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Experimental fractionation of stable carbon isotopes during degassing of carbon dioxide and precipitation of calcite from aqueous solutions

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Processes in the carbonate system of surface waters are in particular sensitive to variations of boundary conditions as, for instance, the partial pressure of carbon dioxide in the atmosphere and the aqueous solution. Examples range from streams, rivers, to coastal marine waters. The flux of carbon dioxide from continental flowing waters was recently included into calculations of the global carbon budget (Butman & Raymond, 2011, Nature Geo.). These solutions, are often supersaturated in carbon dioxide with respect to the atmosphere. The degassing of carbon dioxide is associated with a kinetically controlled fractionation of the stable carbon isotopes, which has to be considered in balancing water-air carbon dioxide fluxes. The degassing process additionally leads to the super-saturation of the aqueous solution with respect to calcium carbonate. Stable isotope fractionation is of particular value to identify and quantify processes at the water-gas phase interface and link these non-equilibrium processes to the formation mechanisms of calcite and the hydrodynamics of surface waters.

Experiments were carried out with or without inert N2 gas flow to degas carbon dioxide from initially supersaturated solutions. Natural solutions used are from different stations of the Elbe estuary, the Jade Bay, the backbarrier tidal area of Spiekeroog Island, carbonate springs of Rügen Island, and the Baltic Sea coastline. Results are compared experiments using bottled mineral waters. By following the (physico) chemical changes in the solutions (pH, TA, Ca PHREEQC modeling) it was found, that two evolutionary stages can be differentiated. Reaction progress led to the preferential liberation of carbon dioxide containing the light carbon isotope, following a Rayleigh-type process. After an induction period, where only degassing of carbon dioxide took place, a second stage was observed where calcite began to form from the highly supersaturated solutions. In this stage the carbonate system of the solution was controlled by both, degassing and carbonate precipitation, still leading to an enrichment of the heavier carbon isotope in the residual DIC. The experimental results are evaluated for both periods, and the influence of salinity and pH is extracted.

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