



Redox sensitivity of P cycling during marine black shale formation: Dynamics of sulfidic and anoxic, non-sulfidic bottom waters

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A high-resolution geochemical record of a 120 cm black shale interval deposited during the Coniacian–Santonian Oceanic Anoxic Event 3 (ODP Leg 207, Site 1261, Demerara Rise) has been constructed to provide detailed insight into rapid changes in deep ocean and sediment paleo-redox conditions. High contents of organic matter, sulfur and redox-sensitive trace metals (Cd, Mo, V, Zn), as well as continuous lamination, point to deposition under consistently oxygen-free and largely sulfidic bottom water conditions. However, rapid and cyclic changes in deep ocean redox are documented by short-term (about 15–20 ka) intervals with decreased total organic carbon (TOC), S and redox-sensitive trace metal contents, and in particular pronounced phosphorus peaks (up to 2.5 wt% P) associated with elevated Fe oxide contents. Sequential iron and phosphate extractions confirm that P is dominantly bound to iron oxides and incorporated into authigenic apatite. Preservation of this Fe–P coupling in an otherwise sulfidic depositional environment (as indicated by Fe speciation and high amounts of sulfurized organic matter) may be unexpected, and provides evidence for temporarily non-sulfidic bottom waters. However, there is no evidence for deposition under oxic conditions. Instead, sulfidic conditions were punctuated by periods of anoxic, non-sulfidic bottom waters. During these periods, phosphate was effectively scavenged during precipitation of iron (oxyhydr)oxides in the upper water column, and was subsequently deposited and largely preserved at the sea floor. After around 15–25 ka, sulfidic bottom water conditions were re-established, leading to the initial precipitation of CdS, ZnS and pyrite. Subsequently, increasing concentrations of H₂S in the water column led to extensive formation of sulfurized organic matter, which effectively scavenged particle-reactive Mo complexes (thiomolybdates). At Site 1261, sulfidic bottom waters lasted for about 90–100 ka, followed by another period of anoxic, non-sulfidic conditions lasting for about 15–20 ka. The observed cyclicity at the lower end of the redox scale may have been triggered by repeated incursions of more oxygenated surface- to mid-waters from the South Atlantic resulting in a lowering of the oxic–anoxic chemocline in the water column. Alternatively, sea water sulfate might have been stripped by long-lasting high rates of sulfate reduction, removing the ultimate source for H₂S production.