# Interlayer structures and binding conformations in the interaction of a tetracycline antibiotic with a smectite clay

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Interactions of antibiotics with soil particles can influence their environmental fate and the extent of their potential effects on soil and aquatic sensitive organisms. Of specific interest are their sorption mechanisms within smectite clay interlayers [1]. We employed a combination of experimental and modeling techniques to investigate the molecular interactions of Oxyteracycline (Oxy) with montmorillonite. Sorption experiments were conducted with a synthetic Fe-free Na-montmorillonite [2] at pH 4, pH 6, and pH 8. The pH-dependent changes in the clay interlayer structures as a function of adsorbed Oxy was revealed through X-ray diffraction pattern analyses of the Oxy-clay systems. These XRD results in conjunction with molecular modeling Monte Carlo simulations were used to probe for the binding conformations of the different Oxy species within the clay interlayer. This study provides for a mechanistic depiction of the sequestration of antibiotics within soil clay particles.

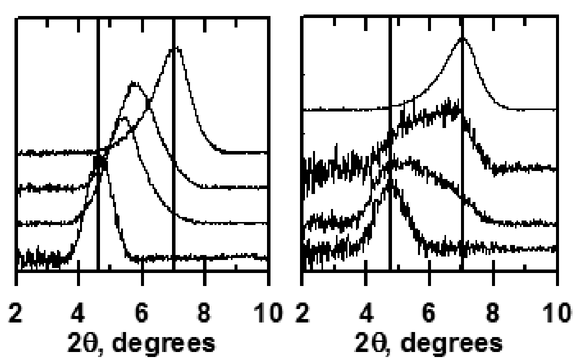


**Figure 1:** Selected X-ray Diffractograms: Interstratification at pH 4 (left) versus segregation at pH 6 (right). Amount of adsorbed Oxy (mmol Oxy/kg of clay) from top to bottom: 0.0, 40.7, 78.4, 284.2 at pH 4 and 0.0, 80.5, 99.6, and 221.7 at pH 6.

[1] Kulshrestha *et al.* (2004) *Environ. Sci. Technol.* **38**, 4097-4105. [2] Reinholdt *et al.* (2001) *Clay Minerals* **40**, 147-190.

# Carbonate ooid formation in a modern freshwater lake: How determinant is the biological role?

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Shallow water sediments in western Lake Geneva, Switzerland, are composed of more than 90% of ooidal sands. The presence of biofilms lining depressions on ooid surfaces has been previously appointed as starting sites for low Mg calcite cortex formation [1]. Field- and laboratory-based experimental results indicate a dominant role of biological versus purely physicochemical processes in the early stages of ooid development.

A special device was placed in the ooid-rich bank of the lake. It contained frosted glass ($SiO_2$) slides, while quartz ($SiO_2$) is the most abundant mineral composition of ooid nuclei that acted as artificial substrates to favour microbial colonization [2]. Microscopic inspection of the slides despicted a seasonal pattern of carbonate precipitates, which were always closely associated with biofilms that developed on the surface of the frosted slides. They contain EPS, cyanobacteria, diatoms and heterotrophic bacteria. Carbonate precipitation peaks during early spring and late summer, and low-Mg calcite crystals mostly occur in close association with filamentous and coccoid cyanobacteria. Further SEM inspection of the samples revealed low-Mg calcite with crystal forms varying from anhedral to euhedral rhombohedra, depending on the seasons.

*In situ* biofilms communities were harvested and cultivated under laboratory conditions. Liquid and solid cultures corroborate the field observations and demonstrate that under the same physicochemical conditions the absence of biofilms prevents low-Mg calcite precipitation. The lack of evidence for the presence of sulphate-reducers further indicate that photosynthetic activity through increasing pH in EPS is the main factor triggering the early precipitation of low-Mg calcite. Hence, these results support the hypothesis of external microbial precipitation of low-Mg calcite as the main mechanism involved in the early stage of ooid formation in freshwater Lake Geneva. Total DNA extractions on natural ooids, biofilms harvested from the *in situ* glass slides, and cultured biofilms in the laboratory indicate a comparable microbial diversity supporting this model.

[1] Davaud & Girardclos (2001) *Journal of Sedimentary Research* **71**, 423-429. [2] Plee *et al.* (2008) *Geobiology* **6**, 341-350.