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# An archaeometric approach to the majolica pottery from alcazar of Nájera archaeological site

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## Abstract

The city of Nájera, located in the north of the Iberian Peninsula, hosts an alcazar of Arab origin, which became the residence of the king of Pamplona-Nájera and later of the duke and duchess of Nájera. From this last period (1500–1600) date the ceramics that were unearthed during the recent excavations of the Alcázar of Nájera. These findings constitute the largest post-Medieval assemblage of ceramic pieces unearthed in the city. They include a large set of plain tin–lead glazed pieces of tableware, as well as some mono or polychrome decorated sherds. In this work, an archaeometric characterization was carried out on a subsample of these ceramics ( $n = 94$ ) by means of a multi-analytical strategy. The pastes were analyzed chemically and mineralogically by ICP-MS and XRD, respectively. Further evaluations on a subsample of ceramic glazes was carried out by SEM-EDS and Raman microscopy. The preliminary results enabled establishing a main large compositional group (NAJ-A) and a smaller one (NAJ-B) which could tentatively be linked to a local production origin. Moreover, exogenous provenances such as Muel and Talavera were identified after the comparison with data from other Spanish contemporary majolica pottery productions.

**Keywords:** Pottery, Nájera, ICP-MS, SEM-EDS, Archaeometry

## Introduction

Located in the Autonomous Community of La Rioja (Iberian Peninsula), in the middle valley of the Ebro (see Fig. 1), the city of Nájera was the royal and episcopal see of the kingdom of Pamplona from the Christian conquest (c. 923) until its incorporation into the kingdom of León-Castilla in 1076. In the following centuries, despite the appearance of other cities such as Calahorra, Logroño or Santo Domingo de la Calzada, Nájera continued to be an important economic, political and religious center of the region [1].

During Roman times, the place where medieval Nájera would emerge was located in a suburban area of Tritium Magallum, one of the main production centers of *Terra Sigillata* pottery from Hispania. Indeed, many remains

of this pottery typology have been found in its vicinity. Their study has revealed an important pottery activity that began in the first century AD and lasted at least during the second and third centuries AD [2]. The decline of the Tritium Magallum that occurred in the Andalusian period and the rise of Nájera to the status of political and military center of the Rioja Alta is still a very poorly known process.

Recent research has dealt with the daily life and artisan activity of medieval Nájera [3–5], although little is known about a local pottery activity that seemingly must have been considerable, judging by various indirect references [6, 7]. The investigations carried out by Sánchez Trujillano on the decoration of the alcazar of Nájera, showed a wide range of ceramic typologies of Moorish influence. A sample of them are the tiles of the *cuerda seca* or *cuenca y arista*, characterized among the materials recovered in the decade of 1930. In the same way, the ostentation that housed the fortress is reflected in the imports from the main majolica producing centers, such as fourteenth century Aragonese monochrome tiles and

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**Fig. 1** Location of Nájera in the Iberian Peninsula (above) and image of the Alcázar of Nájera (below) (Source: LDGP (UPV/EHU))

other architectural decorated features, fifteenth century Sevillian tiles with reliefs or fifteenth century Valencian painted tiles [8]. These production centers were among the most technologically advanced in terms of ceramic production at the time [9].

In contrast to these well-studied sites, the centers of the north of the Iberian Peninsula and in the periphery of Al-Andalus where Nájera was located, barely dragged the attention of ceramologists and archaeometrists, due to their presupposed trade limited to the regional or local

scale and beyond of the main long-distance exchange networks. Furthermore, the lack of research about pottery activity in Nájera in the post-Medieval period is even more dramatic. With regard to local pottery production, historical documentation revealed that in Nájera there were at least four active potters during the sixteenth and seventeenth centuries, namely: Pedro García (1589), Pedro García de Luis (1597), Pedro Gómez (1597), and Francisco de Sagastia (1661). Moreover, potters from the neighbor town of Navarrete going to Nájera as apprentices were also identified [6].

From the ethnographic and art history point of view, the research on the pottery workshops in Rioja carried out by Martínez [6] has attributed ceramic styles to a Nájera origin. The materials studied in his work came from the prospections of the fortress and *Las Viudas* street in Nájera. In addition, the study also mentions a landfill corresponding to a possible local ceramic workshop located in San Lázaro (a land lot within Nájera municipality). However, the origin of these ceramics cannot be unequivocally attributed to Nájera due to the lack of more detailed archaeological or archaeometric studies. Therefore, their tentative production is not discarded in the most active contemporary workshops such as Haro or other Riojan cities such as Logroño [6]. Additionally, the comprehensive study of the ceramic record found in Alava, a northern adjacent region, includes a ceramic group (XLVII) whose provenance is tentatively attributed to Nájera or Logroño [10]. Therefore, until now, there is no direct archaeological evidence of ceramic production in Nájera, such as ceramic kilns or any other equipment required for production, unlike Logroño; where recently, kilns from the thirteenth century–fifteenth period [11] and a kiln from the sixteenth period [12] were discovered.

However, in the excavation carried out in the Alcázar de Nájera in 2002, hundreds of ceramic fragments were unearthed. The chronological framework is given by the reconstruction of the alcazar after the revolts that took place (1520) and until the abandonment of the construction [7]. The modification of the strata that were levelled to cover a difference in level of 12 m to use them as plots implies that the pieces found in this place correspond to those consumed during the Duchy of Nájera and until the moment when the occupants ceased to use the fortress as a residence (end of the sixteenth century). The large number of pieces of similar appearance suggests that many of the fragments could be linked to a local production. In light of this, in the Museo Najerillense a first approximation and typological classification based on stylistic features was carried out [13].

In the current work, an archaeometric approach has been carried in order to characterize the tentative ceramic productions of Nájera. The ceramic assemblage

under study is mainly composed by plain tin–lead glazed earthenware. With such a scarce variety of typologies and decorations, it is especially interesting to carry out an approach based on the compositions of the pastes. In this way, it is possible to shed light on their provenance and technological features, and thus be able to obtain better understanding of the local ceramic production as well as the trade of valuable exogenous productions.

Along these lines, it is known that during the sixteenth century a local market was held every Thursday in Nájera, where pieces from Valencia, Bilbao and Seville were sold [6]. In addition, on a regional scale, Martínez preliminary identified the connections of ceramic workshops in La Rioja with other production centers reporting ceramic exchange. On the one hand, a regional and international provision from Flanders, Pisa and Zamora during the sixteenth century [6]; while on the other hand, a trend towards a regional provision of ceramics from Zamora, Talavera de la Reina, Agreda and Aragón during the seventeenth century. This last link of Aragón, was especially intensified during the eighteenth century, when connections with Talavera de la Reina and Alcora were also reported.

## Experimental

### The alcazar of Nájera

The ceramic samples considered in this work were unearthed in the interventions on the alcazar of Nájera (see Fig. 1). The term alcazar refers to a type of fortification linked to the crown, which must be considered in its double aspect of military and palatial architecture. Thus, the fortress of Nájera, of Islamic origin and whose construction dates back to the ninth century, served as a residence for the kings of Pamplona and maintained its status as a royal fortress until the end of the Middle Ages, when it was ceded to Pedro Manrique (1465). The lineage of the Manrique family reconstructed the ensemble, accentuating its palatial character. However, the assault by the communal rebels in 1520 shows that it maintained its military value even at the beginning of the sixteenth century. It was later transformed into a luxurious Renaissance palace, despite which it was abandoned at the end of the sixteenth century and went into ruin in the following century [7].

### The ceramic sample

The set of ceramics ( $n = 94$ ) consists principally of white plain tin–lead glazed pieces of tableware (27 porringers, 25 plates, 17 jars, 3 pots, and 22 others) from the sixteenth century. Some of the glazes also include blue, green, yellow, black and luster decorations. The ceramics are glazed completely in the interior and either completely, partially or unglazed in the exterior [7]. Other

tin–lead glazed forms include sauce boats, *ataifors*, salt shakers, etc. Moreover, unglazed cooking pots and lids were also analyzed (Table 1).

### Analytical techniques

In order to characterize the compositions and mineralogical phases of the pastes, the whole set of ceramics was analyzed by means of inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD). In addition, a subsample out of these sherds ( $n=15$ ) was analyzed by means of scanning electron microscopy coupled to energy dispersive spectrometry (SEM-EDS) and Raman microscopy in order to better understand the technology used by the potters. Additionally, some micro-XRF and UV-Vis reflectance analyses were performed. The details of the methodology and the results obtained can be consulted in Additional file 1: Figures S2, S3.

### Inductively coupled plasma mass spectrometry (ICP-MS)

For the present work, 15 g of each collected sample was powdered in a planetary mill using tungsten carbide cells for 2–4 min at 300 rpm. Powdered samples were calcined to 1000 °C. These samples, along with the Certified Reference Material from the Geological Survey of Japan used for the calibration of ICP-MS (JB-3, JA-2, JG-1A, JG-2), were fused using a Fluxy automatic gas fluxer (Corporation Scientifique Claisse, Canada). This method, previously optimized for similar matrices [14], involves the melting of approximately 250 mg of sample into a Pt–Au crucible together with 500 mg of a flux ( $\text{LiBO}_2$ ) at more than 1100 °C. The mixture was fused using Program #9 of Claisse with steps F4 and F5 extended to last 100 s and 200 s, respectively (ca. 9 min in total). The melted pearl was then poured into a polypropylene beaker with a solution of nitric acid ( $\text{HNO}_3$ ), which was then diluted in several steps at 1:200 using Milli-Q water (1%  $\text{HNO}_3$ ). This solution was then analyzed by a Nexion 300 ICP-MS (Perkin Elmer).

The internal standards solutions (Sc, Y, Be, Bi and In) were prepared from 1000  $\mu\text{g}/\text{mL}$  stock solutions of Alfa Aesar (Specpure®, Plasma standard solution, Germany) inside a class 100 clean room and using Milli-Q quality water for their dilution. Calibration standards and samples' dilutions were prepared gravimetrically using

analytical balance model Mettler-Toledo XS205 (Columbus, OH, USA) with an uncertainty of  $\pm 0.00001$  g.

The accuracy and reproducibility of the method were checked by repetitive analysis ( $n=3$ ) of the JG-1A, JA-2, JB-3 and JG-2 certified reference materials. In addition, 3 blanks were prepared and analyzed as well for the procedural detection limit calculations following the IUPAC rules, defined as blank signal + 3SD, where SD is the standard deviation of three measurements of a blank ( $n=3$ ).

### Compositional data treatment

The chemometric treatment followed in the current work is based on Aitchison's approach and Buxeda's observations on compositional data [15–18]. Similarity of individuals and subsequently their hypothetical provenance was tested according to the provenance postulate [19]. First of all, in order to compensate for the differences between absolute scales of major and trace elements, a logarithmic transformation was applied. Thus, the underestimation of the contribution of trace elements (that can play a crucial role when differentiating certain compositional groups) is avoided. The comparisons were performed using the ratios of logarithms obtained after dividing all the chemical components by a selected component. Depending on the transformation used (e.g. *alr* or *clr*) it can overcome the compositional data problem called *close to unit sum*, which occurs when data necessarily must add up to 100% and which induces the variables to be codependent [15].

For the principal component analysis (PCA), the component that introduces the lowest chemical variability to the entire set of specimens was taken as a divisor (additive log ratio transformation or *alr*). Whereas, for the hierarchical clustering analysis (HCA), the geometric mean was used as divisor (centered log ratio transformation or *clr*) and the squared Euclidean distance was graphically represented using the centroid agglomerative algorithm. The software employed for all the transformations, statistical analysis and data visualization was R, the routines employed can be accessed on the online repository [20].

### X-ray diffraction (XRD)

For the XRD analysis, powdered samples were used, following the procedure explained before for ICP-MS. The analyses were performed with a PANalytical X'pert PRO powder diffractometer equipped with a copper tube ( $\text{Cu}_{\text{Kmean}}=1.5418$  Å,  $\text{Cu}_{\text{K1}}=1.54060$  Å,  $\text{Cu}_{\text{K2}}=1.54439$  Å), vertical goniometer (Bragg–Brentano geometry), programmable divergence aperture, automatic sample changer, secondary graphite monochromator and PixCel detector. The operating conditions for the Cu tube were 40 kV and 40 mA, and the angular range

**Table 1 Main typologies of ceramics included in the dataset. TLG: Tin–lead glazed**

TIPOLOGY	N	ANID
TLG-plain	72	NAJ001-NAJ073, NAJ090 NAJ091 and NAJ093
TLG-color	15	NAJ074-NAJ089 and NAJ092
Uncoated	7	NAJ094-NAJ100

(2θ) was scanned between 5° and 70°. The treatment of the diffractogram data were carried out using X'pert HighScore Plus software.

**Scanning Electron Microscopy-Electron Dispersive Spectrometry (SEM-EDS)**

The glazes were analyzed by using the FEI Quanta 200 (Thermo Fisher Scientific, USA) scanning electron microscopy (SEM) in combination with the integrated energy-dispersive XFlash 4010 X-ray detector (Bruker, Berlin Germany). The working conditions for this instrument were the following: 20 kV, 100 μA, low-vacuum and 11.5 mm working distance. Secondary Electron mode was used to acquire images and Backscattered Electron mode for EDS measurements.

**Raman microscopy**

The Raman analyses were performed with a Horiba XploRa (Jobin–Yvon, Horiba Group, New Jersey USA) Raman microscope that is equipped with lasers of wavelengths 532 nm, 638 nm and 785 nm. The maximum spatial resolution is 1 μm. Integration times varied between 2 s and 10 s with 10 accumulations. The spectral resolution was 2 cm<sup>-1</sup>. The calibration of the spectrometer was performed at the beginning of the use of the device each working day, by the Raman band of 520 cm<sup>-1</sup> of a crystalline silicon chip. The data obtained were interpreted by comparing the spectra with the pure reference compounds acquired from the Raman e-VISNICH database containing Raman spectra of natural, industrial and cultural heritage objects. Open databases such as RUUFF were also used for other Raman bands identification, in addition to comparing with the spectra of the literature. In-house prepared reference materials were also used for comparison purposes. The interpretation was carried out using the OMNIC (Thermo Scientific™) program.

**Results and discussion**

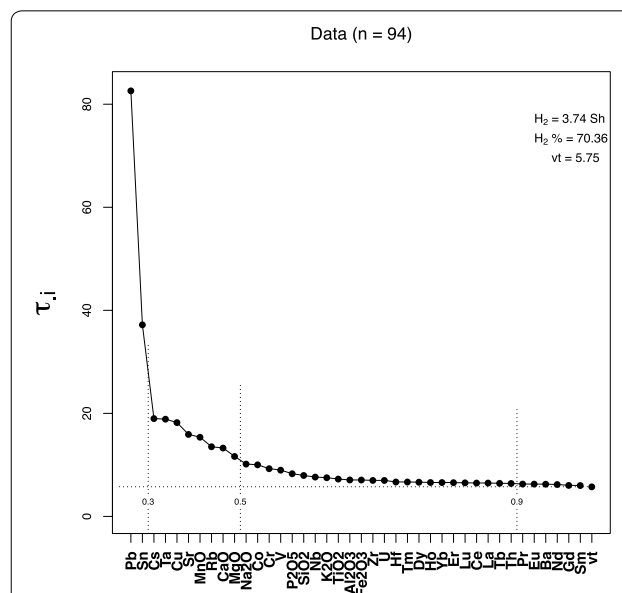
**Identification of compositional groups**

In Table 3 the mean concentrations of each compositional group obtained by ICP-MS are presented. Ideally, for the statistical analysis, the analytical variance should be minimized in such a way that it is originated by natural sources and not because of experimental errors and/or alterations arising from post-depositional processes. Therefore, in this work, several elements were not regarded for the statistical analysis, such as Pb and Sn due to their potential alterations by tin–lead glazes [21] and P, which is known to be retained by the clay body [22, 23]. Moreover, due to the possible alteration by analcime [24] Na, K, and Rb were not considered, either. Moreover, the potential contamination by the wolfram carbide cell used to mill the samples [25] was regarded. Co is a known

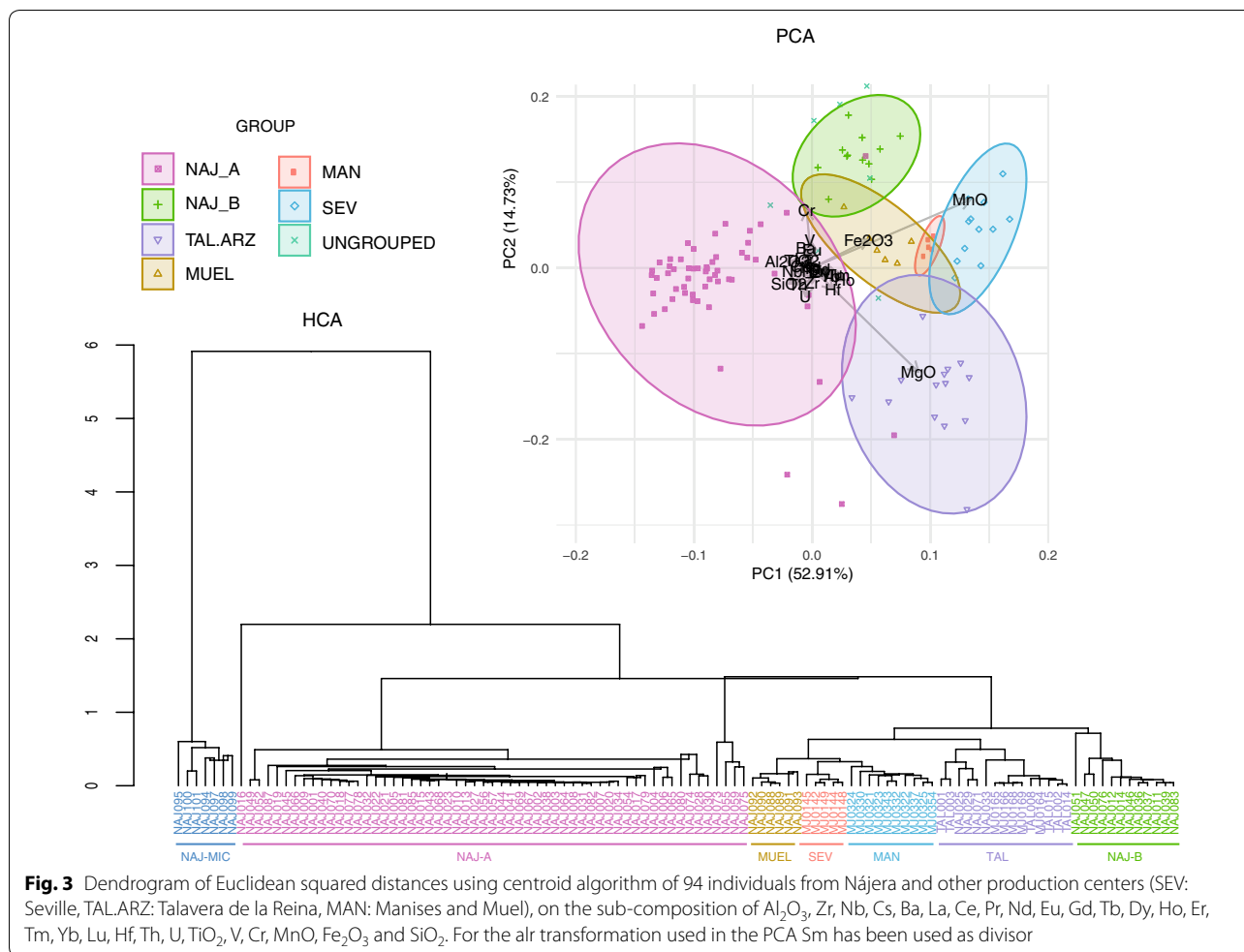
binder in wolfram alloys and usually occurs along with Ta traces. Therefore, Co and Ta were also removed from the statistical analysis. Finally, Cu was not considered, due to the contamination that ceramics can undergo [26]. Likewise, Zn and Ni were omitted since they showed values below or very close to the detection limit.

The compositional heterogeneity was assessed by calculating the compositional variation matrix (MCV), which provides information about the variability introduced by each element into the dataset (Additional file 1: Figure S3). Generally speaking, a large value of the total variation (vt) indicates greater variability and suggests that the dataset is polygenic (i.e. the presence of several compositional groups). In contrast, a small value for vt indicates a possible monogenic nature of the dataset [16]. In this case, the set shows a very high vt (5.75) (see Fig. 2), which reveals the high contribution of the aforementioned elements (Pb, Sn, P, Co, Ta Na, K and Rb). The vt drops down to 0.64 when these are omitted (Additional file 1: Figure S1). This vt can be considered relatively low expecting a low number of compositional groups.

PCA and HCA were carried out in order to extract the compositional groups existing in the dataset (see Fig. 3). Moreover, a comparison was performed to test the possible exogenous provenances. Thus, compositions of ceramics from Seville, Manises and Talavera de La Reina/ Puente del Arzobispo were included in the multivariate statistics. These productions correspond to the main majolica production centers during the fourteenth to the



**Fig. 2** Graphical representation of the evenness of the compositional variability of 94 analyzed Ic-s by ICP-MS. vt = Total variability, H<sub>2</sub> = information entropy, H<sub>2</sub>% = percentage of information entropy over the maximum possible, n = number of specimens (above)



eighteenth centuries and were previously characterized archaeometrically [9].

As a result, 7 compositional groups were identified. The number of groups was established according to the distances observed by HCA, PCA and taking into account the archaeological data available. On the one hand, the results permitted identifying two main compositional groups (NAJ-A and NAJ-B), which are not mixed with exogenous provenances and could be tentatively ascribed to a local origin (see Fig. 3). Micaceous sherds, which are compositionally distinctive, were defined as NAJ-MIC group and is addressed later. On the other hand, ceramics compatible with Talavera reference group were identified. Additionally, some of the sherds showing luster decoration were ascribed to Muel (NAJ088-NAJ093). Despite no ICP-MS reference data from Muel was available, preliminary comparative NAA analyses performed in the ongoing research, pointed out this provenance for NAJ092 and NAJ093 [27]. Thus, the compositional compatibility of the remaining sherds observed by ICP-MS and their coherence in luster

decorations suggested that these could also be ascribed to Muel (Zaragoza). Finally, some sherds could not be ascribed to any provenance due to the lack of a larger sample to compare with. They could neither constitute a compositional group because they showed differing compositions among each other. Thus, NAJ024, NAJ026, NAJ035, NAJ042, NAJ043, NAJ048, and NAJ053 were all tin-lead glazed, whereas NAJ048 and NAJ053 were highlighted by a reddish paste and a very fine coating, which resulted in a glaze with a very poorly white appearance.

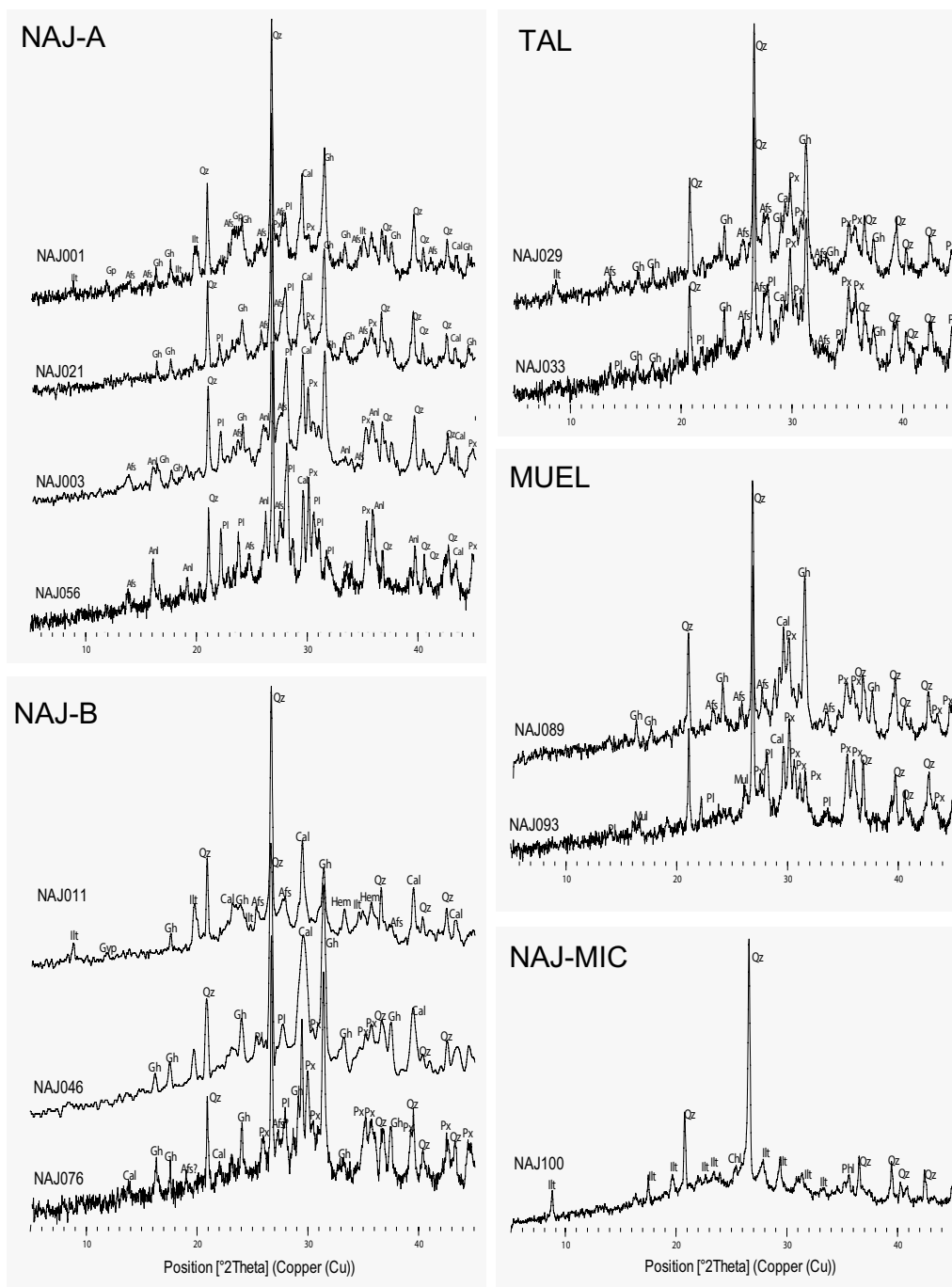
**Characterization of NAJ-A group**  
**Ceramic production of NAJ-A group**

The main compositional group called NAJ-A is the largest (n=56) and include CaO rich (18±3 wt %) pastes. The forms dominating in this group are porringers, jars, plates and bowls, corresponding to tin-lead glazed tableware. Some *ataifors* used for the household are also present in the group. Compositionally, some of the sherds of this group showed differing concentrations of MgO

(NAJ075, NAJ059, NAJ055 and NAJ073). Thus, they remain distanced from this group if MgO is considered in the statistics, but omitting it regroups them within NAJ-A (see the contribution of MgO in the PCA in Fig. 3). Moreover, NAJ016 presents an outlying value of Cr and, likewise, omitting this element regroups the sample within the NAJ-A group.

According to the XRD analysis, four main fabric types were identified in NAJ-A compositional group. Each specific fabric type and compositional groups are listed in Additional file 2: Table S1 and their representative diffractograms are shown in Fig. 4.

The main phases of NAJ-A fabrics are quartz, plagioclases and pyroxenes. The presence of calcite and



**Fig. 4** Representative XRD of each fabric identified in each compositional group. Abbreviations after [44]. \*Indicates basal peak of illite (001)

gehlenite, a phase arising from the reaction of the carbonates with CaO in the clay paste [29], is also ubiquitous among most of the sherds. Since  $\text{CaCO}_3$  decomposes after ca. 750–850 °C, its presence in all cases should be attributed to depositional processes of secondary calcite occurring during burial. These consist on the hydration and subsequent recarbonation of dissociated calcite [30]. Optical microscopy using the thin section of the sherds could help to assess whether the calcites correspond to fine granular mass of the recarbonated form or to the unaltered calcite [31]. The presence of pyroxenes increases from F-I to F-IV, which might be explained by subsequent increasing EFTs. However, the extended presence of pyroxenes can be linked to the temper fraction owing to the presence in the region of high-quartz sandstones and sand deposits produced by the degradation of intrusive rocks [32]. Indeed, its coexistence with low firing temperature firing such as illite (observed in F-I), would reaffirm this hypothesis.

In Fig. 4, NAJ001 is shown as representative diffractogram of F-I ( $n=9$ ). The incipient presence of plagioclases and pyroxenes and the illite-muscovite basal peak at 7 Å detected in all the samples indicates that the ceramics of F-I group were fired at low temperature, ranging between 800 and 900 °C. Moreover, this fabric showed the presence of gypsum. Its presence might be linked to primary sources, due to the evaporites and carbonates-evaporites deposits in the Ebro valley [33], or to secondary sources, that is, to the pollution of the sherds due to the infiltration of gypsum solubilized from the soil by ground waters. The second hypothesis seems to be the most probable owing to the low decomposition temperature of gypsum eventually present in the temper.

While F-II fabric ( $n=20$ ) is mineralogically very similar to F-I, the illite basal peak is completely absent, whereas

the non-basal peak can be still observed at (19 Å). Moreover, a more abundant presence of firing phases such as plagioclases and pyroxenes in coexistence with K-feldspars that have not been fully decomposed permitted estimating the equivalent firing temperature above 850 °C.

According to the mineralogical phases identified, most of the ceramics of NAJ-A show a F-III fabric type ( $n=27$ ). This fabric is very similar to the previous ones, but with an equivalent firing temperature (EFT) higher because the lack of non-basal peaks of illite and indicates that phyllosilicates have been completely decomposed. However, the lack of mullite indicates that the TCE would be at maximum of ca. 950 °C. Additionally, some of the sherds showed the presence of analcime.

There is one sample (NAJ056) showing F-IV fabric type, also with similar mineralogical composition to previous ones, but characterized by the absence of gehlenite. In contrast, the firing phases such as plagioclases or pyroxenes show the most intense peaks, in comparison to other fabrics of NAJ-A group. The higher occurrence of these silicates indicates and the absence of illite suggest a higher EFT, which in comparison to the previous one should be over 950 °C. Moreover, an intense peak of analcime was detected in some of the sherds from this group.

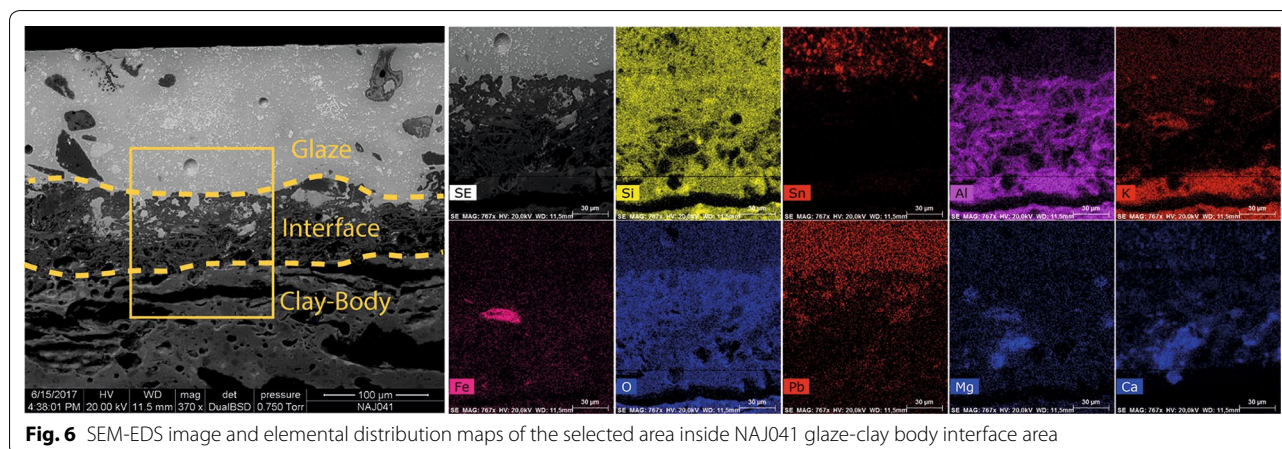
#### Finishing layers of NAJ-A group

As mentioned before, all the pieces of NAJ-A group were coated by white glazes that were opacified by cassiterite ( $\text{SnO}_2$ ). The coating was applied either partially or completely (see Fig. 5). In addition, some ceramics (NAJ074, NAJ075, NAJ077-NAJ082 and NAJ085) include decorative blue motifs (both geometric and vegetal). NAJ085 shows a jasper blue decoration. There is also one with green decoration (NAJ087). From the SEM-EDS



**Fig. 5** Examples of tin-lead glazed and blue decorated ceramics from group NAJ-A





**Fig. 6** SEM-EDS image and elemental distribution maps of the selected area inside NAJ041 glaze-clay body interface area

evaluation it can be concluded that the glazes were applied following two step technology, namely, applying a second firing for the glaze on the bisque ceramic. During this process, the compounds from the glaze are still diffused into the clay body and vice versa. The Pb clearly diffuses into the clay body, while Sn tends to be retained in the glaze (see Fig. 6). In addition, the Al-silicates interact highly with the glazes in comparison to K-bearing phases, as the penetration depth is higher in the former case. Moreover, the observed Ca–Mg accumulations constitute a part of the clay body and most probably correspond to diopsides ( $\text{CaMgSi}_2\text{O}_6$ ) that were previously identified by XRD.

Overall, the glazes of NAJ-A present elevated concentrations of  $\text{SnO}_2$ , being the case of NAJ064 strikingly high one (22.06 wt%). The use of high concentration of  $\text{SnO}_2$  is normally found in the glazes of the so-called “protomajolica” pottery, because sometimes the pastes were darker than the common majolica pottery and the opacifying know-how had not been completely achieved by artisans [9, 27, 34, 35 and references therein]. However, this is not the case of NAJ064, which shows a buffer colored clay body, and is even less common regarding the period under study (sixteenth century). NAJ015 shows the thickest glaze of the whole set of ceramics (0.6 mm), with a 10 wt% of  $\text{SnO}_2$ , ensuring a high opacity in the glaze [21]. In contrast, the thickness of the NAJ044 glaze is smaller (0.11 mm). According to SEM–EDS evaluation, it can be suggested that the use of inclusions in NAJ-A glazes was scarce, although with some exceptions. In any case, these were not very abundant (see Fig. 6). No evident correlation was observed among the coating-type (partial or complete), the  $\text{SnO}_2$  concentration and other factors of glazing technology (inclusions, thickness, etc.). To achieve the mentioned decorations, traditional recipes were used: CoO to obtain the blue and CuO based mixtures for the greens were identified (Additional file 3: Table S2).

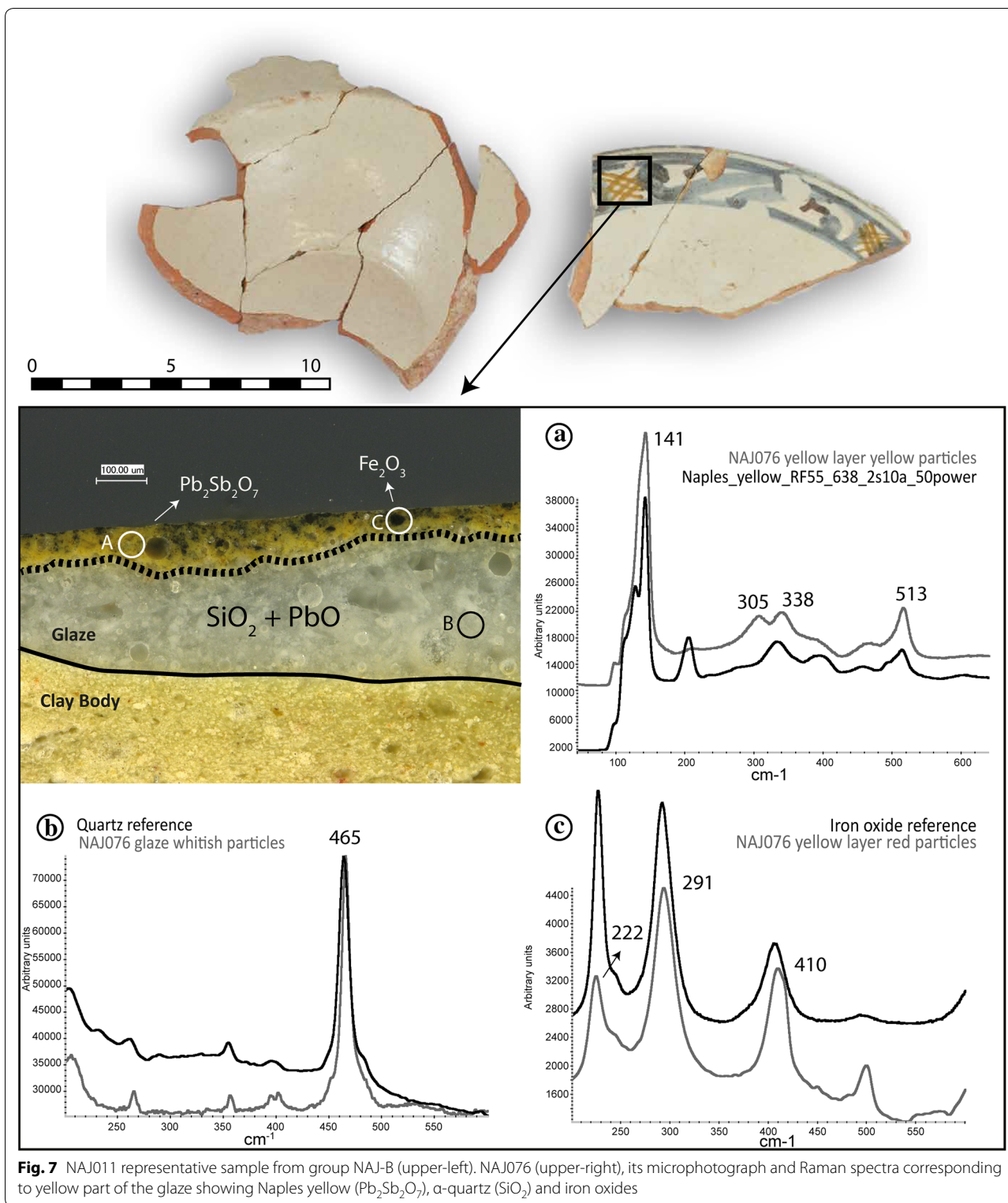
Many of the sherds (NAJ016, NAJ020, NAJ025, NAJ049, NAJ055–NAJ057) present marks of trivet (i.e. the utensil used to separate the ceramic pieces in the kiln that are to be glazed). Moreover, some sherds present drops of honey-glaze (NAJ005, NAJ021, NAJ65). Interestingly, this decoration has not been identified in any of the ceramics. Nonetheless, it can be concluded, that the firing of honey-glazed sherds with tin–lead glazed was performed simultaneously.

### Characterization of NAJ-B group

#### Ceramic production of NAJ-B group

NAJ-B is composed by 14 ceramics and is characterized by a reddish colored clay paste. This color is given by the increment of  $\text{Fe}_2\text{O}_3$  (5.0 wt%) with respect to NAJ-A, whereas the CaO content is still high ( $15.0 \pm 4$  wt%). Likewise, the higher concentration of metals such as V, Cr and Mn was observed in this group (see Table 3 and PCA in Fig. 3). The forms comprising NAJ-B are tableware: mainly plates, porringers and others (atafor, bowl and jar). Beyond the compositional discrimination, the decorations were similar to NAJ-A group, including, largely, plain tin–lead glazes. In contrast, one of the sherds of this group (NAJ076) outlines due to its tricolor decoration, showing the typical decorative motif known as *cenefa castellana*, which includes blue, yellow and black geometric patterns (see Fig. 7 top-right). Furthermore, NAJ083 shows blue colored decorations.

Ceramics showing very similar decoration to these of NAJ-B (especially NAJ076) and described as of “reddish pastes” have been previously reported in the literature [7]. In the mentioned work, their provenance is tentatively ascribed to Haro or Logroño, where these kinds of reddish pastes were more abundant. Nonetheless, preliminary comparisons with productions of Logroño performed in the current research could not confirm this hypothesis [36]. Therefore, its exact provenance remains



unclear. However, according to the high compositional similarity with NAJ-A group, it can be suggested a local origin or a nearby producing location that were exploiting geochemically similar clay beds in the Najerilla basin.

NAJ-B shows three types of fabrics (see XRD results in Table 2). Their common main phases are quartz and Ca-compounds such as calcite and gehlenite. F-I fabric ( $n=6$ ) shows a significant presence of illite coexisting

**Table 2** Fabrics identified in each compositional group and their main mineralogical phases and EFTs

GROUP	Fab.	EFT (°C)	Qz	Ill-Ms	Afs	Cal	Gh	Hem	Pl	Px	Mul	Gp	Anl	Phyllo-Si
NAJ-A	F-I	800–900	x	x	x	x	x		x	x		x		
	F-II	> 850	x		x	x	x		x	x				
	F-III	< 950	x		x	x	x		x	x			x	
	F-IV	> 950	x			x			x	x			x	
NAJ-B	F-I	800–900	x	x	x	x	x	x				x		
	F-II	ca. 900	x			x	x		x	x				
	F-III	> 900	x			x	x	x	x	x				
MIC	F-I	800–900	x	x	x									x
TAL	F-I	800–900	x	x	x	x	x			x				
	F-II	ca. 900	x		x	x	x		x	x				
MUEL	F-I	800–900	x		x	x	x			x				
	F-II	900–1000	x			x	x		x	x	x			

Qz Quartz, *Ill-Ms* Illite-Muscovite, *Afs* alkali-feldspars, *Cal* Calcite, *Gh* Gehlenite, *Hem* Hematite, *Pl* Plagioclases, *Px* Pyroxenes, *Mul* Mullite, *Gp* Gypsum, *Anl* Analcime. Abbreviations after [28]. Phyllo-Si Group (Phyllosilicates): nepheline, phlogopite, chlorite-vermiculite-montmorillonite, biotite, enstatite, orthoclase)

with calcite, gehlenite and K-feldspars. Since the latter start decomposing after 850 °C, the EFT should be close to that temperature (see Fig. 4, where NAJ011 is shown as a representative diffractogram of the fabric). Additionally, gypsum was detected in some of the sherds showing this fabric, whose presence can be linked to contaminations as mentioned in the case of NAJ-A. Moreover, hematite was detected in this fabric, which is highlighted by a richer concentration of Fe<sub>2</sub>O<sub>3</sub>, in comparison to NAJ-A.

F-II fabric (n=6) presents similar mineralogic composition to F-II. In contrast, it shows a complete absence of illite-muscovite, together with a total decomposition of K-feldspars and presence of pyroxenes and plagioclases. The concurrence of these phases places the EFT at ca. 900 °C. In addition, NAJ076 and NAJ063 show an F-III fabric type, which is highlighted by together a higher concentration of pyroxenes and plagioclases. Moreover, the non-basal peak of illite is totally absent. Thus it can be suggested that the EFT is above 900 °C.

#### Finishing layers of NAJ-B group

The coatings of this group present tin–lead glazes with infrequent inclusions. Exceptionally, NAJ076 showed abundant inclusions (see Fig. 8). Moreover, an overall lower concentration of SnO<sub>2</sub> was detected with values that drop down to 5.3 wt% (Additional file 2: Table S1). The high interaction between the ceramic body and the glaze (see Fig. 6) suggests that the coating of this ceramic was applied following one-step-technology, that is, firing simultaneously the ceramic body and the glaze in a single firing [37, 38].

With regard to the tricolor decoration on NAJ076, the spectroscopic characterization by Raman revealed that yellow color was obtained by Pb<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>, known as Naples yellow (see Fig. 7), the yellow layer is evident to the naked

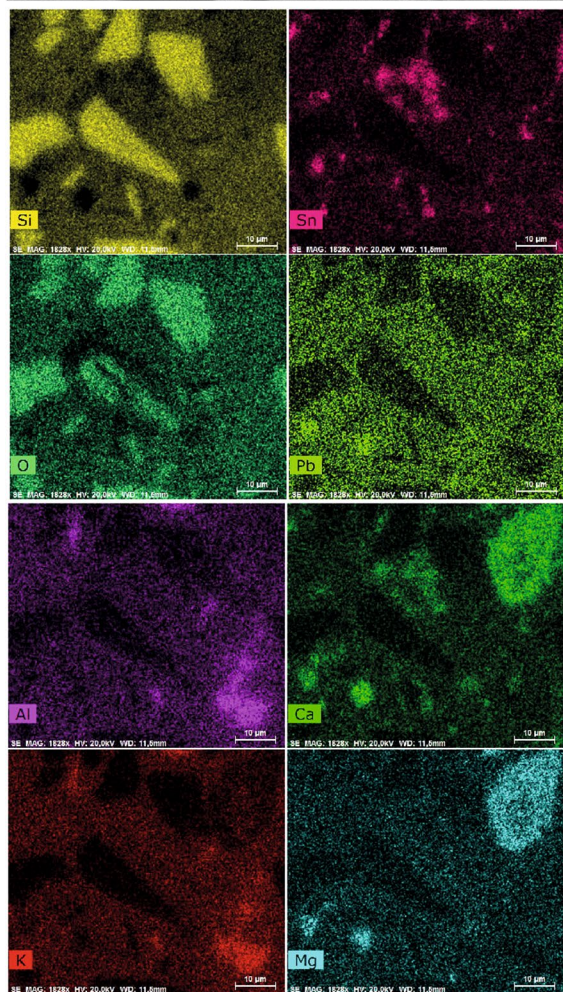
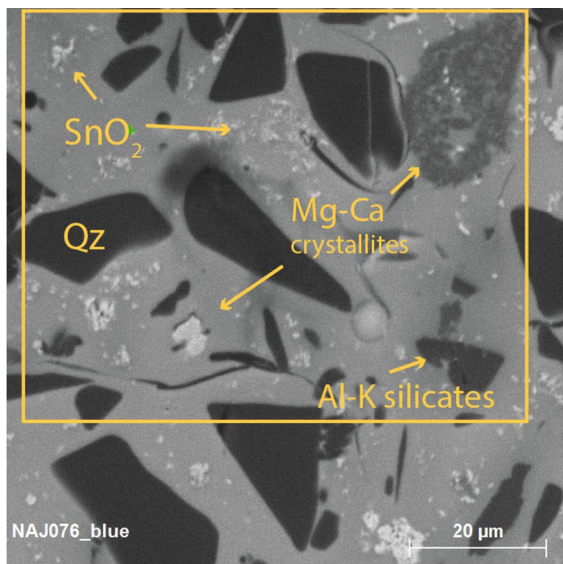
eye since antimony does not dissolve into the glaze, unlike CuO or CoO based pigments. Moreover, the presence of quartz particles and iron oxides which give the reddish hue to the yellow colorant was observed. Naples yellow is light-fast and chemically stable, but may darken with high temperatures (e.g. during the glaze firing), and also with the exposure to iron compounds, which is the case of NAJ076. The presence of iron oxides along with Naples yellow is ubiquitous among majolica pottery from Renaissance.

Interestingly, the blue colorant analyzed in this sample revealed the presence of Mn, As and Ni beyond, Co (see Additional file 3: Table S2 and Additional file 1: Figure S2). Their presence was only observed in this case and suggest differences in the raw material employed, which must be different to cobalt blue used in the other cases, as confirmed by UV–Vis reflectance, (see Additional file 1: Figure S3). According to the elements observed, the alternatives can include asbolan ((Ni,Co)<sub>2-x</sub>Mn<sup>4+</sup>(O,OH)<sub>4</sub>nH<sub>2</sub>O), cobaltite (CoAsS), skutterudite ((Co,Ni)As<sub>3-x</sub>) or erythrite ((Co<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O). Unfortunately, Raman microscopy did not offer any Raman band related with these cobalt compounds due to the high fluorescence registered in the spectra.

#### Characterization of NAJ-MIC group

##### Ceramic production of NAJ-MIC group

The HCA depicts clearly a subset, which is dramatically different from the remaining sherds (see Fig. 3). These ceramics constituted the group called NAJ-MIC (n=6). They are *de visu* recognizable (see Fig. 9) for their heterogeneous pastes showing big sized inclusions (< 1 mm). The compositional differences with respect to the other compositional groups, are mainly given by major elements, especially Al<sub>2</sub>O<sub>3</sub>, but also most of the trace elements (highlight Cr and Ta) show an important decrease



**Fig. 8** SEM-EDS image and mapping of NAJ076 glaze showing inclusions



**Fig. 9** Images of micaceous sherds from NAJ-MIC group (NAJ098 and NAJ101)

(see Table 3). The pastes of this group are highly micaceous, thus, bearing high  $Al_2O_3$  concentrations. As stated in the literature,  $Al_2O_3$  can be positively correlated with the relative abundance of clay minerals and/or the quantity of monomineralic granules of feldspars and mica in the coarser granulometric fractions [39]. For such a study, however, further analyses should be performed of the clay samples and their respective comparison.

According to the literature, the most likely origin of these ceramics would be in Zamora [40]. The region hosts abundant deposits of highly micaceous clays, which show very good refractory properties. For this reason, Zamora has a long-lasting tradition on the production of kitchen ceramics. In the NAJ-MIC group, it can be observed how several ceramics show blackish parts as a result of their exposition to fire, confirming their utility as kitchen utility.

The XRD results were in accordance with the chemical composition showing a very distinctive geochemical situation (see Tables 2 and 3). These pastes show very big sized inclusions (order of mm), which according to the diffractogram (see Fig. 10) correspond to micaceous particles such as chlorite-vermiculite-montmorillonite, and other phyllosilicates such as phlogopite. The presence of illite is very important in this fabric. Moreover, the absence of firing-phases such as plagioclases situates the equivalent firing temperature around 850 °C. The use of phyllosilicates in cooking pots is related to their non-swelling property when exposed to temperature changes. This property, in addition to the higher grain-size distribution and other inclusions such as quartz, is very relevant in pieces that are to be subjected to heating-cooling cycles, such as some kitchenware, thus showing very good thermal-shock resistance. With regard to the coating, none of the micaceous sherds presented glaze or any other decoration.

**Table 3 Mean concentrations and relative deviation (SD) values of each compositional group**

	NAJ-A	SD	NAJ-B	SD	MUEL	SD	TAL	SD	NAJ-MIC	SD
Al <sub>2</sub> O <sub>3</sub>	16.5	1.2	17.6	1.2	13.7	1.3	15.3	0.5	21.8	1.4
CaO	18.2	3.1	15.0	4.5	18.8	3.9	17.8	1.9	3.75	1.5
Fe <sub>2</sub> O <sub>3</sub>	3.2	0.4	5.0	0.6	4.1	0.3	4.2	0.4	2.20	0.09
K <sub>2</sub> O	3.1	0.6	3.5	0.5	3.0	0.3	3.5	0.2	3.4	0.3
MgO	1.8	1.0	2.1	0.3	2.4	0.3	3.9	0.5	0.94	0.07
MnO	0.024	0.006	0.07	0.01	0.062	0.005	0.064	0.004	0.038	0.007
Na <sub>2</sub> O	0.7	0.2	0.8	0.2	0.4	0.1	1.0	0.1	0.5	0.2
P <sub>2</sub> O <sub>5</sub>	0.22	0.06	0.19	0.04	0.18	0.06	0.26	0.05	0.17	0.04
SiO <sub>2</sub>	58	7	53	11	49.9	4.1	59.1	1.6	70.4	4.0
TiO <sub>2</sub>	0.70	0.04	0.76	0.06	0.66	0.08	0.74	0.03	0.27	0.06
Ba	425	47	495	36	435	78	454	23	256	30
Ce	78	5	90	9	77.5	4.7	93.0	3.7	38	7
Co	21	10	24.1	6.9	18.3	5.9	19.4	3.5	21.1	5.5
Cr	69	28	77	12	59.8	5.6	48.3	9.2	23.6	6.6
Cs	13.7	3.5	13.1	2.7	8.0	2.1	9.8	1.3	53.4	9.7
Cu	36	21	34	13	23.8	7.6	43	18	6.9	2.5
Dy	4.5	0.3	4.9	0.4	4.9	0.3	5.7	0.3	5.6	0.4
Er	2.4	0.2	2.6	0.2	2.6	0.1	3.0	0.2	2.8	0.2
Eu	1.2	0.1	1.5	0.2	1.3	0.1	1.35	0.04	0.74	0.08
Gd	5.3	0.4	6.0	0.6	5.6	0.3	6.6	0.3	4.6	0.3
Hf	4.1	0.3	3.8	0.4	4.3	0.4	5.3	0.9	4.1	0.7
Ho	0.79	0.05	0.84	0.05	0.84	0.04	0.96	0.05	0.96	0.07
La	38.9	2.4	45.3	4.9	41.1	2.1	45.4	1.9	19.5	2.3
Lu	0.34	0.02	0.37	0.03	0.36	0.03	0.45	0.04	0.38	0.05
Nb	17.0	1.4	16.4	0.9	15.6	1.4	17.3	0.7	26.0	1.7
Nd	33.6	2.3	38.5	4.0	35.3	1.7	40.9	2.5	19	2
Pb	(487–22 × 10 <sup>3</sup> )		(700–15 × 10 <sup>3</sup> )		6.31 × 10 <sup>3</sup>	2.22 × 10 <sup>3</sup>	(2.89 × 10 <sup>3</sup> – 8.59 × 10 <sup>3</sup> )		(27.6–70.5)	
Pr	9.0	0.6	10.3	1.1	9.3	0.4	10.9	0.6	4.9	0.5
Rb	170	35	180	23	136	21	161	11	528	43
Sm	6.2	0.5	7.1	0.7	6.5	0.3	7.6	0.5	4.5	0.4
Sn	(15.1–1.2 × 10 <sup>3</sup> )		(12.7–220)		36.8	19	41.2	24	91.5	15
Sr	779	1.7 × 10 <sup>2</sup>	585	1.5 × 10 <sup>2</sup>	414	83	389	85	126	20
Ta	1.7	0.3	1.3	0.3	1.33	0.08	1.8	0.1	8.4	3.8
Tb	0.81	0.06	0.88	0.06	0.85	0.04	1.01	0.08	0.92	0.06
Th	13.0	1.0	13.5	0.8	12.0	0.8	15.7	1.3	6.5	1.1
Tm	0.36	0.02	0.40	0.03	0.39	0.03	0.47	0.04	0.44	0.05
U	3.6	0.3	3.9	0.4	3.2	0.2	4.9	0.3	4.6	0.9
V	82.6	9.7	107	19	77.4	6.8	73	11	24.7	3.9
Yb	2.4	0.1	2.6	0.2	2.6	0.2	3.0	0.2	2.9	0.3
Zr	197	24	184	22	228	27	264	61	171	39

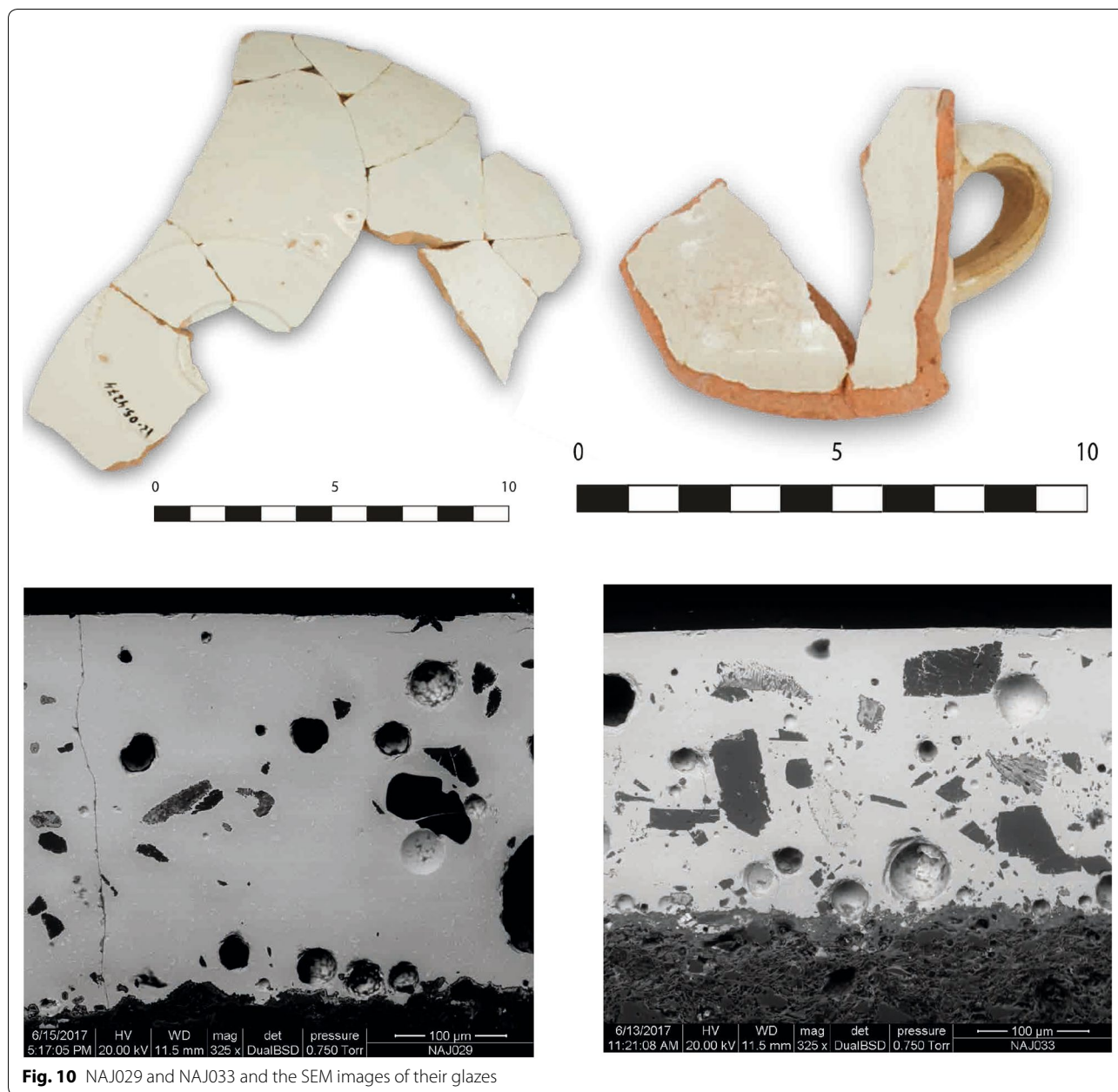
Concentrations obtained by ICP-MS. Oxides are expressed in wt% and the rest in ng/g

### Characterization of TAL group

#### Ceramic production of TAL group

NAJ029, NAJ033, NAJ025 and NAJ071 showed compatible compositions with the productions of Talavera de La Reina (see Fig. 3). Majolica productions of Talavera have been archaeometrically studied by several authors

[9, 31–33]. Compositionally, they are characterized by a high MgO concentration, which was, indeed, the main discriminant element for this group within the current dataset (see Fig. 3). Besides MgO, a higher concentration was observed in trace elements such as Dy, Er, Gd, Hf, Lu, Nd, Sm, Tb, Y, Zr and especially Th (see Table 3).



**Fig. 10** NAJ029 and NAJ033 and the SEM images of their glazes

Along these lines, NAJ029 and NAJ033 ceramics showed chemical compatibility with Talaveran productions when compared with the NAA data published by Iñáñez and coauthors [9]. In addition, from the stylistic perspective, similar pieces produced in Talavera were reported in the literature [37], including both complete glazed and half glazed pieces (see Fig. 10).

In the group of Talavera (TAL) two different fabrics were observed (see Figs. 3 and 8). On the one hand, F-I includes two ceramics (NAJ029 and NAJ025). The basal peak of illite at 7Å and K-feldspars characterize its

mineralogical association. Thus, its EFT can be established between 800 and 900 °C, as no firing phases were detected in significant manner. In contrast, F-II, composed by NAJ033 and NAJ071, shows the lack of illite basal peak and present significant differences on calcite and gehlenite peaks. Therefore, the EFT should slightly higher (ca. 900 °C). These sherds are pieces of tableware that show a finely applied tin–lead glaze resulting in a highly opaque coating. The EDS analysis showed that the white glaze in NAJ029 contained 36 wt% of PbO and 9 wt % of SnO<sub>2</sub>, respectively. The glaze thicknesses

(0.3–04 mm) are the among the biggest of the studied collection. The 20  $\mu\text{m}$  narrow interface between the clay body and the glaze depicts that the glaze was applied on the bisque ceramics, according to the procedures reported in the literature [37, 38]. Remarkably, the recipes used in the glazes from Talavera show abundant inclusions and a low concentration of bubbles.

### Characterization of MUEL group

#### Ceramic production of MUEL group

The statistical analysis (see Fig. 3 and the Table 3) disclosed a group of ceramics (MUEL group) showing the lowest  $\text{Al}_2\text{O}_3$  concentration of the whole dataset (13.7 wt%). These sherds, were not compatible with any other of the tested provenances. Due to the absence of ICP-MS data for Muel production center ceramics, it was not possible to assess unequivocally its provenance to this reference group for these ceramics. Nonetheless, parallel preliminary NAA results performed on NAJ092 and NAJ093 allowed establishing their provenance in Teruel, according to the NAA data published in the literature corresponding to Muel [9]. Thus, their compositional similarity with respect to the remaining sherds of the present group was used as a basis to consider them as a production from Muel. Furthermore, the luster decorations that some of the sherds of this group show are in accordance with the productions of Muel reported in the literature, reinforcing the hypothesis of their Zaragoza provenance [37, 38].

According to XRD analysis, the group of Muel presents two fabric types (see Fig. 4). NAJ089 is representative of F-I fabric ( $n=3$ ) and NAJ093 of F-II fabric ( $n=2$ ). Both contain phases of quartz, calcite and diopsides. In F-I fabric the K-feldspars have not yet fully decomposed, thus the EFT correspond to between 800 and 900  $^\circ\text{C}$ . In contrast, in F-II, the lack of the K-feldspars, and the presence of firing plagioclase phases together with the

incipient presence of mullite, allows estimating the EFT between 900 and 1000  $^\circ\text{C}$ .

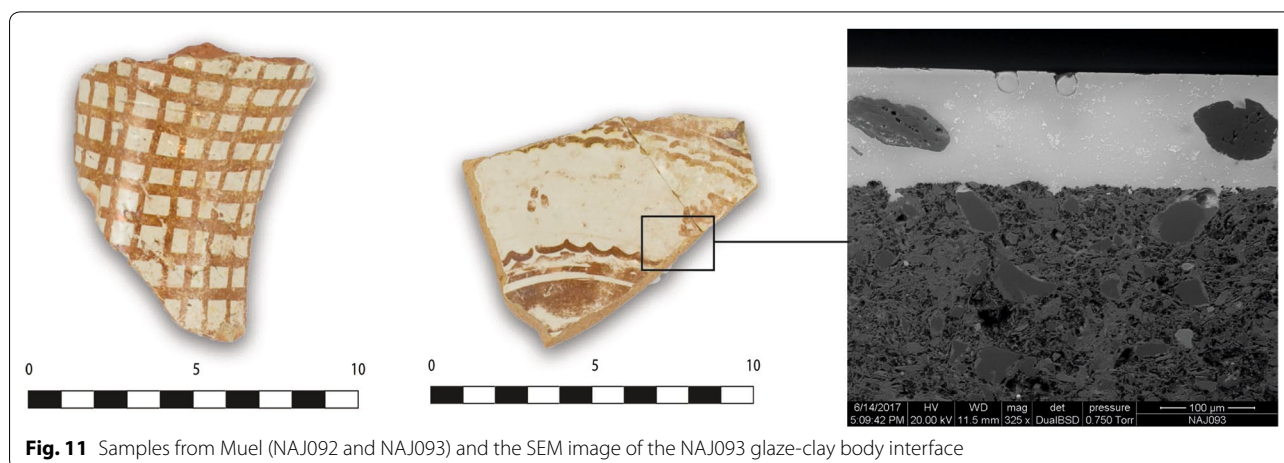
#### Finishing layers of MUEL group

The ceramics ascribed to Muel show mainly luster decorations including also blue painting (see Fig. 11). As all the cases observed before, the tin–lead glazes were applied on the bisque ceramic. However, in order to obtain the luster decoration, historically a third firing was applied [37, 38]. The luster decoration is obtained by the use of a very thin CuO on the outer layer of the glaze, which highly tends to dissolve in the glaze mixture and to be eroded during post-depositional phase [44].

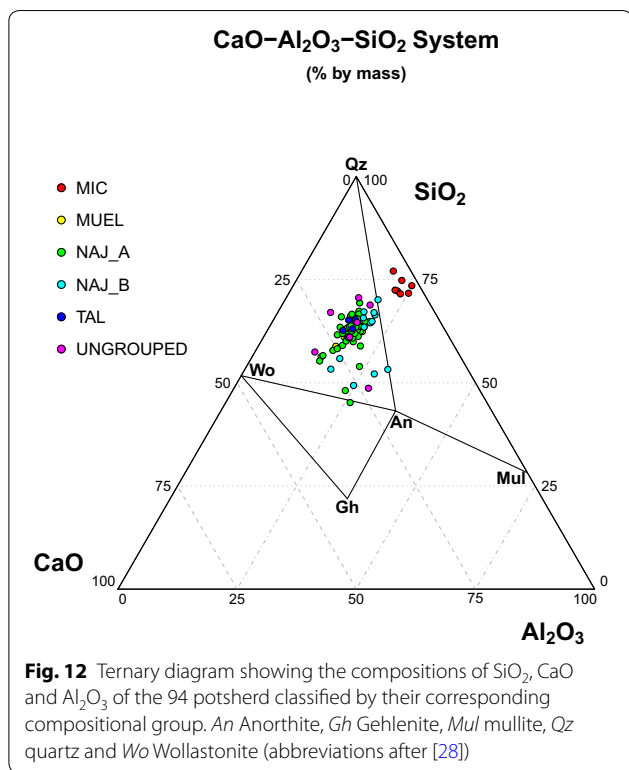
#### Ternary diagram

According to the ternary diagram (see Fig. 12), the six micaceous sherds are strongly differentiated by a higher concentration of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . Their provenance might be ascribed to Zamora according to historic trades of that ceramic typology as has been addressed. The remaining pieces (all tin–lead glazed, some of which include several decorations), fall mostly in the Wollastonite, quartz, anorthite triangle, whereas, some sherds fall within the gehlenite, anorthite, wollastonite triangle, in which a high concentration of CaO can be expected.

The use of marly clays for producing tin lead glazed ceramics is a common technological strategy in post-medieval tin glaze ceramics because the high CaO content produce creamy/buff colored pastes [45]. 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 colored pastes. The higher the firing temperature, the more Fe is incorporated into Ca–Fe silicates, such as pyroxenes (e.g. diopside and fassaite). In addition, and from a technological point of view, a creamy, buff or pink colored paste is desirable since it decreases the



**Fig. 11** Samples from Muel (NAJ092 and NAJ093) and the SEM image of the NAJ093 glaze-clay body interface



need of adding SnO<sub>2</sub> (an expensive material at the time) for obtaining a white opaque glaze. Consequently, glazes can be thinner or contain less SnO<sub>2</sub> than those applied to red pastes [46, 47]. 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 [48].

## Conclusions

This work constitutes the first archaeometric approach published about post-medieval pottery productions of Nájera. The archaeometric characterization performed on the 94 ceramics by ICP-MS, XRD, SEM–EDS and other spectroscopic techniques, with the subsequent chemometric treatment (PCA and HCA), allowed identifying one main compositional group linked to the local pottery production of Nájera during the sixteenth century (NAJ-A), a second group whose provenance could be tentatively ascribed to Nájera (NAJ-B), and three exogenous groups (NAJ-MIC, MUEL and TAL). All of them were tin–lead glazed, except for the micaceous ceramics (NAJ-MIC). With regard to the productions ascribed to a local origin (NAJ-A and NAJ-B), calcareous pastes (showing abundant calcite and gehlenite) were detected in all cases. Moreover, NAJ-B showed a reddish paste which is the result of a higher presence of iron oxides. According to XRD analysis, the EFTs ranged between 800

and 1000 °C. However, in NAJ-A dominated those closer to 900 °C and in NAJ-B those fired at lower temperatures (850 °C). This difference could be connected to a different workshop, kiln or artisan. However, their compositional similarity suggests that NAJ-B was produced nearby, if not in Nájera itself. The elemental compositions responsible for the different decorations, as well as the identification of the chemical compounds that play a main role in those pigments dissolved into the glaze coat were also identified. The use of traditional recipes, such as CuO base greens and lusters, MnO base blacks, CoO blues and opacification by means of SnO<sub>2</sub> on PbO rich glazes was determined. In addition, the characterization of Naples yellow pigment used to obtain the yellowish color was performed in NAJ076's *cenefa castellana* decoration. This sample also showed a different recipe used to obtain the blue, which includes, Mn, Ni and As. Thus, a marked difference in the raw material employed can be inferred.

In brief, the results allowed to link a great part of the ceramics set that was unearthed in the alcazar of Nájera to a local origin related to the ceramic productions during sixteenth century. Moreover, the reception of prestigious ceramics from Talavera and Muel was identified, as well as, most tentatively cooking pots from Zamora. The presence of ceramics from Muel is not surprising when it is known that the neighboring city of Logroño maintained close relations (family ties) with this Zaragoza city, documented as early as the seventeenth century as reported in the literature [6].

## Additional files

**Additional file 1.** Additional Graphics. **Figure S1.** Graphical representation of compositional variation matrix without non-meaningful variables. **Figure S2.**  $\mu$ XRF spectra of blue and yellow pigments in NAJ076. **Figure S3.** UV-Vis reflectance spectra showing the blue colorant in NAJ076 and reference spectrum of Cobalt blue. The nature of these two colorants is very different as the spectra indicate.

**Additional file 2.** List of Ceramics. **Table S1.** List of the ceramics ordered by compositional group. N: number; ANID: analytical ID; TLG: tin-lead glazed; LG: lead glazed; UNC: uncoated; NA: not assigned; UNG: ungrouped; GROUP: compositional group identified by ICP-MS and FAB-RIC: fabric type identified by XRD.

**Additional file 3.** SEM-EDS data. **Table S2.** Semi-quantitative composition (wt. %) of the glazes and the decorations on them obtained by SEM-EDS.

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### Authors' contributions

Jl designed and supervised the project and with EC acquired the analyzed materials and obtained the archaeological documentation. EC, UG and GA carried out preparation and ICP-MS analyses. The remaining analyses were carried out by EC, except those requested to external labs (see "Experimental" section). Jl, MM and EC interpreted the results. EC wrote the initial draft of the manuscript. All authors read and approved the final manuscript.

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### Availability of data and materials

All data generated or analyzed during this study are included as Additional file.

### Ethics approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

### Competing interests

The authors declare that they have no competing interests.

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