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Alkenones as paleoceanographic proxies

Julian P. Sachs

Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Room E34-254, Cambridge, Massachusetts 02139 (jsachs@mit.edu)

Ralph R. Schneider

Fachbereich Geowissenschaften, Universität Bremen, Postfach 330 440, 28334 Bremen, Germany (rschneid@uni-bremen.de)

Timothy I. Eglinton

Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 (teglinton@whoi.edu)

Katherine H. Freeman

College of Earth and Mineral Sciences, 209 Deike Building, Penn State University, University Park, Pennsylvania 16802 (kate@essc.psu.edu)

Gerald Ganssen

Institute of Earth Sciences, Free University, De Boelelaan 1085, 1081 HV Amsterdam, Netherlands (gang@geo.vu.nl)

Jerry F. McManus and Delia W. Oppo

Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 (jmcmanus@whoi.edu; doppo@whoi.edu)

[1] **Abstract:** Alkenone-derived estimates of temperature and CO₂ are contributing to our understanding of Earth's climate history. In order to increase confidence in alkenone-based climate proxies we recommend the following actions. First, the sedimentary component or fraction containing alkenones should be identified in order to assess the impact of horizontal advection and vertical mixing on alkenone-derived temperature and CO₂ estimates. Second, differential mixing rates of alkenone-containing particles and sand-sized foraminifera should be quantified by independent dating of the two phases. Until that is accomplished, apparent temporal offsets of climate proxies in the two phases should be interpreted cautiously. Third, the stability of the unsaturation ratio and carbon isotopic compositions of alkenones during all phases of diagenesis should be confirmed. Both field and laboratory observations are required. Fourth, future alkenone investigations should be coupled with other paleoclimate proxy measurements at high-deposition-rate-sites in a variety of oceanographic settings. In upwelling regions and in the vicinity of river plumes, salinity and nutrient proxies should be measured since changes in these parameters may affect alkenone biosynthesis.

Keywords: Alkenones; biomarkers; paleoclimate; paleoceanography.

Index terms: Paleoceanography; organic marine chemistry; chemical tracers.

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1. Introduction

[2] Molecular fossils (biomarkers) have provided a treasure trove of paleoclimate information during the last 15 years. Of particular importance is the discovery of a biomarker technique for precisely determining sea surface temperatures (SSTs) [Brassell et al., 1986]. Pioneered in the mid 1980s by S. Brassell, G. Eglinton, and coworkers at the University of Bristol, England [Brassell et al., 1986], the unsaturation ratio of C₃₇ methyl ketones is providing some of the most detailed records of Pleistocene SSTs in many locations. Advantages of the method are its (1) potential to determine absolute SSTs. (2) ease of measurement when compared to microfossil-based techniques (i.e., rapid, inexpensive, small sample requirements), and (3) utility in most oceanographic settings, over a wide range of latitudes and depths (including regions where other SST proxies are limited, e.g., below the lysocline depth and where microfossil assemblages are dominated by a single species). Recent analytical advances allow the generation of alkenone time series with temporal resolution that is comparable to those of conventional (inorganic) paleoclimate proxies.

[3] Carbon isotopic measurements of alkenones to determine historical pCO₂ [Andersen et al., 1999; Jasper and Hayes, 1990] levels also hold great promise for paleoclimate reconstructions. Concentrations of greenhouse gases, such as carbon dioxide, increased by 1/3 during glacial terminations [Petit et al., 1999]. Extending the detection of these changes beyond the limit of

polar ice cores (i.e., $> \sim 420$ ka) and to warm periods of the Cretaceous and Tertiary [*Pagani et al.*, 1999a, 1999b], is an important step in predicting the climate response to increased anthropogenic CO₂ concentrations.

[4] In this summary report from the National Science Foundation Sponsored Alkenone Workshop in Woods Hole, Massachusetts, October 3–5, 1999, we (1) assess processes with the potential to affect alkenone-based SST determinations and isotopic paleobarometry, (2) provide indicators of and remedies to these confounding processes, and (3) recommend specific experiments to assess the impact and importance of these processes.

2. Summary of Findings

[5] Physical, chemical, and biological processes may affect alkenone paleotemperature estimates and isotopic records. Physical processes such as sediment mixing and advection can smooth the alkenone SST and isotopic signals, introduce apparent temporal offsets relative to other paleoclimate proxies, and introduce allochthonous alkenones. Chemical factors such as the kinetics and thermodynamics of alkenone degradation can potentially alter alkenone unsaturation and isotopic ratios. Biological processes including growth rate and the depth and season of alkenone production, the biochemical response to changing nutrient and salt concentrations, and the evolution of alkenone-producing flora (prymnesiophytes) can also affect alkenone unsaturation and isotopic ratios preserved in the sedimentary record.



- [6] While certain of these processes are not unique to alkenone-based proxies (e.g., bioturbational smoothing, diagenesis, and variation of depth and seasonality of the paleoceanographic signal carrier), they should be assessed and circumvented if possible by working in high deposition rate locations and where the depth and season of alkenone production are known and believed to have remained unchanged through time. Other processes, such as differential mixing rates of large and small particles, may significantly alter the relative timing of alkenone-based reconstructions (thought to be contained in small particles) relative to those based on the sand-sized foraminifera, including faunal abundance and isotope records and accelerator mass spectrometry (AMS) radiocarbon dates. Similarly, sediments and alkenone-containing particles can be redistributed by benthic processes and by ice, thus affecting estimates of paleotemperature and pCO_2 in certain locations.
- [7] We recommend modeling, laboratory, and field-based studies to determine the size distribution of alkenone-containing particles and to quantify the importance of vertical and lateral redistribution processes on alkenone-derived SST and pCO_2 estimates. Since alkenone biosynthesis and diagenesis were the focus of other working groups, we focus our discussion primarily on the physical processes that can affect alkenone paleotemperature estimates.

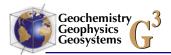
3. Lateral and Vertical Redistribution

[8] Combining faunal and isotopic data from carbonate phases with measurements of alkenone unsaturation and isotopic ratios can provide more detailed paleoclimate information than the individual measurements [Bard et al., 1997; Chapman et al., 1996; Madureira et al., 1997; Rostek et al., 1993; Sikes and Keigwin, 1994; Weaver et al., 1999]. A logical extension of this approach has been the coupling of foram

and alkenone data to derive estimates of salinity [Rostek et al., 1993] and paleo-pCO₂ [Jasper and Hayes, 1990; Jasper et al., 1994]. Successful coupling of sedimentary organic and inorganic climate proxies requires that vertical and lateral transport processes affect each phase similarly and that the depth and season of production of each be the same (or at least known).

[9] Rapidly accumulating pelagic sediments facilitate the resolution of climate events with suborbital (millennial) durations [Bond et al., 1993; Broecker et al., 1988; Chapman and Shackleton, 1998; Keigwin and Jones, 1989; Keigwin et al., 1991; Lehman and Keigwin, 1992]. Rapid sediment accumulation at open ocean sites far from margins, slopes, and upwelling areas is most often caused by lateral "focusing" of fine-grained material, resulting in drift deposits [Hollister et al., 1978; McCave and Tucholke, 1986]. Sediment drifts have accumulation rates that may reach 10-100 times that of typical pelagic sediments [Keigwin and Jones, 1989; Ruddiman and Bowles, 1976; Silva et al., 1976]. A common characteristic of such sites is that during episodes of exceptionally high accumulation rate, coarse particles such as foraminifera tests are heavily diluted by clay and silt-sized grains.

- [10] As an example, one of the drift deposits that is the subject of considerable interest is the Bermuda Rise [Heezen et al., 1966], which preserves a high-resolution climate archive of the warm subtropical northwest Atlantic [Keigwin and Jones, 1994]. This deposit is believed to be maintained by lateral advection of distal, fine-grained detrital components of turbidity flows from the Canadian maritime provinces (Laurentian Fan) by the deep western boundary current [Laine and Hollister, 1981].
- [11] At the Bermuda Rise, alkenone-based temperature estimates indicate a ~5°C degla-



cial increase of SST that is bracketed by winter and summer SSTs derived from planktonic foraminiferal assemblages using the modern analog technique (S. J. Lehman et al., manuscript in preparation, 2000). Notably, coincident with the deglacial warming is a 10-fold decrease in alkenone concentration from ~ 1 to ~ 0.1 µg/gdw. The concentration difference could be related to changes in alkenone preservation, production, or lateral advection. Considering the latter, while coarse, dense particles such as planktonic foraminifera likely derive from overlying surface waters, fine particles, possibly enriched with organic material, can be transported long distances. Thus lateral transport may introduce organic matter from regions of colder or warmer temperatures, compromising interpretation of the regional climate signal. In the Argentine Basin of the western South Atlantic, for example, core top alkenone SST estimates deviate significantly from ambient, surface ocean temperatures, apparently due to lateral displacement of suspended particles and sediments by strong surface and bottom currents, benthic storms, and downslope processes [Benthien and Müller, 2000].

[12] There are several approaches to assessing the impact of lateral advection on sedimentary alkenone unsaturation and isotopic ratios. For example, one can compare alkenone-derived time series to sedimentological parameters such as weight percent CaCO₃. Whereas a variable phase relationship, such as that observed at the Bermuda Rise, is good evidence for a minimal role of advection [Sachs and Lehman, 1999], phase-locked SST and CaCO₃ signals would be consistent with a dominant advective component of sedimentary alkenones. Other approaches include mineralogical or geochemical assessment of the source of fine-grained material. For instance, uraniumseries isotopes can be used to quantify the amount of sediment focusing at a site [Bacon,

1984; Suman and Bacon, 1989], and clay mineralogy and Al/Ti ratios can provide insights into the source of fine-grained material. Consideration of the abundance of the cold water, or tetra-unsaturated C₃₇ methyl alkenone, which is produced only at high latitudes [Rosell-Mele, 1998], can be another indicator of advected sediment in certain locations.

[13] Nevertheless, a critical first-order question in assessing the impact of horizontal (advective) and vertical (mixing) transport on alkenone-derived temperature estimates is determining the sedimentary component in which they reside. Although this may vary with location, an important first step would be to confirm the common inference that they reside within fine-grained particles. Thus alkenone concentrations and distributions in size/density fractionated sediments should be measured in a variety of settings. Hydrodynamic sorting of sediment into size fractions can be accomplished using a split-flow lateral-transport thin (SPLITT) device [Giddings, 1985; Keil et al., 1994]. If indeed alkenones reside in the fine fraction, then it is recommended that attempts be made to place alkenone SSTs on δ^{18} O stratigraphies from the fine-grained (or coccolith) fraction. In this way, reliable paleosalinity reconstructions may be obtainable.

[14] Vertical redistribution, or bioturbation, in oxygenated sediments can diminish the temporal resolution of downcore records [Berger and Heath, 1968; Goreau, 1980; Schiffelbein, 1984]. Biological mixing can also decouple coarse from fine sedimentary components [McCave, 1995; Wheatcroft, 1992]. The smoothing of climate signals that results from bioturbation has been extensively studied and is, in general, inversely dependent on sediment accumulation rate [c.f. Guinasso and Schink, 1975]. This is so because vigorous benthic mixing occurs in a limited zone beneath the



seafloor [Boudreau, 1994; Goldberg and Koide, 1962; Jumars and Wheatcroft, 1989]. As rates of sedimentation increase, residence times within this mixing zone decrease [Berger and Heath, 1968]. Thus locations with high sedimentation rates (e.g., >20 cm/kyr) will yield alkenone-derived time series with only minor smoothing of millennial-timescale climate signals. Another artifact of bioturbation stems from the fact that the depth of mixing is dependent on particle size [Ruddiman and Glover, 1972; Thomson et al., 1988; Wheatcroft, 1992; Wheatcroft and Jumars, 1987]. Small particles are preferentially ingested by deposit feeders and mixed downward, in effect biologically "pumping" coarser particles toward the surface [McCave, 1988, 1995]. If the size fraction of alkenone-enriched particles differs from that of foraminifera, there is the potential for climate proxies to become decoupled or offset in the depth (and time) domain. This process has been cited as a possible cause for the deep penetration of bomb-derived radionuclides in North Pacific sediments [Druffel et al., 1984] and for radiocarbon age differences between forams and bulk carbonate in northeastern Atlantic sediments [Thomson et al., 1995] and between forams and nannofossils (coccoliths) in South Atlantic sediments [Paull et al., 1991].

[15] Although the vertical flux of organic matter through the water column is believed to result from sedimentation of large particles and aggregates [McCave, 1984], these materials rapidly dissociate and become finely disseminated upon arrival at the seafloor [Aufret and Khripounoff, 1994; Lampitt, 1985]. As a result, organic matter can preferentially mix downward during bioturbation. Evidence for such an effect is inferred from subsurface concentration maxima in labile organic compounds [Conte et al., 1994; Santos et al., 1994; Conte et al., 1995] and ²¹⁰Pb [Smith et al., 1986; Thomson et al., 1988].

[16] Presently, the number of high-resolution studies where inorganic and molecular organic proxies have been jointly measured provides limited opportunity to closely examine sediment records for potential offsets. However, Madureira et al. [1997] note that a decrease in alkenone-derived SST appeared to precede the onset of Heinrich events H3 and H6 while maxima in Neogloboquadrina pachyderma (sinistral, left coiling variety) abundances coincided with these layers [Madureira et al., 1997]. While the authors pointed out that better age resolution is needed to determine the origin of these leads and lags, the sense of the observed trends is consistent with differential sediment mixing. A similar apparent offset between alkenone and foram SST records may be discernible in deglacial sediments from the Bermuda Rise (S. J. Lehman et al., manuscript in preparation, 2000).

[17] Potential factors controlling the depth of bioturbation (and thus the magnitude of potential temporal offsets) are numerous and complex [Trauth et al., 1997]; however, the rate and nature of accumulating sediments may play a significant role. Oxygen penetrates deeply into sediments in typical low sediment deposition rate (<5 cm/kyr) pelagic environments but not when sediments accumulate rapidly, particularly if that accumulation is associated with an increased flux of metabolizable carbon. Since an increase in sedimentation rate is not always associated with an increased flux of metabolizable carbon, such as in submarine deltas associated with major river systems and in locations experiencing high dust fluxes, these areas may be especially useful for coupled alkenone and foraminiferal-based paleoclimate studies.

[18] Studies aimed at measuring the ¹⁴C age discrepancy between alkenones and other biomarkers and carbonate phases are underway at the Bermuda Rise and Cariaco Basin (by T. I.



Eglinton). Additional such studies are recommended. These studies will likely never be routine, given the analytical difficulty and large sample sizes required. However, until the effect of differential mixing rates of forams and alkenone-bearing phases are quantified, the climatic significance of apparent temporal offsets between biomarkers and forams should be interpreted cautiously.

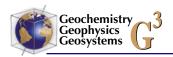
4. Annual Mean Versus Seasonal SST

[19] Global core top sediment calibrations of the alkenone paleothermometer [Müller et al., 1998] are most consistent with mean annual SSTs at 0-m water depth. This is enigmatic since much of the ocean is characterized by seasonal or episodic maxima in haptophyte production [Brown and Yoder, 1994]. The simplest explanation for the apparent inconsistency is that there may be little difference between the annual mean SST and the SST during the season of maximum haptophyte production in many of the studied locations [c.f., Müller et al., 1998]. A second possibility is that much of the fresh organic rain from a bloom is consumed rapidly at the seafloor by a thriving benthic fauna [Prahl et al., 1993]. The slow rain of alkenones the remainder of the year might thus be "over-represented" in the sediments, resulting in an annual mean alkenone SST.

[20] A third possibility is that preferential loss of the tri-unsaturated ketone relative to the diunsaturated ketone during early diagenesis [Gong and Hollander, 1999; Hoefs et al., 1998] results in an apparent "warming," or increase, of the alkenone unsaturation ratio. Laboratory studies provide no evidence for alteration of alkenone unsaturation ratios during microbial [Teece et al., 1998] or photochemical [Rontani and Cuny, 1997] degradation or during grazing [Grice et al., 1998; Volkman et

al., 1980]. However, the timescales of these experiments are vastly different from those over which these compounds reside in the zone of active diagenesis. Field studies have yielded mixed results to date, and although the majority seem to indicate little or no effect of diagenesis on the alkenone unsaturation ratio [Conte et al., 1992; Prahl et al., 1989; Sikes et al., 1991], other reports indicate some diagenetic alteration [Gong and Hollander, 1999; Hoefs et al., 1998]. It should be noted, however, that the conclusions of Hoefs et al. [1998] may not be valid given near-detection-limit concentrations of the tri-unsaturated alkenone (J. Grimalt, personal communication, 1999). Thus, the stability of the unsaturation ratio during all phases of diagenesis should be confirmed. Both field and laboratory observations are required. In the meantime, near-surface, alkenone-derived records of SST cooling that mirror typically exponential declines in the concentration of organic carbon should be interpreted with caution, since this would be consistent with the preferential diagenetic loss of the tri-unsaturated alkenone. Even if selective losses are occurring, downcore studies may not be negatively impacted. Assuming the diagenetic process is constant through time it would simply produce a warm bias to the time series. Alternatively, large changes in sedimentation rate or bottom water oxygen concentrations could alter the magnitude of diagenetic overprinting by altering the duration of active diagenesis or the type of heterotrophic activity and should therefore be assessed.

[21] Finally, it has been suggested that seasonal alkenone production could lead to spurious paleotemperature records if the season of production changed rather than some reference or mean annual SST. In the often cited scenario where haptophyte production precesses from spring to summer in response to colder mean annual temperatures, it is unlikely to result in a spurious alkenone SST time series because the



temporal delay of the bloom would merely result from delayed stabilization of the surface layer. Thus the seasonal alkenone flux would capture the same annual surface water conditions as the bloom precessed in time. The associated SSTs would be close to the annual minimum temperature in much of the subtropics and mid-latitudes [Levitus and Boyer, 1994] since blooms in those regions typically coincide with the cessation of deep, winter mixing. At that time, which marks the onset of thermal stability, nutrients are still abundant in the surface layer [Parsons et al., 1984].

5. Regionality of Alkenone-Derived Climate Signals

[22] Global core top calibrations of the alkenone unsaturation ratio as an SST proxy for latitudes between 60°N and 60°S and mean annual SSTs (at 0 m) of 0°C to 29°C indicate a robust relationship $(r^2 = 0.98, n = 370)$ [Müller et al., 1998] indistinguishable from that derived originally from cultures of Emiliania huxlevi [Prahl et al., 1988]. An analysis of the residuals indicated a standard error of regression of 1.5°C with no latitudinal dependence [Müller et al., 1998]. Regional differences between alkenone-derived and other climate proxies may thus be climatically significant. Alternatively, one or more of the proxies may be affected differently in certain regions (e.g., depth of production and/or calcification), and as discussed above, differential mixing of forams and alkenones could induce or obscure synchroneity as well as asynchroneity. Unfortunately, many late Quaternary time series are from locations with low to moderate (i.e., <10 cm/kyr) sedimentation rates. Despite that caveat, certain patterns of asynchroneity between alkenone and foram-derived climate proxies seem to be emerging on a variety of timescales between tropical and mid-latitude regions, as well as between upwelling and subtropical gyre locations.

[23] While SST records from subtropical gyres closely resemble the pattern of oxygen isotope records from ice cores and marine foraminifera over the last four glacial cycles, those from the tropical ocean indicate significantly warmer temperatures for MIS 6 compared to other glacial intervals (MIS 2-4 and 8) [Eglinton et al., 1992; Herbert and Schuffert, 1999; Rostek et al., 1993; Schneider et al., 1999, 1995, 1996]. Moreover, in upwelling areas and associated boundary current systems, alkenonederived SST records frequently indicate maximum cooling during the middle stages of glacial intervals, with warming trends beginning 10–15 kyr before records of benthic δ^{18} O indicate decreases of ice volume at glacial terminations. This feature has been described for the east equatorial Pacific [Lyle et al., 1992], the Santa Barbara Basin [Herbert et al., 1995], the West African Margin [Eglinton et al., 1992; Kirst et al., 1999; Müller et al., 1997; Schneider et al., 1996], the Cariaco Basin [Herbert and Schuffert, 1999], and the Arabian Sea [Rostek et al., 1993], and may indicate regional differences in the timing of major warming and cooling events between subtropical gyres, upwelling regions, and equatorial current systems.

[24] Relatively few alkenone SST records with high temporal resolution of (i.e., decades to centuries) have been published. Those from the subtropical North Atlantic [Sachs and Lehman, 1999] and the Mediterranean Sea [Cacho et al., 2000] closely covary with isotope paleotemperature records from Greenland ice cores, indicating that the near-polar atmosphere and subtropical surface ocean warmed and cooled together during Dansgaard-Oeschger cycles. By contrast, SST records of moderate to relatively high temporal resolution from the South China Sea [Pelejero et al., 1999; Wang et al., 1999] and the South Atlantic [Kirst et al., 1999] do not show pronounced, millennial-scale SST



variability. This lack of marked Dansgaard-Oeschger cyclicity in alkenone-based SST reconstructions contrasts with oxygen isotope evidence from planktonic foraminifera from the South Atlantic [Charles et al., 1996] and from the South China Sea [Wang et al., 1999], which indicate significant variations in surface hydrography at suborbital time scales. These differences suggest either that the oxygen isotope variations are due solely to salinity changes or that the alkenone records were not sufficiently resolved to capture rapid and short-lived SST changes in these regions.

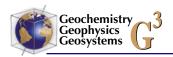
[25] Poleward of the Arctic and Antarctic polar fronts, there are presently no reliable alkenone records owing to very low alkenone production. In such regions, sedimentary alkenones may derive in large part from ancient deposits scoured by glacial ice [Weaver et al., 1999]. Only where warm currents prevailed (at least during the summer season, e.g., in the far northeast Atlantic) have alkenones yielded reasonable SST records. However, in the belt of ice-rafted debris (IRD) deposition, alkenone records can be biased by the admixture of autochthononous with allochthonous alkenones [Weaver et al., 1999]. In such locations, characterized by sporadic widespread delivery of icebergs, the potential effect of salinity changes on the biochemistry of alkenone production may also be important [Rosell-Mele, 1998].

[26] Existing alkenone records have provided important late Quaternary SST histories that often differ from those derived from faunal census data. Regional differences in the apparent timing of alkenone-derived SST and other climate-proxy changes may provide insights into the mechanisms of climate change. Alternatively, they may result from different biological responses of forams and coccoliths in different oceanographic regimes, from differential vertical sediment mixing, or from lateral sediment advection. Until additional alkenone

records are published from high sedimentation rate locations in important oceanographic regimes (e.g., upwelling, equatorial, polar, subpolar, subtropical, tropical), and their SST histories are assessed in the context of benthic δ¹⁸O stratigraphy and other paleoclimate proxies, we recommend caution in interpreting the climatic significance of apparent temporal asynchroneities between alkenone and other climate proxies. We strongly urge that future alkenone investigations be coupled with other paleoclimate proxy measurements at high deposition rate sites in a variety of oceanographic settings. Concurrent studies of alkenone-derived SSTs and salinity and nutrient proxies are also recommended, especially in upwelling areas and in the vicinity of river plumes, since changes in these parameters may effect alkenone biosynthesis [Epstein et al., 1998; Rosell-Mele, 1998].

6. Alkenone δ^{13} C Records

[27] Historical pCO_2 levels in the atmosphere can potentially be estimated from the carbon isotopic composition of alkenones and co-eval carbonate phases [Jasper and Hayes, 1990; Jasper et al., 1994]. A small number of alkenone δ^{13} C records have been used to date to estimate late Quaternary and Miocene pCO₂ [Andersen et al., 1999; Jasper and Hayes, 1990; Jasper et al., 1994; Pagani et al., 1999a, 1999b]. Since both culture and field studies indicate that the δ^{13} C values of alkenones reflect haptophyte growth rates, nutrient levels, and the concentration of dissolved CO₂ in ocean surface waters [Bidigare et al., 1997], reliable paleo-pCO₂ estimates require proxy estimates of nutrient concentrations, growth rates, and/or productivity [Bidigare et al., 1999; Popp et al., 1997]. Downcore studies in tropical and subtropical locations indicate only minor changes in the δ^{13} C value of alkenones for Quaternary [Andersen et al., 1999; Jasper et al., 1994] and Miocene [Pagani et al.,



1999a, 1999b] sections, when compared to the Holocene. This may mean that surface ocean CO_2 concentrations did not undergo pronounced changes over the last several million years. Alternatively, the effect on alkenone $\delta^{13}C$ from CO_2 changes could have been opposed by concurrent changes in growth rate and or nutrient concentrations.

[28] Culture experiments have documented consistent relationships between CO2 concentration and nutrient conditions in controlling the isotopic fractionation associated with haptophyte growth and alkenone production [Bidigare et al., 1997; Popp et al., 1998]. However, recent culture studies indicate that other growth-controlling factors, such as light limitation, are also important [Riebesell et al., 2000]. Nevertheless, it is encouraging that results from the field are consistent with those from cultures [Bidigare et al., 1997], and that environmental conditions most favorable for alkenone production are those that minimize the influence of these additional factors (E. Laws, personal communication, 1999). Alkenone δ^{13} C values should thus be cautiously interpreted in terms of past CO₂ concentrations (or nutrient conditions if the other property is constrained). For such investigations, we strongly recommend that alkenone CO₂ reconstructions be attempted in regions where other proxies imply only minor changes in past nutrient conditions and productivity [Pagani et al., 1999a], and that future such reconstructions be performed concurrently with surface nutrient and paleoproductivity estimates [Bidigare et al., 1999; Popp et al., 1997].

[29] Finally, we recommend widespread core top calibrations of the alkenone δ^{13} C pCO₂ proxy [*Jasper et al.*, 1994] (with concurrent measurements of surface nutrient and light parameters), similar to those performed for the alkenone unsaturation SST proxy. In addition, multisite, high-resolution studies of late

Pleistocene sediments from open-ocean sites should be conducted in order to compare alkenone $p\text{CO}_2$ estimates to ice core records of carbon dioxide variations. Together, these studies will increase confidence in the use of alkenone $\delta^{13}\text{C}$ values for paleo- $p\text{CO}_2$ reconstructions.

7. Conclusion

[30] Molecular tools are gaining widespread acceptance in paleoceanography as new climate proxies are discovered and analytical techniques improve. It is now possible to generate very high resolution time series' of sea surface temperature from alkenone unsaturation ratios in less time, at lower cost, and with smaller samples than with conventional faunal and isotopic methods. Indeed, the quality of the many alkenone-derived SST records published to date is impressive. Nevertheless, there is a great need for additional high-resolution studies in a wide variety of high sedimentation rate environments where smoothing and differential mixing of climate proxies during bioturbation can be minimized. These measurements should be performed in cores with good benthic δ^{18} O stratigraphies and in concert with other paleoclimate proxies. In addition, the importance of advected alkenones must be assessed. Measurements to determine the origin of sedimentary alkenones should be performed wherever possible, and assessment of alkenonederived climate signals should be made in the context of other sedimentological (mineralogical and geochemical) components indicative of laterally advected material. Regional asynchronies between alkenone-derived SSTs and other climate proxies should be interpreted with caution in all but the highest deposition-rate environments. Finally, while the prospect of determining paleo-pCO2 levels from alkenone δ¹³C values prior to 420 ka (the limit of polar ice cores) is promising, additional field studies, including core top calibrations and compari-



sons with late Pleistocene records of atmospheric CO₂ from ice cores, are urged.

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