Isotopic response of Pleistocene coccoliths to an ambient *p*CO_2 change: a calibration experiment

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For geological periods where direct measurements of *p*CO_2 performed on ice cores are not possible, the reconstruction of this key paleoclimatic parameter can only be achieved through proxy data. Results from both *in vivo* cultures and cell modelling biogeochemical studies have demonstrated a link between the biological fractionation of coccoliths and the CO_2 concentration of the living environment of their producers, the coccolithophores. Changes in the CO_2 levels of the surface ocean also drive, on a geological timescale, the isotopic composition (vital effect) of Cenozoic coccoliths. These results have encouraged the use of coccolith vital effects as proxies for seawater CO_2 concentrations. However, a number of potential biases may hinder the application of the empirical calibrations from culture experiments to wild coccolith populations. This work formalizes a transfer function linking the vital effects of fossil coccoliths to the constrained values of Pleistocene [CO_{2aq}], with a view to develop a new tool to reconstruct older *p*CO_2 levels.

The calibration relies on the carbon and oxygen isotopic analyses of purified fractions of coccoliths from the North Atlantic core MD95-2037 across Termination II (ca. 140-130 ka). Using the alkenone-based sea-surface temperature (SST) record available at the site and atmospheric CO_2 concentrations from the Antarctic ice cores, we derived values for surface ocean CO_2 concentrations across the deglaciation. We quantified the changing magnitude of the vital effect of the coccoliths to the presumed forcing by CO_2 and formulated a transfer function between the two parameters. We evidence a control of CO_2 concentrations on the isotopic difference ($\Delta^{18}O$, $\Delta^{13}C$) between coccoliths of different sizes produced across the penultimate glacial-interglacial transition. We discuss the factors complicating the obtained relationship, including the effect of growth rate changes and/or air-sea disequilibrium. As a perspective to this work, we discuss the possible application of this calibration to more ancient periods in the Cenozoic, where direct measurements of *p*CO_2 are not available.