From bone to fossil: early diagenesis of apatite

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Bones are geochemically stable in living organisms, comprised of hydroxyapatite (HAP) with compositional control from the host's metabolic and biochemical (e.g. Ca, Na exchange). Once introduced into the environment, HAP alteration is mediated by direct and indirect, abiotic and biotic interactions and processes. Significant gaps in our understanding highlight the need to study the chemical and structural changes experienced by HAP for bone preservation during early diagenesis because thermodynamic models predict that HAP is unstable in a range of geochemical conditions, such that bone must undergo rapid alteration to a more stable phase (e.g. fluorapatite) for fossil preservation to occur. We combined laboratory and synchrotron sourced (i.e. X-ray near edge structure, XANES) spectroscopy methods to gain insight into bone alteration, on time scales ranging from days to years, from abiotic and biotic experiments. Our results demonstrate that structural modifications to HAP crystallites, including increased crystallinity and loss of phosphate, occur within days and correlate with collagen release. After three years, incorporation of Fe at the expense of Ca emphasizes that early changes are critical for preservation. From Ca K-edge XANES spectra, comparisons of fossil Pleistocene- to Cretaceous-aged bones indicate similar structural alterations caused by increased p-orbital occupancy that likely reflects Ca(II) site substitutions within the HAP lattice. Despite variable bone geochemistry, convergence of HAP lattice configuration may afford stability over geologic time.