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A multi-technique approach by XRD, XRF, FT-IR to characterize the diagenesis of dinosaur bones from Spain

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ABSTRACT

A combined investigation by X-ray fluorescence (XRF), Fourier Transform Infrared spectroscopy (FT-IR), Raman spectroscopy and powder X-ray Diffraction (XRD), supplemented with the Rietveld analysis, was conducted on sixty Spanish dinosaur bone specimens from Upper Jurassic/Lower Cretaceous to Upper Cretaceous age to investigate taphonomy and diagenetic processes. The diffraction approach assessed in all specimens the presence of fluorapatite at various levels of percentage as the mineral phase constituting the fossil bone. In addition to fluorapatite, calcite and quartz were also found as main secondary phases in many specimens. The infrared spectra of fossil bones show significant changes in the phosphate and carbonate band intensity with respect to a non-fossil bone. Conversely, the X-ray fluorescence spectra turned out to be mainly dominated by the presence of Ca, obviously accompanied by phosphorus. Simultaneously, other elements accompanying Ca, such as Fe and Sr were found at significant concentration levels.
A considerable amount of Fe and Sr ions were incorporated in the structure of fluorapatite, but when their concentration was found elevated in the fluorescence spectrum, the diffraction data revealed the presence of goethite (FeOOH) and celestite ($SrSO_4$) phases. While the X-ray diffraction phase analysis also revealed the presence of kaolinite, dolomite, barite and gypsum, in some fluorescence spectra further elements like Y, As, Pb, Ti, Mn, Cr, Cu, Zn were present in concentration at trace level. The introduction/substitution of new elements with the infiltration of new phases due to diagenesis is also affecting to various extent the Raman and FT-IR spectra with modification of some bands and/or the appearance of new bands. The average crystallite size of the "apatitic" constituent phase was found to vary from a minimum of ca. 183 Å to an upper level of 2107 Å. No systematic relation between apatite crystallite size and age of the dinosaur bones was found that suggests a high variability of diagenetic processes affecting the growth of bone crystallites even in the same site.

1. Introduction

The study about chemical and mineralogical composition of fossil animal and human bones may be a precious source of information about the past. However, a large fraction of these studies have focused on archaeological samples and biomaterials and only to a little extent on dinosaur fossils (Zocco and Schwartz, 1994; Hubert et al., 1996; Bocherens, 1997; Trueman et al., 2003a, 2003b; Tütken et al., 2004; Fricke et al., 2008; Dumont et al., 2011; Heuser et al., 2011; Pfretzschner and Tütken, 2011; Tütken, 2011;). Changes involving the structure and chemical composition of bones may occur in two different periods, i.e., first during the animal's life, and second during the fossilization process. The time scale of these two stages may be incommensurable and a distinction is made between biostratinomy and fossildiagenesis. During the biostratinomic stage, micro-organisms and other biotic processes can attack the organic and inorganic content of bones, degrading mineral bone phases (e.g. Trueman and Martill, 2002; Jans et al., 2004). In addition, abiotic factors can degrade the bones both before or after burial (e.g. Denys, 2002). If the bones are not subjected to microbial or biotic erosion or the processes are affected by drastic physical or chemical changes, fossilization may occur soon after burial (Trueman and Martill, 2002; Pfretzschner, 2004; Farlow and Argast, 2006).

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Table 1
List of the Spanish dinosaur bones with classification, geological period and provenance location.

Sample code	Classification	Epoch and geological stage	Formation and basin	Location
Serrat del Corb	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Isona (Lleida)
Serrat-R2	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Isona (Lleida)
Molí del Baró	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Isona (Lleida)
La Penella	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Peramola (Lleida)
Lo Bas	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Abella de la Conca (Lleida)
La Llau de Bas	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Abella de la Conca (Lleida)
Nerets	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Villamitjana (Lleida)
Pous	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Basturs (Lleida)
Basturs Poble	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Basturs (Lleida)
Basturs Poble-07	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Basturs (Lleida)
Boiga	Dinosauria (unclassified)	Upper Cretaceous (Maastrichtian)	Tremp Tremp Basin	Conques (Lleida)
Peguera 1-Figols	Dinosauria (Hadrosauria)	Upper Cretaceous (Maastrichtian)	Tremp Fígols-Vallcebre Basin	Figols (Barcelona)
Psm-Mila	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Puebla de San Miguel (Valencia)
Psm-Maite	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Puebla de San Miguel (Valencia)
Psm-Andres	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Puebla de San Miguel (Valencia)
Psm-Carles	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Puebla de San Miguel (Valencia)
CerroTadon	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
HTCO4-3	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
Rascaña	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
Yac-David	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
Corral de Marin	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
229	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
Losilla	Dinosauria (Eusauropoda)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
Aras de Alpuente	Dinosauria (Eusauropoda)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
La Ventura	Dinosauria (Eusauropoda)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	Alpuente (Valencia)
El Collado	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	La Cuevarruz (Valencia)
El Collado 1	Dinosauria (unclassified)	Upper Jurassic/Lower Cretaceous	Fm. Villar del Arzobispo; Southwestern Iberian Basin	La Cuevarruz (Valencia)
Patiras	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Todolella (Castellón)
SAV-39	Dinosauria (Eusauropoda)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
SAV-67	Dinosauria (Eusauropoda)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
Povet	Dinosauria (Ornithopoda)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
Camino	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
EAP 38	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
EAP 40-39	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
EAP 43	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Morella (Castellón)
Comptadors A1	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Cinctorres (Castellón)
Todolella 1	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Todolella (Castellón)
Torre Julian	Dinosauria (unclassified)	Lower Cretaceous (Aptian)	Arcillas de Morella Maestrat Basin	Todolella (Castellón)

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