

Taphonomy, geochemistry, and diagenesis of bone accumulations in the lower Horseshoe Canyon Formation, Alberta, Canada

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Vertebrate remains in the 210-meter thick lower Horseshoe Canyon Formation (LHCF; latest Campanian) in south-central Alberta accumulated under locally high aggradation rates and collectively describe an unusual but non-unique "floodplain" mode of fossil taphonomy in which the vast majority of bone (>90%) was buried rapidly and fossilized in fine-grained, non-channel facies. Bones in the LHCF are commonly found as widely dispersed, solitary elements or in high-area, low-concentration bonebeds, generally organized along subtle, laterally extensive surfaces reminiscent of and analogous to marine condensed sections. Individual specimens show a mosaic of bone modifications that fall into three categories: abrasion, destruction, and mineralization. Abrasion is the most common modification in the assemblage and includes polish (on 39% of the specimens), fine striations (45%), and fungal mottling (26%); one or more of these features occur on specimens in ~90% of the 521 sites documented in this study. Over one-third of the fossils show partial removal of cortical bone. One-third are partially encased in large-scale siderite nodules, whereas other forms of mineralization, including permineralization, are less common. Fossilization in the LHCF must have occurred rapidly after burial, occurring even at minimal depth, to preserve coprolitic material, undistorted plant structures, and delicate microfossils include seeds and eggshell fragments in similar siderite concretions. Although analyses of trace-element content in tyrannosaur tooth enamel from the LHCF indicate significant enrichment, particularly in divalent cations, enamel from these teeth preserves an unaltered stable oxygen isotopic record, useful on an individual scale for examination of annual seasonality and also at the formational scale as a record of gross climate change through the succession.

Ion-substituted apatites: Standards for Raman analysis of bone

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Bone is a living tissue having mineral components similar to hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ which contains other inorganic ions, such as CO_3^{2-} , Na^+ , Mg^{2+} , K^+ , Cl^- and F^- . These constituent ions, found in bone matrix, affect its properties and growth. Investigations of these effects may be done by studying bone in a variety of growth and stress conditions through micro-Raman spectroscopy. A model material was developed to both interpret the effect of ion substitutions on the spectra and to calibrate the amount of mineral versus matrix (collagen, lipid, *etc.*) in the bone samples.

Our model bone sample, B-type carbonated apatite, was synthesized in the laboratory by aqueous precipitation. In our methodology, IR spectroscopy was used to determine the carbonate concentration while the proportions of the other inorganic ions were determined by ion-chromatography. The synthesized apatites have carbonate ranging from 0.3% to 11.2%. We studied effective ways to mix an internal standard, sodium sulphate, with the apatite. We investigated several mixing methods in order to maximize uniformity on the micron scale. Averaging spectra collected from 20 to 30 sites on the sample minimized error.

We investigated the effect that changes in concentrations of CO_3^{2-} , Mg^{2+} , Na^+ , and Cl^- in the apatite structure have on the Raman spectra of the phosphate ions. We found that ions that replace phosphate (*e.g.* carbonate) and calcium (*e.g.* Mg^{2+}) do not affect the wavenumber of the phosphate A_1 symmetric stretch (961 cm^{-1}) but ions that replace hydroxide (*e.g.* Cl^-) cause shifts to lower wavenumbers.