



Do biofilms and clays alter the chemistry and fabric of a hyper-alkaline, saline, non-marine carbonate precipitate?

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Non-marine carbonates comprise a hugely diverse family of deposits, which reflect a constellation of forcing factors from local hydraulics to regional climatology. However, the two dominant controls on precipitation are solution chemistry and benthic microbial biogeochemistry. Here, we present a unifying concept for understanding how these controls influence deposit characteristics, and re-emphasise the importance of biofilms. It is generally accepted that biofilms play an important part in the precipitation of authigenic minerals in a wide variety of settings. In carbonate settings, biofilms are recognised to increase the amount of calcite precipitation and alter the geometry and coarse scale petrography of the precipitate. They determine at what water marginal water chemistries calcite starts to precipitate and microbialites give way to chemical limestones. Biofilms also interact with ambient water, controlling chemical accumulation transport.

New evidence, drawn from unique experimental approaches, is demonstrating that biofilm influence extends to control of calcite trace element composition, and crystal scale fabric. Under tightly controlled temperature and chemical conditions, fully replicated experiments show that Mg incorporation into tufa carbonate defies the expected thermodynamic control. However, there is a pronounced influence on (Mg/Ca)calcite from precipitation rate, so that rapidly forming precipitates develop with very low magnesium content indicating kinetic control on fractionation. Calcite precipitation rate in these experiments is controlled by biofilm growth rate and reflects kinetic fractionation arises from the electrochemical activity of extracellular organic acids. These effects are therefore likely to occur wherever these molecules occur, including stromatolites, soil and lake carbonates and (via colloidal organic acids) speleothems.

The presence of Extracellular polymeric substances (EPS), even without the presence of cells, also alters precipitation style. Spherular and shrubby calcite growths are well known from the geological record, but their environmental significance is not clear. Sterile, microcosm experiments have shown that these forms occur in saline, hyperalkaline settings — but only in the presence of organic acid molecules in solution. The presence of inorganic materials (hydrated magnesium clays) does not impact on precipitate morphology, and reduces the precipitation rate of calcite.