Global to nano-scale relevance of Ca-carbonate biosignatures

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This short note addresses the recent advances in geobiociences and nanotechnologies focused on developing the capacity to resolve at very fine scale mineral biosignatures and traces of life left behind long after living organisms are gone. In recent years, expansion in research on early terrestrial life as well as on organic compounds found in meteorites has delivered a wealth of high-magnification and high-resolution data to aid characterization and detection of the most puzzling biosignatures, which led to a number of scientific publications related to this topic. Therefore, geobiocience-oriented international journals are flourishing, and conferences on these subjects occur regularly throughout the world.

Scientific progress is often fuelled by the development of industrial needs and demands. Nanotechnology, as one example, is focused on discoveries of new materials and novel properties of the existing materials in which size, shape, orientation pattern and other morphological properties are of critical importance in determining their function (e.g., magnetic, optical, and mechanic). In the effort to control a variety of parameters during the synthesis of inorganic materials, it is important to study how these materials were formed in nature. Ca-carbonate (CaCO$_3$) is an example of biogenic inorganic compound with a wealth of micro-/nanostructures and unique properties that have been extensively investigated in nanotechnologies.

Ca-carbonate minerals are among the most abundant minerals on Earth and their study has a great scientific relevance because they represent the most frequent type of biomineralization; they form extensive accumulations of biological and geological origin and are of an obvious economic interest (e.g., oil industries and nanotechnologies). Carbonates have also been identified on Mars surface using hyperspectral remote sensing techniques and, more recently by ground-truth analyses from MER Spirit rover and Phoenix lander (Niles et al., 2013). Martian carbonates may hold important clues about the evolution of the planet, possible history of life and habitability (i.e., potential to develop and sustain life). On Earth, Ca-carbonate is the most abundant biomineral formed directly via enzymatic control or indirectly via metabolic activity, followed by silica, Ca-phosphate and few others. Natural Ca-carbonates may occur as anhydrous polymorphs including vaterite, aragonite, and calcite, whereas, as hydrous polymorphs, they may occur as monohydrate calcite, ikaite, and amorphous calcite carbonate (ACC), with calcite showing the highest thermodynamic stability. All these Ca-carbonates can be precipitated through biologically induced and controlled mineralization processes. Metastable crystalline Ca-carbonate is often bio-induced and it is relatively rare in nature as well as in the geological record. As such, it may be difficult a direct observation due to its submicron size and since it easily and completely converts into calcite over the time. For instance, ikaite may instantaneously convert into its polymorph glendonite (granular calcite) moving from few to 6°C. Ca-carbonate mineral in a biological system is well known to be produced in form of nanoparticles, and nanoparticles have a thermodynamic behavior that can follow different equations of the bulk materials and thus in some cases forming more stable varieties. Therefore, when formed under biological control, metastable Ca-carbonate minerals (including nanoparticle clouds) can be stable for the entire (mineral) lifetime (if adequate conditions are maintained) when formed under biological control. These conditions are much more common than it is currently believed.

Since bio-crystallized Ca-carbonates are commonly occurring as nano-scale minerals with specific morphologies and remarkable mechanical properties, their formation processes became focus of industrial and technologic research in the synthesis of advanced materials. The mechanical properties of aragonite fibers are widely used as filler in paper and biomedical materials. Hence, nanotechnology and environmental sciences (e.g., bioremediation) demonstrated that a wide range of natural and artificial biomolecules are able to template mineral nucleation of micro- and nano- Ca-carbonate particles, as well as to control their growth and spatial alignment. It is well know that microbes can promote Ca-carbonate formation. Researchers are striving to address the microbial biogeochemistry involved in the formation of Ca-carbonate nanoparticles, and recent discoveries have provided the evidence for their biogenicity and biosignatures potential (Benzerara et al., 2006; Lepot et al., 2008; Westall et al., 2011). The Ca-carbonate nanoparticles when associated to fossil microbial remains are now interpreted as biogenic signature of photosynthetic activity.

Using modern in situ high-resolution techniques, such as synchrotron X-ray and high-resolution electron microscopy, 30-100 nm-sized aragonitic nanoparticles...
have been observed within modern biofilms forming calcareous microbial mats and stromatolites in the alkaline Lake Van (Turkey) (Benzerara et al., 2006). This nano-aragonite has been interpreted as a distinctive signal of photosynthetic activities in microbial mats and proposed to be a key biosignature of photosynthesis in the geological record. By using in situ high-resolution techniques, among others High Resolution Transmission Electron Microscopy (HRTEM), Secondary Ion Mass Spectrometry (SIMS), and Synchrotron Radiation, to address their biogenicity, Lepot et al. (2008) and Westall et al. (2011) recently reported for the first time reliable biosignatures in form of aragonitic nanoparticles from 2.72 and 3.33 billion-years-old rocks in Western Australia and South Africa, respectively. The South African aragonitic nanoparticles are particularly important as they represent the oldest known natural aragonite (Fig. 1). These pioneering works have the purpose to illustrate the potential of the nanoparticles study in geo-materials coupled with advances in high-resolution instrumentation. The Ca-carbonate nanoparticles might have a great potential as a biosignature of biological processes (i.e., photosynthesis) and, therefore, they could be of great utility in early life research and astrobiology.

The technical advances present unprecedented opportunities for dissecting causal relationships between patterns of biological and environmental interactions recorded in the sedimentary record of the deep geologic time. As paleontologists we can take advantage of the extraordinary opportunities offered by combining nano-scale investigations, high-resolution microscopy and nanotechnology, which will definitively provide opportunities for the next generations too.

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