

## Analysis of Red Pigment Found on Red Shroud Mummies

### Project Overview

The J. Paul Getty Museum's mummy (91.AP.6) is the subject of an ongoing collaboration between the Getty Conservation Institute Museum Research Laboratory and the Getty Museum Antiquities Conservation Department designed to answer questions about the traditions surrounding Romano-Egyptian mummification, about the preparation and use of Roman pigments, and about the long term preservation of this object and others like it. Preliminary results of this study have revealed considerable information regarding the materials, fabrication, and rituals used to create and preserve this mummy.

The mummy—known by the name “Herakleides” from a painted inscription on the feet of its shroud—dates to the first century. It is wrapped in linen with an attached painted portrait. The wrappings enveloping Herakleides are painted entirely red with mythological images decorating the front surface. The portrait, executed on a wooden panel, has been expertly rendered using a beeswax medium. Herakleides belongs to a small group of similar Romano-Egyptian mummies known collectively as “red-shroud mummies” due to their comparable decorative schemes and because they are painted from head to toe with the pigment red lead,  $Pb_3O_4$ .

In an effort to learn more about fabrication technology and the person within the wrappings, a study of Herakleides began in 2002 after a conservation treatment. Herakleides was subjected to a number of investigations including computer-aided tomography (CT) scanning, carbon-14 dating, and multispectral imaging. The major thrust of the analytical efforts, however, was on developing an understanding of the red surface of the mummy. The liberal use of red lead on red shroud mummies was new in the Roman period and unusual considering reddish iron earth pigments had traditionally been used in Egypt to embellish decorative and funerary objects. Certainly, the use of this red color was appealing to the Romano-Egyptians for its symbolic benefit to ward off evil and protect the individual in death.

In this project, the composition of samples of red lead pigment from Herakleides and six other red shroud mummies was analyzed to assess how this pigment was made and from where the



Figure 1: JPGM 91.AP.6



pigment may have come (i.e., Egypt or elsewhere in the Roman world). The overarching goal was to understand the early Roman history of pigment mining and preparation, to establish trade patterns of these materials, and to document the use of red lead pigment as part of Romano-Egyptian funerary display.

## Analytical Methodology

In this study, a combination of inductively coupled plasma time-of-flight mass spectrometry (ICP-TOFMS) and Raman microspectroscopy was employed. Recent studies have demonstrated the effectiveness of using standard geochemical trace element and radiogenic isotope tracer tools to determine the origins of archaeological raw materials. Time-of-flight detection for mass spectrometry allows the complete mass range of major and trace elements in a sample (from lithium to uranium) to be monitored in a pseudo-simultaneous manner (the entire mass spectrum can be collected in less than 30 ms). The analytical advantage of this technique is that the correlated noise sources associated with the plasma source (i.e., flicker noise) may be minimized due to the rapid detection of mass. These instrumental features contribute to a superior isotope ratio precision compared to quadrupole mass detection techniques. To complement the detailed elemental and isotopic analysis, molecular characterization by Raman spectroscopy was employed to establish major and trace mineralogical phases in the red lead pigment. Since Raman microspectroscopy can characterize single pigment grains, it is an effective tool to assess minor mineralogical phases that might otherwise be below the detection limits of conventional mineral identification techniques such as powder X-ray diffraction.

## Results of Analysis: The Red of the Red Shroud Group

### *Visual Appearance*

A sample of red pigment from Herakleides shows that the particles are polygonal in shape and on the order of 1–3  $\mu\text{m}$ . The particles are dispersed within the original medium identified as beeswax by gas chromatography–mass spectrometry. These large particle sizes suggest the pigment was ground after production. Subtle color differences may also be seen among the particles. Some of the particles appear red-yellow, while others are more intensely red.

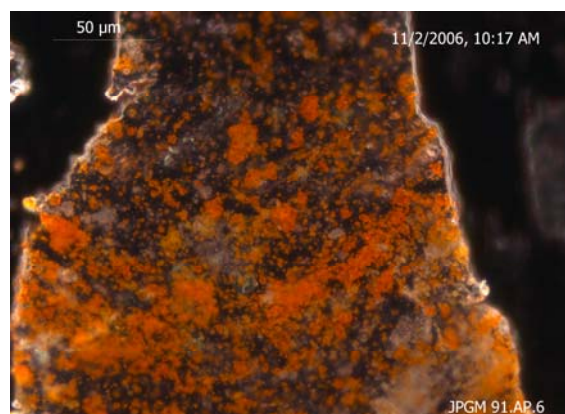


Figure 2: Red pigment sample from Herakleides flattened to view particle morphology

### *Elemental Composition by ICP-TOFMS*

Samples of red pigment from each of the seven red shroud mummies in this study were composed primarily of lead (83%–92% by weight), with tin (Sn) present at concentrations ranging from approximately 1900 ppm to 19,900 ppm in the solid material (~ 0.2%–2.0% by weight).



To compare the relative distribution of trace elements between the samples and evaluate any anomalously high trace element abundances that may indicate the origin of the pigment, all data were normalized to the average upper continental crust composition. The upper continental crust compositional values are often used as a proxy for typical sediment to assess geochemical variability within ore deposits. Some of the normalized trace element data may be seen at right in a "spider plot" of transition metals. A strong compositional relationship among all samples may be readily observed in this plot, and the similarity of the patterning suggests the samples originated from a single source. In comparison to the upper continental crust, the samples show elevated levels of many trace elements, with particularly high values (~1000 times greater than upper continental crust) for Ag, Au, Cd, In, Sn, Sb, and Bi.

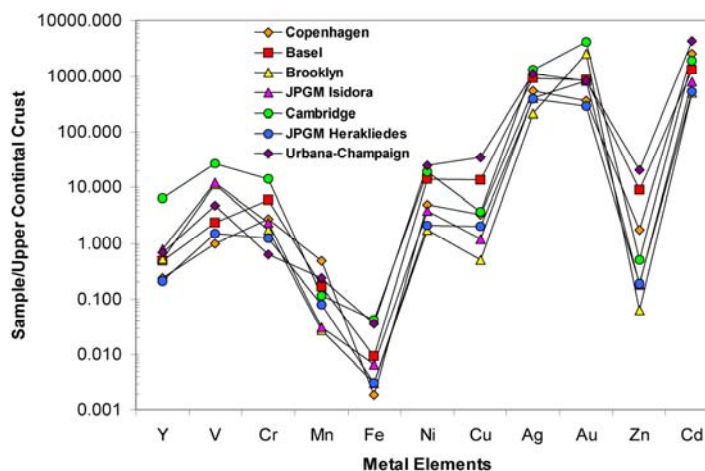


Figure 3: Spider plot of transition metals

The high levels of these trace elements within a lead matrix are consistent with a litharge (PbO) in which trace metals associated with an ore body become enriched during silver refinement (known as cupellation), as opposed to an unprocessed native lead ore. The elevated silver and gold content (at 100 ppm) suggests the parent lead ore source would have been rich enough in these metals to be exploited for its metallurgical content. The metallurgical associations of the material are further underpinned by the abundant presence of Sn. In a typical geologic deposit of lead, Sn is not present, due to its geochemical incompatibility with lead ores (i.e., galenas, cerrusites, and anglesites). Therefore, the Sn can only enter into lead through nonnatural routes (i.e., processing of ores).

#### Lead Isotope Composition

The excellent mass resolution achievable by ICP-TOFMS allows for the measurement of the individual isotopes of lead. By comparing ratios of these individual isotopes of lead ( $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ , and  $^{206}\text{Pb}/^{204}\text{Pb}$ ) to the ratios from known geological sources of lead, the provenance of lead material can be determined. Therefore, to further assess the possibility that the lead in red samples came from metallurgical processing of a silver or gold bearing ore body, lead isotope ratios were measured and compared to known isotopic values associated with lead ore

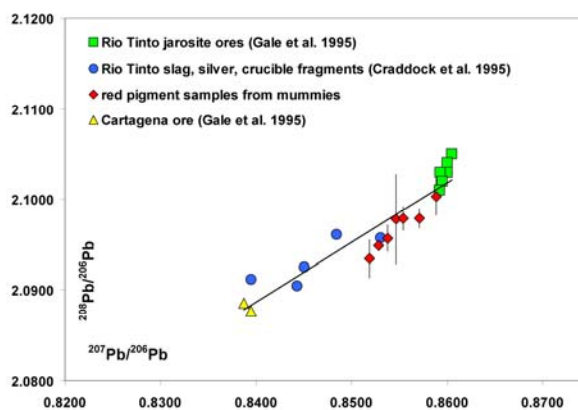


Figure 4: Plot of  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$



bodies from Egypt, and throughout the Mediterranean and Near East. The  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{206}\text{Pb}$ , and  $^{206}\text{Pb}/^{204}\text{Pb}$  lead isotope ratios measured for each of the seven red pigment samples are seen in the plot of  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$ .

It was found that the closest matches to the red lead isotope composition were lead-rich slags, silver, and other smelting debris from mining and metal refinement at the early-Roman site of Rio Tinto in Spain.

#### *Molecular Composition by Raman Microspectroscopy*

Molecular characterization of all seven samples was undertaken by Raman microspectroscopy to explore whether the slight color differences observed among the particles within the samples were an optical effect or corresponded to different chemical species. The use of a 1064 nm excitation source significantly reduced fluorescence from the beeswax binding medium, allowing Raman spectra of the individual pigment particles to be collected with virtually no fluorescence background interference. In all samples, the major phase was confirmed to be red lead ( $\text{Pb}_3\text{O}_4$ ); a representative Raman spectrum showed the characteristic peaks of  $\text{Pb}_3\text{O}_4$  at 64, 122, 152, 226, 314, 391, and 549  $\text{cm}^{-1}$ . Raman spectra from an area containing yellow as well as red particles showed additional peaks at 82, 131, 198, 275, 293, and 458  $\text{cm}^{-1}$ , indicating the presence of lead stannate ( $\text{Pb}_2\text{SnO}_4$ ) together with red lead.

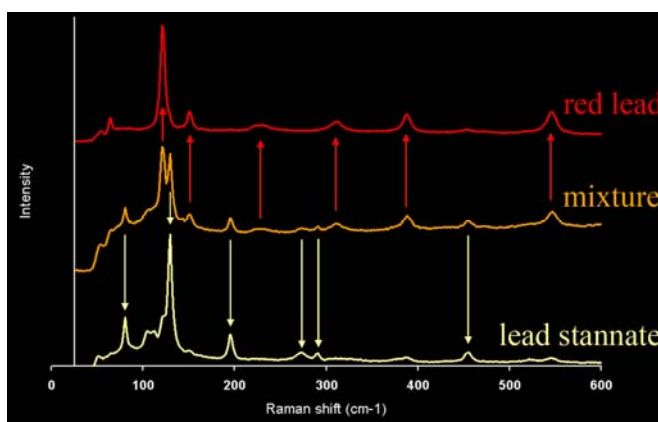


Figure 5: Raman spectra of individual pigment particles

The discovery of lead stannate was somewhat surprising, as this material does not occur in nature, but is produced by heating mixtures of lead and tin oxides to temperatures between 650° C and 800° C, with the final color depending on temperature. Significantly, lead stannate was not known to have been produced for use as a pigment until the fourteenth century when it was termed *lead-tin yellow*. Lead stannate was detected together with red lead in all of the red pigment samples examined in this study.

## Conclusion

The trace element and lead isotope data point to silver production at Rio Tinto, Spain, as the source of the red lead pigment. The trace element data, in particular the detection of elevated levels of Sn, point to litharge formed during cupellation of silver as the likely immediate precursor of the pigment material. The discovery that the Sn is present in the form of lead stannate provides additional evidence that litharge was reheated to produce the red lead pigment used on the mummies. Red lead decomposes rapidly to  $\text{PbO}$  when heated above 500° C under oxidative conditions. However, lead stannate only forms under oxidative calcination at temperatures above 650° C. Therefore, if the red lead pigment had been produced directly from a Sn-bearing lead ore, lead stannate could not have been formed



without also decomposing the red lead. Instead, the Sn-bearing material must have first been subjected to oxidative conditions at temperatures in excess of 650° C, such as those associated with cupellation, to produce litharge containing lead stannate. Subsequent roasting of this litharge at temperatures below 500° C would form red lead with the lead stannate phase remaining entrained, resulting in the trace lead stannate observed.

That this pigment was found on Romano-Egyptian mummies might be evidence of trade in either pigments or raw litharge between Spain and Egypt during this period.

### **Project Participants**

Marie Svoboda, J. Paul Getty Museum Antiquities, Conservator: Conservation treatment and surface characterization of the Mummy.

Karen Trentelman, Getty Conservation Institute, Senior Scientist: Raman analysis of red lead.

Marc Walton, Getty Conservation Institute, Assistant Scientist: Trace element and lead isotope analysis of red lead.

### **Bibliography**

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