

# **Carbon isotopic vital effects in planktonic foraminifera: A mechanistic proxy for DIC through the Paleogene**

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The  $\delta^{13}\text{C}$  of planktonic foraminifera, whilst easy to measure, have largely been overlooked as a quantitative proxy for past seawater isotopic composition and conditions. This is in large part due to uncertainty over a potentially variable vital effect as a result of symbiont activity and a multitude of environmental conditions demonstrated to influence shell chemistry in culture. However a review of both the biological evidence and isotopic composition of the size-dependence of the  $\delta^{13}\text{C}$  of planktonic foraminifera suggests that the vital effect can be mechanistically understood by a simple mass balance of carbon from two sources, and can be applied as a novel proxy for past ocean DIC (dissolved inorganic carbon), a crucial component of reconstructing past  $\text{pCO}_2$ .

The  $\delta^{13}\text{C}$  of small planktonic foraminifera are consistently isotopically lighter than larger foraminifera and offset to light values compared to equilibrium. Experimental evidence demonstrates that the carbon pathway for symbiotic photosynthesis is independent from the carbon pool for calcification. Calcification sources carbon only from dissolved inorganic carbon (DIC) through seawater vacuolisation and carbon from metabolic respiration. A simple mass balance model is proposed for the size-dependence of the  $\delta^{13}\text{C}$  vital effect via mixing of DIC with a contribution of respiratory carbon proportional to the size-normalised metabolic rate. Application of this model towards a compilation of size-dependent planktonic foraminiferal  $\delta^{13}\text{C}$  suggests that the reduced size-dependence for periods of the Paleogene may be attributed to the increasing dilution of metabolic carbon by elevated surface ocean DIC. Surface ocean DIC fluctuated up to 2-fold compared to modern seawater but could have changed by up to 5-fold through carbon isotope perturbations of the Paleogene. Such changes in surface ocean DIC amplify the atmospheric  $\text{pCO}_2$  inferred from boron isotope-derived pH for periods of the Paleogene. The size-dependence of carbon isotopic vital effects in foraminifera offers a novel approach to constraining past surface ocean DIC levels and surface ocean  $\delta^{13}\text{C}_{\text{DIC}}$ .