Reconstructing the phytoplankton community of the Cariaco Basin during the Younger Dryas cold event using chlorin steryl esters

Kristina A. Dahl

Massachusetts Institute of Technology, Woods Hole Oceanographic Institution Joint Program in Oceanography and Ocean Sciences, Woods Hole, Massachusetts, USA

Daniel J. Repeta

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

R. Goericke

Scripps Institution of Oceanography, La Jolla, California, USA

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[1] A record of the downcore distribution of chlorin steryl esters (CSEs) through the Younger Dryas was produced from Cariaco Basin sediments in order to assess the potential use of CSEs as recorders of the structure of phytoplankton communities through time. Using an improved high-performance liquid chromatography method for the separation of CSEs, we find significant changes in the distribution of CSEs during the Younger Dryas in the Cariaco Basin. During the Younger Dryas, enhanced upwelling in the Cariaco Basin caused an increase in the diatom population and therefore an increase in the relative abundance of CSEs derived from diatoms. In contrast, the dinoflagellate population, and therefore CSEs derived from dinoflagellates, decreased in response to the climate change during the Younger Dryas. These community shifts agree well with the shifts observed in the present day on a seasonal basis that result from the north-south migration of the Intertropical Convergence Zone over the Cariaco Basin. We also identify changes in the abundance of several CSEs that seem to reflect rapid warming and cooling events. This study suggests that CSEs are useful proxies for reconstructing phytoplankton communities and paleoenvironments. *INDEX TERMS:* 1055 Geochemistry: Organic geochemistry; 4267 Oceanography: General: Paleoceanography; 4855 Oceanography: Biological and Chemical: Plankton; *KEYWORDS:* Younger Dryas, Cariaco Basin, chlorin steryl esters

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1. Introduction

[2] Chlorin steryl esters (CSEs) (Figure 1) consist of pyropheophorbide-a (a chlorophyll-a degradation product) and various sterols [e.g., *King and Repeta*, 1991]. Chlorophyll-*a* is the major photosynthetic pigment of all oxygenic photoautotrophs and can be used as a biomarker for phytoplankton-derived organic matter in sediments. Chlorophyll-*a* is rapidly degraded in the water column during zooplankton ingestion. One of the major degradation products is pyropheophorbide-*a*. Because chlorophyll-*a* degrades so rapidly and cannot be uniquely linked to a single class of phytoplankton, it cannot be used to track changes in the composition of the phytoplankton community through time.

[3] Sterols are a subset of the lipid class that has been well studied due to their ubiquity in algae and heterotrophs. Sterols that are geochemically important biomarkers have 27–30 carbon atoms and consist of a four-ring system onto which a variety of side chains are attached. The side chains, or R groups, attached to the ring structures allow for a wide range of sterol structures (Figure 2). Sterols have been utilized extensively because they exhibit the traits of good biomarkers: they are relatively refractory in the water column, and they can be traced back to known biological precursors [e.g., *Volkman*, 1986; *Volkman et al.*, 1993; *Meyers*, 1997; *Volkman et al.*, 1998]. The main issue confronting the use of sterols as biomarkers, however, is that sterols degrade at different rates. More specifically, 4-methyl sterols, found mainly in dinoflagellates [*Volkman et al.*, 1998], exhibit enhanced preservation relative to 4-desmethyl sterols [*Gagosian et al.*, 1980; *Wolff et al.*, 1986; *Harvey et al.*, 1989]. The free sterol distribution could therefore overestimate the dinoflagellate constituent of the phytoplankton community [e.g., *Pearce et al.*, 1998]. Furthermore, the ability to reconstruct the relative abundances of different phytoplankton classes could be affected by the amount of diagenesis that has taken place in the sediments.

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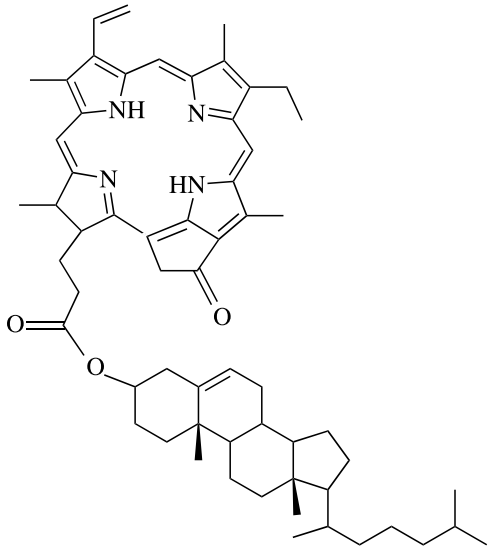

Figure 1. Structure of pyropheophorbide-*a* cholesteryl ester, a typical chlorin steryl ester.

While this problem may not be significant in recent sediments, it could become more significant in sediments heavily affected by diagenesis.

1.1. Formation of CSES in the Marine Environment

[4] Recent studies of zooplankton grazing and senescence-induced changes [*Harradine et al.*, 1996; *King and Wakeham*, 1996; *Talbot et al.*, 1999a, 1999b, 2000] have confirmed the finding of *King and Repeta* [1991, 1994] that CSEs are formed during zooplankton herbivory when the sterols produced by phytoplankton become esterified to pyropheophorbide-*a*, a chlorin. Several studies suggest that the conversion of sterols to CSEs occurs nonselectively during the grazing process [*King and Repeta*, 1991; *Harradine et al.*, 1996; *Talbot et al.*, 1999a]. That is, the structure of a sterol does not affect whether or not it esterifies to the pyropheophorbide-*a* molecule. Thus the distribution of CSE sterols reflects the sterols in algae that are grazed by herbivorous zooplankton and therefore the distribution of different classes (e.g., diatoms, dinoflagellates, red algae, etc.) of phytoplankton in the water column [e.g., *Pearce et al.*, 1998].

[5] After their formation in the water column, CSEs and other chlorins arrive at the seafloor via fecal pellets [*King*, 1993; *Talbot et al.*, 1999a]. Within sediments, CSEs exhibit enhanced preservation relative to both other chlorins [*Talbot et al.*, 1999a, and references therein] and free sterols [*King and Repeta*, 1991, 1994; *Talbot et al.*, 2000]. The enhanced preservation of CSE sterols relative to free sterols has been inferred from stanol/stenol ratios of the two groups of compounds [*King and Repeta*, 1991, 1994; *Pearce et al.*, 1998], which provide an estimate of the amount of degradation each type of compound has experienced [*Wakeham*, 1989]. CSE sterols have a low stanol/stenol ratio relative to free sterols, which indicates that they are less affected by microbial degradation [*King and Repeta*, 1991, 1994; *Pearce et al.*, 1998]. While several studies have now noted the enhanced preservation of CSE sterols relative to free sterols, a definitive mechanism for this phenomenon has not yet been demonstrated. As a result of their enhanced preservation, the distribution of CSE sterols in sediments reflects the distribution of water column sterols more closely than the sedimentary free sterol distribution does [*King and Repeta*, 1991, 1994; *Pearce et al.*, 1998]. Although CSEs do degrade once they reach the seafloor, the best available evidence suggests that the distribution of esterified sterols does not change during degradation; that is, there is no preferential degradation of a given CSE [*Talbot et al.*, 2000].

[6] CSEs exhibit the structural diversity of water column sterols while circumventing the problem of differential degradation that affects free sterol distributions. This feature of CSEs has prompted many to suggest that sedimentary CSEs could record the structure of phytoplankton communities through time [*King and Repeta*, 1994; *Harradine et al.*, 1996; *Pearce et al.*, 1998; *Talbot et al.*, 1999a]. However, only one study to date [*King and Repeta*, 1994] has made correlations between community structure and CSE sterol distributions. Our study evaluates the potential

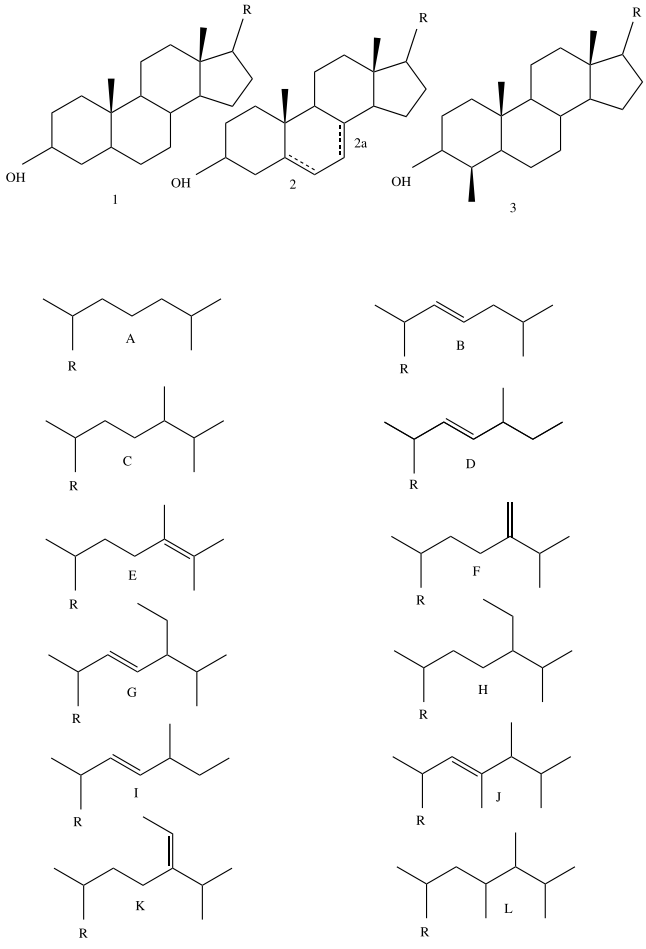

Figure 2. Sterol structures. R refers to the attachment point between the tetracyclic structure and the carbon chain.

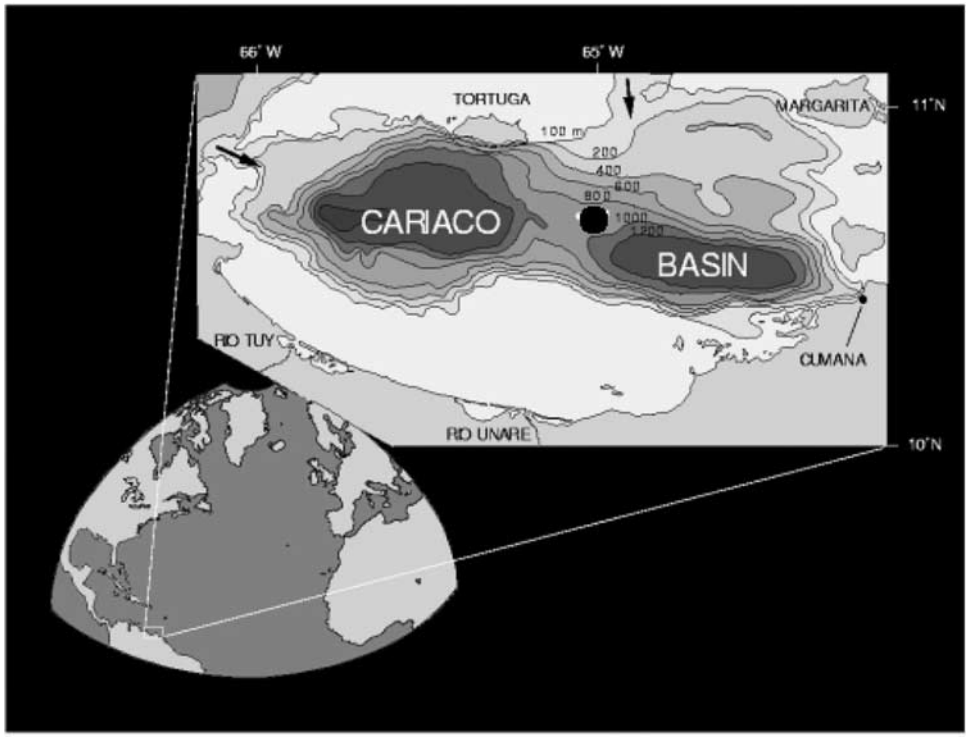

Figure 3. Location and bathymetry of the Cariaco Basin. The location of core 56-PC is shown as a black dot. Arrows indicate sills that control exchange with the Caribbean Sea. (Figure provided by K. Hughen.)

of CSE sterols as proxies for the phytoplankton community through time. In order to assess this possibility, we examined Younger Dryas-aged sediments from the Cariaco Basin, Venezuela.

1.2. Cariaco Basin: Setting and Background

[7] The Cariaco Basin is a small, anoxic, marine basin off the coast of Venezuela in the southern Caribbean Sea (Figure 3). Shallow (<146 m) sills separate the basin from the rest of the Caribbean Sea. The sills restrict flow to and from the basin and prevent oxygenation of deeper waters. Consequently, the basin has been anoxic below ~300 m for the past 12.6 kyr (^{14}C age; *Peterson et al.* [1991]). Owing to its latitude, the Cariaco Basin is subject to seasonal [*Peterson et al.*, 1991] and long-term [e.g., *Black et al.*, 1999; *Haug et al.*, 2001] fluctuations in the Intertropical Convergence Zone (ITCZ). During the Northern Hemisphere winter the ITCZ is at its farthest latitude south. Trade winds blow along the northern coast of South America, inducing upwelling and, subsequently, high production [*Muller-Karger et al.*, 2001]. During this upwelling season, diatoms dominate the phytoplankton community [*de Miro*, 1971; *Ferraz-Reyes*, 1983]. The ITCZ migrates northward during the Northern Hemisphere summer, causing trade winds and upwelling in the basin to diminish. Primary production during the nonupwelling season is lower [*Muller-Karger et al.*, 2001] and dominated by cyanobacteria and dinoflagellates [*Ferraz-Reyes*, 1983]. Sediments in the basin exhibit seasonal laminae, which are indicative of the basin's high sediment preservation potential. Furthermore, the lack of significant bioturbation and high deposition rates (20–100 cm/kyr; *Peterson et al.* [1991]) make the Cariaco Basin an ideal site for paleoceanographic reconstructions [*Lin et al.*, 1997].

[8] Much like the seasonal migrations of the ITCZ, longer-term (i.e., millennial-scale and longer) changes in trade wind strength cause changes in primary productivity and, most likely, phytoplankton community structure in the Cariaco Basin [*Haug et al.*, 1998]. The Younger Dryas is the most thoroughly researched millennial-scale climate event. Its timing is well constrained by radiocarbon dates from the varved sediments of the Cariaco Basin [*Hughen et al.*, 1996, 1998, 2000]. The Younger Dryas began about 13 kyr (calendar age) BP and lasted roughly 1300 years. It has been proposed that the Younger Dryas occurred as a result of a shutdown of North Atlantic Deep Water (NADW) formation [*Broecker et al.*, 1985; *Boyle and Keigwin*, 1987; *Broecker et al.*, 1988]. Such a change in thermohaline circulation would have caused changes in the meridional sea-surface temperature gradient and therefore the strength of trade winds and subsequent upwelling over the Cariaco Basin [*Hughen et al.*, 1996, and references therein]. Strengthening of the trade winds has been invoked as a mechanism to explain lithologic, climatologic, and faunal evidence from Younger Dryas-aged sediments from the basin [*Hughen et al.*, 1996; *Lin et al.*, 1997; *Lea et al.*, 2003].

[9] At the onset of the Younger Dryas, increases in trade wind intensity, and therefore upwelling, in the basin would have increased the concentration of nutrients in surface

waters. Under these high nutrient conditions, diatoms likely became the dominant primary producers [*Schrader et al.*, 1993]. Easing of the trade winds at the Younger Dryas termination should have shifted the dominant primary producers to cyanobacteria and dinoflagellates, as is observed during present-day Northern Hemisphere summer [*Ferraz-Reyes*, 1983]. If CSE sterols do indeed accurately reflect the phytoplankton community at the time of formation, then the assemblage of CSE sterols should undergo major changes at the onset and termination of the Younger Dryas in the Cariaco Basin. More specifically, we expected that the distribution should reflect an increase in the diatom population and a decrease in the dinoflagellate population during the Younger Dryas. As cyanobacteria do not produce large amounts of sterols, CSEs are unlikely to yield information regarding the abundance of this class of phytoplankton through time.

[10] *Werne et al.* [2000] performed a study of the distribution of free sedimentary sterols and a C_{37} alkenone in the Cariaco Basin during the Younger Dryas. These authors concluded that diatoms were the dominant primary producers during the Younger Dryas, while alkenone-producing coccolithophorids dominated during warm periods, such as the Holocene. While these shifts do exhibit the trends that one would expect, there are several uncertainties with this type of analysis. First, it has been widely noted that free sterols are more susceptible to selective degradation than are CSE sterols [*King and Repeta*, 1991, 1994; *Talbot et al.*, 1999a, 2000]. Second, although sterols and alkenones are both relatively refractory compound classes, it is expected that one class of lipids would undergo preferential degradation relative to the other [e.g., *Wakeham et al.*, 1997]. In contrast, CSEs all belong to the same class of compounds and therefore do not preferentially degrade relative to one another [*Talbot et al.*, 2000]. Because the Cariaco Basin is largely anoxic, it is unlikely that free sterol degradation and preferential degradation of one compound class over another will have a great effect on the accuracy of downcore records [*Wakeham and Ertel*, 1988]. In fact, *Werne et al.* [2000] noted that the highest accumulation rates of sterols (which are labile relative to alkenones) were found in the deepest sediment layers that they studied, which indicates that differential degradation is not a significant factor in the Cariaco Basin. Given the robustness of the free sterol record from the Cariaco Basin, the findings of *Werne et al.* [2000] provided an ideal backdrop for testing the potential of CSEs as proxies for phytoplankton community reconstructions.

2. Methods

2.1. Extraction and Isolation of CSES

[11] Core-top sediments were obtained from a box core taken from the center of the western basin of the Cariaco Trench (10°40N, 65°36′W, 700 m water depth) by the R/V *Iselin* [*Wakeham and Ertel*, 1988]. Pigments were extracted ultrasonically from ~300 g of wet sediment with acetone (3x, 400 mL each) followed by methylene choloride (3x, 400 mL each).

[12] Chlorin steryl esters were purified from the bulk extract using a combination of solid-phase extraction and reverse-phase high performance liquid chromatography (RP-HPLC). Solid-phase extraction was performed by packing a 6 cm diameter glass column with 75 g octadecylsilane (J.T. Baker, 40–140 mesh size) and eluting the pigments in several fractions, which were then further purified by RP-HPLC prior to structural identification. CSEs were purified on two Nucleosil C18 columns (Alltech, 3μm, 150 × 4 mm) connected in series. The CSEs were eluted isocratically with 25/75 (v/v) methylene chloride/acetonitrile at 1.5 mL/min and detected at 410 and 666 nm. In method development experiments this solvent composition provided an optimal separation of seventeen individual CSEs, which eluted between 25 and 65 min in our samples (Figure 4). Individual CSE peaks were collected manually as they eluted from the columns.

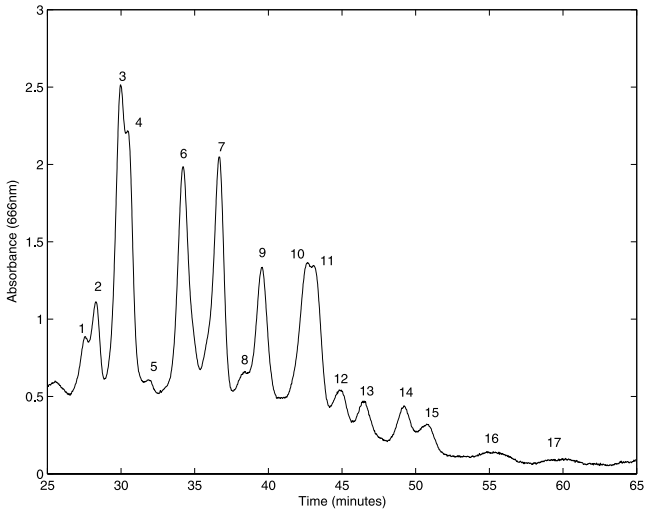

Figure 4. High-performance liquid chromatogram of the CSEs in a typical Cariaco Basin sample, showing the numbering scheme used in this study. Seventeen CSEs eluted between 25 and 65 min (refer to text for specific conditions). See Table 1 for CSE sterol identifications.

[13] Downcore samples are from piston core PL07-56PC in the Cariaco Basin [*Hughen et al.*, 1998]. This core was retrieved at 10°40.60′N, 64°57.70′W from 810 m water depth and has a sedimentation rate of ~50 cm/kyr. Samples (0.3 grams dry weight (gdw)) were taken every 10 cm from 300–800 cm across the Younger Dryas as determined from previous work [*Hughen et al.*, 1998]. The samples were freeze-dried overnight and extracted using automated solvent extraction (ASE) (100% methylene chloride, 1000 psi, 100°C). Total chlorins were quantified at 666 nm using UV/Vis spectrophotometry assuming an extinction coefficient of 5×10^4 L mol^{-1} cm^{-1}.

2.2. Sterol Identification

[14] CSE sterols were structurally identified for the bulk core-top sediment extraction using a combination of liquid chromatography-mass spectrometry (LC-MS) and Gas chromatography- mass spectrometry (GC-MS). LC-MS was performed on the individually collected CSEs from the core-top sediments in order to determine the molecular weight of the each CSE. The same columns and conditions

Table 1. Identification of CSE Sterols[a]

Peak	CSE Sterol Structure[b]	Precursor	MW	Basis[c]	Reference
1	24-norcholesta-5,22E-dien-3β-ol (2B)	dinoflagellates	887	G,L	*Goad and Withers* [1982] *Leblond and Chapman* [2002]
2	27-nor-24-methylcholesta-5,22E-dien-3β-ol (2I)	dinoflagellates	901	L	*Goad and Withers* [1982] *Mansour et al.* [1999]
3	24-methylcholesta-5,24(28)-dien-3β-ol (2F)	diatoms	915	L	*Barrett et al.* [1995, and references therein] *Volkman et al.* [1998]
4	cholesta-5,22E-dien-3β-ol (2B)	diatoms, red algae[d]	901	G,L	*Barrett et al.* [1995] *Véron et al.* [1998] *Volkman et al.* [1998]
5	24-methylene-cholest-5-en-3β-ol (2F)	many	915	L	*Goad* [1978, and references therein]
6	24-methylcholesta-5,22E-dien-3β-ol (2D)	diatoms, chryptophytes, coccolithophorids	915	G, L	*Volkman et al.* [1998] *Leblond and Chapman* [2002]
7	cholest-5-en-3β-ol (2A)	zooplankton, phytoplankton	903	G,L	*Volkman* [1986]
8	23,24-dimethylcholesta-5,22E-dien-3β-ol (2J)	diatoms, dinoflagellates	929	L	*Volkman et al.* [1993] *Leblond and Chapman* [2002]
	24-ethylcholesta-5,22E-dien-3β-ol (2G)	haptophytes, green and golden algae diatoms			*Volkman et al.* [1998] *Véron et al.* [1998]
	24-ethylcholesta-5,24(28)E-dien-3β-ol (2K)	haptophytes, prasinophytes			*Volkman et al.* [1994]
9	24-methylcholest-5-en-3β-ol (2C)	green algae	917	G,L	*Volkman* [1986] *Véron et al.* [1998]
10	24-ethylcholest-7-en-3β-ol (2aH) 24-ethylcholest-22-en-3β-ol (1G)		931	L	
	23,24-dimethylcholest-5-en-3β-ol (2K)	green algae, prasinophytes diatoms dinoflagellates			*Volkman et al.* [1998] *Véron et al.* [1998] *Volkman et al.* [1984] *Goad and Withers* [1982]
	23,24-dimethylcholest-22-en-3β-ol (1J)	green algae, prasinophytes			*Volkman et al.* [1998]
11	24-ethylcholest-5-en-3β-ol (2H)	many	931	G,L	*Volkman et al.* [1998]
12	24-ethylcholest-7-en-3β-ol (2aH) 24-ethylcholest-22-en-3β-ol (1G)		931	L	
	23,24-dimethylcholest-5-en-3β-ol (2K)	green algae, prasinophytes diatoms dinoflagellates			*Volkman et al.* [1998] *Véron et al.* [1998] *Volkman et al.* [1984] *Goad and Withers* [1982]
	23,24-dimethylcholesta-22-en-3β-ol (1J)	green algae, prasinophytes			*Volkman et al.* [1998]
13	4α,23,24-trimethylcholest-22E-en-3β-ol (3J)	dinoflagellates	945	L	*Withers* [1987]
	4α,23,24-trimethylcholest-N-3β-ol[e]	dinoflagellates			*Volkman et al.* [1998]
14	4α,23,24-trimethylcholest-22E-en-3β-ol (3J)	dinoflagellates	945	L	*Withers* [1987]
	4α,23,24-trimethylcholest-N-3β-ol[d]	dinoflagellates			*Volkman et al.* [1998]
15	23,24-dimethyl-5α(H)-cholestan-3β-ol (1L)	dinoflagellates	933	L	*Volkman et al.* [1998]
	4α,24-dimethyl-5α-cholestan-3β-ol (3C)	dinoflagellates			*Robinson et al.* [1984] *Withers* [1987, and references therein]
16	4α,23,24-trimethyl-5α-cholestan-3β-ol (3L)	dinoflagellates	947	L	*Talbot et al.* [2000] *Leblond and Chapman* [2002]
17	unknown		ND		

[a]Sterol identifications for peaks shown in Figure 4. For peaks with uncertain sterol identities, all possible sterol identities, on the basis of molecular weight, are listed. These CSE sterols have not been firmly identified.
[b]Structure numbers refer to Figure 2.
[c]Basis refers to the methods used to identify the CSE sterol. L, LC-MS; G, GC-MS.
[d]The red algae that produce this sterol are generally not found in seawater [*Volkman*, 1986].
[e]N indicates that the position of the double bond is unknown.

were used for the LC-MS as described above for RP-HPLC. The instrument used was a Shimadzu HPLC fitted to a Finnegan MAT LCQ operated in the positive ion mode and using atmospheric pressure electrospray ionizaton.

[15] Individual CSEs, collected from core-top sediments by RP-HPLC, were then hydrolyzed to liberate the CSE sterols. GC-MS was then performed on the individual CSE sterols in order to determine the structure (and therefore the identity) of each sterol. We apply these identifications to our downcore record, assuming that the sterols present in the core-top sample will be present downcore. Given the uniformity of RP-HPLC retention times in our downcore record, this is assumption is likely a good one.

[16] For cases in which the identity of a sterol was uncertain despite LC-MS and GC-MS, we have made certain assumptions in order to make the identifications listed in Table 1. CSEs 2 and 4 have the same molecular weight. GC-MS of CSE sterol 4 enabled us to identify it as cholesta-5,22E-dien-3β-ol. Results from GC-MS of the total CSE sterol fraction revealed that the only other CSE sterol present in our samples with the same molecular weight was 27-nor-24-methylcholesta-5,22E-dien-3β-ol. This is there-

fore our identification of CSE sterol 2. This identification is consistent with the elution order of the CSEs during RP-HPLC. The identifications of CSEs 3 and 5 are based on their relative abundances in seawater. 24-methylcholesta-5,24(28)-dien-3β-ol is more abundant in seawater than 24-methylenecholest-5-en-3β-ol [*Volkman*, 1986]. By analogy with their relative peak areas, we have identified CSE sterols 3 and 5 as indicated in Table 1.

2.3. Data Analysis

[17] In order to determine the distribution of CSEs in each downcore sample, the area of each CSE peak in each chromatogram was determined using the HP Chemstation software's data analysis program. The areas were determined as follows: A baseline was drawn between the beginning of CSE 1 and the end of CSE 15. Vertical lines were then drawn between each of the peaks, using the lowest point of the valley between peaks when obvious, and the area was calculated. For cases in which no distinct minimum separated two CSEs this area of the two peaks were combined. This was done throughout the downcore record for peaks 1 and 2, peaks 3 and 4, and peaks 10 and 11. The downcore records of peaks 3 and 4 (as well as 10 and 11) are mirror images of one another, which is an artifact of the integration rather than a true signal. The resolvability of peaks 1 and 2 varied throughout the record. Combining the peaks of two CSEs has implications for the reconstruction of phytoplankton classes through time in that if the combined peaks do not have the same biological source, then the combined peak will be a reflection of multiple classes of phytoplankton. As will be shown in the "sterol identification" section of the results, this does not pose a significant problem in the interpretation of our record. Peaks 16 and 17 were not included in the integration because the peak heights were generally very low and the boundaries of the peaks were not consistently defined. The area of each peak was then divided by the total area of the CSEs in order to determine changes in the distribution of the CSEs relative to one another. The average error for two sets of integrations was 0.23 ± 0.095%.

[18] Principal component analysis was performed using Matlab software. For this analysis, peaks 1 and 2 (hereafter 1 + 2), peaks 3 and 4 (3 + 4), and peaks 10 and 11 (10 + 11), which were not well resolved, were combined so as to prevent the introduction of erroneous changes in the distribution of the CSEs with depth. Elemental CHN analysis was performed on ten samples throughout the core to determine changes in the organic carbon content of these sediments through the Younger Dryas. These analyses were performed using a Carlo Erba Elemental Analyzer (model 1108).

3. Results

3.1. Bulk Parameters

[19] Stadial events, such as the Last Glacial Maximum (LGM) and the Younger Dryas, are characterized by relatively low percentages of organic carbon in comparison to interstadial events (Figure 5b). The lowest organic carbon contents (<2%) occurred during the LGM. The

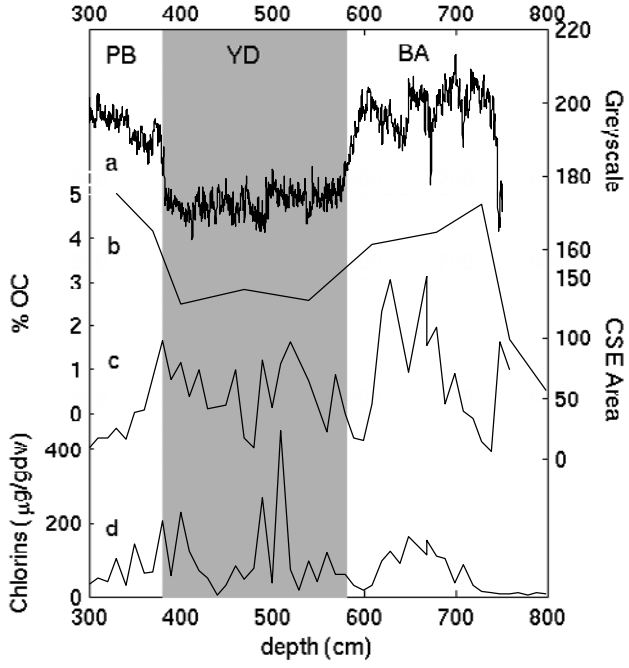

Figure 5. (a) Gray scale, (b) percent organic carbon, (c) total CSE area per gdw (arbitrary units), and (d) total chlorins versus depth. The Younger Dryas period is denoted by the shaded bar. PB, YD, and BA refer to the Preboreal, Younger Dryas, and Bølling/Allerød periods, respectively.

organic carbon content rose to 4–5% during the Bølling/Allerød warm period then dropped again to ~2.5% during the Younger Dryas. At the Younger Dryas termination the organic carbon content rose once again to 4–5%. These results are in good agreement with higher resolution data from a neighboring piston core, PL07-39PC (K. Hughen, personal communication, 2001). The shifts toward a lower percent organic carbon during stadials reflect a dilution of the organic carbon signal rather than a decrease in the preservation of organic carbon. During the Younger Dryas, increased productivity drove a roughly 3-fold increase in the bulk sedimentation rate [*Hughen et al.*, 1996]. The increased sedimentation of biogenic debris (i.e., diatom and foraminifera tests) during the Younger Dryas therefore diluted the organic carbon reaching the sediments. It should be noted, however, that the accumulation rate of organic carbon was elevated during the Younger Dryas relative to the Bølling/Allerød and Preboreal periods [*Werne et al.*, 2000] due to a decrease in the oxygen content of the water column [*Dean et al.*, 1999; *Lyons et al.*, 2003].

[20] Increased primary productivity during the Younger Dryas is also reflected in the gray scale record of this core, previously published by *Hughen et al.* [1996] (Figure 5a). Gray scale is a measure of the reflectivity of sediment. In the Cariaco Basin, gray scale is determined primarily by the relative inputs of terrestrial (dark) and biogenic (light) material and can therefore be used as a proxy for primary productivity. During the Younger Dryas the increase in sedimentation of biogenic material relative to

terrestrial material caused a decrease in the gray scale of the sediments.

[21] The concentration of total chlorins in the Cariaco Basin through time varies from nondetectable to 448 μg/gdw with an average value of 72 μg/gdw (Figure 5d). The ratio of chlorin concentration to percent organic carbon varies through time as well, which suggests that either there are different mechanisms controlling the preservation of chlorins and organic carbon in sediments or the contribution of CSEs to the total organic carbon pool varies through time. The total CSE area, defined as the integrated area under all of the CSE peaks in a given HPLC chromatogram, corresponds well to total chlorin concentration, determined by the absorbance at 666 nm, through time (Figure 5c).

3.2. CSE Fraction

[22] The CSE fraction is composed of at least 17 distinct CSEs (Figure 4), all of which have pyropheophorbide-*a* as the chlorin component. We did not find any CSEs with pyropheophorbide-*b* (CSEs b) as the chlorin component in our samples. As shown by *Talbot et al.* [1999b], sterols are incorporated into CSEs of pyropheophorbide-*a* and pyropheophorbide-*b* in equal proportions. The pigment precursor to pyropheophorbide-*b* (chlorophyll-*b*) is much less abundant in algae than the precursor to pyropheophorbide-*a* [e.g., *Svec*, 1991]. The concentrations of CSEs b are therefore generally lower than those of CSEs a, which have pyropheophorbide-*a* as their chlorin [*Gall et al.*, 1998; *Kowalweska et al.*, 1999; *Tani et al.*, 2002].

[23] The HPLC chromatogram shown in Figure 4 is typical of CSE distributions in core-top and downcore sample extracts. The largest peaks in each chromatogram are 3 + 4, 6, 7, 9, and 10 + 11. These CSEs, on average, constitute roughly 80% of the total CSEs. The remaining 12 CSE peaks are consistently smaller than those mentioned above and collectively constitute ~20% of the total CSE area.

3.3. Sterol Identification

[24] LC-MS data enabled us to identify the molecular weights of each CSE (Table 1). The molecular weights of the CSEs (i.e., the combined weight of the chlorin and the sterol of a given CSE) range from 887 to 947 Daltons and generally increase with retention time. These molecular weights correspond to sterols with carbon numbers of 26–30 and molecular weights of 352–412 Daltons. In general, the diunsaturated 5,24(28) sterols eluted before 5,22 sterols, and monounsaturated 5-stenols eluted after diunsaturated 5,24(28) and 5,22 sterols. Sterol identifications, made via a combination of LC-MS, GC-MS of individual CSE sterols, and GC-MS of a total CSE sterols sample, are shown in Table 1.

[25] In many cases the molecular weight alone is enough to make a definitive identification of the CSE sterol. Identifications based solely on LC-MS become problematic, however, given that several sterols can have the same molecular weight if they differ in structure simply by the position of a double bond. Because GC-MS was performed on just the CSE sterols, we were able to clarify many of the ambiguous LC-MS data. The combination of LC-MS and GC-MS allowed us to identify 10 out of the 17 CSEs.

[26] Our sterol identifications provide further justification for combining the peaks for CSEs 1 + 2 and CSEs 3 + 4. As shown in Table 1, CSE sterols 1 and 2 are both derived from dinoflagellates while CSE sterols 3 and 4 are both derived from diatoms. CSEs 10 and 11 are not derived from the same phytoplankton class; we therefore do not interpret CSEs 10 + 11 as a reflection of a given phytoplankton class.

3.4. Downcore CSE Records

[27] As shown in Figure 6, the relative percent of some CSEs varies very little (e.g., CSE 13, which varies between 2 and 3%) while the relative percent of others varies quite dramatically downcore (e.g., CSE 7, which varies between 12 and 24%). It is clear that the distribution of some CSEs changes through time and that these changes are often synchronous with changes in the climate of the Cariaco Basin (Figure 6).

[28] Five CSE peaks that vary significantly downcore, along with variations in gray scale from the same core, are shown in Figure 7. As mentioned above, gray scale can be used as a proxy for primary productivity in the Cariaco Basin. The gray scale record from this core correlates very well with the accumulation rate of the GISP2 ice core from central Greenland, which has been interpreted as a proxy for North Atlantic sea- surface temperature [*Kapsner et al.*, 1995; *Hughen et al.*, 2000]. This correlation implies that gray scale in the Cariaco Basin is a reflection of climate. We use gray scale here primarily as a reference for the rapid transitions into and out of the Younger Dryas. On the basis of our sterol identifications we can draw several conclusions about the nature of the phytoplankton community during the Younger Dryas in the Cariaco Basin.

[29] CSEs 1 + 2 decrease in abundance during the Younger Dryas (Figure 7a). The mean abundance of CSEs 1 + 2 during the Younger Dryas is significantly different from the mean abundance during the Bølling/Allerød and Preboreal periods at the 99% confidence level, as determined by a *t* test for two sample populations. Furthermore, CSEs 1 + 2 may reflect some of the centennial-scale variability during the Bølling/Allerød that can be seen clearly in the pattern of gray scale. CSE sterols 1 and 2 (24-nor-cholesta-5,22E-dien-3β-ol and 27-nor-24-methylcholesta-5,22E-dien-3β-ol, respectively) are produced by dinoflagellates [*Goad and Withers*, 1982; *Mansour et al.*, 1999; *Leblond and Chapman*, 2002]. We can therefore infer from Figure 7a that the relative abundance of dinoflagellates in the Cariaco Basin is high during warm weak trade wind intervals and low during cold increased trade wind intervals such as the Younger Dryas. The decrease is gradual over the Bølling/Allerød-Younger Dryas transition. At the Younger Dryas-Preboreal transition, however, CSEs 1 + 2 increase very rapidly. The downcore relationship between CSEs 1 + 2 and gray scale is consistent with the observation that the dinoflagellate population increases during the nonupwelling (lower productivity) season in the Cariaco Basin today [*Peterson et al.*, 1991].

[30] Figure 7b shows the distribution of CSEs 3 + 4 through the Younger Dryas. The sterols of CSE 3 (24-methylcholesta-5,24(28)-dien-3β-ol) and CSE 4 (cho-

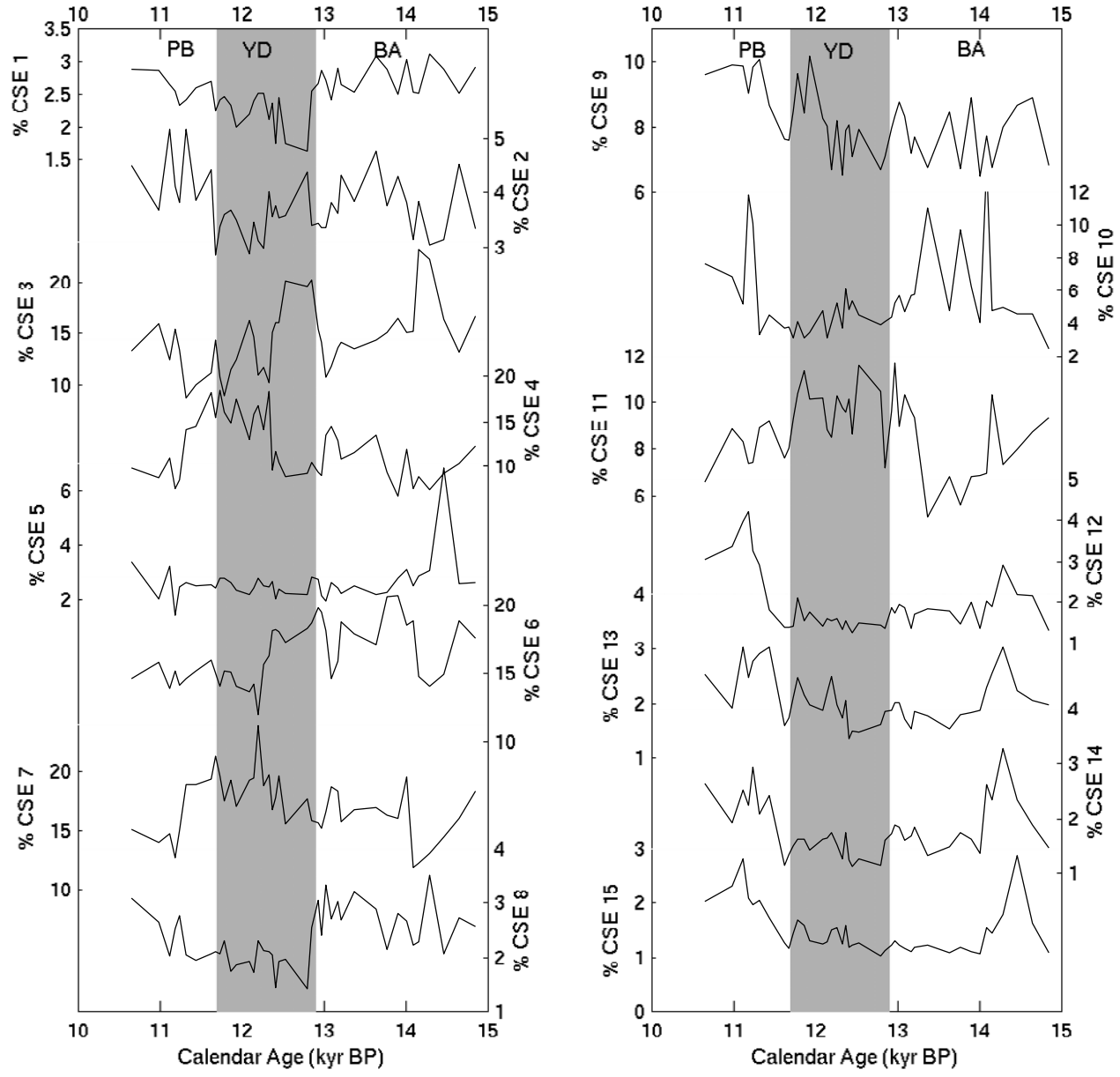

Figure 6. Downcore changes in the relative percentage of each CSE relative to the total CSE area through time. CSE numbers refer to the peaks in Figure 4. The Younger Dryas period is represented by the shaded bar. BA and PB refer to the Bølling/Allerød and Preboreal periods, respectively.

lesta-5,22E-dien-3β-ol) are both abundant in diatoms [e.g., *Barrett et al.*, 1995; *Véron et al.*, 1998; *Volkman et al.*, 1998]. CSEs 3 + 4 increased in abundance during the Younger Dryas and decreased during the Preboreal period. The increase in abundance at the onset of the Younger Dryas was very rapid, while the decrease coming out of the Younger Dryas lagged slightly behind that of the increase in gray scale. The mean abundance of CSEs 3 + 4 during the Younger Dryas is different from that of the Bølling/Allerød and Preboreal periods at the 99% confidence level. This downcore distribution suggests that the diatom population of the Cariaco Basin increased during the Younger Dryas, which was expected a priori, given that the increase in trade wind intensity and upwelling during the Younger Dryas would have favored the growth of diatoms just as it does during the present-day upwelling season [*Peterson et al.*, 1991].

[31] CSE 6 shows an interesting pattern of high abundance during the Bølling/Allerød and the first half of the Younger Dryas followed by a rapid decrease about halfway through the Younger Dryas (Figure 7c). The abundance stays relatively low throughout the rest of the Younger Dryas and the Preboreal period. CSE sterol 6 is 24-methylcholesta-5,22E-dien-3β-ol, a sterol that is found in many types of phytoplankton including diatoms and coccolithophorids [*Volkman et al.*, 1998, and references therein].

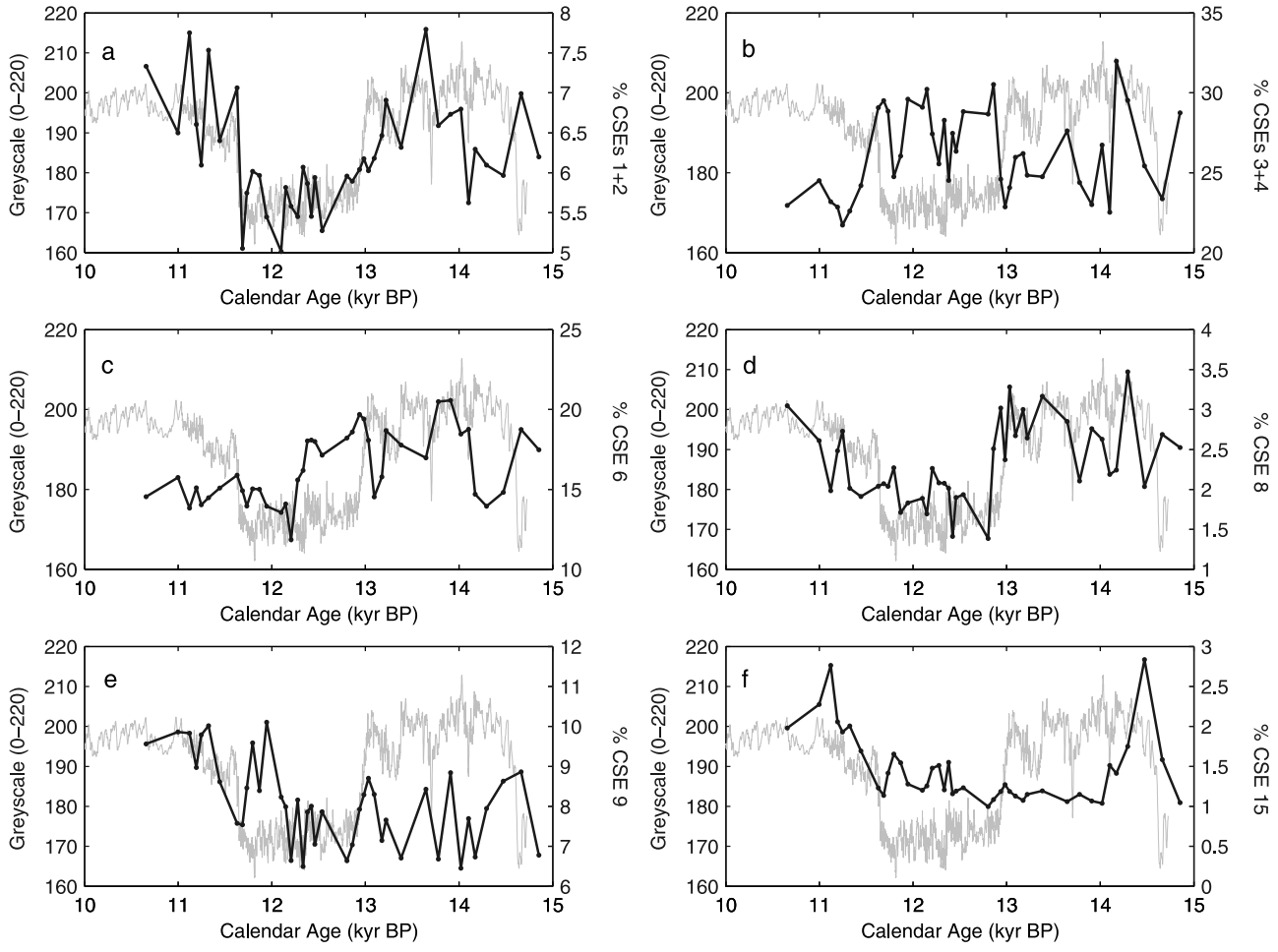

Figure 7. Changes in the relative percentage of different CSEs (black) and gray scale (gray) in core PL07-56PC. (a) CSEs 1 + 2, (b) CSEs 3 + 4, (c) CSE 6, (d) CSE 8, (e) CSE 9, and (f) CSE 15.

[32] The relative percentage of CSE 9 (24-methylcholest-5-en-3β-ol), derived from green algae [*Volkman*, 1986], generally increases from low during the Bølling/Allerød to high during the Preboreal period (Figure 7e). Much of this increase takes place during the second half of the Younger Dryas. Interestingly, this trend is opposite that of CSE 6, which shows a decrease in abundance in the middle of the Younger Dryas. CSE 9 also undergoes major changes in relative abundance at each climate transition. During transitions into interstadials (stadials) the relative percent of CSE 9 increases (decreases). While higher-resolution data is needed, this relationship appears to hold true for the centennial-scale variability exhibited in the gray scale record during the Bølling/Allerød.

[33] CSEs 8 and 15 remain unidentified. It is evident from their downcore trends, however, that they may be useful climate proxies (Figures 7d and 7f). CSE 8, which could originate from a number of different classes of phytoplankton, including dinoflagellates and diatoms, exhibits a rapid decrease in abundance at the onset of the Younger Dryas but does not respond rapidly to the warming at the end of the Younger Dryas. This CSE might therefore be a useful indicator of rapid cooling and/or increased upwelling events. Although CSE 15 has also not been identified, all of the sterols that are consistent with its molecular weight are dinoflagellate sterols (Table 1). CSE 15 (as well as CSEs 12 and 14, Figure 6) responds rapidly to warming events or decreases in upwelling intensity but does not appear to respond to cool increased upwelling events such as the Younger Dryas. Shifts in the abundance of these CSEs take place not only at rapid climate transitions (e.g., the Bølling/Allerød-Younger Dryas transition) but also within "stable" climate regimes (e.g., the rapid decrease in the abundance of CSE 15 during the Bølling/Allerød). Thus the biological sources of CSEs 8 and 15 are responding to changes in the environment of the Cariaco Basin that are not reflected in the gray scale record. Identification and downcore analysis of these CSE sterols would therefore allow for reconstruction of specific aspects of the paleoenvironment that cannot be inferred from gray scale changes. In addition, the downcore records of CSEs 1 + 2 and CSE 15 are markedly different from one another despite the fact that each of these CSEs originates from dinoflagellates. That different sterols, each presumably being produced by different species of dinoflagellates, can exhibit independent trends suggests that the

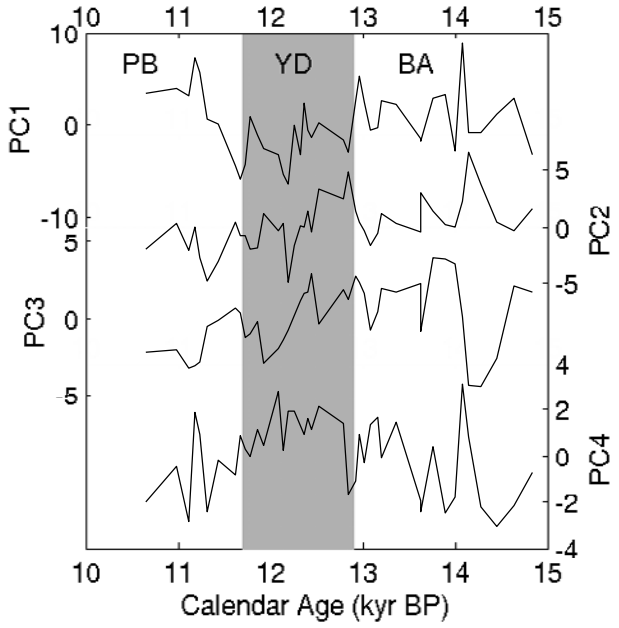

Figure 8. Principal components 1–4 plotted through time. the younger Dryas is defined by the shaded bar. BA and PB refer to the Bølling/Allerød and Preboreal periods, respectively.

suite of CSEs can offer a very in-depth detailed view of paleoenvironments.

3.5. Principal Component Analysis

[34] Principal component analysis of the downcore CSEs demonstrated that 94% of the total variance in the data set could be explained by four principal components (PCs). These four PCs are shown plotted against age in Figure 8. PC1, which explains 46.1% of the variance, becomes more negative during the Younger Dryas. This reflects a greater influence of CSEs 3 + 4 (diatoms) and 7 (many sources) during this time. Positive values of PC1, such as those that occur during the Bølling/Allerød and Preboreal periods, reflect a greater influence of CSEs 6 and 10 + 11, both of which come from a number of different phytoplankton sources. PC2, explaining 18.8% of the variance, shows a generally decreasing trend from the Bølling-Allerød to the Preboreal period. This decrease represents a trend from a greater influence of CSEs 3 + 4 (diatoms), 6, and 7 (many sources) to a greater influence of CSE 9 (green algae). PC3, which explains 18.6% of the variance, becomes more positive at the onset of the Bølling-Allerød, which reflects an increase in the influence of CSEs 6 and 7 (many sources) and a decrease in the influence of CSEs 3 + 4 (diatoms) and 9 (green algae). PC4 explains 10.6% of the variance and has very positive values during the Younger Dryas. These positive values reflect an increased influence of CSEs 10 + 11 and 7 (many sources) and a decreased influence of CSEs 1 + 2 (dinoflagellates) and 5 (diatoms). The results of the PCA therefore support the results of the downcore distribution trends. The increased influence of diatom CSEs and the decreased influence of dinoflagellate CSEs during the Younger Dryas (Figure 8) support the trends seen in the downcore CSE records. Furthermore, the trend toward a greater influence of green algae is consistent with a generalized warming and/or decreased upwelling in the Cariaco Basin since the LGM.

4. Discussion

[35] The successful application of CSEs as biomarkers requires the identification each CSE sterol as well as the generation of accurate downcore records of the CSE distribution. With respect to both of these requirements, the results presented here represent an important step toward successful reconstruction of phytoplankton communities. One of the main benefits of our approach is that it can be performed using relatively small (0.3 gdw) samples. In addition, the analyses can be done very quickly using automated RP-HPLC technology. In contrast, the use of gas chromatography (GC) to do such work would require larger samples and longer preparation time for several reasons. Prior to GC analysis, CSEs would have to be purified using RP-HPLC, yielding the same information we have utilized for this study. Owing to their high molecular weights, the CSEs would then need to be hydrolyzed in order to liberate the CSE sterols. Furthermore, given the sensitivity of the GC-MS we have been using, we estimate that we would need to start with double the amount of sediment.

[36] In this study, we have doubled the previous number of CSEs [*King and Repeta*, 1994] that can be separated by optimizing the HPLC solvent composition and the columns. By only resolving about half of the CSEs reported in this study, earlier studies could not represent the full suite of phytoplankton sterols. Furthermore, substantial coelution prevented accurate determination of the relative contribution of each CSE. Our improved separation represents a critical step toward accurate reconstruction of phytoplankton communities through time. With further method development and more complete CSE sterol identification, our ability to reconstruct phytoplankton communities will continue to improve.

[37] One limitation of using CSE sterols or free sterols as indicators of phytoplankton communities is that most sterols do not have a single biological precursor. For example, 24-methylcholesta-5,22E-dien-3β-ol (CSE 6) has been identified not only in diatoms, but also in haptophytes and cryptophytes [*Goad and Withers*, 1982; *Volkman*, 1986; *Volkman et al.*, 1998]. Furthermore, the sterol composition in a given class of phytoplankton can be diverse. As shown by *Volkman et al.* [1998], while some diatoms contain an abundance of 24-methylcholesta-5,24(28)-dien-3β-ol, others have cholesterol as their major sterol. Still others contain only cholesta-5,24-dien-3β-ol [*Barrett et al.*, 1995], which demonstrates there may not be a single definitive sterol biomarker for diatoms. With further method development and statistical analysis of trends within groups of CSEs downcore, however, CSEs could be very powerful biomarkers.

[38] There is evidence that zooplankton may preferentially take up certain sterols during the CSE formation process. A culture study by *Talbot et al.* [2000] showed that copepods discriminated against 4-methyl sterols (predominantly from

dinoflagellates) during CSE production. It has been observed that the abundance of 4-methyl sterols is lower in CSE sterols than in free sterols [*King and Repeta*, 1991; *Eckardt et al.*, 1992; *King and Repeta*, 1994; *Pearce et al.*, 1998]. As a result, it is possible that the distribution of CSEs will underestimate the contribution of dinoflagellates to the community of the overlying water column [*Talbot et al.*, 2000]. However, the discrimination against 4-methyl sterols may depend upon the setting [*Pearce et al.*, 1998]. Reconstructions of the dinoflagellate population using free sterols have the opposite problem: 4-methyl sterols are more refractory than 4-desmethyl sterols, which could lead to an overestimation of the dinoflagellate contribution to the phytoplankton community. In this study, we have used 4-desmethyl sterols (24-norcholesta-5,22E-dien-3β-ol and 27-nor-24-methylcholesta-5,22E-dien-3β-ol, CSEs 1 + 2), as opposed to the more traditional 4-methyl sterol, dinosterol, as dinoflagellate indicators. Using these 4-desmethyl sterols, we see evidence for changes in the dinoflagellate community through time in the direction that we would expect. This may be a potential solution to the problem of 4-methyl sterol exclusion from CSE formation, although it is clear from a comparison of CSEs 1 + 2 and CSE 15 that different dinoflagellate biomarkers can yield different results.

[39] Our results are broadly consistent with paleoceanographic studies of the Cariaco Basin during the Younger Dryas. *Peterson et al.* [1991] showed that the relative abundance of the planktonic foraminifer *Globigerina bulloides*, which is commonly used as a proxy for upwelling conditions [*Duplessy et al.*, 1981; *Ganssen and Sarnthein*, 1983; *Prell*, 1984; *Prell and Campo*, 1986], was higher during the Younger Dryas than during the Bølling/Allerød and the Preboreal periods. Further evidence for increased upwelling in the Cariaco Basin during the Younger Dryas comes from oxygen isotopes of several taxa of planktonic foraminifera [*Lin et al.*, 1997]. Our finding of an increased abundance of diatoms during the Younger Dryas is consistent with an increase in upwelling in the basin.

[40] *Werne et al.* [2000] also demonstrated that diatoms increased in abundance during the Younger Dryas through the use of free sterols and other organic biomarkers. Similar to our results for CSEs 6 and 9, *Werne et al.* [2000] found that significant changes in the phytoplankton community took place in the middle of the Younger Dryas. *Werne et al.* [2000] observed a decrease in the diatom and dinoflagellate populations during the Younger Dryas, while in this study we find a decrease in the relative abundance of CSE 6, which is derived from a variety of phytoplankton classes including diatoms and coccolithophorids. While the specific classes involved in this decrease may differ between this study and that of *Werne et al.* [2000], the biomarkers used in both studies suggest that phytoplankton community reconstructions potentially record changes in environmental conditions that take place during periods of seemingly stable climate. In contrast to our observations of a strong decrease in the relative abundance of dinoflagellates during the Younger Dryas, *Werne et al.* [2000] found relatively little change in the dinoflagellate population through time. There are several potential reasons why this discrepancy exists. First, *Werne et al.* [2000] use dinosterol (4α,23,24-trimethylcholest-22E-en-3β-ol, CSE 13 or 14) as their sole indicator of dinoflagellates, whereas we use a suite of CSE sterols (1 + 2 and 15) as dinoflagellate indicators. Given the fact that CSEs 1 + 2 and CSE 15 show such different trends, it is apparent that using different dinoflagellate biomarkers can yield different results. Second, free 4-methyl sterols, such as dinosterol, are known to exhibit enhanced preservation relative to free 4-desmethyl sterols [*Gagosian et al.*, 1980; *Wolff et al.*, 1986; *Harvey et al.*, 1989]. Thus changes in the diagenetic conditions of the water column or sediments could alter the abundance of dinosterol relative to other sterols. Given the anoxic nature of the Cariaco Basin, however, it is unlikely that this is the reason for the discrepancy between the two records. In more oxic settings this would become a more likely scenario.

[41] The differing approaches of this study and that of *Werne et al.* [2000] each have their strengths. For example, *Werne et al.* [2000] were able to detect large changes in the coccolithophorid population by using an alkenone biomarker for coccolithophorids and by assuming that their sterol and alkenone biomarkers would not have experienced differential degradation. Unfortunately, there is no CSE sterol that uniquely corresponds to coccolithophorids; therefore our study cannot yield information regarding coccolithophorid populations. Through the use of CSEs, however, we have been able to detect changes in the green algae population; a phytoplankton class that was not identified by *Werne et al.* [2000].

5. Conclusions

[42] In this study, we have examined the paleoceanographic potential of chlorin steryl esters. We find that during the Younger Dryas cold event in the Cariaco Basin, the phytoplankton community shifted such that there were fewer dinoflagellates and more diatoms than there were during the Bølling/Allerød warm period. These shifts are consistent with both the seasonal shifts in productivity in the basin today and the hypothesis that trade wind-induced upwelling in the Cariaco Basin increased during the Younger Dryas. The ability to detect these changes in the downcore distribution of CSEs has been made possible via optimization of the separation of CSEs using RP-HPLC. These results represent an important step in the development of CSEs as paleoenvironmental indicators. As we continue to improve the separation as well as the identifications of the CSE sterols, the nature of these downcore distribution changes will become more salient and CSEs may become more robust proxies for environmental conditions through time.

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K. A. Dahl, Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, MS#22, Woods Hole, MA 02543, USA. (kdahl@whoi.edu)

R. Goericke, Marine Life Research Group, Scripps Institution of Oceanography, 9500 Gilman Dr., La Jolla, CA 92093, USA. (rgoericke@ucsd.edu)

D. J. Repeta, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MS#4, Woods Hole, MA 02543, USA. (drepeta@whoi.edu)