



Rapid redox changes during Late Cretaceous black shale formation - A high-resolution geochemical study of OAE 3 (Demerara Rise)

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The Oceanic Anoxic Event (OAE) 3 was the last of several periods of wide-spread oceanic anoxia in the late Cretaceous. We investigated two OAE 3 intervals of 100 cm and 122 cm from ODP Leg 207 Sites 1259 and 1261, respectively, in 1 cm resolution for their inorganic and organic carbon contents as well as for their major and trace elemental composition. We chose a high-resolution approach to reveal the importance of small-scale compositional variations on the overall geochemistry of the sediments. Our results show that the contents of TOC, carbonate and most major and trace elements are generally of the same order of magnitude as in OAE 2 black shales from the same drill sites. But, as most geochemical investigations performed until present on OAE sediments have a maximum resolution of 10 cm, we find significant differences when looking at the elemental profiles in detail. A pronounced cyclicity is documented in most parameters, which is more regular at Site 1261 due to more continuous deposition than at Site 1259. Here we focus on redox-sensitive/sulphide-forming trace element and phosphorus profiles, as these reveal most pronounced deviations from other, comparable black shale successions. Most obvious are the distributions of V/Al and Zn/Al over depth: In most studies of anoxic sediments, they show a good correlation with TOC or sulfur, which is not the case in the investigated interval of OAE 3. We rather observe an anti-correlation, as highest V/Al and Zn/Al values are paralleled

by lowest TOC contents. Calculation on a carbonate-free basis (CFB) does not alter this fact. We therefore conclude that the potential primary trace metal-organic matter relationship was somehow altered after sediment deposition. A similar, even more extreme pattern is observed for phosphorus. In more or less regular intervals, phosphorus contents rise rapidly around TOC maxima to peak values of several wt%, then drop again to very low background values. When calculated on CFB, however, phosphorus peaks fall together with TOC minima. We applied a sequential phosphate extraction procedure to identify in which phase phosphorus is present in the sediments. Comparing the phosphorus data set with the bulk Fe, Fe/Al and Fe/S profiles, we find a close coupling of phosphorus with iron rather than with TOC. Based on our results, we can infer several, probably linked causes for the observed millennial-scale fluctuations: Periodic oxidation of bottom water, shifts in primary production/primary producers and/or variation in continental runoff and nutrient input.