



Evolution of $\delta^{13}\text{C}$ and $\delta^{44}\text{Ca}$ in calcite and spring water (Carinthia, Austria)

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In order to shed light on fractionation mechanisms of Ca isotopes during calcite precipitation in a natural surface hydrological system we have conducted research along a stream in Carinthia (Austria) where precipitation of calcite is triggered by CO_2 degassing from low mineralized spring water. We compared $\delta^{13}\text{C}$ and $\delta^{44}\text{Ca}$ variations in water and corresponding calcite deposits. $^{44}\text{Ca}/^{40}\text{Ca}$ ratios (expressed as $\delta^{44}\text{Ca}$) were analyzed by TIMS using a ^{42}Ca - ^{48}Ca double spike. $^{44}\text{Ca}/^{40}\text{Ca}$ ratios are normalized to seawater ($\delta^{44}\text{Ca} = 0$), which is used as a standard. The genesis of Ca-HCO_3 -type spring water is related to the infiltration of meteoric water to an unconsolidated sediment aquifer. Seepage water takes up CO_2 from the soil zone, and subsequently dissolves CaCO_3 from conglomerates and moraines along the underground flow path. After reaching the surface, rapid degassing of CO_2 causes a progressive increase in pH and in the saturation of the water with respect to calcite. Calcite precipitates in the streambed and in small ponds with stagnating water flow. The formation of calcite is accompanied by a steady decrease in HCO_3^- - and Ca^{2+} concentrations in the stream water. $\delta^{13}\text{C}$ of dissolved inorganic carbon changes systematically towards "heavier" values from -13.3 to -11.5 permil (PDB) due to the release of CO_2 gas. $\delta^{44}\text{Ca}$ values of dissolved Ca^{2+} are close to the value for seawater, while calcite is enriched in the light ^{40}Ca isotope (-2.2 to -1.2 permil relative to seawater). $\delta^{44}\text{Ca}$ values of calcite are significantly correlated with dissolved Ca^{2+} and HCO_3^- concentrations, indicating a strong effect of the precipitation rate on the Ca isotope composition. In addition, there is a significant correlation with precipitation temperature.