Carbonization Studies on Mammut americanum Tusk

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Carbonization Studies on Mammut americanum Tusk

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Introduction

In 1933, a large mastodon tusk was discovered in a gravel pit near Hampton, Iowa, shown in Figure 1. It has been held by the University of Northern Iowa since that time. The tusk, pictured in Figure 1, has undergone many documented and undocumented restoration attempts, but it has also been damaged, as shown in Figure 2.

What is known or was suspected about the tusk initially:
• Very little information uncovered about the tusk's original preservation in the ground.
• Little information is known about the tusk's current state.
• Reported to be highly carbonized (fragile).
• Its position in the gravel pit was slightly inclined.
• No other bones or remains of the mastodon were found nearby the tusk.
• Observations suggest the tusk may have been carried by water currents away from where the mastodon died.

Why Carbonization?
As a tusk fossils in its ground, its organic contents are exchanged for carbonate, namely calcium carbonate. The process is known as carbonization or mineralization.
• During the mastodon's life, the main chemical composition of its tusk included collagen and hydroxyapatite, \( \text{Ca}_9(\text{PO}_4)_6(\text{OH})_2 \).\(^2\)
• Hydroxyapatite (HAp) is mainly found on the outer layers of bones and teeth. It is the component that makes a tusk rigid and strong.\(^3\)
• Collagen is mineralized. This process can occur with mineral-containing water moves through the porous structure of the tusk and leaves mineral deposits,\(^4\) or it can occur in the presence of bacteria that replace organic contents with calcium carbonate.\(^4\)
• Examining the extent of carbonization of the tusk can provide conservators with an idea of the delicacy of the tusk.
• Carbonization studies can also provide a better clue about the conditions of the ground preservation of the tusk.

Elemental Analysis

Elemental analysis (EA) is a selective chemical analysis technique that is able to provide the percent composition of carbon, hydrogen, nitrogen, and sulfur present within a sample. A diagram of a typical elemental analyzer is shown in Figure 3.

Results
Data obtained from the EA is presented in Table 1.

Table 1: Percent carbon and hydrogen by weight of tusk sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon (% by weight)</th>
<th>Hydrogen (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.971</td>
<td>0.574</td>
</tr>
<tr>
<td>2</td>
<td>0.851</td>
<td>0.523</td>
</tr>
<tr>
<td>3</td>
<td>0.668</td>
<td>0.571</td>
</tr>
<tr>
<td>4</td>
<td>1.288</td>
<td>0.661</td>
</tr>
<tr>
<td>Average</td>
<td>0.945</td>
<td>0.582</td>
</tr>
</tbody>
</table>

• The tusk is not homogenous, as shown by the fluctuation in the percent carbon between the 4 samples.
• On average, the tusk contains about 1% carbon.
• The hydrogen content is from water picked up by the powder and not from the HAp, as the combustion temperature was not high enough to incinerate the compound.

Raman Spectroscopy

Raman spectroscopy relies on the polarizability of the molecules present in an analyte. Raman, a scattering technique, requires a monochromatic light source to excite virtual states of molecules.\(^5\) A different wavelength of light is emitted by the sample after it has been excited. The energy difference between the source and the emitted photon is unique for every compound, remaining constant even when different incident wavelengths (lasers) are used.\(^5\) A diagram of the Raman spectrometer is shown in Figure 4.

Results
The Raman spectra obtained from the tusk fragments and tusk plaster are presented in Figure 6.

• The source, a 785 nm diode laser, reflects off of mirrors, is focused by a lens, and hits the sample. The sample emits a photon of a different energy. The emitted light travels through a notch filter to block interference from Rayleigh scattering, towards a grating, where it is dispersed, and to a charge-coupled device detector.
• There are many excitation lasers. Data was collected with the 785 nm laser for the best signal-to-noise ratio, as shown in Figure 5.
• 36 spectra (64 scans) were collected for 12 different tusk fragments at 30mW.

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

A high resolution cross sectional picture of the tusk’s layers was obtained on the SEM shown in Figure 7. Energy dispersive X-ray spectroscopy revealed the location of the calcium and carbon.

• Calcium was detected in two layers. The left most layer is part of the ivory tusk, while the right most layer in blue is plastic.
• The carbon is almost exclusively present in plaster and shellac layers, not in the tusk material.

Conclusions

• The tusk is not highly carbonized. This means the tusk fragments are not as delicate as previously suspected.
• The artificial outer shellers and plaster layers of the tusk are the main sources of carbon. Once these layers are removed, pristine tusk, composed mainly of the strong and rigid hydroxyapatite, will be exposed.
• Josh Prybil was able to extract nucleobases from the tusk, accounting for some of the tusk carbon content.
• Not enough data was collected to make any conclusions about the carbonization in terms of the tusk’s ground preservation, but this is a topic of interest for future work.

Literature Cited

Acknowledgements
Thank you to the Roy J. Carver Charitable Trust for providing the funding for the conservation of the tusk and the Raman spectrometer. Thank you to the UNI Museum and Nathan Arndt for providing tusk fragments for analysis. Thank you to Dr. Colin Weeks and Dr. Joshua Seebregts for assisting in the data collection process. Thank you to Nick Bonde and Katie Platzie for sharing their SEM/EDX pictures, and thank you to Josh Prybil for sharing the results of his nucleotide sublimation experiments.

Figure 1: (A) The gravel pit where the tusk was first discovered. (B) A picture of the tusk after some initial restorations.\(^1\)

Figure 2: (A) The tip has broken off from the rest of the tusk. Most of the fragments (B) collected for analysis came from this area of the tusk.

Figure 3: A diagram of a typical elemental analyzer.

Figure 4: A diagram of a typical Raman spectrometer.

Figure 5: The spectra show the 785 nm laser provides the best signal-to-noise ratio, improving resolution of small peaks.

Figure 6: The spectra obtained for the tusk fragments, plaster, and positive HAp and calcite controls are plotted above.

Figure 7: The tusk fragment used for analysis is pictured (left). A high resolution SEM picture of the fragment was taken (middle). EDXS highlighted which layers contained calcium (blue) and carbon (green) (right picture).