

Biogeochemical pathways in Holocene and latest Pleistocene sediments of the anoxic Cariaco Basin: Linkages to palaeoceanographic and palaeoclimatic variability

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The present study examines, at high-resolution, the biogeochemical cycling of organic carbon (OC), nutrients, sulphur, and a broad suite of trace metals in the uppermost sediments collected at Site 1002 in the Cariaco Basin during Ocean Drilling Program Leg 165 (Sigurdsson *et al.*, 1997). Our primary goal was to evaluate variability in coupled organic-inorganic geochemical systems within the context of temporal palaeoredox gradients and their palaeoceanographic controls. The relevant deposits span almost 8 m of depth and record the oxic conditions present during the last glacial lowstand, the anoxic regime that has persisted throughout the Holocene, and the productivity-driven transition from oxic to anoxic deposition at roughly 12.6 ka.

Background. The Cariaco Basin, a pull-apart basin located on the northern continental shelf of Venezuela, is the world's second largest modern anoxic basin. Lateral exchange of waters with the Caribbean is limited by sills that currently come to within 150 m of the sea surface, and the basin is presently anoxic below 300 m water depth (Peterson *et al.*, 1991). Although longer-term records indicate oscillations between oxic and anoxic conditions over the last 500 ka, the basin has been permanently anoxic for the last 12.6 ka.

Results from a complementary high-resolution biogeochemical study have revealed significant changes in productivity, nutrient cycling, and planktonic community structure as a direct result of variability in upwelling in the Cariaco associated

with abrupt changes in global climate over the last 12.6 ka (Werne *et al.*, 1998). Despite increasing strength in the marine connection with the rise of sea level, the basin switched from oxic to anoxic conditions at roughly 12.6 ka with the increase in Ekman-induced upwelling that characterized the cooler Younger Dryas (12.6 to 11 ka) [Peterson *et al.*, 1991]. Climatic patterns in the Cariaco Basin, both seasonal and longer term, have been linked to north-south excursions of the Intertropical Convergence Zone (ITCZ). During cool periods such as the Younger Dryas, the ITCZ occupies a more southerly average position leading to increased trade wind strength and correspondingly greater upwelling intensity and productivity. The transition to anoxic conditions marks the increase in OC loading and concomitant respiratory consumption of O₂ and is characterized by abrupt increases in the accumulation of OC and biogenic opal, as well as foraminiferal indicators of increased productivity (Peterson *et al.*, 1991).

Geochemical parameters, such as temporal patterns for $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ for organic and inorganic species, faithfully record the dynamic balance between upwelling intensity and nutrient utilization by biological productivity over the last 12.6 ka (Werne *et al.*, 1998). Furthermore, molecular biomarker analyses have illuminated the variability in the planktonic ecosystem associated with climatic and oceanographic changes over the same time period. The recognition of climatically forced

oscillations within the region of the Cariaco Basin indicates that the tropical marine environment is a sensitive recorder of climate change and that nutrient cycling and ecosystem dynamics in low latitudes can be effectively linked to global changes in climate. This palaeoceanographic/palaeoredox framework is ideal for our investigation of redox-dependent biogeochemical cycles.

C-S-Fe systematics. For the present study of redox chemistry, we have focused on the sediment record of continuous basinal anoxia spanning the last 12.6 ka and, in particular, the sharp redox interface that marks the transition from oxic to anoxic conditions at 12.6 ka. Analytical efforts have produced down-core evaluations of the Fe sulphides (contents and isotopic compositions), distributions of organic carbon (OC) and organically bound S, a fourfold speciation of the solid-phase Fe reservoir, a broad range of solid-phase trace metal data, and profiles for dissolved phases within the interstitial waters including sulphate and nutrients.

In the postglacial microlaminated deposits, down-core trends for the Fe sulphides (concentrations, isotopics, and extents of Fe sulphidation), in conjunction with an apparent decoupling between OC and pyrite accumulation, are consistent with significant water-column (syngenetic) formation of Fe sulphides. These results agree with published records of modern anoxic-sulphidic (euxinic) water-column conditions in the Cariaco. Despite the persistence of Holocene water-column anoxia, Fe limitations in combination with comparatively high levels of OC have precluded S enrichments relative to oxically deposited marine sediments with comparable levels of OC. In further contrast to the established geochemical paradigm for euxinic deposition (e.g. low C/S ratios and high extents of Fe sulphidation), degree of pyritization values (DOP: the ratio of sulphidized iron to total reactive iron) for these samples are comparatively low despite independent evidence for Fe limitation, with mean values in the range of 0.56. This relationship challenges widely held views on the utility of DOP as a palaeoredox proxy. These data are strongly compatible with a new model based on data from the Black Sea that links variations in extents of Fe sulphidation to palaeoceanographic controls, in addition to depositional redox, that are manifested in basic temporal and spatial differences within the Fe reservoir (e.g. Canfield *et al.*, 1996; Lyons, 1997). These additional controls include variability in the relative and absolute fluxes of biogenic particles and Fe-bearing siliciclastic sediment which, in part, modulate the balance between diagenetic and

syngenetic mineralization.

The oxic-anoxic transition. We have further addressed the sediment record of trace metal cycling within the context of a complex matrix of temporally varying palaeoceanographic/palaeoclimatic conditions, with particular emphasis on the transition from oxic to anoxic deposition at 12.6 ka. Elements of interest include V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ba, which were assessed relative to corresponding trends for OC and pyrite S. The most striking first-order observation is the presence of high levels of pyrite S below the redox interface despite the low levels of OC in the oxic sediments. We attribute this relationship to the downward diffusion of sulphide following the initiation of increased productivity and OC accumulation and the corresponding inception of water-column anoxia. The downward limit of sulphide diffusion is marked by an abrupt transition from gray to red sediment. Consequently, we are provided with a unique opportunity to evaluate the mechanics of metal partitioning across a well-constrained tripartite downward redox gradient from: (1) anoxic deposition with high levels of OC and pyrite S to (2) oxic deposition with low levels of OC but elevated concentrations of pyrite S and ultimately to (3) oxically deposited sediments with low levels of OC and pyrite S.

Molybdenum reveals a clear relationship to depositional redox with likely linkages to the accumulation of OC. Manganese varies in a nonsystematic way but generally is enriched in the microlaminated anoxically deposited muds and gray bioturbated (sulphide-overprinted) oxic deposits relative to the red oxic muds, which challenges a common model for Mn that invokes Mn depletions in euxinic sediments relative to oxic sites as a palaeoredox indicator (Calvert and Pedersen, 1993). Barium shows no appreciable increase across the 12.6 ka transition to high productivity, which was expected given the highly reducing conditions. Distributions of Fe are linked to siliciclastic fluxes, interstitial diffusion in response to redox/sulphide gradients, and the likelihood of scavenging of dissolved Fe within the anoxic water column. The remaining elements are either comparatively insensitive to the geochemical gradient (Cu) or show varying degrees of coupling to OC, solid-phase sulphide content, and depositional palaeoredox (V, Cr, Co, Ni, and Zn). Beyond our specific interest in the Cariaco Basin, the climatically induced palaeoredox gradient provides a definitive natural laboratory for testing a wide range of palaeoenvironmental proxies.