A Compositional Analysis Of Historic & Pre-historic Pigments

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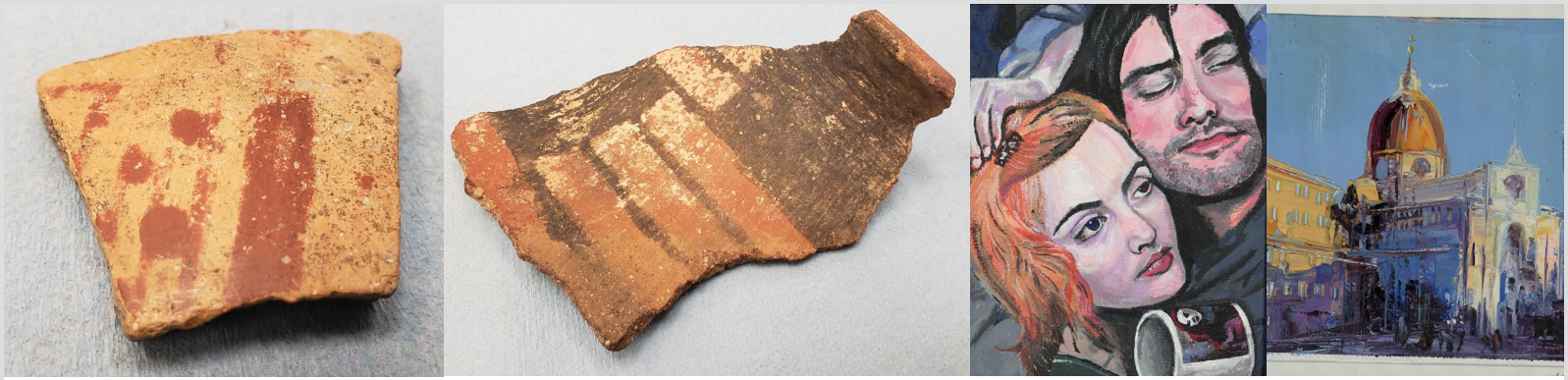
Introduction

- 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 florescence energy dispersive spectrometer by iXRF Systems.

X-Ray Florescence 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

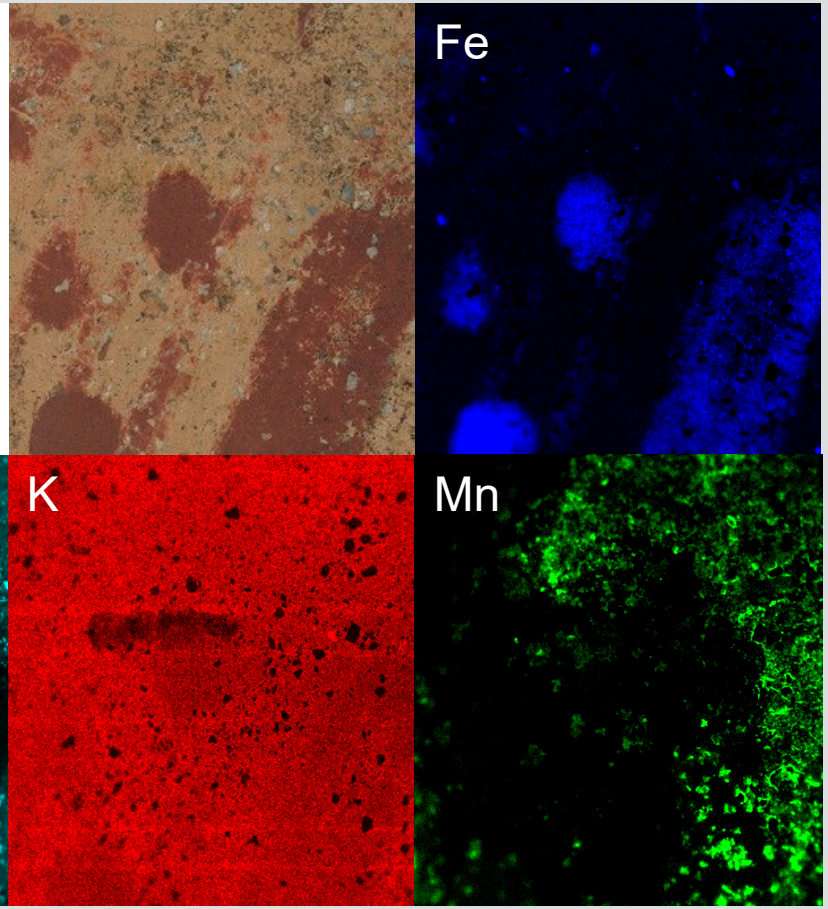


Left to Right: Southeastern Pottery, Southwestern Pottery, Acrylic Painting, Oil Painting

- 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

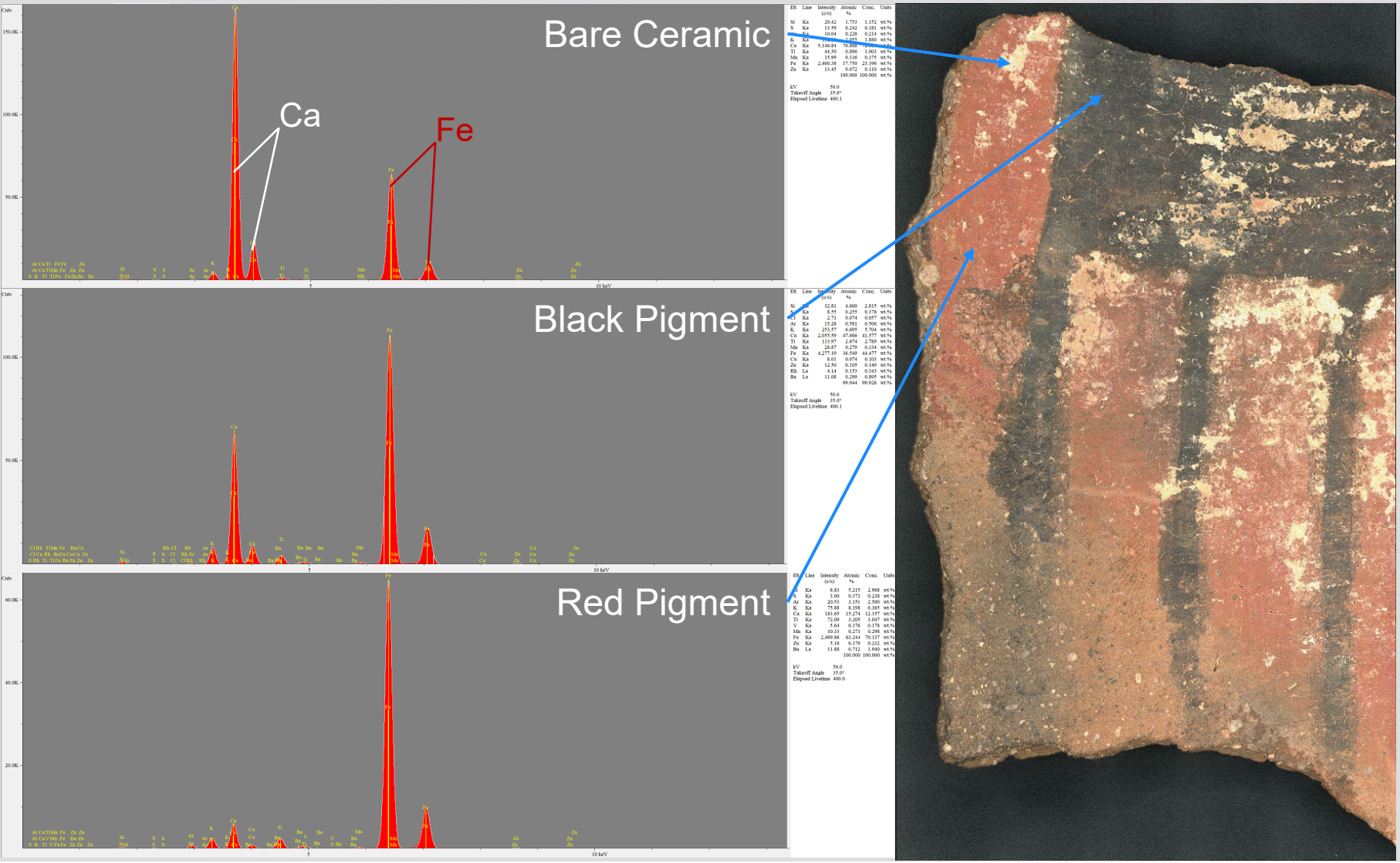
Southeastern Ceramic Results

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.

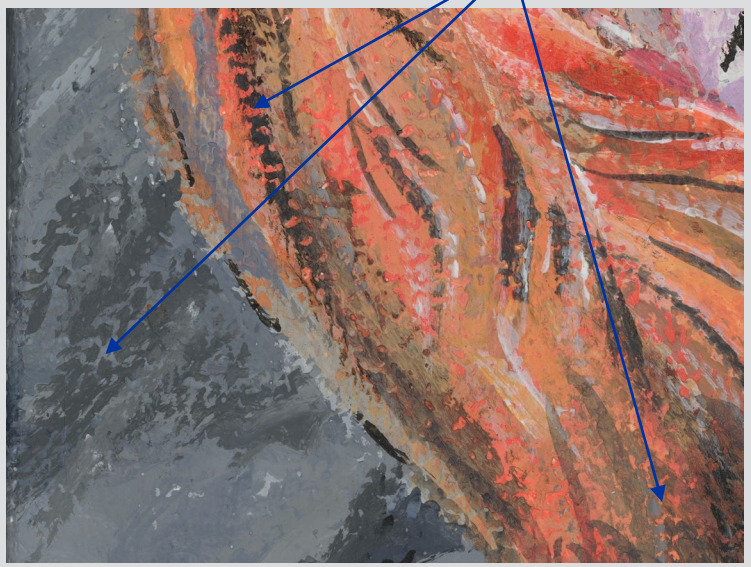
Southwestern Ceramic Results



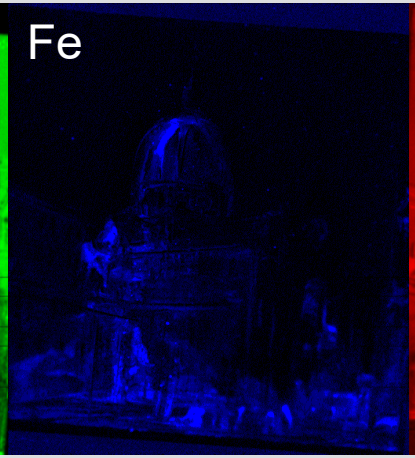
Acrylic Painting Results

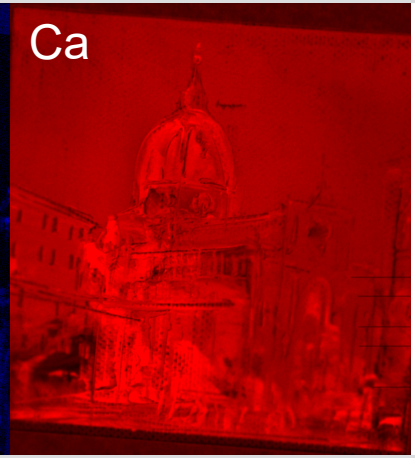
Clockwise from top-left: Optical, Manganese vs. Iron (Red and Blue respectively), Titanium, Zinc, Sulfur, Barium.

- 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 ($CaSO_4 \cdot H_2O$)
  - Orpiment (As_2S_3) or Realgar (As_4S_4)
  - Red (Anhydrate) or Yellow (Hydrated) Ochre
  - Titanium White (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/.

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

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