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Geochemistry of fossiliferous carbonate concretions from the Cretaceous Santana Formation – assessing the role of microbial processes

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Exceptional fossil preservation (incl. soft-tissue phosphatization) within organic-rich black shales is often associated with the formation of a protective carbonate shell surrounding the fossil specimen. Whereas the mechanisms controlling soft-tissue mineralization during the earliest stage of fossilization are considerably well understood (e.g. Briggs and Kear, 1993), only limited information is currently available on the complex biogeochemical processes which lead to the precipitation of the concretionary carbonate mantle around the fossils. This study focuses on the organic and inorganic geochemistry of carbonate concretions derived from black shale deposits of the Early Cretaceous Santana Formation, Araripe Basin, NE Brazil (Martill, 1993; Heimhofer et al. 2008). This konservat-type fossil lagerstätte is world famous for its fossiliferous concretions hosting an exceptionally preserved fish and reptile fauna. The principle aim is twofold including (1) identification of the type and source of organic matter trapped within the Santana concretions and (2) assessment of the different microbial or microbially-mediated processes associated with successive concretion growth during early burial. Based on sedimentological evidence and palaeoenvironmental considerations, the involvement of a prokaryotic mat in early fossilization of the Santana biota has been proposed (Martill, 1988). At this stage, 3 different carbonate concretions hosting fossil fish remains (incl. Notelops brama, Calamopleurus sp. und an unknown specimen) have been analysed with a combined approach including organic molecular geochemistry, high-resolution stable isotope analysis, micro-XRF scanning and sedimentary petrography. Petrographic inspection shows a distinct zonal pattern of the carbonate shell surrounding the fossils. The innermost zone I shows an undulating and discontinuous lamination superimposed on a clotted fabric. Zone II is characterized by the frequent abundance of finely dispersed pyrite aggregates and a less pronounced lamination pattern, whereas the outmost zone III consists of a layer of medium to coarse-grained bundles of calcite crystals showing a “cone-in-cone” pattern. This zonal pattern is also visible in the distribution of elemental intensities derived from micro-XRF scanning results. In particular, variations in pyrite content are well displayed in the distribution of Fe and S intensities, probably reflecting the occurrence of BSR during concretion formation. Preliminary high-resolution carbon isotope profiles of the carbonate perpendicular to bedding show values varying between -9.1 and -19.7 permil and display a distinct trend throughout the concretion rim with relatively stable values of -12 permil in zones I and II. A distinct shift to less negative values occurs in the uppermost part of zone II. In contrast, the “cone-in-cone” calcitic fabric shows the most negative C-isotope signature with values as low as -19.7 permil. Organic geochemical analyses of sample material taken from the different zones confirm the low thermal maturity of the sedimentary organic matter. The biomarker composition is dominated by acyclic isoprenoids, steranes and by isorenieratane and its derivatives, whereas n-alkanes and hopanoids are of only subordinate importance. Biomarker composition and concentration shows considerable variations with the innermost sample displaying only few compounds occurring in relatively low concentrations (incl. squalane, phytane and isorenieratane derivatives). In contrast, the outermost sample shows a much broader biomarker spectrum probably indicative of marine background sedimentation. In summary, the preliminary petrographic and geochemical results provide convincing evidence for the involvement of different microbial processes actively influencing concretion growth. Analyses of new sample material as well as compound-specific carbon isotope measurements will provide further insights into the role of microbes in

concretion formation.

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