

## The stable carbon isotopic composition of marine phytoplankton throughout the Phanerozoic

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<sup>12</sup>C is preferentially discriminated over <sup>13</sup>C during the incorporation of external environmental inorganic carbon into the internal structures and through the synthesis of carbon into metabolic pathways in primary producers. To better understand the environmental factors influencing this discrimination, the stable carbon isotopic fractionation associated with autotrophic inorganic carbon fixation ( $\epsilon_p$ ) was calculated from the stable carbon isotopic composition ( $\delta^{13}\text{C}$ ) of the general phytoplanktonic biomarker phytane, a diagenetic product from chlorophyll-a. The compilation (data from the literature with complementary laboratory work) comprises of approximately 400 sediment and oil samples from open marine environments, and considers both free and sulfur-bound phytane. The resulting  $\epsilon_p$  ranges from 12–24‰, agreeing the literature's postulated maximum Rubisco fractionation of 25‰. The trend in  $\epsilon_p$  mirrors the compiled pCO<sub>2</sub> record from ~125 Ma to modern day, though  $\epsilon_p$  has a negative offset from the pCO<sub>2</sub> record prior to 125 Ma and a larger offset prior to 350 Ma. The timing of these offsets coincide with the emergence of diatoms (radial centric at 142–97 Ma) and haptophytes (375–285 Ma), both of which have higher maximum fractionation than other phytoplankton due to their carbon fixing enzyme Rubisco, which has evolved in response to decreasing pCO<sub>2</sub>. This factor should be considered when applying the  $\delta^{13}\text{C}$  of phytane as a quantitative pCO<sub>2</sub> proxy in the Phanerozoic.