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Lustre and glazed ceramic collection from Mas Llorens, 16-17th centuries (Salt, Girona). Provenance and technology

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Abstract

Lustre pottery unearthed at Mas Llorens constitutes one of most interesting collections of late 16th and early 17th centuries lustre pottery from Catalonia. The collection is formed by an unparalleled set of more than 200 complete dishes and bowls, which were buried in the same place and at the same time, thus becoming of paramount archaeological interest. Consequently, this set of lustre pottery has become of pivotal importance for the study of this type of ceramic not only because of the number and integrity of the pieces that were found, but also by its homogeneity. This multidisciplinary study has revealed the importance of this pottery in terms of economy, trade, and social status in Modern times Catalonia. The main purpose of this paper is to determine provenance and technology of production of lustre and other glazed wares from Mas Llorens. We present the results of the archaeometrical characterization of 21 ceramic sherds, recovered from the excavations of Mas Llorens. The sampling includes 11 lustre ceramics, 4 blue-on-white tin-lead-glazed ceramics, and 6 plain lead glazed objects. Chemical and mineralogical composition of the ceramic pastes were analyzed by XRF, NAA, and XRD, and statically compared to 16th-17th tin-lead glazed pottery produced by the main Catalan workshops (e.g. Barcelona, Reus, Vilafranca del Penedès). The chemical data show a high homogeneity in the composition of lustreware pastes, as seen in other proto-industrial fine ceramic productions, evidencing a Barcelonan provenance. Chemical composition and microstructures of the glazes and lustre decorations were observed and analyzed by Scanning Electron Microscopy (SEM), Electron Probe Microanalyzer (EPMA) and Elastic

ion backscattering spectroscopy (EIBS). Successful lustre exhibits a red-copper color and metallic shine; it contains more copper than silver (average concentration, 9.5 wt% and 3.4 wt% respectively) with a ratio of $\text{wt\% Cu}/(\text{Cu}+\text{Ag}) = 62\%$, in the form of copper and silver nanoparticles which are concentrated in a thin layer ($< 300 \text{ nm}$) very close to the surface. On the contrary, in the unsuccessful brown lustre lacking metallic shine, although the copper to silver ratio is similar - $\text{wt\% Cu}/(\text{Cu}+\text{Ag}) = 63\%$ -, the copper nanoparticles are distributed in a thick layer (1 micron thickness) but in lower concentration (average concentration in the layer 3.4 wt%), while the silver nanoparticles appear concentrated on a thinner surface layer. The lack of metallic shine in those samples is explained by the low concentration of silver and copper nanoparticles in the layer. This may be related to a deficient reducing firing capable of reducing copper to the metallic state and stopping its diffusion into the glaze.

Key words: Lustre; tin glaze, post-medieval; Catalonia; NAA; SEM; EIBS.

Introduction

The ancient fortified house of Mas Llorens is located in the old town of Salt, nowadays a small city located in the outskirts of Girona city, (NE Catalonia) (Figure 1). During the modern rehabilitation works of the remains of the house several rescue archaeological campaigns were carried out during the late 80's and early 90's (Alberch and Burch, 1989). As a result of these archaeological fieldworks, several human burials and an important set of pottery were discovered.

Mas Llorens is a magnificent building that combined functionality and austerity, constituting a great example of the Late Medieval and post-Medieval rural wealthy families. Abundant documentary evidence exists about the presence and activities of the Llorens family in Salt since early 13th century AD. Architecturally, the old house of Mas Llorens is visibly dominated by a defensive three-story squared tower with several arrow slits and ornamental gargoyles. However, direct archaeological evidence states only the use of the solid defensive tower during the 16th and 17th centuries, since reconstruction works carried out within the first third of the 16th century removed any older evidence. However, indirect archaeological evidence, like human

burials and the neighbouring church building, as well as documentary evidences enable setting its construction back to the 14th century. Presumably the house was built originally earlier than the defensive tower, and 13th century written sources already mentioned the existence of the Mas Llorens fortified house. The existence of such fortification in this rural environment is consequence of the need of protection of the vicinity family croplands and cattle. Besides, the Mas Llorens property was strategically placed near the main road, Camí Reial, which connected the main villages and cities in Catalonia, and several mills.

Documentary evidences point out a date around the year of 1633, with the death of Gaspar Llorens, as the moment when the fortified house lost its functionality as the main home of the family, becoming a simpler tenant farming. The reasons behind the loss of importance of the house are still unclear, although historians consider that one possibility was the marriage of the heiress, Maria Llorens, to a man from a richer family, Narcís Cortada (Alberch and Burch, 1991). It is in this context that archaeologists circumscribed the moment when more than 200 complete dishes and bowls of lustre pottery were buried in a hole dug next to the main building. The ware was buried in



Figure 1. Location map of Salt and different tinglaze workshops during post-medieval ages in Catalonia.

the same place and at the same moment, then becoming of high archaeological interest since it provides researchers with a sealed picture of late 16th and early 17th centuries Catalan pottery (Figure 2). Besides the large quantity of lustre ware, some monochrome glazed wares (honey and green coloured), and blue decorated tin glaze wares were also unearthed. Vegetal ornaments and some animal and human motifs define the main decorations of the lustre dishes meanwhile bowls and porringers were decorated with geometrical elements. Chronologically, this ware set is dated between the last decades of the 16th century and end of the first third of the 17th century, fact that is in agreement with the decease of Gaspar Llorens in 1633 (Alberch and Burch, 1994). A similar contemporary finding of lustre pottery buried into a hole is documented also in the Montsoriu

Castle when it was definitively abandoned (Font et al., 2008).

The main goal of this study is, on the one hand, to evaluate the provenance and, on the other, to determine the technology of production of the glazed wares and in particular of the lustreware of this chronologically closed set of ceramics unearthed at Mas Llorens de Salt. A third goal is to assess the inner trade within Catalonia, paying special attention to Barcelonan ceramic productions. This adds valuable information to the survey about the rural wealthy class society in NE Catalonia.

Samples and Analytical Methodology

The sampling strategy consisted of the random selection of 21 ceramics from Salt, selecting



Figure 2. Images of representative samples. A) Salt-1, Salt-6; B) Salt-2, Salt-9, Salt-10; C) Salt-3, Salt-5, Salt-7, Salt-11; D) Salt-4, Salt-8; F) Salt-18, Salt-19, Salt-20, Salt-21; G) Salt-15, Salt-16, Salt-17; H) Salt-12, Salt-13, Salt-14.

several individuals for each of the decorative types present in the ceramic collection. Thus, 11 lustre sherds (6 plates and 5 leaf-handle and non-handle porringers), 4 fragments corresponding to blue decorated plates, and 6 monochrome glazed (3 honey-glazed and 3 green-glazed) ceramics were selected for analysis (Figure 2). Glazed ceramics were analyzed by means of x-ray diffraction (XRD), x-ray fluorescence (XRF) and neutron activation analysis (NAA). Chemical results were compared against one of the largest databank of post-medieval majolica and glazed ceramics from the Iberian Peninsula, formed by more than 1000 individuals from the main Catalan (Barcelona, Reus, Vilafranca del Penedès, Lleida), Valencian (Manises) and Castillian (Talavera de la Reina, Puente del Arzobispo, Seville) production centers (Iñáñez, 2007; Iñáñez et al., 2008).

Chemical composition of the ceramic bodies was carried out by means of NAA at

the University of Missouri Research Reactor (MURR). The analytical routine for NAA has been described at length elsewhere (Glascock et al., 2007), and will be only summarized here. At MURR, INAA of pottery consists of two irradiations and a total of three gamma counts. Short irradiations involve a pair of samples being transported through a pneumatic tube system into the reactor core for a 5 s neutron irradiation using a thermal flux of $8 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. After 25 min of decay, the samples are counted for 720 s using a high-resolution germanium detector. For the long irradiation, quartz vials are irradiated for 24 h at a flux of $5 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Following the long irradiation, samples decay for seven days, and then are counted for 1800 s on a high-resolution Ge detector coupled to an automatic sample changer. After additional two-week decay, a second count for 9000 s is carried out on each sample. These measurements allow quantification of 33 elements: Al, Ba, Ca, Dy,

K, Mn, Na, Ti, V, As, La, Lu, Nd, Sm, U, Yb Ce, Co, Cr, Cs, Eu, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn and Zr. Besides, elemental analysis of the ceramic bodies by means of X-ray Fluorescence (XRF) was carried out at SCT-UB of the University of Barcelona. A thorough description of the XRF analytical routines used in this study can be also seen elsewhere (Hein et al., 2002). For major elements determination, 30 mm glassy beads obtained after the fusion of 0.3 g of sample mixed with 5.7 g of lithium tetraborate flux (dilution 1:20) using an automated Philips Perl'X-3 glass bead casting instrument. Elemental quantification was obtained by means of a Philips PW2400 spectrophotometer with a Rh exciting source, obtaining quantitative data for 10 elements: Al_2O_3 , Fe_2O_3 , MnO , P_2O_5 , TiO_2 , MgO , CaO , Na_2O , K_2O , and SiO_2 . The chemical data were examined using an array of multivariate statistical procedures. The application of multivariate statistical techniques to chemical data facilitates identification of compositional groups. The similarity between specimens, and subsequently to their hypothetical provenance according to the provenance postulate (Weigand et al., 1977), was examined using Cluster Analysis (CA) and Principal Components Analysis (PCA), whereas Canonical Discriminant Analysis (CDA) was performed to further assess the archaeological classifications and the chemical groups shown by PCA. Statistical analysis of the chemical data followed Aitchison's approach and Buxeda's observations of compositional data (Aitchison et al., 2000; Buxeda, 1999; Buxeda and Kilikoglou, 2003). The statistical procedure consists of the use of ratios of logarithms obtained by dividing all the components by the element that introduces the lowest chemical variability to the entire set of specimens or the calculated geometric mean. The use of logarithms compensates for differences in magnitudes between major elements, such as Al and Fe, and trace elements, such as the rare earth

elements. Additionally, log-transformed data can sometimes highlight possible perturbations in the chemical data as a result of diagenesis, contamination, or other alteration processes (Buxeda, 1999).

Ceramic bodies and glazes were also analyzed by micro x-ray diffraction (XRD) at European Synchrotron Radiation Facility (ESRF) in order to assess the sintering degree and alteration of the clay bodies, as well as to compare the mineralogical phase identification with the reference groups. Synchrotron radiation micro-X-ray diffraction (SR- μ -XRD) was performed on beamline BM16 at the ESRF in transmission geometry, using 1.2398 Å wavelength and taking advantage of the layered structured, a 70 μm x 50 μm spot size and recorded using a CCD detector.

Glaze microstructures were studied by means optical microscopy and Scanning Electron Microscopy (SEM-EDX at University of Girona) preparing paste-glaze metallographic polished cross sections for each sample. Glazes chemical composition and microstructure were analysed by means an Electron Probe microanalyzer (EPMA at University of Barcelona). Analyses were performed at 15 kV and 15 nA, using an electron beam thickness of 2 μm . Chemical profiles of diffusing elements from the ceramic body to the glaze (between 10 and 25 points depending on the glaze thickness) were measured. We have to mention that the bulk SnO_2 content in the glazes is not successfully measured due to the fact that cassiterite crystals (SnO_2) are heterogeneously distributed in the glassy matrix, and the incident electron beam is about a 2 μm spot, too small to obtain bulk data.

Furthermore, lustre decorations were analysed by Elastic ion backscattering spectroscopy (EIBS), also known as Rutherford backscattering spectroscopy. Lustre decoration consists on a superficial Ag and Cu nanocrystals layer embedded in the glassy matrix (Pérez-Arantegui et al., 2001). Typical thicknesses

usually range from 200 nm to 1000 nm, being too thin for satisfactory SEM and EPMA analysis of the cross section preparations. Therefore, the silver and copper were measured directly on the surface by EPMA, although the ionization energy also surpassed the outer layer of decoration and a small area of the subjacent glaze was also excited and, consequently, measured, the metal ratio is still valid (Pradell et al., 2005). EIBS allows the evaluation of the elemental composition of a few micrometre thick surface layers, and in particular it provides thickness and elemental compositional profile of the lustre layers. EIBS measurements were obtained from three samples showing different optical properties (colour and shine). The analysis were performed with the 5 MV tandem accelerator at the Centro de Micro-Análisis de Materiales of the Universidad Autónoma de Madrid (CMAM) as described elsewhere (Pradell et al., 2007).

Results and Discussion

Pastes

The colour of the pastes is straightly related to the chemical composition and mineralogy of the pastes, as well as to the temperature and atmosphere reached during firing. Lustre and blue decorated specimens are made of calcareous pastes (around 15 wt% of CaO) characterized by creamy or pinkish bodies. Green and honey monochrome glazed ceramics are also calcareous pastes but containing less CaO than the former and exhibit a red or brownish colour; this is shown in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ ternary diagram of Figure 3. Chemical composition of Salt lustre wares is quite homogeneous, containing about 15.4 wt% CaO, 54 wt% SiO_2 , 15.5 wt% Al_2O_3 , and 5.3 wt% Fe_2O_3 (Table 1). However, the blue-glazed ceramics show a larger chemical variability; two of them have a composition very similar to the lustre wares, while the other two are calcium richer. Salt-21, a polychrome (yellow and blue)

ware, contains greater CaO (18.6 wt%), as well as MgO (2.59 wt%), and lower Al_2O_3 and Fe_2O_3 amounts than the plain blue decorated ceramics (Salt-18, 19, 20). Monochrome ware also exhibit greater variability in the CaO contents (from 10.5 wt% to 13.2 wt%).

The use of marly clays for producing blue and lustre decorated ceramics is a common trend in medieval and post-medieval tin glaze ceramics. The high CaO content produce creamy coloured pastes (Molera et al., 1998). During firing, the calcium silicates developed incorporate Fe in their mineralogical structure lowering the free Fe to form hematite, which is ultimately responsible for the red coloured pastes. The higher the firing temperature, the more Fe is incorporated into Ca-Fe silicates such as the pyroxenes (diopside and fassaite). From a technological point of view, a creamy coloured paste is desirable, since it decreases the need of adding SnO_2 (an expensive material at the time) for obtaining a white opaque glaze. Consequently, glazes can be thinner or contain less SnO_2 than those applied to red pastes (Vendrell et al., 2000). Besides, the thermal shrinkage is less pronounced for calcareous pastes than for red pastes and, therefore, much more adequate for the tin-lead glazes, which also show low shrinkage (Tite et al., 1998).

Mineralogical composition of the pastes was determined by XRD at ESRF. Lustre ware pastes contain mainly diopside and anorthite as principal firing compounds, and calcite was residual or completely absent, indicating that the calcareous clays were well fired at temperatures above 950 °C. Monochrome lead glazed wares pastes contains illite or dehydroxylated muscovite, and neither calcite, nor diopside are found. However, large amounts of lead bearing feldspars are found in the interface between the ceramic paste and the glaze as shown in Figure 4. Lead bearing feldspars of sanidine crystallographic structure are known to grow at the interface between lead glazes and illitic clays

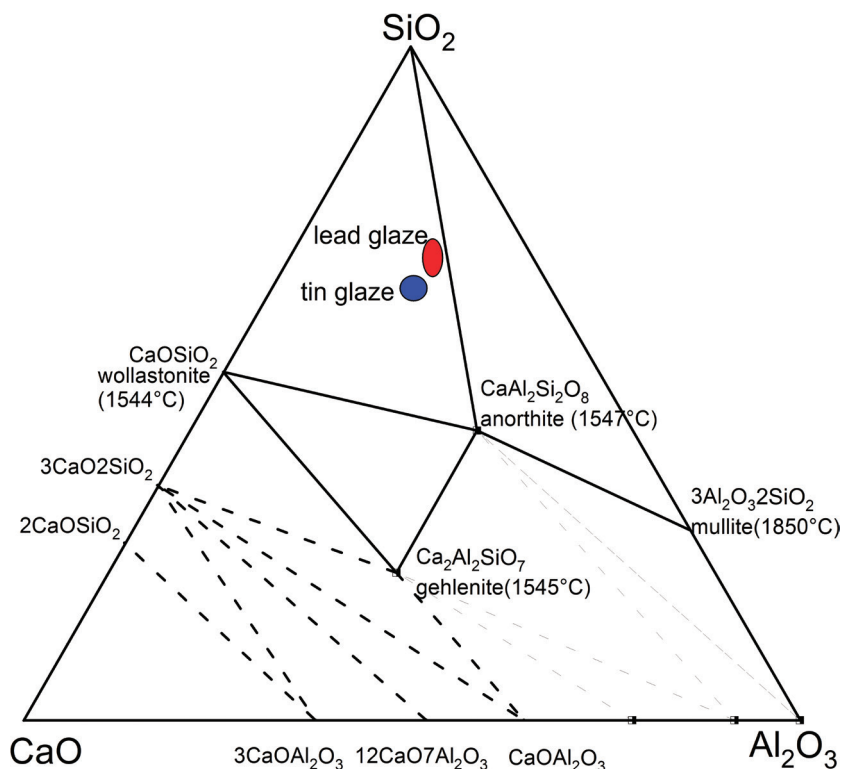


Figure 3. Ternary diagram of chemical composition of ceramic bodies. Tin glaze samples are grouped in the blue circle and lead monochrome samples in the red ellipse.

(Molera et al., 2001). In the interface of lustre and blue tin glaze wares together with sanidine analcime is found, most probably a weathering product (Figure 4). Analcime is currently found at the interface between calcium rich pastes and glazes as is reported in Pradell et al. (2010).

With regard to the lustre and blue decorated wares, it is also observed that creamy pastes appear more altered and have a lower toughness than the pinkish ones, associated to the presence of analcime, which is commonly attributed to a post-depositional weathering mineral formed during burial, (Buxeda, 1999). Analcime is a sodium zeolite, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$, usually determined by XRD in those ceramic pastes

exhibiting a high degree of vitrification, (see Figure 4) thus in those ceramics that were fired at higher temperatures. Furthermore, this process reports the leaching of K and, sometimes, Rb, from the matrix, with a subsequent enrichment of sodium because of the analcime crystallization (Schwedt et al., 2006). As a consequence, this process affect the ceramic paste composition, without possibility of satisfactory correction. This is, for instance, the case for Salt-2 (Figure 4), which exhibits abundant analcime, anorthite and diopside; contrarily to Salt-5, showing higher amounts of calcite and fewer of anorthite and pyroxene characteristic of lower firing temperature. As a result, Na, K, and Rb were

Table 1. Chemical compositions of ceramic pastes by XRF (except Salt-3 and Salt-21) (wt%).

REF.	decoration	Fe ₂ O ₃	MnO	TiO ₂	CaO	K ₂ O	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O
Lead Glazes	green	5.60(0.26)	0.08(0.02)	0.77(0.05)	10.66(0.22)	3.15(0.09)	1.38(0.02)	60.83(0.74)	15.66(0.25)	1.43(0.08)	0.44(0.24)
	honey	5.50(0.11)	0.06(0.01)	0.74(0.05)	11.62(0.17)	3.27(0.04)	2.57(0.31)	57.90(0.46)	16.35(0.03)	1.50(0.03)	0.49(0.09)
	dishes	5.30(0.19)	0.07(0.01)	0.71(0.01)	15.80(1.01)	2.56(0.69)	3.03(1.53)	53.47(1.92)	15.62(0.64)	2.10(0.10)	1.34(0.46)
Lustre	bowls	5.23(0.16)	0.07(0.01)	0.71(0.03)	15.16(0.39)	2.74(0.36)	3.36(2.72)	54.11(1.92)	15.37(0.50)	2.03(0.13)	1.21(0.25)
	bowls with handles	5.35(0.22)	0.06(0.01)	0.70(0.03)	14.87(0.31)	3.42(0.51)	2.30(1.11)	55.06(1.53)	15.31(0.21)	2.02(0.02)	0.90(0.34)
	all lustre	5.26(0.17)	0.07(0.01)	0.71(0.02)	15.14(0.82)	2.93(0.60)	2.63(1.71)	54.24(1.72)	15.33(0.51)	2.07(0.10)	1.07(0.37)
Tin glaze	Blue	5.35(0.22)	0.07(0.02)	0.71(0.01)	15.38(0.29)	2.61(0.60)	4.60(3.34)	53.01(1.69)	15.34(0.46)	1.79(0.34)	1.14(0.42)
Barcelona	B2	5.25(0.20)	0.07(0.01)	0.70(0.02)	15.85(1.22)	2.70(0.55)	3.76(2.22)	53.21(1.98)	15.29(0.51)	2.03(0.26)	1.15(0.34)

Table 2. Chemical composition of ceramic pastes by NAA ($\mu\text{g/g}$).

	B1		B2		B3		SALT lustre		SALT Blue		SALT G/H		SALT21 concentration
	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	mean	σ	
La	41.54	0.76	38.86	1.55	36.11	1.90	35.94	2.31	38.65	0.17	42.57	0.50	38.78
Lu	0.43	0.03	0.40	0.03	0.37	0.03	0.35	0.03	0.36	0.04	0.44	0.01	0.35
Nd	34.80	1.81	33.55	2.05	31.24	2.18	30.71	3.27	34.32	3.39	38.27	3.72	32.82
Sm	7.38	0.13	6.86	0.29	6.36	0.34	6.24	0.42	6.97	0.14	7.88	0.27	6.90
U	3.38	0.27	3.39	0.33	2.57	0.46	3.11	0.38	3.16	0.34	3.30	0.52	2.85
Yb	3.31	0.29	2.98	0.20	2.72	0.23	2.63	0.17	2.84	0.03	3.28	0.18	3.02
Ce	85.64	5.19	77.33	3.60	72.63	3.85	72.74	4.66	79.37	0.91	88.77	2.98	81.03
Cr	73.16	2.10	69.25	4.54	63.78	5.97	65.64	4.63	67.57	4.12	75.62	3.92	69.61
Cs	17.55	1.63	17.95	2.40	6.39	1.54	18.29	2.32	17.56	1.71	8.36	0.54	7.09
Eu	1.36	0.03	1.27	0.05	1.21	0.07	1.19	0.08	1.26	0.02	1.42	0.04	1.29
Fe (%)	3.77	0.10	3.52	0.22	3.20	0.25	3.36	0.24	3.67	0.14	3.80	0.25	3.37
Hf	6.59	0.43	5.14	0.47	5.03	0.24	4.65	0.46	4.85	0.04	5.97	0.83	5.33
Sc	13.97	0.38	13.55	0.64	12.21	0.82	12.79	0.83	13.66	0.22	14.51	0.45	13.21
Sr	125.23	13.88	164.01	39.87	233.83	46.06	225.79	57.13	214.74	35.65	272.02	42.71	273.38
Ta	1.27	0.04	1.21	0.08	1.09	0.15	1.11	0.07	1.19	0.01	1.25	0.05	1.11
Tb	1.00	0.10	0.93	0.09	0.83	0.06	0.87	0.09	0.90	0.03	1.07	0.10	0.94
Th	14.18	0.30	13.53	0.58	12.06	0.62	12.82	0.90	13.75	0.17	14.68	0.53	13.18
Zn	113.10	17.13	117.00	19.28	90.74	12.62	179.99	65.07	176.09	26.61	153.01	49.69	261.33
Zr	162.20	26.18	128.15	19.96	130.88	19.44	113.58	14.10	125.79	11.62	138.09	19.50	100.45
Al (%)	7.71	0.20	7.53	0.34	6.76	0.42	7.42	0.26	7.65	0.01	8.04	0.25	7.59
Ba	482.03	57.47	539.78	134.07	363.19	39.76	477.59	63.52	493.70	61.80	544.48	47.39	753.40
Ca (%)	8.18	0.83	10.76	1.12	16.85	1.16	10.71	0.86	10.68	0.14	8.12	0.59	13.03
Dy	5.07	0.20	4.88	0.25	4.46	0.35	5.07	0.28	4.90	0.09	5.76	0.44	4.95
Mn	673.01	82.16	572.69	50.87	527.39	63.00	501.38	48.02	540.29	3.09	552.45	124.21	677.25
Ti (%)	0.40	0.03	0.38	0.05	0.35	0.02	0.38	0.03	0.35	0.01	0.38	0.02	0.37
V	100.38	9.30	94.61	7.32	88.92	13.65	85.31	10.72	77.89	10.49	103.44	13.42	105.77

Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Sm, Sr, Ta, Th, Zn, Zr, Al, Ba, Ca, Dy, Mn, Ti and V, using La as divisor because it introduced the lowest variability to the data set (Table 2).

The study of the statistical NAA data is summarized in the Figures 5 and 6. An examination of a bivariate plot using as axis the two first principal components calculated after the latter subcomposition, and accounting for 75% of the variance, facilitated the identification of several discrete chemical reference groups from the primary production centres of the Iberian Peninsula during the 16th-17th centuries: Catalan (Barcelona, Reus, Vilafranca del Penedès,

Lleida), Valencian (Manises) and Castillian (Talavera de la Reina, Puente del Arzobispo, Seville) (Figure 5). A closer examination of the PCA study allows identifying that the lustre and blue-glazed ceramics from Salt clearly match the geochemical composition of the B2 reference group from Barcelona (Figure 6). However, chemical features of monochrome ceramics from Salt do not easily enable discerning their belonging to any reference group from the Iberian Peninsula. According to the PC analysis, all 6 monochrome seem to show a relatively similar chemical composition than Barcelona productions (B2 and B3) and Vilafranca del

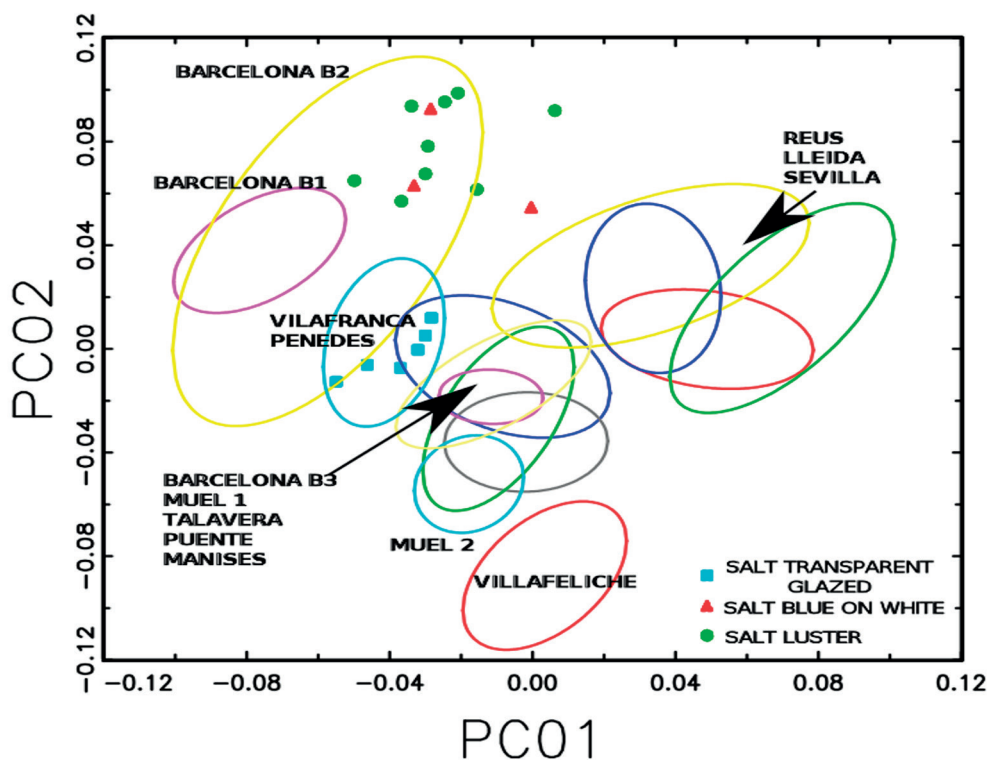


Figure 5. Principal Components Analysis of the variance-covariance matrix of the ceramics data. Ellipses represent 90% confidence level for membership.

Penedès group. Furthermore, NAA chemical data of monochrome ceramics differs from the rest of the lustre and blue ceramics, especially regarding their lower Cs and Ca and higher Sr and Zn contents.

In order to assess the robustness of the assignment to groups identified by PCA and to further explore the clustering of Salt monochrome ceramics, a Canonical Discriminant Analysis was performed over the following subcomposition: Lu, Nd, U, Yb, Ce, Cr, Cs, Eu, Fe, Hf, Sc, Sm, Sr, Ta, Th, Zn, Zr, Al, Ba, Ca, Dy, Mn, Ti and V, using La as divisor because it introduced the lowest variability

to the data set. Interpretation of the graphical scatter plot of the two first discriminant factors enables confirming the strength of the group assignments projected by PCA. Furthermore, CD analysis enables confirming that monochrome glazed ceramics do not match any of the Catalan reference groups, due to the relatively small differences in their Cs, Ca, Sr and Zr contents.

Regarding the XRF chemical data, cluster analysis (CA) was performed in previous studies over the major chemical subcomposition: Al_2O_3 , Fe_2O_3 , MnO, TiO_2 , MgO, CaO, and SiO_2 , using the calculated geometric mean

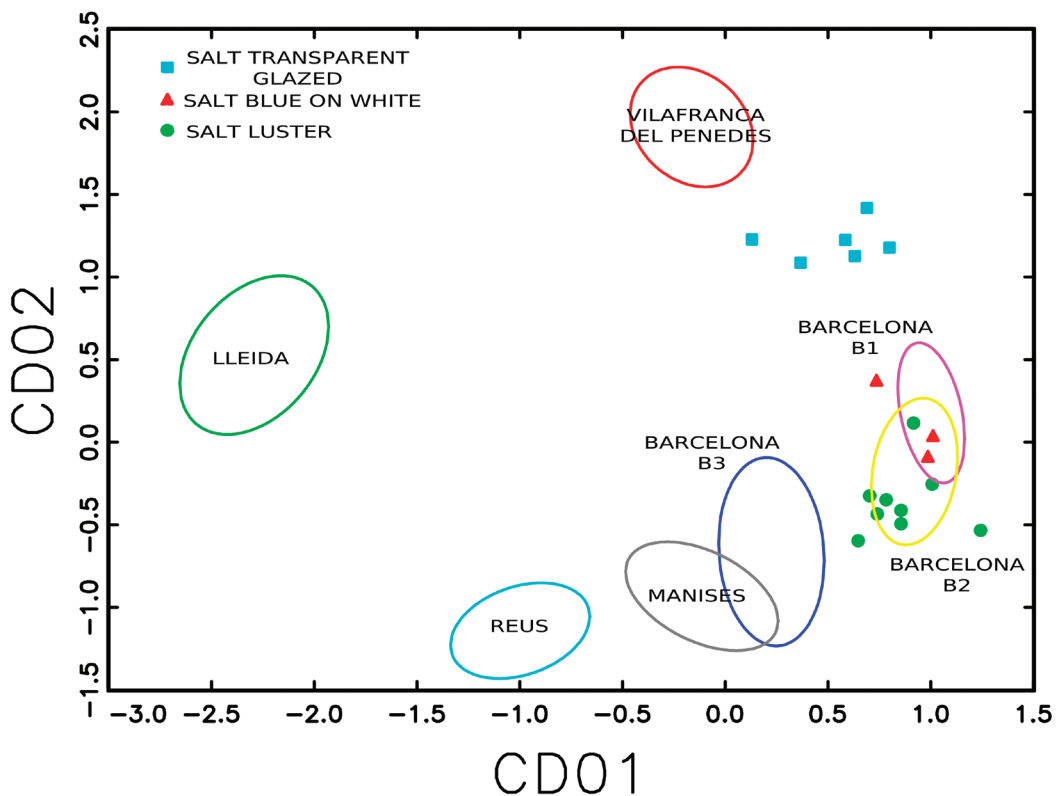


Figure 6. Canonical Discriminant Analysis of the variance-covariance matrix of the ceramics data. Ellipses represent 90% confidence level for membership.

as divisor (Molera et al., 2007). According to Table 1, chemical differences within lustre wares and blue ceramics are minimal, always within one standard deviation, and no relationship between the chemical fingerprint and typology or decoration was observed. Furthermore, the XRF data reveals a similar classification than that obtained from the NAA data. Thus, lustre and blue glazed ceramic chemical data is clearly compatible with the B2 reference group, so confirming the Barcelona provenance for these ceramics. However, the chemical assignment of monochrome ceramics to any of the reference groups established so far has produced inconclusive results. Thus, it is not possible to confirm or to clearly rule out a Barcelonan origin for these ceramics.

Glazes

Lead glazes were used for the monochrome wares and tin glazes on lustre and blue decorated samples, as is shown in Table 3. The lead content of the tin glazes ranges from 37

to 40 wt% PbO, silicon between 47 to 49 wt% SiO₂ (Table 3) and the aluminum is about 3.3 wt% Al₂O₃. Monochrome glazes contain greater lead (49-56 wt% PbO), less silicon (33-36 wt% SiO₂) and more aluminum (5-5.5 wt% Al₂O₃). Potassium and sodium are higher in the tin glazes than in the lead monochrome glazes. This may be related to the need of higher amounts of flux but also because they are required for the lustre decoration development as discussed in the followings paragraphs. Finally, the tin content cannot be measured properly, because the chemical analyses were obtained from spot analyses by microprobe (EPMA) and most of the tin appears forming tin oxide crystals distributed through the glaze, but similar lustre samples from Barcelona contains around 4% of SnO₂ measured by SEM (forthcoming paper about Blue and lustre production from Barcelona, by the same authors).

Figure 7 show back scattering electron images (BSE) of the glazes microstructure

Table 3. Chemical composition of glazes by EPMA (wt%).

	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	SiO ₂	PbO	SnO ₂	TiO ₂	Fe ₂ O ₃	Cu ₂ O	CoO
Lustre	0.86 (0.21)	3.38 (0.87)	2.24 (0.96)	0.31 (0.09)	3.40 (1.40)	47.02 (2.57)	39.74 (2.51)	2.17 (1.23)	0.13 (0.05)	0.68 (0.51)	0.04 (0.02)	nd
Blue tin glaze	1.44 (0.22)	3.85 (0.16)	2.12 (0.36)	0.52 (0.09)	3.25 (0.38)	48.76 (2.04)	37.24 (1.90)	1.17 (0.51)	nd	1.26 (0.37)	0.03 (0.01)	0.32 (0.30)
Honey lead glaze	0.16 (0.02)	1.02 (0.26)	4.47 (0.70)	0.50 (0.15)	5.57 (1.39)	35.83 (0.20)	49.65 (2.80)	0.03 (0.01)	0.31 (0.06)	2.39 (0.37)	0.05 (0.01)	nd
Green lead glaze	0.21 (0.06)	0.79 (0.35)	0.94 (0.36)	0.35 (0.09)	5.03 (1.77)	33.41 (3.91)	55.87 (5.03)	0.07 (0.03)	0.32 (0.13)	1.31 (0.34)	1.67 (0.52)	nd

from cross-sections of the samples. Some significant differences can be observed between the glazes from the lustre wares and those from the blue wares. Lustre ware glazes show tin oxide crystals more or less grouped in clusters which resemble the original grains. There are few grains of quartz and potassium feldspar and bubbles dispersed in the glaze. Most of the individuals exhibit a thin paste-glaze interface, indicative of a double firing process, resulting from the application of the raw glaze mixture on the previously fired ceramic body also called

biscuit ceramic. Some samples, like Salt-2 exhibit a thicker interface, with significant crystallite growths, more characteristic of a single firing process, although it could also be associated to a higher firing temperature during the second firing (Molera et al., 2007; Molera et al., 2001) in good agreement with reaction phases formed in the ceramic body as is shown in Figure 4b.

Blue decorated glazes show great amounts of quartz and feldspar crystals into the glaze and less tin oxide crystallites. These microstructure

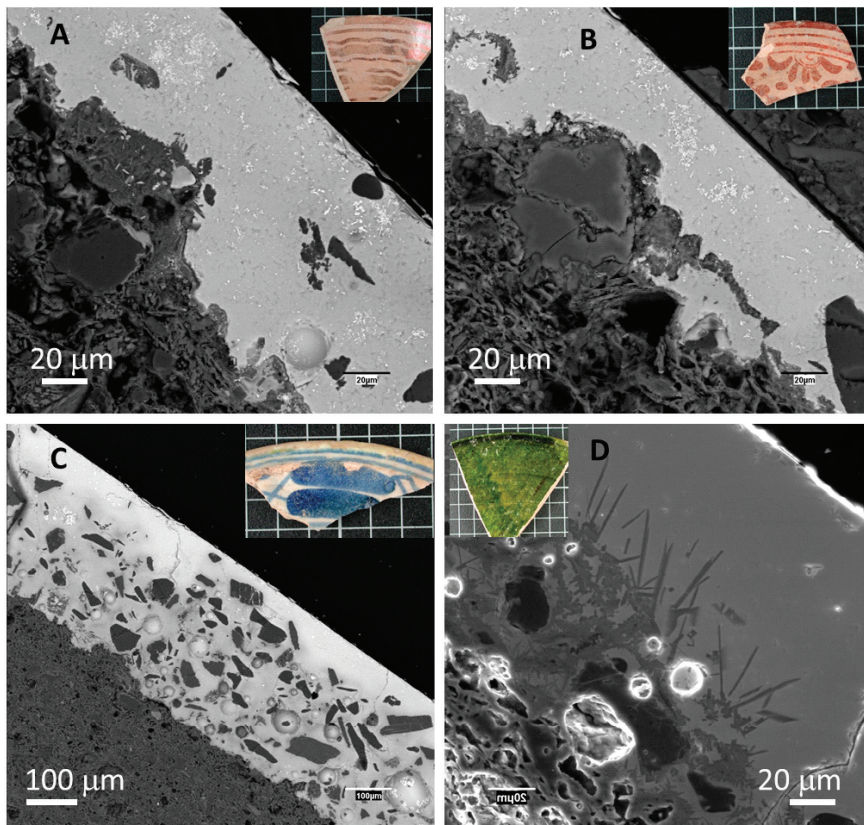


Figure 7. SEM Images. A) Lustre pottery Salt-4: white crystals are tin oxide; B) Lustre pottery Salt -5; C) Blue tin glaze pottery Salt-19: white crystals are tin oxide and grey inclusions are quartz and feldspars and D) Green lead monochrome glaze Salt 13: prismatic crystals are K-Pb feldspars grown into the interface.

is common in the blue tin glaze wares from Barcelona during the 17th period, when other cheaper alternatives were documented to obtain white glazes adding a lower content of tin oxide (expensive material in that epoch). Blue-tin-glazed ceramics also exhibit the thin interfaces characteristic of a double firing process. Cobalt, dissolved in the glaze, is the main responsible for the blue color. It was applied on the outer surface of the glaze, as the chemical analysis of the cross-sections of the glazes shows. Fe is related to the Co as shown by the more or less constant Co-Fe ratio of 0.5 except for Salt-20 which shows a significantly higher Co-Fe ratio of 0.75 than the rest of blue glazes and, which may indicate a different provenance for the cobalt used. Polychrome (yellow and blue) decorated dishes (Salt-19 and Salt-21) contain lead antimonate particles responsible for the yellow colour. Lead antimonate crystallites appear forming a thin layer in Salt-21 glaze, while they appear forming small aggregates scattered on the surface of Salt-19 glaze.

Finally, monochrome glazed ceramics do not show many quartz or feldspar crystallites, but exhibit thicker paste-glaze interphases, containing growths of lead potassium feldspars needle-like crystallites related to a likely single firing process (Figure 7D and Figure 4), and some bubbles. In the green glazes, Cu^{2+} is the main chromophore and Cu/Fe ratio is about 1.5 to 2. Honey-coloured glazes show also a high Fe content (between 1.5wt% to 1.9 wt%), indicating that iron is responsible for such coloration. Salt-14 shows a thin clay slip applied on the outer surface of the paste before glazing.

The composition of the glazes show also some alteration related to the burial conditions and generally speaking the tin glazes appear more weathered than the lead monochrome. Moreover, the undecorated white glaze areas appear also more altered than the lustre decorated areas. Being lustre produced by ionic exchange between sodium and potassium from

the glaze and the silver and copper ions from the lustre precursor mixture, lustre acts as chemical temper which increases the toughness and weathering resistance.

With regard to the lustre decoration, Cu contents is always higher than Ag contents, although the Ag/Cu ratio may vary a lot on different areas Cu and Ag ions enter the glaze surface by ionic exchange with the Na and K ions present in the glaze. Given that K is present in higher amounts than Na, K is mainly exchanged with Cu (Pradell et al., 2005). It is also worth to highlight that the glazes corresponding to lustre wares contain more Na and K than those of lead monochrome wares and less Al. This seems to corroborate that Na and K were added intentionally to the glaze.

The EIBS analysis corresponding to the Salt-2 and Salt-11 lustre decorations shows how the good metallic shine is achieved by the formation of a thin copper rich lustre layer close to the surface (Figure 8). Pradell et al. (2007) established that the introduction of lead in the glaze formulation is important in order to obtain a good metal like lustre decoration. A lead richer glaze decreases the diffusion of Cu^+ into the glaze after ionic exchange takes place and prior to the copper reduction and formation of the metal nanoparticles. This reduced diffusivity may be consequence of either a lower solubility of Cu^+ in the lead glaze and to a more complex diffusion path involving other elements from the glaze (large divalent cations such as lead are known to reduce the diffusivities of alkali cations such as Na^+ and K^+). In “metallic” shining lustre samples such as Salt-11 and Salt-2 the copper nanoparticles are concentrated in a thin layer of 200 or 300 nm thickness. In this case the concentration of particles in the layer is high enough to obtain the metallic like effect (increased reflectance). On the contrary, samples such as Salt-1 or DB-10 (Barcelona lustre production Figure 8C) that do not exhibit metallic shine show a low concentration of

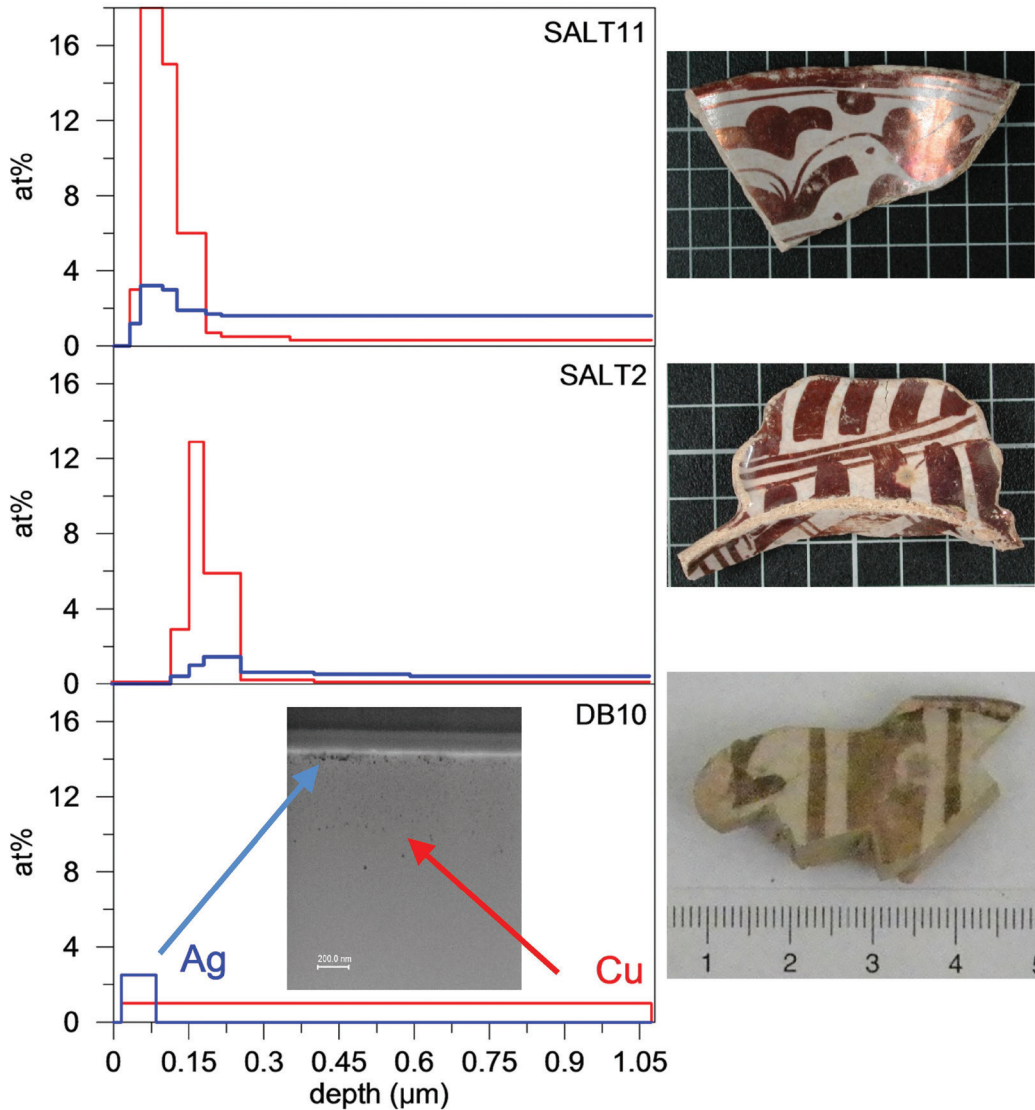


Figure 8. Elemental profile concentration obtained from the EIBS data for the three lustre layers of samples Salt-11, Salt-2 and DB10 (Barcelona lustre production of the same period).

copper and silver in the lustre decoration. The SEM-FIB image shown in Figure 8C shows that in this case silver is concentrated close to the surface while copper appears diffused into the glaze at a depth as large as 1 micron. As the

lead content in these cases is similar than in the others, this may be related to a light reduction not strong enough to reduce the copper into the metallic state.

Conclusions

In this study a combined archaeological, analytical and historical study of the Catalan pottery production during the 16th and 17th centuries is performed for the first time. The results presented here provide solid evidence of the regional distribution of lustre ware within Catalonia, demonstrating that it was largely supplied by the Barcelona workshops. Interestingly, none of the decorated ceramics found in the deposit of Mas Llorens de Salt were produced by any other of the known important production centers from Catalonia, Aragon Crown (Reus, Vilafranca, Lleida, Manises, Muel) or Castilian Crown (Seville, Talavera). This fact provides an important insight into the regional distribution of goods within the Aragon Crown at that time, which appears dominated by the commercial importance of Barcelona in the Mediterranean, an interesting contrast with their Castilian counterparts which shows as Atlantic influence.

The multivariate statistical approach carried out on the chemical data of the clay pastes from Salt has confirmed the Barcelonan origin of the lustre and blue ware. However, the green and honey transparent glazed ware cannot be clearly attributed to any of the Catalan productions known so far. The major chemicals of such green and honey glazed pottery do not seem to differ greatly from the ones found in Barcelona, especially group C and group B1. But the NAA data shows some discrepancies between the reference groups from Barcelona and these green and honey glazed ceramics from Salt, especially regarding the lower Cs and Ca and higher Sr and Zn contents shown by the latest. Therefore, and taking into account that there are historically known similar productions in nearby locations (Quart, Girona), we cannot rule out a local origin.

Green and honey monochrome glazes are PbO richer than tin glazes and show also some

differences between them. Green glazes contain copper oxide as colorant (1.7% of CuO) and around 1% of Fe₂O₃ meanwhile honey glazes contain 2.4 of Fe₂O₃ and 4.5% of CaO. Their high aluminum content (5-5.5 wt% of Al₂O₃) may be related to the addition of clay to the glaze. Monochrome glazes were fired in a single firing process meanwhile tin-lead glazes were fired in a double firing.

Both blue and lustre decorated tin glazes show the same basic glaze composition, poorer in PbO and richer in SiO₂ than the monochrome glazes. Lustre contains more tin oxide as opacifier than the blue decorated glazes. For the blue decorated glazes in order to achieve a white glaze with so low tin oxide content, sand was added to the glaze (clearly seen by the large number of quartz and feldspar inclusions) and the cobalt pigment was applied on top of the raw glaze. Lustre decorations were painted over the previous fired glaze containing more K and Na than the corresponding lead monochrome glazes, indicating that these elements were intentionally added to favour the lustre development. The successful lustre show a red-copper colour and metallic shine and contain more copper than silver. In these cases copper and silver nanoparticles are concentrated in a thin layer very close to the surface; on the contrary, the brown lustre without metallic shine contains copper nanoparticles distributed in a thicker layer, and silver appearing concentrated on the top of the lustre layer. The lack of metallic shine in those samples is explained by the insufficient silver and copper concentration in the layer. This may be related to a deficient reduction able to reduce copper into the metallic state.

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