## Threshold adaptations of marine algae to CO<sub>2</sub> in the late Cenozoic

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Paleoclimate calibration of the climate sensitivity to greenhouse forcing requires the proxy reconstruction of atmospheric  $CO_2$  during periods with higher than preindustrial levels. The sensitivity of photosynthetic algae to  $CO_2$  limitation, reflected in the carbon isotopic fractionation in organic biomarkers produced by marine coccolithophorid algae, has been exploited as one proxy. We show that the carbon isotopic fractionation in the coccolith calcite is also sensitive to  $CO_2$  limitation. This occurs because at limiting  $CO_2$ , coccolithophorid cells reallocate cellular HCO3-transport from calcification to photosynthesis, resulting in greater fraction of diffusive  $CO_2$  to carbon used for calcification and more depleted isotopic composition of coccoliths especially in larger cells.

The carbon isotopic signature of coccoliths isolated from Cenozoic sediments indicates that a threshold of carbon limitation was passed in the Late Miocene. The carbon isotopic signatures of large and small coccoliths diverge, as happens in culture experiments when  $\text{CO}_2$  aq concentrations fall below 19 uM. The threshold is passed first starting at 7 Ma in warm (28C) tropical location and subsequently starting at 5 Ma in the cooler (18C) higher latitude location. We propose that decreasing atmospheric pCO2 caused first tropical waters to fall below a critical CO<sub>2</sub> aq threshold, but due to the higher solubility of CO<sub>2</sub> in cold waters, this same CO<sub>2</sub> aq threshold was not passed in the high latitude site until pCO<sub>2</sub> decreased by a further 150 ppmv. This inferred period of decreasing CO2 has not been well resolved by previous proxy reconstructions but is consistent with inverse modeling of climate data [1] Since the late Miocene, further decrease in pCO<sub>2</sub> is accomodated by reduced calcification, attenuating its manifestation in the isotopic composition of coccoliths. We compare this pattern of coccolithophorid response to CO2 limitation since the late Miocene with that of diatoms, whose wide range of diffusive area to volume confer a different sensitivity of isotopic fractionation in organic matter to CO<sub>2</sub>.

[1] van de Wal, de Boer, Lourens, Kohler, & Bintanja (2011), *Clim. Past* **7**, 1459-1469.