



# Elemental Characterization of Fresco Pigments and Cistern Walls

## via X-Ray Fluorescence Spectrometry

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### 1. Background

Excavations commenced on a subterranean structure, a hypogeum in the shape of an inverse pyramid, below the city of Orvieto in Umbria, Italy in 2012. Based on ceramic evidence the structure was filled in the late fifth century BCE with architectural materials that seem to be a disassembled temple. This season we explored an associated cistern that was of Etruscan construction but clearly reused in the medieval period. The cistern is a contaminated locus as evidenced by the material recovered - some Etruscan pottery amidst a large amount of medieval ceramics that date from the mid-10th to the beginning of the 14th century CE. In the 17th century the cistern was enclosed in a renovation project. The other site examined was Coriglia, specifically in Trench C. Coriglia is the primary excavation site that is believe to have been an Etruscan healing shrine. After the Romans conquered the Etruscans, it is most likely the site became a complex bath system. This area was discovered by a farmer who was plowing.

The elemental characterization of the hydraulic cement cistern together with pigments on architectural terra cotta fragments also recovered from the hypogeum are presented here. The chemical compositions were determined via portable X-Ray Fluorescence Spectrometry (XRF) due to its sensitivity to elements found in pigments and cements, its portability, as well as its non-destructive capability to preserve the fragile, ancient remains. Elements found in the black, white, and red pigments included Ca, Fe, and Sr, while Ca, Fe, and Sr, were determined to make up the cistern wall cements. In the Coriglia site, the mortar was determined to contain Sr, Fe, and Ca. Multivariate statistics was used to evaluate the spectral data.

### 2. Method

The pigments and walls were categorized by physical color and analyzed using the Bruker Tracer III-V+ portable XRF. Each pigment color was analyzed in duplicate at two different locations on each artifact for 120 s each; the instrument was operated upright in a stand in a laboratory setup. The cements were analyzed in duplicate at many locations on each wall for 120 s each; the instrument was operated handheld for *in situ* measurements of the materials. A 40 keV x-ray tube energy with 25  $\mu$ A tube current was used for all measurements. Spectra were exported to Excel and imported into the multivariate statistical software, Unscrambler.

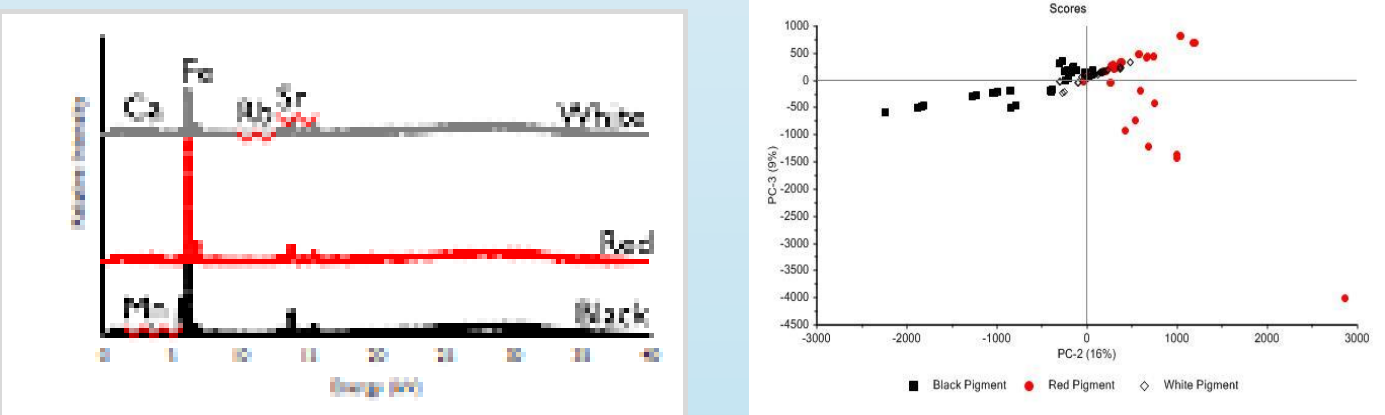
### 3. Instrument Setup



**References:**  
1.Redente, M. Saint Anselm College Chemistry Department Senior Thesis, December 2013.  
2. Donais, M. Saint Anselm College Chemistry Department Report on Terraced Wall Study, March 2017.

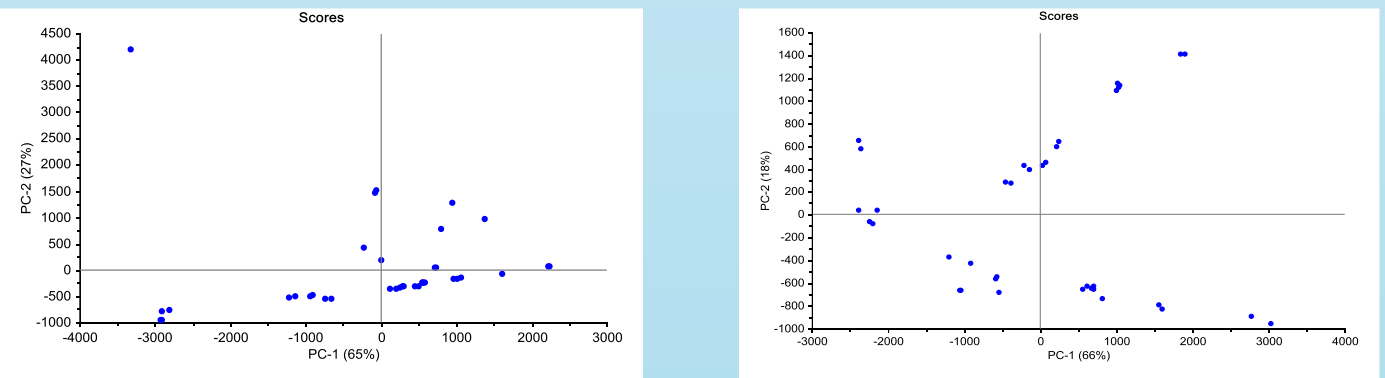
### 4. Pigment Results

#### All Pigments



•  $PC_1$ : Fe, Mn;  $PC_2$ : Ca;  $PC_3$ : Sr

#### Individual Pigments



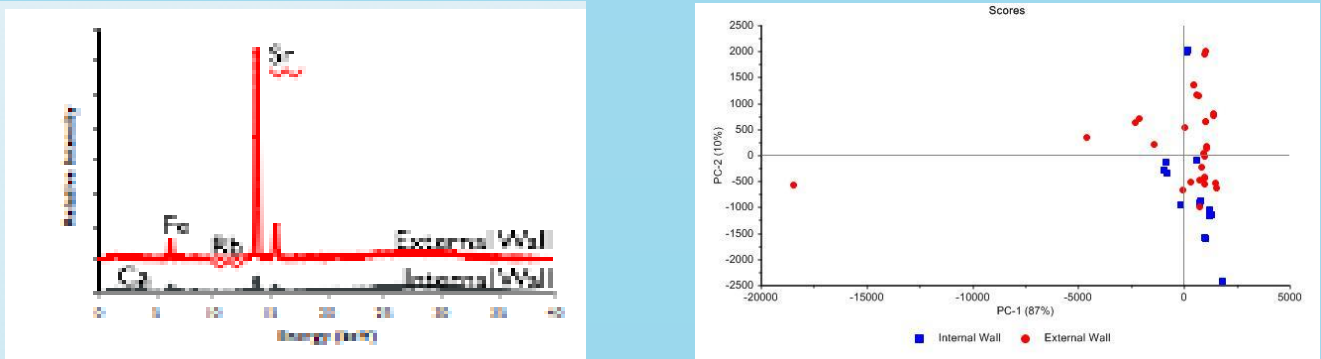
Black Red

### 5. Conclusions

- XRF data and principal component analyses (PCA) permitted identification of the key compositional elements in the pigments.
- The three pigments show different elemental compositions with white and red being the most similar and only black containing Mn.
- The black pigment and the white pigment may have more than one source whereas the red pigment has likely only one source.

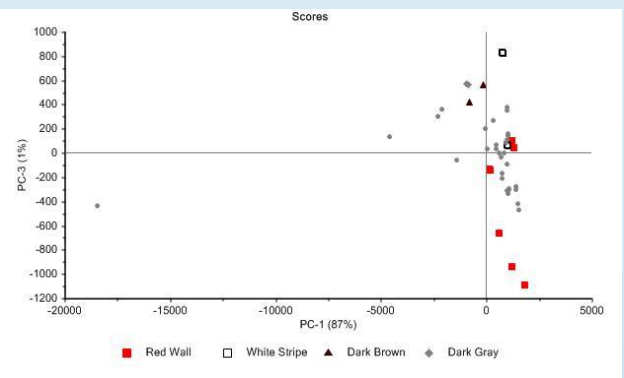
### 6. Cistern Wall Results

#### Internal and External Walls



$PC_1$ : Sr;  $PC_2$ : Fe;  $PC_3$ : Ca

#### Internal Wall by Color



•  $PC_1$ : Sr,  $PC_2$ : Fe,  $PC_3$ : Ca

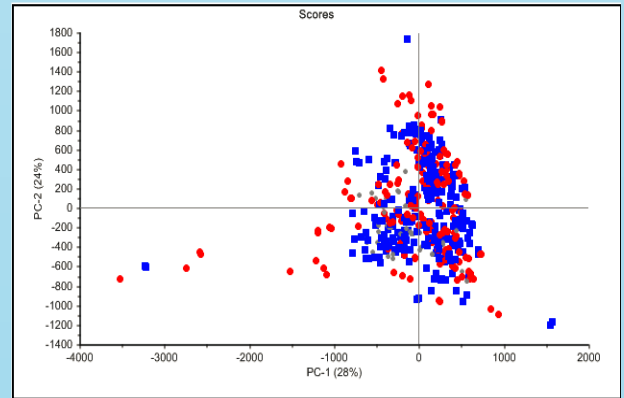
### 7. Conclusions

- The outer and inner hydraulic cement walls appear to have different elemental compositions.
- Colored areas on the walls also have different elemental compositions than the non-colored main wall areas.

### 8. Trench C Mortar Results

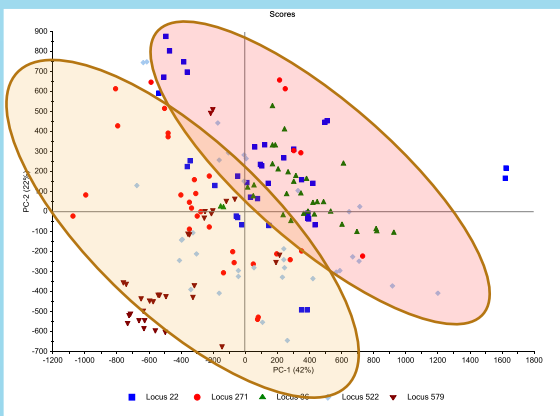
#### Top vs. Side Mortars

- No difference regarding mortar location observed



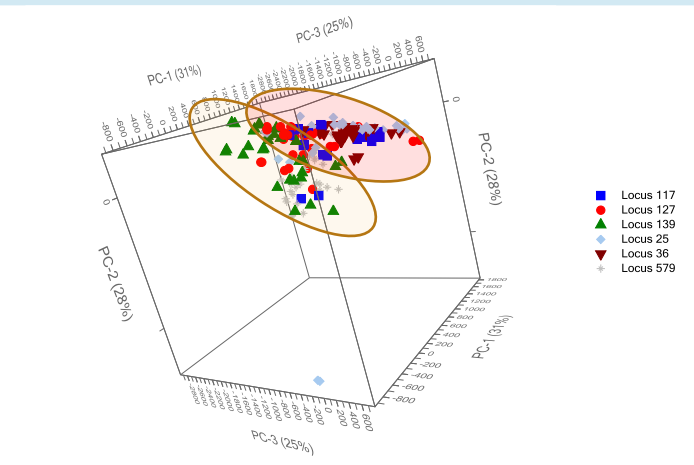
#### Select Loci Comparison

- Loci 271/579 clustered and 22/36 clustered
- Locus 522 dispersed throughout plot



#### East-West Wall Mortars

- Loci 139/579 clustered and 25/36/177 clustered
- Locus 127 dispersed throughout



#### Coriglia Trench C Loci Map



### 9. Conclusions

- Majority of samples were determined to be similar in elemental composition regarding the major elements
- The top mortar is a bit more dispersed which may be the results of contamination due to weather and/or navigating as walk ways to reach other areas of Coriglia.

#### Acknowledgements

I would like to thank Dr. Donais and Dr. George for their endless guidance and support throughout my research. I would also like to thank the Chemistry Department at Saint Anselm College for the Fr. Michael Custer O.S.B. Award, that allowed my research and journey to Italy to be possible.