Determination of sediment provenance at drift sites using hydrogen isotopes and unsaturation ratios in alkenones

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Abstract—The large (∼20‰) hydrogen isotopic gradient in surface waters of the northwest Atlantic Ocean is exploited to track changes in the source of alkenones to the Bermuda Rise sediment drift. Cultures of the predominant alkenone-producing coccolithophorid, E. huxleyi, were grown in deuterium-enriched seawater and shown to possess alkenones with a D/H ratio that closely tracked the water D/H ratio (r² = 0.999, n = 5 isotopic enrichments) with a fractionation factor (α) between 0.732 and 0.775. A hydrogen isotopic depletion of −193 ± 3‰ (n = 9) was measured in alkenones from suspended particles relative to seawater in the subpolar and subtropical northwest Atlantic Ocean. This value was used to calculate the water ∆D values in which alkenones from Bermuda Rise sediment were synthesized, and by extension, the water mass in which they were produced. Applying this technique we find that 60% to 100% of the alkenones in late Holocene Bermuda Rise sediment were produced in deuterium-depleted subpolar water to the northwest of the drift. To reconcile values of the alkenone unsaturation ratio (U'k), a widely used proxy for sea surface temperature, with the ∆D values of alkenones in late Holocene sediments from the Bermuda Rise at least three sources of sediment must be invoked: a cold, very isotopically depleted source, likely to be the Scotian Margin; a warm, moderately isotopically-depleted source, likely to be the northwestern edge of the subtropical gyre; and a cold, isotopically enriched source, which we hypothesize to be the subpolar waters overlying the main branch of North Atlantic Deep Water flowing southwest from the Nordic Seas.

1. INTRODUCTION

Paleoclimates 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 paleoclimatic investigations, but a major potential concern for this approach arises from the possibility that the fine fraction of sediment (e.g., <63 µm), and the climate proxies within it, may represent conditions far from the deposition site. Here we propose and test the hypothesis that hydrogen isotope ratios of alkenones, a class of lipids from phytoplankton, may provide insight into the source of fine-grained 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. The sedimentary abundances, extents of unsaturations, and isotopic compositions of alkenones provide quantitative and near-continuous records. We isolated alkenones from cultured unicellular algae (haptothye Emiliania 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_{18} compounds. We then compared the ∆D values of the alkenones in surface sediments between the Bermuda Rise and the Scotian Margin above which a large (∼20‰) ∆D 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 ∆D values during the Medieval Warm Period–Little Ice Age climate transition (cf. Keigwin, 1996) at the Bermuda Rise.

Emiliania huxleyi, a cosmopolitan coccolithophorid, is an abundant species in both open ocean and coastal waters and are distinguished by their synthesis of a suite of C_{17}-C_{20} methyl and ethyl ketones, collectively called alkenones (Volkman et al., 1980, 1995). 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). 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 (Craig, 1961; Dansgaard, 1964). Fractionation from non-equilibrium processes such as evaporation lead to imperfections in the correlation between δ^{18}O and ∆D values, but the first order signals of δ^{18}O and ∆D may be used interchangeably (Dansgaard, 1964). Using the relationship, [δD ≈ 88.9δ^{18}O + 10], and the extensive surface ocean δ^{18}O data set available, a map of surface ocean δD values has been constructed and reveals a strong gradient in surface ocean ∆D in the northwest Atlantic.

At low temperatures, water hydrogen exchanges quickly and reversibly with labile organic hydrogen, most of which is

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bound to organic nitrogen, sulfur, and oxygen (Koepf, 1978; Werstuk 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). The D/H ratios of n-alkanes are conserved at diagentic temperatures well above 150°C, and it has been documented that water at neutral pH and low temperature in the absence of a catalyst does not readily exchange with most carbon-bound hydrogen (Koepf, 1978; Hoering, 1984).

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 submersed aquatic plants and found hydrogen isotopes fractionate at a predictable rate, thereby recording the D/H ratio of environmental water. Sessions et al. (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 values in different 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 signatures of individual lipids in each class generally fell within a range of <50‰, (Sessions et al., 1999).

Using geochemical (e.g., Sachs and Lehman, 1999; Sachs et al., 2001; Sachs and Anderson, 2003; McManus et al., 2004), 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. In addition, multiple proxies of the same physical parameter, such as SST, can be measured in a single core to determine how depth and seasonality may have contributed to the “temperature history” recorded by different proxies whose measurement in isolation would have been interpreted as the definitive temperature history. 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.

Because lateral transport predominates over vertical sedimentation at drift deposits, careful consideration must be given to the role horizontal advection of sediment may play in shaping down-core records of proxies that are part of the fine fraction of sediment. A major potential concern for utilizing the multiple proxy approach at drift sites arises from the possibility that the climate proxies associated with the fine fraction of sediment (e.g., alkenone unsaturation ratios, biomarkers, clay mineralogy, detrital Sr and Nd isotopic ratios) may be chrono-

logically and spatially decoupled from those associated with the coarse fraction of sediment (e.g., abundance, isotope ratio, and trace metal concentration of foraminiferal tests) (Sachs et al., 2000). The recognition and determination of the magnitude of offsets between proxies is particularly important when records of abrupt climate change are sought from high accumulation-rate sites. On the Bermuda Rise, for example, high rates of sediment accumulation result from lateral advection and focusing of distal fine-grained sediments (Laine and Hollier, 1981; Keigwin and Jones, 1989; Suman and Bacon, 1989) that are believed to derive from “pelagic fallout, turbidity-current material from the Laurentian Fan swept over the rise by deep currents, and resuspended sediment from the Grand Banks and United States/Canada margins entrained in the deep circulation” (McCave, 2002, and references therein; Fig. 1).

Ohkouchi et al. (2002) demonstrated that at the same level in a Bermuda Rise sediment core, the radiocarbon ages of alkenones exceed those of coeval planktonic foraminifera by 2 to 8 ka. Using a simple two-endmember mixing calculation, they estimated that 0% to 75% of the material at the Bermuda Rise was transported from elsewhere. They concluded that the Bermuda Rise is influenced by highly variable processes with more than two sources, and in the deglacial sediments studied, some aspects of the fine material cannot be interpreted as a time history of events at the sea surface directly above the site.

Subsequent studies of the radiocarbon age difference between coeval alkenones and planktonic foraminifera in open ocean (Keigwin et al., 2005) and margin sediments (Mollenhauer et al., 2003) indicate smaller or no age discrepancies of 0.5 to 4.5 ka, with the alkenones usually older than the planktonic foraminifera (Mollenhauer et al., 2005). It is noteworthy too that the radiocarbon ages of different species of planktonic foraminifera in the same sediment sample—which can be as large as 4.7 ka (Broecker et al., 2004)—display a comparable amplitude and range of age difference as observed for the alkenones relative to planktonic foraminifera (Broecker et al., 1999; Broecker et al., 2004; Lowemark and Groothes, 2004).

The purposes of this study were to: (1) determine the fidelity by which alkenone δD values reflect the deuterium concentration of water in which coccolithophorids grow, both in culture and in the field; (2) determine if D/H ratios of sedimentary alkenones reflect the δD values of suspended particles in surface waters over the site; and (3) apply alkenone δD measurements to determine the origin of fine-grained sediment at the Bermuda Rise during key climate transitions.

2. METHODS

2.1. Study Sites and Field Sampling

Water, particulate and sediment samples were collected from four sites in the western North Atlantic Ocean (Table 1 and Fig. 1). Sargasso Sea sediment (KNR 161-8, Box Core 1), suspended particles and water samples were collected over the abyssal plain to the southwest of the Bermuda Rise (31°30’N, 63°30’W, 4450 m) June 10 to July 10, 2000, during cruise 161-8 of R/V Knorr. Bermuda Rise box core OCE 326-BC01 (33°42’N, 57°37’W, 4420 m) was collected from the southwestern central region of the Bermuda Rise in July, 1998 on cruise 326 of R/V Oceana. Scotian Margin sediments were collected from the Emerald Basin, ~60 mi southeast of Nova Scotia, with a multicorer (OCE326-MC29; 45°53’N, 62°48’W, 250 m) in July, 1998 on cruise 326 of R/V Oceana. Emerald Basin surface waters were collected in April 2004 on cruise HUD2004-009 of R/V Hudson, Gulf of Maine surface water
and suspended particulate samples were collected from the waters west of Nova Scotia (43°15' N, 68°17' W) on May 14, 2001 on cruise 377 of R/V Oceanus. Water samples for hydrogen isotopic analysis were collected simultaneously with suspended particulate samples. Suspended particles were collected by filtration of 500 to 5000 L of near-surface seawater (from the ship's clean seawater intake) through 293 mm Gelman A/E filters and immediately storing at 20 to 40°C until extraction.

Table 1. Description of marine samples analyzed in this study. Sample numbers in parentheses correspond to identification numbers found in Tables 4 and 5, and in Figure 1.

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Sample type (no.)</th>
<th>Cruise/sample name</th>
<th>N lat.</th>
<th>W lon.</th>
<th>Collection date</th>
<th>Water depth (m)</th>
<th>Sample depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sargasso Sea</td>
<td>Water (6–9)</td>
<td>KNR 161-8-W</td>
<td>31°50'</td>
<td>63°30'</td>
<td>June 2000</td>
<td>4450</td>
<td>0–3</td>
</tr>
<tr>
<td>Sargasso Sea</td>
<td>Particulate (6–11)</td>
<td>KNR 161-8-SP</td>
<td>31°50'</td>
<td>63°30'</td>
<td>June 2000</td>
<td>4450</td>
<td>0–3</td>
</tr>
<tr>
<td>Sargasso Sea</td>
<td>Sediment (12)</td>
<td>KNR 161-8-BC1</td>
<td>31°50'</td>
<td>63°30'</td>
<td>June 2000</td>
<td>4450</td>
<td>0–0.02</td>
</tr>
<tr>
<td>Bermuda Rise</td>
<td>Sediment (25–34)</td>
<td>OCE 326-BC9J</td>
<td>33°42'</td>
<td>57°37'</td>
<td>July 1998</td>
<td>4420</td>
<td>0–0.1</td>
</tr>
<tr>
<td>Gulf of Maine</td>
<td>Water (13)</td>
<td>OCE 377-W</td>
<td>43°15'</td>
<td>68°17'</td>
<td>May 2001</td>
<td>185</td>
<td>0–3</td>
</tr>
<tr>
<td>Gulf of Maine</td>
<td>Particulate (13)</td>
<td>OCE 377-SP</td>
<td>43°15'</td>
<td>68°17'</td>
<td>May 2001</td>
<td>185</td>
<td>0–4</td>
</tr>
<tr>
<td>Emerald Basin</td>
<td>Sediment (14–16)</td>
<td>OCE 326-MC29</td>
<td>45°53'</td>
<td>62°48'</td>
<td>July 1998</td>
<td>250</td>
<td>0–0.03</td>
</tr>
</tbody>
</table>

Fig. 1. Turbidity currents (salmon) from the Laurentian fan (LF) are entrained by deep-ocean flows (blue arrows) and trapped in regions of recirculation (pale blue areas) (Schmitz and McCartney, 1993). Resuspension from the upper continental margin of Nova Scotia and the northern US feeds into the recirculating gyre and may find its way to the Bermuda Rise. North Atlantic Deep Water (NADW) (thick blue arrow). WBUC, Western Boundary Undercurrent. Locations of samples analyzed in this study (black filled circles) are detailed in Table 1. Sample identification numbers (parentheses) correspond to Tables 4 and 5. Figure from McCave (2002).
Sediment samples were taken from box cores (Sargasso Sea and Bermuda Rise) or multi-cores (Emerald Basin) which had been stored at \(-20^\circ\text{C}\) (Sargasso Sea) or 4°C (Bermuda Rise, Emerald Basin), and stored in plastic bags at \(-20^\circ\text{C}\) until extraction.

2.2. Algal Cultures

*Emiliania huxleyi* strain CCMP374 was obtained from the Center for Culture of Marine Phytoplankton (CCMP), Bigelow Laboratory, Maine. The coccolithophorids, originally collected from the Gulf of Maine (42.5°N, 69°W) in 1989, were batch cultured at 18°C under a 14:12-h dark cycle with cool-white fluorescent lighting with a scalar irradiance of 150 to 250 \(\mu\text{E}\) m\(^{-2}\) s\(^{-1}\) during the light cycle; light levels were measured with a QSL-100 (Biospherical Instruments) light meter. The cultures were grown at five different enrichment spanning \(-500\%\) (Table 2) in 2 L of f/2 nutrient medium (Guillard, 1975). The f/2 medium was prepared from sterile filtered and autoclaved seawater provided by Vineyard Sound, MA, which has a salinity of 31.5 to 32.0 psu; f/2 medium was prepared from sterile filtered and autoclaved seawater. Media were acclimated over an 8-h period at 18°C before inoculating the cultures at cell densities of \(1 \times 10^3\) to \(3 \times 10^5\) cells mL\(^{-1}\) using stocks growing in their logarithmic phase. Cultures were harvested 10 to 12 days after inoculation, when cell densities reached \(3 \times 10^5\) to \(5 \times 10^5\) cells mL\(^{-1}\); Samples were collected by filtration through prebomed (450°C, >8 h) 47-mm Whatman GF/F filters, and immediately stored at \(-20\) to \(-40^\circ\text{C}\) until extraction.

2.3. Lipid Extraction and Fractionation

The alkenone purification procedure was adapted from Xu et al. (2001). All materials were prebomed at 450°C for \(>8\) h or solvent washed (methanol [3\(\times\]), dichloromethane [DCM] [3\(\times\)], hexanes [3\(\times\)]); cotton was soxhlet extracted in DCM/hexane. Silver nitrate-coated silica gel (Aldrich, 10% wt wt on 200+ mesh) was activated at 110°C overnight. After activation, silica gels were stored in 70°C drying oven.

Filters and sediments were freeze-dried (Viris Benchtop 6.6) before extraction. Dried filters were cut into 1-cm strips and loaded into a stainless steel cell with 6 g Na\(_2\)SO\(_4\), while dried sediment (2–40 g) was loaded into a stainless steel cell with an equivalent quantity of Na\(_2\)SO\(_4\). Samples were then back extracted (1×) with water, and applied to a Na\(_2\)SO\(_4\) drying column. The column was rinsed (3×) with hexane, adding the rinses to the combined hexane fractions, and the solvent was evaporated under N\(_2\). The dried extracts were then redissolved in hexane and applied to a glass 6-mL Supelco SPE tube containing 0.5 g activated 100 to 200 mesh silica gel in hexane. The sample was eluted with 10 mL hexane (F1: hydrocarbons), 16 mL 1:1 DCM/hexane (F2: alkenones), and 10 mL MeOH (F3: pigments). Branched and cycled molecules were then removed from the alkenone-containing fraction via the formation of urea clathrates. F2 was dissolved in 2:1 hexane/DCM and urea-added (3×) using methanolic urea (40 mg urea/mL MeOH). Next, polyunsaturated ketones were separated by argelation column chromatography in a 5.75-in pipet containing 4 cm silver nitrate-coated silica gel. DCM was used to apply the sample to a prewetted (DCM) column, then the sample was eluted using 16 mL DCM (F1), 4 mL ethyl ether (F2, alkenones), and 4 mL MeOH (F3). In the final silica column purification, hexane was used to apply the sample to a prewetted (hexane) 5.75-in pipet containing 4 cm 100 to 200 mesh silica gel, and the sample was eluted using 4 mL hexane (F1), 6 mL DCM (F2: alkenones), and 4 mL MeOH. Before gas chromatographic analyses, dried TLE were dissolved in toluene and silylated with bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 60°C for 1 h.

The purified fractions contained a distribution of \(C_{37-2-4}\) alkenones and most of the chromatographic baseline that interferes with both accuracy and precision in hydrogen isotopic measurements was removed. Comparing the concentration of \(C_{37-2-4}\) alkenones in the purified fraction to the concentration of \(C_{37-2-4}\) in the TLE, we calculated a recovery of \(-30\%\) in both culture and marine samples. The loss of product during urea adduction was substantial, with additional losses from numerous chromatography steps and physical transfers during the purification process. Although \(-70\%\) of the alkenones were lost during purification we do not expect hydrogen isotopic fractionation to have occurred as a result of the purification procedure. First, no bonds to hydrogen were produced or broken. Second, only minor interaction is expected between the \(-70\) hydrogen atoms (covalently bonded to carbon along the length of the molecule) and the silica gel used to purify the alkenones. Third, urea adduction, the step associated with most of the loss of alkenones, operates on the basis of molecular size and geometry, rather than chemical constituents on the molecule.

2.4. Instrumentation

2.4.1. Gas chromatography and gas chromatography–mass spectrometry

To identify and quantitate alkenones, gas chromatography was performed with Hewlett Packard 6890 Series II gas chromatographs (GC) using either a flame ionization detector or Agilent 5973 Mass Selective Detector. Both GCs were equipped with a Hewlett Packard 7683...
autoinjector, a pressure-temperature vaporization (PTV) inlet and a 60-m Chrompack CP Sil 5 capillary column (Varian). The columns were 0.32 mm i.d. with a 0.25-µm phase and a constant 1.6 mL/min flow of helium carrier gas. Both instruments used ChemStation (Agilent) acquisition software. The PTV temperature program was 60°C for 0.85 min, 60 to 320°C at 720°C/min, hold for 2.35 min, then 320 to 450°C at 720°C/min, followed by a 5-min isothermal step. The oven temperature program was 110°C for 2 min, 110 to 270°C at 40°C/min, 270 to 320°C at 2°C/min, followed by an 18 min isothermal step.

2.4.2. Isotope ratio monitoring gas chromatography mass spectrometry (irmGCMS)

Unless otherwise noted, hydrogen isotopic measurements were obtained at the MIT Earth, Atmospheric and Planetary Sciences Organic and Isotope Geochemistry Laboratory (OIGL). The facility consists of a Trace GC with a splitless PTV inlet coupled via GC Combustion III graphitization furnace to a DELTAplus XP stable isotope ratio mass spectrometer (ThermoFinnigan, Bremen, Germany). All irmGCMS work used a 30-m capillary column with a 0.32 mm i.d. and 25-µm DB-5 phase. The PTV program was 100 to 325°C at 13°C/s, followed by a 60 min isothermal step. The oven temperature program was 100°C for 1 min, 100 to 150°C at 20°C/min, 150 to 315°C at 10°C/min, followed by a 40-min isothermal step. Using helium carrier gas, the effluent from the GC is fed into a graphite-lined alumina tube held at 1400°C, at which temperature organic compounds are quantitatively pyrolyzed to graphite, H2, and CO (Burgoyne and Hayes, 1998). An open split transmits 200 µL/min of the resulting gas stream to the mass spectrometer. Data were collected and analyzed using Isotof Dat NT 2.0 (Thermo Electron) acquisition software.

Raw mass-3 currents are corrected for contributions from H3 using a H2 factor that is determined daily. Interference in measurements of HD can occur because H3 is formed in the ion source, and generally, the higher the hydrogen concentration in the ion source, the greater amount of H3, formed. A linearity correction is performed by measuring different H2 concentrations in the ion source (i.e., different peak heights) and for each peak, a background correction is performed and the ratio of (area mass-3):(area mass-2) is calculated and a regression line is established covering all peaks.

Analytical results are reported as parts per thousand difference in the D/H ratio as compared to a standard reference material:

$$\delta D = \left( \frac{(D/H)_x - (D/H)_s}{(D/H)_s} \right) \times 10^3$$

where x refers to the unknown sample and s refers to the standard, Vienna Standard Mean Ocean Water (VSMOW) distributed by the International Atomic Energy Agency

Alkenone δD values were determined by reference to coinjected n-alkane standards obtained from Biogeochemical Laboratories, Indiana University, Bloomington, IN, USA. A mixture of 15 homologous n-alkanes (C16 to C30; alkane mix “B”) spanning a six-fold range in carbon number and concentration was used to calibrate the instrument. A linear regression of δD values to the VSMOW scale. Because deuterium is in such low abundance in natural materials, 500 to 1000 ng compound were injected on-column per δD measurement. Intensities (peak areas) of 60 to 100 Vs typically gave the most reproducible results.

3. RESULTS

3.1. Estimates of Uncertainty

The accuracy and precision of D/H analyses of lipids is influenced by a number of factors, including variations in the H3 factor and chromatographic challenges related to closely eluting compounds. For all alkenones, chromatographic resolution required reporting a pooled isotopic value for all compounds of a given chain length (i.e., C37:2, C37:3, C37:4 reported as a pooled “C37:2-4”). It is likely that isotopic differences between unsaturations of a given chain length are small, given the relatively few exchangeable hydrogens. δD values from both C37:2-4 and C38:2-4 alkenones are listed in Tables 2 to 4, and in most cases the results of each chain length were very similar, varying by <1‰ to 13‰, with a median difference of ~4‰ for C38:2-4. We therefore propose that δD values from the C38:2-4 alkenones be used to confirm the δD value of the C37:2-4 alkenones if sufficient material is unavailable to perform duplicate isotope analyses. C39 alkenones were also detected in the samples, but concentrations were too low for reliable isotopic measurements.

The precision of replicate analyses of a single sample was 2.9‰ (n = 34). This combines uncertainties associated with ion-current-ratio measurements, short-term variations in the pyrolysis procedure, and comparisons between sample and standard peaks in the same chromatogram. To evaluate accuracy, Sessions et al. (1999) used root mean square (RMS) error for hydrogen-isotopic analyses of a mixture of well-resolved n-alkanes of known isotopic composition. Regression of the isotopic compositions of these standard mixes measured by irmGCMS vs. offline provided a normalization line analogous to that used in batchwise analyses (Coplen, 1988). The RMS error represents the RMS difference between the analytical result and the known isotopic composition, and is therefore a measure of both accuracy and precision. In this study, the RMS error of hydrocarbon standards was 5.8‰ (n = 16). This combines the noise sources listed above with all other factors, long- and short-term, affecting the placement of the samples on the δD_VSMOW hydrogen-isotopic scale. At the 95% confidence interval, the accurate value of δD_VSMOW for the compounds analyzed is within 2 RMS errors of the value reported.

3.2. Hydrogen Isotope Ratios in Alkenones

3.2.1. Emiliania huxleyi cultures

Hydrogen isotopic compositions of alkenones from cultures of E. huxleyi increased linearly with increasing deuterium enrichment of water according to the equations

$$\delta_{\text{alk}} = 0.732 \times \delta_{\text{w}} - 225 (R^2 = 0.9997, n = 5)$$ for C37 alkenones.

$$\delta_{\text{alk}} = 0.745 \times \delta_{\text{w}} - 233 (R^2 = 0.9997, n = 5)$$ for C38 alkenones.
Table 4. Isotopic compositions of marine particulate (p) and sediment (sed) samples from Sargasso Sea (SS), Gulf of Maine (GM), and Emerald Basin (EB), and water (w) samples collected simultaneously with particulate samples.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample type</th>
<th>Alkenone δD</th>
<th>Water</th>
<th>δD (‰)</th>
<th>δ18O (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>SS p/w</td>
<td>–182 1</td>
<td>C37</td>
<td>10.35</td>
<td>1.12</td>
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<tr>
<td>7</td>
<td>SS p/w</td>
<td>–181 3</td>
<td>C38</td>
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<td>1.18</td>
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<tr>
<td>8</td>
<td>SS p/w</td>
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<td></td>
<td>10.37</td>
<td>1.09</td>
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<tr>
<td>9</td>
<td>SS p/w</td>
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<td>10.29</td>
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<tr>
<td>10</td>
<td>SS p/w</td>
<td>–159 7</td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>SS p/w</td>
<td>–161 8</td>
<td></td>
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<td></td>
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<td>PSD</td>
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<tr>
<td>12</td>
<td>SS sed (0–2 cm)</td>
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<td>EB</td>
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</tr>
<tr>
<td>13</td>
<td>GM p/w</td>
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<td>16</td>
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<tr>
<td>17</td>
<td>EB water (1–40 m)</td>
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<tr>
<td>18</td>
<td>1 m</td>
<td>–194 2</td>
<td></td>
<td>12.07</td>
<td></td>
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<tr>
<td>19</td>
<td>10 m</td>
<td>–212 2</td>
<td></td>
<td>11.78</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>10 m</td>
<td>–194 2</td>
<td></td>
<td>11.96</td>
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</tr>
<tr>
<td>21</td>
<td>20 m</td>
<td>–192 2</td>
<td></td>
<td>11.91</td>
<td></td>
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<td>20 m</td>
<td>–195 2</td>
<td></td>
<td>11.92</td>
<td></td>
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<tr>
<td>23</td>
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<td>–193 2</td>
<td></td>
<td>11.93</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>40 m</td>
<td>–198 2</td>
<td></td>
<td>11.94</td>
<td></td>
</tr>
</tbody>
</table>

The pooled standard deviation (PSD) of the 13 injections of Sargasso Sea particulate sample is reported. Abbreviations are described in Table 2. Water δD and δ18O values have an estimated standard deviation of 1‰ and 0.35‰, respectively, and were measured at the Stable Isotope Laboratory, Dartmouth College (Hanover, NH), and the Laboratory for Geochemical Oceanography, Harvard University (Cambridge, MA), respectively.

* Measured in Isotope Organic Geochemistry Laboratory, Brown University, Mar 2001. δD values were not used in final statistical analyses because raw isotope values were based on comparison to reference gas pulses rather than coinjected standards, as were used for evaluation and normalization of the remainder of the data. On both OIGL and WHOI irmGCMS instruments, reference hydrogen tanks have been observed to "drift" throughout the sample runs by 7 to 10‰ (S. Sylva, pers. comm.).


Average value of water samples 6 to 9, used in calculation of ε37:2–4/w for comparison purposes only.

Average value of water samples 17 to 24, used in calculation of ε37:2–4/w for comparison purposes only.

Determining the hydrogen isotopic fractionation associated with alkenone biosynthesis in cultured *E. huxleyi* is somewhat complicated by the fact that the slopes of the δalk vs. δw regressions are offset from unity by significant amounts, a principle described by Sessions and Hayes (2005). From the relationship

$$\delta_p = \alpha \delta_w + e$$

where $\delta_p$ is the δD value of the products (alkenones), $\alpha$ is the fractionation factor, $\delta_w$ is the δD value of the reactant (water), and $e$ is the per mil enrichment factor, the isotopic fractionation associated with alkenone biosynthesis can be determined in two ways, both of which have been used in the literature (cf. Sessions and Hayes, 2005, and references therein). The slopes of the regressions, $\alpha_{C37} = 0.732$ and $\alpha_{C38} = 0.745$, represent one ‘fractionation factor’, while the intercepts, $\epsilon_{C37} = –225$‰ and $\epsilon_{C38} = –233$‰, often called the per mil enrichment factors and most often used to determine isotopic fractionations in the biogeochemical literature, represent another. The two values are equivalent when the slope of the regression is 1, in which case

$$\epsilon_{\text{intrcpt}} = (\alpha_{\text{slope}} - 1) \times 1000$$

However, when the slope differs substantially from unity, as it often does with hydrogen isotopes, the two measures of isotopic fractionation can be quite different (Sessions and Hayes, 2005).

In the case of alkenones from cultured *E. huxleyi* the α value calculated from the intercept of the regression using Eqn. 2, $\alpha_{\text{intrcpt}} = \epsilon_{\text{intrcpt}} / 1000 + 1$, is 0.775 and 0.767, respectively, for C$_{37}$ and C$_{38}$ alkenones (Table 3). Though different from the α values obtained directly from the slope of the regressions, $\alpha_{\text{slope}} = 0.732$ and 0.745, respectively for C$_{37}$ and C$_{38}$ alkenones, the differences are small in comparison to published studies of hydrogen isotopic fractionation during lipid biosynthesis in plants and algae (cf. Sternberg, 1988; Sauer et al., 2001; Huang et al., 2002, cited in Sessions and Hayes, 2005). (Following the analysis by Sessions and Hayes, 2005, we have used the subscripts ‘slope’ and ‘intrcpt’ to distinguish between fractionation factors calculated from the intercept $[\epsilon_{\text{intrcpt}}]$ of the regression $[\alpha_{\text{intrcpt}}]$ from those taken directly from the slope of the regression $[\alpha_{\text{slope}}]$). The three different expressions of the hydrogen isotopic fractionation between alkenones and water (concentrations of C$_{37}$ and C$_{38}$) are shown in Table 3.

That α values calculated from ε values derived from the intercept of a linear regression result in different apparent
Hydrogen isotopes in alkenones

The range of surface water δD values in the north Atlantic is mirrored by alkenone δD values of suspended particles; the amplitude of ΔδD between the Sargasso Sea and the Gulf of Maine is similar for both water (17‰) and suspended particulate alkenones (19‰) (Table 4 and Fig. 3). The mean ε_{37:2-4/w} between C_{37:2-4} and surface waters in the marine samples was −193 ± 3‰ (n = 9). Alkenones in the field were thus 32‰ more enriched than predicted from the aggregate E. huxleyi culture experiments, −225‰. Operating under the assumption that our field results are more likely to be representative of wild populations of coccolithophorids than those obtained from batch cultures we later apply the isotopic fractionation of −193‰ observed in field samples to infer the δD value of water in which the algae grew.

The D/H ratio of particulate alkenones was very similar to the δD value of core-top sediments from each region (Fig. 3). In the Sargasso Sea, southwest of the Bermuda Rise, the particulate alkenones had a mean δD value of −181 ± 2‰ (n = 13), while the alkenones in core-top sediment had a δD value of −184‰ (n = 1). Particulate alkenones from the Gulf of Maine had a δD value of −200‰ (n = 1), while alkenones in core-top sediments from the Emerald Basin had a δD value of −204 ± 1‰ (n = 3). Further, on a time scale of days, alkenone δD values in the Sargasso Sea particles varied little, averaging −181 ± 2‰ (n = 13) with a range of −180‰ to −182‰. Although the particulate samples represent a snapshot in time whereas the sediments average over tens to thousands of years, the difference in δD values for each was within our measurement error. In addition, alkenone δD signatures distinguish northern (more depleted) and southern (less depleted) source waters, but do not vary greatly within those regions (Fig. 3).

For ease of discussion, Emerald Basin and Gulf of Maine samples have been loosely grouped as Scotian Margin (SM). The mean δD values of all alkenones (particulate and sedimentary) analyzed in the Sargasso Sea and Scotian Margin regions, respectively, were −182 ± 3‰ (n = 14) and −203 ± 2‰ (n = 4).

Data from box core subcore OCE326-BC9J are summarized in Table 5 and Figure 4. Keigwin (1996) and Ohkouchi et al. (2002) previously examined this same box core to investigate late Holocene and glacial-interglacial climate change. Weight percent CaCO₃ decreases from a maximum at 4.5 cm to a pronounced minimum centered on 1.5 cm and we follow the work of Keigwin (1996) in attributing the carbonate minimum and preceding maximum to the climate events loosely known as the Little Ice Age (LIA) and Medieval Warm Period (MWP), respectively. δD values increase from a low before and including the MWP, to a high at 2.5 cm, then return to more depleted values at the core-top. δD values indicate a SST maximum centered at 5 cm followed by a minimum at 1.5 cm.

4. DISCUSSION

4.1. Alkenone δD in Suspended Particle

Because we cultured a single strain of E. huxleyi, the difference between culture and field results may reflect real differences in the hydrogen isotopic fractionation associated with alkenone biosynthesis in different strains or species of coccolithophorids. Discrepancies between culture and field results are common in alkenone unsaturation calibrations (e.g., González et al., 2001; Herbert, 2001) and are generally ascribed to different responses of cells in culture vs. natural field environments. It is not immediately clear whether batch or continuous growth models better represent natural conditions or whether the sinking flux of alkenones and alkenoates in the ocean comes from populations in exponential, late logarithmic, or stationary growth state. Different biochemical responses can be obtained from the same strain of alkenone-producing algae cultured in batch or continuous modes (Popp et al., 1998) and...
from the phase of growth from which alkenones are harvested (Conte et al., 1998; Epstein et al., 1998).

*E. huxleyi* is the dominant coccolithophorid in many of the world’s oceans (Berge, 1962; Okada and Honjo, 1973, 1975; Okada and McIntyre, 1977, 1979; Nishida, 1986), is believed to be the main producer of alkenones in the open ocean (Volkman et al., 1980; Marlowe et al., 1984a, 1984b, 1990), and constitutes between 40% to 87% of the coccoliths in surface sediments from the greater part of the North Atlantic Ocean (Geitz-Ennauer et al., 1977). However, the species exists as genetically different strains, and it is apparent that these can have different lipid compositions that respond differently to temperature change (e.g., Conte and Eglinton, 1993; Sikes and Volkman, 1993; Conte et al., 1994). Variability in intracellular alkenone composition has also been noted to have a physiologic as well as genetic component (Conte et al., 1998; Epstein et al., 1998), and algal cells are well known to undergo complex modifications of their intracellular and membrane compositions (e.g.,

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Fig. 3. δD values of water (*w*), particulate alkenones (*p*), and near-surface sedimentary alkenones (*s*) from the Sargasso Sea (SS), Gulf of Maine (GM), and Emerald Basin (EB). Detailed site locations can be found in Table 1.
Table 5. Carbonate content for Bermuda Rise core OCE326-BC9J (this study) as well as alkene $^{14}$C age and $U_{37}^{K}$, from Ohkouchi et al. (2002), n.a.: not analyzed.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sediment depth (cm)</th>
<th>% CaCO₃</th>
<th>$(\text{Ohkouchi et al., 2002})$ 14C age</th>
<th>$U_{37}^{K}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.5</td>
<td>24.9</td>
<td>6230</td>
<td>0.577</td>
</tr>
<tr>
<td>26</td>
<td>1.5</td>
<td>17.8</td>
<td>5060</td>
<td>0.524</td>
</tr>
<tr>
<td>27</td>
<td>2.5</td>
<td>20.4</td>
<td>7810</td>
<td>0.495</td>
</tr>
<tr>
<td>28</td>
<td>3.5</td>
<td>23.9</td>
<td>n.a.</td>
<td>0.601</td>
</tr>
<tr>
<td>29</td>
<td>4.5</td>
<td>45.5</td>
<td>5780</td>
<td>0.675</td>
</tr>
<tr>
<td>30</td>
<td>5.5</td>
<td>31.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
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<td>32.4</td>
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<tr>
<td>32</td>
<td>7.5</td>
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<tr>
<td>33</td>
<td>8.5</td>
<td>32.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>9.5</td>
<td>30.1</td>
<td>3100</td>
<td>0.848</td>
</tr>
</tbody>
</table>

Shuter, 1979, and references therein) in response to growth regulating environmental factors such as nutrient availability, light, and trace micronutrient concentrations (e.g., Sunda and Huntsman, 1995).

While these points have contributed to general ambiguity surrounding the use of alkene unsaturation calibrations, our observed 32‰ difference in $f_{E}$, $f_{R}$, between single species cultures and mixed field populations could potentially be explained by differing biochemical responses driven by genetics alone. Using an average $\epsilon_{\text{field}}$ of $-190\%$e and $\epsilon_{\text{culture}}$ of $-230\%$e, a two-end-member mixing calculation indicates that 20% to 100% of the $\delta D$ variability observed in the top 10 cm of core BC9J can be accounted for by a mixed population of alkene-producers. Clearly, a two-end-member mixing calculation is not sufficient to constrain the nuances of the natural coccolithophorid assemblage, but these differences in H isotopic fractionation should be considered when examining time scales in which the coccolithophorid assemblage may have changed. The possibility remains that $\delta D$ measurements can potentially be used to infer the proportion of alkenones coming from a single species, and therefore, unsaturation calibration is more appropriate for a given location and time.

4.2. Provenance of Alkenones at the Bermuda Rise Using $\delta D_{\text{alkenone}}$

At the Bermuda Rise, it is likely that carbonate flux was relatively constant and the flux of terrigeneous sediment delivered by deep currents increased during the LIA (Keigwin, 1996), just as it did during earlier carbonate minima in the Holocene and during glaciation (Bacon and Rosholt, 1982; Suman and Bacon, 1989). Bacon and Rosholt (1982) recognized a strikingly cyclic variation in $^{230}$Thex, $^{231}$Paex, and a number of transition metals with depth. The variations closely followed the fluctuations in carbonate content across glacial-interglacial periods, and a simple model was proposed in which the supply of CaCO₃ and the metals scavenged from the water column remains constant with time and concentration changes are caused mainly by variations in the supply of aluminosilicate detritus from the continents. Suman and Bacon (1989) observed similarly coupled $^{230}$Thex and carbonate content within the Holocene section of a Bermuda Rise core. The terrigeneous sediment most likely was resuspended from the Scotian Rise during abyssal storms (Hollister and McCave, 1994) or eroded from the northeast scarp of the Bermuda Rise (Laine et al., 1994).

Geochemical evidence for changes in late Holocene NADW production is ambiguous, so it is not known if there was actually a change in the source of deep waters associated with the LIA, as there was for similar events in the Pleistocene (Keigwin and Jones, 1989). But alkene $U_{37}^{K}$, and $\delta D$ signatures could distinguish between the two sources, leading to a “cold” $U_{37}^{K}$ signal and depleted alkene $\delta D$ value during periods when the sediment was Scotian Margin-derived and a “warmer” $U_{37}^{K}$ signal and relatively less depleted alkene $\delta D$ value when it was Bermuda Rise-derived.

A strong SST gradient exists in summer directly south of the Scotian Margin (Fig. 5). If alkenones from middle and subpolar latitudes are produced primarily in summer, as a global dataset of coccolithophorid blooms observed from space indicates (Iglesias-Rodriguez et al., 2002), subtle changes in the transport of fine-grained sediment (and alkenones) from the region south of the Scotian Margin to the Bermuda Rise could potentially cause $U_{37}^{K}$ values to vary between 0.45 and 0.85.

The large summer SST gradient south of the Scotian Margin is offset to the north of a strong isotopic (H and O) gradient of surface waters (Fig. 5). By combining the unsaturation ratio of alkkenones with their hydrogen isotopic composition it ought to be possible to evaluate the source of alkenones in Bermuda Rise sediment. Doing so requires that the $\delta D$ value of surface waters in the NW Atlantic either remained constant through time, or that any change can be quantified.

Keigwin (1996) showed that oxygen isotope ratios of the surface-dwelling planktonic foraminifera Globigerinoides ruber (white variety) in the upper 50 cm of Bermuda Rise sediment (spanning the last ~3 ka) spanned a range of 0.75‰. Two thirds of that signal was attributed to changes in SST, leaving 0.25‰ attributable to changes in the oxygen isotopic composition of the surface water. According to the relationship between $\delta^{18}$O and $\delta D$ in meteoric water, this equates to 2‰ of $\delta D$ variation in the northern Sargasso Sea during the last 3 ka.

In the Emerald Basin, located on the Scotian Margin, Keigwin et al. (2003) showed that the oxygen isotopic composition of the planktonic foraminifera N. pachyderma (sinistral)
spanned a range of \(-0.75\%_e\) during the last 1.6 ka. Half of that variation can be attributed to temperature, leaving \(0.4\%_e\) arising from water isotopic variations (Keigwin et al., 2003). This equates to \(3\%_e\) of surface water \(\delta D\) change during the last 1.6 ka on the Scotian Margin.

We therefore estimate that \(-5\%_e\) of down-core alkenone \(\delta D\) variation might be attributable to temporal changes in the H isotopic composition of surface waters in any one geographic location during the late Holocene. This value is a factor of 5 to 6 lower than the observed range in alkenone \(\delta D\) in the upper 10 cm of Bermuda Rise sediment (Fig. 4).

By utilizing the present-day spatial patterns of both SST and \(\delta D\) values and assuming these patterns have remained constant during the deposition of the upper 10 cm of sediment at the Bermuda Rise, a period spanning the last \(-1\) ka, we can begin to map out the source region of the alkenones.

Based on SST and \(\delta D\) values of alkenones we distinguished three likely source regions of alkenones to the upper 10 cm of Bermuda Rise sediment. These regions are labeled A-C in Figure 5, a contour map of surface water \(\delta D\) and Summer SST values in the North Atlantic. Constraining the relative contribution of alkenones from three sources is not possible with two parameters (\(\delta D\) and \(U_{\text{K}}\)), and there may be additional sources that are not well represented by our zonation. But using this initial data, we can move closer to understanding the origin of clay and silt sized material in Bermuda Rise sediment.

Region A, on the northwestern edge of the subtropical gyre, is characterized by warm SSTs and relatively low \(\delta D\) values of surface waters (Fig. 5, region A). Alkenones at 4 to 7 cm depth (Fig. 4), corresponding in time approximately to the Medieval Warm Period (Keigwin, 1996), are relatively depleted in deuterium and exhibit high unsaturation ratios, indicating they may have come from region A.

Alkenones at 2 to 3 cm, corresponding to the beginning of the Little Ice Age (Keigwin, 1996), are enriched in deuterium and have a low unsaturation ratio (Fig. 4). We surmise that they came from subpolar water to the northeast of the Bermuda Rise. This region, which is labeled B in Figure 5, is characterized by cold SSTs and high D/H ratios of water. While this region lies to the northeast of the expected source region of sediment to the Bermuda Rise (cf. McCave, 2002, and Fig. 1) we note that it lies along the main branch of NADW flow from its source in the Nordic Seas. A reconstruction of bottom water current velocities along the path of NADW flow southeast of Iceland based on the mean size of particles in the 10- to 63-\(\mu\)m range appears to indicate a decrease in flow of bottom water during the LIA (Bianchi and McCave, 1999). But there is no clear relationship between bottom current velocities, as reconstructed by the sortable silt parameter of Bianchi and McCave (1999), and sediment accumulation rates at their core site on the Gardar Drift. So lower bottom (NADW) current velocities during the LIA do not preclude the possibility that a substantial fraction of alkenones in Bermuda Rise sediment at the beginning of the
LIA were transported from the northeast in association with the main branch of NADW.

Deuterium enrichment in both C_{17:2-4} and C_{18:2-4} alkenones from the 2- to 3-cm depth interval corresponds to a particularly large 14C age difference between alkenones (7.81 14C ka) and total organic carbon (7.99 14C ka), presumably in the fine fraction of sediment, and coeval sand-sized G. ruber planktonic foraminifera (0.715 14C ka) reported by Ohkouchi et al. (2002). Thus we conclude that alkenones deposited at the continental margin east of the Canadian Maritime provinces enriched in deuterium but have low unsaturation ratios indicating a relatively young and deuterium-depleted alkenone source which would be expected to be with a pelagic source for the alkenones at 2 to 3 cm, rather than a continental margin source which would be expected to be enriched in deuterium.

Alkenones from the top 2 cm of Bermuda Rise sediment are enriched in deuterium but have low unsaturation ratios indicative of cold SSTs (Fig. 4), conditions characteristic of the continental margin east of the Canadian Maritime provinces (Fig. 5). Thus we conclude that alkenones deposited at the Bermuda Rise during the last few centuries likely were produced and transported from the Scotian Margin region, denoted C in Figure 5.

Alkenones from 7 to 10 cm are depleted in deuterium but have unsaturation ratios intermediate (~0.55) between those characterizing the MWP (~0.7) and the LIA (0.45) (Fig. 4). Their low δD values of < 200‰ require a significant, if not predominant, Scotian Margin source (Fig. 5). Yet with higher unsaturation ratios than would be expected from the subpolar waters of the Scotian Margin there must have been a contribution of alkenones from the northwestern subtropical gyre (region A).

5. CONCLUSIONS

The hydrogen isotopic composition of alkenones from marine particles and sediments can be measured by isotope ratio-monitoring gas chromatography-mass spectrometry with a combined accuracy and precision (i.e., RMS error) of 6‰. Culture experiments with the coccolithophorid E. huxleyi, and analyses of suspended particulate samples from the northwest Atlantic Ocean, indicate that the hydrogen isotopic ratio of alkenones closely tracks that of water. The hydrogen isotopic depletion of surface waters from the Emerald Basin (~12‰) and the Gulf of Maine (~7‰) relative to the Sargasso Sea (~10‰) was 22‰ and 17‰, respectively. This isotopic depletion was reflected in the hydrogen isotopic composition of alkenones in suspended particles from the Gulf of Maine (~200‰) relative to those in the Sargasso Sea (~181‰), which were lower by 19‰. It was also reflected in the ~20‰ isotopic depletion of alkenones in surface sediments from the Scotian Margin (~204‰) relative to those in the Sargasso Sea (~184‰). The ~20‰ hydrogen isotopic depletion of alkenones in the Scotian Margin relative to those in the Sargasso Sea was used in conjunction with alkenone unsaturation ratios to determine the source of alkenones to sediments of the Bermuda Rise drift.

Alkenone δD values varied by 45‰ in the top 10 cm of Bermuda Rise sediment, suggesting a change in the source of phytoplankton detritus during the climate periods loosely known as the Medieval Warm Period and Little Ice Age. Alkenone δD values indicate that > 60% of the sedimentary alkenones were produced to the north and west of the drift in the region of deuterium-depleted waters. To reconcile alkenone unsaturation ratios (δD, 14C) with their δD values a simple linear mixing model of sediment from the Sargasso Sea with that from the Scotian Margin and Laurentian Fan does not suffice. Instead we suggest that a third source of alkenones is necessary, characterized by cold SSTs and high δD values. The main branch of NADW flowing southwest from the Nordic Seas is a likely candidate.

Hydrogen isotopic analyses of alkenones are a complementary approach to the radiocarbon method developed by Ohkouchi et al. (2002) for determining the origin of alkenones and other components of the clay and silt fractions of sediment (i.e., the majority of the sediment) at drift sites such as the Bermuda Rise, and most likely anywhere a large hydrogen isotopic gradient exists. Alkenone δD values provide a better constraint on the surface water mass in which the alkenones were synthesized. They also require far less sediment per analysis than alkenone δ13C measurements, and they permit sediment sequences older than ~30,000 yrs—the upper limit for precise radiocarbon dating—to be evaluated.

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