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Isotope and elemental geochemistry of Cretaceous fossiliferous concretions (Santana Formation, Brazil)

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Exceptional three-dimensional fossil preservation (incl. phosphatization of soft-tissues) within organic carbon-rich mudstones is often associated with the formation of a protective carbonate shell surrounding the fossil specimen. Examples for this type of preservation are the Early Cretaceous fishes, turtles and pterosaurs from the Brazilian Santana Formation. Numerous studies proposed different conceptual models for concretion formation. Having new state-of-the-art geochemical tools at hand we revisited these models for the Santana Formation as an exemplary case. Differential compaction clearly indicates early precipitation of micritic calcite surrounding a central cavity containing the still decomposing fossil. The presence of pyrite forming a circular rim around the fossil and carbonate with negative carbon isotope compositions suggest intense sulphate reduction whereby the production of ammonium from the decay of proteins led to an increased alkalinity, which induced early carbonate precipitation. By means of micro-XRF scanning we found that pyrite is absent from the interior part of the concretions and that total iron content is very low, which indicate absence of sulphate reduction at the center of the concretions and possibly local onset of methanogenesis. We postulate that the central cavity may even have been filled with methane gas that evolved from the decaying animal. Methane diffusing outward was anaerobically oxidized in the surrounding sulphate reduction zone. Carbonate clumped isotopes revealed that micritic calcite formed early, but that these early precipitates are overprinted by two different late diagenetic cements precipitated at elevated temperatures. The occurrence of an outermost “cone-in-cone” calcite rim can be associated with burial showing temperatures of up to 60°C. Strontium-isotope ratios of matrix calcite and cement phases show radiogenic values (0.710416 to 0.712465), which are significantly higher than typical marine Cretaceous carbonates. These radiogenic strontium-isotope signatures support late diagenetic overprinting of early carbonate phases and may reflect the particular tectono-sedimentary regime in this region during early rifting of the evolving Atlantic. Results from the Santana concretions demonstrate how the application of new geochemical tools can help to advance our understanding of early diagenetic processes and fossil preservation in the geological record.