Miocene climate change: A molecular approach

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Alkenones are diagenetically resistant lipids known to be produced by only coccolithophorid Haptophyte algae (for example, *Emiliania huxleyi* today). These compounds are present ubiquitously in marine sediments of at least Miocene to Recent age, but are known from sediments as old as Cretaceous in age. The alkenones can be readily isolated from the organic fraction of sediment samples from DSDP/ODP sites. Field and experimental data have established that fractionation of carbon isotopes during photosynthesis (carbon fixation) for the Haptophyte algae is primarily controlled by the concentration of ambient CO_2(aq) (a function of pCO_2, the partial pressure of CO_2 in the atmosphere and/or surface- water mass) and cellular growth rate. These relationships have been calibrated, relating ε_p (the difference between the carbon isotopic composition of the organic compound and the inorganic carbon source) to [CO_2(aq)] and phosphate concentration in surface waters. This technique constitutes a paleo-pCO_2 barometer, provided that the $\delta^{13}C$ of alkenones and dissolved inorganic carbon (DIC) can be measured, directly or indirectly, and growth rates estimated using various paleochemical proxies. Fortunately, a close approximation of $\delta^{13}C_{(CO2aq)}$ can be made by measuring the carbon isotopic composition of coeval planktic foraminifera and assuming equilibrium conditions among the carbon species in surface waters; required temperature estimates are derived from the oxygen isotopic compositions of selected planktonic foraminifers.

Using these techniques, we have been developing a detailed record of the $\delta^{13}C$ of di-unsaturated alkenones for the early through middle Miocene from sequences recovered in DSDP/ODP sites in order to assess the role of postulated changes in pCO_2 in climate change. The middle Miocene is a pivotal time of the Cenozoic, bridging times of fluctuating glacial conditions and with that of large, permanent continental ice sheets. Decreasing pCO_2 and/or alterations in heat and vapor transport via rearrangement of deep-water circulation are commonly cited drivers of late Cenozoic global cooling. Our approach is to establish ε_p records from low-productivity regions in the world's oceans, thereby mitigating the effect of variable growth rates on the $\delta^{13}C$ of alkenones. As an example of the approach,

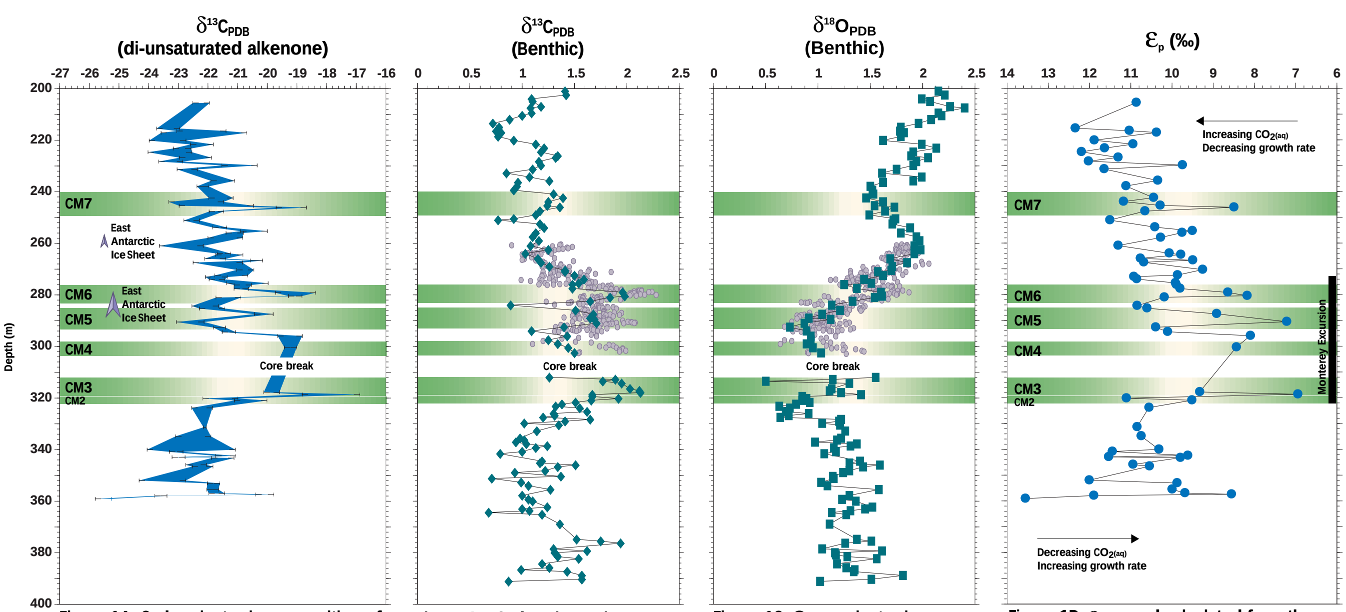

Figure 1A: Carbon isotopic composition of di-unsaturated alkenone from Site 588 in the southwest Pacific. Green banding indicates the range of $\delta^{13}C$ maxima (CM2-CM7) within and outside the "Monterey Excursion."

Figure 1B: Carbon isotopic composition of benthic foraminifera from Site 588 [*Kennett*, 1985; *Flower and Kennett*, 1993].

Figure 1C: Oxygen isotopic composition of benthic foraminifera from Site 588 [*Kennett*, 1985; *Flower and Kennett*, 1993].

Figure 1D: ε_p record calculated from the $\delta^{13}C$ of di-unsaturated alkenones (figure 1A) and the $\delta^{13}C$ of coeval planktic foraminifera.

we present preliminary data and interpretation from DSDP Site 588 (figure 1) in the southwest Pacific ocean. Site 588 records a continuous Miocene section with a low organic content and a low, steady sedimentation rate.

Results for the interval from ≈22 to 8 Ma exhibit both long-and short-term trends in alkenone ε_p. A sharp and rapid decline followed by an equally rapid rise in ε_p at ≈21.5 Ma indicates a dramatic fall and return in [CO_2(aq)] and inferred pCO_2. A trend toward lower ε_p follows this event, reaching a minimum throughout the 'Monterey excursion' of the middle Miocene (≈17.5-13.5 Ma). The 'Monterey excursion' is a broad, 1‰ positive shift in the $\delta^{13}C$ of benthic foraminifera attributed to increased organic-carbon burial, that resulted in lower pCO_2 and global cooling [*Vincent and Berger,* 1985].

Sharp positive shifts in ε_p coincide with inorganic $\delta^{13}C$ carbon maxima (CM2-CM7) within and outside the "Monterey excursion". These carbon maxima are associated with positive shifts in benthic $\delta^{18}O$ and increased carbonate preservation [*Woodruff and Savin,* 1991], again suggesting a relationship between episodes of enhanced organic-carbon burial, decreasing pCO_2, and deep-water cooling. Our results support such interpretations. Furthermore, a trend toward higher pCO_2 , inferred from the increasing ε_p values following East Antarctic ice sheet growth at ≈14.5 Ma [*Flower and Kennett,* 1993], may highlight the importance of ice albedo in the regulation of global temperatures. Once global albedo increases a new climate system equilibrium is reached, allowing ice sheets to persist a higher pCO_2 than that required to initiate global glaciation.