Holographic interferometry study of the inhibition of gypsum dissolution

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The knowledge of the dissolution properties of gypsum in aqueous solutions is of primary importance in many situations, among which the weathering of rocks, the gypsum karst formation, the quality of drinking water, the scale formation in the oil and gas industry, and the liberation of calcium ions, useful for the geological storage of CO_2 .

In standard dissolution experiments, the mineral is dissolving in stirred water. So the dissolution kinetics is blurred by diffusive and convective contributions. For hard minerals, dissolution is so slow that it drives the whole kinetics and the convection contribution can be neglected. But for softer minerals like gypsum, dissolution, diffusion and convection timescales are of the same order of magnitude and their respective contribution can be difficult to distinguish.

We have collected dissolution rates of gypsum in water measured by various methods found in the literature. The deduced dissolution rate constants span over several decades. Therefore we have analysed the hydrodynamics of the experimental setups, eliminated the convective contribution and deduced from them the pure surface reaction rate constant of gypsum in water. It appears to be much smaller than expected from the literature results. An holographic interferometry experiment, performed in still water, is carried out and enables to measure directly this rate constant. Both values agree within experimental uncertainty.

We have made use of this methodology to investigate the influence of various salts, known for their calciumcomplexing influence, on the dissolution rate of gypsum. These agents provoke a decrease of the surface reaction rate constant of gypsum of up to more than one order of magnitude (cf. Fig. 1).

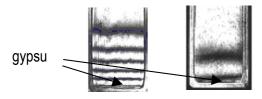


Figure 1: Holointerferograms of the dissolution of a gypsum sample in pure water (left) and in a phosphate salt aqueous solution (right) at rest.

Viruses: A key role in microbial mat mineralization

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In microbial mats, microbes mediate the formation of mineral layers, most commonly carbonates, through the process of organomineralisation, and in doing so enhance their preservation potential in the geological record; Cell walls, sheaths and extracellular polymeric substances (EPS) matrix are currently thought to be the main templates for such mineral precipitation. Nanometer-scale spheroids (20-200 nm) have been widely found in the geological record and are thought to initiate precipitation. Previously, these nanospheres have been interpreted as fossilised bacterial remains [1] such as nannobacteria, proteins and, more recently, EPS [2].

This study focuses on organomineralisation in a living, hypersaline, non-lithifying microbial mat from Lagoa Vermelha, Brazil, where mineralized nano-scale spheroids have been found. Correlative NanoSIMS and TEM analyses of the same sample area show a one-to-one correlation of nanoscale spheroid morphology, organic material and mineralogy. These results indicate that viruses, which cause the death of the bacteria and then become mineralized upon release, are the most likely origin of these spheroids. The infection of microbial mats by viruses appears to be significant in preserving one of Earth's most primitive and enduring ecosystems in the fossil record.

[1] Kirkland, B.L. Lynch, F.L. Folk, R.L. Lawrence, A.M. & Corley, M.E. (2008) Nanobacteria, organic matter, & precipitation in hot springs, Viterbo, Italy, distinctions & relevance. *Microscopy Today* **16**, 58–60. [2] Benzerara, K. Menguy, N. Lopez-Garcia, P. Yoon, T-H. Kazmierczak, J. Tyliszcazak, T. Guyot, F. Brown & G.E. Jr. (2006) Nanoscale detection of organic signatures in carbonate microbialites. *Proc. Natl. Acad. Sci.* **103**, 9440–9445.

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