SCIENCE IN THE SERVICE OF ART:

ER:YAG LASER ABLATION OF A ROMAN URN, WITH RAMAN, GC/MS AND SEM ANALYSIS.

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Cinerary Urn, mid-1st–2nd century; Roman, Imperial period; marble; body: 13 1/2 x 12 1/2 inches, lid: 7 1/4 x 12 inches; Saint Louis Art Museum, Museum Purchase 47:1922

Abstract: A Roman Cinerary urn , 67-100 CE, was acquired by the St. Louis Art Museum in 1922 and never exhibited because of the intractable encrustation on the surface of the marble. It was sent to the conservation laboratory at Duke University for cleaning with the Erbium:YAG laser at 2.94µm. Testing demonstrated that the encrustation was a combination of organic materials which over the millennia had transformed to oxalates. The Er:YAG laser successfully removed much of the encrustation.

Introduction: The Roman Cinerary urn was incrusted with an intractable layer of calcite that covered the decorative area of the body of the marble surface. None of the traditional conservation methods for cleaning the surface was effective in removing the dark crystal structure (Figure 1).

The marble urn was sent to the Duke University conservation laboratory for testing to remove the calcite without changing the marble substrate or disturbing the original polished surface of the marble. Tests were carried out with Er:YAG laser at 2.94 µm to determine whether the calcite could be removed by laser ablation (Figure 2).

In a number of areas located over the surface of the urn, round or oval black fungi nests have eaten in to the marble. Laser ablation was able to remove these nests and follow into the stone to remove the embedded fungi. A bright white flash of black-body light occurred during the ablation process that is a reaction to Er:YAG laser ablation of the thick cell wall of the fungi, which are comprised of long chain polysaccharides that are made up of many C–OH bonds (Figure 3).

A literature review of Roman burial customs gave an indication that the encrustation on the marble surface was caused by the oxidation of organic materials that were applied to the surface of the urn on the anniversary of the death of the person whose ashes were interned in the urn. The intent of these rituals was to assure abundance in the afterlife.

Roman funerary urn, 67 – 100 CE. Acquired by the St. Louis Art Museum in 1922.

Figure 1.

Figure 2. The Er:YAG laser at 2.94µm in the mid-infrared corresponds to a strong absorption peak in the infrared spectra of OH- or NH-containing organic molecules. The energy of photons at this wavelength excites bond vibrational stretching mode. Any substance containing a high concentration of -OH bonds at its surface has a strong affinity for photons at 2.94 μm, and confines the absorption of these photons to a surface depth of no more than a few microns. An object's organic contaminant, which either contains the --OH bonds or has been treated with a thin liquid film (water, alcohol, -NH) immediately before lasing, acts as a stain of relatively high concentration and very high absorption, providing a natural barrier to energy penetration into underlying layers. Laser ablation offers a gradual, homogeneous, cleaning which enables the conservator to complete the cleaning using mild solvent mixture, which in themselves are not
Effective.

Figure 3. In a number of areas located over the surface of the urn, round or oval black fungi nests dematiaceous fungi have eaten in to the marble. Laser ablation was able to remove these nests and follow into the stone to remove the embedded fungi. A bright white flash measured by emissions spectroscopy as black-body light occurred during the ablation process that is a reaction of the thick cell wall of the fungi, which are comprised of long chain polysaccharides that are made up of many C–OH bonds.

Figure 4. Thick crust before and after ablation

GC/MS

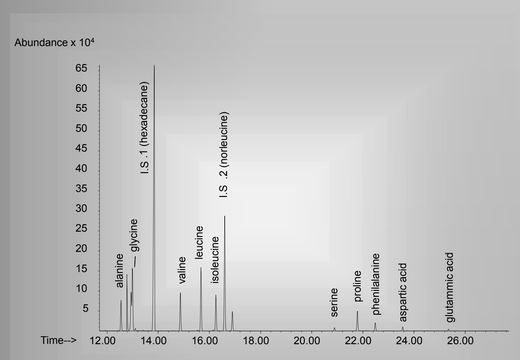

Figure 5. Gas Chromatographic Mass Spectrometric analysis: Single Ion Monitoring (SIM) of the amino acid fraction.

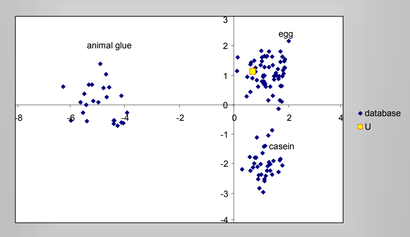

Figure 6. PCA Score Plot

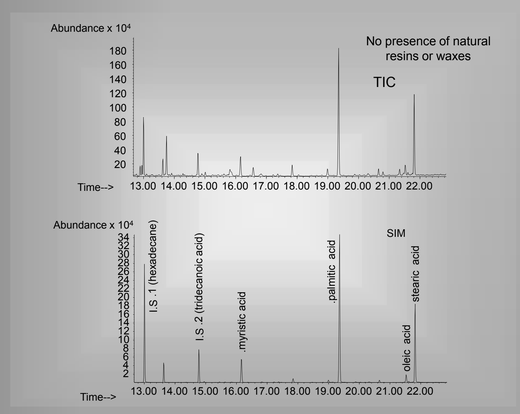

Figure 7. Gas Chromatographic Mass Spectrometric analysis: Total Ion Chromatogramm (TIC) and Single Ion Monitoring (SIM) of the lipid resinous fraction.

PALM/STEA	1.7	AZE/PALM	0.005	Dicarboxilic.%	0.3

Total amount of lipid material: 7.2 µg (corresponding to the 0.25% in weight of the sample)

	Linseed oil	Walnut oil	Poppy oil	Egg	Tempera grassa
P/S	<2	2.2-3.0	>3	2.0-3.2	1.8-2.3
A/P	>1	>1	>1	<0.3	0.5-1
D	>40	>40	>40	<10%	10-20%
col	No	No	No	Si	Si

Figure 8. Lipid resinous fraction: characteristic ratio values

The GC/MS analysis was performed in order to identify the organic material. The analytical procedure is based on a multi step sample pre-treatment that is able to separate the various organic components into different fractions (polysaccharide, lipid-resinous and proteinaceous), which are separately analysed by GC-MS after purification and derivatisation. The analysis of the proteinaceous fraction of a sample collected from the superficial encrustation evidenced the presence of protein. In Figure 5 the Single Ion Monitoring (SIM) of the amino acids is shown. Their relative percentage was compared with those of 122 reference materials of the Department of Chemistry of Pisa (Scibec group) database. The Principal Component Analysis performed identified egg as proteinaceous component in the sample from the urn (Figure 6). The analysis of the lipid/resinous fraction was performed and the resulting Total Ion Chromatogram (TIC) and Single Ion Monitoring Chromatogram(SIM) are shown in (Figure 7). The fatty acids, being the palmitic and stearic acids the most abundant, have been quantified. The characteristic ratio values of the fatty acid (Figure 8) of the sample have been compared with those of reference materials (see Table in Figure 8). As we can see the values of the palmitic over stearic acid is not exactly the one expected for egg (>2), probably due to a contamination. Finally the GC/MS analysis excluded the presence of beeswax, natural resins, or saccharide material.

Figure 17. Abundance in the after life is reflected in the sculptured garlands of the urn. Fruits, vegetables and nuts are the repeated decorative motif of the swages, which wrap around the cylindrical form of the urn.

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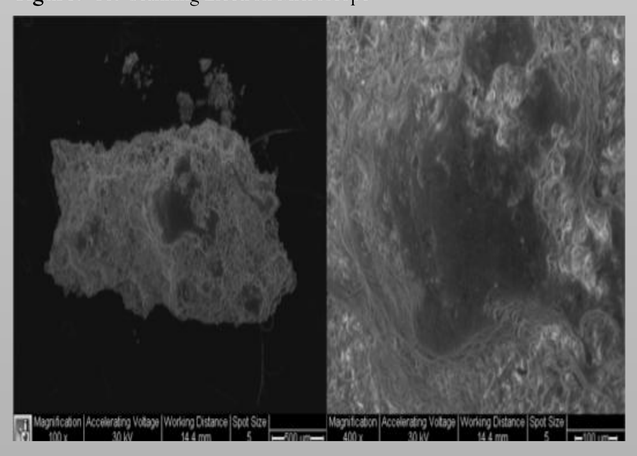
Figure9-10. Scanning Electron Microscope



Micrographs have identified the structure of the marble and of the material that encrusted the marble surface. The crystalline marble is a loosely defined lattice-like structure that can deteriorate through the loosening of the crystals (Figure 9-10). The organic materials that have been identified with GC/MS have penetrated into the crystal structure of the marble and as the oxalates formed caused the excretion of the $CaCo_3$ crystals (Figure 11-12).
The SEM composition analysis shows that the elements in the marble are predominately Ca with traces of iron, magnesium and aluminium (Figure 13). The organic elements of Carbon, sulphur and oxygen derive from the decomposed materials identified by GC/MS and are interspersed in the crystal structure.

Figure 11-12

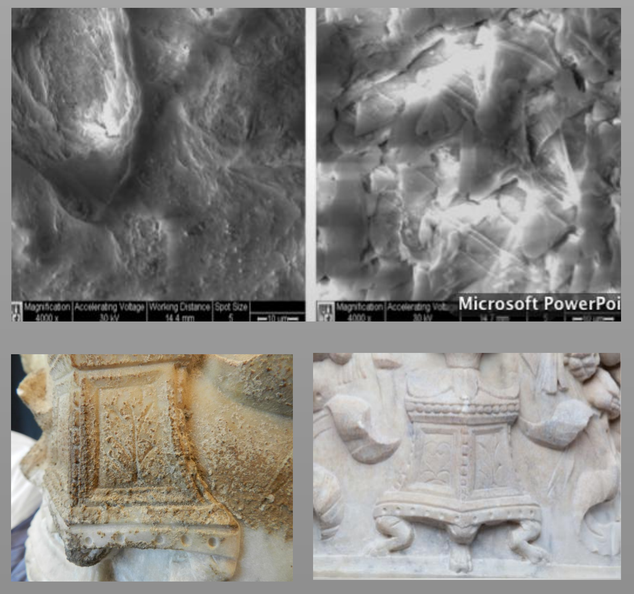


Figure 15-16. Gratis benedictum before and after laser ablation

Figure 13. SEM Elemental Report

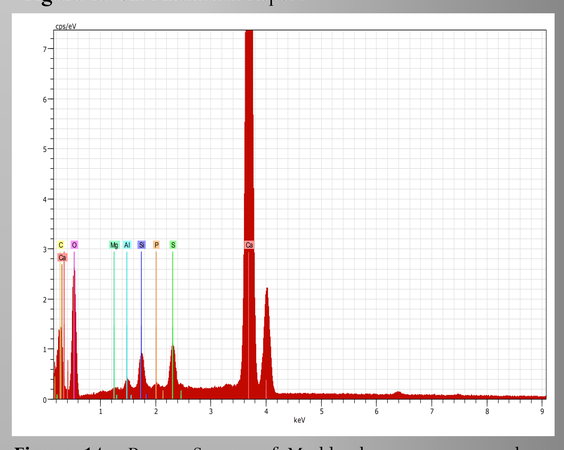


Figure 14. Raman Spectra of Marble shows a strong peak at wavelength of 1077cm2, which represents amorphous calcium carbonate (CaCo3-(x)H2O).

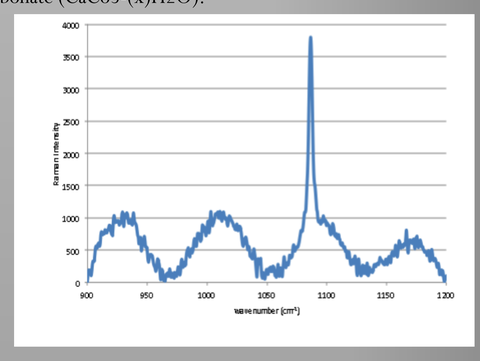


Figure 18. Roman Urn after cleaning.

Conclusions:

The Roman urn made of marble has been studied for the identification of materials that covered the original carved surface and obscured the marble and its sculpted ornament. The removal of encrustations from the marble surface is a delicate operation, which demands that the substrate and original polish remain intact while the material that obscures the original decorative carving is removed. The excretions on the surface have been identified as oxalates. They are the degraded compounds of organic materials that were applied as a part of Roman ritual for the dead.
The removal of the encrustation from the marble surface was done by laser ablation using an Er:YAG laser at 2.94µm. The energy per pulse used were between 100-125 mJ (corresponding to a fluence ranging from 3 to 4 J/cm^2) at 7Hz. A wetting agent enabled effective ablation. The components of the materials that we removed were studied with analytic processes that identified the type of marble used, the calcite that covered the surface, and the biological materials that were embedded in the stone.