

Introduction

The impact of production methods on the color and chemical composition of charred bone pigments was investigated by UV-Vis-NIR spectroscopy, X-ray fluorescence spectroscopy, and lightfastness testing. Contemporary, commercially available bone black pigment was analyzed alongside twelve pigments prepared from fresh bovine femur—the same feedstock currently used for commercial pigment production. The prepared pigments varied in three degrees of cleanliness and were fired to four temperatures to produce a range of twelve brown, black, and gray colors, some of which were subsequently washed. Preparation and washing procedures were synthesized from those offered by Cennino Cennini (1437)¹, Nicholas Hilliard (ca. 1600)², and George Field (1835)³. This is the first study to analyze the impact of feedstock cleanliness and washing procedures in artists' pigments prepared from animal bone, and it also offers spectroscopic data from freshly prepared bone brown.

Method



boiled bone

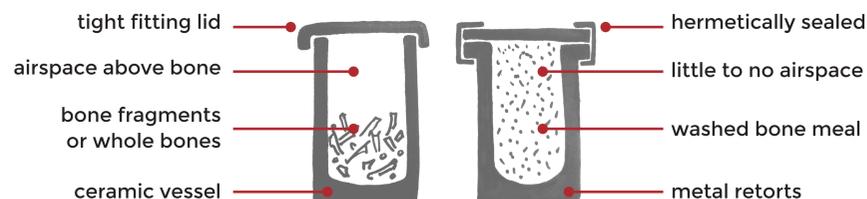


scraped bone



crude bone

Bovine femur segments were obtained from a local butcher and prepared to three degrees of cleanliness: "crude" (with some meat and marrow left intact on the bone), "scraped" (with meat and most of the marrow scraped away), and "boiled" (bones were scraped clean then boiled in distilled water). The bone matter was dehydrated briefly, crushed into rough segments, and heated in fused silica crucibles with lids. The resultant fragments were crushed into a fine powder for spectroscopic analysis and mixed with gum Arabic binder for lightfastness testing. Selected pigments were subsequently washed in gum Arabic solution in a manner described by Hilliard⁴, dried, and analyzed. Detailed information about instruments used can be found in the notes section below.



Traditional, small batch production vs contemporary, large scale production⁵

Results

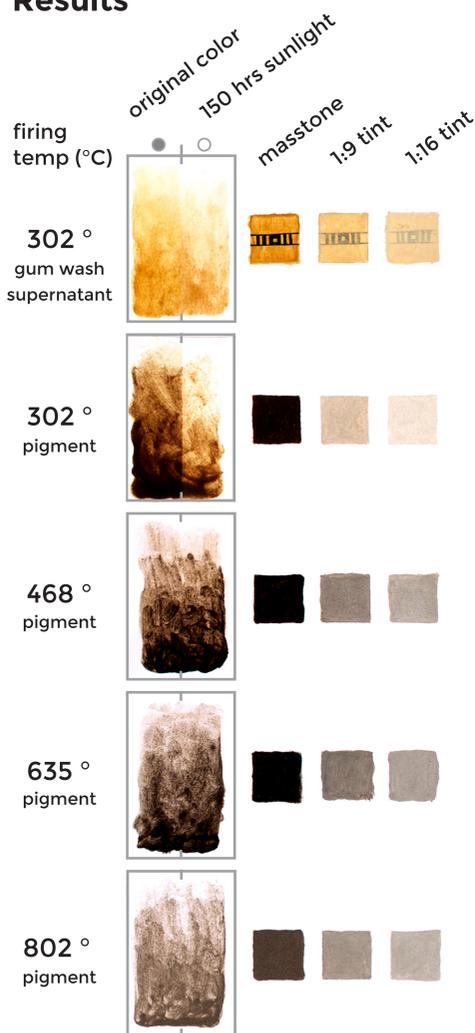


Figure 1: Crude bone pigments

As the maximum firing temperature increased, the color of bone pigments progressed from pale brown to deep brown and black. Bone fragments heated from 302 °C to 635 °C were homogenous in color, though bone heated to 802 °C were variegated black, white, and blue. Pigments fired to 302 °C faded rapidly when exposed to direct sunlight. When washed in a gum Arabic solution, most pigments settled to the bottom after resting. However, pigments heated to 302 °C turned the solution a yellowish-brown color that did not settle over time. The supernatant from one of these brown solutions was decanted and evaporated, producing a transparent color that was relatively more lightfast than pigment that settled from the same solution (figure 1). Tinting strength of pigments is shown in mass ratios of bone pigment : titanium white mixed in Liquitex Gloss Gel medium.

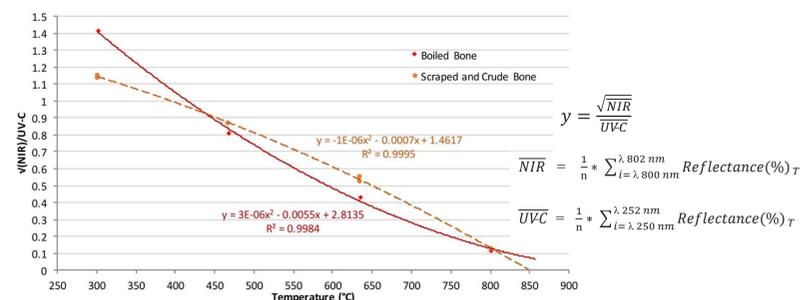


Figure 2: Relationship of temperature and reflectance data

To determine the impact of temperature and cleanliness on pigment color, two-way ANOVA tests with replication were conducted on UV-Vis-NIR reflectance data over 2 nm window averages at 50 nm increments from 250 nm to 802 nm. In all cases the amount of heat, degree of cleanliness, and interaction of cleanliness and heat were found to have a significant impact on reflectance data. These findings were then used to model relationships between reflectance data and firing temperatures. Two successful models were developed: one for crude and scraped bones and another for boiled bones (figure 2). These models can be used to estimate the maximum firing temperatures from UV-Vis-NIR reflectance data of bone pigments fired in similar environments. XRF data is often useful in discerning which temperature model to use.



19th century photo of two men standing on a pile of bison skulls. The rise of the bone char industry in the United States was closely linked with railroad development, westward expansion, and the near extinction of the American buffalo.

In XRF spectra, a well-defined K, K α peak with moderate separation from the adjacent Ca, K α peak is a good indication that meat was still present on bone before firing, if the pigment was not subsequently washed (figure 3). Bones of all levels of cleanliness also exhibited this peak behavior after being washed in a gum Arabic solution. Bones from the boiled group exhibited a clear, negative skew in the range of ~3.2-3.4 KeV, while similar peaks of bones that had not been boiled exhibited symmetry. However, all K, K α peaks were poorly defined in pigments fired to 802 °C. XRF data also revealed industrially produced pigment contains high levels of iron and other metals, likely a result of the milling process (figure 4).

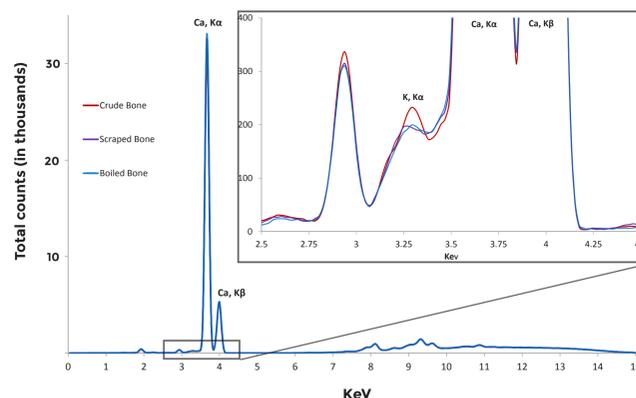


Figure 3: XRF spectra of pigments heated to 635 °C

	Crude Bone	Boiled Bone	Ebonex
K	847 ± 150	215 ± 141	1175 ± 148
Ca	> 25 %	> 25 %	> 25 %
Ti	-	-	137 ± 22
Cr	-	-	27 ± 3
Mn	8.1 ± 3.9	8.7 ± 4.1	50 ± 4
Fe	33* ± 25	42 ± 24	2160 ± 59
Ni	31** ± 26	31* ± 27	35 ± 23
Cu	-	-	41 ± 7
Zn	89 ± 8	77 ± 7	95 ± 6
Rb	3.5* ± 2.2	-	9 ± 1.5
Sr	180 ± 7	118 ± 6	211 ± 7
Zr	18 ± 3	14 ± 4	30 ± 3
Mo	2.7 ± 0.4	2.3 ± 0.4	1.6 ± 0.4
Sb	-	-	17 ± 11
Ba	22 ± 10	20 ± 10	48 ± 9
Pb	-	-	50 ± 5

Figure 4: Concentrations (ppm) of selected metals from commercial bone black and pigments heated to 635 °C

Conclusions

XRF spectra were useful in determining the cleanliness of bone substrates, identifying industrially manufactured pigments, and observing characteristic changes after washing pigments in a gum Arabic solution. Exposure to 150 hours of light confirmed that pale bone brown pigments are highly susceptible to photodegradation while black-char and white-ash pigments did not fade. UV and NIR reflectance data were successfully used to model the maximum firing temperature of pigments produced in the study. Compared to industrial processes and related studies of bones heated in open-air environments⁶, these models are highly specific to bone fired in lidded but unsealed vessels. Future directions include developing additional temperature models, investigating other charred materials, and analyzing historical charred bone pigments from bulk and in situ samples.

References

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Notes

An electric Skutt Automatic Kiln, model KM-1227, was used to heat the samples, and its temperature gauge was found to be accurate ± 6 °C using Orton pyrometric cone standards. UV-Vis-NIR diffuse reflectance spectroscopy was carried out with an Ocean Optics USB4000 Spectrometer and an Ocean Optics DH-2000-BAL balanced deuterium-halogen light source. An Ocean Optics WS-1-SL Spectralon standard was used for calibration. X-ray fluorescence spectroscopy was carried out on an Olympus X-5000 X-Ray Fluorescence Spectrometer calibrated with an Innov-X Systems alloy-grade 316 steel standard. XRF spectra used in peak area analysis and presented above were smoothed with a 7-point Savitzky-Golay filter.