

Stable isotope and trace element discrimination, and barite formation in modern carbonate sinters of the temperate climate zone

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Processes in the dissolved carbonate system of surface waters may contribute and are sensitive to variations of boundary conditions associated with climate change. Groundwaters saturated in CaCO₃ and supersaturated in carbon dioxide that emerge from springs start to degas carbon dioxide to the atmosphere. When exceeding a critical value, solid carbonates precipitate. The distribution of trace elements and stable isotopes associated to the mineral precipitation leads to proxy formations.

Two examples of recent sinter formation from streams in the temperate climate zone were investigated: One from the cliff zone of Rügen Island at the southern Baltic Sea coast line (Site R), and another one from Westerhof in the south-western Harz foreland (Site W). We find two phases of process development: (i) An induction period starting at the spring, where only degassing of carbon dioxide takes place, and (ii) a stage where calcite formation from highly supersaturated solution is driven by further degassing. The liberation of CO₂ is associated with an enrichment of the heavy carbon isotope in the remaining DIC. Isotope and trace element discrimination between the aqueous solutions and calcite precipitates yield distribution coefficients that are compared to calibrated experimental studies to estimate calcite precipitation rates. The trace-element based rate estimates for Site W are higher than published direct measurements, which is presumably due to hydrodynamic boundary conditions impacting the in-situ growth experiments. The geochemical observations at Site W can be compared with observations dating back to the late 60s, now allowing for an analysis for ecosystem changes during more than 6 decades. The occurrence of BaSO₄ in recent carbonate sinter is reported for the first time, which agrees with slight supersaturation conditions modeled for the stream water. This new finding indicates that barite may have potential proxy potential in fresh water deposits. At Site R (bottom of the cliff), the carbonate stream water finally encounters the Baltic Sea and mixing with brackish surface waters occur. There, the