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Climate-induced variations in productivity and planktonic ecosystem structure from the Younger Dryas to Holocene in the Cariaco Basin, Venezuela

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Abstract. A high-resolution molecular organic geochemical study of sediments in the anoxic Cariaco Basin indicates significant changes in primary productivity and planktonic community structure associated with the transition from the Younger Dryas to the Holocene. Variations in climate conditions over the past 12 ^{14}C kyr have induced large-scale changes in upwelling intensity, which directly affected levels of primary productivity as reflected in accumulation rates of bulk productivity proxies. Concentrations and accumulation rates of sterol and alkenone biomarkers have been used to identify how productivity changes affected the structure of the planktonic ecosystem. A shift in the dominant primary producer from diatoms (Younger Dryas) to coccolithophores (Holocene) is identified. If productivity and ecosystem variations like those identified in the tropical upwelling zone of the Cariaco Basin region, occur throughout the tropical oceans, they have the potential to affect global climate through perturbations in the biogeochemical cycle of carbon.

1. Introduction

Detailed climate records that document abrupt changes associated with the transition from the last glacial to present conditions are well preserved in high-latitude sedimentary environments (e.g., > ~45° [*Bard and Broecker*, 1992]) such as ice cores (Greenland Ice Sheet Project, GISP [*Taylor et al.*, 1997]), lacustrine sediments (Soppensee, Switzerland [*Lotter et al.*, 1992]), and marine sediments [*Broecker et al.*, 1988; *Troelstra et al.*, 1995]. Initially, it was thought that such climate variation, as reflected in large temperature changes and associated ice volume responses, was largely limited to high latitudes. Because the low latitudes were assumed to be much less prone to large temperature variations, it was thought that signals of high-frequency climate oscillation would be reduced or absent at these locations [e.g., *Bard and Broecker*, 1992]. Contrary to this assertion, recent work has identified climate signals associated with deglaciation, such as the Younger Dryas (YD) cold period (11-10 ^{14}C kyr), in low-latitude settings in both continental [cf. *Islebe et al.*, 1995; *Troelstra et al.*, 1995] and marine environments [cf. *Flower and Kennett*, 1990; *Keigwin and Jones*, 1990; *Kennett*, 1990; *Linsley and Thunell*, 1990; *Peterson et al.*, 1991; *Hughen et al.*, 1996a, b; *Hughen et al.*, 1998]. Some of these low-latitude climate signals have been positively correlated with variations in ice volume and sea surface temperature (SST) recorded at higher latitudes. For example, *Hughen et al.* [1996a, b] presented high-resolution correlations between sedimentological signals inferred to reflect productivity in the Cariaco Basin and signals from both ice cores and high-latitude lacustrine sediments. Thus it appears that global climate change may be manifested as variations in productivity in low-latitude environments where temperature variations are less significant.

The correlations presented by *Hughen et al.* [1996a, b] and others provide compelling evidence for a low-latitude response to global climate perturbations. If global climate changes such as the YD cold period are indeed manifested in the tropical oceans primarily as variations in productivity, they should be recognizable in sediments such as those in the Cariaco Basin that tend to preserve organic matter (OM) and/or inorganic indicators of productivity (e.g., carbonate and opal remains) at high resolution.

In order to examine changes in biological productivity and the planktonic community structure we have undertaken an organic geochemical study in sediments deposited over the last 12 kyr in the Cariaco Basin. Our goal was to assess climate-induced change in the intensity of primary productivity and the structure of the planktonic ecosystem assemblage within the Cariaco Basin over the period beginning at ~12 ka and spanning the YD and Holocene. Bulk geochemical proxies (organic carbon and carbonate accumulation rate) were used to assess changes in the level or primary production associated with the transition from YD to Holocene. Molecular (biomarker) accumulation rates have been used to identify unambiguously the source(s) of the organic matter (i.e., marine versus

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terrestrial) and the dominant primary producers in the basin and assess variations in the planktonic ecosystem structure associated with the proposed productivity changes as a result of climate-induced variability in coastal upwelling. Molecular accumulation rates have been compared to bulk indicators (organic carbon and carbonate) to ground truth the notion that bulk accumulation rates reflect real variations in primary productivity and ascertain whether reconstructions based on bulk proxies were the same as those based on molecular proxies. It is possible that climate-induced changes in low-latitude production and ecosystem structure such as those identified in this study could affect climate through feedbacks in the global biogeochemical cycle of carbon.

2. Regional Setting and Background

The Cariaco Basin (Figure 1), the world's second largest anoxic marine basin after the Black Sea, is a pull-apart basin located on the northern continental shelf of Venezuela. Exchange with the Caribbean is restricted by sills located ~150m below the present sea surface [*Richards and Vaccaro*, 1956; *Heezen et al.*, 1959]. These sills allow circulation between the upper water column of the Cariaco Basin and the Caribbean Sea, which provides a steady source of nutrients to stimulate productivity in the photic zone. Below the sills, however, circulation is restricted, thereby limiting the flux of oxygen needed to replenish that consumed by respiration of settling organic matter in the deeper waters of the basin. As a result of this imbalance in the oxygen budget, the basin has been anoxic for the last 12.6 kyr [*Peterson et al.*, 1991]. Currently, the waters of the Cariaco Basin are anoxic and sulfidic from ~300m to the maximum water depth of ~1400m [*Wakeham*, 1990; *Fry et al.*, 1991]. There is also evidence for water column sulfide production throughout much of the period from 12.6 ka to the present [*Lyons et al.*, 1998].

The climate in the region of the Cariaco Basin is strongly influenced by seasonal migration of the Intertropical Convergence Zone (ITCZ) and therefore undergoes significant variation from monsoonal to arid extremes. During the winter months, when the ITCZ is located at its southernmost position, strong trade winds develop above the Cariaco Basin [*Herrera and Febres-Ortega*, 1975; *Aparicio*, 1986]. These easterly trade winds induce Ekman transport of surface waters northward away from the basin, which in turn induces strong upwelling [*Herrera and Febres-Ortega*, 1975; *Aparicio*, 1986]. Upwelled waters bring a large supply of nutrients and dissolved inorganic carbon to the surface, which are then available for biological utilization and can support elevated productivity in the surface waters [*Ballester*, 1969; *Muller-Karger and Aparicio*, 1994; *Astor et al.*, 1997]. Conversely, the trade winds are weaker during the summer months when the ITCZ assumes its northernmost position more nearly over the basin, which leads to less intense Ekman-induced upwelling and ultimately to reduced, though still comparatively high, productivity [*Muller-Karger and Aparicio*, 1994; *Astor et al.*, 1997].

Evidence of these large seasonal changes is preserved in the laminated (varved) sediments which accumulate on the Cariaco Basin floor [*Peterson et al.*, 1991; *Hughen et al.*, 1996a, b]. High winter productivity during the upwelling season produces a thicker, light colored, millimeter-scale microlamina composed predominantly of opaline and carbonate tests. The biogenic remains are predominantly diatoms in the deeper sediments where laminae are thickest, but there are significant contributions from coccolithophorids, silicoflagellates, and

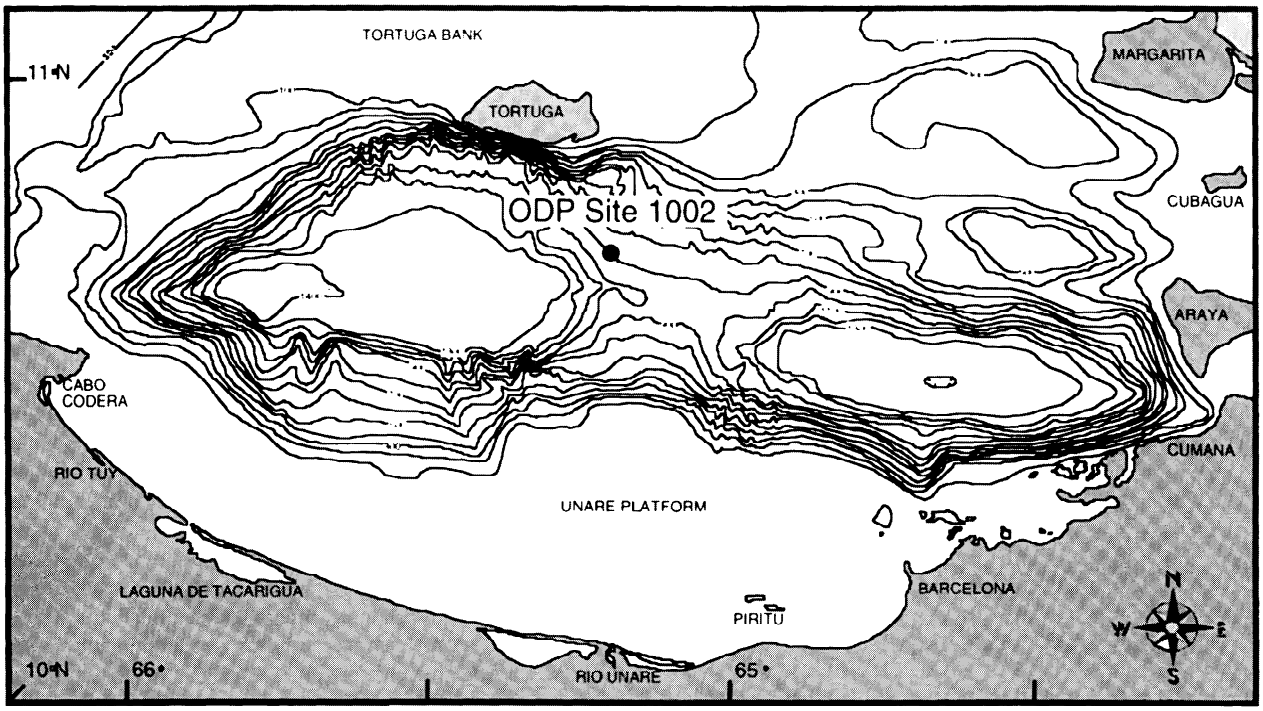

Figure 1. Location and bathymetry of the Cariaco Basin showing position of Site 1002, Ocean Drilling Program (ODP) Leg 165.

foraminifera [*Hughen et al.*, 1996a]. The summer record in the annual couplet contains mostly terrigenous mineral grains, dominantly quartz and feldspars, deposited during the local rainy season [*Hughen et al.*, 1996a]. For reasons developed below the varves are thicker and more distinct during the period from 12 ka to ~10 ka than during the Holocene [*Hughen et al.*, 1996a, b], suggesting a greatly increased bulk sedimentation rate at that time.

The existence of pronounced productivity differences in the Cariaco Basin as a result of seasonal climatic oscillations led *Peterson et al.* [1991] to propose an analogous model for longer-term changes in productivity and oceanographic conditions in the Cariaco region as a result of climatic variability. They proposed that during cooler periods in Earth history (e.g., the YD) the overall climate pattern in the Cariaco Basin was similar to the present day winter climate with a more southerly position of the ITCZ causing increases in trade wind strength and upwelling intensity and a higher level of primary productivity. During warmer periods the climate was generally more like present day summer, with a more northern locus of the ITCZ associated with weaker trade winds, less intense upwelling, and a lower level of productivity. The hypothesis of *Peterson et al.* [1991] stresses the necessity for increased zonal atmospheric circulation, which is consistent with a recent conclusion of *Webb et al.* [1997] that increased atmospheric and oceanic circulation intensity may have been a partial causal factor in cooling of the tropics during the Last Glacial Maximum.

3. Methods

Cariaco Basin samples were acquired from Ocean Drilling Program (ODP) Site 1002 drilled during ODP Leg 165 (Figure 1). Core 1002B, consisting of a single, continuous 6 m core collected from 900 m water depth for dedicated geochemical studies, was subsampled at 5 cm intervals [*Shipboard Scientific Party*, 1997]. Following pore water isolation within hours of collection, the sediment samples were immediately frozen, stored frozen for a few months, and subsequently dried at 50°C prior to analysis. Frequency of analysis (ranging from 5 to 40 cm) was dictated by the effort required for a given analytical procedure (e.g., bulk measurements were made at higher resolution than molecular analyses).

3.1. Bulk Concentration/Accumulation Rates

Concentrations of total carbon and total inorganic carbon (IC) were determined using a UIC Carbon Coulometer. Total organic carbon (OC) was determined by difference. Calcium carbonate concentrations were calculated stoichiometrically, assuming all inorganic carbon is present as calcium carbonate. To normalize for dilution effects resulting from known temporal changes in bulk sedimentation rate (ranging from ~30 to ~100 cm/kyr over the interval of interest [*Shipboard Scientific Party*, 1997], concentrations were converted to accumulation rates using sedimentation rates and bulk density data from adjacent cores [*Shipboard Scientific Party*, 1997]. This conversion was facilitated by correlating core 1002B with well-dated piston core PL07-39PC [*Lin et al.*, 1997] using high-resolution records of magnetic susceptibility. A suite of 20 accelerator mass spectrometry (AMS) ^{14}C dates from core PL07-39PC spanning the time interval of overlap was used to create an age model for which a standard reservoir correction of 420 years was applied [*Lin et al.*, 1997]. Ages are reported as reservoir-corrected radiocarbon years rather than calendar years, which could possibly affect the calculation of mass accumulation rates because of the effects on sedimentation rates. The correlations of magnetic susceptibility indicate continuous deposition in core 1002B, with a basal age of the sediment sequence of ~12 ^{14}C kyr.

3.2. Lipid Extraction and Separation

Lipid analysis was performed following a procedure modified from S. G. Wakeham and T. K. Pease [unpublished manuscript, 1992]. Dried sediments were Soxhlet-extracted with a 2:1 methylene chloride:methanol solution for 24 hours to obtain the total lipid extract (TLE). Extracts were washed with 5% aqueous NaCl solution and dried over Na_2SO_4. The TLE was then saponified in 3 mL 0.5 N KOH/methanol plus 1 mL extracted-distilled water at 100°C for 2 hours. Neutral fractions of TLE were obtained by extracting the saponified TLE with hexane three times. The remaining TLE was acidified to pH 2 with 6 N HCl and extracted with hexane three times to obtain acid fractions, which will not be discussed in this paper. The neutral fraction was separated into different compound classes by column chromatography (9 mm internal diameter (ID) column with 8 g of 5% deactivated 70-230 mesh silica gel). The separate fractions were isolated as follows: alkane/alkene fractions in hexane, ketone fractions (including long-chain unsaturated alkenones) in 10% ethyl acetate/hexane, alkanols and 4-methyl sterols in 15% ethyl acetate/hexane, and 4-desmethyl sterols in 20% ethyl acetate/hexane. The latter two fractions were derivatized to their trimethylsilyl-ethers in 100 mL bistrimethylsilyltrifluoroacetamide (BSTFA) and 100 mL acetonitrile at 60°-70°C for 2 hours.

3.3. Gas Chromatography

Quantification of compounds was performed on a Hewlett-Packard 5890 Series II Plus gas chromatograph (GC). On-column splitless injection was used with an HP-1 capillary column (50 m x 0.32 mm), a He flow rate of 1 mL/min, and a flame ionization detector. The oven temperature program initiated at 60°C and increased at rates of 10°/min to 200° and 3°/min to 320° and remained at 320°C for 30 min. Concentrations of individual compounds were determined assuming that concentration is proportional to chromatogram peak area and that the response factor is the same as for the internal standard (androstane). Concentrations of biomarker compounds were converted to accumulation rates by the methods described for bulk OC and $CaCO_3$.

3.4. Gas Chromatography-Mass Spectrometry

Molecular identification of compounds was carried out using a Finnigan MAT TSQ 700 mass spectrometer coupled to a Hewlett-Packard 5890 Series II gas chromatograph. Conditions for the injection, column, flow and oven temperature were similar to those described for the GC methods. Operating conditions for the mass spectrometer were as follows: accelerating voltage 200 V, 1500 multiplier, source temperature 170°C, manifold temperature 70°C, and transfer line temperature at

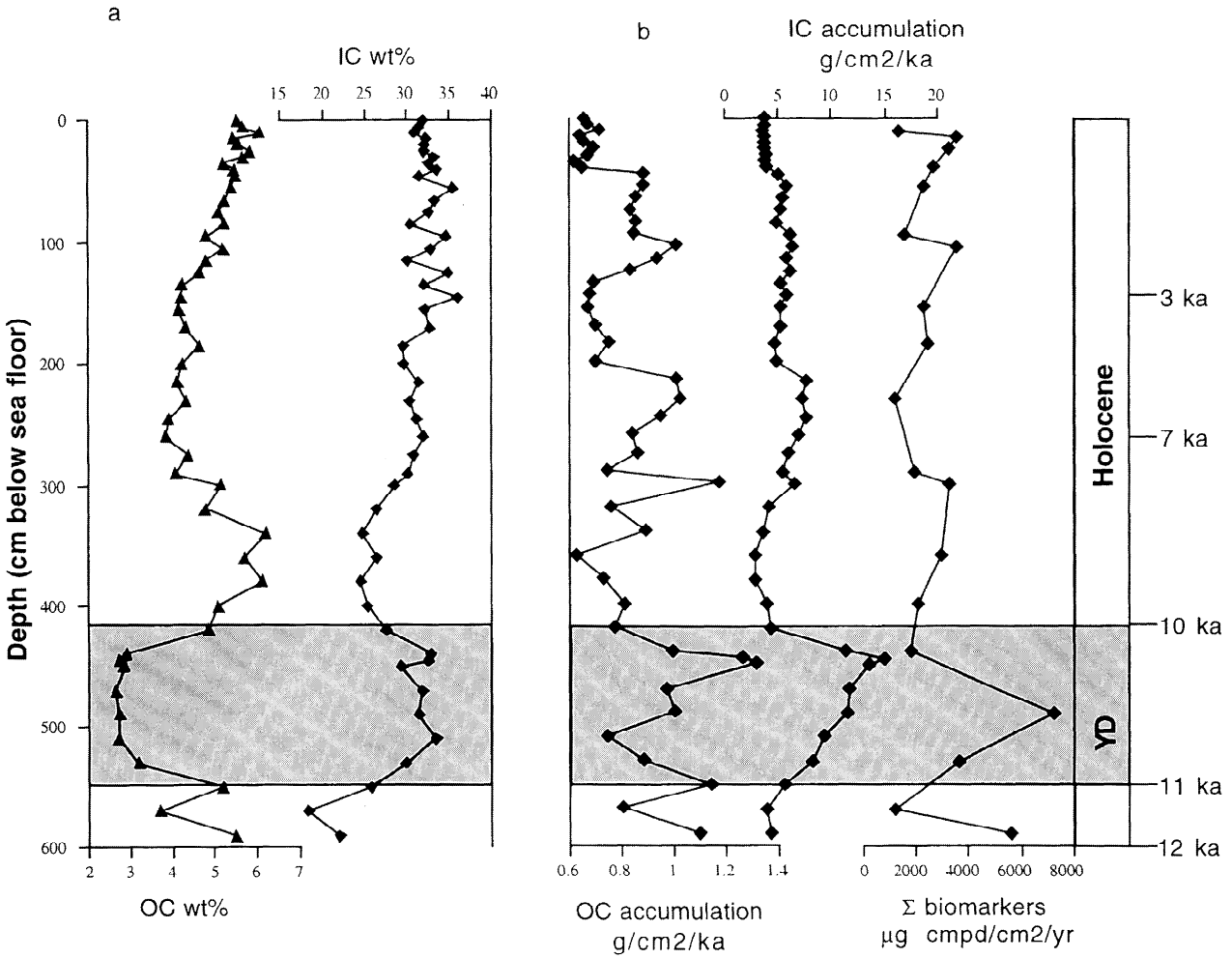

Figure 2 (a). Concentration (weight percent) of organic carbon and inorganic carbon (as carbonate). Note that it appears from this plot that productivity increased from the Younger Dryas (YD) to the Holocene. (b). Accumulation rate of organic and inorganic carbon and sum of biomarkers indicative of planktonic community (fucosterol, C_{37} alkenone, dinosterol, and cholesterol), calculated on the basis of Accelerator mass spectrometry (AMS) ^{14}C dates from core PLO7-37PC [*Lin et al.*, 1997] and correlated to 1002B using magnetic susceptibility measurements. Highest accumulation rates of organic and inorganic carbon and cumulative biomarkers occur during the YD, suggesting highest primary productivity at that time.

320°C. Mass scan was 1 scan/0.8 sec over the mass interval 50-600.

4. Results

4.1. Bulk Parameters

OC weight percent is much lower during the YD than during the Holocene and increases throughout the Holocene (Figure 2a), ranging from a low of ~3 wt % during the YD to >6 wt % during the early and late Holocene. $CaCO_3$ wt % is less variable, ranging from just over 20 wt % before the beginning of the YD to 35 wt % during the late Holocene. Because of changes in bulk sedimentation rate in the Cariaco Basin (i.e., varying dilution effects) over the last 12 kyr, which ranged from ~30 cm/kyr during the Holocene to almost 100 cm/kyr during the YD [*Shipboard Scientific Party*, 1997], concentrations of bulk OC and $CaCO_3$ have been converted to accumulation rates to achieve a more accurate perspective on primary OC and $CaCO_3$ inputs to the sediments.

Bulk organic carbon accumulation rates are more variable but generally higher during the YD than the Holocene, ranging from a low of 0.6 g/cm^2/kyr during the late Holocene to a peak of almost 1.4 g/cm^2/kyr during the YD (Figure 2b). Accumulation rates of $CaCO_3$ peak during the YD at almost 15 g/cm^2/kyr and decrease to <5 g/cm^2/kyr during the Holocene (Figure 2b).

4.2. Molecular Parameters

Bulk organic matter can be a mixture of compounds from many different sources (e.g., terrestrial higher plants, marine algae, and bacteria) and as such is useful only for determining gross changes in total productivity. It is difficult, for example, to assess the relative contributions from terrestrial and marine sources or the ecosystem structure using only bulk data. Biomarker trends were therefore utilized to determine whether the bulk geochemical and sedimentological productivity signals preserved in the sediments are marine in origin or simply reflect variations in the relative contributions of terrestrial versus marine organic matter. To achieve this goal,

Table 1. Name, Common Name, Source Organism(s), and Reference(s) for Biomarker Compounds Used in This Study

Compound	Common Name	Source organism(s)	Reference(s)
Cholesta-5,22-dien-3β-ol	Δ22-cholesterol	diatoms, red algae	Volkman [1986]
24-methylcholesta-5,22-dien-3β-ol	brassicasterol	diatoms, coccolithophorids	Volkman [1986] and Meyers [1997]
24-methylcholesta-5,24(28)-dien-3β-ol	fucosterol	diatoms, brown algae	Volkman [1986] and Saliot and Tusseau [1984]
24-ethylcholesta-5-en-3β-ol	β-sitosterol	diatoms, higher plants	Volkman [1986] and Meyers [1997]
4,23,24-trimethylcholesta-22-en-3β-ol	dinosterol	dinoflagellates	Boon, et al. [1979] and Brassell et al. [1987]
Cholesta-5-en-3β-ol	cholesterol	zooplankton, phytoplankton	Volkman [1986] and Meyers [1997]
Heptatriaconta-15E,22E-trien-2-one	C_{37} alkenone	coccolithophorids	Marlowe et al. [1984]
Nonacosane	n-C_{29} alkane	terrestrial higher plants	Meyers [1997]

Though several compounds have multiple possible sources, the lack of significant amounts of terrestrial OM in sediment traps [*Thunell et al.*, 1997] suggests that the marine planktonic sources are more likely. Also, the accumulation rate of the n-C_{29} alkane is more than an order of magnitude lower than other biomarkers.

concentrations of C_{29} n-alkanes, C_{37} alkenones, and several sterol biomarkers were determined. Specific biomarkers and their precursor organisms are listed in Table 1. To correct for dilution effects from bulk sedimentation rate changes and gain a more accurate representation of surface water conditions at the time of deposition, we have converted the biomarker concentrations to accumulation rates.

The terrestrial biomarker, C_{29} n-alkane, has a maximum accumulation rate in the most surficial sediments at almost 300 μg compound/cm^2/yr. Through the majority of the sedimentary sequence, however, the accumulation rate of n-C_{29} never gets above 200 μg compound/cm^2/yr (Figure 3). This accumulation rate is an order of magnitude lower than the maximum of all other biomarkers (as detailed below), suggesting that the supply of terrigenous organic matter to the sediments in the Cariaco Basin has been negligible over the past 12 kyr.

The accumulation rates for each of the four diatom biomarker compounds (Δ22-cholesterol, brassicasterol, fucosterol, and β-sitosterol) peak during the YD at values up to 3000 μg compound/cm^2/yr and decrease to values <1000 μg compound/cm^2/yr in the early Holocene (Figure 3). The rates remain consistently low for the remainder of the Holocene. The accumulation rates for the zooplankton biomarker, cholesterol, reveal a similar trend, peaking in the YD at >3000 μg compound/cm^2/yr and decreasing to a level below 1000 μg compound/cm^2/yr for most of the Holocene (Figure 3). The dinoflagellate biomarker, dinosterol, displays a very similar trend during the YD and early Holocene but diverges from these other biomarkers during the later Holocene (Figure 3). The accumulation of dinosterol peaks at a rate of almost 900 μg compound/cm^2/yr during the YD, which is a lower level than for the diatom and zooplankton biomarkers over the same interval. During the mid-Holocene, dinosterol accumulation rates are consistently below 200 μg compound/cm^2/yr. Conversely, the accumulation rates for the biomarker for coccolithophorids, C_{37} di-unsaturated alkenone, are generally lowest during the YD (values range from 50 to 800 μg compound/cm^2/yr; see Figure 3). Holocene rates are more variable and reach a maximum of >2500 μg compound/cm^2/yr.

To determine whether the bulk productivity proxies are accurately representing conditions in the surface waters, we have compared them to the cumulative aquatic biomarker accumulation rates ($\Sigma biomarker_{acc}$). For this comparison we have added the accumulation rates of of the most representative biomarker of each of the major planktonic organisms: diatoms, dinoflagellates, zooplankton, and coccolithophorids. $\Sigma biomarker_{acc}$ is similar, but not identical to, the bulk productivity indicators (Figure 2b). $\Sigma biomarker_{acc}$ peaks during the YD at almost 8000 μg compound/cm^2/yr and drops to between 2000 and 4000 μg compound/cm^2/yr during the Holocene. The peak in $\Sigma biomarker_{acc}$ is offset from the peaks for OC and $CaCO_3$ accumulation; however, the peaks in OC and $CaCO_3$ accumulation are between adjacent biomarker samples, so it is possible that the peaks are much closer than is apparent from Figure 2b. It is also possible that the peaks in OC and $CaCO_3$ are due to some source other than planktonic production in the surface waters; however, as presented above and discussed more fully below, there is no evidence for a substantial contribution of terrestrial organic matter to the sediments of the Cariaco Basin.

5. Discussion

5.1. Constraining Sources and Diagenetic Alteration of Organic Matter

In any organic geochemical study it critical to be certain of the sources of organic matter under study and also to take into account any potential diagenetic alteration of that OM that

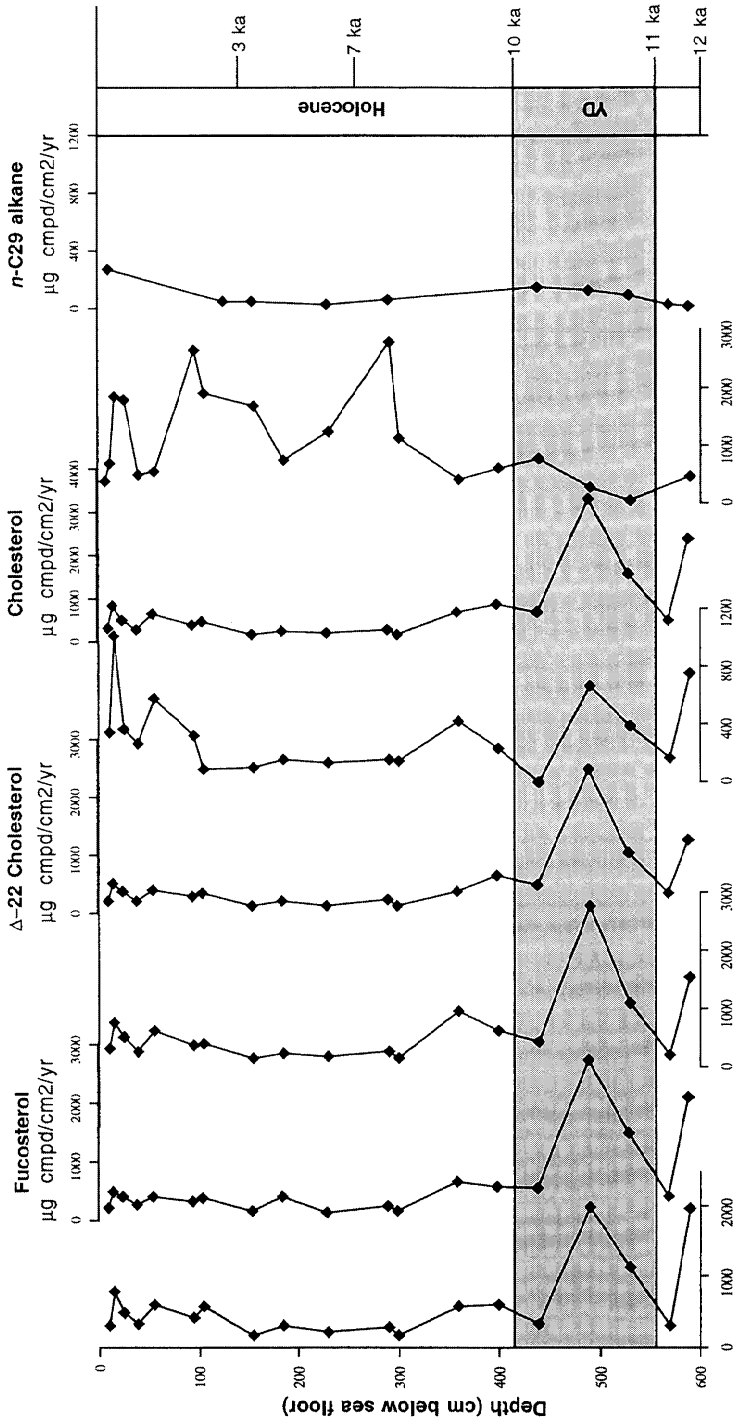

Figure 3. Accumulation rates of biomarkers indicative of diatoms, dinoflagellates, zooplankton, coccolithophorids, and terrestrial organic matter (OM). The accumulation rate of n-C_{29} is more than an order of magnitude lower than the marine biomarkers, indicating that there is not a significant input of terrestrial OM to the sediments of the Cariaco Basin. The excellent correlation of sterols compared to alkenones suggests that coccolithophorids are not responding to the environmental changes in the same way as the diatoms, dinoflagellates, and zooplankton. Note how well the accumulation rates of sterols indicative of diatoms match the bulk OC accumulation rates during the YD, indicating that these are the organisms providing the dominant supply of OM at that time.

may affect interpretations. The depositional environment in the Cariaco Basin has been consistently anoxic throughout the period of study, so we can assume that any changes in bottom water oxygenation that might induce differential degradation of organic matter are insignificant. The work of *Wakeham and Ertel* [1988] indicates that organic material is altered dominantly in the water column of the Cariaco Basin but not significantly once it reaches the sediments. Furthermore, although enhanced preservation can be attributed to increased rates of bulk sedimentation, this effect appears to be less significant in euxinic settings [*Henrichs and Reeburgh*, 1987; *Canfield*, 1989, 1994]. Also, given the relative magnitudes of present-day water column remineralization versus diagenetic remineralization and the range of sedimentation rates over the past 12 kyr in the Cariaco Basin, sedimentation-related preservational artifacts are thought to be of secondary importance in the present study. Thus, assuming constant degradation in the water column over the interval of study, the organic matter in the sediments of the Cariaco Basin can be utilized as a reliable indicator of changes in marine primary production.

Differential degradation among different compounds during diagenesis is another factor that can potentially affect interpretations of biomarker data (e.g., sterols appear to be more labile than alkenones [*Teece et al.*, 1994; *Wakeham et al.*, 1998]). In the sediments of the Cariaco Basin, however, the highest accumulation rates of sterols, the more labile biomarkers, occur in the deepest sediment layers; the opposite is true for the more refractory alkenones. In other words, the relative proportions of these biomarkers are opposite of what would be predicted by stability relationships alone, and removal of a diagenetic signal would not alter the observed relative trends of these biomarkers. Therefore it appears that the concentrations of biomarkers in the sediments of the Cariaco Basin are controlled dominantly by inputs from primary production, and differential degradation is not a significant factor. While accumulation rates of biomarker compounds cannot be used as a direct indicator of the number of organisms living in the water column at the time of deposition (given complications associated with processes like degradation and heterotrophy), biomarkers are still useful reconstructive tools. Temporal changes in their accumulation rates can be related to changes in the intensity of productivity and ecosystem structure.

A potential complication in the interpretation of biomarker data is that certain compounds can be produced by multiple organisms (e.g., 24-ethylcholesta-5-en-3β-ol is produced by diatoms and higher plants [*Volkman*, 1986]). However, there is not a significant present-day input of terrestrial OM to the waters of the Cariaco Basin, as evident in studies of water column particulates [*Wakeham*, 1990; *Freeman et al.*, 1994] and sediment trap materials [*Thunell et al.*, 1997]. In the 12 kyr sediment record, *n*-alkanes are dominated by short C-chain compounds (e.g., C_{17}), and both *n*-alkenes and *n*-alcohols display strong even-over-odd and short C-chain predominance (J. Werne, unpublished data, 1998), also suggesting that terrestrial OM is an insignificant fraction of the extractable organic matter over the time period of the present study [*Meyers*, 1997]. Finally, the accumulation rate of the C_{29} *n*-alkane is more than an order of magnitude lower than the aquatic biomarkers (Figure 3), indicating that terrestrial OM is not a significant portion of the sedimentary OM in the Cariaco Basin. We conclude from these data that higher plant contributions to the sedimentary biomarker pool are insignificant and therefore that our assignments of biomarkers to marine organisms are valid.

5.2. Climate-Induced Changes in Productivity and Ecosystem Structure

5.2.1. Bulk and molecular indicators of autotrophic and heterotrophic production. Accumulation rates of bulk productivity proxies and biomarkers have been used to evaluate the productivity in the Cariaco Basin over the past 12 kyr. There is good agreement between the bulk OC and $CaCO_3$ accumulation rates, opal accumulation rates [*Peterson et al.*, 1995] and $\Sigma biomarker_{acc}$ (Figures 2a and 2b), suggesting that marine planktonic production was the dominant source for OM and carbonate to these sediments. With the exception of the coccolithophorid alkenone, accumulation rates for individual biomarker compounds (Figure 3) are similar to those for bulk OC and $CaCO_3$ and published results for opal [*Peterson et al.*, 1995]. We attribute these increased accumulation rates during the YD (Figure 2b) to elevated primary and secondary productivity driven by the increased supply of nutrients associated with intensified upwelling. Evidence of intensified upwelling and productivity during the YD relative to the Holocene also exists in foraminiferal [*Peterson et al.*, 1991], oxygen isotope [*Lin et al.*, 1997], and sedimentological indicators [*Hughen et al.*, 1996a, b].

Accumulation rates of sterols indicative of diatoms and zooplankton (see Table 1 for specific biomarkers) peaked during the YD (Figure 3), suggesting that high rates of primary production by diatoms and high rates of heterotrophy by zooplankton may be coupled. The dinosterol accumulation rate also peaked during this period but at a much lower level than diatom sterols, indicating that dinoflagellates were probably not as significant in the planktonic community as diatoms, but generally followed the same productivity trends. During the Holocene, accumulation rates of all sterol biomarkers decreased by at least a factor of 3 relative to the YD. This decrease is thought to reflect a decrease in primary productivity of diatoms and dinoflagellates due to decreased upwelling and the concomitant decrease in zooplankton consumers feeding on them. Conversely, accumulation rates of C_{37}-alkenones (indicative of coccolithophorids) were very low during the YD and increased during the Holocene (Figure 3). Thus it would appear that during periods of high upwelling, diatoms are the dominant primary producer in the planktonic ecosystem of the Cariaco Basin, and during periods of lower upwelling, such as the Holocene, coccolithophorids become a significantly more important part of the planktonic ecosystem.

5.2.2. Ecosystem structure variations, YD to Holocene. Analysis of the accumulation rates of this suite of plankton biomarkers suggests changes in the planktonic community assemblage over the last 12 kyr. Although interpretations based on the absolute abundances of biomarkers are misleading owing to their susceptibility to dilution effects as-

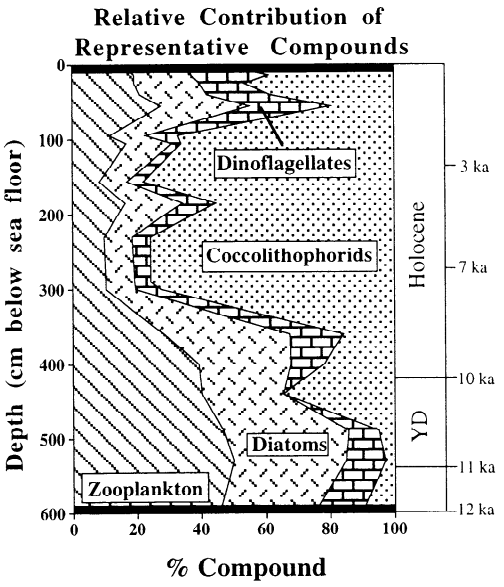

Figure 4. Relative percent of biomarkers indicative of diatoms, dinoflagellates, coccolithophorids, and zooplankton, illustrating the change in dominant primary producer from diatoms during the YD to coccolithophorids during the Holocene. One biomarker compound representative of each organism was chosen and the total normalized to 100%.

sociated with changing sedimentation rates, the general structure of the planktonic community can be interpreted from changes in the relative abundances of different biomarkers. To illustrate the transition in community dominance clearly, the relative abundances of compounds indicative of diatoms, dinoflagellates, coccolithophorids, and zooplankton have been plotted (Figure 4). As different numbers of biomarkers have been identified for different organisms, one compound was chosen as representative of each organism, and the total normalized to 100%. It is evident from Figure 3 that the absolute accumulation rates of these different compounds have varied temporally, but Figure 4 clearly demonstrates the change in relative dominance of the phytoplanktonic community assemblage from diatoms during the YD to coccolithophorids during the Holocene.

These results are not unexpected considering the preferred habitat of the organisms studied. Diatoms are known to compete well in high-nutrient, cold water upwelling systems [*Schrader et al.*, 1993; *Guillard and Kilham*, 1977] such as existed in the Cariaco Basin region during the YD. In fact, it has been shown that diatoms bloom only when silicate concentrations are ≥ 2 μM/kg [*Egge and Aksnes*, 1992], thus the necessity for strongly upwelling waters. Conversely, coccolithophorids compete well in low-nutrient, warm water environments [e.g., *Nanninga and Tyrrell*, 1996; *Brand*, 1994] which existed in the Cariaco during most of the Holocene.

5.3. Comparative Ecosystem Reconstructions: Molecular Versus Bulk and Micropaleontological Records

The biomarkers used in this study have been compared to bulk and micropaleontological data to determine whether reconstructions made on the basis of different data are in agreement. For this comparison we will be using our bulk OC and $CaCO_3$ data, opal data from *Peterson et al.* [1995], and microfossil data (foraminifera and coccoliths) from *Lynn* [1998]. Correlations between individual biomarkers and bulk parameters (e.g. OC, $CaCO_3$, and opal) are useful for identifying the part of the planktonic ecosystem that contributes different bulk parameters. For example, the accumulation rates of diatom biomarkers and opal [*Peterson et al.*, 1995] correlate well, both peak in the YD and decrease significantly during the Holocene, because diatoms are generally considered the dominant source of opal in tropical upwelling environments. The sum of aquatic biomarker accumulation rates correlates reasonably well with the TOC accumulation rate, suggesting that the organic matter in the Cariaco Basin sediments is dominantly derived from primary production of plankton and that gross production during the YD was, in fact, higher than during the Holocene.

It is interesting to note, however, that the $CaCO_3$ accumulation rate peaks in the same interval as the zooplankton biomarker accumulation rate rather than that of the coccolithophorid biomarker (Figures 2b and 3), suggesting that coccolithophorids are not as significant a source of carbonate to the Cariaco Basin sediments as are the dominant zooplankton, foraminifera. This offset between the molecular data and the carbonate data demonstrates the utility of molecular paleontology for paleoenvironmental reconstruction. On the basis of microfossil analyses, *Lynn* [1998] has estimated the contribution of coccoliths to the total carbonate in the Cariaco Basin sediments to be between 5 and 20% over the past 12 kyr, with values generally near 10-15% during the Holocene, the time of maximum coccolithophorid production. The majority of the carbonate in the Cariaco sediments is actually derived from planktic foraminifera [*Lynn*, 1998]. Conversely, C_{37}-alkenones contribute 5-75% of the total normalized biomarkers, averaging 60-65% during the Holocene (Figure 4). Had the reconstruction been based on carbonate alone (i.e., the abundance of shells and tests), coccolithophorids would likely not have been recognized as a significant contributor to primary production. In fact, the significance of coccolithophorids has been potentially overlooked in studies of the modern planktonic ecosystem in the Cariaco Basin region that were based on plankton tow or satellite imagery data rather than molecular analyses of organic matter [e.g. *Margalef* 1965; *Muller-Karger et al.*, 1989]. The lack of recognition of the importance of coccolithophorids in the planktonic community from micropaleontological and modern planktonic studies is probably due to their small size and the fact that coccolithophorids are not commonly obtained by traditional plankton tow collection techniques.

From comparison with bulk (i.e., carbonate and opal) and microfossil data (i.e., coccoliths and foraminiferal tests) it is evident that biomarker studies such as this one can potentially preserve a better record of paleoenvironmental conditions than carbonate or opal under certain conditions. For example, where there is the possibility of poor preservation of carbonate or silica in the form of shells or tests, such as in the deep ocean below the carbonate compensation depth (CCD), it is likely that molecular studies of organic matter will give a more accurate depiction of actual conditions of primary and secondary production in the surface waters than carbonate tests. The difference in the size of the shells or tests synthesized by dif-

ferent organisms and the fact that a number of primary producers do not produce carbonate or opal shells or tests suggest that contributions of carbonate and/or opal from different producers may not accurately represent the actual relative contribution of the different organisms to the planktonic ecosystem. These proxies would therefore not be as likely to provide an accurate representation of paleoenvironmental conditions as preserved sedimentary organic matter.

6. Implications: Ecosystem Variations and Abrupt Climate Change

Upwelling zones cover a significant portion of the low-latitude oceans, including the equatorial upwelling zone and coastal upwelling zones such the Peru and west African margins. These zones of upwelling should be affected by global climate change in a manner similar to the upwelling zone in the Cariaco Basin region. Studies have shown that dust flux to the worlds oceans increased during the YD [*Dansgaard et al.*, 1989] and the last glacial period [*Petit et al.*, 1981, 1990; *Hammer et al.*, 1985; *Edwards et al.*, 1997]. An increased dust flux has been interpreted to indicate increased aridity, which is a condition observed in the Cariaco Basin region during the winter months (when the ITCZ is at its southernmost position), and it has been proposed that similar conditions existed during cold periods such as the YD [*Peterson et al.*, 1991]. This increased aridity is associated with intensified atmospheric circulation and stronger trade winds, which would increase dust flux to the oceans and stimulate equatorial upwelling. In the Cariaco basin region the increased atmospheric circulation intensity stimulates Ekman-induced upwelling, providing a large supply of nutrients, such as nitrate, that limit productivity in coastal zones.

In the open ocean, increased atmospheric circulation intensity can also stimulate productivity by providing limiting micronutrients such as iron though an increased dust flux to the oceans [e.g., *Edwards et al.*, 1997]. During glacial times, increased oceanic circulation and upwelling intensity occurred off the coast of northwest Africa [*Abrantes*, 1992; *Shimmield*, 1992], in the Peru upwelling margin [*Schrader*, 1992], and in the Benguela Current upwelling system [*Diester-Haass et al.*, 1992; *Meyers*, 1992]. Additional studies also suggest increases in equatorial productivity in glacial intervals in both the Atlantic [*Abrantes et al.*, 1994; *Gingele and Dahmke*, 1994; *Sikes and Keigwin*, 1994] and Pacific [*Pedersen*, 1983; *Paytan et al.*, 1996; *Herguera*, 1994; *Zahn et al.*, 1994]. Thus the factors (e.g., atmospheric circulation intensity) that combine to increase upwelling and productivity in the Cariaco Basin during cold periods such as the YD seem to be occurring throughout the tropical ocean.

Variations in gross primary production and planktonic community structure may be an important mechanism for influencing global climate through carbon cycle feedbacks, if the variations are of sufficient magnitude. We have shown that in the region of the Cariaco Basin, a significant increase in primary productivity and, consequently, carbon burial during the YD has occurred as a result of increased upwelling intensity stimulated by cooler climate and the associated variations in atmospheric circulation. If primary productivity increased throughout the tropical oceans during cold periods in a fashion similar to that in the Cariaco Basin region, the deposition of carbon (as organic matter and carbonate) to the sediments would probably have increased as well. It is possible that the upwelling region around the Cariaco Basin responded in a similar fashion during glacial periods as well, with generally increased upwelling-induced productivity due to colder climate and the associated increased zonal atmospheric circulation. However, this is not evident in the Cariaco sediments because sea level was not sufficiently high relative to sills surrounding the basin to maintain an adequate nutrient flux to the basin. Because of limited circulation (nutrient inputs) during sea level lowstands, glacial periods in the Cariaco are characterized by lower productivity levels, leading to oxic basinal conditions and, consequently, poor organic matter preservation [*Peterson et al.*, 1991; *Haug et al.*, 1998]. The process of enhanced upwelling during glacial periods stimulating surface water productivity in the region surrounding the Cariaco Basin is still valid, however, and should be investigated in future studies of the southern Caribbean.

It is likely that the additional organic carbon sequestration or variation in planktonic assemblage could affect global climate through perturbations to the biogeochemical cycle of carbon. For example, during cold periods characterized by diatoms as primary planktonic producer the elevated formation of opal and organic matter would remove dissolved inorganic carbon from the water column and sequester it in sediments as organic matter. Conversely, during warmer periods characterized by increased coccolith production, the increased formation of carbonate relative to opal, and the overall decrease in organic matter production would serve to reduce the amount of carbon sequestered in sediments. Such interrelationships would thereby act as potential positive feedback loops for affecting the biogeochemical cycling of carbon in low-latitude environments during cold to warm period transitions.

7. Conclusions

We have examined the effects of known climatic and oceanographic changes on primary productivity and ecosystem dynamics within the Cariaco Basin region over the last 12 kyr. Accumulation rates of OC, $CaCO_3$, and cumulative aquatic biomarker compounds indicate that levels of planktonic primary production during the YD were almost 3 times higher than during the Holocene and are directly attributable to variations in climate associated with the Younger Dryas cold period. Our data support the hypothesis of *Peterson et al.* [1991] that the YD was characterized by a more southerly displacement of the ITCZ, enhanced zonal atmospheric circulation, and increased Ekman-induced upwelling of cold, nutrient-rich waters. This enhanced nutrient flux stimulated primary productivity in the surface waters, leading ultimately to water column anoxia and organic enrichment in the sediments. Conversely, the Holocene was characterized by a more northern locus for the ITCZ, weaker atmospheric circulation, weaker upwelling, and weaker (though still sufficient to maintain anoxic conditions) primary productivity.

Ecosystem dynamics within the Cariaco Basin region have been complex over the last 12 kyr. During the YD, high accumulation rates of biomarkers indicative of diatoms, dinoflagellates, and zooplankton suggest high rates of produc-

tivity of these organisms. During the Holocene, however, accumulation rates of these biomarkers decline, and those of coccolithophorid biomarkers increase significantly. Thus the dominant primary producer in the Cariaco Basin appears to have changed from diatoms to coccolithophorids as a result of the variations in climatic and oceanographic conditions associated with the YD to Holocene transition. The transition in planktonic assemblage associated with this climate change could have affected carbon cycling and organic matter sequestration in the Cariaco Basin region. Additionally, the increased deposition of organic and inorganic carbon to the Cariaco Basin sediments during the YD is likely to have affected the biogeochemical cycling of carbon in the basin during this period. Evidence that the tropical oceans respond to global climate change in a similar fashion to the Cariaco Basin [e.g., *Abrantes et al.*, 1994; *Pedersen*, 1983] suggests that the tropical oceans may be able to influence and be influenced by global climate to a larger extent than previously recognized through feedbacks in the biogeochemical cycle of carbon.

This study has also demonstrated the utility of molecular paleontology for deciphering paleoecological relationships (such as between diatoms and coccolithophorids in this study). Biomarker studies such as this one are particularly useful in environments in which (1) there is the possibility of poor preservation of carbonate or siliceous tests such that preserved organic matter will give a more accurate depiction of actual conditions of primary and secondary production in the surface waters, (2) the primary producers do not produce carbonate or opal shells or tests, again allowing better and more accurate interpretations to be made from molecular organic analyses, and (3) contributions of carbonate and/or opal from producers do not accurately represent the relative proportion of the different organisms in the planktonic ecosystem due to differences in the amount of carbonate or opal produced by different organisms, such as was the case for carbonate from zooplankton and coccolithophorids in the sediments of the Cariaco Basin.

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