



## Origin of the formation of calcite on rock art: abiotic or biotic process?

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Palaeolithic rock art present in the south-western of Europe (Lascaux, Altamira, ...) is threatened by numerous alteration phenomena including very often the formation of calcite ( $\text{CaCO}_3$ ) in the karstic caves. This phenomena is particularly well known in the cave of Arcy-sur-Cure (24500-28000 BP, Yonne, France), where calcite formation was followed during the last 20 years. These studies revealed the presence of at least two calcite types: one thin translucent yellow layer protecting the paintings as a varnish and one thick opaque white layer obstructing the visibility of the paintings. However, the origin of these calcites was not determined.

Calcium carbonate minerals are formed either by biotic (biomineralization) or abiotic processes (dissolution-recrystallisation). Concerning the biogenic calcite, many bacteria were involved in calcite formation (*Bacillus cereus*, *B. megaterium*, *Pseudomonas calcis*, cyanobacteria, ...). At least three kinds of macromolecules have been implicated in the biomineralisation process: proteins, polysaccharides, and membrane lipids (Wustman *et al.*, 2003). Interestingly, cyanobacteria are both at the origin of the calcite formation and an early life form on Earth. The abiotic formation of calcite and crystal morphology depends on several conditions ( $\text{pCO}_2$ , pH, temperature, ...). The two

main steps (nucleation and crystal growth) are affected by these factors. The crystal morphology is not sufficient to assess the origin of the calcite.

In order to assess the origin of the different calcites from the cave of Arcy-sur-Cure, we have submitted these samples to a multidisciplinary study including microscopic, spectroscopic and microbiological methods. The morphology of the yellow and the white calcite are established by microscopic observation at different scales by SEM and TEM (Chalmin and Menu, 2003). The elemental composition is also measured by PIXE and the structure by XRD, IR and Raman spectroscopy (Reiche *et al.*, 2003). The bacterial effect on the calcite mineralization is assessed by culture and molecular methods. Both total DNA and micro-organisms were isolated from the surface water of underground lake. *In vitro* experiments of biogenic calcite formation (using isolated bacteria) will allow comparing its morphology and structure with the yellow and white calcite.

These data will be used to model the biogeochemical mechanisms of the two types of calcite formation. And thanks to this analytical approach and to *in vitro* synthesis, it will be possible to establish a conservation strategy for rock art menaced by calcite formation.

#### References:

Wustman, B.A., Weaver, J.C., Morse, D.E., Evans, J.S. (2003) *Langmuir*, 19 (22): 9373-9381

Chalmin and Menu (2003) *Journal of Measurement Science and Technology*, Vol.14, 1590-1597

Reiche *et al.* (2003) *Journal of Measurement Science and Technology*, Vol.14, 1608-1619