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CHEMICAL TAPHONOMY OF A WELL-PRESERVED FOSSIL OF FEATHERED DINOSAUR: A MULTI-TECHNIQUE APPROACH

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The preservation of labile soft-tissues of ancient organisms is scarce through the geological record as only the mineralized parts (bones, teeth) are usually preserved. In some rare cases, these fragile organic structures are fossilized and bring insights into the taphonomy of fossils and the biology of extinct organisms. Fossils of feathered dinosaurs constitute significant findings that allow the study of the origin of flight in modern birds. Here, we applied a multi-technique approach to study the chemistry of a fossil plumage preserved around the skeleton of a Jurassic small theropod dinosaur, *Anchiornis huxleyi*, excavated from the Tiaojishan Formation in Liaoning, China (Fig. 1A). The specimen is embedded in varved, carbonated and clayed, lacustrine sediments. The chemical composition of fossil feathers and their embedding sediment was investigated by ion beam analyses (particle-induced X-ray emission - PIXE - and elastic backscattering spectrometry - EBS), nuclear magnetic resonance (^{13}C CP-MAS NMR) and pyrolysis in the presence of TMAH (TMAH Py-GC-MS). The ultrastructure and mineralogy of the feathers and sediment have been studied with scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). Feathers from a modern buzzard (*Buteo buteo*) were analyzed for comparative purposes.

SEM of the fossil feathers shows traces of ancient pigmentary organelles, melanosomes,

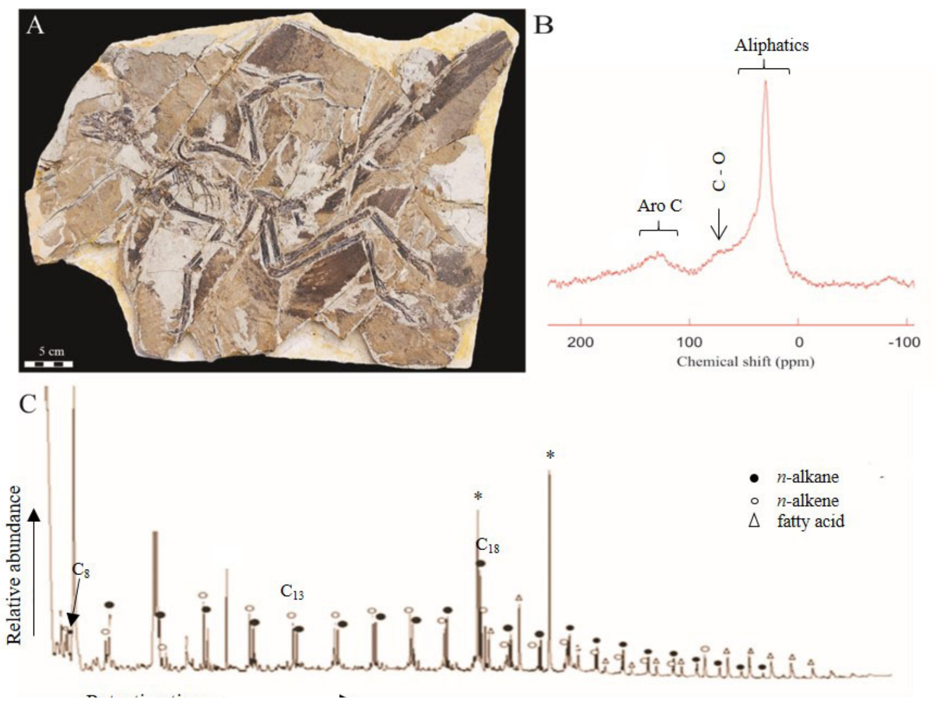

Figure 1 *(A) Picture of the theropod dinosaur, Anchiornis huxleyi, with preserved feathers around the skeleton, (B) ^{13}C CP-MAS NMR spectrum of fossil feathers, (C) Pyrochromatogram of the fossil feathers; * = unidentified compounds.*

mainly in the form of imprints, along with elongated structures. PIXE and EBS analyses showed that carbon and oxygen are more abundant in the fossil feather than in the sediment. Sulfur was also detected in the samples, and exhibited concentrations in the fossil feather twice higher than in the embedding sediment, and twenty times higher than in the remote sediment. This may suggest a preservation of S-rich original compounds in the fossil plumage, such as cysteine and/or phaeomelanin, or a selective enrichment in some elements associated with organic matter. The ^{13}C NMR spectrum of the fossil feather (Fig. 1B) is dominated by an aliphatic peak at 30 ppm with a broad shoulder in the C-O range, along with an aromatic peak of low intensity at 129 ppm. The embedding sediment led to a spectrum similar to that of the fossil. The modern feathers yielded much more complex NMR spectra, with many resolved peaks in the aliphatic region as well as additional signals at 173 ppm (carboxylic), 158 ppm and 55 ppm (methoxyl carbons). The 158 ppm peak can be assigned to the guanidino carbon of arginine or to phenolic carbon, including that of tyrosine. Along with the multiple aliphatic signals, it reflects the protein contribution in the feathers

Pyrolysates of the fossil feather (Fig. 1C) and its embedding sediment are typical for sedimentary organic matter. They are dominated by *n*-alkane/*n*-alkene doublets, but also comprise fatty acids, toluene, and benzene derivatives. However, substantial differences can be noted between the two pyrochromatograms. First, the fossil feather yields two abundant compounds, which are not yet identified (likely comprising a C_{17} moiety) but are lacking in the sediment pyrochromatogram. Secondly, the *n*-alkane/*n*-alkene doublets range from C_8 to C_{26} in the fossil feather and from C_8 to C_{27} in the sediment and the fatty acids range from C_{18} to C_{32} and from C_{14} to C_{20} in the fossil feather and in the sediment, respectively. Taken together, these differences in molecular composition between the fossil feather and its embedding sediment suggest an endogenous origin for at least part of the fossil organic matter. Nevertheless, the pyrolysate of the fossil feather exhibits none of the characteristic constituents of that of the modern feather. Indeed, the latter is dominated by cyclic molecules containing nitrogen, including diketopiperazine derivatives, which reflect the presence of amino acids, likely originating from keratin, the main constituent of modern feathers.

This geochemical characterization of the plumage of one of the most ancient feathered dinosaurs thus shows that despite the excellent morphological preservation of the fossil, its constitutive organic matter has undergone severe diagenetic transformation. Components exclusive to the fossil and alkane/alkene patterns though suggest in situ polymerization of original constituents of the dinosaur feathers.