



## **Stable isotope and trace element partitioning in recent carbonate-precipitating streams, Rügen Island**

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Processes in the carbonate system of near-surface waters of the temperate climate zone are in particular sensitive to variations of boundary conditions as, for instance, soil activity, humidity, temperature etc. associated with climate change. Calcium carbonate-saturated ground waters that emerge from springs may lose dissolved carbon dioxide to the atmosphere due to degassing. This leads to super-saturation of the aqueous solution with respect to several carbonates, including calcite. Stable isotope and trace element fractionation are of particular value to link these non-equilibrium processes to the formation mechanisms of calcite and the hydrodynamics of flowing streams. These are influenced by the ground water formation rate, temperature, and the CO<sub>2</sub> partial pressure of the atmosphere.

An example linking the past and present terrestrial and marine carbon cycles is found at the cliff coast line of Rügen Island, Baltic Sea: Fossil marine calcium carbonate that forms the cliffs, is nowadays dissolved on the Island by CO<sub>2</sub>-loaded soil solutions reaching saturation with respect to calcite in the water-saturated zone. When these ground waters emerge as springs, their dissolved carbonate system is in dis-equilibrium with respect to the recent Earth atmosphere. By following the chemical changes downstream it is found, that two regions of stream water evolution can be differentiated: After an induction period, where only CO<sub>2</sub>-degassing takes place, a second stage is observed where calcite begins to form from the highly supersaturated solutions. In this stage the carbonate system of the stream water is controlled by both, degassing and carbonate precipitation. At the bottom of the cliff, the carbonate stream water is finally entering the Baltic Sea mixing with the brackish coastal waters.

In the present study, trace element and stable isotope (C, O) isotope fractionation was followed in several carbonate-precipitating streams. Major, minor and trace element concentrations and delta<sup>13</sup>C and delta<sup>18</sup>O values of carbonate solids and aqueous solutions were analyzed as a function of the flow path. In addition, marine and older travertine carbonate samples were analyzed for a comparison with recent precipitates.

Sr/Ca and Mg/Ca ratios were lower in the newly formed calcium carbonate compared to the aqueous solution. The partition coefficients are larger than previous experimental close-to-equilibrium calibrations and indicate relatively fast calcite precipitation rates. The spring carbon isotopic composition indicates ground water evolution under conditions, essentially closed with respect to a carbon dioxide gas phase. The delta<sup>13</sup>C values of DIC increased along the flow path, due to preferential degassing of <sup>12</sup>CO<sub>2</sub>. Travertin samples displayed a slight enrichment in <sup>13</sup>C compared to the solution which is consistent with experimental and theoretical studies. Some seasonality in the composition of the spring waters carbonate system as well as the degassing efficiency from the stream waters, however, can not be completely ruled out and require further investigations. Finally, the delta<sup>18</sup>O values preserved in the carbonates indicate influence of precipitation kinetics.