



## Submerged and reused: An archaeometric approach to the early Modern ceramics from Aveiro (Portugal)

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### ABSTRACT

Aveiro, a city located in northern Portugal that lies next to the Atlantic Ocean, has a long potting tradition. Indeed, during the 15<sup>th</sup>–17<sup>th</sup> centuries, this region played an important role in the maritime trade between the north of Europe, the Iberian Peninsula and the Atlantic. Historical records reflect regular trade contacts between ship-owners and masters of Aveiro with English, Irish, Flemish, Galician and Basque entrepreneurs, in Europe and overseas.

The archaeological research carried out on the Ria de Aveiro A (RAVA) shipwreck collection (16<sup>th</sup> – beginning 17<sup>th</sup> centuries), revealed a large amount of ceramics as cargo, tentatively produced in Aveiro Region. That was compared to a collection from *Santo António* church, in Aveiro, which includes ceramics used to fill the upper choir dome, with an exact chronology (1524), also manufactured in Aveiro. Such set of pottery enabled the establishment of a typology divided in three groups, used in everyday life at that time in Aveiro (tableware, long-distance storage and transportation and sugar moulds) and combining red and black pastes and shiny and matte black finished surfaces.

With a view to characterize and to assess the provenance of local or regional origin of this Post-Medieval pottery assemblage from the two sites, an archaeometric approach of 25 unglazed ceramics showing red and black pastes has been performed. In this way, chemical and mineralogical analyses have been carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X-Ray Diffraction (XRD), and microstructural analysis by Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS) analytical techniques. The results show that ceramics from RAVA have a compatible chemical fingerprint with those from the church, forming the A-1 local production reference group. Moreover, the A-1 reference group has been further assessed by comparing against the main reference groups from the Iberian Peninsula.

### 1. Introduction

Aveiro, a city located in the west of the Iberian Peninsula, in Portugal, lies next to a large lagoon area called Ria de Aveiro (Fig. 1). Separated from the Atlantic Ocean by a line of dunes more than 50 km long, the lagoon influenced the life of the inhabitants from Medieval times to the Early Modern age; and settlements, which were strongly related to maritime activities and trading, combined agriculture with salt production and fishing. As a consequence, it became an important

maritime port. Moreover, these economic activities -often seasonal and complementary- marked the landscape of the lagoon (Alves et al., 2001; Amorim, 2011; Carvalho et al., 2014).

Nevertheless, Aveiro not only was famous because of its maritime activities and trading; the city was, and nowadays still is, a traditional ceramic production region, with high variety and availability of clay reserves. The chemical and mineralogical properties of these clays led to their use as a raw material for the ceramic manufacturing. Pottery production increased in the early 16<sup>th</sup> century, due to the growth of the

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city and the maritime trade, which demanded pottery to supply ships and commerce (Barbosa et al., 2009; Bettencourt and Carvalho, 2008; Carvalho and Bettencourt, 2012).

Aveiro featured both red and black coarsewares, showing similar paste features. The red ware assemblage, fired in an oxidising environment, is composed of pieces of an orangey to red colours, with darker grey surfaces. Many exemplars have different shades and even black stains on the outer surfaces as a result of variations in the firing environment and kiln temperature. A small percentage of the assemblage is represented by black vessels, fired in a reductive environment, with pastes of grey and black tones, sometimes with a visible metallic shine. The macro-visual observation revealed a very fine and hard paste, and the two groups show the same inclusions: quartz and mica, fine to medium grained, well distributed throughout the matrix. Mica is more abundant, being very visible on the exterior surfaces. Most of the vessels may have received some surface treatments which consisted mainly on smoothing the surfaces, in some cases after the application of a slip of the same colour as the paste, but slightly darker (Bettencourt and Carvalho, 2008; Carvalho and Bettencourt, 2012).

Those ceramics can be classified in different groups, such as for domestic use, like tableware (e.g. cups, bowls, jars), kitchenware (cooking pots) and personal hygiene (bacins); long-distance storage and transportation (e.g. olive jars); and sugar moulds (*formas de açúcar*) (Fig. 2).

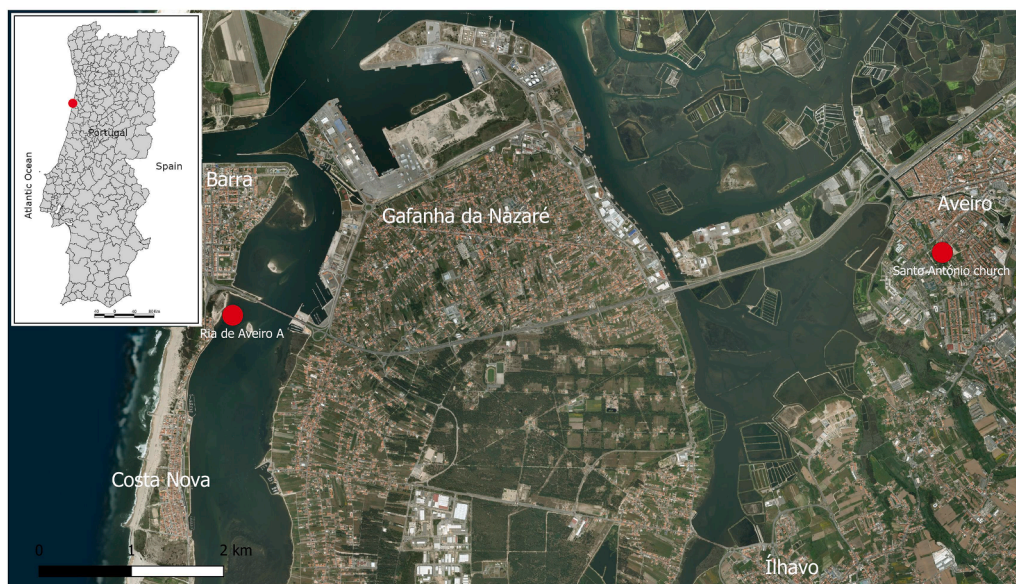
Sugar moulds were essential for the sugar production process. They are conical moulds, with a hole in their top. Nowadays, it is common to find discarded pieces as a constituent element of the wall of the old buildings in the old town of the city (Bettencourt and Carvalho, 2008; Morgado et al., 2012). In recent years, sugar moulds, as well as pottery with different typologies from Aveiro, have been identified in international locations. According to Silva (2018), Aveiro was, probably, since the 16th century, the main producer and supplier of sugar moulds in the sugar production areas of the Kingdom of Portugal, such as Madeira, Azores, Cape Verde and had a strong impact in other markets like Canaries. Ceramics from Aveiro were also found in England and Newfoundland. All these facts are evidence of the Atlantic and transatlantic trade flows during the Medieval, Post-Medieval and Modern Periods. Portugal was certainly a major consumer of English-caught Newfoundland cod (Bettencourt and Carvalho, 2008; Carvalho and Bettencourt, 2012; Newstead, 2014; Silva, 2018).

On the other hand, the traditional salt production in the region is well known since the 10th century and the production was increased

after the 13th century, due to the constant salinity levels of the lagoon water as well as the favourable landscape and environmental conditions. In fact, several maps show the salt production locations in the lagoon, such as the map made by the Dutch cartographer Lucas Janszoon Waghenaer in 1584 (Fig. 3). In this way, Aveiro also played an important role in the supply of salt since the Middle Ages, not only to North-western Europe (England, the Low Countries, Finland and Sweden), but also to the north of Spain, in particular Galicia and Asturias, as well as to the Dutch market, during the 16th and 17th centuries (Amorim, 2019; Antunes, 2008a). Salt was used in manufacturing and preservation of food and hides. Fishing and other activities were heavily dependent on this by-product of the sea (Antunes, 2008b).

The Atlantic distribution of the Aveiro ceramics is documented, in addition to the discovery of Aveiro wares in other localities, thanks to a diverse underwater archaeological record, with nearly a dozen archaeological sites (Carvalho et al., 2014). Some of the examples belong to the archaeological sites called Ria de Aveiro A, B and C. In the two latter places, a large assemblage of Aveiro ceramics as well as several artefacts related to maritime activities were discovered, suggesting that Aveiro was connected to the routes with the North and the South of Europe since the Middle Ages (Bettencourt, 2009; Carvalho et al., 2014). Moreover, the former case, in which this work will focus on, corresponds to a shipwreck. Ria de Aveiro A (RAVA) was discovered in the Aveiro lagoon (Ílhavo) in 1992. The site preserved the aft end of a small wooden vessel, ca. 18-meter-long ship of Ibero-Atlantic tradition, which transported a coarseware cargo. The cargo was located in the hold of the ship, and the ceramics were protected by a dunnage “mattress” about 200 mm thick, made of interwoven sticks, undergrowth, straw, mats and pine needles (Alves et al., 2001). Carbon-14 analysis conducted at an initial research stage, attributed the context to a chronology from mid-15th century (Alves et al., 2001), but the excavation and study of the ceramic cargo indicates a more recent date, from early modern period, 16th or beginning of the 17th centuries (Carvalho and Bettencourt, 2012). RAVA was interpreted as containing a local ceramics cargo destined to be sold in markets outside the lagoon, but the final destination could not be defined. The size of the cargo and the archaeological context suggest, however, a port located in Portugal as the most probable destination (Bettencourt and Carvalho, 2008).

The large number of recovered ceramic pieces allowed the establishment of a typology with the shapes used in everyday life at that time. Some big ceramics, such as large pots, were carrying smaller pots inside



**Fig. 1.** The location of Aveiro in the map of Portugal (red circle) and the location of Ria de Aveiro A (RAVA) and *Santo António* church in the principal map (red circles). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

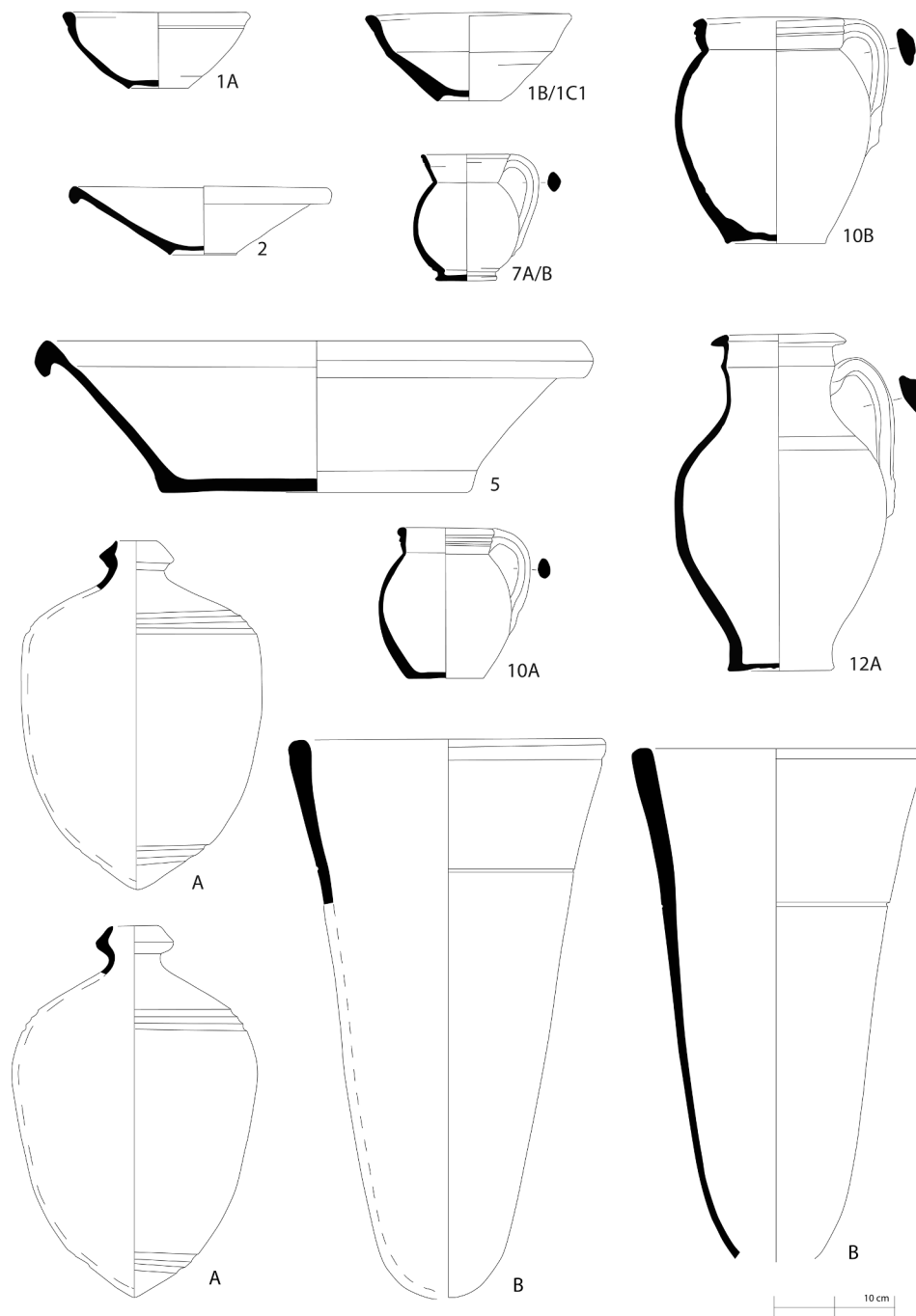


Fig. 2. Main pottery forms: A – olive jars; B – sugar moulds; 1A/1B/1C – bowls; 2 – plate; 5 – basins; 7A/B – mugs; 10A/B – cooking pots; 12A – jar.

them. Similar ceramics were found in Portugal, particularly in the North (Viana do Castelo, Porto, Coimbra), but also in the Atlantic, in places like Azores, Madeira, Newfoundland, in sites related to seasonal fishing settlement, or on England contexts (Alves et al., 2001; Bettencourt and Carvalho, 2008; Carvalho and Bettencourt, 2012). It should also be noted that several pieces of evidence indicative of a fire on board were documented. These are visible in a set of ceramics, which are burnt, deformed and vitrified (Carvalho and Bettencourt, 2012). Since the ceramics were located in the hold of the ship and they were wrapped, the firing environment produced around the ceramics could have been a reducing environment.

The present work also focuses on the ceramics recovered in a terrestrial environment, specifically in the filling of the upper choir dome of *Santo António* church in Aveiro. It is estimated to have around

90 pieces of different typologies. The primitive Franciscan convent of *Santo António*, of which only the church and part of the cloister remains, was founded in 1524. It was classified as a National Monument. The use of ceramics in the construction of domes is a peculiar technique of remote origin, probably Roman, which was developed in the Christian Medieval Era. After cleaning the surface remains, it was discovered that the ceramics were methodically placed and surrounded by very fine and loose clay soil. The conditions and context of finding, allowed to assign this lot to a precise chronology (1524). As many of them had manufacturing defects, it is generally assumed that ceramics reused in these contexts were of local production. There was a predominance of red and unglazed earthenware, although some big black cooking pots were also recovered. In addition to the assemblage of household ceramics and sugar moulds already well known in Aveiro, the finding of a



**Fig. 3.** Sea map of Portugal made by the Dutch cartographer Lucas Janszoon Waghenaer in 1584. The salt production centers of Aveiro could be seen in the fourth river starting to the left. [Title: Gedaente en vodoeninge vant Landt van Portugal; from: Mariner's Mirror (T'eerste deel vande Spieghel der zeevaerdt, van de navigatie der Westersche zee, innehoudende alle de custen van Vranckrijck, Spaingen ende 't principaelste deel van Engelandt, in diversche zee caerten begrepen", Leiden, Christoffel Plantijn, 1584). Source: University of Texas at Arlington Libraries].

group of several olive jars (*anforetas/botijas*) was remarkable because they constituted the main part of the retrieved collection in the church. One of the most characteristic aspects of the olive jars is the distinctive exterior surface treatment by the white slip. This slip is not uniform and does not cover the entire pieces (Silva, 2018).

Regarding the archaeometric analyses of the ceramic materials from Aveiro and surroundings, few studies have been carried out. Among them, the archaeometric investigation by Alves and collaborators (1998), concerning the ceramics recovered in the ship of Ria de Aveiro A, should be noted. In their research, Alves and colleagues catalogued those ceramics as local products after comparing them with the ceramics recovered in *Bairro das Olarias* (Aveiro) and *Casa do Infante* (Porto) by means of X-Ray Fluorescence (XRF). The authors additionally have identified, by XRD, the iron oxide as the common colouring agent, giving different colours (red, brown, grey and black) depending on the oxidation state of the iron. Other relevant study includes the one carried out by Sousa et al. (2005). Sousa and colleagues characterized sugar moulds exhumed in Machico (Madeira Island) concluding that these ceramics could have been produced in Aveiro. Additionally, Vieira and collaborators (2013) compared the spectroscopic data obtained by different techniques, such as micro-Raman, from Portuguese faience production from *Mata da Machada* (South of Lisbon) and tin-lead glazed shards found in a medieval house in Aveiro. The obtained results indicate a similarity in the micro-Raman spectrum in their glaze and clays (Vieira et al., 2013). Recently, Iñáñez et al., 2020 suggested a probable Aveiro provenance for two unglazed red pots recovered in the shipwreck Angra D (Terceira Island, Azores archipelago), after their archaeometric study.

With a view to characterize and to assess the provenance of local or regional origin of the Post-Medieval pottery assemblage, an archaeometric approach of 25 unglazed ceramics from RAVA and the church showing red or black pastes has been performed. In this way, chemical, mineralogical and microstructural analysis by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-Ray Diffraction (XRD) and Scanning Electron Microscopy coupled to an energy dispersive X-ray analyzer (SEM-EDS) have been carried out. Moreover, their provenance has been further assessed by comparing them with well-known archaeometric reference groups from the main production centres of the Iberian Peninsula (Buxeda i Garrigós et al., 2015; Calparsoro et al., 2019; Iñáñez et al., 2008, 2009; Sanchez-Garmendia et al., 2020) shedding light on the local consumption patterns and Atlantic and transatlantic trade during the Medieval, Post-Medieval and Modern

Periods.

## 2. Materials and methods

### 2.1. The ceramic wares

The group of household ceramics (AVR001, AVR002, AVR003, AVR004, AVR005, AVR006, AVR007, AVR008, AVR009, AVR010, AVR011, AVR012, AVR013, AVR014, AVR015, AVR016, AVR022, AVR023, AVR024, AVR025 and AVR026) corresponds to red and black unglazed pottery production, and all ceramics are wheel-made evidenced by concentric marks and lines in their surfaces (Fig. 4). There is a predominance of red earthenware, with variations in the colour of the pastes between red–orange and beige. The pastes of this red earthenware are compact, medium hard and with laminar aspect, either purified or with the inclusion of small and medium non-plastic elements (essentially quartz, calcite and mica), well distributed throughout the matrix. The black pastes are similar to the previous ones, distinguished only by the reducing cooking environment. Among these ceramics, AVR003 and AVR005 are the most uncommon ceramics. The former shows a two-coloured surface and a black paste, whereas the latter is composed by two ceramic shards stuck together (Fig. 4). Additionally, there are three pieces of sugar moulds (AVR018, AVR019 and AVR020) (Fig. 4). These are distinguished by compact pastes, a sandy texture, light orange colour and little purification, with poorly distributed abundant small-medium non-plastic elements (like quartz grains, mica and small, dark-coloured ferruginous particles) and their surfaces are black matte. Finally, the specific group of containers intended for long-distance storage and transportation is formed by an olive jar (AVR017) (Fig. 4). The orange, fine and purified paste differentiates the manufacture of the olive jars. Its surface is not glazed; however, it shows the distinctive exterior surface treatment by the white slip.

The finish of some black ceramics of this assemblage is also worthy of note: four ceramics show a black shiny metallic surface (AVR003, AVR005, AVR015 and AVR016), whereas eight show a black matte one (AVR001, AVR002, AVR012, AVR018, AVR019, AVR020, AVR022 and AVR025) (Fig. 4). Regarding the evidence of the firing produced in the ship, AVR005 seems to be totally burnt, showing black pastes and vitrified surfaces. Another shard showing evidence of fire on its surfaces is AVR013. This information is summarized in Table 1.

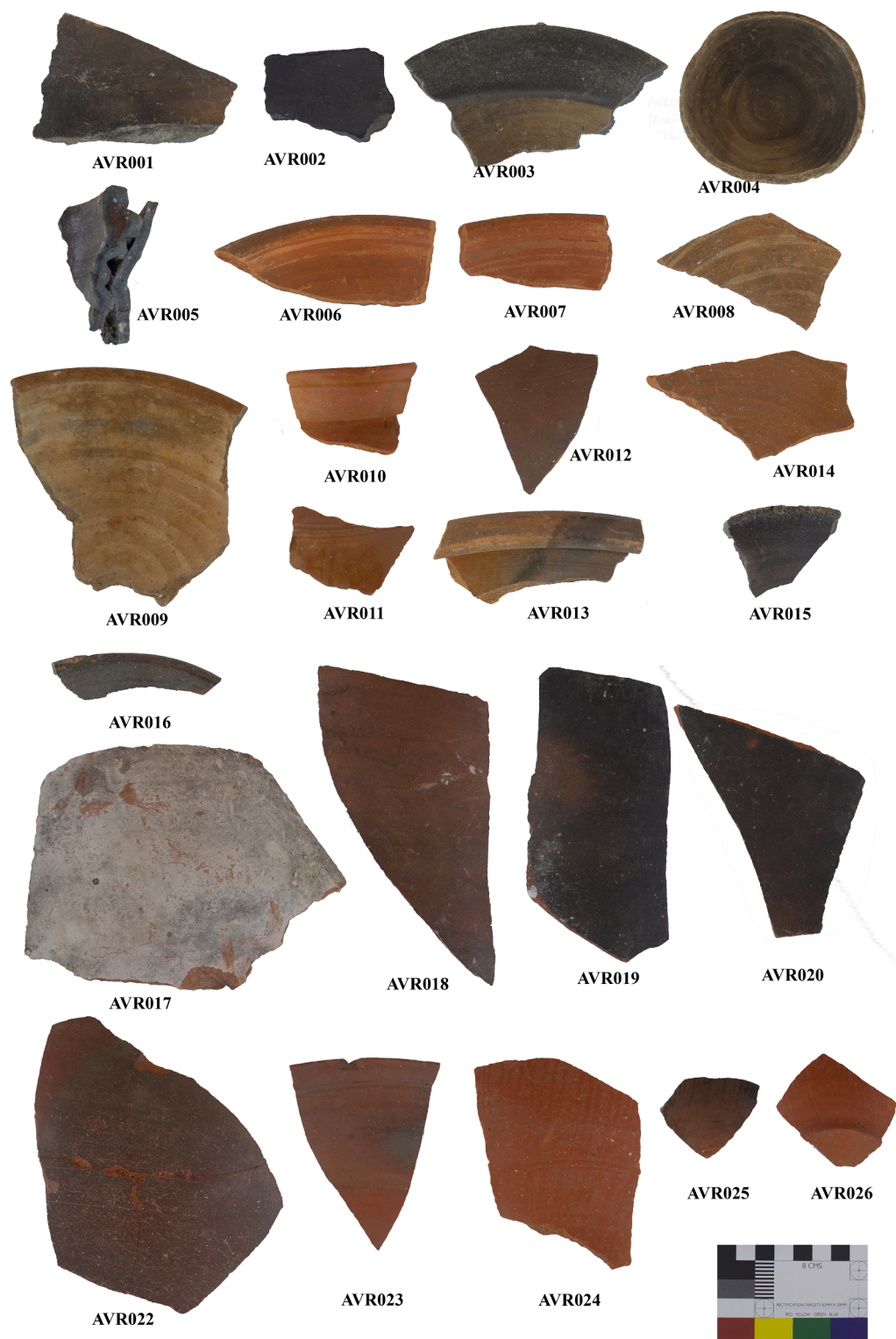


Fig. 4. 25 unglazed red and black pieces unearthed in Ria de Aveiro A and in Santo António church, showing red and black pastes and surfaces.

## 2.2. Methodology

The set of ceramics ( $n = 25$ ) was characterized by a multi-analytical approach. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X-Ray Diffraction (XRD) have been carried out for the chemical and mineralogical analyses. In addition, microstructural characterization, and assessment of the extent of vitrification, alterations and contaminations of a subsample out of the shards ( $n = 16$ ) have been also studied

by Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS).

### 2.2.1. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

These analyses were performed with a Nexion 300 ICP-MS (Perkin Elmer), provided with an Oneneb pneumatic concentric nebulizer, cyclonic spray chamber and standard nickel cones. Prior to the analyses, the ceramic shards followed a fusion sample treatment as in [Sanchez-](#)

**Table 1**

Analytical Identification (ANID), archaeological site, form and the colour of the pastes and surfaces of the 25 ceramics from RAVA and Santo António church.

Anid	Archaeological site	Form	Paste	Surface
AVR001	RAVA	Basin ( <i>alguídar</i> )	Beige	Black matte
AVR002	RAVA	Basin ( <i>alguídar</i> )	Black	Black matte
AVR003	RAVA	Plate ( <i>prato</i> )	Black	Shiny black and beige
AVR004	RAVA	Mug ( <i>púcaro</i> )	Beige	Beige
AVR005	RAVA	Storage jar ( <i>talha</i> )	Black	Shiny black
AVR006	RAVA	Bowl ( <i>tigela</i> )	Red	Red
AVR007	RAVA	Bowl ( <i>tigela</i> )	Red	Red
AVR008	RAVA	Basin ( <i>alguídar</i> )	Beige	Beige
AVR009	RAVA	Bowl ( <i>tigela</i> )	Beige	Beige
AVR010	RAVA	Mug ( <i>púcaro</i> )	Red	Red
AVR011	RAVA	Mug ( <i>púcaro</i> )	Red	Red
AVR012	RAVA	Jar ( <i>cântaro</i> )	Red	Black matte
AVR013	RAVA	Basin ( <i>alguídar</i> )	Red	Red and black matte
AVR014	RAVA	Basin ( <i>alguídar</i> )	Red	Red
AVR015	RAVA	Plate ( <i>prato</i> )	Black	Shiny black
AVR016	RAVA	Plate ( <i>prato</i> )	Dark red	Shiny black
AVR017	Church	Olive jar ( <i>anfqueta/botija</i> )	Red	White
AVR018	Church	Sugar mould ( <i>forma de açúcar</i> )	Red	Black matte
AVR019	Church	Sugar mould ( <i>forma de açúcar</i> )	Red	Black matte
AVR020	Church	Sugar mould ( <i>forma de açúcar</i> )	Red	Black matte
AVR022	Church	Cooking pot ( <i>panela</i> )	Red	Black matte
AVR023	Church	Bowl ( <i>tigela</i> )	Red	Red
AVR024	Church	Jar ( <i>cântaro</i> )	Red	Red
AVR025	Church	Jar ( <i>cântaro</i> )	Red	Black matte
AVR026	Church	Mug ( <i>púcaro</i> )	Red	Red

Garmendia et al. (2020), based on the method optimized by García de Madinabeitia et al. (2008).

The solutions obtained from the fusion of each ceramic were then treated inside a class 100 clean room, following the methodology described in detail in the study carried out by Sanchez-Garmendia et al. (2020). The difference of the present method with the method followed by those authors is that different weights of the Certified Reference Materials used as standards were treated to get solutions of different concentrations in order to obtain external calibrations with wider concentration ranges. First, the solutions were diluted gravimetrically 200 times in a 1% HNO<sub>3</sub> solution. 10 g of dilution were prepared for each primary solution. The internal standards solution (In) was prepared from 1000 µg/ml stock solutions of Alfa Aesar using Milli-Q quality water for their dilution. Argon was used as carrier gas in the ICP-MS measurements. In total, 42 elements and compounds were measured: Al<sub>2</sub>O<sub>3</sub>, Ba, CaO, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe<sub>2</sub>O<sub>3</sub>, Gd, Hf, Ho, K<sub>2</sub>O, La, Lu, MgO, MnO, Na<sub>2</sub>O, Nb, Nd, Ni, P<sub>2</sub>O<sub>5</sub>, Pb, Pr, Rb, SiO<sub>2</sub>, Sm, Sn, Sr, Ta, Tb, Th, TiO<sub>2</sub>, Tm, U, V, Yb, Zn and Zr. The experimental conditions and sample introduction of the ICP-MS are collected in the study carried out by Sanchez-Garmendia et al. (2020).

### 2.2.2. Data interpretation

The chemical results have been treated by a chemometric procedure in order to test the similarity of ceramics and subsequently their hypothetical provenance in accordance with the provenance postulate (Weigand et al., 1977). This treatment has followed a statistical procedure following observations on compositional data by Aitchison (1982), Aitchison (2008), Buxeda i Garrigós (1999), and Buxeda i Garrigós and Kilikoglou (2003). The software employed for all the transformations, statistical analyses and data visualization was R (Core Team 2019). The routines employed are published in a reproducible manner elsewhere (Calparsoro, 2018).

On the one hand, a logarithmic transformation was applied and the comparisons between individuals were performed after dividing all the chemical components by a selected component. In the present work, as a Hierarchical Clustering Analysis (HCA) has been represented, the divisor used was the geometric mean (centered log ratio transformation or clr) and the squared Euclidean distance was graphically represented using the centroid agglomerative algorithm. Therefore, this approach overcomes the problem of the compositional data called “close to unit sum”, when data necessarily sums 100%. It is important to highlight that the use of logarithms not only compensates the differences in magnitudes between major elements (e.g. Si or Al) and trace elements (e.g. the lanthanides or rare earth elements), but also it serves to make the distributions of geochemical data more nearly normal. In addition to that, the log-ratio transformation also detects possible perturbations in the chemical data because of contamination, diagenesis or other alteration processes (Buxeda i Garrigós and Kilikoglou, 2003; see Martín-Fernández et al. (2015) for a thorough discussion on the use of log-ratio principles).

On the other hand, in order to test the variability that each chemical element and compound introduced into the dataset, the compositional heterogeneity was evaluated calculating the compositional variation matrix (MCV). Thus, when the variability is high (indicated by a large value of the total variation, vt), it suggests that the dataset is polygenic (i.e. presence of several compositional groups). On the contrary, a small vt value indicates a possible monogenic nature of the dataset (Buxeda i Garrigós and Kilikoglou, 2003).

### 2.2.3. X-Ray Diffraction (XRD)

A PANalytical X'pert PRO powder diffractometer was used for these analyses. For this, powdered ceramic pastes obtained following the procedure carried out by Sanchez-Garmendia et al. (2020) were used but calcination was not performed.

The instrument was equipped with a copper tube ( $\lambda$ CuK $\alpha$ mean = 1.5418 Å), programmable divergence aperture, vertical goniometer (Bragg-Brentano geometry), automatic sample changer, PixCel detector and secondary graphite monochromator. The operating conditions for the Cu tube were 40 mA and 40 kV. The angular range (2  $\theta$ ) was scanned between 5 ° and 70 °. The treatment of the diffractogram data was carried out using X'pert HighScore (PANalytical) software in combination with the powder diffraction file database PDF2 (International Centre for Diffraction Data – ICDD, Pennsylvania, USA).

### 2.2.4. Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS)

The microstructural characterization and examination of the extent of vitrification, alterations and contaminations of the ceramics were analyzed using the EVO 40 Carl-Zeiss Scanning Electron Microscopy (SEM) coupled to an Energy Dispersive X-ray analyzer (EDS) X-Max. This study was conducted on 11 ceramic pieces after being transversally cut, embedded in epoxy resin, polished and gold coated, as well as in 5 freshly fractured surfaces that were cut perpendicularly to the outer/inner surfaces. The working conditions for SEM were the following: 20 kV, 100 mA, full vacuum conditions and 7.5–10.5 mm working distance. Then, for EDS the intensity is increased to 500 mA to improve the signal. The elemental composition of the ceramics was determined by an Energy Dispersive Spectrometry (EDS) analysis; the EDS spectra were acquired and treated using the INCA software.

## 3. Results and discussion

### 3.1. Identification of the compositional groups by the ICP-MS

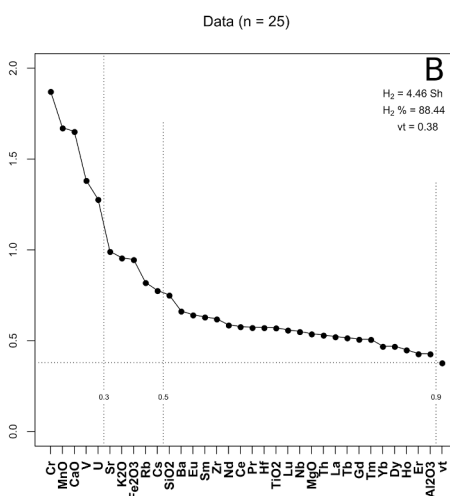
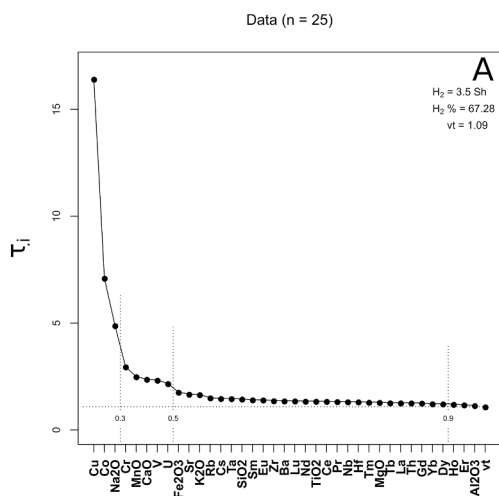
The mean, minimum and maximum concentrations of each element and their average expanded uncertainties (U) as well as the relative standard deviation (RSD) for the 25 ceramics obtained by ICP-MS, are presented in Table 2. The expanded uncertainty of the results has been

**Table 2**

Elemental concentrations, minimum and maximum values and their average expanded uncertainty (U) as well as the relative standard deviation (RSD) for the 25 ceramics obtained by ICP-MS. The RSD has been calculated using all the values of the same component in the 25 ceramics. The concentrations of the elements are expressed in ng/g, whereas for oxides in wt %.

	Mean	Min	Max	RSD	$\bar{U}(\%)$
Al <sub>2</sub> O <sub>3</sub>	17.9	15.0	21.5	10	6.0
Ba	407	364	475	7	5.0
CaO	4.15	3.08	5.66	16	84
Ce	97.6	71.5	121	14	6.0
Co	29.4	16.0	88.6	51	26
Cr	44.5	22.9	74.8	27	38
Cs	26.3	20.7	32.5	11	4.0
Cu	12.2	3.00	37.1	74	24
Dy	5.25	3.84	6.70	14	13
Er	2.64	2.06	3.18	11	22
Eu	1.28	0.999	1.83	16	11
Fe <sub>2</sub> O <sub>3</sub>	5.01	3.68	7.62	19	8.0
Gd	6.35	4.90	8.06	14	10
Hf	6.23	5.05	8.18	11	6.0
Ho	0.751	0.577	0.946	13	20
K <sub>2</sub> O	4.56	3.99	5.72	8	4.0
La	48.3	36.4	60.2	13	5.0
Lu	0.437	0.312	0.584	15	17
MgO	1.76	1.35	2.22	11	18
MnO	0.0208	0.0142	0.0348	24	28
Na <sub>2</sub> O	0.606	0.365	1.11	28	34
Nb	20.5	15.4	25.4	13	4.0
Nd	41.6	30.8	52.7	15	6.0
Pr	11.0	8.32	13.6	15	5.0
Rb	302	252	362	8	3.0
SiO <sub>2</sub>	73.7	66.8	83.5	5	5.0
Sm	7.53	5.40	10.1	17	6.0
Sr	89.9	74.6	125	11	19
Ta	3.03	2.33	3.70	13	8.0
Tb	0.855	0.614	1.12	15	8.0
Th	17.3	13.3	21.0	12	13
TiO <sub>2</sub>	0.735	0.593	0.941	12	9.0
Tm	0.423	0.322	0.516	13	22
U	5.19	3.47	8.96	25	17
V	59.9	40.1	96.7	27	16
Yb	2.60	2.04	3.10	12	19
Zr	230	180	316	13	6.0

calculated following the Guide to the Expression of Uncertainty in Measurement (GUM) (Possolo, 2015) with  $k = 2$ , which is equivalent to a 95% confidence level, as in Calparsoro (2019) and Sanchez-Garmendia et al. (2020), considering the whole analytical procedure. Average values were calculated with the expanded uncertainty of the concentrations corresponding to all ceramics. It should be highlighted that



**Fig. 5. A:** Graphical representation of the evenness of the compositional variability of 25 analyzed ceramics by ICP-MS. P<sub>2</sub>O<sub>5</sub> and Zn were omitted since they showed values below the detection limit and Ni, Pb and Sn because their high uncertainty values. // **B:** Graphical representation of the evenness of the compositional variability of 25 analyzed samples by ICP-MS, after excluding Co, Ta, Na<sub>2</sub>O and Cu for the statistical analysis. (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)).

shipwreck and ceramics recovered in the church and produced in Aveiro, in which all of them define a single compositional group A-1 (Fig. 6). Three ceramics (AVR004, AVR019 and AVR020) are slightly different from the rest due to some differences in their chemical composition, but these are not so significant to discriminate these three ceramics from the rest.

Then, a HCA was performed to compare A-1 ceramics against several reference groups of productions of the Iberian Peninsula such as Seville, Zamora, Barcelona, Manises, Talavera, Nájera and some from Lisbon and Toro based on results obtained through ICP-MS, in order to test the possible exogenous provenances (Buxeda i Garrigós et al., 2015; Calparsoro et al., 2019; Iñáñez et al., 2008, 2009; Sanchez-Garmendia et al., 2020) (Fig. 7).

### 3.1.1. Provenance

Examination of the resulting dendrogram allows establishing a well-defined single group, named as A-1, structure that corresponds to the production of Aveiro, only formed by ceramics unearthed in Ria de Aveiro A and in the dome of *Santo António* church. This fact is in accordance with the article published by Alves and collaborators (1998), which was explained in section 1. Regarding the main chemical features of this reference group, it can be said that it is a low-calcareous group, averaging 4.15 wt% of CaO. The forms dominating in this group are all unglazed olive jars, pots, cups, sugar moulds, plates and bowls, developing reddish and, in some cases, black pastes to visual appearance. The difference between the two sample sets (shipwreck and church) are those which could be seen in a macroscale: while the ceramics retrieved in the church have only red pastes and do not show shiny black surface

and vitrified material, ceramics from the shipwreck show also black pastes and a shiny finish as well as some concretions or alterations in the paste.

### 3.2. Technological assessment by XRD

After identifying the compositional groups, XRD was conducted to identify the mineral phases and different production fabrics. A fabric is the final result that reaches the paste, after completing the technological process of the fabrication of the ceramics (Buxeda i Garrigós and Cau, 1995; Buxeda i Garrigós and Madrid i Fernández, 2016), which can be observed by the array of mineralogical composition and paste textures. In addition, the Firing Temperature (FT) in which the fabrics were fired was also evaluated.

The ceramics from Aveiro form five different production fabrics (F-I, F-II, F-III, F-IV and F-V) (Table 3). The main mineral phases of these four fabrics are quartz, potassium feldspars (principally microcline, sanidine and orthoclase) and plagioclases (principally albite and anorthite). The main differences between the fabrics are the existence or not of illite, hematites and hercynite, all depending on the firing temperatures and oxidizing/reducing conditions (Broekmans et al., 2008; Cianchetta et al., 2015; Nodari et al., 2004).

As regards the F-I group, it is completed with beige paste ceramics from RAVA and is divided in three subgroups: F-I<sub>a</sub>, F-I<sub>b</sub> and F-I<sub>c</sub> (Table 3). The common phases are quartz, illite, potassium feldspars, hematite and plagioclases. On the other hand, the differences between these three groups are the amount of potassium feldspars, plagioclases, hematite and the appearance of secondary phases. It has to be

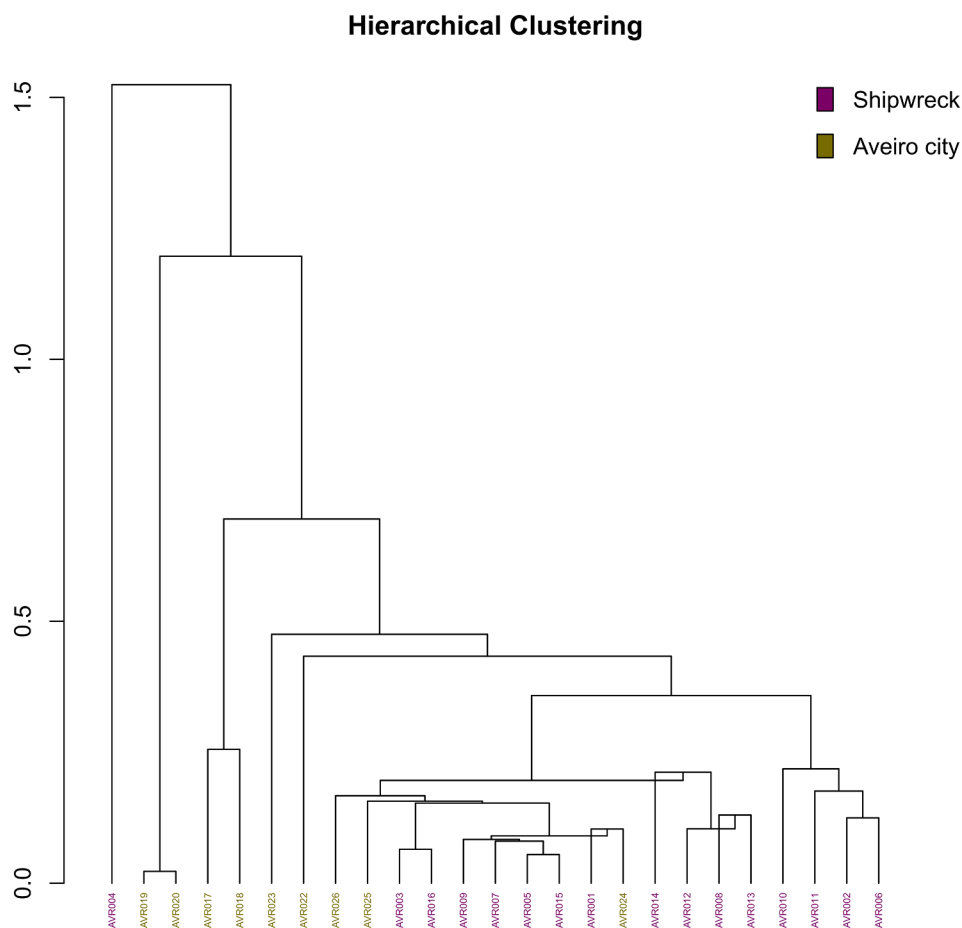
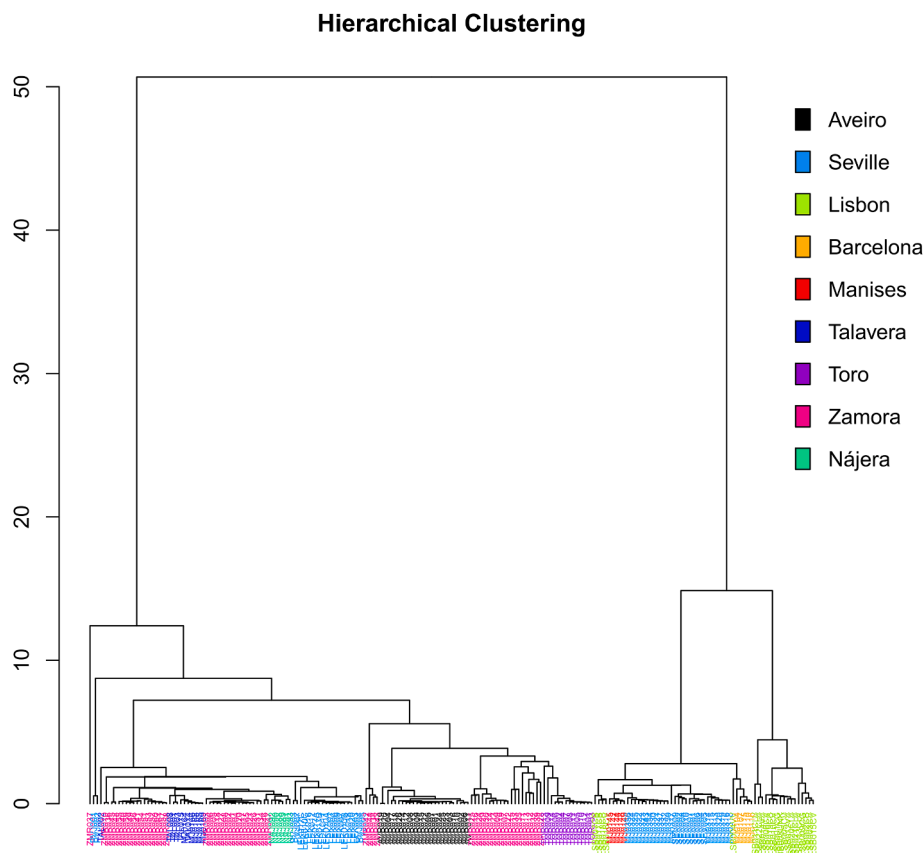


Fig. 6. Dendrogram of Euclidean squared distances using centroid algorithm of 16 ceramics recovered in the shipwreck and 9 recovered in the church and produced in Aveiro, on the sub-composition of Al<sub>2</sub>O<sub>3</sub>, Ba, CaO, Ce, Cr, Cs, Dy, Er, Eu, Fe<sub>2</sub>O<sub>3</sub>, Gd, Hf, Ho, K<sub>2</sub>O, La, Lu, MgO, MnO, Nb, Nd, Pr, Rb, SiO<sub>2</sub>, Sm, Sr, Tb, Th, TiO<sub>2</sub>, Tm, U, V, Yb, Zr.





**Fig. 7.** Dendrogram of Euclidean squared distances using centroid algorithm of 25 individuals from Aveiro (A-1 reference group) and different places from Iberian Peninsula, on the sub-composition of Al<sub>2</sub>O<sub>3</sub>, Ba, CaO, Ce, Cr, Cs, Dy, Er, Eu, Fe<sub>2</sub>O<sub>3</sub>, Gd, Hf, Ho, K<sub>2</sub>O, La, Lu, MgO, Nb, Nd, Pr, SiO<sub>2</sub>, Sm, Sr, Tb, Th, TiO<sub>2</sub>, Tm, V, Yb, Zr.

**Table 3**

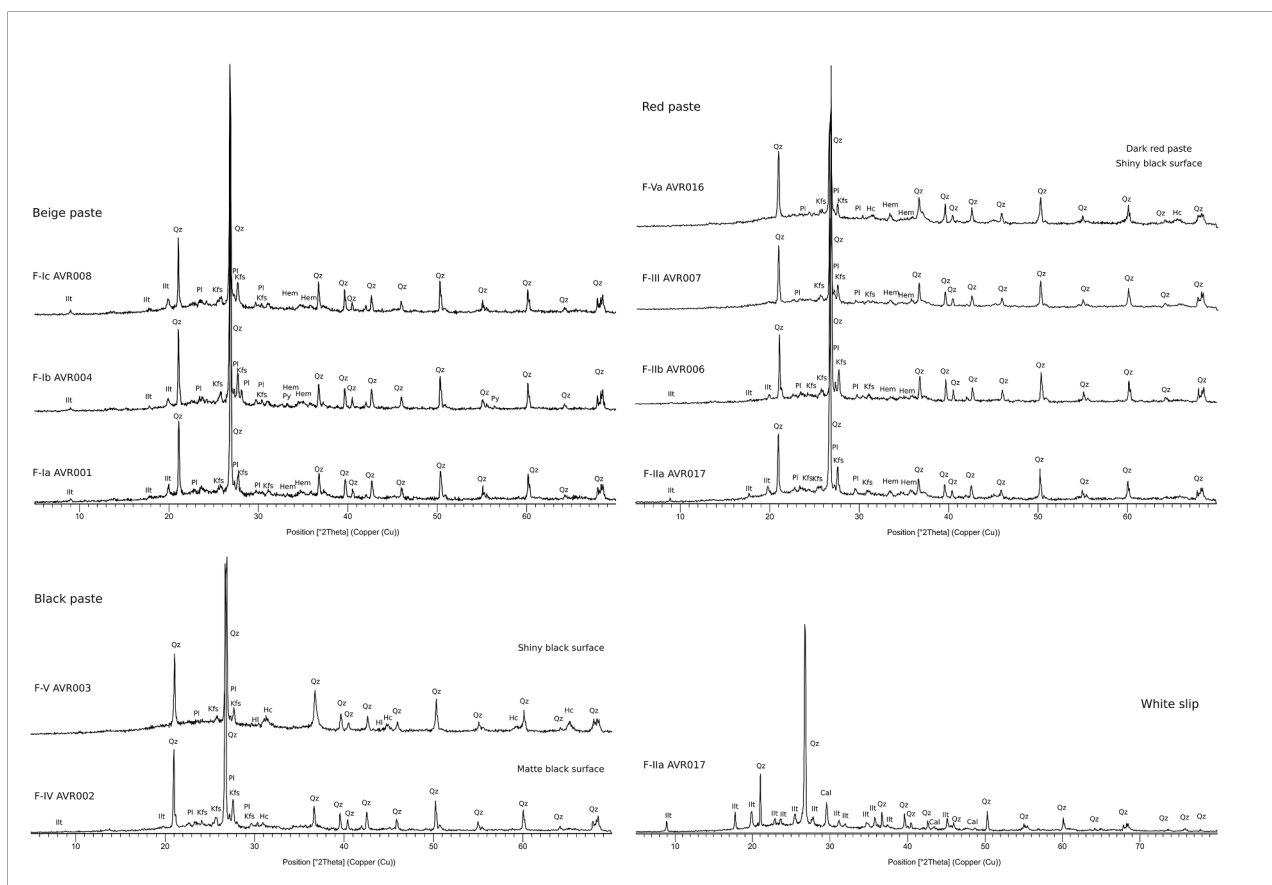
The composition of each fabric and Summary of the results obtained by XRD (the FT, subgroups, ceramics and typology and composition of each fabric). Qz = quartz; Illt = illite; Kfs = potassium feldspar; Pl = plagioclase; Hem = hematite; Hc = hercynite; Py = pyrite; Hl = potassium halite; Cal = calcite, abbreviations according to Whitney and Evans (2010).

FT (°C)	Fabrics	Ceramics	Subgroups	Typology	Qz	Illt	Kfs	Pl	Hem	Hc	Py	Hl	Cal
800	F-I	AVR001	F-I <sub>a</sub>	Beige paste	X	X	X	X	X				
		AVR004	F-I <sub>b</sub>		X	X	X	X	X		X		
		AVR008, AVR009	F-I <sub>c</sub>		X	X	X	X	X				
800–850	F-II	AVR013, AVR017, AVR025	F-II <sub>a</sub>	Red paste	X	X	X	X	X				X (surface of AVR017)
		AVR006	F-II <sub>b</sub>		x	x	x	x	x				
900	F-III	AVR007, AVR010, AVR011, AVR012, AVR014, AVR018, AVR019, AVR020, AVR022, AVR023, AVR024, AVR026	F-III	Red paste	X		X	X	X				
850–900	F-IV	AVR002	F-IV	Black paste and black matte surface	X	X	X	X		X			
950	F-V	AVR016	F-V <sub>a</sub>	Dark red paste and black shiny surface	X		X	X	X	X			
		AVR003, AVR005, AVR015	F-V <sub>b</sub>	Black paste and black shiny surface	X		X	X		X		X (AVR003)	

highlighted that the ceramic that forms the F-I<sub>a</sub> subgroup, is the only one that has a black matte surface in F-I. F-I<sub>b</sub> seems to have more potassium feldspars and plagioclases than the rest, whereas the main difference between F-I<sub>a</sub>, F-I<sub>b</sub> and F-I<sub>c</sub> is the amount of hematite: F-I<sub>c</sub> has much more hematite than the others do. This fact could be related to the reduction of hematite in marine environments, suggesting that the iron of the hematite (Fe<sup>3+</sup>) of F-I<sub>a</sub> and F-I<sub>b</sub> is lower because it was reduced to the iron

of pyrite and/or jarosite (Fe<sup>2+</sup>), whereas F-I<sub>c</sub> did not suffer any or not too much hematite reducing reactions (see Section 3.3) (Secco et al., 2011). This fact could be proven by the appearance of pyrite in the F-I<sub>b</sub> fabric. Therefore, in the fabric F-I, the high presence of illite and the appearance of potassium feldspar allows establishing a Firing Temperature (FT) of 800 °C (Fig. 8).

The fabric F-II is formed by red paste ceramics and divided in two



**Fig. 8.** Reference diffractograms of the fabrics divided by the colour of the pastes (beige paste, red paste and black paste). Qz = quartz; Ill = illite; Kfs = potassium feldspar; Pl = plagioclase; Hem = hematite; Hc = hercynite; Py = pyrite; HI = potassium halite; Cal = calcite, abbreviations according to [Whitney and Evans \(2010\)](#).

subgroups: F-II<sub>a</sub> and F-II<sub>b</sub>, completed by ceramics from RAVA and the church. The common phases are quartz, illite, plagioclases, potassium feldspars and hematite and the differences between these two subgroups is that F-II<sub>a</sub> contains much more illite than F-II<sub>b</sub>. Moreover, inside the group of F-II<sub>a</sub>, ceramics from the church (AVR017 and AVR025) show more hematite than ceramics from RAVA (AVR013). This could be in accordance with the fact that in marine environment hematite could be reduced ([Secco et al., 2011](#)). As illite is present but is decreasing in the amount, the FT of the fabric F-II is in the range of 800–850 °C ([Fig. 8](#)).

When it comes to the fabric F-III, formed by red ceramics from RAVA and the church, it presents quartz, potassium feldspars, plagioclase and hematite. As the no appearance of illite suggests its decomposition, the FT is of 900 °C ([Fig. 8](#)).

The F-IV fabric is formed by one black matte ceramic (surface and paste) from RAVA and it presents quartz, little illite, plagioclases, potassium feldspars and hercynite. There is no hematite, and this fact could suggest that the hematite could have been reduced to hercynite, in addition to the reductions that could happen in the marine environment ([Broekmans et al., 2008](#); [Cianchetta et al., 2015](#); [Nodari et al., 2004](#)). The total reduction of hematite could be explained by the black colour of AVR002 ceramic shard. In this fabric, the presence of a little amount of illite, potassium feldspar and hercynite permits establishing an FT in the range of 850–900 °C ([Fig. 8](#)).

Finally, F-V fabric, divided in two subgroups, is formed by four metallic shiny black surface ceramics from RAVA, showing quartz, potassium feldspars, plagioclases and hercynite. F-V<sub>a</sub> is formed by a ceramic which shows a dark red paste, whereas F-V<sub>b</sub> is formed by ceramics with black paste. The main difference between these two sub-fabrics is the appearance of hematite in F-V<sub>a</sub>, suggesting that the reduction conditions were not fully achieved in AVR016 ceramic (see

Section 3.3). Additionally, some secondary phases in some shards, as well, were identified, like potassian halite (AVR003). According to literature, sodium–potassium chloride (potassium halite) was also detected in an Italic amphora recovered in an underwater marine environment ([López-Arce et al., 2013](#)). Given these conditions, the FT of this fabric is of 950 °C. The amount of hercynite particularly draws the attention in F-V<sub>b</sub>, because it is the highest peak in comparison with the rest of the fabrics ([Fig. 8](#)).

Additionally, the white slip of AVR017 ceramic (olive jar) has been analyzed. The phases that are clearly differentiated are quartz, calcite and clay minerals ([Fig. 8](#)). Thus, this slip was made mainly by a calcareous substrate likely mixed with clay to facilitate bonding to the ceramic surface while providing a white surface that covered the whole piece. However, the reason for applying such slip, beyond aesthetic features or for marking specific product containing the olive jar, remains unknown.

### 3.2.1. Black ceramic production

The ICP-MS analyses allowed to know that the source of clay used for the manufacture of these 25 ceramics was the same. Additionally, as it could be noticed by XRD analyses, the pastes are not the same, so the only reason for this fact that one can think about, is the different technology (e.g. different atmosphere conditions during firing, different finishing) applied with a view to obtaining red and black pastes. According to literature, the black coloration of ancient ceramics was obtained mainly in three ways: using carbon, adding manganese oxides to the clays and reducing iron oxides in a reducing atmosphere, during firing ([Edwards and Chalmers, 2005](#); [Gillies and Urch, 1983](#)). The first case (the use of carbon) is based on using clays naturally rich in organic material or to which carbonaceous material has been added. Then, they

are fired in reducing conditions and carbon is formed. This gives the black colour to the ceramic (Gillies and Urch, 1983). The third case (firing in reducing conditions) is probably the oldest of all ceramic-decoration processes (Noll et al., 1975). When iron oxides are fired, their colour is affected by temperature, duration of heating and atmosphere (Shepard, 1976). In an oxidizing atmosphere, iron oxides are mainly in the form of hematite. However, in a reducing atmosphere, iron oxides form spinel phases, like hercynite ( $\text{FeO}\cdot\text{Al}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ), which are predominantly black (Longworth and Tite, 1979; Maggetti et al., 1981; Noll et al., 1975). One of the hypotheses of the black ceramics that form F-IV and F-V, is that they were fired in reducing conditions in order to get the black colour. This black colour could have been obtained due to the reduction of hematite ( $\text{Fe}_2\text{O}_3$ ) to hercynite, indicating strong reducing firing conditions (Ibarra, 2006; Nodari et al., 2004).

According to archaeological evidence, it was common in Aveiro to produce these black ceramics for the forms related to kitchen wares, like cooking pots (Carvalho and Bettencourt, 2012; Fernandes and Castro, 2012; Ibarra, 2006). The reason for doing this could have been the good qualities that the ceramics obtain in these reducing firing conditions: the carbon element that is caught in the ceramic paste during the process decreases the permeability of the paste, so that these shards are suitable for retaining liquids. The same circumstances provide also better and more hygienic food preservation because the dirt and bacteria are not able to pierce in the pores, preventing the ceramic pastes, in this way, from the reproduction of these microorganisms (Sempere, 1982). On the other hand, the reduced wares are harder than the common wares, so that they are more resistant in the use (Sempere, 1982).

### 3.3. SEM-EDS assessment

Finally, ceramics of each fabric were selected to study them by SEM and SEM-EDS in order to analyze the microstructure, the extent of vitrification, alterations and contaminations.

#### 3.3.1. Extent of vitrification

Five freshly fractured surface ceramics were selected for SEM analysis, because their SEM examination provides information about the internal morphology developed during the original firing, the extent of vitrification and pore structure (Maniatis and Tite, 1978). Among the selected ceramics, two are from F-I (AVR008, AVR009), one from F-II (AVR017), one from F-IV (AVR002), and one from F-V (AVR003) (Table 4). In this way, the results of SEM demonstrate that the F-I and F-II fabrics show an early initial vitrification due to the appearance of isolated smooth-surfaced areas, whereas the F-IV shows a medium vitrification (Maniatis and Tite, 1978). Finally, the F-V shows a

**Table 4**  
Elemental concentrations of Na (in wt %) in different regions obtained by SEM-EDS of the ceramics shown in Fig. 12.

ANID	Glassy-layer	Spectrum	Position	Na
A. AVR003	Yes	Spectrum 3	Surface	9,99
		Spectrum 2	Lower than the surface	1,97
		Spectrum 1	Body	0,29
B. AVR016	Yes	Spectrum 1	Surface	5,37
		Spectrum 2	Surface	6,03
		Spectrum 3	Body	0,64
C. AVR015	Yes	Spectrum 3	Surface	5,87
		Spectrum 2	Lower than the surface	2,79
		Spectrum 1	Body	0,77
D. AVR004	No	Spectrum 4	Surface	0,41
		Spectrum 3	Body	0,43
E. AVR014	No	Spectrum 1	Surface	0,39
		Spectrum 2	Surface	0,26
		Spectrum 3	Body	0,17

continuous vitrification, because a continuous smooth vitrified layer is formed over the whole fracture surface (Fig. 9) (Maniatis and Tite, 1978). All these results are in accordance with their FTs.

Additionally, 11 transversally cut and polished pieces were selected for SEM-EDS analyses: 2 from F-I (AVR004, AVR008), 1 from F-II (AVR017), 4 from F-III (AVR007, AVR014, AVR016, AVR018) and 4 from F-V (AVR003, AVR005, AVR015, AVR016).

#### 3.3.2. The glassy-layer

According to SEM-EDS results, none of the ceramics has any alkaline or tin-lead glaze, although a glassy-layer is observed in the shiny black ceramics from F-V (Fig. 10). For the ceramics of F-V<sub>b</sub>, a glassy-layer that contains vacuoles could be observed, whereas for F-V<sub>a</sub> (AVR016), the vacuoles are less abundant. The reason for the appearance of the glassy-layer could be that, at high temperatures, iron compounds may act as a flux when they are exposed to a reducing atmosphere, resulting in the change of the colour of the shard (from red to black) and also the formation of a glassy-layer in the surface (Rice, 2015). Additionally, Noll and colleagues (1975) explain that, for example, Cretan wares black painting was obtained reducing (by the iron reduction technique) iron-rich clays, which were added as a slip. The authors explain that in Cretan wares a high content of vacuoles were formed in the black paint layer. These vacuoles could have been formed due to the fact that during firing, some gases were formed in the form of bubbles (e.g. carbon dioxide) that attempt to escape through the layer. At higher temperatures, more of this glassy-layer is formed and the large number of bubbles/vacuoles could indicate a relatively high firing temperature (Noll et al., 1975). Thus, the existence of the vacuoles in the ceramics from Aveiro could be explained by the fact that Noll and collaborators report in their study. In these lines, a hypothesis is thought for AVR016 ceramic; it is from F-V<sub>a</sub> subgroup, which shows a dark red paste and fewer vacuoles in the glassy-layer. Thus, this ceramic probably was red in origin but it was refired during the firing produced in the ship. As the firing environment around the ceramic cargo was probably a reducing environment (because they were covered), the hematite of the paste was reduced partially to hercynite, as it has been reported in Section 3.2. Thus, the fewer vacuoles of the glassy-layer and the partial reduction of hematite to hercynite could suggest that the interaction between the ceramic and the fire was not very strong when time exposed and temperature reached are considered. On the contrary, a strong interaction case could be the case of AVR005; this ceramic was probably red in origin, as well, but the reduction of hematite in this case was a total reduction. Moreover, the reason for thinking that AVR005 was red in origin, is that there is no archaeological evidence for black storage jars in Aveiro A excavation context. All storage jars recovered are red.

#### 3.3.3. The shiny black surface

The shiny black surface finishes found on ceramics studies here, have been applied in pottery from their earliest production. The reasons for applying them were both practical -because they provide more impermeable surface layer- and decorative (Tite et al., 1982). In some cases, the fine particle fraction of the body clay has been used to produce the black coating (in the case of Greek Attic black ceramics, for example) (Gillies and Urch, 1983). This is not the case of our ceramics, as no clay slip has been identified by SEM-EDS. In other cases, the metallic shiny black surface has been achieved by applying a burnished finishing in addition to the firing in high temperatures and reducing atmosphere. In this way, the shiny black surface is produced due to the alignment of the clay particles in the surface region on account of reducing firing conditions and burnishing (Gillies and Urch, 1983). According to Berg (2008), burnishing consists of the use of a hard, smooth object like wood, stone or bone, to rub the ceramic surface, often resulting in narrow parallel facets. By compressing the clay, burnishing creates a characteristic luminous shine (Berg, 2008). Burnishing produces a uniform and compact surface, and it causes specular reflection, giving to the ceramics a "lustrous", "shiny" or "glossy" surface like that obtained by

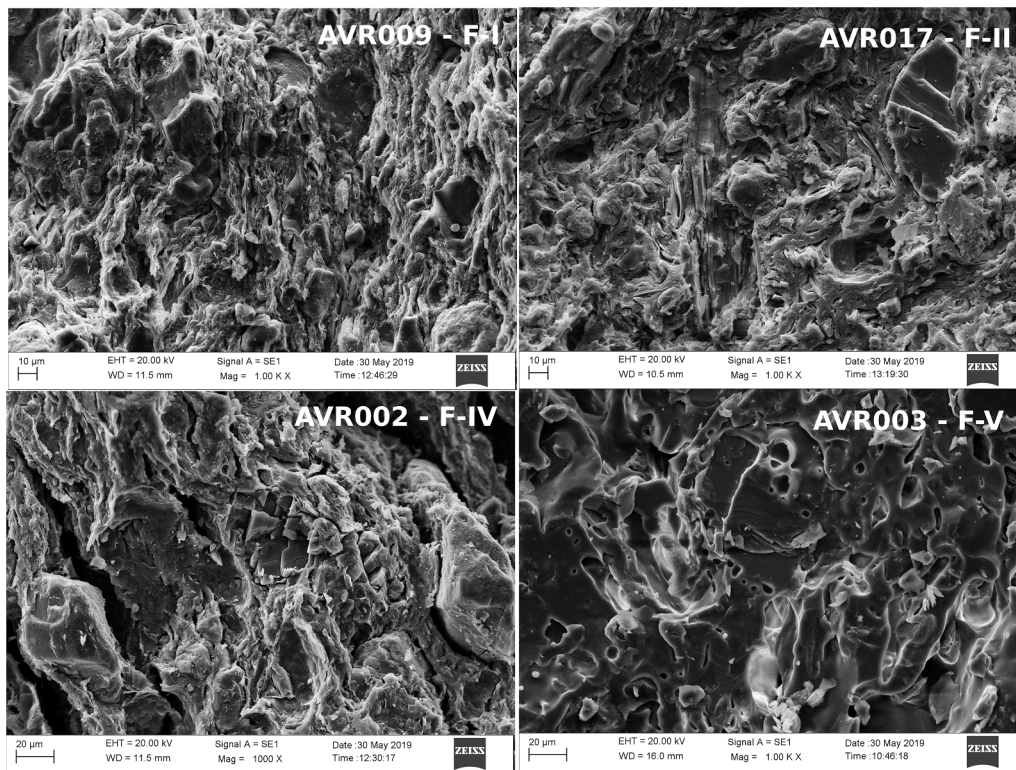


Fig. 9. The grade of vitrification of A) F-I (ceramic AVR009), B) F-II (ceramic AVR017), C) F-IV (ceramic AVR002) and D) the grade of vitrification of F-V (AVR003).

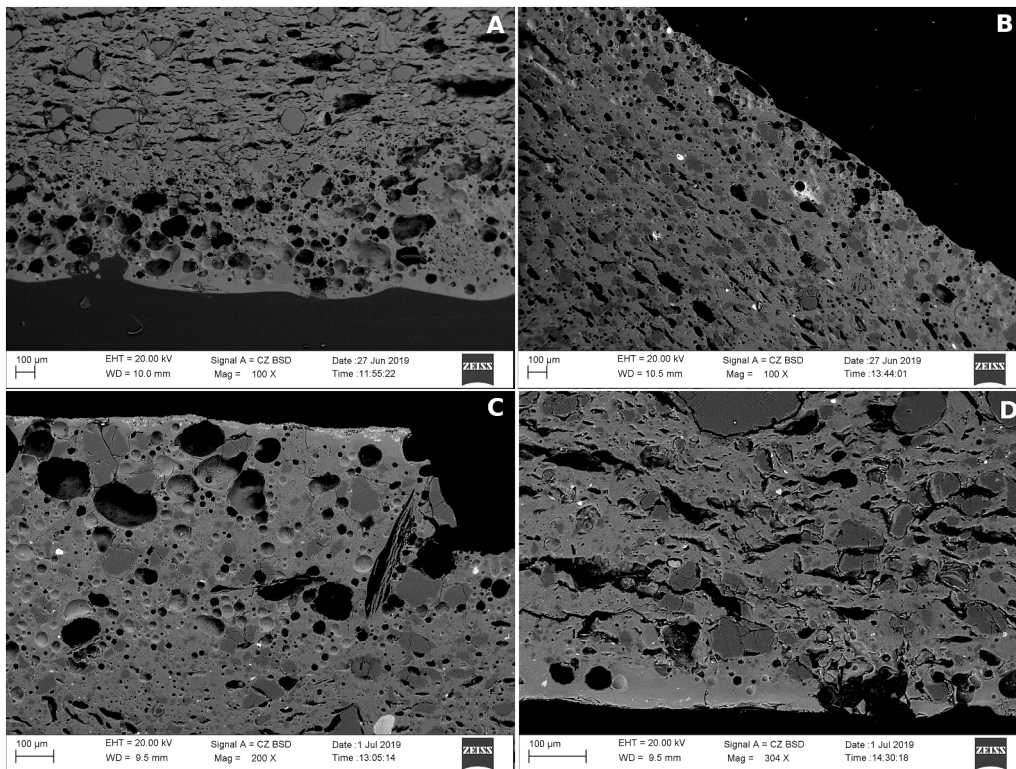


Fig. 10. Four ceramic pieces from F-V showing a glassy-layer (A: AVR003, B: AVR005, C: AVR015 and D: AVR016).

different coatings (e.g. paints, slips, glazes). Contrariwise, smoothing makes ceramics appear “matte” or “dull” and this difference is because of different light reflections; the uniform surface allows for a large amount of light to be reflected directly back to the observer and thus the

surface appears “lustrous” or “shiny” (Ionescu et al., 2014). This is the case for some black ceramics from Marginea (Romania) (Ionescu et al., 2014), Orsett (Essex, England) (Gillies and Urch, 1983), Indian “Northern Black Polished Ware” (Gillies and Urch, 1983) and Attic

ceramics (Maniatis et al., 1993). Regarding the present case, burnished ceramics are well documented in Aveiro red and black ceramics, sometimes in vertical and crossed lines, creating geometric motifs in some of the closed forms (mugs, jugs/water jugs and storage jars) (Bettencourt and Carvalho, 2008; Carvalho and Bettencourt, 2012). Additionally, Fernandes (2012) studies the black ceramic production from Portugal in her doctoral thesis and mentions that burnishing the surface of the pieces was, and still is, a technique widely used to decorate the surfaces of black or red pottery, leaving the surface shiny (Fernandes, 2012). Therefore, according to the literature presented, ceramics from F-V have been probably burnished because of the

appearance of their shiny black surface.

### 3.3.4. Salt-glaze hypothesis

Additionally, the elements Na and Cl have been identified in an aggregate of AVR009, in the surfaces of AVR004 and AVR005 and in the ceramic body of AVR015 (Fig. 11). Moreover, Na has been identified in the surface and body of some ceramics (AVR003, AVR004, AVR005, AVR006, AVR007, AVR008, AVR014, AVR015, AVR016) (Fig. 11). Potassium halite has been identified as described in the Section 3.2, as well. Although the sodium could be related to the sodium feldspars, especially in the ceramics that do not have a glassy-layer, the NaCl or Na could be

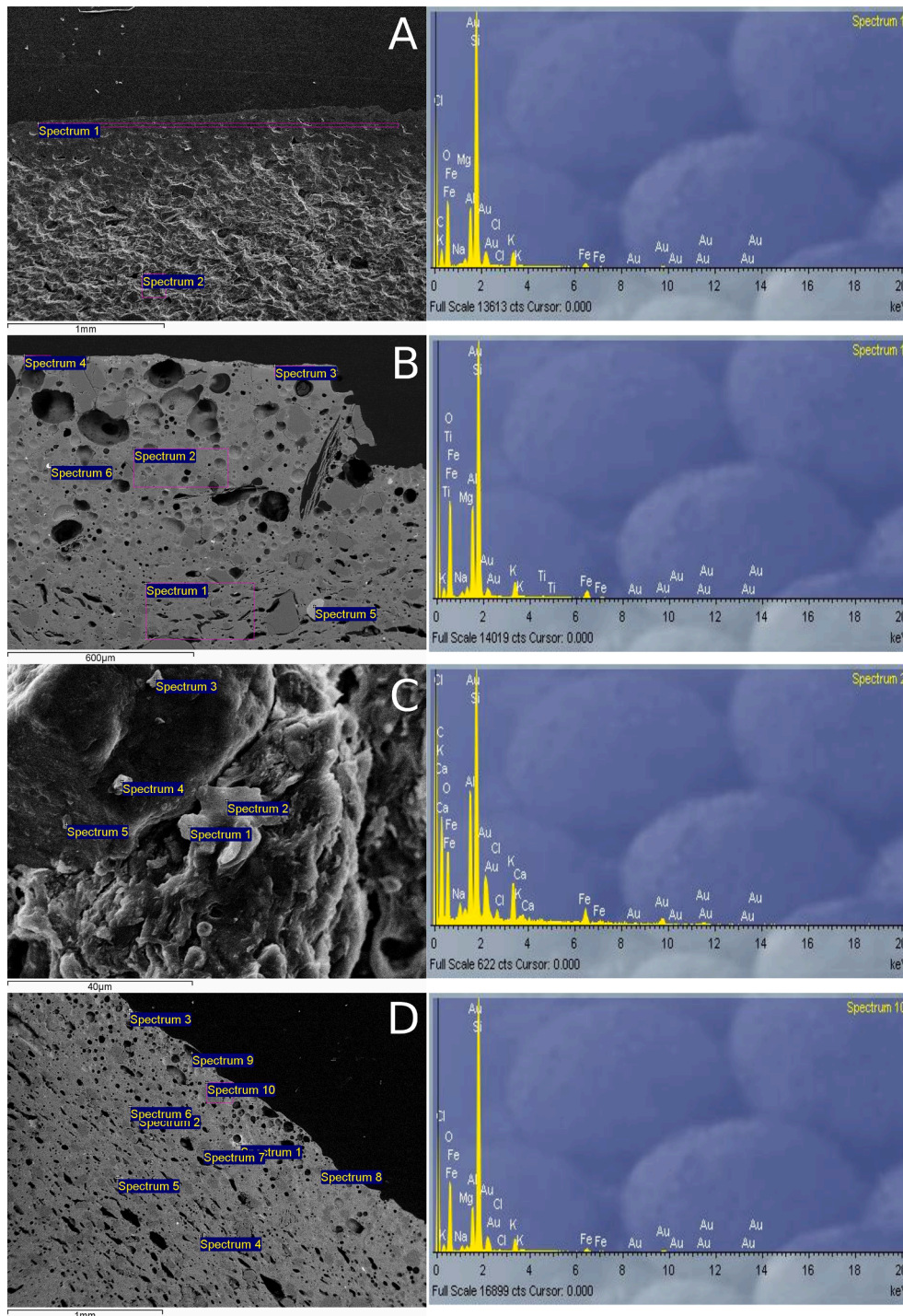


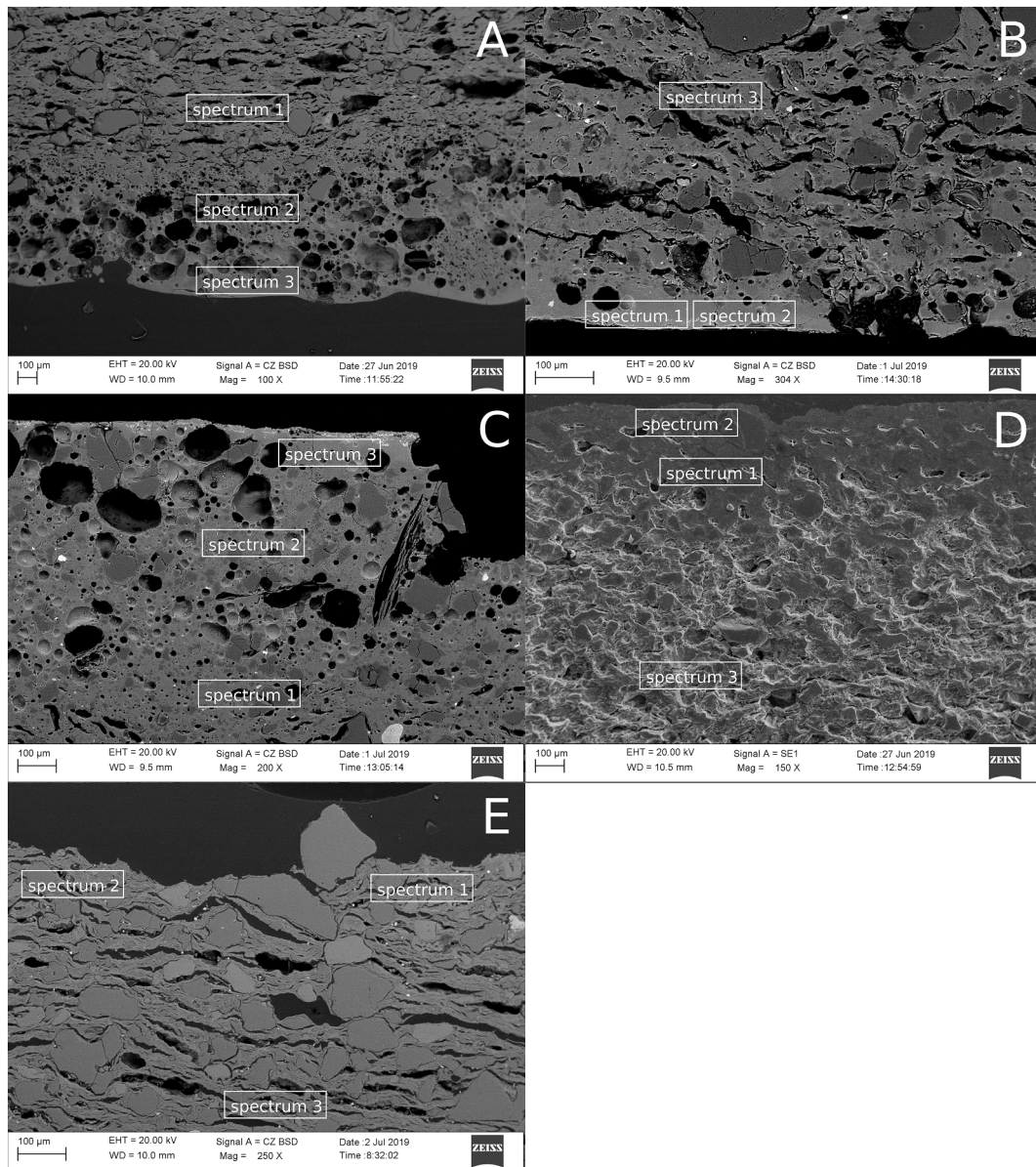
Fig. 11. A: Na and Cl in the Surface of AVR004. B: Na in the body of AVR015. C: Na and Cl in an aggregate of AVR009. D: Na and Cl in the surface of AVR005.

related to the salt of the water environment from RAVA. Moreover, it could be related to the salt production and trade of Aveiro because fragments of a wood piece belonging to the shipwreck were discovered in the archaeological site of Ria de Aveiro A. By comparison with materials from other underwater contexts, it was recognized as a part of a shovel made of a single piece of log. It seems that the shovels were destined to load, unload and move the salt, although another function on board is not excluded. A similar shovel was also recovered in Newfoundland, associated with the conservation treatment of fish caught by European fishers who move there annually (Bettencourt and Carvalho, 2008). Therefore, it could be thought that the ship was carrying salt in a location next to the ceramics or above them.

As has been reported in Section 1, several indications of a fire on board have been documented. The adiabatic flame temperature is the highest temperature achieved without any heat loss or any other external factor affecting the combustion process and, in the case of wood, the calculated adiabatic value is 1980 °C (Annamalai and Puri, 2006; Nolan, 2000). However, in a real fire event, like the underwent by the RAVA shipwreck, many factors play a role when determining the

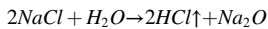
temperature (e.g. timber thickness and density, amount of available combustible material, humidity, atmospheric pressure, oxygen supply, among others). In any case, flame temperature can be around 1000 °C (Elvira Martín, 1984; Stroup et al., 2013), or even higher if it is an enclosed fire, in which flame temperature easily reaches 900°C but showing peak temperatures up to 1200 °C depending on the size of the fire (Babrauskas and Williamson, 1978, 1979). However, when considering pottery firing, flame temperature is not the only factor to consider; surrounding gas temperature should be also of importance regarding the effect of firing. In this regard, and according to software simulations, the expected gas temperature in the near field of a wood fire will vary between 600 and 1100 °C (Degler and Eliasson, 2015; Kawagoe and Sekine, 1963). Moreover, in enclosure fires, gas temperature may easily exceed a temperature above 1000 °C (Elvira Martín, 1984), sustaining the gas temperature for over 50 min under optimal conditions of amount of combustible, humidity and oxygen (Karlsson and Quintiere, 2000).

In this context, it is possible to hypothesize about the relation between the salt and the fire present on board. As the fire started in the ship, the salt could have reacted with the water in high temperatures

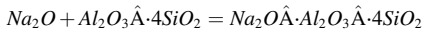


**Fig. 12.** Elemental analyses in the different regions (surface, lower than the surface and body) of **A:** AVR003; **B:** AVR016; **C:** AVR015; **D:** AVR004 and **E:** AVR014, marked by the name of the spectrum.

(the temperatures of the fire), giving hydrogen chloride and sodium oxide (alkaline flux) as a product, according to the following reaction (Rice, 1987):



The important role of the alkaline fluxes is to lower the very high melting point of silica, which is normally 1710 °C (Rice, 1987). Hence, this alkaline flux could have reacted with the silica of the pot surface ( $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ), giving a glassy-layer as a product ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ):



Therefore, temperature achieved during a fire like the one in the RAVA shipwreck might be high enough and sustained long enough as to produce vitrification and glassy-layers on the vessel surfaces, probably with a rapid temperature increase when the vegetable cover that wrapped the cargo ignited.

These reactions can explain the presence of Na and not Cl in some ceramics and some concretions of some ceramics as well as the vacuolar aspect of the glassy-layers: the Cl was evaporated in the form of hydrogen chloride, leaving holes where before there were bubbles. This reaction and the formation of a glassy-layer also can be explained by the compositional difference of Na between the surface and the body of the ceramics that have the glassy-layer (Fig. 12 and Table 4). These values demonstrate that the concentration of Na is higher in the surface than in the body, due to probably the formation of  $\text{Na}_2\text{O}$  in the surface. The difference in the concentration of Na also occurs in a lesser degree, that is, not with big differences, in other ceramics that do not have a glassy-layer (e.g. AVR014), but not in all of them (e.g. AVR004) (Fig. 12 and Table 4). Moreover, this hypothesis can also explain the case of AVR005: the two ceramics that were next to each other in the ship could have reacted with the salt following the reaction explained, so that finally

they got stuck.

### 3.3.5. Marine environments

Some aggregates composed by Fe, S, and in some cases, K have also been identified in the cavities and cracks of the ceramics (Fig. 13).

According to the literature, these aggregates could be pyrite ( $\text{FeS}_2$ ) and/or jarosite ( $(\text{K}, \text{Na})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ) (Secco et al., 2011). The presence of these two aggregates is a common alteration in marine environment ceramics, produced due to the decomposition of hematite ( $\text{Fe}_2\text{O}_3$ ), from ferric ion ( $\text{Fe}^{3+}$ ) to ferrous ion ( $\text{Fe}^{2+}$ ), by the reduction and solubilization with hydrogen sulphide ( $\text{H}_2\text{S}$ ) in water solution (Iñáñez et al., 2020; Secco et al., 2011). In saline water environments, the microorganisms can reduce sulphate ions ( $\text{SO}_4^{2-}$ ) to sulphur (S) or hydrogen sulphide, in the presence of sulphate-reducing bacteria (*Desulfovibrio desulfuricans*) (Neal et al., 2001; Secco et al., 2011). Then, this  $\text{H}_2\text{S}$  is the responsible for hematite being reduced. Two main mechanisms could happen for this reduction, giving as a product framboidal aggregates or euhedral crystals of pyrite (Secco et al., 2011). On the one hand, hematite could hydroxylate to goethite ( $\text{FeOOH}$ ), and subsequently, goethite could be reduced by  $\text{H}_2\text{S}$  to  $\text{Fe}^{2+}$ . On the other hand, hematite could be reduced directly to  $\text{Fe}^{2+}$  in the presence of  $\text{H}_2\text{S}$ . After these two reduction mechanisms, the ferrous ion reacts with additional hydrogen sulphide and forms pyrite as euhedral crystals or framboidal aggregates depending on the different sequences of reactions and the amount of organic matter and hydrogen sulphide (Neal et al., 2001; Schoonen, 2004; Secco et al., 2011). Then, jarosite could be formed due to the oxidation of pyrite and reaction with dissolved alkali (Secco et al., 2011).

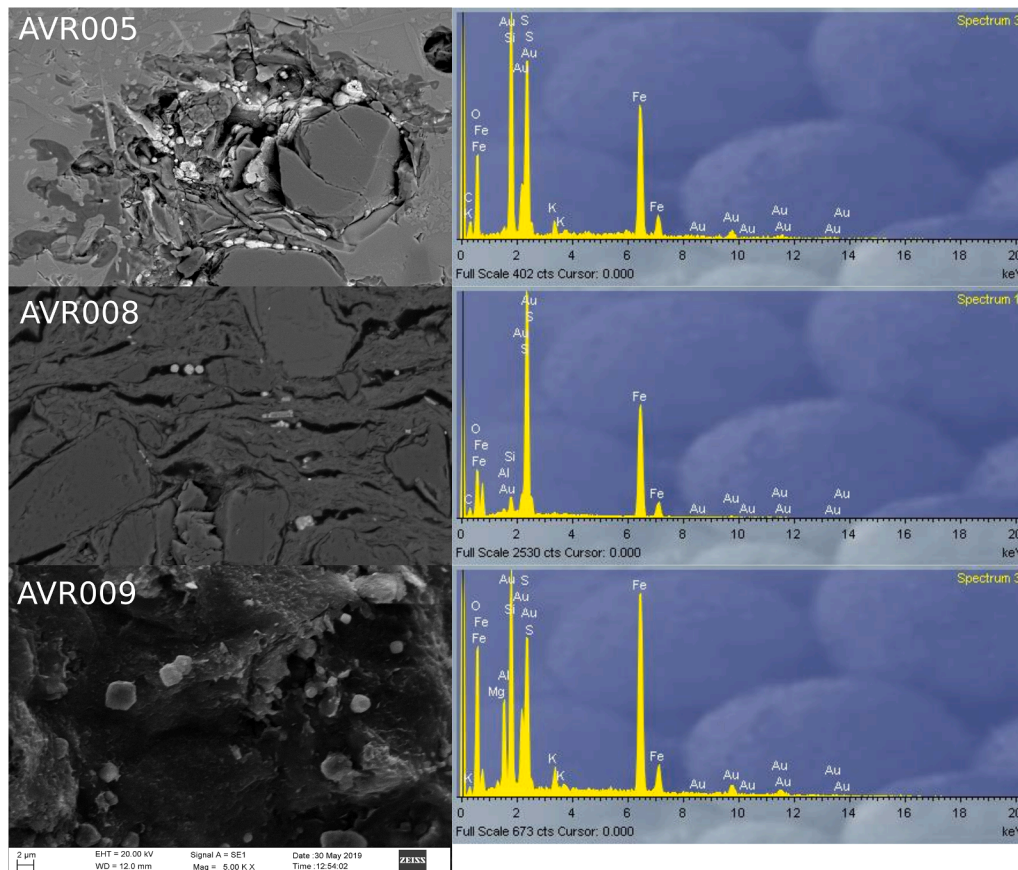


Fig. 13. Aggregates in the cracks and cavities of AVR005, AVR008 and AVR009 composed mainly by Fe and S, and, sometimes, K.

#### 4. Conclusions

This study provides a deeper understanding of pottery production and trade in Aveiro during the Post-Medieval period after the archaeometric characterization performed on 25 unglazed red and black low-calcareous ceramics unearthed in the archaeological site Ria de Aveiro A and the *Santo António* church. Thus, chemical analysis allowed establishing their provenance as belonging to A-1 local reference group, which is related to the local pottery production of Aveiro during the 16th to the beginning of 17th centuries. These results are in accordance with the study carried out by [Alves et al. \(1998\)](#), which was explained in section 1.

As far as the manufacture technology is concerned, two main colours are distinguished among the pastes inside A-1 reference group: low-calcareous red and black, fired at temperatures ranging from 800 °C to 950 °C. Considering that all ceramics are formed with the same clays, the difference in the colour suggests that there is no specialization concerning the paste. Instead, in the first place, potters played with the temperature and the atmosphere of the kiln to obtain the colour of the paste they desired and, in the second place, they played with the different finishing of the ceramics. Thus, probably, they applied reducing conditions and high firing temperatures (850–950 °C) for AVR002, AVR003 and AVR015 ceramics and this fact would be explained by the appearance of hercynite -after the reduction of hematite- in all of these ceramics. [Echallier \(1984\)](#) states that black pastes should therefore not be considered a priori as an indubitable index of technological poverty, but, on the contrary, as a conscious mastery of a simple and effective technique. However, two ceramics, which form the F-V fabric (AVR005 and AVR016), present a different case of study; probably, they were red ceramics in origin, however, the reducing firing conditions of the fire of the ship turned their surfaces to black. On the other hand, with respect to the shiny finishing of the ceramics, the potters probably burnished the shiny black shards of F-V fabric (AVR003, AVR005, AVR015 and AVR016), evidencing the burnishing technique in ceramics with red and black pastes ([Fernandes, 2012](#)). However, AVR002 from F-IV draws the attention because of its black matte surface. In order to obtain the metallic black finishing the potters used the technique of burnishing, as it produces an even and compact surface, which causes specular reflection and gives to the ceramics a shiny surface ([Ionescu et al., 2014](#)). Therefore, the reasons for this difference could be that, maybe they did not give this finishing to AVR002 or that, AVR002 could have been smoothed instead of burnished because, according to the literature, smoothing makes ceramics appear matte ([Ionescu et al., 2014](#)).

Besides, SEM-EDS analyses have also facilitated the identification of the nature of a glassy-layer mainly of vacuolar aspect. One of the reasons for the formation of that layer is that iron compounds may act as a flux when they are exposed to a reducing atmosphere at high temperatures ([Rice, 2015](#)). In this case, the vacuoles could have been formed because of the gases (such as the carbon dioxide) formed during the original firing of high temperature or due to the fire produced in the ship. Therefore, the thickness of the glassy-layer would depend on the contact between the fire and the shards. On the other hand, the glassy-layer could have also been produced because of the reaction between the salt (NaCl) and the water. If the salt that was transported in the ship reacted with seawater (thanks to the high temperature of the fire), HCl and sodium oxide were formed according to the reaction of [Rice \(1987\)](#). Then, sodium oxide could have reacted with the silica of the ceramics, lowering its melting point, and giving as a product a glassy-layer. The vacuoles could be the product of the evaporation of HCl. Therefore, in this case, the thickness of the glassy-layer would depend on the amount of salt that reacted with the ceramics. The clear example would be the AVR005 ceramic, which has two ceramics stuck together: they were fused and melted together during the process. Furthermore, it is probably that the layers of the rest of the ceramics from F-V were also formed due to this reaction, as the higher concentration of Na in the surface of F-

V ceramics suggested, probably due to the formation of Na<sub>2</sub>O in the surface.

Moreover, the fire produced in the ship possibly did not act with the same intensity on all the shards, so some black spots may have appeared because the fire impacted directly on them (like in the case of AVR001, AVR012 or AVR013). Maybe, as with AVR005 and AVR016 happened, AVR002 was also burnt by the fire developed in the ship. Additionally, the beige surface of AVR003 could have been reoxidized during this process ([Gillies and Urch, 1983](#)).

In addition, XRD and SEM-EDS analyses have also shown the appearance of some secondary phases, such as pyrite or jarosite and evidences of potassium halite, related to alterations and contaminations of the ceramics in the post-depositional scenery. The presence of pyrite and jarosite aggregates is a common alteration in marine environment ceramics, produced due to the decomposition of hematite (Fe<sub>2</sub>O<sub>3</sub>), from ferric ion (Fe<sup>3+</sup>) to ferrous ion (Fe<sup>2+</sup>), by the reduction and solubilization with hydrogen sulphide (H<sub>2</sub>S) in water solution ([Secco et al., 2011](#)). On the other hand, halite can crystallize in porous materials, especially in marine environments ([López-Arce et al., 2013](#)).

Finally, the present work reinforces the idea that local production from Aveiro, included in A-1 compositional group, clearly predominates in the city production pattern and was also a valuable object in the Atlantic trade. The fact that the ceramics from RAVA show a chemical fingerprint compatible with ceramics from the church, reinforce the conclusion of the study carried out by [Carvalho and Bettencourt \(2012\)](#); that ceramics from RAVA were from a latter period than it was thought, despite the ship being dated to the mid-15th century ([Alves et al., 2001](#)).

#### CRedit authorship contribution statement

**Uxue Sanchez-Garmendia:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization, Project administration. **Patricia Carvalho:** Conceptualization, Investigation, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **José Bettencourt:** Conceptualization, Investigation, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Ricardo C. Silva:** Conceptualization, Investigation, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Gorka Arana:** Methodology, Validation, Investigation, Resources, Data curation, Writing - review & editing, Supervision. **Javier G. Iñañez:** Conceptualization, Methodology, Software, Validation, Investigation, Resources, Data curation, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jasrep.2020.102648>.

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