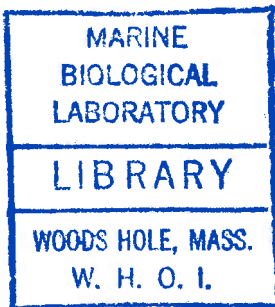


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Determination of Sediment Provenance at Drift Sites Using Hydrogen Isotopes in Lipids



by

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B.S. Geology
B.S. Environmental Science
Lake Superior State University, 2001

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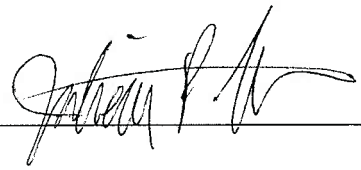
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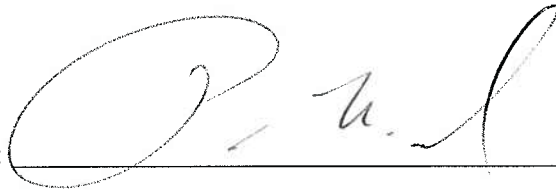
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-Drift-

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Determination of sediment provenance at drift sites using hydrogen isotopes in lipids

Amy C. Englebrecht

Abstract--Paleoclimate records with sufficient length and temporal resolution to study the occurrence and causal mechanisms of abrupt climate change are exceedingly rare. Rapidly deposited ocean sediments provide the best archive for studying these events through geologic time, but such sites in the open ocean are limited to sediment drift deposits such as the Bermuda Rise in the northwest Atlantic. Using multiple climate proxies in a single core is becoming more common in high-resolution paleoclimate investigations, but a major potential concern for this approach arises from the possibility that the fine fraction of sediment ($< 63 \mu\text{m}$), and the climate proxies within it, may represent conditions far from the deposition site. We hypothesize that hydrogen isotope ratios of alkenones, a class of lipids from phytoplankton, may provide insight into the source of fine fraction sediment. Because of their restricted sources, broad geographic distribution, and excellent preservation properties, alkenones are of particular interest in the emerging field of compound-specific hydrogen isotopic analysis, and the sedimentary abundances, extents of unsaturations, and isotopic compositions of alkenones provide quantitative and near-continuous records. We isolated alkenones from cultured unicellular algae (haptophyte *Emiliana huxleyi*), surface ocean particulate material, and open ocean sediments to determine the extent and variability of hydrogen isotopic fractionation in the di-, tri-, and tetraunsaturated C_{37} compounds. We then compared the δD of the alkenones in surface sediments between the Bermuda Rise and the Scotian Margin above which a large ($\sim 20\text{‰}$) δD gradient exists. We determined the fractionation between alkenones from suspended particulate samples and the water in which the phytoplankton lived, and examined the variability of alkenone δD during key climate transitions at the Bermuda Rise.

Thesis Supervisor: Julian P. Sachs

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Chapter 1: Introduction

1.1 Goals of Thesis

The goals of this thesis were to: 1) confirm predictability of $\Delta\delta D$ between environmental water and alkenones; 2) determine if initial D/H ratios of alkenones persist downcore in sediments; 3) use alkenone δD to elucidate origin of fine fraction sediment at the Bermuda Rise during key climate transitions.

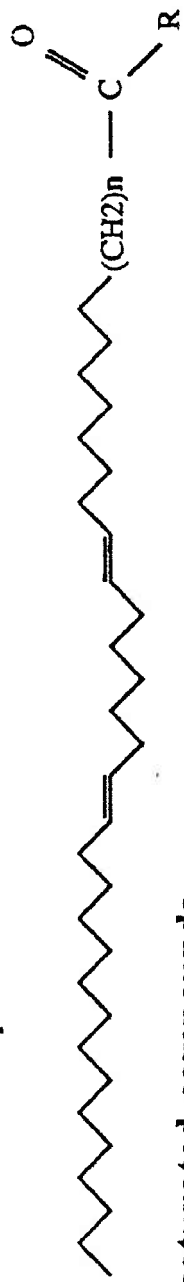
1.2 Overview of Alkenones as a Paleocceanographic Proxy

Temporal records in cores from lakes and ocean sediments, in coral reefs, and in polar ice encode information on natural variations of the climate system. One of the most fundamental and important parameters needed to study ocean-climate linkages is sea surface temperature (SST). Geochemical proxies that reflect past environmental conditions are employed to understand large-scale shifts in climate, and in the mid-1980's a new paleo-SST proxy based on a class of sedimentary organic compounds called alkenones was introduced (Brassell et al., 1986b). This formed the basis for a new approach to paleoclimate study: molecular stratigraphy.

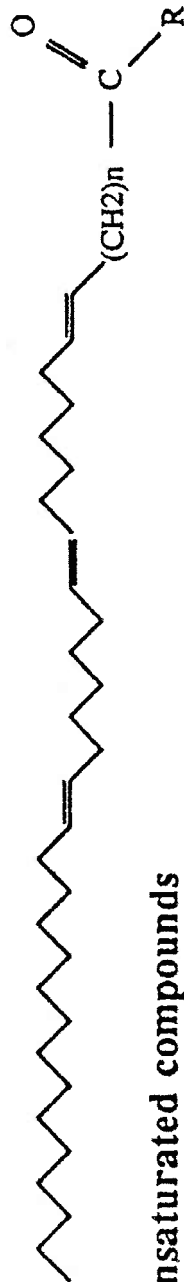
Emiliana huxleyi, a cosmopolitan coccolithophorid, is an abundant species in both open ocean and coastal waters and is noted for its propensity to form immense blooms that have a major impact on the biological carbon cycle and on atmosphere/ocean fluxes of carbon dioxide and volatile sulfur compounds (reviewed in Westbroek et al., 1993). *E. huxleyi* and *Gephyrocapsa oceanica*, a member of the genus from which *E. huxleyi* is believed to have evolved (Marlowe et al., 1990), are distinguished by their synthesis of a suite of C₃₇-C₃₉ methyl and ethyl ketones, collectively called alkenones (Volkman et al., 1980; 1995; Figure 1). Although the location and biochemical function of these compounds within the cell is not presently known, it is recognized that the synthesis of alkenones is restricted taxonomically and has been documented only within the haptophyte order Isochrysidales (reviewed in Conte et al. 1994).

Alkenones gained attention after recognition that their degree of unsaturation is strongly controlled by the growth temperature of their producers (Marlowe, 1984) and that downcore

I Diunsaturated Compounds:



II Triunsaturated compounds



III Tetraunsaturated compounds

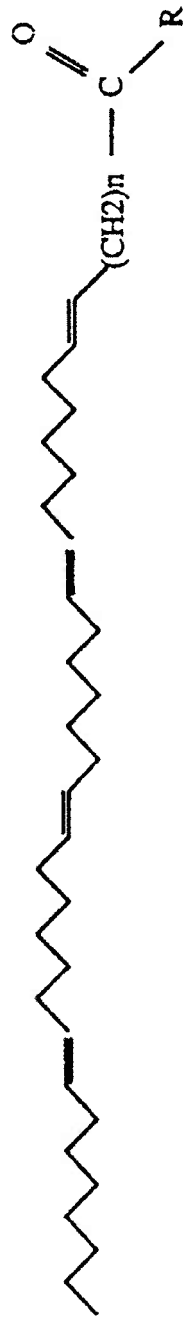


Figure 1.

(glacial-interglacial) variations in the ratio of di-, tri-, and tetraunsaturated alkenones closely corresponded with shifts in oxygen isotopic compositions of planktonic foraminifera (Brassell et al., 1986b). The unusual trans geometry of the double bonds (Rechka and Maxwell, 1988) may be responsible for preservation of the unsaturation ratios downcore, and alkenones have been demonstrated to be stable over time in the water column and during early diagenesis in sediments (Conte et al., 1992). Brassell et al. (1986a,b) defined an alkenone unsaturation index, $[U_{37}^K = (37:2 - 37:4)/(37:2 + 37:3 + 37:4)]$ and proposed U_{37}^K could be used as an indicator of paleo-SST. Prahl et al. (1988) calibrated C_{37} alkenone unsaturation with growth temperature for a NE Pacific strain of *E. huxleyi*, and Prahl and Wakeham (1987) demonstrated that a modified index, $U_{37}^{K'} [= (37:2)/(37:2 + 37:3)]$ varied linearly with SST, with an accuracy in $U_{37}^{K'}$ value of ± 0.02 units. This corresponds to a growth temperature precision of $\pm 0.6^\circ\text{C}$ (Prahl and Wakeham, 1987; Sikes and Volkman, 1993).

The sedimentary abundances, extents of unsaturations, and isotopic compositions of alkenones provide quantitative and near-continuous records, and along with restricted sources, broad geographic distribution, and excellent preservation properties, alkenones provide an opportunity to reconstruct paleo-SST on a global scale. These same characteristics make alkenones of particular interest in the emerging field of compound-specific hydrogen isotopic analysis.

1.3 Hydrogen Isotopes in the Environment

Stable hydrogen isotope ratios of modern and fossil organic substrates contain potentially valuable climatic information (Buchardt and Fritz, 1980; Yapp and Epstein, 1982; Smith et al., 1983; Schimmelmann et al., 1986; Miller et al., 1988; Friedman et al., 1988; Miller 1991). Trends in the distribution patterns of deuterium and oxygen-18 concentrations in meteoric waters (rain and snow) reveal a close correlation among some climatically relevant meteorological parameters, such as surface air temperature or amount and isotopic composition of precipitation (Craig, 1961; Dansgaard, 1964). Fractionation from non-equilibrium processes such as evaporation lead to imperfections in the correlation between $\delta^{18}\text{O}$ and δD , but the first order signals of $\delta^{18}\text{O}$ and δD can be used interchangeably (Dansgaard, 1964). That near-linear relationship is often plotted as the Global Meteoric Water Line (Figure 2). Using this

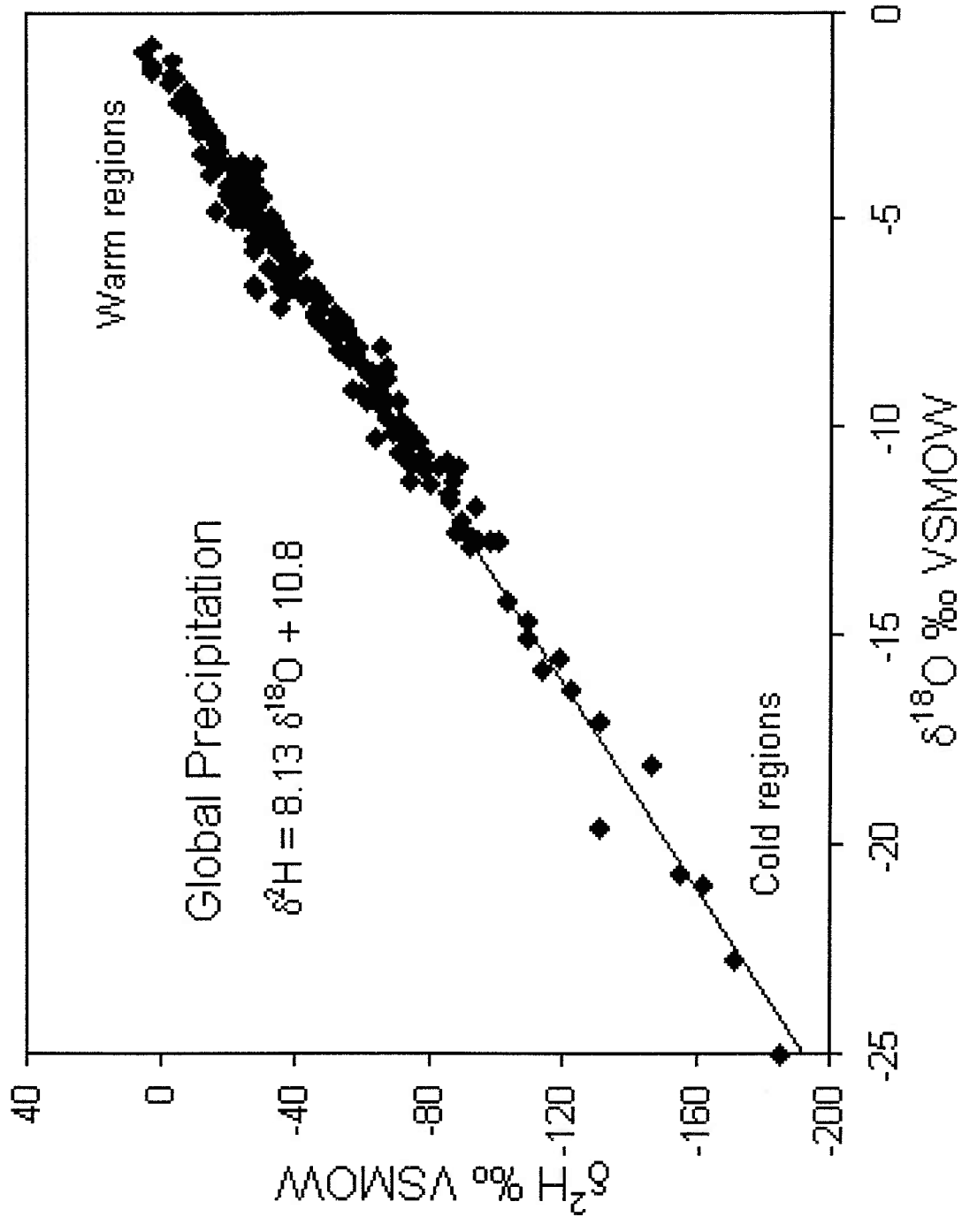


Figure 2.

relationship, [$\delta D \cong 8\delta^{18}O + 10$], and the extensive surface-ocean $\delta^{18}O$ data set available, a map of surface ocean δD has been constructed (Figure 3) and reveals a strong gradient in surface ocean δD in the northwest Atlantic. Analyses of water samples from this region confirming this gradient are presented in Chapter 2.

At low temperatures, water hydrogen exchanges quickly and reversibly with labile organic hydrogen, most of which is bound to organic nitrogen, sulfur, and oxygen (Koepp, 1978; Werstiuk and Ju, 1989), limiting the usefulness of measuring total D/H ratios in most organic compounds. Known exceptions are hydrocarbons and lipids (Schoell, 1984; Sternberg, 1988), nitrated cellulose (Epstein et al., 1976) and chemical derivatives of chitin (Schimmelmann and DeNiro, 1986; Miller et al., 1988). Water at neutral pH and low temperature in the absence of a catalyst does not readily exchange with most carbon-bound hydrogen, thereby conserving the D/H ratios of *n*-alkanes at temperatures well above 150°C (Koepp, 1978; Hoering, 1984). Only hydrogen in a few aromatic and alkyl sites adjacent to branching and carbonyl positions may start to reversibly exchange around 100°C (Alexander et al., 1981; Werstiuk and Ju, 1989), especially at low pH. In addition to these reversible processes, irreversible hydrogen isotopic exchange may occur as a consequence of chemical reactions of organic matter. Sufficient activation energies to break carbon bonds, such as that provided by exposure to radiation (Dahl et al., 1988) or high temperatures (Hoering, 1984; Seewald et al., 1998), as well as reactions involving radicals (Schoell, 1984) facilitate isotopic exchange between C-H and ambient water hydrogen.

1.4 Hydrogen Isotopes in Lipids

Hydrogen isotopic compositions of lipids are controlled by three factors: isotopic compositions of biosynthetic precursors, fractionation and exchange accompanying biosynthesis (Martin et al., 1986), and hydrogenation during biosynthesis (Smith and Epstein, 1970; Luo et al., 1991). Sternberg (1988) examined lipids in submerged aquatic plants and found hydrogen isotopes fractionate predictably, thereby recording the D/H ratio of environmental water. Sessions and coworkers (1999) developed a reliable analytical system capable of measuring the D/H ratio of individual organic compounds, leading to the discovery that while different compounds within a given class (e.g. sterols) can have substantially different δD in different

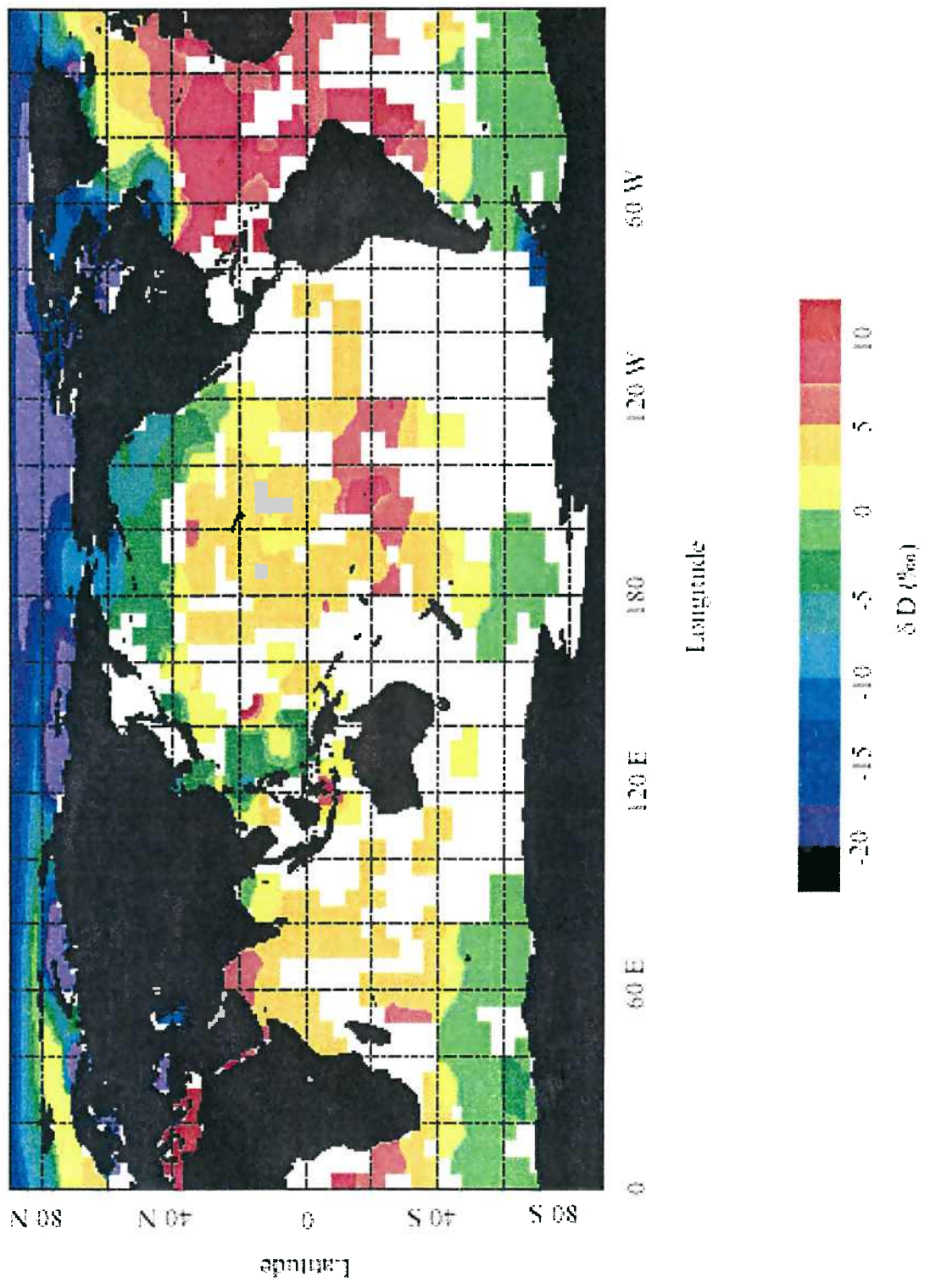


Figure 3.

organisms despite growing in water with the same hydrogen isotopic composition, there was little isotopic variability within specific compound classes in individual organisms, and δD of individual lipids in each class generally fell within a range of $< 50\text{‰}$ (Sessions et al., 1999).

1.5 Studying Paleoclimate at the Bermuda Rise

Paleoclimate records with sufficient length and temporal resolution to study the occurrence and causal mechanisms of abrupt climate change are exceedingly rare. Rapidly deposited ocean sediments provide the best archive for studying these events through geologic time, but such sites in the open ocean are limited to sediment-drift deposits such as the Bermuda Rise in the northwest Atlantic Ocean (Figure 4). In the deep ocean away from continental margins, sediments consist entirely of material from the upper ocean that is a mixture of sand-sized ($>63 \mu\text{m}$) particles, mostly of foraminiferal origin, and fine particles ($<63 \mu\text{m}$) that consist of wind-blown dust and phytoplankton detritus. But sedimentation rates at open ocean sites are extremely low, on the order of a few centimeters per 1000 years, or in the case of the North Pacific, less than one centimeter per 1000 years. In drift deposits, however, flux of laterally transported sediment exceeds vertical flux, leading to high accumulation rates (Bacon and Rosholt, 1982; Bacon, 1984; Suman and Bacon, 1989), sometimes up to 1-2 m of sediment per 1000 years.

Using geochemical (e.g. Sachs and Lehman, 1999; Sachs et al., 2001), faunal (e.g. McManus et al., 1994; Keigwin and Pickart, 1999; Lehman et al., 2002), and isotopic (e.g. Keigwin and Jones, 1989; Charles et al., 1996; Keigwin, 1996; Adkins et al., 1997; Raymo et al., 1998; Draut et al., 2003) proxies, many studies have targeted drift sites to construct detailed paleoclimate records and improve understanding of abrupt climate change. To avoid mistaken interpretations, it is important to develop parallel, independent proxy records that can provide constraints and confirmations. The use of multiple climate proxies in a single core is becoming more common in high-resolution paleoclimate investigations and, in this approach, the assumption is made that climate proxies measured in the same depth interval of sediment represent the same interval of time. This circumvents chronological uncertainties associated with comparing proxy records from different cores whose age models have substantial uncertainties. In addition, multiple proxies of the same physical parameter, such as SST, can be

