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doi:10.1017/S1431927621010461
Microsc. Microanal. 27 (Suppl 1), 2021

Orpiment in Colonial Williamsburg: Challenges with the Identification of Yellow Arsenic Sulphides in Historic Housepaints

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Scholars of historic architectural finishes have generally agreed that orpiment (As_2S_3), the yellow arsenic sulphide pigment also known as "Yellow Arsenic" or "King's Yellow", was relegated to the artist's palette and rarely, if ever, used in common housepaints [1]. This consensus was based on the numerous disadvantages associated with the lemon-yellow pigment including its toxicity, odor, expense, and difficulty to grind. These properties were well known to early housepainters such as John Smith, the author of "The Art of Painting in Oyl" (1723), who wrote that orpiment was of a "poisonous nature" and one needed to take care that the fumes did not "offend the brain" during its preparation [2]. Over a century later, T. H. Vanherman wrote that it was "necessary to caution the use of [Orpiment], unless any one has a wish to be driven out of house and home…" and criticized its "antipathysing" with other colors [3]. In recent years, evidence-based architectural paint research, including that carried out by the Colonial Williamsburg Foundation, suggests that oil-based yellow paints in vernacular settings were prepared primarily with yellow iron oxide (ochre), a more stable, cheaper, and non-toxic yellow, until the introduction of chrome yellow in the early nineteeth century.

Yet, recent analysis of 18th- and early-19th-century housepaints with cross-section microscopy, scanning electron microscopy – energy dispersive spectroscopy (SEM-EDS), and polarizing light microscopy (PLM) has discovered the use of orpiment in a number of building interiors in Colonial Williamsburg's historic area. For example, at the George Reid house (mid-18th c.), orpiment was found in two separate interior paint generations: first, in a green paint from the mid-18th century, and later, in a yellow paint dated to the early 19th century. Initially the orpiment in the 18th c. paint was identified with PLM, but instrumental confirmation was elusive. Extensive SEM-EDS analysis of the green paint in cross-section failed to detect any arsenic. Eventually, the presence of orpiment was confirmed by dispersing a paint scraping on a carbon stub and analyzing with SEM-EDS repeatedly through spot and line-scan functions until, finally, peaks for arsenic emerged. The failure of SEM to identify arsenic within the cross-section could be attributed to matrix effects arising from the heterogeneity of the green paint layer, which contained other pigments including lead white, yellow ochre and associated clays, chalk, and Prussian blue. Were it not for PLM, the orpiment would have gone undetected. In the same building, in the "best" parlor, a paint layer dating to the early 19th-century was again found to contain orpiment, this time mixed with chrome yellow, and used as a bright yellow base coat for an imitation wood-graining finish. The combination here of orpiment with chrome yellow suggests a transition period from using more traditional pigments with newer (unpredictable) ones. This raises the interesting possibility that orpiment might have been considered more a reliable pigment than previously recorded.

These findings have led to a re-examination of early yellow-pigmented housepaints at Colonial Williamsburg, where almost every original building has been sampled at least once in the past century. Architectural paint samples (sometimes decades old, housed in our Architectural Fragments collection) are being re-analyzed with the goal of identifying yellow arsenic sulphides that might have been overlooked before the establishment of our Analytical Laboratory in 2014. To date, our findings suggest that orpiment, despite its reported disadvantages in housepaints, was used more often than previously thought. These results give us a better understanding of the housepainter's palette, and, considering orpiment's relative expense, a more nuanced understanding of the status of certain spaces within a structure. This study also underscores the importance of light microscopy in association with analytical methods. The identification of orpiment has been most successful with PLM, as the pigment exhibits distinct optical and morphological characteristics not shared by

other yellows, and these characteristics, and additional analytical challenges, will be discussed in further detail with supporting photomicrographs and data.

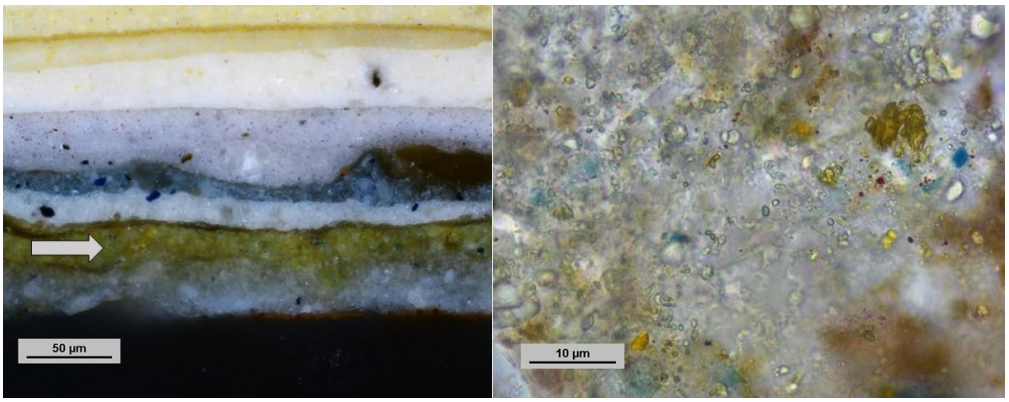

Figure 1. Left: Paint cross-section of sample RE 24b, visible light, 200x; taken from George Reid house interior, second-floor west chamber, door architrave. Arrow indicates mid-18th c. green paint containing orpiment. Right: Dispersion of pigments from green paint at left, plane polarized light, 1000x. Orpiment, lead white, yellow ochre, and Prussian blue were identified.

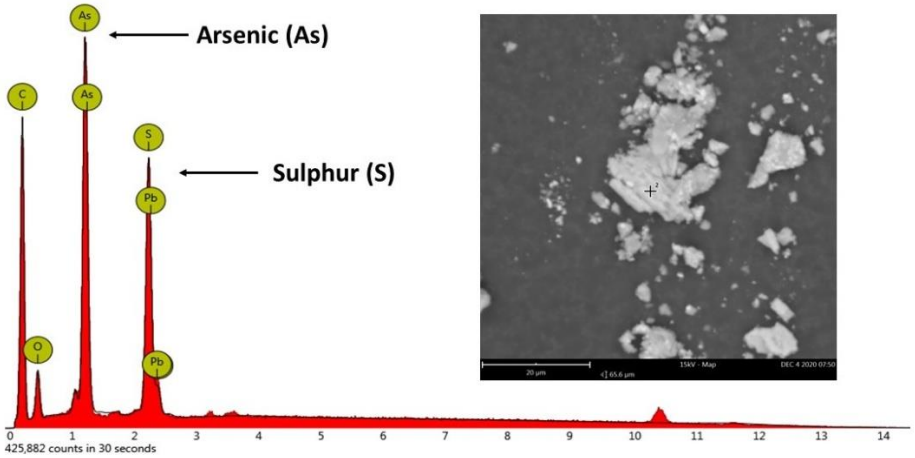

Figure 2. EDS spectrum from a dispersion of the green paint shown in Figure 1, showing arsenic and sulphur. These elements were not detected with SEM-EDS point analysis or elemental mapping of the paint cross-section. Inset: SEM-BSD image of dispersion containing orpiment. Cross indicates EDS target. Scale bar at bottom left is 20 microns.

References

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https://doi.org/10.1017/S1431927621010461 Published online by Cambridge University Press