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Chemical Analysis of prehistoric pottery complex of Valcorrente - Sicily (Italy)

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Abstract. This paper is aimed at studying different pottery sherds excavated in the site of Valcorrente, located in Sicily, occupied in three main periods, dating respectively to the end of the Neolithic period, to the end of the Chalcolithic period, and to the Early Bronze Age. The chemical composition of the pottery sherds has been analysed with Ion Beam techniques at AGLAE facility at Centre de Recherche et Restauration des Musées de France and the results have been treated with principal component analysis in order to extract indications about the ceramic production technology in the area and the evolution in time.

1. Introduction

Pottery, thanks to the evidence of changes in technology, style, and use, is one of the best indicators for the definition of chronological sequences, reconstruction of economic, domestic, social, and symbolic activities, as well as the definition of areas and exchange system, connections, and relations between communities, sometimes even through long distances. The typological and stylistic analysis, associated with archaeometric studies of the fabrics, allows us to analyze the changes in both the manufacture processes adopted by the craftsmen and in the practical and symbolic uses

Valcorrente site is situated on a low hill on the south-western slopes of the volcano Etna, on the outskirts of the plain of Catania, less than 20 km from the sea. It was fortuitously identified in 2005 during some agricultural works and was systematically excavated from 2012 to 2015 by the University of Catania and the Local Archaeological service with three large trenches: two located in proximity to a rescue excavation conducted in 2005, and another one 80 m to the east, to ascertain the overall extension of the site. This issue was also tackled through an extensive survey that was carried out in 2013 and led to a hypothesis that during the EBA an area of about two hectares had been frequented [1-3]. The excavations revealed three main periods of frequentation, which date respectively to the end of the Neolithic period, to the end of the Chalcolithic period, and to the Early Bronze Age, dated with C14 and TL and OSL methods [4] between the end of fifth mill. BC and the half of the second mill. BC.

The different pottery fabrics recognized, belonging to different periods, seem to be mostly locally produced, although it is likely that different technological choices are related to the function of the different classes of materials. The aim of the work is to study similarities and difference in sherd coming from different periods to look for an evolution in production techniques and raw material origin.

2. Materials and methods

2.1. The samples
A set of 33 ceramic sherds among all the excavated ones has been chosen for this study; they are illustrated in figure 1. According to archeology classification, two sherds are remains of furnace, and they are identified as 101 and 102. The other fragments (numbers from 1 to 40) refer to similar vase forms, mainly closed vessels, with various fabric type. The production period ranges from Neolithic (NEO) to Final Copper – Bronze Age (FC-BA) and to Bronze Age (BA). The details about the identification code, and the dating are shown in Table 1.

Figure 1. Picture of analysed sherds

2.2. The PIXE analysis
The chemical composition of all the sherds has been obtained with PIXE analyses, widely used in archaeometry to obtain for different materials the major and minor components, with very low detection limits and small uncertainties. Measurements have been performed at the New AGLAE facility (ANR-10-EQPX-22) of the Centre de Recherche et Restauration des Musées de France (C2RMF) in the Louvre Palace in Paris [5].
A 3 MeV proton beam was extracted through a 0.1 μm thick Si_3N_4 window (surface 1 mm^2) and delivered to the samples 2 mm downstream, with a magnetic focus allowing a beam spot about 50 μm wide. Three 50 mm^2 SDD detectors were used with 50 μm aluminium filter to enhance the detection of high energy X-Rays, while one SDD with a smaller solid angle was used in helium atmosphere to enhance the response to low energy X-Rays. The sherds have been abraded by sandpaper and cleaned with ethylic alcohol to eliminate the contribution to the PIXE analysis of surface secondary alteration product due to the burial environment. For each sample several measurements were done, on internal and external surfaces and over the broken edge, i.e., in the bulk of the sherd. Inhomogeneity effects of sample were reduced in each measurement by analysing a 0.5×0.5 mm^2 wide area, scanned by combining rapid vertical magnetic deflection of the beam with horizontal mechanical translation of the sample holder. PIXE data sorting was performed with TRAUPIXE [6] AGLAE's software using the GUPIX code.

In Table 1, the PIXE analysis results, in terms of major (MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, Fe_2O_3, minor (P2O5, Cr_2O_3, MnO) and trace elements (NiO, CuO, ZnO, Ga_2O_3, Rb_2O, SrO, Y_2O_3, ZrO_2), are listed.

Table 1. Major, minor and trace elements (ppm) of the analysed sherds

Sample	Type	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	NiO	CuO	ZnO	Ga_2O_3	Rb_2O	SrO	Y_2O_3	ZrO_2
S1	BA	29514	182881	573425	5426	23489	73862	14314	202	928	81263	63	66	737	36	115	494	55	336
S2	BA	23230	176957	608679	10538	24007	49804	14007	203	832	83965	59	50	204	31	125	519	37	270
S3	BA	21400	157024	637077	15859	18837	40394	16748	230	773	85058	83	78	280	27	108	429	26	267
S4	BA	25148	190539	603792	10989	20497	46532	13909	178	1952	82115	76	88	318	33	155	368	38	250
S5	BA	20398	194424	544988	13117	15473	45448	27767	65	1680	118765	81	68	209	30	53	718	27	322
S6	BA	32975	186477	570617	7321	22901	68979	14013	187	1240	81690	69	55	393	28	100	661	30	273
S7	BA	17200	187610	607776	16913	18435	50741	14214	171	1064	74660	80	61	183	32	77	854	40	351
S8	BA	20088	162522	581003	8695	24536	110887	10797	167	725	72425	68	28	157	28	138	520	41	438
S9	FC-BA	23981	185783	621017	7966	16437	33243	15355	215	1309	88669	88	82	293	35	122	892	34	268
S10	BA	29392	185963	567690	8916	20114	53862	18112	280	1478	104452	79	98	284	31	94	429	34	360
S11	BA	25857	164098	580564	37311	19754	70167	13758	191	2060	78510	74	191	373	36	108	419	72	699
S12	FC-BA	20361	158326	616629	15659	21905	56483	15883	139	1139	82514	45	351	365	29	109	827	38	456
S13	FC-BA	36371	159548	561713	11704	14941	88952	17577	168	1893	98938	91	110	219	30	64	597	21	246
S14	FC-BA	27970	166498	611266	8964	16232	36487	17233	188	1742	105809	132	123	312	30	130	467	32	318
S15	FC-BA	35318	166245	570864	5743	17681	92919	15130	413	1392	82536	71	275	283	32	90	572	47	386
S16	FC-BA	21971	181160	581964	6657	22218	80457	13964	171	989	78995	49	583	439	31	114	750	38	406
S17	FC-BA	22375	179352	570846	6545	22134	86750	15066	138	1081	82823	44	73	169	35	79	858	43	390
S18	BA	27681	176764	576003	15003	20686	60555	17841	278	1243	97086	91	82	237	32	114	577	34	373
S19	BA	24966	186491	582013	10468	21787	65110	14115	169	995	81880	67	64	160	27	98	673	32	329
S20	BA	29296	171971	610825	11598	21197	48406	14870	235	1028	81343	117	82	190	27	90	555	29	262
S21	FC-BA	17137	182932	602427	14649	20349	66780	13865	203	688	75562	85	68	211	28	99	578	35	308
S22	FC-BA	15383	151338	655756	22734	20226	50363	13103	150	1012	62156	48	69	187	24	97	576	60	382
S23	BA	22703	172473	578980	20231	20784	80036	13804	175	1377	79777	51	121	248	30	128	511	35	402
S24	BA	25764	170202	590798	5914	21969	76927	14386	208	1098	83674	71	73	176	33	125	479	42	537
S25	BA	21648	170808	591199	16902	19531	61188	17476	129	1718	86894	45	171	280	30	94	771	50	427
S26	BA	22742	177221	630144	10498	23169	39402	13070	208	624	77394	116	54	229	34	125	438	34	303
S27	BA	18141	180472	631655	8601	20096	39704	13534	217	596	80595	111	53	182	30	99	464	31	309
S34	NEO	20890	177540	573068	8412	21378	95951	13508	194	1277	82412	56	65	161	36	116	649	34	312
S35	NEO	19920	169389	599404	15057	22587	56038	13949	153	1235	92741	51	96	199	31	114	667	36	547
S39	NEO	23110	161142	554559	41620	23524	87963	15231	168	1316	81326	59	44	200	29	113	673	37	330
S40	NEO	21781	166969	617492	9427	20665	68249	12099	186	974	74707	45	70	160	30	113	556	29	341
S101	NEO	19990	169500	644600	14350	16700	35590	9810	126	1200	78360	78	83	209	27	121	553	38	659
S102	NEO	23850	168300	571700	43690	17080	74680	9070	91	2190	79890	61	102	345	32	152	538	42	217

Results have been analysed with Principal Component Analysis; a multivariate technique used to simplify the structure of compositional data. In this work, the PCA calculations have been performed with the Statistica software on the standardized set of data.

3. Results

The chemical compositions of all the 33 samples have been studied with PCA in order to look for possible similarities and differences among the various observed ceramic typologies using all the elements and excluding only the Calcium because it is susceptible to be attacked by groundwater circulation and it can be interested in the formation of secondary products [7-8].

The scatter plot of the data set in the plane of the two principal components PC1 and PC2, accounting for 18.9 % and 15.9 % respectively, is presented in Figure 2. The PC1 *vs* PC3 and PC2 *vs* PC3 plots are not presented because they did not provide different results.

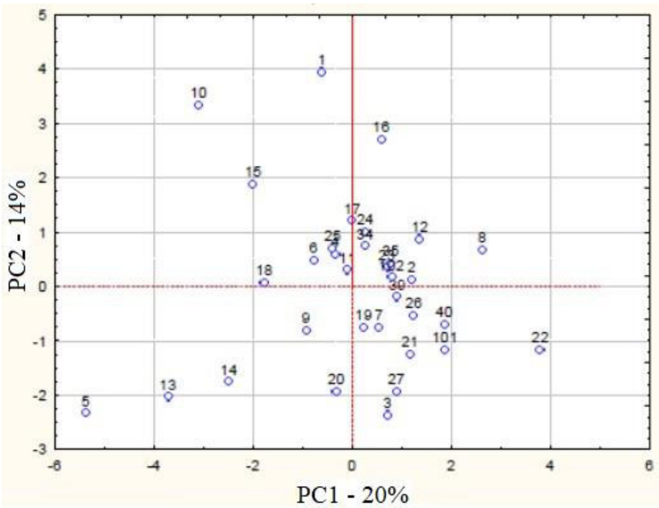
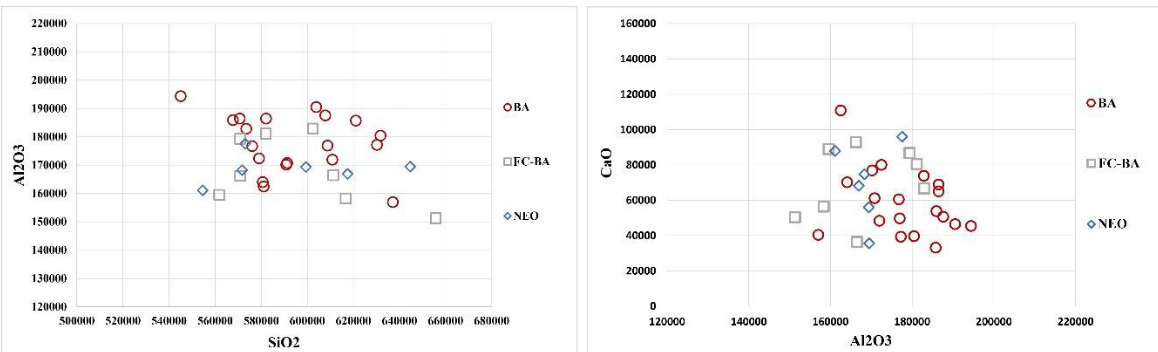


Figure 2. Data sample scatter plot in PC2-PC1 for all sherds

The Figure 2 shows how data does not present any particular pattern related to sample characteristics, as for example production period. It seems thus that all the specimens are homogeneous in composition and thus in provenance of the raw materials.

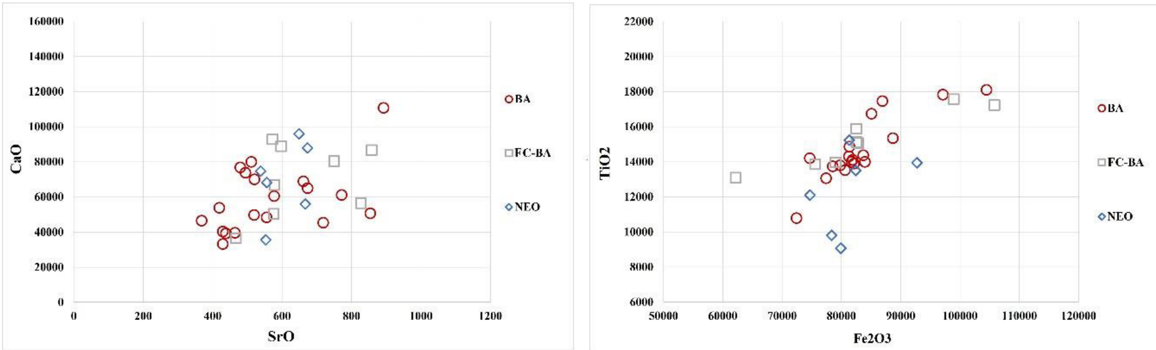
The correlation between the single elements can be studied to look for further confirmation of observed similarities and to search for peculiarities of some given single sample. Furthermore, the binary plots provide us information about the peculiar aspect of the technology and manufacturing phase. In order to acquire indications about the main components of the bulk, correlations among some elements (Al_2O_3 vs SiO_2 and CaO vs Al_2O_3) are plotted in Figure 3 a-b.



(a) (b)

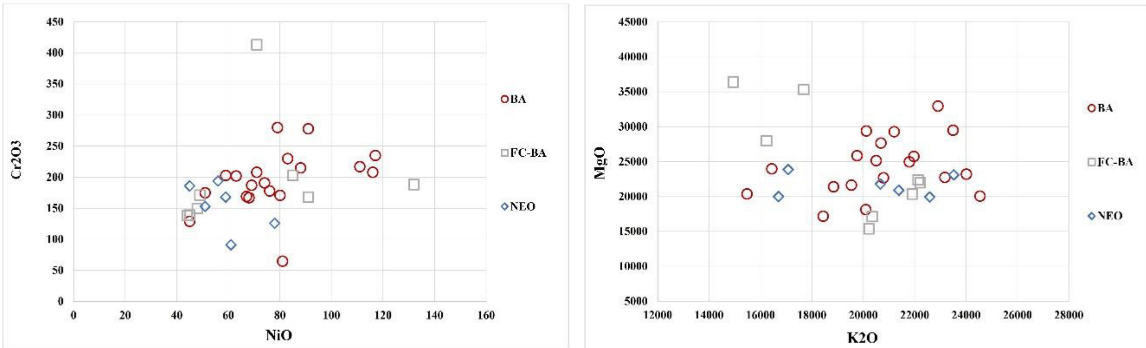
Figure 3. Al_2O_3 vs SiO_2 (a) and CaO vs Al_2O_3 (b) concentrations (ppm) for all analysed samples

Figure 4 reports the CaO *vs* SrO (a) and the TiO_2 *vs* Fe_2O_3 (b) concentrations for the samples. In the last case, the plot shows the expected linear relationship between these major elements, related to the sand used for the terracotta manufacturing. In Figure 5, the binary plots relating to the trace elements Cr_2O_3 vs NiO (a) and MgO vs K_2O (b) concentrations for all analysed samples are displayed.



(a) (b)

Figure 4. CaO vs SrO (a) and TiO_2 vs Fe_2O_3 (b) concentrations (ppm) for all analysed samples



(a) (b)

Figure 5. Cr_2O_3 vs NiO (a) and MgO vs K_2O (b) concentrations (ppm) for all analysed samples

In all the figures, it can be observed that no particular differences are present among samples of different periods (Bronze age, Final Copper-Bronze age, Neolithic) as well as among the sherds and two pieces of the remains of furnace.

4. Discussion and Conclusions

Chemical compositions of a set of ceramic sherds coming from the Valcorrente and produced in three different historical periods site has been determined with PIXE technique. The obtained data have been analysed with PCA, showing a quite homogeneous pattern, confirmed by the study of correlation plot between major elements. These results seem to suggest a common origin of raw materials and a similarity in realization techniques along all the concerned periods as we all the local provenance. This evidence is proved also by the analysis of two sherds of furnace, typically realized with local material. A further confirmation of this conclusion could be given by petrological analysis presently in course on the studied samples.

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