Archaeopteryx Feathers and Bone Chemistry Fully Revealed via Synchrotron Imaging

Archaeopteryx specimens are important but extremely rare fossils. Due to their possession of both reptilian (jaws with teeth, long bony tail) and avian (feathered wings) characters, *Archaeopteryx* has been crucial in the development of Darwinian evolution. Despite their importance, no *Archaeopteryx* specimen has ever been chemically analyzed. This in large part may be explained by the analytical obstacles which preclude applying standard methods to such valuable specimens; destructive sampling is not an option and most non-destructive methods cannot handle large specimens. Furthermore, mapping using conventional methods is far too slow to enable chemical zonation to be reasonably determined. Mapping of trace element chemistry is of tremendous interest, however, because it opens a window into understanding several critical questions about *Archaeopteryx* in particular, and about fossil specimens in general. Preserved trace chemistry in bones and soft tissue may be remnants of the living organism, and therefore may give insight into life processes of extinct organisms. When mapping includes the embedding rock matrix, mass transfer between the fossil and the matrix can be constrained, hence giving information about mode of preservation. Chemical analysis can also resolve artefacts of the curation process. Finally, accurate chemical maps can also be useful for directing future work by highlighting regions that may be promising for other types of analysis including structural methods (CT, diffraction) or techniques that use other parts of the electromagnetic spectrum (infra-red).

We were given access to perhaps the best preserved *Archaeopteryx* out of the ten known, and overcame the analytical problems inherent in analysis by applying Synchrotron Rapid Scanning- X-ray Fluorescence imaging. SRS-XRF is a unique and powerful tool available at SSRL, because scan control and readout electronics have been purpose-built to allow rapid scanning simultaneous with rapid data read out. When combined with the extreme brightness of the beam as compared to laboratory sources of X-rays, SRS-XRF at SSRL allows us to map the concentrations of trace elements (several ppm) within large objects (over 900 cm^2) within reasonable time scales (several hours). Our results show that Zn and Cu levels in the *Archaeopteryx* bone are measurably higher than in the limestone matrix, indicating that the concentrations of these trace metals most likely reflect minimum concentrations in the original bone. That is, the mass transfer vector must flow from bone to rock, not vice versa. This result is exciting, because the Zn and Cu levels determined are comparable to levels found in extant bird species. Figure 1 presents a false

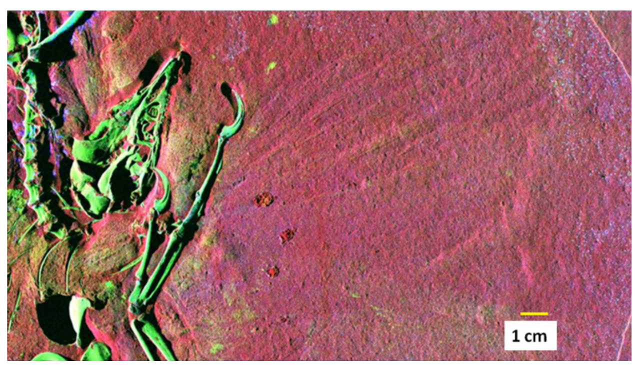

Figure 1. False colour SRS-XRF map of *Archaeopteryx*. Colour code is: Calcium-red, Zn-green, Mn-blue. Higher intensities correspond to higher concentrations, Almost the entire Zn inventory in this image is associated with the *Archaeopteryx* bone material. Zinc apparently was present in appreciable concentrations in the original bone (as in many extant organisms) and has been well-sequestered within the bone over 150 million years of burial. (PNAS)

colour composite view of the specimen's skull region. The bright green associated with the skull shows the high Zn levels associated with the bone. In order to make sense of the observed zoning patterns we also completed XRF point analyses so that we could quantify the trace element concentrations. PyMCA was used to analyze full EDS spectra from a number of points.

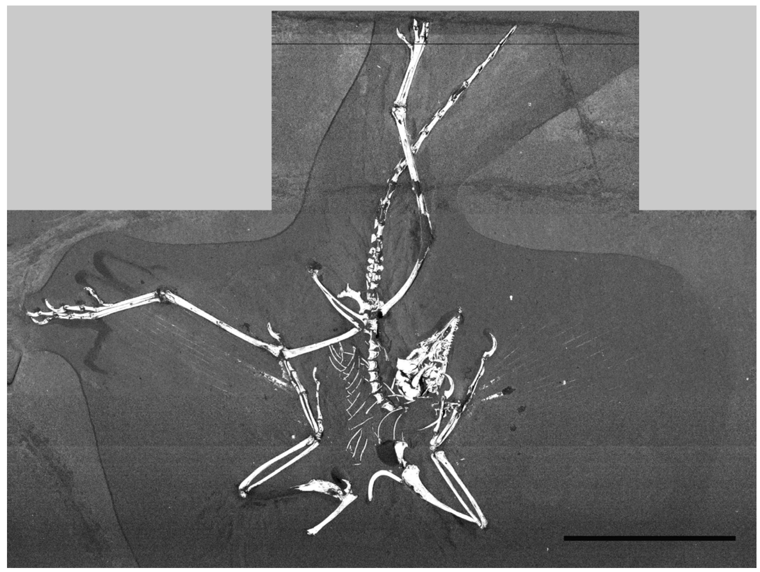

Figure 2. Grayscale Synchrotron Rapid Scanning X-ray Fluorescence map of the phosphorous distribution in the Thermopolis *Archaeopteryx.* The fossil bones are obvious, as expected, but when imaged in this way the chemistry of the feather shafts is also shown to be high in this element and different from the rock matrix, indicating part of the feather chemistry has survived. Scale bar = 10 cm. (PNAS)

Analysis and mapping of relatively high atomic number elements (such as Zn and Cu) was made simple by the fact that at those characteristic energies absorption by air is small. However, for biological entities such as fossils, it is necessary to also map macronutrient elements with lower atomic numbers such as P and S. For those elements, we developed a method to almost entirely exclude any air pathway between sample and detector by building a sample holder which could be sealed with a large polymer window and purged with helium gas. The detector was placed such that its aperture grazed the window surface during scanning thus almost completely eliminating transmission through air, and by this method we were able to produce amazing detail in the distribution of light elements. Perhaps the most important result of this study was produced in this way.

The most famous aspect of the *Archaeopteryx* is that is has preserved feather structure. It had been assumed up until now that these were merely feather impressions and that none of the original chemistry of this soft-tissue had been preserved. By scanning the matrix along with the fossil, we showed that phosphorous and sulfur distributions in the wing regions are controlled by the biological structure of the organism, such that the feather shafts (rachises) are still visible and partially preserved as shown in Figure 2. These results show the power of the SRS-XRF method in resolving the chemical fossil since it can produce such clear results from 150 million year old soft tissue, as well as from the much more degradation resistant bony material.

We also for the first time explored the application of X-ray absorption spectroscopy to complement SRS-XRF scanning. Sulfur within the bone was shown to be almost entirely present as sulfate, thus indicating that a well-known geochemical process which deposits iron sulfide (pyritization) into fossil bones had not affected this *Archaeopteryx* specimen.

Primary Citation

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