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Classification of Tusk Layers by Means of Raman Spectroscopy

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Introduction and Past Preservation Methods Used

The American Mastodon tusk was donated to the University of Northern Iowa, and Dr. J. Cable took the lead on preserving it for museum display at UNI. Dr. Cable's notes stated that it would be possible to preserve the entire tusk, because the outside was "covered with a hard enamel-like substance".[1]

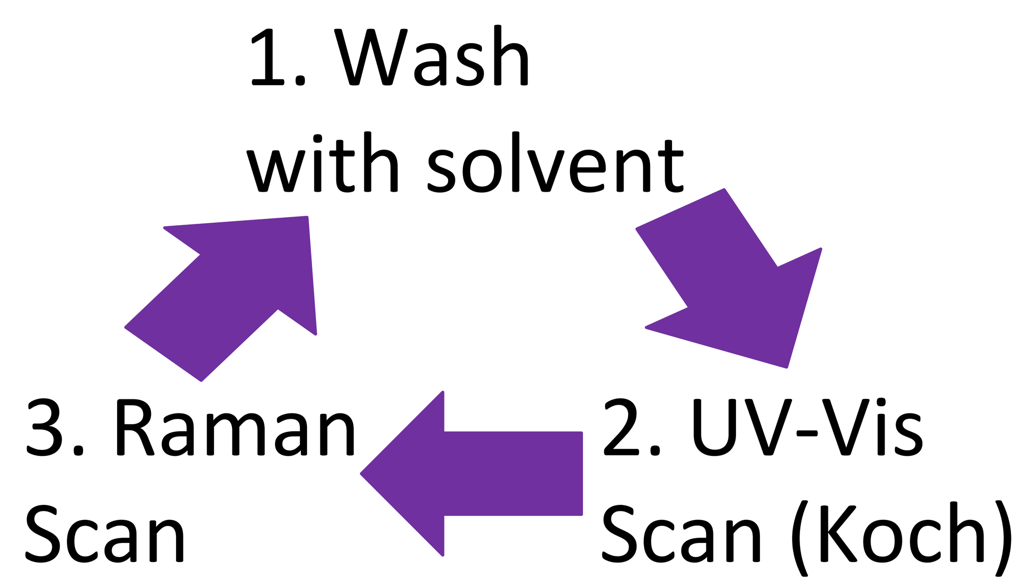
Some notes were taken as to what materials were used to preserve the tusk early on, but their exact composition was not noted.

- Glazed and varnished between 1933 and 1960
- 1960 – canned patching plaster on chipping areas, glazing liquid (brown), two coats of varnish (satin finish with some gloss added)
- 1966 – wood brace and steel band added near tip to prevent cracking[2]

No notes were taken on the preservation process after 1966, so the materials used are completely unknown.

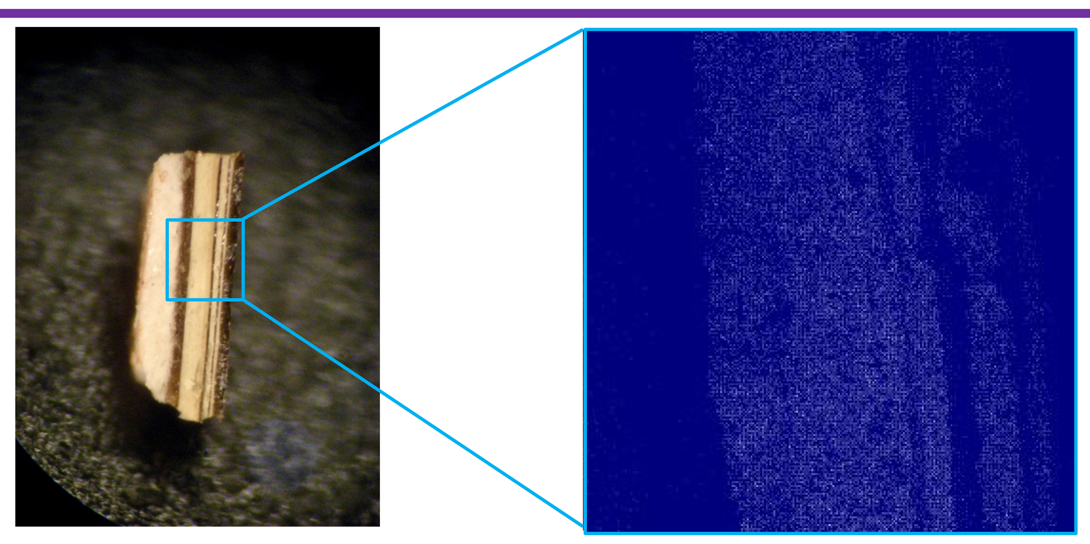
The goal of this project is to analyze the composition of the restoration materials used on the tusk and to strip the restoration materials off of the tusk without harming the tusk itself.

Methodology



Use dichloromethane to remove varnish/lacquer layers, and use methanol to remove plaster layers.

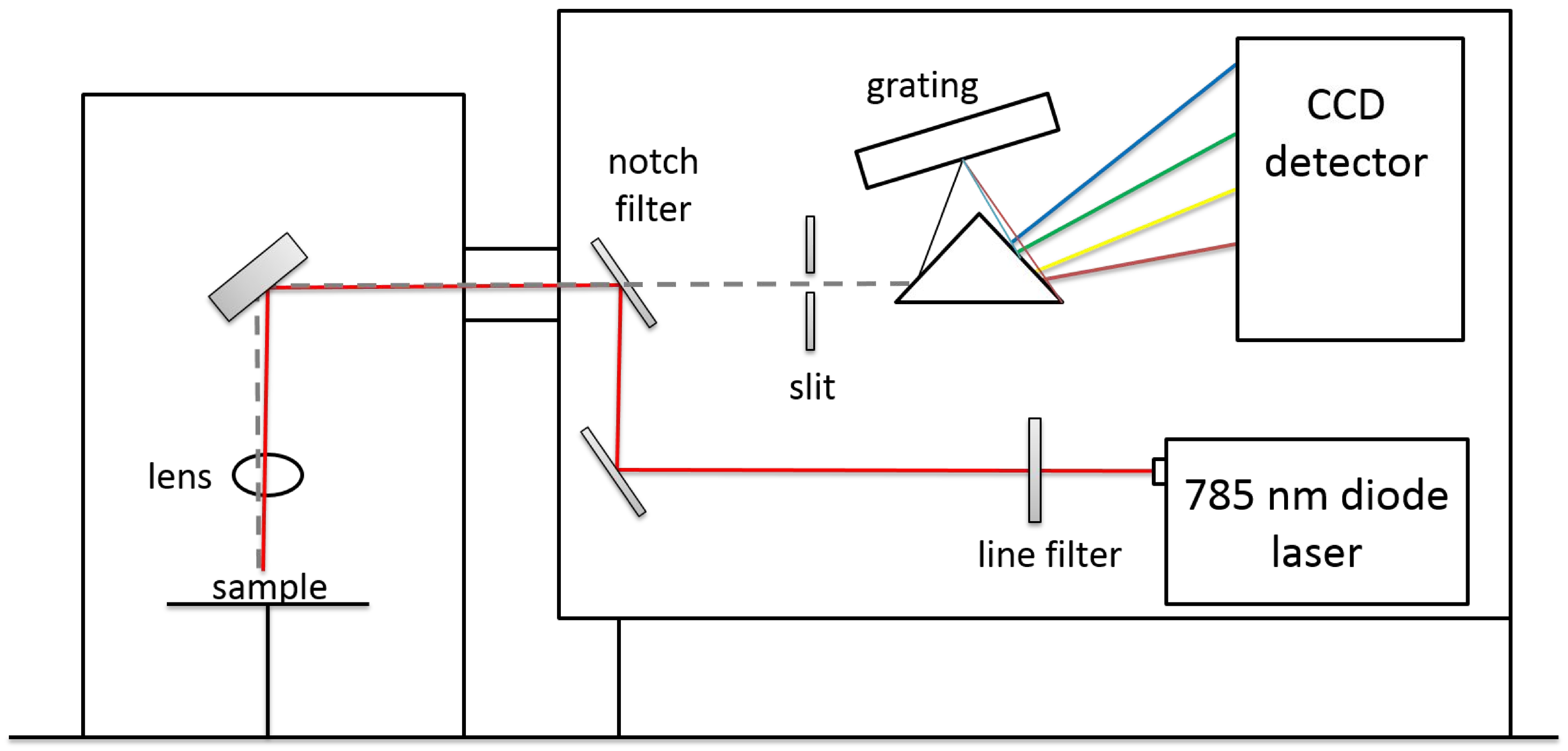
Microscopy



Optical (45x) SEM/EDX (200x)

A small piece of the tusk was broken off of the tusk and turned on its side to view all the layers. It was viewed on an optical microscope at 45 times magnification and on the SEM/EDX at 200 times magnification. The SEM/EDX picture shows the different types of materials that each layer is made of: red is the tusk itself, green represents organic layers, and blue represents inorganic (plaster) layers. The identification of the materials in each layer by SEM/EDX was used to help identify the compounds represented by the peaks on the Raman Spectra.

Raman Spectroscopy



Raman Diagram

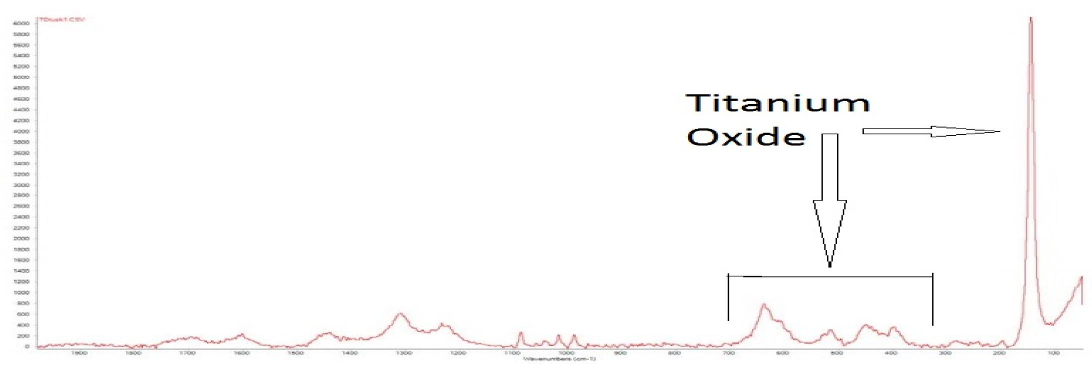
- Raman spectroscopy uses scattered light from a laser to change the vibrational properties of a molecule. A molecule must be polarizable in order for it to be Raman active, therefore the selectivity directly related to the polarizability of the molecule.
- The Rayleigh scattering effect occurs when electromagnetic radiation induces an oscillating dipole.
- Raman scattering occurs from the laser's light being scattered by the molecule. The scattering weakens the energy of the photon based on the characteristic frequencies of the molecule. The CCD detector then detects the lower energy photons.
- Electrons are moved into a higher "virtual state" in the molecule (stokes emission – used when molecules are actively vibrating).[3]
- A CCD detector generally allows for higher sensitivity, but it is more susceptible to fluorescence.
- Fluorescence shows up as oscillating peaks on Raman spectra, therefore it contributes to noise issues.[4] This is especially important to note when working with the tusk, because the whole tusk fluoresces (Laubenthal).

Parameter Table

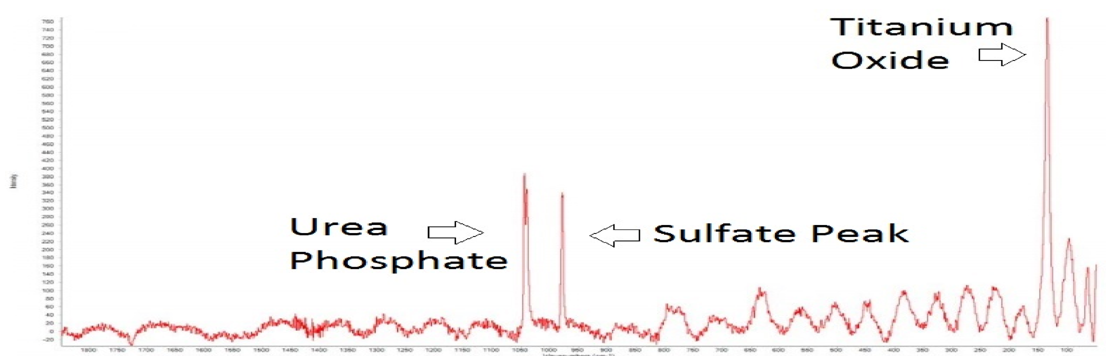
Resolution	1.859
Grating	400 lines/mm
Slit Width	25µm
Laser/ Wavelength	GaAlAs diode 785nm
LTD	Caused by Raleigh lines
Selectivity	Polarizability

Results

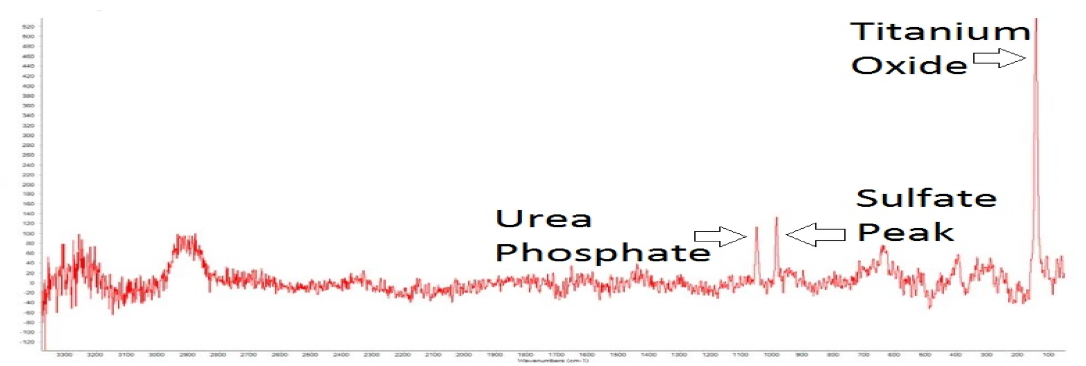
Layer 1



Layer 2

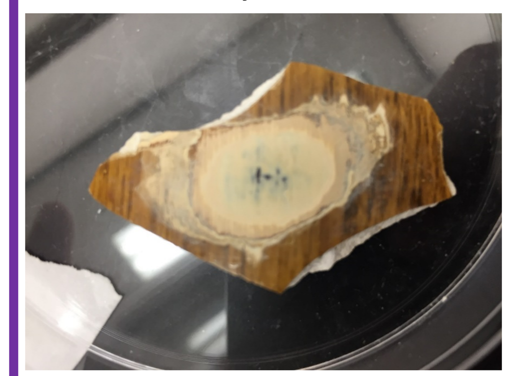


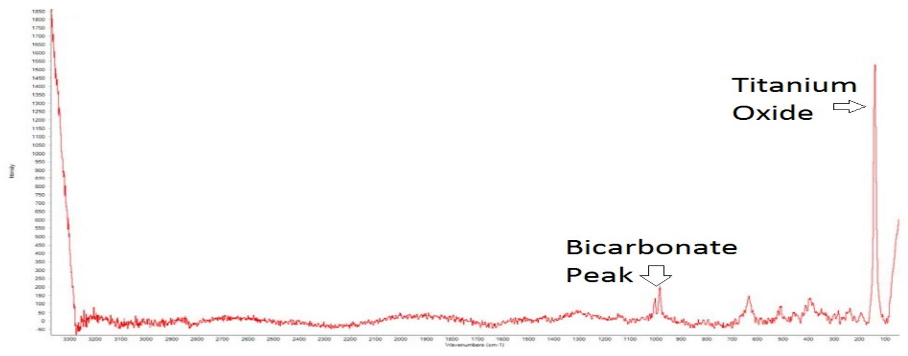
Layer 3



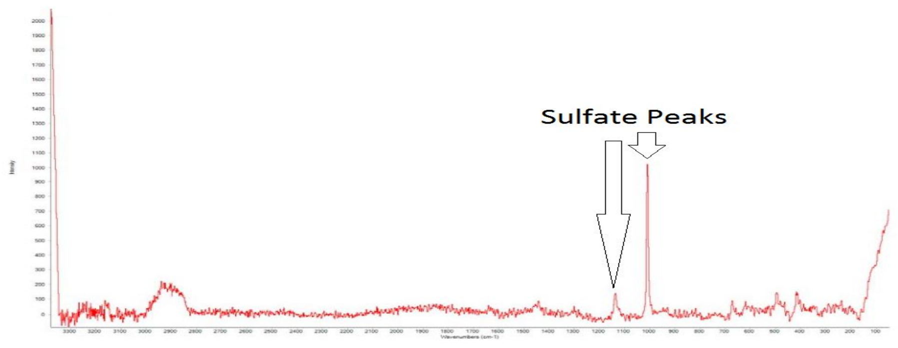
Results continued

Layer 4

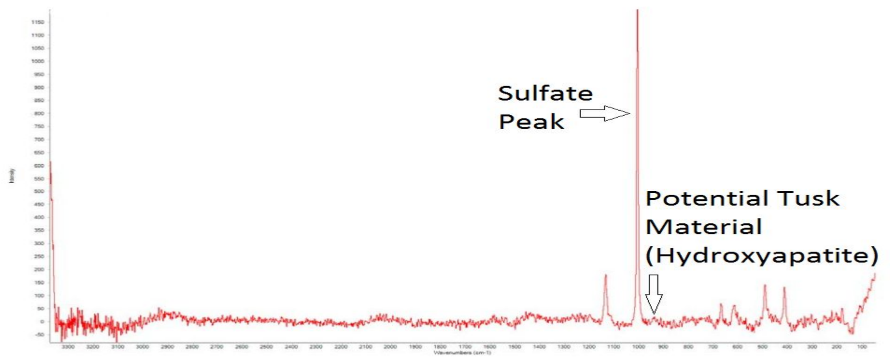




Layer 5



Layer 6



Analysis and Identification

- Titanium Oxide – Primary component of paint
- Sulfate Peaks – Likely from Calcium Sulfate found in Plaster of Paris
- Bicarbonate Peak – Used in several types of plasters, typically used as a buffer to keep the plaster neutral
- Urea Phosphate Peaks – Likely came from the ground in which the tusk was found

Conclusions

I am reasonably confident that I have identified all of the layers correctly, however not all of the plaster has been removed, as shown by the large sulfate peak in layer 6. There is a small peak (950 wavenumbers) that may indicate tusk material in layer 6, however it is not large enough to confidently conclude it is above the noise level. Given more time, more methanol could be used to take off the rest of the plaster to reveal the raw tusk material.

Acknowledgements

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- Thank you to the UNI Museum for making this opportunity possible.
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- Nina Jocic (Raman Diagram).
- Clare Laubenthal (Fluorescence of tusk data)
- Thank you to Vaughn Koch for selecting the solvents to remove each layer from the tusk sample and working on the project with me.

References

1. Cable, J. *The Hampton Tusk*, 1934.
2. University of Northern Iowa Museum, Mastodon Tusk (conservation history), 1966.
3. Granger, R. M.; Yochum, H. M.; Granger, J. N.; Sienerth, K. D. Instrumental analysis; Oxford University Press: New York ; Oxford, 2017.
4. Walker, D.; Bies, M.; Surovell, T.; Frison, G.; Miller, M. Raman in Art and Archeology, 2014.