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Anomalous Carbon Isotope Biogeochemistry in the Cariaco Upwelling System: Balancing the Effects of Biological and Oceanographic Processes

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The carbon isotopic composition of sedimentary organic matter ($\Delta^{13}C_{org}$) has been utilized in numerous studies as a proxy for variations in the supply of $[CO_2]_{aq}$ and in primary productivity ($[CO_2]_{aq}$ utilization). Traditional models relating productivity and isotope systematics have focused primarily on the tendency of organisms, dominantly photoautotrophs, to utilize the lighter isotope (i.e. ^{12}C) preferentially. According to these models, an increase in the $\Delta^{13}C_{org}$ indicates an increase in the rate of primary production, and the consequent decrease in the selectivity of the organisms assimilating $[CO_2]_{aq}$. Recent studies, dominantly theoretical and culture studies, have suggested that a number of processes can potentially affect C-isotopic fractionation ($<Epsilon>_p$), and thereby the preserved $\Delta^{13}C_{org}$, including $[CO_2]_{aq}$, growth rate, cell size and geometry, pH, temperature, plankton species (e.g. Bidigare et al., 1997; Popp et al., 1998; and references therein).

The Cariaco Basin, Venezuela, provides an ideal "natural laboratory" in which to study the effects of competing biological and oceanographic processes on $<Epsilon>_p$ and $\Delta^{13}C_{org}$ preserved in the sediments. The surface waters of the Cariaco Basin receive a large supply of nutrients from upwelling waters in the open Caribbean, which stimulates a high level of primary production. Circulation in the deeper basin is restricted by sills that come to within 120 m of the sea surface, resulting in anoxic conditions below ~300 m water depth and excellent preservation of organic matter. The existence of continuous laminations and absence of benthic foraminifera suggest that the bottom-waters of the Cariaco Basin have been anoxic for the past 12.6 kyrs. As a result of the CARIACO time series program, a wealth of data exists characterizing the annual cycle in the Cariaco region (e.g. Walsh et al., 1999; Muller-Karger et al., submitted; Thunell et al., in press), which can be used to constrain interpretations based on sedimentary data. The region undergoes a seasonal oscillation in the intensity of upwelling due to the seasonal migration of the inter-tropical convergence zone, which directly affects the supply of $[CO_2]_{aq}$ and nutrients delivered to the basin. This fluctuation in nutrients directly affects the level of primary production in Cariaco surface waters. Evidence of these large seasonal variations is well-preserved in the laminated sediments of the Cariaco Basin, and significant fluctuations in primary productivity have been documented in the Cariaco Basin over the past 12 kyrs (e.g. Werne et al., 2000).

In order to assess the relative impacts of biological and oceanographic processes in a natural environment on ε_p and the resulting sedimentary $\Delta^{13}C_{org}$, we have carried out a bulk and molecular organic/isotopic geochemical study of the sediments in the Cariaco Basin. We have also utilized water-column and sediment trap data available from the CARIACO time series study to place constraints on the sedimentary data. This study identifies three fundamental discrepancies in the isotopic data that are in direct contrast to traditional models. First, the bulk carbon isotopic composition of organic matter is most depleted at a time when the organic carbon accumulation rate indicates that productivity was maximized. Second, maximum isotopic depletion of biomarkers is associated with relatively low and constant ε_p. Third, measured ε_p values in both sediments and sediment traps are of a significantly lower magnitude than those predicted by theoretical relationships. Based on analysis of sedimentary data within the framework of the documented variations in the annual cycle of the Cariaco Basin and also within the framework of interpreted variations over the past 12.6 kyrs, we propose that the discrepancies in the isotopic signature of the Cariaco Basin can be explained by a combination of several factors. These factors include:1) the ratio of $[CO_2]_{aq}$ supplied through upwelling to that utilized by biological production, 2) the timing of formation of organic matter in the annual cycle, 3) the ratio of various nutrients (C:N:P) in the upwelling water mass, 4) the contribution of chemo-autotrophic biomass to the sediments, and 5) the existence of de-nitrification and nitrogen fixation in the Cariaco Basin.

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