Chemical characterization of an Early Cretaceous coprolite assemblage (Angeac-Charente, France).

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From the Lower Cretaceous Lagerstätte of Angeac-Charente (SW France), more than 6000 fossilized faeces were discovered, alongside abundant vertebrate remains (teeth/bones) including dinosaurs, crocodylomorphs, turtles, and actinopterygians. This study aims to understand the preservation of coprolites, by examining several chemical elements and their spatial distribution within these fossil objects. Combining µXRF, FTIR, and LIBS analyses revealed that the analysed coprolites were mainly composed of Ca bonded with F, P within phosphate groups, and carbonate groups, all forming carbonate-fluorapatite (CFa). Main other major elements originated either from pyrite precipitation (Fe, S) in cracks and outer rim of the coprolites, or from the surrounding sediment reaching up to the inner parts of the coprolites (Si, Al). A few minor elements are repeatedly found concentrated in the coprolites compared to their surrounding sediment. Among them, Y and Ce show a higher concentration at the margin compared to the coprolite cores. For Sr and La, this pattern occurs only in some specimens. Other minor elements such as Mn, Cu, Zn, As, Pb, U are found in higher concentrations alongside pyrite inclusions. The main component of the coprolites, carbonate-fluorapatite, is assumed to partly originate from a carnivorous diet, and completed by microbial diagenesis adding extra apatite. The presence of fluorine suggests a diagenetic alteration of the coprolites since this element is absent in bioapatite.

The high concentration of these minor elements within the coprolites is interpreted as diagenesis represented by two different patterns. The first one, increasing the elements concentration in the coprolites, is their adsorption into the apatite, slowly diffusing toward the inner parts, as evidenced by the observed gradient. The second pattern is the incorporation of other minor elements in pyrite during its precipitation. The sequence of alteration within the coprolite can be inferred from these analyses. An episode of microbial alteration occurred prior to adsorption of minor elements. Pyrite most likely precipitated only after the microbial alteration, but its relationship with minor element adsorption remains unclear.

Among the measured REE, as for the bones and their