Sensitivity of coccolithophorid physiology to CO_2 concentrations on geological time scales

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Coccolithophorid algae play a key role in the biological pump and therefore the oceanic uptake of atmospheric CO_2, as they are the main drivers of the carbonate counter pump. Future responses of coccolithophorid algae under elevated atmospheric CO_2 concentration scenarios are unknown, as most studies to date have focused on short-term laboratory experiments. It is of key importance to understand the interplay between this algal group and atmospheric CO_2 concentration on geological timescales, especially when CO_2 concentrations were higher than today.

Bolton and Stoll (2013) [1] reported the long-term appearance of stable isotope vital effects in coccolithophore calcite in the Caribbean Sea (ODP site 999) over the last 15 Ma. These authors infer, based on an inverse model, that $\delta^{13}C$ vital effects appeared as a result of the reallocation of carbon (HCO_3^-) from calcification to photosynthesis after ~7 Ma in response to decreasing aqueous CO_2 concentrations in tropical waters. Here, we model various proxy datasets from the same ODP site using a model of cellular cabon fluxes. We evaluate the interplay between CO_2 concentrations and coccolithophorid physiological responses from 14 to 4 Ma. Our simulations reveal that under specific scenarios (e.g. decreasing CO_2 concentrations with time and variable growth rates), only a large change in the relative allocation of HCO_3^- to photosynthesis versus calcification affects the carbon isotope fractionation during calcification (ε_{cal}) after 7 Ma. In contrast, substantial effects on the carbon isotope fractionation during photosynthesis (ε_p) only occur when CO_2 concentrations decrease in combination with an increase in algal growth rates and a substantial amount of HCO_3^- diverted to the chloroplast. Our model reveals a high sensitivity of ε_p to growth rate changes. This highlights the importance of taking into account algal physiology when reconstructing pCO_2 from the geological record, and undescores the limitations of the alkenone $\delta^{13}C$ paleobarometer.

[1] Bolton & Stoll (2002), *Nature* **500**, 558-562.