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GEOCHEMICAL EVIDENCE FOR INTEGRATED CERAMIC AND ROOF TILE INDUSTRIES AT THE ETRUSCAN SITE OF POGGIO COLLA, ITALY

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ABSTRACT

We conducted a geochemical study to characterize the composition of ceramics, tiles, and local sediments from the Poggio Colla Etruscan archaeological site north of Florence, Italy. We consider whether these wares were locally produced, as well as address the broader question of the organization of the ceramic industry at Poggio Colla. X-ray fluorescence was used to determine sample geochemistry. We also used X-ray diffraction and petrography to infer the mineral content; thermogravimetic analysis to consider the effects of firing; and macroscopic observations for qualitative content and textures. The mineral constituents in typical Podere Funghi and Poggio Colla pottery sherds and tile fragments included abundant quartz, some feldspar, and minor amounts of mica. Lithics (including a red sandstone) and grog were also observed. Comparing groups using principal component analysis showed that the compositions of the Podere Funghi and Poggio Colla tile and pottery groups are similar but the rock and sediment specimens were compositionally different. This lends support to the hypothesis that diverse components of a ceramic industry co-existed in close proximity to the Poggio Colla acropolis, although neither a kiln nor a specific local source has yet been identified.

KEYWORDS: X-ray fluorescence, X-ray diffraction, thermogravimetry, petrography, provenance, principal component analysis, Etruscan ceramics

1. INTRODUCTION

The Etruscan site of Poggio Colla is located in the Mugello Valley, Tuscany, Italy, approximately 35 km northeast of Florence (Figure 1). Archaeologists from Southern Methodist University, Franklin & Marshall College, and the University of Pennsylvania Museum of Archaeology and Anthropology have been investigating the site since 1995. Two types of settlement, spanning the mid-seventh century BCE to the second quarter of the second century BCE, have been uncovered in these excavations (Warden et. al., 2005).

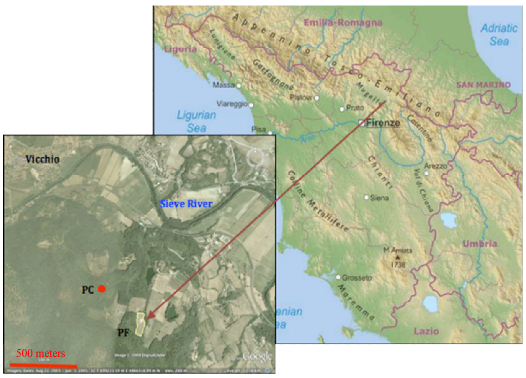

Figure 1. Location map of Poggio Colla.

The first is an acropolis with significant architectural foundations on the hill known as Poggio Colla. The architecture along with a number of deposits of votive material, including bronze objects, jewelry, and a statue base, suggest a sanctuary space, with at least three distinct building phases (Warden, 2009). On the northeast slope of Poggio Colla, a second excavated area, known as the Podere Funghi, has produced a smaller structure dating to the mid-fourth to mid-second centuries BCE. This simple rectangular building with a hearth at its center has been interpreted as a domestic space that also functioned as a rural ceramic workshop. Ceramic production is evidenced by at least four kilns adjoining and beneath the structure, a nearby midden containing ceramic wasters, and the results of a shovel test survey in the Podere Funghi (Bon-Harper, 2011). In addition, a deposit of heavily broken and re-used roof tiles utilized as floor packing for the second building phase of the Podere Funghi structure may indicate that roofing tiles were also produced in the area. Although a kiln for the firing of roof tiles has not yet been found, the size (approximately 62 cm x 48 cm for a standard pan tile) and weight of the tiles suggest it is highly unlikely that they would not have been made in close proximity.

Previous studies have examined the geochemistry of Etruscan ceramics and tiles in conjunction with various archaeological questions. These have focused on the acquisition and location of raw clay sources (Ammerman et al., 2008; Fermo et al., 2004; Gliozzo et al., 2011); the relationship between production and regional trade distribution patterns (Gliozzo and Memmi Turbanti, 2004); kiln temperatures and firing procedures (Maritan, 2004); and the specific collaboration and influence of distinct workshops and techniques (Winter et al., 2009).

We have conducted a geochemical study to characterize the composition of the various ceramics and tiles from the Poggio Colla site, including the fine ware sherds from the Podere Funghi midden, which were likely produced on-site because they were mixed with the wasters. If the chemical compositions of the tiles, coarse wares, and bucchero ceramics were similar to the Podere Funghi fine wares' geochemical fingerprint, a reasonable conclusion would be that all the tile and pottery groups were made from the same raw clays and tempers, which would then support a local production hypothesis (Buxeda i Garrigós, 2001).

Our study thus considers a broader question about the organization of the ancient ceramic industry by utilizing geochemical results to consider the full spectrum of ceramic production on the slopes of Poggio Colla. Although several standard archaeological techniques (i.e. excavation, typological and stylistic analysis) have been employed and point to a ceramics industry that was producing wares for local usage, geochemical data allow for a more precise understanding of the integrated relationship between the production and usage of ceramics and tiles (Meyers et al., 2010). Our current research not only seeks to ascertain whether or not geochemical composition supports the hypothesis of local production, but also asks whether there are compositional similarities between different ceramic types (bucchero, fine ware, and coarse ware) or between diverse artifacts, such as utilitarian pottery and terracotta roofing elements. Such similarities would suggest a collaborative ceramics industry, capable of diversifying production among traditional ceramic products and architectural elements such as roof tiles. While a few Etruscan sites, such as Poggio Civitate, Marzabotto, and Laurentina-Acqua Acetosa, have provided evidence for such incorporated industry through the excavation of workshop remains alone, our documentation of integrated ceramics and tile production at Poggio Colla through both archaeological and geochemical methods provides a convincing example of a long-standing local ceramic industry in ancient Etruria. In addition, as a sanctuary with ceramic production space in such close proximity, our research at Poggio Colla provides rare evidence for the economic life of an Etruscan religious center.

2. CERAMICS AND GEOCHEMISTRY

Since the 1950s, archaeometric studies of ceramics have revealed information on the life cycle of pottery (Tite, 2008). Ceramic provenance studies can use geochemistry and petrography to provide evidence for local production of pottery in four ways (Stoltman, 2001): comparing ceramic temper material with possible local sources; comparing ceramic pastes with possible local sources; comparing a vessel with others known to be locally produced; comparing variability within a class of vessels. Stoltman (2001) refers to the first and second approaches as the provenance postulate, the third as the local-products-match postulate, and the fourth as the "spatial pattern postulate." Examples of these approaches include provenance studies to determine: sources of raw clay (Ammerman et al., 2008); the source area of tempers (Pecchioni et al., 2007); and trade patterns (Gliozzo and Memmi Turbanti, 2004). While it is possible to provenance ceramic materials to original clay beds, it has proven notably difficult due to: possible removal of the source due to erosion of the landscape over time (Grave et al., 2009); compositional modification of clays during refinement and tempering (Nijboer, 1998); and post-depositional chemical alteration of artifacts (Freestone, 2001; Maritan and Mazzoli, 2004; Mommsen, 2001; Buxeda i Garrigós, 1999). Nevertheless, it is noteworthy that ethnographic studies have found that potters prefer raw clay and temper sources lie within one kilometer, and at most seven kilometers, of a ceramic workshop (Nijboer,1998).

In the archaeometric and archaeological literature, one finds several provenance/production studies that have been successful in determining the raw sources of clay at Etruscan sites (Ammerman et al., 2008; Fermo et al., 2004), characterizing ceramics from various Etruscan sites to test local production hypotheses (Fermo et al., 2004; Maritan, 2004), and discovering ancient trade patterns in Etruria (Gliozzo and Memmi Turbanti, 2004). These studies also used firing tests to determine the kiln temperatures used to produce the analyzed pottery (Maritan, 2004), assessed the suitability of clay for ceramic/tile manufacture (Ammerman et al., 2008), and tested how firing temperatures affected the chemical composition of clays and ceramic sherds (Fermo et al., 2004). Notably, Fermo et al. (2004) found no significant variation after heating the clays and ceramic sherds to 700, 900, and 1000°C. Geochemical analytical methods -- e.g., flame atomic emission spectrometry (AES), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA), and XRF analysis -- combined with various types of statistical analyses formed the backbone of all these provenance studies, with petrographic and mineralogical (e.g., X-ray diffraction) analyses making important contributions to some.

The research presented here continues this line of study. We primarily use geochemical data from XRF analyses of fine wares, coarse wares, bucchero ceramics, tiles, and local sediments (potential clays) to test the hypothesis that local manufacture of many ware and tile types occurred. Furthermore, through comparison of the pottery and tile to the sediments, we consider whether these sediments could represent the potential sites of ancient raw source material used in local production.

3. MATERIALS AND METHODS

Several groups of samples are included in this study. The first group was studied by Weaver et al. (2006), who used X-ray diffraction (XRD) and X-ray fluorescence (XRF) on ceramics and tiles from the Podere Funghi midden and on Poggio Colla bucchero pottery. In 2006, a second group of roof tile fragments from both Podere Funghi and Poggio Colla was added to this sample. Finally, a third group of ceramics and raw clay specimens from Poggio Colla and Podere Funghi were analyzed by Didaleusky (2009). The complete set of samples measured at Franklin & Marshall College (F&M) comprised 37 Poggio Colla tile fragments, 37 Podere Funghi tile fragments, 22 Podere Funghi coarse ware sherds, 38 Podere Funghi fine ware sherds, one Podere Funghi black gloss sherd, and one Podere Funghi mud brick (Weaver et al., 2006). The group measured at Smith College is made up of ceramics from Poggio Colla (three bucchero sherds, 19 coarse ware sherds, 13 fine ware sherds), 18 sediments/clays from the Podere Funghi, and three rock specimens (lithified clay-like material such as mudstone and sandstone) from road cuts in the surrounding area (Didaleusky, 2009).

Trace element and major oxide analyses by XRF were the primary techniques we used. The XRF spectrometer at F&M is a Panalytical 2404 with a 4 kW Rh energy source. A flux-fusion technique was employed to determine major and minor element concentrations, while a sample powder-copolywax binder technique was used in the measurement of trace element concentrations. Working curves for each element were determined by analyzing geochemical rock standards (Abbey, 1983; Govindaraju 1994). Accuracy and precision of this instrument is given by Mertzman (nd). The methodology and equipment used in preparing the F&M specimens ensure essentially no contamination, with a maximum of a few percent enrichment in Al_2O_3 from the alumina pulverizer. However, given the relatively high Al_2O_3 compositions of the analyzed specimens (~15 to 21 wt% Al_2O_3) and the precision of the XRF spectrometer, this contamination is inconsequential. The same cannot be said of the Smith specimens, which are likely to be contaminated in Co, Nb, Zr, (trace elements) and possibly TiO_2 (a minor oxide) due to pulverization in tungsten-carbide shatterboxes. Therefore, the compositional results of the Smith samples should be regarded with caution.

We used XRF to determine the major element oxide compositions of all F&M and Smith specimens, except for two Smith fine ware sherds (CER 8 and CER 13). Most of the F&M coarse ware Podere Funghi sherds (total n = 20), Poggio Colla tile fragments (n = 30), Podere Funghi tile fragments (n = 26), and some Podere Funghi fine ware (n = 6) were also analyzed for trace element composition by XRF. For the Smith specimens, trace element XRF analyses were carried out on 11 Poggio Colla fine wares, 20 Poggio Colla coarse wares, three rock (lithified clay-like material) specimens, and 15 sediment/clay specimens.

Samples were also examined by: macroscopic viewing of uncrushed pottery sherds and tile fragments using a 10x hand lens for 101 F&M specimens; use of a stereoscopic microscope to analyze the uncrushed F&M pottery sherds and tile fragments; microscopic viewing of 27 thin sections using a petrographic microscope; XRD analysis of four hydrous F&M (<80 mesh) specimen powders and 31 Smith specimens; thermogravimetric analysis (TGA) of four hydrous F&M specimen powders after crushing to a finer size than 80 mesh.

Whereas the TGA, XRD, macroscopic, and petrographic analyses serve a qualitative role in our provenance study, the XRF analyses provide quantitative chemical compositions. Statistical analysis of compositional data is discussed by Aitchison (1986), Buccianti et al. (2006), and Baxter and Freestone (2006). The major oxide and trace element data were prepared for analysis with CoDaPack3D software (Comas-Cufí and Thió-Henestrosa, 2011) by normalization to 100 wt%. We applied a centered log-ratio transformation (Howel, 2007) to improve the compositional data distribution for multivariate statistical analysis (Krzanowski, 2000). For multivariate statistical analyses (Baxter, 2001) with software packages SPSS and JMP, we primarily used principal component analysis (PCA). Cluster analysis and discriminant analysis were used to support hypotheses based on PCA, especially when groups could not be geochemically distinguished. Principal components representing a high fraction of the data's variability (usually 70 to 80%) were plotted in 3-dimensional scatterplots. Tentative hypotheses about group relationships based on PCA were corroborated by cluster analyses and discriminant analyses. For example, if groups appeared geochemically similar in a 3D principal components plot, cluster analysis was used to test that clusters were composed of specimens from multiple groups, and discriminant analysis was used to test that classification schemes worked poorly, implying little discrimination among groups and substantial compositional overlap of the groups.

4. RESULTS

The XRD analyses, petrographic analyses, and macroscopic observations indicate that the dominant mineral constituents in typical Podere Funghi and Poggio Colla pottery sherds and tile fragments include much quartz and some feldspar, together with lesser amounts of several types of mica. Additional visible components are lithics and older ceramic fragments (i.e., grog). Microcrystalline to cryptocrystalline to amorphous matrix-forming material constitutes the "glue" that holds all the other constituents together. A common lithic element of note is what appears to be a dark red, quartz-rich sandstone; for the macroscopically analyzed F&M pottery sherds and tile fragments, this "red sandstone" was observed in ~51% of Poggio Colla tiles, ~30% of Podere Funghi tiles, ~55% of Podere Funghi coarse wares, and ~50% of Podere Funghi fine wares. Notable mineralogical and petrographic peculiarities include: the presence of dolomite in Smith coarse ware specimen CER 31 as evidenced by XRD analysis; a pyroxene crystal in Smith coarse ware CER 31 and a gastropod fossil in Smith coarse ware specimen CER 28 found in petrographic analysis; and abundant large feldspar crystals as inclusions in some of the Podere Funghi and Poggio Colla tiles and coarse wares.

Macroscopic examination indicates that a typical Poggio Colla or Podere Funghi tile is generally heterolithologic in nature; that is, it is a coarse mixture of mineral grains, rock, and grog pieces that are several millimeters in their longest dimension and are situated in a very fine-grained matrix. That being said, there is high variability in the sizes, shapes, abundances, and colors of the quartz, feldspar, mica, rock, and grog inclusions found in the Poggio Colla and Podere Funghi tiles. Most tile specimens (~81% of F&M Poggio Colla tile fragments; ~86% of F&M Podere Funghi tile fragments) contain abundant quartz grains that are conspicuous under a 10x hand lens, and commonly visible without any magnification. In other specimens, the quartz grains are smaller and less abundant. While feldspar grains are commonly present as small and sparse inclusions, several tile specimens (Poggio Colla specimens IPW#20 and IPW#25; Podere Funghi specimens PFCW19 and PFCW30) lack easily discernible quartz grains and contain abundant large feldspar crystals up to 4 mm in their longest direction.

The XRD analysis of the four previously mentioned F&M specimens produced quite

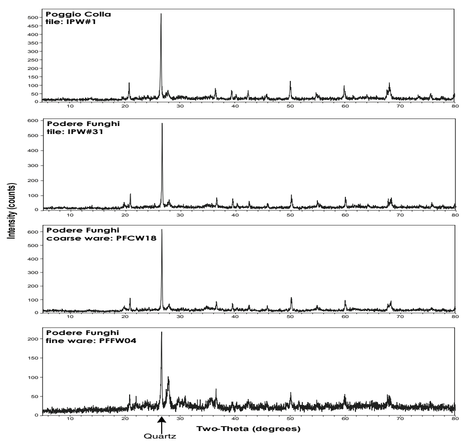

Figure 2. X-ray diffractograms from a Poggio Colla tile and a Podere Funghi tile, coarse ware, and fine ware. The quartz peak is labeled.

similar results, as seen in the X-ray diffractograms of Figure 2.

The patterns are basically the same; the mineral quartz consistently produces the highest intensity peak, consistent with its abundance in the majority of the tile and pottery samples as seen in thin sections and hand samples. The much smaller peaks result from a mixture of two feldspars, plagioclase and a potassium feldspar. That no other minerals (such as the micas observed in macroscopic analysis) are evident in XRD means that all other mineral constituents of these tiles and pottery comprise less than a few percent of the sample. The XRD analyses of the Smith specimens also indicated the presence of quartz and plagioclase feldspar; one coarse ware specimen (CER 31) had a dolomite signal in its diffractogram. Montmorillonite/illite, kaolinite, and quartz peaks were present in the Smith clays' X-ray diffractograms; montmorillonite/illite and quartz were also found in the Smith rock specimens by XRD analysis.

Petrographic analyses of thin sections detect some mineral constituents missed by XRD, most notably micas. Figure 3, a photomicrograph taken with uncrossed polarizers, shows one such mica grain, a 0.4 mm long muscovite that possesses very prominent (0001) cleavage traces. This image also reveals abundant quartz grains of very diverse sizes (e.g., those marked by the lower right arrows), highlights the heterolithologic nature of the tiles, and provides evidence that quartz was a major component of the temper used by the ancient tile maker. Other studies of ancient Etruscan and early Roman tiles suggest that certain inclusions may have been added to the clay to improve drying without cracking and reduce shrinkage (Winter, et. al. 2009; Wikander 1993).

Figure 4 displays the same image as Figure 3, but with crossed polars. The characteristic highly colorful nature of the birefringent muscovite under crossed

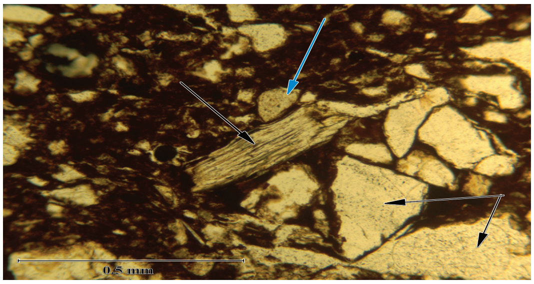

Figure 3. Photomicrograph of Podere Funghi tile PFCW06. The central arrow shows a muscovite mica crystal; the lower right arrows indicate a couple of the abundant quartz grains; the blue arrow points towards a possible lithic fragment.

polars is in stark contrast to the white of the quartz crystal, which has low birefringence. Much of the matrix surrounding these crystals is essentially black, identifying this material as amorphous.

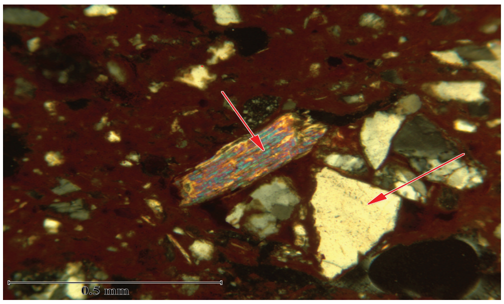

Figure 4. This photomicrograph shows the same image as Figure 3, but with the polarizers of the petrographic microscope crossed (scale 0-5mm).

In the four F&M specimens analyzed with TGA, any ferrous iron (Fe^{+2}) present should be oxidized to ferric iron (Fe^{+3}), which would result in a small weight gain. However, this effect was overwhelmed by weight loss, as shown in Figure 5. The weight loss can result from dehydration of structural water released from clay and micaceous minerals, or devolatilization loss from the amorphous matrix-forming materials. Figure 5 shows that the general shapes of the weight-vs-temperature curves are similar for all ware types, suggesting that the specimens are made of a similar mix of mud-sized and sand sized materials

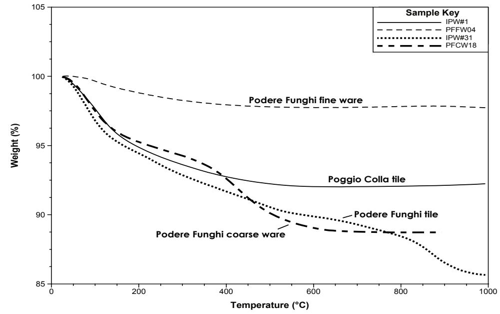

Figure 5. TGA results for normalized weight-vs.-temperature plots of four tile, coarse ware, and fine ware specimen (scale 0-5mm).s.

with some coarser fragments. What appears to be a systematic difference between the curve shapes for the tiles and coarse ware vs. the curves exhibited by the fine ware might be attributable to differences in original firing temperatures or to variable processes in post-burial alterations of these different ceramic fabrics.

Table 1 is a summary of the XRF results; the full compositional data set is available from the authors. Principal component plots of these results are illustrative of the multivariate structure and inter-group relationships of the Podere Funghi and Poggio Colla data, so we present a few examples here that summarize our observations. Figure 6 plots the first three principal components of XRF trace element data (14 elements: Ce, Cr, Cu, Ga, La, Ni, Pb, Rb, Sc, Sr, Th, V, Y, and Zn) for a number of the F&M and Smith Podere Funghi and Poggio Colla samples (n = 117: 55 tiles, 13 fine wares, 34 coarse wares, three bucchero ceramics, nine sediments/clays, and three rocks/lithified sediments). The results were center log-ratio transformed prior to PCA. The Ba data were removed from the PCA due to barium's potential as a post-burial contaminant. The Co, Nb, and Zr results were not included in the analysis due to probable contamination of these trace elements in the Smith specimens during pulverization.

Figure 6 shows three-dimensional principle component scatter plots with the

Table 1. Geochemical data by group. PC - Poggio Colla; PF – Podere Fughi. Only the major and minor oxides and trace elements for the Smith specimens that are thought to not be contaminated by pulverization are presented. The values in standard font represent the centers of the groups. The italic numbers are standard deviations for a group's oxide and trace element components. These data have been normalized.

Group/type	#	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Ba	Ce	Cr	Cu	Ga	La	Ni	Pb	Rb	Sc	Sr	Th	V	Y	Zn
F&M	29	68.1	17.7	6.45	0.07	1.78	1.13	1.36	2.22	1.13	558	69	114	34	20	34	50	20	105	15	95	11	109	28	79
PC tile		*2.8*	*1.2*	*0.68*	*0.04*	*0.74*	*0.83*	*0.30*	*0.27*	*0.55*	*77*	*9*	*37*	*36*	*2*	*4*	*23*	*5*	*18*	*3*	*21*	*2*	*19*	*4*	*17*
F&M	26	67.2	18.4	7.10	0.07	1.72	1.06	1.17	2.18	1.06	536	65	110	34	21	31	56	19	103	16	93	11	117	25	90
PF tile		*2.6*	*1.3*	*0.54*	*0.04*	*0.75*	*1.05*	*0.17*	*0.25*	*0.64*	*98*	*9*	*61*	*10*	*2*	*5*	*27*	*4*	*19*	*2*	*30*	*1*	*16*	*6*	*21*
F&M	20	66.7	18.1	7.30	0.10	1.70	0.89	1.22	2.07	1.76	662	78	124	44	20	35	75	21	98	16	107	11	123	30	114
PF cw		*2.7*	*1.3*	*0.82*	*0.04*	*0.57*	*0.42*	*0.28*	*0.18*	*0.72*	*163*	*13*	*44*	*21*	*2*	*4*	*55*	*3*	*13*	*2*	*16*	*1*	*23*	*9*	*43*
F&M	6	64.1	18.9	7.31	0.12	2.50	1.49	1.04	2.52	1.93	687	84	150	49	22	37	89	22	119	17	128	15	125	36	126
PF fw		*4.6*	*1.7*	*1.06*	*0.02*	*0.55*	*1.07*	*0.21*	*0.33*	*1.48*	*123*	*8*	*20*	*9*	*2*	*2*	*25*	*5*	*22*	*2*	*48*	*2*	*24*	*4*	*15*
Smith	5	63.8	19.7	6.45	0.07	2.54	1.89	0.89	2.80	1.66	814	93	150	36	19	40	82	18	137	19	140	15	130	39	148
PC w		*1.6*	*1.0*	*0.36*	*0.02*	*0.37*	*1.11*	*0.27*	*0.18*	*1.47*	*98*	*9*	*13*	*8*	*0*	*4*	*7*	*4*	*20*	*1*	*36*	*1*	*15*	*2*	*7*
Smith	13	67.4	18.7	6.79	0.07	1.59	0.63	0.88	2.22	1.59	768	78	120	34	18	35	62	22	99	16	88	12	132	27	114
PC cw		*2.9*	*1.7*	*1.02*	*0.05*	*0.52*	*0.43*	*0.33*	*0.22*	*0.87*	*282*	*8*	*33*	*13*	*2*	*4*	*42*	*6*	*17*	*2*	*34*	*1*	*25*	*4*	*45*
Smith	3	67.1	18.3	6.96	0.07	1.80	0.39	1.24	2.40	1.58	640	81	143	36	18	40	78	24	121	17	77	14	131	31	115
PC bucchero		*1.3*	*0.8*	*0.45*	*0.02*	*0.27*	*0.07*	*0.07*	*0.08*	*1.02*	*55*	*8*	*12*	*7*	*2*	*3*	*8*	*3*	*12*	*1*	*4*	*0*	*13*	*5*	*32*
Smith	9	63.1	21.0	8.22	0.16	2.60	0.97	0.48	3.14	0.11	380	105	148	50	22	63	73	15	177	17	77	14	162	54	131
clay/sed		*1.5*	*1.0*	*0.95*	*0.13*	*0.30*	*0.28*	*0.26*	*0.58*	*0.05*	*90*	*27*	*19*	*21*	*2*	*28*	*42*	*5*	*26*	*1*	*10*	*1*	*10*	*38*	*26*
Smith	3	55.5	15.9	7.31	0.08	3.65	13.13	0.96	3.16	0.17	314	46	174	24	14	29	71	7	147	23	249	12	148	30	118
rock		*2.7*	*1.2*	*1.74*	*0.01*	*1.68*	*3.94*	*0.07*	*0.13*	*0.04*	*35*	*4*	*59*	*4*	*3*	*5*	*21*	*2*	*10*	*2*	*43*	*1*	*19*	*7*	*5*

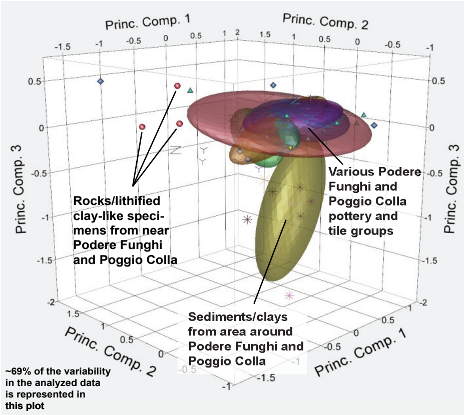

Figure 6. 3D principal components plot of center log-ratio transformed trace elements of the Podere Funghi and Poggio Colla geochemical data set (55 tiles, 13 fine wares, 34 coarse wares, three bucchero ceramics, nine sediments/clays, and three rocks/lithified sediments). The 50% confidence regions are shown as ellipsoids for all groups except the Poggio Colla bucchero ceramics and the rocks/lithified clays due to too few specimens. Symbols: PC - Poggio Colla; PF - Podere Funghi; Bucc. - bucchero; FW - fine ware; CW - coarse ware; lith. - lithified; unlith. - unlithified.

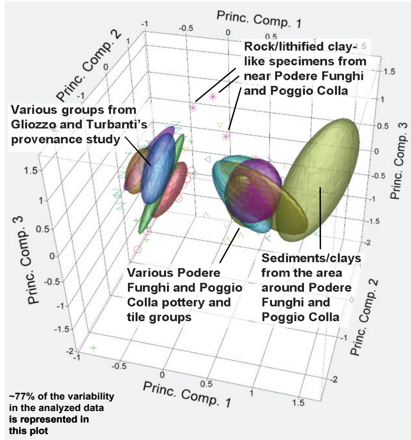

Figure 7. Same as Figure 6, but including 144 samples from Gliozzo and Memmi Turbanti (2004), and without the element gallium.

50% confidence ellipsoids for all groups except the Poggio Colla bucchero and the rocks/lithified clay groups, which contain too few specimens. The compositions of the Podere Funghi and Poggio Colla tile and pottery groups overlap substantially, but the rock and sediment specimens are compositionally different than the tiles and pottery. The geochemical reference group, the Podere Funghi fine wares, overlaps most other pottery and tile groups. The Poggio Colla fine wares overlap the least of all the pottery groups, possibly due to natural differences in gallium concentration. Although the rock specimens and most sediments are compositionally different from the Poggio Colla and Podere Funghi groups, there is some overlap of the sediment/clay ellipsoid and the Podere Funghi/Poggio Colla groups.

The similarities between the Podere Funghi and Poggio Colla groups become even more clear when ceramics known to be produced elsewhere are introduced into the PCAs (Figure 7). For this we used trace element data from Gliozzo and Memmi Turbanti (2004), who used ICP-OES, XRF, and INAA for different elements to analyse 144 black gloss specimens from other Etruscan sites to the South of Poggio Colla: Arezzo, Campania, Chiusi, Lazio, Populonia, and Volterra. Gallium was not analyzed by Gliozzo and Memmi Turbanti (2004), so was excluded. Figure 7 shows that the Podere Funghi and Poggio Colla tile and pottery groups have a chemical signature distinct from the black gloss pottery from other Etruscan sites. Furthermore, one sees that the variabilities of the Podere Funghi and Poggio Colla pottery and tile groups are relatively high compared to those of the black gloss groups. A few Poggio Colla and Podere Funghi compositional outliers are also visible on the plots. The overlap of the Podere Funghi and Poggio Colla ceramic and tile groups implies that these groups can be broadly categorized as one group.

These two principal components plots demonstrate the similarity of all the Podere Funghi and Poggio Colla pottery and tile groups. The apparent similarities of the Podere Funghi and Poggio Colla groups in these plots are supported by additional PCAs, cluster analyses, and discriminant analyses. The Smith data, while generally similar to the F&M data, show some systematic differences that suggest contamination or calibration effects. For example, one can see that the Poggio Colla fine ware ellipsoid (all these samples from Smith) is somewhat offset from the other Poggio Colla and Podere Funghi groups. Preliminary tests suggested this may be the result of systematic differences in the concentration of the trace element gallium (Ga). The systematic differences of the F&M and Smith data sets may either reflect true chemical difference between ceramics excavated at the Poggio Colla and Podere Funghi sites or effects of the different laboratory preparations for the F&M and Smith specimens. The fact that the F&M Poggio Colla tile samples do not show such systematic discrepancies compared to the Podere Funghi ceramic and tile groups supports the latter hypothesis.

The locally produced Podere Funghi fine ware specimens from the midden are chemically similar to all the other Podere Funghi and Poggio Colla fine wares, coarse wares, bucchero ceramics, and tiles. We conclude that in spite of some systematic geochemical differences, there are overall compositional similarities between the Podere Funghi and Poggio Colla pottery and tile groups that, when combined with mineralogical and petrographic similarities of these groups, suggest that that they were manufactured from raw materials with similar mineralogy and chemistry; a reasonable assumption would be that the same raw materials were used for all these ceramics. Thus inference would support the local production hypothesis.

The sediments and clays are clearly distinct from the chemically overlapping Podere Funghi and Poggio Colla pottery and tile groups, so we cannot claim to have found potential raw clay source areas in any of the Smith sediments/clays or rock. The rock specimens were distinctive in all chemical comparisons, so do not represent identifiable sources of raw clay material for the ceramics studied. Uniquely matching a ceramic to a clay source is problematic anyway, considering that the ancient potters tempered and possibly levigated their raw clay to form the pastes for different wares and tiles, processes that could have altered the raw clay's chemical compositions. Our observations suggest that a great deal of quartz, some feldspars, some lithics (which often included a "red sandstone"), and varying amounts of grog were commonly added as temper to the Podere Funghi and Poggio Colla raw clays.

Our consideration of only the trace elements in the clays and sediments might remove a large part of the geochemical effect of the tempering and better reflect the trace element composition of the raw clay. In the PCA of the sediments plus pottery and tile groups (Figure 6), a few of the sediment/clays appear relatively close in composition to some of the pottery and tile specimens. Sediment/clay specimens CL 19 and CL 44 are consistently most similar in trace element chemistry to that of the average Podere Funghi and Poggio Colla ceramic or tile. However, in the analyses, these two sediment compositions are outside or at the very edge of the chemical ranges of the current ceramic and tile specimens. We remain cautious about the implications of this observation because of the low number of similar clay/sediment specimens, their possible contamination, and the unresolved effects of raw clay tempering and refinement.

5. CONCLUSIONS AND ARCHAEOLOGICAL IMPLICATIONS

Overall, the archaeometric studies herein provide several lines of evidence that support the local provenance hypothesis:

1. The Podere Funghi and Poggio Colla fine wares, coarse wares, bucchero ceramics, and tiles are consistently (and not surprisingly) quartz-rich, as implied by the relatively high SiO_2 concentrations. Quartz was a major component of the temper the ancient potters used.

2. Plagioclase and potassium feldspars are other common temper components.
3. Lithic fragments are typical temper components; the presence of "red sandstone" lithics in all F&M tile and pottery groups, in addition to the all-around similar temper mineralogy, suggests the same source(s) of temper in these groups.
4. The geochemical compositional similarities between the Podere Funghi fine ware reference group and all other Podere Funghi and Poggio Colla tiles and pottery, especially for the trace element geochemistry, support the hypothesis that these tiles and pottery were made from the same raw materials.
5. A few specimens are geochemical, petrographic, and mineralogical outliers, likely of non-local provenance.
6. The sediment/clay survey has not conclusively identified any of the ancient clay bed sources, but two sites bear closer examination in future research. Although the size of plain tiles makes the geochemical possibility of a non-local provenance unlikely, this could be the case for ceramics.
7. We note that the variability of the Poggio Colla/Podere Funghi geochemistry is greater than that for the black gloss samples of Gliozzo and Memmi Turbanti (2004). An interesting speculation is whether the variability might reflect the level of control and uniformity in the production process.

Thus, the analyses of the pottery and tile groups from Podere Funghi and Poggio Colla provide important evidence for the usage and production of roof tiles and pottery in northern Etruria. The primary archaeological implications for the interpretation of the site fall into two categories: 1) the relationship between roof tiles from the two excavated areas of the Podere Funghi structure and the Poggio Colla acropolis; and 2) the role of tile production within the larger ceramic industry at the site.

The results indicate that the major and minor oxide and trace element compositions of the tiles from Podere Funghi are similar to those of the tiles from Poggio Colla. We reiterate that "similarity," as used in this study, means significant overlap in the multivariate compositional ranges/ellipsoids of the studied groups. Although the pottery and tile groups were all found to be compositionally similar, there were still large differences in variance and covariance structures that cannot currently be explained. Any differences in chemical composition ranges and variance/covariance structures of the different pottery and tile groups could be due to a variety of factors such as different paste recipes, raw sources, or compositional variability within raw source areas. Furthermore, we point out that the concept of "local" is not currently constrained. While the chemical data demonstrate a local compositional signal, the data are highly variable, and it is not known what potential combinations of raw materials might produce such compositions nor across what geographical range the raw materials exist.

It is evident that these geochemical, petrographic, and mineralogical studies reveal important information about tile and pottery production at Poggio Colla. The results point to a similarity between the chemical and mineralogical compositions of tile from Poggio Colla and Podere Funghi and ceramics from both sites, including fine ware, coarse ware, and bucchero. These similarities lend additional support to the hypothesis that diverse components of a ceramic industry were all being conducted in close proximity to, and perhaps somewhere on, the Poggio Colla hill.

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REFERENCES

Abbey, S., (1983) Studies in "standard samples" of silicate rocks minerals 1969-1982: *Geological Survey of Canada* Paper 83-15, Ottawa.

Aitchison, J. (1986) *The statistical analysis of compositional data*, Blackburn Press, Caldwell, NJ.

Ammerman, A.J., Iliopoulos I., Bondioli, F., Filippi, D., Hilditch, J., Manfredini, A., Pennisi, L. and Winter, N.A. (2008) The clay beds in the Velabrum and the earliest tiles in Rome. *Journal of Roman Archaeology,* vol. 21, 7-30.

Baxter, M.J. (2001) *Multivariate analysis in archaeology.* In Handbook of archaeological sciences, D. R. Brothwell and A. M. Pollard (eds.), John Wiley and Sons, Chichester, 685-694.

Baxter, M.J. and Freestone, I.C. (2006) Log-ratio compositional data analysis in archaeometry. *Archaeometry*, vol. 48, 511-531.

Bon-Harper, S. (2011). Investigating Etruscan Ceramic Production at the Podere Funghi. *Etruscan Studies,* vol. 14, 125-140.

Buccianti, A., Mateu-Figueras, G. and Pawlowsky-Glahn, V. (eds.) (2006) *Compositional data analysis in the geosciences: from theory to practice,* Geological Society, Special Publications No. 264, London.

Buxeda i Garrigós, J. (1999) Alteration and contamination of archaeological ceramics: the perturbation problem. *Journal of Archaeological Science,* vol. 26, 295-313.

Buxeda i Garrigós, J., Kilikoglou, V. and Day, P.M. (2001) Chemical and mineralogical alteration of ceramics from a Late Bronze Age kiln at Kommos, Crete: the effect on the formation of a reference group. *Archaeometry*, vol. 43, 349-371.

Comas-Cufí M. and Thió-Henestrosa S. (2011) CoDaPack 2.0: a stand-alone, multi-platform compositional software, Egozcue JJ, R. Tolosana-Delgado and M. I. Ortego (eds.), CoDaWork'11: *4th International Workshop on Compositional Data Analysis.* Sant Feliu de Guíxols.

Didaleusky, J. (2009) Geochemical and mineralogical comparison between clays and ceramics from the Etruscan archaeological sites of Poggio Colla and Podere Funghi, Tuscany, Italy. *Proceedings of the twenty-second annual Keck Research Symposium in Geology.* April 2009, Franklin & Marshall College, A.P. de Wet (ed.), Lancaster, Pa.

Fermo, P., Cariati, F., Ballabio, D., Consonni, V. and Bagnasco Gianni, G. (2004) Classification of ancient Etruscan ceramics using statistical multivariate analysis of data. *Applied Physics A: Materials Science & Processing*, vol. 79, 299-307.

Freestone, I.C. (2001) *Post-depositional changes in archaeological ceramics and glasses.* In Handbook of archaeological sciences, D. R. Brothwell and A. M. Pollard (eds.), John Wiley and Sons, Chichester, 615-624.

Gliozzo, E. and Memmi Turbanti, I. (2004) Black gloss pottery: production sites and technology in northern Etruria, part I: provenance studies. *Archaeometry*, vol. 46, 201-225.

Gliozzo, E., Comini, A., Cherubini, A. Ciacci, A. Moroni, A. and Memmi Turbanti, I. (2011) Ceramic production and metal working at the Trebbio archaeological site (Sansepolcro, Arezzo, Italy), Memmi Turbanti, I. (ed.), *Proceedings of the 37th*

International Symposium on Archaeometry, Springer-Verlag Berlin, 61-69.

Govindaraju, K. (1994) 1994 Compilation of working values and sample description for 383 geostandards. *Geostandards Newsletter,* vol. 18, 1-158.

Grave, P., Kealhofer, L., Marsh, B., Sams, G. K. Voigt,M. and DeVries, K. (2009) Ceramic production and provenience at Gordion, Central Anatolia, *Journal of Archaeological Science*, vol. 36, 2162-2176.

Howel, D. (2007) Multivariate data analysis of pollutant profiles: PCB levels across Europe. *Chemosphere*, vol. 67, 1300-1307.

Krzanowski, W.J. (2000) *Principles of multivariate analysis: a user's perspective.* Oxford University Press, Oxford.

Maritan, L. (2004) Archaeometric study of Etruscan-Padan type pottery from the Veneto region: petrographic, mineralogical and geochemical-physical characterization. *European Journal of Mineralogy,* vol. 16, 297-307.

Maritan, L. and Mazzoli, C. (2004) Phosphates in archaeological finds: implications for environmental conditions of burial. *Archaeometry*, vol. 46, 673-683.

Mertzman, S. (nd) Precision and accuracy. http://www.fandm.edu/earth-and-environment/precision-and-accuracy, accessed 3 Aug. 2012.

Meyers, G.E., Jackson, L.M., and Galloway, J. (2010) The production and usage of non-decorated Etruscan roof-tiles, based on a case study at Poggio Colla. *Journal of Roman Archaeology,* vol. 23, 303-319.

Mommsen, H. (2001) Provenance determination of pottery by trace element analysis: problems, solutions, and applications. *Journal of Radioanalytical and Nuclear Chemistry,* vol. 247, 657-662.

Nijboer, A.J. (1998) *From household production to workshops; archaeological evidence for economic transformations, pre-monetary exchange and urbanisation in central Italy from 800 to 400 BC.* Ph.D. thesis, Groningen University.

Pecchioni, E. Cantisani, E., Pallecchi, P., Fratini, F., Buccianti, A., Pandeli, E., Rescic, S. and Conticelli, S. (2007) Characterization of the amphorae, stone ballast and stowage materials of the ships from the archaeological site of Pisa-San Rossore, Italy: inferences on their provenance and possible trading routes. *Archaeometry*, vol. 49, 1-22.

Stoltman, J.B. (2001) The role of petrography in the study of archaeological ceramics, In Earth sciences and archaeology, P. Goldberg, V. T. Holliday and C. R. Becker (eds.), Kluwer Academic, New York, NY, 297-326.

Tite, M. S. (2008) Ceramic production, provenance and use–a review. *Archaeometry*, vol. 50, 216-231.

Warden, P. G. (2009) Remains of the ritual at Poggio Colla. In Votives, places and rituals in Etruscan religion: studies in honor of Jean MacIntosh Turfa, M. Gleba and H. Becker (eds.), Brill Academic Publishers, Leiden, 107-22.

Warden, P.G., Thomas, M. L. Steiner, A. and Meyers, G. (2005) Poggio Colla: a N Etruscan settlement of the 7th-2nd c. B.C. (1998-2004 excavations). *Journal of Roman Archaeology,* vol. 18, 252-266.

Weaver, I.P., Steiner, A. R., Mertzman, S. A. and Vaden, C. (2006) Ceramics from the Etruscan settlement of Poggio Colla in Tuscany: a chemical characterization and provenance study. *Abstracts with Programs - Geological Society of America,* vol. 38.7, 215.

Wikander, Ö. (1993). Acquarossa VI.2. The Roof Tiles. Typology and Technical Features. Acta Instituti Romani regni Sueciae, series 4, vol. 37.

Winkler, J.J., Taylor, R.H. and Warden, P.G. (2005) Ceramic production and distribution in Late Iron Age Etruria: an example from the Mugello Basin. *Geoarchaeological and Bioarchaeological Studies*, vol. 3, 283-286.

Winter, N., Iliopoulos, I. and Ammermann, A. J. (2009) New light on the production of decorated roofs of the 6th century B.C. at sites in and around Rome. *Journal of Roman Archaeology,* vol. 22, 6-28.

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