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### Sponge-like hosted mineralization on silica gardens: Implications for natural systems

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The so-called sponge-like porous microstructures are common in natural systems involving silica precipitation [1]. In several cases, these microstructures can act as a host to the mineralization of authigenic phases such as clay minerals, iron oxo-hydroxides and sulfides. Laboratory modelling of these processes can be useful to understand the silicification processes and/or the formation of authigenic phases in small confining systems (ie. during the early diagenesis). In this work, materials related to natural honeycomb or sponge-like structures have been synthesized from hollow silica fibers by using reactions kinetically driven by the silica garden process [2]. The dependence on the average composition of the precursor sol and the dissolving salts has been analyzed.

The fibers were obtained by adding different Fe and Al salt crystals. Two situations, oxic and anoxic, have been analyzed. In the later case, sodium dithionite was used to limit the extent of Fe<sup>2+</sup> oxidation. Likewise, the starting solutions contain Si, K, and Mg. In most cases, the fibers consist of a hierarchical structure composed of an amorphous silica matrix and an internal honeycomb structure filling the inner space. The growth of these microstructures takes place by means of a process of heterogeneous nucleation at the sites provided by the porous silica matrix and show variable mineralization from outer to inner silica walls.

Further structural and compositional characterization was done at several resolution-scales by TEM, SAED, SEM-EDX, TOF-SIMS and XPS to determine the internal architecture of the fibers as well as the related structural domains. A novel procedure based on the application of the Rietveld method to polycrystalline SAED diagrams was applied in order to structurally characterize the nano-sized crystalline domains hosted by porous mesostructure. These analyses show that in many cases, the crystals have a layer-silicate structure (2:1) C/2m, related to celadonite, as well as iron oxo-hydroxides. As a consequence, this study suggests that silica gardens can be a good laboratory analogous to understand the processes of authigenic minerals formation at low temperature, in particular clays and iron oxides.

#### References

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### Competition between iron- and carbon-based nanoparticle carriers for trace metals in freshwater, seawater and sediment porewaters

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Here we show that geochemical nanophases (natural colloids) are the dominating phase for most trace elements in freshwaters, coastal seawater and sediment porewaters. These colloids are mainly composed of two carrier phases, organic dominated and iron dominated colloids, and the relative importance of these two depends on pH, dissolved iron and carbon concentration and redox conditions. Different elements are shown to be prevailing in the different nanophases e.g. Cu, U and I is preferentially bound in the organic rich nanoparticles, while Pb, P and V are dominated by the iron rich colloids. It is mainly in the lower nanometer scale that these colloids are found and it is also the small dimensions that makes them so efficient in binding the elements. It is by development of a combination of a relatively mild size fractionation technique (Flow Field-Flow Fractionation) coupled on-line to a high resolution ICPMS that new knowledge of metal reactivity of these colloids have been gained for 47 elements. Thermodynamic speciation modeling of the experimental results show good agreement.

