



Authigenic barite formation triggered by black shale-fueled anaerobic methane oxidation in the deep biosphere of ODP Leg 207

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Biogenic barite in sediments is often used for the estimation of paleoproductivity. High productivity results in organic-rich sediments characterized by sulfate depletion due to microbial sulfate reduction during decomposition of organic material. Deeply buried Cretaceous black shales at Demerara Rise (ODP Leg 207, tropical Atlantic) provide a suitable substrate for ongoing metabolic activity in a deep biosphere several hundred meters below present sediment surface. In this study we identify those processes that take part in the formation and modification of barite in the sediment column. Inorganic and stable isotope geochemical investigations have been carried out on pore waters, bulk sediments and separated barites. The history of the pore water-sediment-microbes interactions is additionally subjected to diagenetic modeling.

High methane in combination with low sulfate concentrations indicate that organic matter degradation is still active in the deep-seated black shale sequence deposited nearly 100 Ma ago. It is dominated by methanogenesis which gives rise to a diffusive flux of microbial methane out of the black shales. Upward diffusing methane as well as downward diffusing sulfate are totally consumed in the course of anaerobic methane oxidation (AOM). Complete depletion of sulfate within the black shale sequence promotes the remobilization of biogenic barite. Barium is released, diffuses upwards and

reprecipitates as authigenic barite. The process is clearly indicated by a co-enrichment of heavy S and O isotopes. Different Ba/Sr ratios in the barite concretions indicate dynamics in pore water gradients in the course of diagenetic crystallization. Barite dynamics are controlled by the availability of sulfate and rate of AOM, and thus by the upward flux of methane from the black shale unit. Coexisting isotopically heavy barite and pyrite are introduced as a new proxy for the occurrence of AOM.