Reverse stable Sr and Ca isotope fractionation in marine sulfates: Biogenic $SrSO_4$ (acantharia) vs. inorganic $CaSO_4 \cdot 2H_2O$ (gypsum)

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The combination of stable Sr ($\delta^{88/86}$Sr) and Ca ($\delta^{44/40}$Ca) isotope analyses on marine sulfates provides new perspectives for the quantification of element fluxes within the water column and new insights into the principles of precipitation-related fractionation processes.

Acantharia are widespread distributed protozoans with a $SrSO_4$ skeleton, common in the upper 400 m of the oceans and suggested as potential driver of seasonal changes in Sr/Ca ratios of the upper water column by depletion in Sr. After their lifetime these celestite spines (σ = 3.96 g/cm^3) sink and dissolve in the deeper water column, thereby potentially transfering large amounts of Sr (Sr/Ca$_{\text{celestite-spines}}$ >40 mol/mol) to the deep sea. The initial data set of this study provides $\delta^{88/86}$Sr signatures of Acantharia from the North East Atlantic (Bay of Biscay) and Eastern Indian Ocean (off Western Australia) with values down to 0.03 and 0.11 ‰ (referred to NIST-SRM 987), respectively. This corresponds to a precipitation related fractionation $\Delta^{88/86}$Sr $_{\text{(acanth.-sw)}}$ of up to -0.36 ‰, referred to the IAPSO seawater (SW) standard of this study (0.39±0.03 ‰, 2SD). In a case study we combined high resolution chemical composition and growth structure analyses (EMP) on single Acantharia with double spike Sr and Ca isotope analyses (TIMS). Providing also precise concentration data the latter imply a Sr transfer in the order of 50 ng/skeleton. One aim of the study is to develop an isotope based model for the threshold value of Acantharia blooming (n/liter SW) for significant Sr/Ca$_{\text{SW}}$ and $\delta^{88/86}$Sr$_{\text{SW}}$ changes and its potential impact on coincident carbonate archives.

In contrast to this carbonate analogue fractionation systematic, Sr coprecipitates as trace element in Ca sulfate ($CaSO_4 \cdot 2H_2O$, gypsum) from pore waters in marine sediments and in lab experiments with a positive $\Delta^{88/86}$Sr $_{\text{(precip.-fluid)}}$ value of up to 0.2 ‰. This direction is also reverse to the fractionation of Ca as main constitutent in gypsum ($\Delta^{44/40}$Ca $_{\text{(precip.-fluid)}}$: -0.9±0.2 ‰, 2SD) and implies lattice and element coordination as controlling factor.