Chemical Characterization of a Tower in Monterubiaglio, Umbria (Italy) Utilizing Portable X-Ray Fluorescence Spectrometry

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Objective

The mortar on two faces of a stone masonry tower in Monterubiaglio, Umbria was analyzed using portable X-ray fluorescence spectrometry (pXRF). From an autopsy of the building the lower part is of Roman technique and the upper is of medieval engineering (Figures 1 & 2).

The objective of this research was to:

- Determine whether mortar identified as visually different also differed chemically
- Assuming chemical differences did exist, determine the specific elements that did differ between the two mortars
- Compare the tower mortar to that found at the excavation site (Coriglia)

Note that funding for this research was through Saint Anselm College and the Institute for Mediterannian Archaeology under the auspices of the Soprintendenza per I Beni Archeologici dell'Umbria and the Parco Archeologico e Ambientale dell'Orvietano.

Figure 1: Tower of Study

Figure 2: North side of Tower

Background

The samples explored in this research were located on a town square tower in Monterubiaglio near Orvieto, Italy. The tower was part of the castle that was in the possession of the Monaldeschi della Cervara family from 809 until 1698. The records indicate that the base of the tower was in good shape in 809 and was recognized as an old Roman tower of unspecified date. No documented repairs have been made to areas pertaining to the study. The most extensive repair of the tower was reported in 1299 when Cardinal Theudoric ordered the building of a defensive wall into the base of the tower. He also expanded the piazza at the base (*fundò la torre de Monterubialio*) which would indicate work on the substructure of the tower below its Roman phase. The tower and castle were then passed to the current family whose archives are confidential. The next major event in its history was during World War II when the castle was bombed by the Allies. There was substantial damage, but the lower sections remained completely intact. These documentations assure that the Roman portion of the tower was preserved and could be analyzed for composition and then compared to the other sections and the excavation site.

Figure 3: Lower mortar of Roman origin, locations marked with arrows

Figure 4: Upper mortar of Medieval origin, locations marked with arrows

Instrumentation & Procedure

A Bruker AXS Tracer III-SD (Kennewick, WA) pXRF was used for analyses.

- Rh target X-ray tube excitation source, 40 kV excitation, 21 μA tube current
- Green Filter composed of 0.006 in Cu, 0.001 in Ti, and 0.12 in Al, were used for all analyses.
- Signal was collected for 120 seconds for each analysis in triplicate at each location on the tower.
- Smooth, flat sample locations were used for the analyses.
- The chosen sample locations were cleaned with a brush, marked, and digitally photographed; GPS coordinates were recorded (Figures 3 &4).
- Data were collected for cement reference materials throughout mortar analyses to assure quality control. The reference materials were: SRM 1881a Portland Cement and SRM 1886a Portland Cement (National Institute of Standards and Technology, Gaithersburg, MD).
- Two faces of the tower were analyzed for this study- one facing north and the other west.
- 12 analysis locations on lower and upper mortar in triplicate on north face.
- 5 analysis locations on lower and upper mortar in triplicate on west face.
- Data were exported as spectra and analyzed using a fully cross validated principle components analysis (PCA) with centering and no weighting of the data.

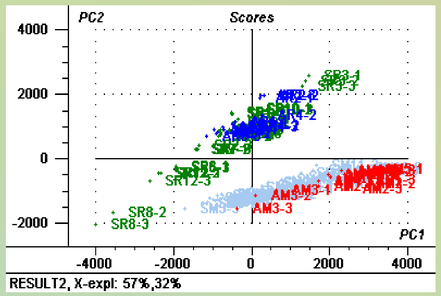

Figure 5: 2-Dimensional PCA scores plot of all mortar samples
SR – West wall, Roman mortar
AR – North wall, Roman mortar
SM – West wall, Medieval mortar
AM – North wall, Medieval mortar

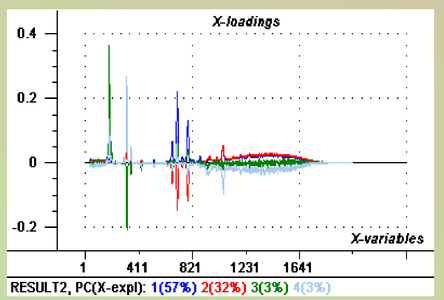

Figure 6: PCA Loadings plot of all mortar samples

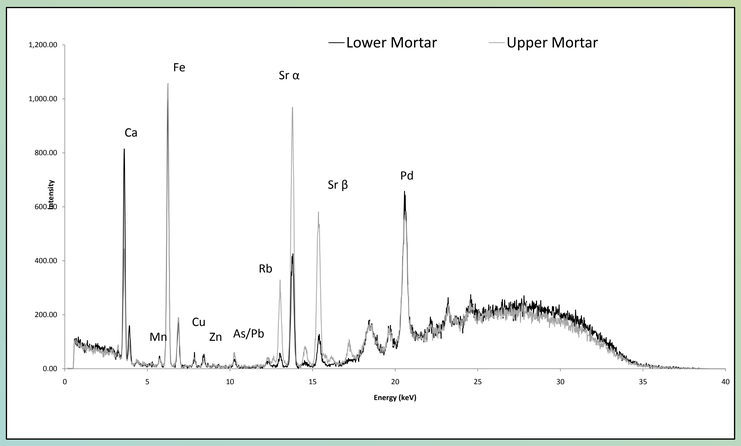

Figure 7: Overlay of XRF spectra with the **Roman (Lower)** mortar having a darker and more full accent, and the Medieval (Upper) mortar having a lighter appearance.

Results & Discussion

The 2-dimensional scores plot (Figure 5) shows

- The Roman mortars on the two different walls are in one cluster showing they are similar in chemical composition.
- The Medieval mortars on the two different walls are in one cluster showing they are similar in chemical composition.
- The Roman mortar and Medieval mortar are in separate clusters showing they are different in chemical compostion.

The loadings plot (Figure 6) was used to determine which elements explained the variance for each PC.

- PC 1: Sr & Rb PC 2: Fe PC 3: Ca

Figure 7 is the overlay of the Roman and Medieval mortar spectra.

- Roman mortar has a significantly higher signal for Ca.
- Medieval mortar has a slightly higher signal for Fe, Sr and Rb.

Calcium is the major component of mortar in various forms such as calcite, dolomite, and gypsum. The lower calcium signal for the Medieval mortar indicates that non-calcium containing materials are used in higher amounts in the this mortar, possibly as filler.

Two-way analysis of variance (ANOVA) with replicates was performed on peak areas (Ca, Cu, Fe, Mn, Pb, Rb, Sr, Zn, and Zr) for the lower and upper.

- Statistically significant difference at 95% confidence
- $F_{crit} = 7.13$, $F_{table} = 3.85$, for 32 degrees of freedom

Figure 8 shows pXRF spectra collected for wall mortars at the Coriglia excavation site. Instrument conditions were identical to those for the tower mortars analyses.

- Mortars from trench C are of similar compositions.
- The Roman Tower mortar is not similar to the Trench C mortars.
- Roman Tower mortar and Trench B mortar.

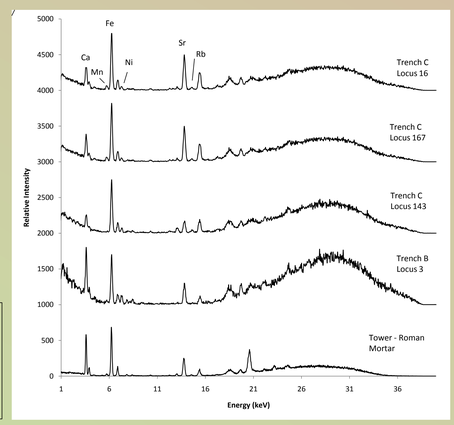

Figure 8: A comparison of tower mortar to mortar found at the excavation site, organized by Trench and Loci identification.

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