

A Mammoth Task: Identifying Mammoth Ivory Using Raman Spectroscopy

A mammoth tusk contains an inner mineralized protein matrix of dentine and an outer layer of cementum. Enamel is only present on the tips of the tusks of young mammoths, and is worn away in older mammoths. Dentine is a mineralized connective tissue containing the inorganic component of dahlite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)\text{H}_2\text{O}]$. To determine the species from which ivory originated, often destructive methods are used. Raman spectroscopy is a non-invasive laser-based technique that has proven applications in study of bone and mineral chemistry. Ivory and bone have similar biochemical properties. The aim of this study is to test the hypothesis that mammoth ivory is identifiable using Raman spectroscopy.

Mammoth tusks were kindly loaned from the Natural History Museum, London, UK. All tusks were from the species *Mammuthus primigenius* discovered either in Lyakhov Islands or next to the Yenisei river, Krasnoyarsk (Siberia, Russia) and span the Pleistocene epoch, Cenozoic era. The ivory was scanned with an *inVia* Raman micro spectrometer (Renishaw Ltd) equipped with a x50 objective lens and a 785nm laser. Spectra were acquired using line maps on cross sections of two samples, and individual spectral points were acquired independently at random or at points of interest on all samples. Data was analysed with principal component analysis (PCA) using an in-house Matlab script.

To date, the results of this study establishes that well preserved mammoth ivory can be characterized through the comparison of peak intensity ratios between organic $\nu(\text{CH})$ collagen peaks and inorganic $\nu(\text{PO})$ hydroxyapatite peaks. Differences were observed in the hydroxyapatite peak from spectra acquired near the medulla of the tusk compared to the cortex. This suggests that the tusk is more mineralised towards the cortex compared to dentine found closer to the medulla. A comparison of the average data from each mammoth tusk demonstrated that the mammoth spectral 'fingerprint' remains similar for all samples, though there was some inter-variation in the mineralisation of the tusks from mammoths of the same species.

Further work in this study aims to compare the Raman spectra between mammoth and elephant ivory. This will have direct applications in archaeology, as the species from which an ivory sample is found could be identified without the need for more traditional, destructive techniques of valuable artefacts. Additionally, international trade regulations require proof of the species from which ivory is obtained. The information obtained in this study will be valuable in developing quick and non-destructive methods for the identification of ivory from an unknown origin.