Constraining the mechanisms driving coccolith $\delta^{44/40}$Ca and Sr/Ca variations: new perspectives from cultures, cellular models, and the sediment record

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Coccoliths comprise a major fraction of the calcium carbonate (CaCO$_3$) production, with contributions varying from 95% of the global carbonate sink during the Cenozoic, to 50% in the modern ocean. Therefore, significant changes in coccolith Ca isotopic fractionation could have affected past seawater Ca isotopic composition ($\delta^{44/40}$Ca), with potential important implications for the interpretation of the global Ca cycle and related changes in seawater chemistry.

Here we evaluate the mechanisms driving coccolith Ca isotopic fractionation in a quantitative framework, by deriving a steady-state mass balance geochemical model (CaSri-Co), which assumes that fractionation is solely associated with desolvation (i.e. dehydration) of Ca during cellular transport through membranes. The application of the CaSri-Co model to previously published and to our new $\delta^{44/40}$Ca and Sr/Ca results from cultured coccolithophores (Emiliania huxleyi, Gephyrocapsa oceanica and Calcidiscus leptoporus) allowed us to identify calcification rates, Ca retention efficiency and water structure strength as main regulators of the Ca isotopic fractionation and Sr/Ca ratios of cultured coccolith calcite. Higher calcification rates, higher Ca retention efficiencies and higher water structure strength (slower Ca solvation-desolvation reactions) increase both coccolith Sr/Ca and Ca isotopic fractionation. The CaSri-Co model shows that coccolith Ca isotopic fractionation is especially sensitive to changes in water structure strength. On the other hand, Ca retention efficiency appears to be the main driver of the observed Sr/Ca trends, which results from the incomplete usage of the Sr transported to the calcification vesicle and subsequent Sr enrichment of the cytosol, while Ca inside the calcification vesicle is assumed to be completely utilized in the model.

In this study we also measured $\delta^{44/40}$Ca and Sr/Ca in two coccolith size fraction from site 925 in the Western Equatorial Atlantic representing the last 11 Ma. We observe an increase of Sr/Ca ratios in both size fractions which may indicate an enhanced Ca retention efficiency during a period of increasing carbon limitation. The rather large changes in Ca isotopic fractionation measured in both cultures (up to 5 %o ) and the sedimentary record (up to 0.32 %o ), could be in part explained by changes in sea surface temperature (SST) and/or changes in the amount/type of cellular exudates, both of which modify the water structure strength around the cell. Since changes in Ca isotopic fractionation of the magnitude of those observed in this study and in others could potentially affect seawater $\delta^{44/40}$Ca, we would recommend future modeling studies to include coccolith-based studies for a better interpretation of the Ca cycle.