



In situ experimental study of the formation and physicochemical circumstances of thermal water-related biogeochemical precipitates and calcites

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The formation and evolution (and so the age) of biogeochemical precipitate and calcite of thermal springs are difficult to study in their natural environment and in laboratory. In situ experiments are useful tools to better understand the physicochemical circumstances, growth and the role of microbes in mineral formation.

A 12-week-long in situ experiment was conducted in a 37°C warm flowing water (with a $\sim 1.5 \cdot 10^{-4}$ m³/s volume discharge) in a 130-m-long trapezoid-shaped channel. Physicochemical parameters (temperature, specific electrical conductivity, pH, dissolved oxygen content) of the water was measured continuously. The concentration of major ions, trace elements (in filtered and unfiltered water), and the specific activity of ²²⁶Ra and ²²²Rn were followed along the flow path three times during the experiment. The formation of precipitates was followed on glass slides (put perpendicular to the water flow into the channel at 1, 8, 20, 40, 60, 80, 100 and 120 m far from the source of the water) under stereo, transmitted light and scanning electron microscopes.

The attachment of rod-shaped bacteria to the surface of the slides could be seen after one day along the whole flow path. After two days, calcite crystals formed after 80 m. By the 6th week, there was enough precipitate for analytical measurements. At the first 15 m, red, amorphous iron-oxyhydroxide formed. Around 20 m, light red calcite formed, built-up by rhombohedral crystals. Between 30 and 120 m, yellowish grey calcite could be seen, composed by dendritic crystals with trapped microbial filaments inside them. These precipitates were sampled again for detailed analysis after 12 weeks.

The analysis (gamma spectroscopy, ICP-MS) of the six and twelve-week-old precipitates suggests that the iron-oxyhydroxides have high adsorption capacity, resulted in elevated trace element (e.g. As, Fe, Mn, P, S) and radionuclide (²²⁶Ra) content. The effect of calcite precipitation and evaporation of water can be detected in the changing stable isotope (δD , $\delta^{18}O$) composition of the precipitates along the flow path. Mössbauer spectroscopy proved that the concentration of Fe(III) (in the form of ferrihydrite/goethite) is decreasing along the flow path until 20 m, then it is undetectable.

The simultaneous study of the physicochemical parameters of the water and the forming precipitates during an in situ experiment can help to improve our understanding of the circumstances and processes of mineral formation.

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