

# A Compositional Analysis Of Historic & Pre-historic Pigments

BY: BENJAMIN R. SAMPSON, MICHAEL J. DETISCH,  
JILLIAN CRAMER, W. BRENT SEALES, T. JOHN BALK



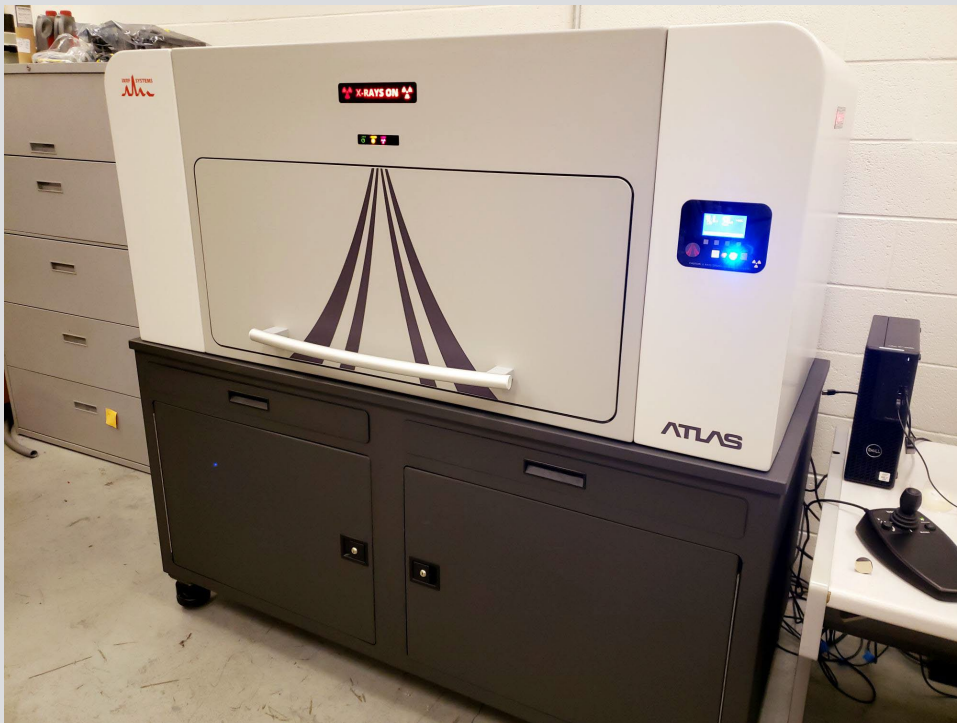
# Introduction

- X-ray Fluorescence spectroscopy (XRF) was developed as a technique for studying composition of historic and pre-historic pigments in ceramics and paintings.
- XRF techniques were applied to Native American pottery fragments from the southeastern and southwestern United States were analyzed, as well as two modern paintings.
- While the modern paintings analyzed were not artifacts in a strict sense, they served well as a stand-in for actual artifacts. However, some of the modern pigments used are not identifiable by their composition alone.
- XRF techniques were applied using an “Atlas X” X-ray fluorescence energy dispersive spectrometer by iXRF Systems.



# X-Ray Fluorescence Energy-Dispersive Spectroscopy

- In XRF/EDS, atoms in a material are bombarded by a high-energy X-ray beam. This beam takes electrons belonging to those atoms up to an excited state. Eventually, the electrons return to their ground state, releasing a characteristic X-ray that can be used to identify the atom that release it based on its energy.
- Similar working principle to the energy dispersive spectroscopy (EDS) used in electron microscopy, except that an X-ray beam is used, rather than an electrons beam.
- Pros (compared to electron microscope EDS) are higher compositional accuracy, faster measurements, no need for vacuum-pumping, and, most importantly, the ability to create large area maps.
- Cons are lower spatial resolution and an inability to detect some lighter elements.



# Background on Paintings and Pottery

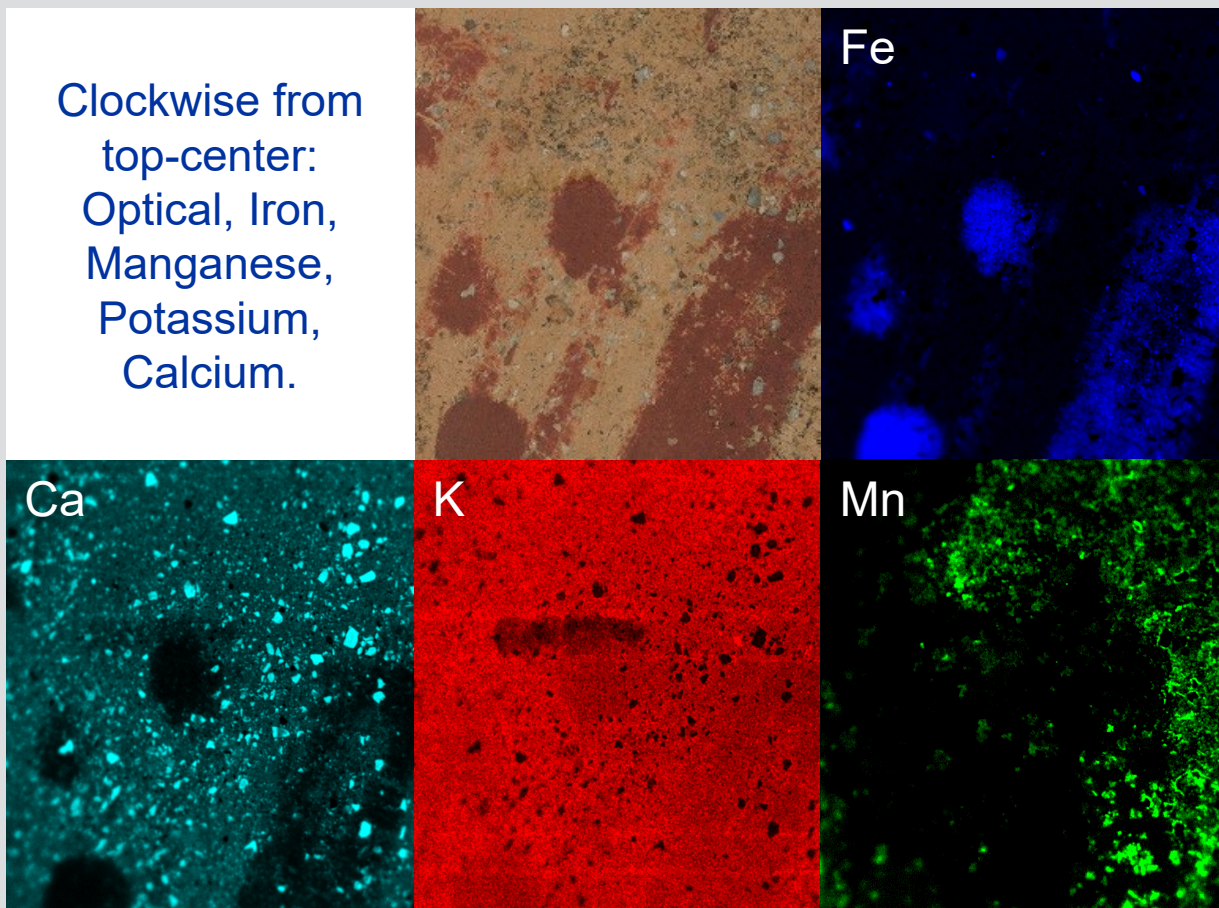


Left to Right: Southeastern Pottery, Southwestern Pottery, Acrylic Painting, Oil Painting

- Southeastern Fragment (Left): The fragment features a slip, temper, and pigmentation
- Southwestern Fragment (Center-Left): The fragment features a slip, temper, and two different types of pigmentation
- Acrylic Painting (Center-Right): This painting features mixed pigments and undercoating
- Oil Painting (Right): This painting features mixed pigments, undercoating, and scraping

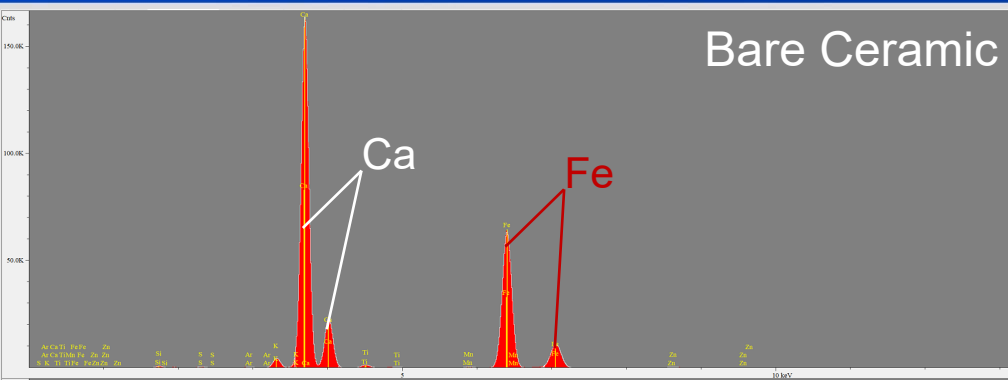
# Southeastern Ceramic Results

Clockwise from  
top-center:  
Optical, Iron,  
Manganese,  
Potassium,  
Calcium.



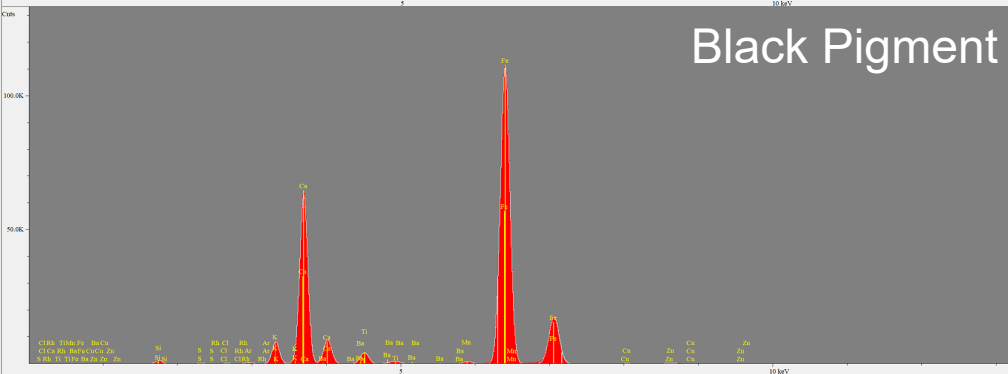
- The darker blue image indicates that the red pigment contains high levels of iron.
- The light blue image indicates that the white temper seen on the surface contains high levels of calcium.
- The red image indicates that there is calcium present on the clay and pigment surface that is not present in the white temper.
- The green image indicates that there is manganese present in unidentified dark flecks on the surface.

# Southwestern Ceramic Results



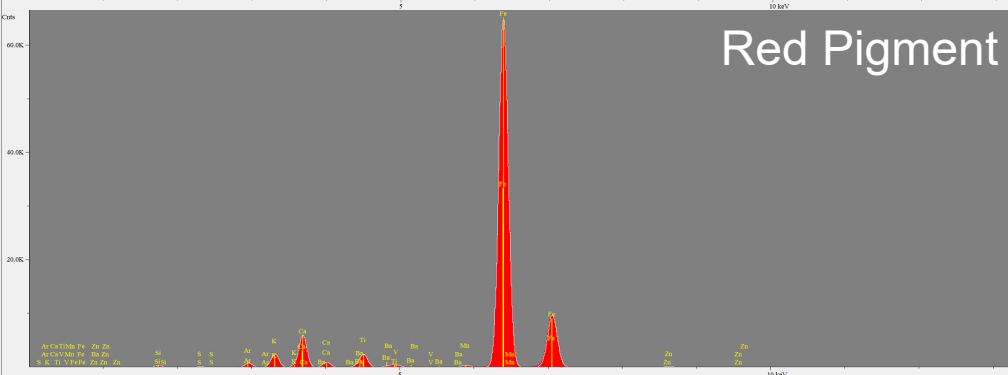
El.	Line	Intensity (cps)	Atomic Conc. (%)	Units
Si	Kα	20.42	1.753	1.552 wt%
Al	Kα	13.50	0.242	0.183 wt%
K	Kα	10.04	0.228	0.214 wt%
Ca	Kα	8.146	0.244	0.183 wt%
Fe	Kα	4.50	0.180	0.138 wt%
Mn	Kα	15.99	0.156	0.175 wt%
Pb	Kα	2.693	0.175	0.130 wt%
Zn	Kα	13.45	0.072	0.110 wt%
			100.000	100.000 wt%

50.0  
Takeoff Angle 35.0°  
Dispersed Line(s) 400.1



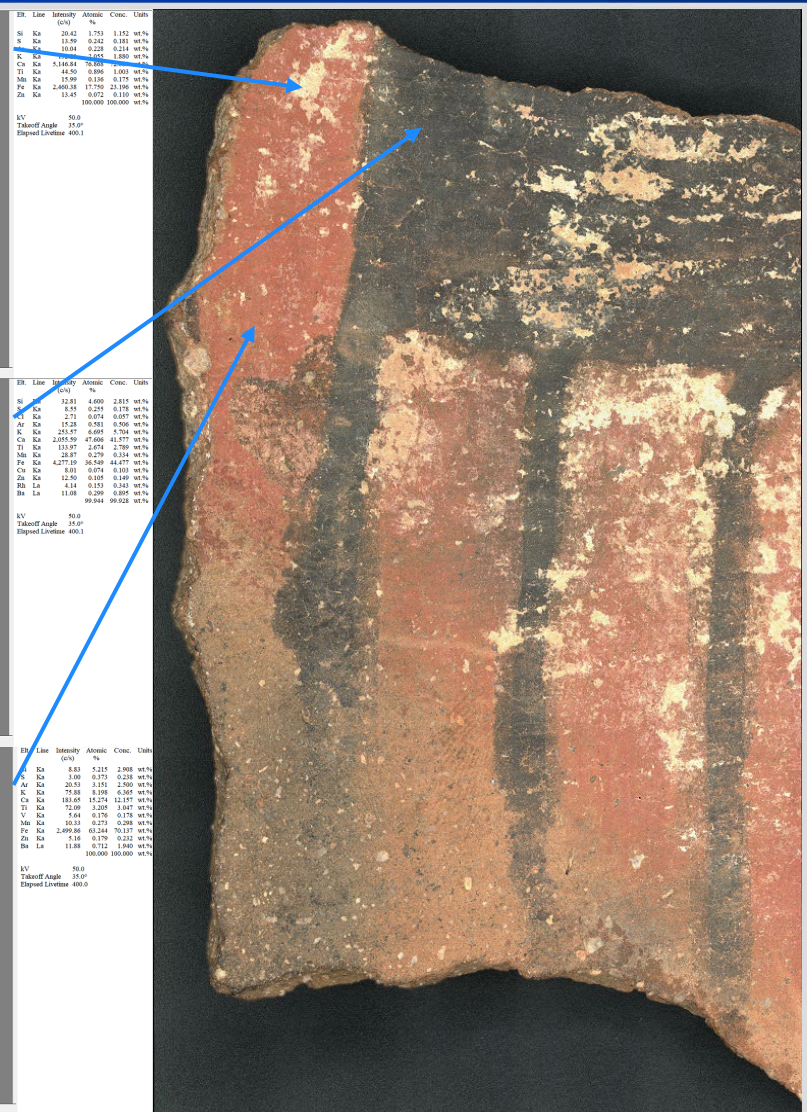
El.	Line	Intensity (cps)	Atomic Conc. (%)	Units
Si	Kα	32.81	4.000	2.815 wt%
Al	Kα	8.51	0.245	0.175 wt%
Ca	Kα	2.71	0.074	0.057 wt%
Fe	Kα	15.26	0.581	0.500 wt%
K	Kα	253.57	6.695	5.704 wt%
Ca	Kα	2,055.50	47.666	41.577 wt%
Fe	Kα	133.97	2.674	2.789 wt%
Mn	Kα	23.87	0.270	0.134 wt%
Pb	Kα	4,277.19	36.549	44.477 wt%
Ca	Kα	1.01	0.074	0.101 wt%
Zn	Kα	12.50	0.185	0.140 wt%
Br	Lα	1.14	0.153	0.242 wt%
Br	Lα	11.08	0.209	0.895 wt%
			99.944	99.928 wt%

50.0  
Takeoff Angle 35.0°  
Dispersed Line(s) 400.1



El.	Line	Intensity (cps)	Atomic Conc. (%)	Units
Ca	Kα	8.83	5.215	2.898 wt%
Al	Kα	3.80	0.375	0.228 wt%
Ar	Kα	20.53	3.151	2.500 wt%
K	Kα	75.68	8.196	6.500 wt%
Fe	Kα	181.68	15.274	12.157 wt%
Fe	Kα	10.35	0.271	0.200 wt%
V	Kα	5.64	0.176	0.178 wt%
Mn	Kα	10.33	0.271	0.200 wt%
Fe	Kα	2,489.86	63.244	70.137 wt%
Zn	Kα	5.16	0.170	0.232 wt%
Br	Lα	11.88	0.712	1.840 wt%
			100.000	100.000 wt%

50.0  
Takeoff Angle 35.0°  
Dispersed Line(s) 400.0

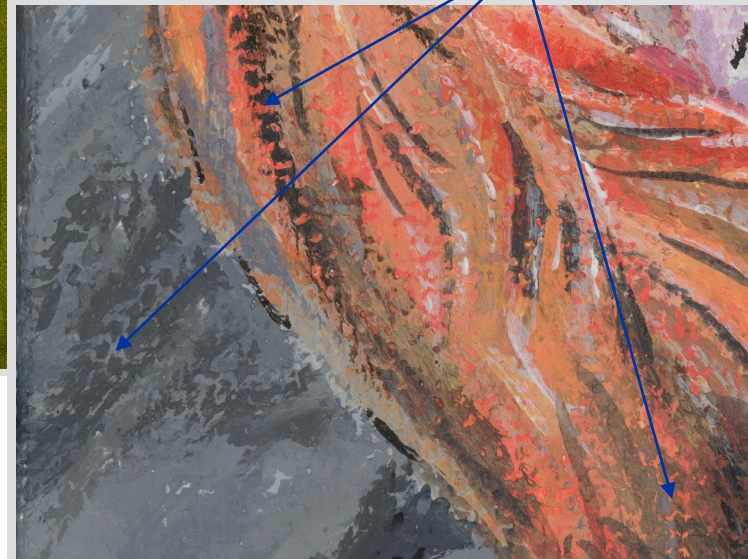


# Acrylic Painting Results

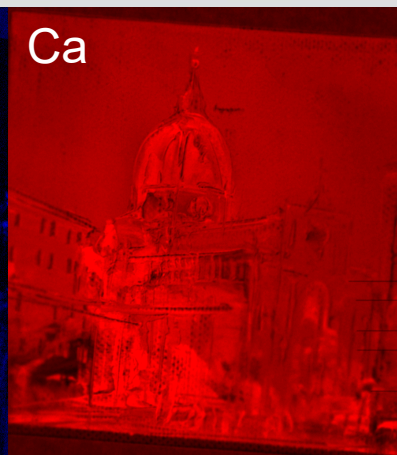
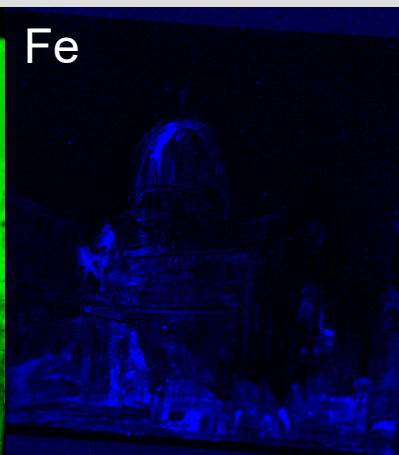


Clockwise from top-left: Optical, Manganese vs. Iron (Red and Blue respectively), Titanium, Zinc, Sulfur, Barium.

- Identified Pigments:
  - Lithopone ( $BaSO_4$  and  $ZnS$ )
  - Titanium White ( $TiO_2$ )
  - Umber/Sienna ( $Fe$  &  $Mn$  Oxides)
- Undercoating can be viewed in the image below:

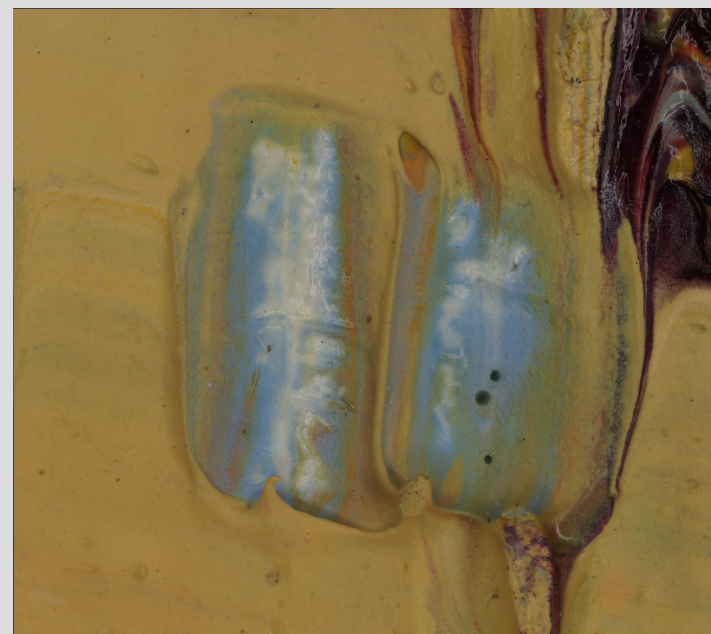


# Oil Painting Results



Left to right:  
Optical,  
Titanium,  
Iron,  
Calcium

- Pigments Identified:
  - Gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ )
  - Orpiment ( $\text{As}_2\text{S}_3$ ) or Realgar ( $\text{As}_4\text{S}_4$ )
  - Red (Anhydrite) or Yellow (Hydrated) Ochre
  - Titanium White ( $\text{TiO}_2$ )
- Undercoating and scraping can be viewed to the right:



# Work Cited

“Pigments Checker V.5.” *Cultural Heritage Science Open Source*,  
[chsopensource.org/pigments-checker/](https://chsopensource.org/pigments-checker/).

Y Leng, and Inc Ebrary. *Materials Characterization : Introduction to Microscopic and Spectroscopic Methods*. Weinheim, J. Wiley, Copyright, 2013.

**EduceLab is a 2021 National Science Foundation Mid-Scale Research  
Infrastructure Project: Award Number 2131940**

