

A Pigment of the Imagination: The Role of Melanin Pigment in the Preservation of Archaeopteryx Feathers, Solnhofen Limestone (Upper Jurassic), Germany

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Abstract

Charles Darwin acknowledged the importance of color in the natural selection of bird plumage. color can indicate age, sex, and diet, as well as play roles in camouflage, mating and establishing territories. Feather and integument color depend on both chemical and structural characteristics and so both structure and chemistry can be used to infer color and pigment patterns in a range of extant and fossil organisms. A specific cell controls pigment patterns, the melanocytes, during feather growth. There are two main melanin pigments in animal tissues, eumelanins and pheomelanins. The former are more prevalent (>75%) and furnish dark black or brown hues in both invertebrates and vertebrates. A diagnostic and functional component of the molecular structure of melanin is their carboxyl substituents.

These negatively charged end-groups function as cation chelators, selectively binding positively charged particles, such as free radicals and transition metals. Consequently, melanin granules in bird feather melanosomes display high concentrations of zinc, copper, calcium and iron. Birds may have evolved this ability to accumulate toxins in feathers to avoid the chemotoxic affects of minerals and contaminants in their diet. The mere presence of trace-metals in melanin may play a key role in the preferential preservation of feathers. When the black and white feathers of domestic chickens are exposed to feather-degrading bacteria (*Bacillus licheniformes*), white feather breakdown significantly faster than the black melanised feathers. Such studies suggest plumage color might be an evolutionary response to the presence of feather-degrading bacteria, with high melanic content being more resistant to decay. The distribution of metal chelates in soft tissue has been preserved in *Archaeopteryx* and provides a useful biomarker for eumelanin patterning.

The biocidal properties and non-biodegradability suggest that trace-metal distributions may represent the definitive method for revealing eumelanin pigmentation patterns. Synchrotron-based elemental mapping and spectroscopy of trace-metal inventories in *Archaeopteryx* have made it possible to make progress in understanding pigmentation. Results from the synchrotron-based imaging show clear evidence for the presence of Cu-O/Cu-N complexation, indicative of endogenous melanin pigments being preserved within the exceptionally preserved feathers of this early bird. However, it is the trace-metal coordinated biochemistry of melanin-type pigments in this iconic fossil that potentially played a key role, both in the life and preservation of this organism. Feathers, rich in trace-metals, functioned as a 'natural-biocide' protecting these structures from bacterial decay in life, but also delivering the multitude of selective advantage through color. The very same trace-metals inhibited the natural processes of decay after death, resulting in rare and remarkable fossils that display soft tissue structures.

