Constraining the mechanisms driving $\delta^{44/40}$Ca variations in coccolithophores: A mixed culture and fossil study approach

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Culture studies have suggested temperature and kinetic effects as potential drivers for changes in coccolith Ca isotopic composition ($\delta^{44/40}$Ca) and Ca isotopic fractionation. However, the specific mechanisms affecting $\delta^{44/40}$Ca are still unclear. Moreover, additional interacting factors, such as carbon limitation under low CO_2 could also play a role.

We measured $\delta^{44/40}$Ca and Sr/Ca from cultured *Emiliania huxleyi, Gephyrocapsa oceanica* and *Calcidiscus leptoporus* at varying CO_2 levels, and from two coccolith size fractions from site 925 in the Western Equatorial Atlantic representing the last ~11 Ma. We propose a simple model (CaSri-Co) for transmembrane Ca and Sr transport, assuming Ca desolvation as the sole source for Ca fractionation. This model identifies three main potential factors driving Ca fractionation in coccolith calcite, based on our culture results and those from other studies for which calcification rates have been reported.

The model shows that higher calcification rates decrease Ca fractionation, while an increased Ca retention efficiency (Ca incorporated/Ca taken up) tends to increase it. Ca efficiency was found to have a larger effect on Sr/Ca than in Ca fractionation. The model also shows that Ca fractionation is very sensitive to the solvation environment, which affect the solvation (Rb) and desolvation (Rf) rates via modification of the water structure strenght. A decreased solvation rate could explain the observed increasing Ca fractionation at decreasing calcification rates for the small fossil coccolith size fraction observed form ~5 to ~4 Ma. Between the potential factors that could have produced decreases in the Rb are increases in the seawater Mg concentrations, decreases or modifications in the cellular exudate production, possibly associated to physiological adaptations to limiting carbon availability, changes in the affinity of the protein to which Ca attaches upon uptake, and decreases in seawater temperatures in part driven by seawater CO_2 variations.