# Technical Study of an Attic Skyphos with Ancient Lead Repairs


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## KEYWORDS

Ceramic · Attic · X-radiography · X-ray fluorescence · ICP-MS



***Figure 1.*** *Skyphos. ca. 480-420 BCE, red terracotta, black slip, historical lead staple repairs, H 13.9 cm × W 27.3 cm × Diam. 18.2 cm. Bryn Mawr College, P.2493/ACP1691b*

## INTRODUCTION

An ancient Greek skyphos that was donated to Bryn Mawr College did not come with substantiated provenance and was in poor condition due to a failing previous intervention (Figure 1). As the focus of a technical study and treatment project in the Winterthur/University of Delaware Program in Art Conservation (WUDPAC), many analytical techniques were used to help determine the best course of treatment and gain information that might add to the vessel's provenance and value as an educational tool. These techniques included ultraviolet light induced fluorescence (UV), x-radiography, x-ray fluorescence spectroscopy (XRF), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Fourier-

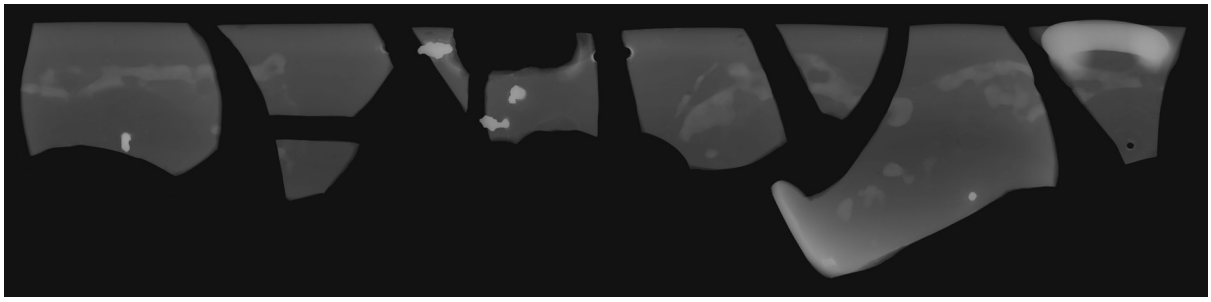

***Figure 2.*** *X-radiograph of the disassembled rim sherds of skyphos P.2493/ACP1691b, exposed at 35 kV and 4 mA for 30 seconds*

transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GCMS), and inductively coupled plasma-mass spectrometry (ICP-MS). As could be expected, some techniques simply confirmed presumed facts, while others did not provide clear answers. However, certain analyses led the study down an evolving research path, revealing radiopaque formations throughout the body of the ceramic and lead isotope attribution less straightforward than initially assumed.

## BACKGROUND AND CONDITION

The subject of this study was a terracotta black-slipped vessel, the style of which is referred to as an Attic skyphos. It was a gift of Howard Comfort, Professor of Classics at Haverford College, to Bryn Mawr College in Pennsylvania, and its approximate date of manufacture is likely between 480 and 420 BCE. Both the slip and body were stable, but the skyphos as a whole had broken at least twice in the past. It notably included multiple potentially ancient repairs in the form of lead staples attached through holes drilled through the body of the ceramic on either side of the breaks. This was a standard method of ceramic repair during ancient times, though variations did occur in the execution of the technique (Elston 1990; Dooijes and Nieuwenhuyse 2007).

At some point after the lead staples were applied, the skyphos suffered additional breakage. No previous treatment record exists for this object, but an image of the skyphos from 1956 shows it was already joined with adhesive. Upon its arrival to WUDPAC, the vessel consisted of 19 joined fragments with minor associated losses. For the most part, the lead staples were no longer functioning as mends, and many were lost or incomplete. The adhesive was instead holding the joins in place with limited success, as many gaps between sherds were visible, and there was movement at some of the joins. The excess adhesive was also pulling away from the surface of the ceramic.

## ANALYSIS AND RESULTS

Examination under long-wave ultraviolet light and analysis with FTIR confirmed the assumption that the failing adhesive was cellulose nitrate. However, before reversing these joins, x-radiographs were taken to observe any possible hidden weaknesses or hallmarks of manufacture. What was revealed was a series of anomalous smudge-like radiopaque features most concentrated at the top half of the vessel, but also present throughout. These resemble smudges caused by fingers or handling, but are not related to anything on the exterior of the vessel detectable in normal or ultraviolet light. The x-radiographs were taken of side views of the joined vessel (before any treatment commenced), making it complex to interpret. It was decided that once the sherds were separated and cleaned, they would be x-rayed again in their disassembled state. For the second round of x-radiography, the rim sherds were laid flat and organized in a way to make the pattern of the smudges clearer (Figure 2). The formations do not maintain any correlation or relationship with the breaks.

It should be noted that upon disassembly and cleaning, it was discovered there are three different colors present in the clay body of the skyphos, visible on the break edges. These will henceforth be referred to as “green,” “red,” and “dark” (Figure 3a). The colors often remain constant through the entire thickness of the sherd, not changing depending on whether the location is nearer to the core or the slipped exterior, and the “dark” spots line up approximately with

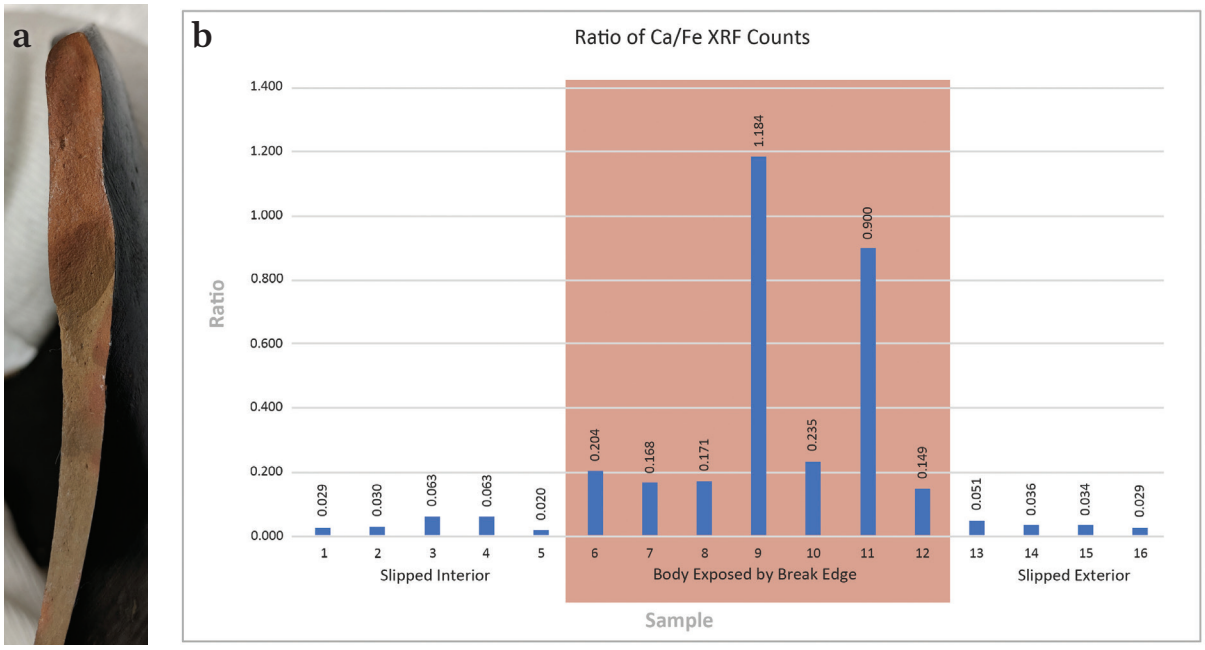


***Figure 3.*** *a) A cleaned break edge displaying all three of the clay body colors; b) graph of the ratio of calcium and iron in each XRF sample location*

where the radiopaque smudges meet the edges of the sherds. Initial XRF analysis of the skyphos had been done prior to disassembly, confirming the general elemental content of terracotta clay and lead staples. XRF was revisited on one of the disassembled sherds, analyzing various points on the interior slip, a break edge displaying the various clay body colors, and exterior slip, in hopes of detecting elemental differences that might explain the radiopaque features. Taken in conjunction with the results of SEM-EDS analysis of two samples of the vessel of differing radiopacity, a hypothesis was formed that this skyphos was made with poorly mixed clay and the "dark" radiopaque areas may contain a larger portion of calcium than the red areas (Figure 3b). To roughly test this hypothesis, tiles were made with a modern terracotta clay, some of which was calcium-enriched and poorly mixed with the unenriched clay. X-radiographs were taken of the fired tiles at the same parameters used on the skyphos sherds. Unfortunately, no difference in radiopacity was observed.

Lastly, it was hoped that the lead-isotope ratio analysis through ICP-MS would place the lead used for the skyphos' staple mends clearly within a pre-established data set. The fact that lead was used for these mends presented an opportunity for scientific analysis to produce additional information about the provenance and history of this object. While not all elements exhibit source-specific ratios of their isotopes, lead does. The ratios of $^{204}$Pb, $^{207}$Pb, and $^{208}$Pb, each to $^{206}$Pb in a given sample, can help indicate the locality from which the lead was mined (Tite 1981). The ratios of lead isotopes in a number of objects are plotted graphically using the ratio of two isotopes on one axis, and a different ratio of two isotopes on the other axis. Plotting the data often allows it to fall into distinct groupings, demonstrating their relationships. A sample from a lead staple on the skyphos was taken, processed, and run three times through ICP-MS analysis. These three data sets were then plotted along data collected for selected sites known as archaeological and geological lead sites from Oxford Archaeological Lead Isotope Database OXALID (2014). Results clearly suggest that this lead is not likely from India, but it is not clearly part of the overlapping groupings from Mediterranean and Near Eastern sites. Plotting the same samples by different ratios does not completely clarify this issue but more securely places the source of the skyphos' lead within the Mediterranean (Figure 4). However, this determination is based solely on the available data on OXALID; it is not a complete resource, and as additional studies are added to the database, the attribution to the lead of this object may be changed or refined.

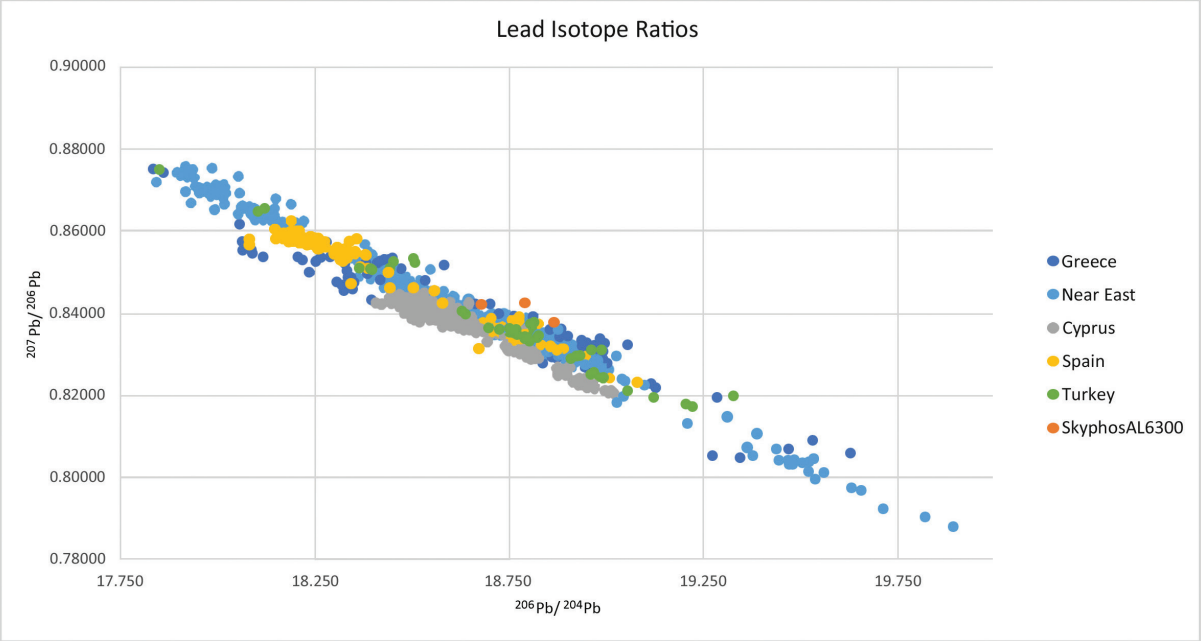


***Figure 4.*** *Scatter plot of lead isotope ratio analysis of skyphos P.2493/ACP1691b (orange), as well as data collected from other locations and published on a lead isotope research database (OXALID 2014)*

## CONCLUSION

Multiple scientific techniques were used to analyze a Greek skyphos to help determine the course of its conservation treatment and partially provide scientific backing for its presumed provenance. These analyses also uncovered oddities within the body of the ceramic. These were not completely characterized and are so far matchless in the field of archaeological ceramics. It is hoped that this freshly conserved object will be the focus of future education and research, and that its remarkable features will be properly explained.


## ACKNOWLEDGEMENTS

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