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Dynamics of redox-sensitive tracers through the C/T in the southern North-Atlantic (ODP Leg 207): A high-resolution study

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Cretaceous black shales deposited under severe oxygen-depleted conditions are carriers of proxy signals for paleoenvironmental conditions. Changes in the water column redox conditions lead to dynamics in biogeochemical sulfur-carbon-metal cycles. Therefore, distribution patterns of iron and sulfur speciation, sulfur isotope partitioning, and enrichments of redox-sensitive and sulfide forming trace metals provide important paleoenvironmental informations on dynamics of biogeochemical element cycles and corresponding water column redox-conditions during black shale deposition.

Here we present a high resolution study from black shale sequences of Sites 1258 and 1260 using high-resolution patterns of iron and sulfur speciation, stable sulfur isotope discrimination, and trace element enrichment to identify changes in redox-conditions of the depositional environment during the Cenomanion/Turonian boundary Event (OAE2) in the southern North-Atlantic (ODP Leg 207, Demerara Rise). Sediments were analyzed for different iron (total, pyrite, Na dithionite, and HCl leachable) and sulfur (total, pyrite, acid volatile, organic, and barite bound) fractions, in addition to major and minor elements as well as total organic and total inorganic carbon. The S-34/S-32 ratios of the sulfur species were measured by means of gas irmMS.

Chemical changes in the depositional environment during the OAE 2 are suggested: High ratios of reactive to total iron indicate that pyrite was formed both in the water column and within the sediment. This corresponds to euxinic paleoenvironmental conditions with free hydrogen sulfide present in the water column, a situation similar to the modern deep Black Sea. In addition, besides fixation of sulfide as iron sulfide, organic matter acted as an important sulfur trap during early diagenesis. Stable sulfur isotope fractionation went through a minimum with a downcore pattern similar to observations made at other C/T sites from the southern North Atlantic.

Elevated Fe/Al and Co/Al values within the C/T interval confirm euxinic conditions but, at the same time, require a zone where reducing but non-sulfidic conditions prevail, allowing reductive Fe and Co mobilization in oxygen-depleted nearshore sediments. The existence of an extended coastal upwelling oxygen-minimum-zone (OMZ) is demonstrated by extremely low Mn/Al ratios.