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PRECIPITATION OF CALCITE FROM SPRING WATER (CARINTHIA, AUSTRIA) AND THE EVOLUTION OF ^{13}C/^{12}C- AND ^{44}CA/^{40}CA-SIGNATURES

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Biologically induced and abiotic fractionation processes of stable calcium isotopes are subjects of numerous recent studies. Research in marine environments is focused on calcium isotope fractionation patterns in foraminifera and coral species. Complementary investigations show a systematic fractionation during abiotic precipitation of $CaCO_3$ from supersaturated solutions under controlled laboratory conditions (e.g. Gussone et al. 2003). However, little is known about calcium isotope fractionation in terrestrial environments and natural hydrological systems.

A systematic study was undertaken along a stream in Carinthia (Austria), where calcite precipitation is induced by degassing of CO_2 from spring water. The temperature of the water increases at about 4°C along the flow path of 120 meters. Precipitation of calcite can be followed by a continuous decrease of dissolved HCO_3^- and Ca^{2+} along the stream ($[HCO_3^-]:[Ca^{2+}] = 2:1$). Evolution of $\delta^{13}C_{HCO3}$ values shows a systematic change towards "heavier" values from -13.3 to -11.5 $^{o}/_{oo}$ (PDB). $^{12}CO_2$ is liberated from the solution into the atmosphere somewhat faster than $^{13}CO_2$. A kinetic fractionation factor $\alpha = 0.990$ is obtained. Accordingly, ^{13}C is enriched in the remaining dissolved HCO_3^-.

^{44}Ca values of dissolved Ca^{2+} and corresponding calcite precipitates along the stream were analyzed by thermal ionization mass spectrometry using a ^{42}Ca-^{48}Ca double spike to correct fractionation during the analytical procedure. ^{44}Ca/^{40}Ca ratios are normalized to seawater (^{44}Ca = 0). While rather heavy ^{44}Ca values close to seawater are observed for dissolved Ca^{2+}, the precipitates show "light" calcium isotope compositions with a difference of up to -2.4 ‰ relative to the liquid phase. The differences among calcite along the profile are within a range of 1 ‰. $^{44}Ca_{calcite}$ values show a significant correlation with temperature (0.23 ‰ per 1 °C increase in temperature). These results indicate the potential use of calcium isotopes in future hydrological studies in carbonate systems.

References

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