Biomineralization in hydrothermal systems

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Due to heat production in the bulk Earth, temperature increases with depth. Convection cells of water between the surface and the Earth's interior remove internal heat thus generating hot aqueous fluids which can reach temperatures of up to 400°C. These high temperature hydrothermal fluids are discharged into the ocean, often as "black smokers" characterized by steep gradients of temperatures between 400°C and 2°C over centimeter spatial scales. Abundant minerals grow in such temperature gradients leading to the formation of hydrothermal chimneys. The sequence of nucleation and growth of the main mineral phases (e.g. pyrite, sphalerite, chalcopyrite,...) is relatively well known. I will first discusss the mineral assemblages observed in these systems using a geochemical code (Chess). Predictions regarding nucleation and growth of accessory minerals, some of them having not been described in these environments yet, will then be made using the same geochemical code. This modeling will be used in further studies as a guide for searching such phases in natural samples collected from oceanographic campaigns lead by IFREMER, Brest, France.

Hyperthermophilic microorganisms (i.e. optimally living above 80°C), mostly archaea, inhabit hydrothermal chimneys, although their direct imaging within the porosity of the rocks has not been accomplished yet. Organic matter is observed in close association with minerals, in particular pyrite, but it is not clear whether that organic matter is related to hyperthermophilic microoganisms or to abiotic organic synthesis which is known to occur in these natural environments. The main questions we will discuss in this lecture are thus related to the nucleation and growth of minerals induced by such microorganisms living under the most extreme conditions (for life) as listed below :

(1) Are biomineralization processes at work in these hydrothermal chimneys?

(2) Can mineral traces of hyperthermophilic microorganisms be recognized in these environments?

(3) What is the interplay between biological and abiotic synthesis of reduced carbon compounds in these systems and which role minerals might play in those processes?

Among archaea inhabiting hydrothermal chimneys, the genus Thermococcus been shown to be dominant at several locations. In recent experiments specifically designed to study the biomineralization by hyperthermophilic microoganisms, we have shown that nucleation and growth of pyrite and of greigite occur at 85°C in close association with cells of several species of the genus *Thermococcus*. FeS_2 pyrites were formed by reaction of sulfur-rich vesicles with Fe^{2+} and since most vesicles were still attached to the cells, there was a remarkable co-localization of pyrite minerals with the cells. Fe_3S_4 greigite precipitated on extracellular polymeric substances (EPS) in the immediate vicinity of cells and we could show that the adsorption of Fe^{3+} on the EPS prevented pyrite precipitation and favored the formation of greigite. This result is particularly significant because greigite has a strong catalytical potential toward CO_2 reduction thus promoting abiotic organic synthesis. Such situations in which biominerals promote abiotic organic synthesis illustrate the complexity of the abiotic/biotic conundrum of the organic matter production in hydrothermal systems.Thermodynamic models using Chess show that the nucleation of greigite is not favored in any possible precipitation sequence and that the presence of iron (III) phosphate on EPS might be the only way to prevent the thermodynamically stable pyrite formation. In that sense, greigite in the environment of hydrothermal chimneys could consitute a biosignature but this difficult notion will be then discussed.

In addition to the metabolism of S(0) reduction described above, both metabolisms of Fe(II) oxidation and Fe(III) reduction are favourable to biomineralization. Iron (III) reducing bacteria and archaea are particularly interesting because they commonly produce magnetites. Magnetites are extremely valuable environmental markers amenable to concentration by magnetic separation techniques permitting the accumulation of sufficient material for detailed geochemical studies often lacking due to low abundances of biominerals. We recently have demonstrated the quality of the magnetite geochemical biomarker in the specific case of (non hyperthermophilic) magnetotactic bacteria. Although not directly relevant to hydrothermal biomineralization, I will show how this example might contribute to the strategy of search for biomineral signatures in hydrothermal chimneys.

Finally, in a more prospective way, I will discuss three applications that might be generated by a better understanding of nucleation and growth of minerals induced and/or controlled by hyperthermophilic microoganisms.

(1) Hyperthermophilic strains have the potential to immobilize metal elements in insoluble mineral phases. Having a bioremediation reactor based on biomineralization by hyperthermophilic microorganisms would enable all the advantages of bio processes (e.g. green chemistry, high specificity) while taking advantage of better kinetics and avoidance of any contamination of the reactor with undesired microorganisms.

(2) Interactions between minerals and microorganisms thriving at high temperature could be highly beneficial for bio-extraction of specific elements from minerals in bio-hydrometallurgical processes.

(3) One particular area which has not been explored above 90°C yet is the bio-production of solid phases of interest for technological applications such as catalysis, electrochemistry (e.g. battery materials) thus filling a gap existing between low temperature bio-assisted synthesis of technological nanomaterials and higher temperature hydrothermal synthesis or processing. The bio-assisted synthesis of materials above 100°C could allow to combine the interests of two synthesis routes for now still antagonistic.