Refining the alkenone-*p*CO₂ method: Nutrient constraints and the effect of growth rate

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The alkenone- pCO_2 method is one of the most widely used approaches to reconstruct the atmospheric CO₂ level in the Cenozoic. Based on the fractionation of stable carbon isotopes between dissolved CO2 and biomass of haptophyte algae, this relationship (known as $\epsilon_{\rm p})$ scales inversely with growth rate and positively with CO₂ [1]. Recently published records of alkenone-derived CO2 from late Pleistocene samples, however, are poorly correlated with ice core CO₂ records, indicating that improvements to the current methodology are needed. Models and experiments indicate that algal growth rate as represented by the physiological parameter b' – which must be specified in order to reconstruct CO₂ levels - are sensitive to nutrient concentrations (e.g., phosphorous, [2]) as well as other environmental conditions [3]. Here we revise the relationship between seawater reactive phosphate concentration and b using published core-top $\epsilon_{\scriptscriptstyle D}$ data. The sediment-based data show a shallower slope of the phosphate-b regression than the widely used relationship derived from suspended organic matter. Further, we show that the archaeal lipids often co-occuring with alkenones in the sediments may be used to estimate past changes of seawater nutrient levels and therefore to calibrate 'b'. Applications of this refined alkenone- pCO_2 method to two published datasets yield similar trends and magnitude of pCO_2 changes over the last glacial-interglacial cycle, matching the ice-core records.

[1]Laws, E.A., Popp, B.N., Bidigare, R.R., Kennicutt, M.C., Macko, S.A., 1995: *Geochim. Cosmochim. Acta* 59, 1131-1138.[2]Bidigare, R.R. et al., 1997: *Global Biogeochem. Cyc.* 11, 279-292.[3]Laws, E.A., Popp, B.N., Cassar, N., Tanimoto, J., 2002: *Funct. Plant Biol.* 29, 323-333.

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