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Biomarkers, chemistry and microbiology show chemoautotrophy in a multilayer chemocline in the Cariaco Basin

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A B S T R A C T

The Cariaco Basin is the world's largest truly marine anoxic basin. We have conducted a comprehensive multidisciplinary investigation of the water column (42–750 m) bracketing the redox boundary (a 250-m thick "chemocline") of the Cariaco Basin to evaluate linkages between lipid biomarkers, distributions of major dissolved chemical species, and the microbial community and associated redox processes. Our multidimensional data set includes: hydrography, water column chemistry, microbial distributions and rates, and lipid biomarkers. Multivariant statistical analysis of this data set partitions the investigated water column into 5 distinct zones, each characterized by different chemistries, microbiologies and biomarker compositions. The core of this chemocline is a 25-m thick suboxic zone where both dissolved oxygen and sulfide were below detection limits, bacterial and archaeal cell numbers and the rate of chemoautotrophic (dark) carbon fixation are elevated, and dissolved chemical species and bacterial and archaeal lipid biomarkers are indicative of tightly coupled cycles of carbon, nitrogen, and sulfur through chemoautotrophy.

1. Introduction

Permanently anoxic marine basins such as the Cariaco Basin are ideal natural laboratories for investigating relationships between physical controls on nutrient dynamics and primary production, biogenic particle export and transformations under oxic, suboxic and anoxic conditions, and preservation of paleoceanographic records in underlying sediments. The US-Venezuelan CARIACO Ocean Time Series Program (Carbon Retention in a Colored Ocean; http://www.imars.usf.edu/CAR/) has collected more than 15 years of monthly measurements of physical, chemical and biological properties in the Cariaco Basin, complemented by SeaWIFS satellite observations and biannual process-study cruises (Thunell et al., 2001, 2007; Muller-Karger et al., 2004; Goñi et al., 2009 for background). High seasonal coastal surface productivity and restricted water exchange between the Caribbean Sea and the deep Cariaco Basin maintain a sulfidic ("euxinic") zone from ~260 m to the seafloor at ~1400 m (Astor et al., 2003; Scranton et al., 2006). Between oxygenated surface waters and sulfidic bottom waters lies a well-developed ~250-m thick zone of strong chemical gradients and associated microbiological community, hereafter termed "the chemocline", in which lipid biomarker distributions are markedly different.

Biogeochemical redox processes within the chemocline support a diverse microbial community (Madrid et al., 2001; Lin et al., 2006, 2007, 2008; Stoeck et al., 2003; Taylor et al., 2006) that produces diagnostic lipid biomarkers (Wakeham, 1990; Freeman et al., 1994; Wakeham et al., 2004). Various oxidants (O_2, MnO_2, Fe_2O_3, NO_3^- $S_2O_3^{2-}$, SO_3^{2-}, S^0) and reductants (H_2S, NH_4^+, CH_4, Fe^{2+}, Mn^{2+}) could

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support chemoautotrophy (Scranton et al., 2001; Scranton, 1988; Taylor et al., 2001; Ho et al., 2002, 2004; Hayes et al., 2006; Percy et al., 2008; Li et al., 2008, 2012). Denitrifying, metal-reducing, and ammonium and sulfide oxidizing microbial populations are all active within different depth intervals. Chemoautotrophy in the Cariaco Basin equates to 10–130% of contemporaneous primary production and responds to interannual and decadal changes in surface productivity and deep-water ventilation rather than short-term surface processes of seasonal upwelling and blooms (Taylor et al., 2001). As a result, the flux of organic carbon (OC) captured in sediment traps below the chemocline frequently exceeds the flux exported from above, further implicating mid-water chemoautotrophic production as an important secondary source of OC in the water column and to the sediments in addition to surface water photoautotophy (Taylor et al., 2001). Anoxic and laminated sediments of the Cariaco Basin preserve a record of Holocene climate change, including changes in upwelling intensity, planktonic community structure and regional rainfall resulting from the shifting position of the Inter-Tropical Convergence Zone (ITCZ) (Goñi et al., 2009, and references cited). Recognizing the significance of mid-water chemoautotrophy from a lipid biomarker perspective aids in identifying water column sources of biomarkers as proxies for biological processes and climate change, especially for past oceans characterized by euxinic conditions and extensive organic carbon deposition. The underlying causes of oceanic anoxic events (OAEs) that may lead to organic-rich sediments deposited under oxygen-deficient water column conditions are the subject of ongoing investigations, given recent suggestions that ocean warming and increased stratification caused by global climate change lead to declining dissolved oxygen in the interior of the ocean (Keeling et al., 2010).

This study uses a high resolution sampling scheme to generate a multidimensional data set to help define linkages between lipid biomarkers, distributions of major dissolved chemical species, and the microbial community. Our data set includes: hydrography [temperature, fluorescence, transmissivity and dissolved oxygen], chemistry [particulate organic carbon (POC), total particulate nitrogen (TN), $\delta^{13}C_{POC}$, CH_4, nutrients (NO_3^-, NO_2^-, NH_4^+), sulfur species (H_2S, $S_2O_3^{2-}$, SO_3^{2-}, S^0)], microbial distributions and rates [bacterial and archaeal cell numbers, abundances of β-, and ε-proteobacteria, sulfate-reducing and anammox bacteria; heterotrophic and chemoautotrophic production rates] and lipid biomarkers [intact polar lipids, bacteriohopanepolyols, ladderane lipids, fatty acids and free apolar compounds]. Our results show that a multilayered chemocline spans roughly 250 m of the water column, from the oxycline into the anoxic zone. Within this greater chemocline, a 25-m suboxic zone and the transition into anoxic waters together harbor a complex assemblage of chemoautotrophic microorganisms that connect the cycles of carbon, nitrogen and sulfur and act as a “hotspot” of production of new organic matter (OM).

2. Methods

2.1. Site description and sampling

The Cariaco Basin is located on the continental shelf of northern Venezuela (Fig. 1). A shallow sill (<150 m) isolates it from the Caribbean Sea, and a second, deeper saddle ($\sim$1000 m) restricts circulation between the two deep 1400-m sub-basins. Upwelling, regional rainfall, primary productivity and particle export are all driven by the seasonal migration of the ITCZ. In winter, the ITCZ is below the equator promoting sustained easterly Trade Winds, strong upwelling and export of autochthonous OM. During summer the ITCZ is farther north, bringing high precipitation and increased sedimentation of allochthonous lithogenic material from the Venezuelan uplands (Muller-Karger et al.,

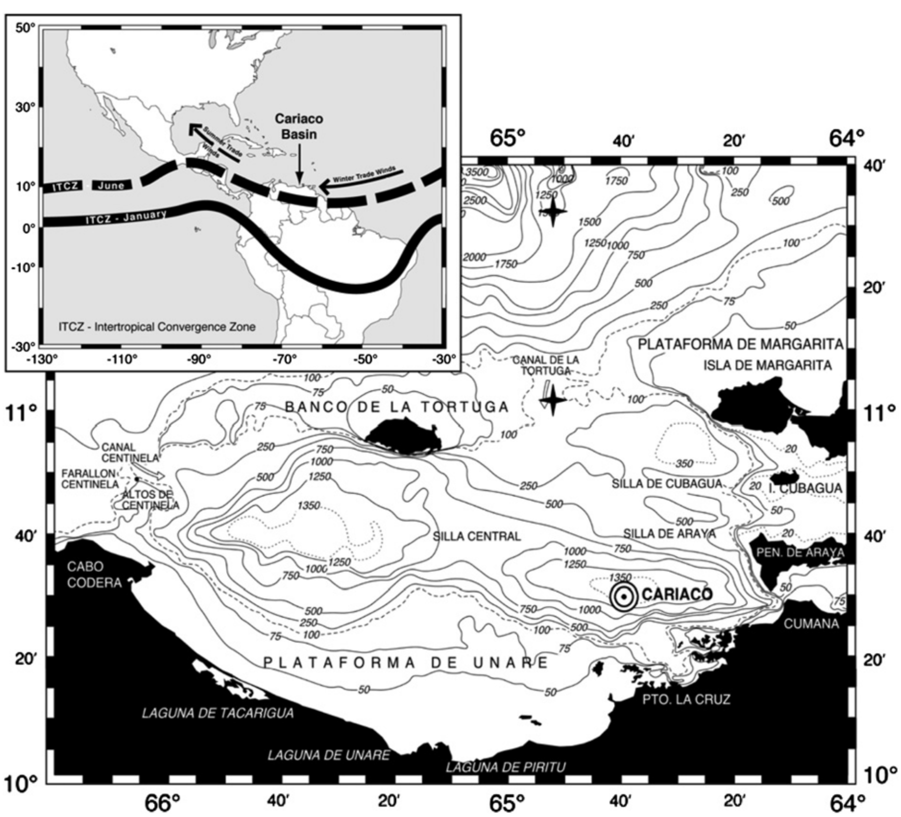

Fig. 1. Map showing the location of the Cariaco Basin, and the effect of the ITCZ position on seasonal upwelling (boreal winter) during November sampling, and high precipitation and run-off (summer). Suspended particles were collected in November 2007 (CAR-139) at the CARIACO time-series site in the Eastern Basin.