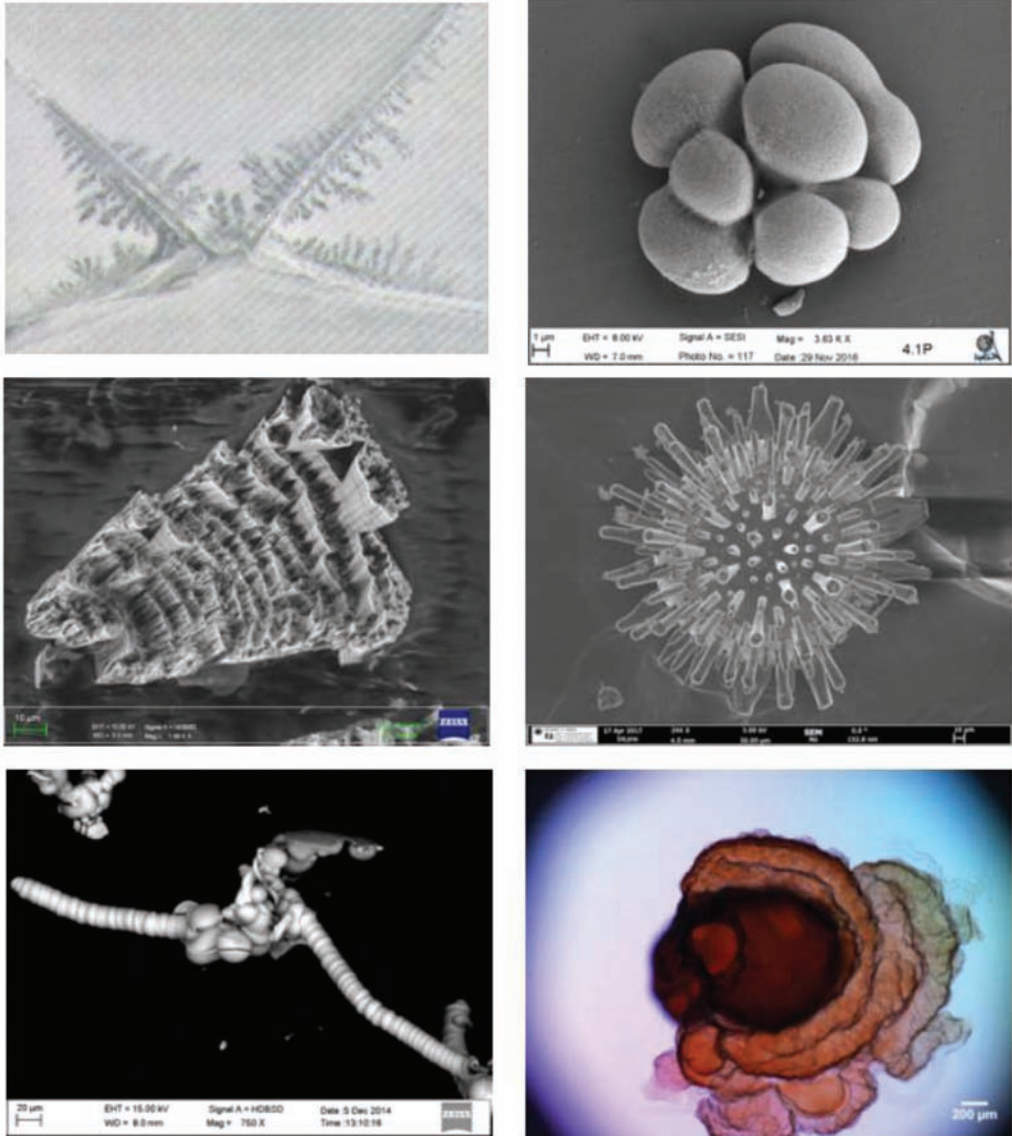


Fig. 3. Several examples of self-organized biomimetic structures. All pictures are from the lab's author.

### **Globular and embryo-like structures.**

Polymeric compounds have been shown to induce splitting of the ends of elongated single crystals. These have been shown for the case of barium, strontium and calcium carbonate but also for calcium phosphates (*Kniep & Simon (2007)*). The continuous splitting leads the formation of dendrites with non-crystallographic branching that ends into random globular structures or embryo like cell partition (*Yin et al., 2007*).

### **Calcite single crystals with non-singular faces.**

The ability of bacteria to induce distinctive features in the morphology and crystal arrangement of  $\text{CaCO}_3$  precipitates has been widely reported. The subject is of great importance in the interpretation of limestone petrogenesis and a huge literature on field and laboratory studies has been published (*Buczynski & Chafetz, 1991*). The catalogue of forms included crystal bundles, rod-shaped crystals, dumbbell-shaped crystal aggregates, barrel-like, comb-like and brush-like forms (*Fig. 3*). There is no doubt that these bizarre habits of calcium carbonate occur linked to bacterial activity. In fact, they can be also observed in mineralized tissues of higher organisms, as they appear, for instance in eggshells, exoskeletons and otoliths. When looking in detail for the origin of these forms, it is clear that they arise because of the interaction of calcite and aragonite crystal faces with biological macromolecules. I will discuss how prebiotic chemical compounds and silica are able to mimic exactly the textural and morphological features of biological induced calcium carbonate precipitation.

### **Acknowledgments**

This study has been supported by the Ministerio de Economía y Competitividad of Spain through the project CGL2016-78971-P.

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