Resolving the physiological parameter '*b*' for alkenone-based pCO_2 reconstructions

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The haptophyte algal biomarkers called alkenones are wildly used to reconstruct atmospheric CO_2. This method is based on the notion that the algal carbon isotope fractionation during photosynthesis, $\varepsilon_{p37:2}$, is a function of seawater CO_2 concentration and algal physiology such as growth rates (μ), cell size (V/S) and plasamembrane permeability (P). These variables are aggregated collectively as the parameter '*b*'. The lack of constraint on *b* is the largest source of uncertainty for the alkenone-CO_2 approach.

Here we show that based on the interdependence between haptophyte cell size and growth rate, the length of the fossil coccolith produced by ancient alkenone-synthesizers can be used to estimate *b*. Combined with the P value determined by chemostat cultures [1], the *b* parameter can be computed for each sample. By combining calculated *b* values with a newly generated $\varepsilon_{p37:2}$ record from the South China Sea, pCO_2 was calculated over the last three glacial – interglacial cycles. Overall, the alkenone-based CO_2 estimates replicate the ice core CO_2 records both in trends and absolute values.

Previously reported Southern Ocean $\varepsilon_{p37:2}$ values across the Eocene-Oligocene boundary are close to the maximum allowed fractionation (~25‰). Therefore, the calculated pCO_2 levels are about 10,000 ppm, which is inconsistent with other records [2]. We postulate that the large size of the Southern Ocean alkenone-producers indicates very slow growth rates. Using the V/S-μ relationship, the reevaluated pCO_2 values from these sites are reduced and more in line with other records. Interestingly, this result depends on a significantly smaller permeability of haptophytes during the E-O, relative to Pleistocene haptophytes, highlighting the evolutionary control on the carbon uptake of phytoplankton.

[1] Popp, B.N. et al., 1998., *Geochim. Cosmochim. Acta* 62, 69-77; [2] Pagani, M. et al., 2011., *Science* 334, 1261-1264.