Controls on paleo-alkenone $\delta^{13}C$

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The carbon isotopic fractionation that occurs during marine photosynthetic carbon fixation (ε_p) is primarily a function of surface-water [CO_{2aq}], growth rate, and cell geometry. Although modern data suggest that haptophyte growth rates exert a dominant control on the value of $\varepsilon_{p37:2}$, some patterns of paleo-$\varepsilon_{p37:2}$ change are contrary to changes in nutrients inferred from foraminiferal trace element concentrations. Further, comparison of $\varepsilon_{p37:2}$ values for the past ~45 million years with $\varepsilon_{p37:2}$ values from modern growth environments, spanning oligotrophic to eutrophic sites, indicate that changes in algal growth rate is not the first-order control on the long-term trend. If changes in cell geometry of alkenone-producers were minimal, then long-term trends in $\varepsilon_{p37:2}$ qualitatively reflect a decrease in [CO_{2aq}] from the middle Eocene to the early Oligocene. Atmospheric carbon dioxide concentrations can be estimated using the modern calibration for $\varepsilon_{p37:2}$ as a function of surface-water [PO_4^{3-}] and [CO_{2aq}], assuming the range of paleo-[PO_4^{3-}] for each site was similar to modern distributions. This approach yields middle Eocene pCO_2 levels ~3 to 5 times that of modern levels. pCO_2 rapidly declined following the Eocene/Oligocene boundary reaching modern concentrations near the end of the Oligocene.

Recent measurements of coccolith geometries suggest changes in algal geometries of alkenone-producing algae did occur. These results and their impact on carbon dioxide estimates will be discussed.

The importance of a vital effect on the Ca isotopic composition of foraminiferal tests

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The influence of temperature on Ca isotope fractionation during biomineralisation was investigated through the paired analyses of $\delta^{44/42}Ca$ (via MC-ICP-MS) and $\delta^{18}O$ on the calcite tests of twelve species of planktonic foraminifera from core-top sediments [1]. No significant correlation between temperature and Ca isotopes was observed in any of the twelve species of foraminifera investigated. The results suggest that the theoretically-expected relationship [2-3] between Ca isotopes and temperature can be obscured by, as yet, unquantified metabolic and physiological processes in nature. Variable growth-rate could be a reason for this vital effect [3] but cannot explain inter-species variations. Vital effects on Ca-isotopes are particularly relevant to the globorotaliid species and *G. bulloides* in core-top studies but could also explain the discrepancy between laboratory-determined temperature calibrations and core-top data for *G. sacculifer* [4]. It is doubtful that the effects of metabolic and physiological processes remained constant through time. This could complicate models of the temporal evolution of the Ca isotopic composition of seawater by introducing a variable fractionation factor between seawater and the carbonate sink.

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