Archaeometric analysis of Islamic Pottery from *Pollentia*, Mallorca, using XRF, XRD and SEM techniques

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Figure i: Visual representation of Islamic water jars [ii]

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ABSTRACT

A sample-set of twenty-one Type 3-Å1 water jar pottery fragments excavated from the northern peninsula of Pollentia, Mallorca, Balearic Islands were chemically and compositionally evaluated using archaeometric techniques. The applications and principle working parameters of artefactual analytical techniques have been investigated in this dissertation, paying particular attention to XRF, XRD and SEM as analytical tools in archaeometry.

The study has provided strong evidence for the requirement of three compositionally similar chemical groups for the sample-set (with two sub groups and an outlier), as well as the identification of the evolution of crystalline mineral phases and vitrification intensities, in order to estimate equivalent firing temperatures (EFTs), ranging from < 800°C-850°C to between 900°C-1000°C. Further research may be done in order to better evaluate the provenance and EFTs of the calcareous-based artefacts, and associate the consumption site to the production site kiln. This thesis is a continuation from a future co-published dissertation entitled “Caractérisation archéométrique de pichets d’eau du période musulmane dans la ville de Pollentia (Alcúdia, Majorque, Îles Baléares)” by the author and members within the ERAAUB research group at the Universitat de Barcelona.

All the scientific equipment described in this dissertation in order to undergo archaeometric analysis were used in collaboration with the Centres Científics i Tecnològics at Edifici Prevosti, Facultat de Biologia, a faculty of Universitat de Barcelona.

Keywords: Pottery, Islamic Period, Balearic Islands, archaeometry, artefact, SEM, EDX, WD-XRF, XRD, calcareous ceramics, equivalent firing temperature

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INTRODUCTION

A sample-set of twenty-one Islamic Type 3-A water jar fragments were analysed in this dissertation, discovered in the Roman and late antiquity city of Pollentia on the island of Mallorca, part of the Balearic Islands in the Western Mediterranean. The samples were dated to around the 10th and 11th century AD, when Pollentia was under Islamic ruling.

The main objective in this dissertation is to chemically analyse the samples (using XRF), in order to define and differentiate between Paste Compositional Reference Units\textsuperscript{[3]} (also defined as Chemical Groups, CGs, in this dissertation), for compositionally similar samples. Additionally, the equivalent firing temperatures (EFTs)\textsuperscript{[4][5][6]} for the calcareous based ceramic fragments were determined by mineral phase analysis (using XRD). The study of the microstructure, sintering state, vitrification effects, heavy minerals and glaze were also identified in this dissertation, using SEM.

In order to complete this type of archaeometric analysis, wave-dispersive X-ray Fluorescence (WD-XRF), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) were used as scientific techniques, in conjunction with multi-variate statistical analysis (principal component analysis) and hierarchical cluster analysis, using a log-ratio transformation. The SEM and XRF are techniques which provide a non-destructive mode of artefactual analysis, and their quick and effective elemental characterisation provide a structured reasoning in their selection as analytical methods, and XRD provided a similar analysis as a sample destructive method of analysis.

Kiln-fired pottery presents various predicted EFTs for the samples, since the firing temperature within a kiln does not necessarily correlate with a uniform firing temperature for all ceramics within that kiln. Therefore, the crystalline mineral phases identified in the samples using XRD provided a first-step insight into an estimated EFT for each sample. The intensity of vitrification in the clay matrix using SEM was utilised in order to analyse how the extent of vitrification varies as the EFT increases from below 800\textdegree C-850\textdegree C up to between 900\textdegree C-1000\textdegree C.\textsuperscript{[4][5][6]} Additionally, the SEM characterization of heavy minerals, slip and glazes were evaluated for particular calcareous samples.

It must be highlighted that the findings in this dissertation provide an archaeometric study of pottery from the Islamic period in the Balearic Islands which is an area of research still in an incipient state, to the authors knowledge. All research was carried out as part of an internship agreement and Master thesis requirement with the Institut Polytechnique de Grenoble-PHELMA, Grenoble, France, and the ERAAUB research team at the Universtat de Barcelona, Barcelona, Spain.
2.1 ARCHAEOLOGY: AN INTERDISCIPLINARY SUBJECT

In order to understand archaeometry as a subject with more clarity, one distinct property of the topic area must be clear: archaeometry is, innately, an interdisciplinatory subject. In order to provide a complete technical and contextual analysis of a historic artefact of significance, both the archaeological approach and the scientific analysis must be fully understood and appreciated. Efficient progress is made, therefore, when there is a “close association between classical archaeologists, physicists, and computer specialists sharing all of the different parts of the work (...); it gives a very useful mutual understanding.”[7] Therefore, this dissertation attempts to analyse Islamic pottery by utilizing specific scientific testing methods as its fundamental objective, whilst considering more archaeologically-based questions which may be further imposed, upon the dissertation’s conclusion.

It is common practice that several archaeometric techniques are used in combination, in order to characterise and analyse complex ceramic artefacts. Since certain archaeometric techniques provide specific information about the artefact, it was deemed unnecessary to further complicate the artefactual analysis by implementing additional archaeometric techniques in this dissertation. This is not to say that the techniques used were inadequate, rather that further analysis would neither vastly benefit nor enhance the outcome of this dissertation. It would therefore be appropriate to summarise these points by quoting an infamous proverb from Confucius (and as M. A. Cau mentions in his article) “never use a cannon to kill a fly.”[8] In other words, “it is important to adjust the techniques and the methodological approach to the question being asked.”[8]

Considering this in mind for the analysis of Islamic pottery, this dissertation aims to highlight both perspectives of this archaeometric approach, highlighting a stronger reference to the scientific viewpoints, and in partial consideration of the archaeological viewpoints.

2.2 ARCHAEOLOGICAL PERSPECTIVE

2.2.1 HISTORICAL CONTEXT

The Roman settlement of Pollentia was the capital of the Island of Majorca and the Balearic Islands under Roman ruling. Situated strategically in the north east side of the island such that it could control territory due to its elevation, the ancient city of Pollentia was founded in 123 BC and was led by the Roman ruler General Quintus Caecilius Metellus.[9] In the 21st century, the modern town
of Pollença is regularly cited as a historic town with an important Roman-archaeological site in the Balearic Islands\[10\] and is situated the municipality of Alcúdia (Fig. 1).

![Figure 1- Pollentia location in the Balearic Islands (Spain) in the Western Mediterranean\[11\]](image)

In terms of the chronological order for the occupations of the city, it is documented that a fire destroyed many parts of the city at the end of the 3rd century, however the city survived the event and continued to be populated across the Vandal (455 AD), Byzantine (534 AD) and the Islamic (902/903 AD) periods.\[11\][12][13][14][15][16]

In terms of previous research throughout the Balearic Islands (specifically in relation with archaeometry for Islamic pottery), there has been an increase in Islamic pottery found in different areas of the city, though archaeometric studies remain limited. In an article written in 2001 by J. Molera, M. Vendrell-Saz, and J. Pérez-Aranteuoi, Islamic pottery in the Balearic Islands were briefly described through the analysis of tin glazes of jars from the eleventh century, although no remains of kilns or workshops were found, therefore a local production could not be suggested.\[17\][18] Additionally, only recently an excavation of Almohad materials was analysed in the site of Puig de Sa Morisca (Southwestern Mallorca) by Albero et al. in 2019.\[19\]

As an underlying objective therefore, this dissertation aims to provide the initial steps into better understanding the pottery production and archaeometric analysis of ceramics during the Islamic period in the region highlighted in Fig. 1.
2.2.2 SAMPLE SET

A total of twenty-one water jars are analysed in this dissertation, of which a large proportion included a painted decoration on the rim and/or the neck of the water jar. A depiction of where each fragment location was believed to have been, and it’s given corresponding abbreviation (which is utilised throughout this dissertation) is shown in Fig. 2 below.

The discovery of water jars in the area is not uncommon, and a majority of finds have been uncovered along the northern peninsula of Pollentia (Fig.1). These Type 3A Islamic water jars were dated to between the 10th and 11th century AD, and their presence related to a local well near the excavation site.\cite{10}
2.2.3 CERAMIC COMPOSITION

2.2.3.1 CERAMIC MANUFACTURE

Pottery was most likely the first artificially created material manufactured and used by humankind as a vessel for utilitarian uses, for example: storage, cooking and food or drink consumption, etc. Due to its high durability, broken pottery fragments are among the most common artefacts found in excavations over the world, and the earliest known evidence of a non-figurine related ceramic was found in Yuchanyan Cave, China, and dated to around 18,000 BC. Archaeologically-speaking, ceramics also represent an important historical insight into the power and social successes of cultural communities and civilisations, as the manufacturing process of higher quality pottery improved with each time period’s advancement of knowledge. By analysing well preserved ceramic fragments, therefore, certain physical features and styles can be used to distinguish between prehistoric cultures.

Geologically, clay is formed through erosion, sedimentation and an interaction with weathering environments, from which a particular distribution and abundance of a hydrous, aluminium-silicate minerals are produced, with a layered crystal structure. Clay minerals are commonly found as extremely small fine-grain structures in sedimentary rocks and can be either allogetic (originally deposited with the other sediments) or authigenic (formed by chemical reactions in the subsurface). These clay minerals are composed of tetrahedral layers and surrounded by four oxygens, three of which are shared. Additionally, they may contain octahedral layers of aluminium or magnesium surrounded by six oxygens, whereby all the oxygens are shared, and a layer of loosely-bound atoms or molecules are exchanged. In general, clays are classified into two separate categories: calcareous and non-calcareous (with high or low levels of alumina) clays. Calcareous clays have a CaO content above ~5% whereas non-calcareous clays are clays lacking in CaO abundance. Furthermore, this distinction between the two types of clay are also described by their different fundamental physical properties, such as their mechanical and thermal properties.

In terms of the manufacturing process, naturally occurring clayey sediments are composed of some combination of clays, silts and sands, and may have a finer or coarser microstructure. This raw clayey material may be further refined by sieving or used as it is, as well manipulated using an artificial tempering with sand and/or mixing of two separate raw clay, depending on the sediments, type and function of the final ceramic product. This malleable clay material is then shaped at ambient temperature with water and subsequently fired at high temperatures, before allowing to cool down. It is with this vital decorative and shaping stage with which one can determine various parameters of
a society, such as: social classes, dietary habits, religious practices and economical movements in a region.

It is well documented that the moulding of fabric clays in ancient ceramics may have been achieved through hand manipulation by: the ‘pinching pot’ method (formed by pinching a single lump of clay), the ‘coil method’ (using a small coil tube of clay surrounding scored edges to reinforce and build a connection) and the ‘slab pot method’ (formed by joining flat clay slabs together), or by using the wheel as an aid (either a manually foot or hand-turned wheel). To get a better understanding of how handles, spouts or rims were welded together for example, radiography may represent an accurate archaeometric technique, though this will not be utilised as a technique in this dissertation.

2.2.3.2 FIRING PHASE

The firing phase in ceramic production creates an irreversible physiochemical and structural change in the clay paste. Since the ability for potters to maintain a desired firing temperature has a large dependency on the type of kiln being utilised, a general variability is produced in the structural changes in each clay’s matrix structure. Furthermore, the ceramic production from a specific production site can provide a basis for associating the kiln type with a certain time period. It must be taken into account, however, that not all ceramics produced from the same flame kiln, using the same clay, will show the exact same evolution of structural change. A study completed by O.P. Gosselain in 1992 describes a brief evaluation of the differences in firing temperatures for different kiln types, using ethno-thermometric data acquired from fieldwork conducted around the globe (Fig.3).

Figure 3- Temperature ranges for different types of fire kiln structures (1) Open firing, (2) Open firing with sherds covering pots, (3) Pit firing, (4) Pit firing with sherds covering the pots (5) Updraft firing.
It can be clearly defined that in Fig. 3, the shaded region represents roughly two thirds of all the data and that between 600°C and 900°C, all the firing temperature data overlaps i.e. it cannot be known for certain exactly which type of flame kiln was used if the ceramic analysed shows properties of temperatures between 600°C and 900°C in its clay paste matrix. Finally, if the drying process is not uniform and controlled, then there is a possibility for stresses to build around the body, which can lead to cracks, clay body deformation and volume reduction, especially if the water is lost too rapidly.

Above the boiling point for and up to around 200°C, the absorbed H₂O in the clay paste (i.e. the ‘hydrated’ interlayer cations) are liberated. Above this temperature, the chemically-bonded H₂O is released and the loss of oxides (e.g. CaO₂) produce important definitive mineralogical and compositional changes in the final ceramic product. Since water is expelled in the firing process (from not just the H₂O between the clay particles but also the water bound at the mineral lattice), there is a second volume reduction in proportion to the increase in firing temperatures, over time. “In the vitrification range, the shrinkage increases systematically with firing temperature and time; the kinetics are those of sintering in the presence of a liquid phase.”[26] Water is also an important reason for flame kilns to have a controlled ventilation during the firing phase, since large masses of clay-ware may decompose due to large thermal stresses created from a rapidly escaping steam.

At 573°C, a chemical process known as ‘quartz inversion’ occurs, where quartz crystals rearrange their chemical ordering caused by an α-β phase inversion of the quartz.[27] Proportionally, as vitrification increases, the apparent porosity (i.e. the apparent decrease in water absorption) in the ceramic decreases. Vitrification is defined as the transformative phase which occurs at temperatures ~700°C (dependant on the fluxing impurities in the clay e.g. Na₂O, CaO), as the clay particles begins to partially fuse into an amorphous, glassy phase. At high temperatures (up to ~1000°C), new minerals may form in the clay paste- it is therefore evident that the larger the vitrification which appears in the microstructure of a ceramic, the larger the likelihood that the ceramic was fired at higher temperatures. Furthermore, if vitrification presence has a higher abundance near the ceramic surface rather than the central clay body matrix, then the probability of the firing temperature being closer to 800°C is greater than the firing temperature of 1000°C.

These microstructural changes of the clay material through sintering and vitrification described above are analysed in this dissertation using SEM techniques, in an attempt to directly contrast and compare the equivalent firing temperatures found for the Islamic pottery fragments from Pollentia, Mallorca, Balearic Islands.
2.2.3.3 CLAY MINERALOGY AND MICROSTRUCTURE

Clay minerals which are found in ceramics provide certain characteristics of the ceramic material itself, including: hardness, plasticity and firing temperature. For example, the colouring of the clay matrix, or glaze, is due to the mineral components exhibiting their chemical changes after firing (or prior, if the clay body is decorated beforehand). Other mineral compounds in the clay may even lower the vitrification temperature of clay bodies, by acting as a flux. Traditional ceramics are manufactured from raw materials based on silica (SiO₂), or alumina (Al₂O₃) plus silica. The raw materials are most commonly classified into three groups: clay, silica, and feldspar (KAlSi₃O₈).[28]

Clay minerals are formed by hypogene processes resulting from the action of gases, vapours, or solutions which originate below Earth (from extremely high, several hundred-degree centigrade temperatures and compressed water vapor pressures) and force their way upward through rocks in the Earth's crust. Most of the elements found in clay minerals are contributed by the invaded rocks; few, other than water, are derived from deeper sources. The main materials removed from the crustal rocks are alumina, silica, alkali or alkaline earth elements, and iron; these are transformed into clay minerals at a temperature ranging from slightly below 100°C to about 450°C in an environment that may be acidic, neutral, or alkaline, depending upon the pH of the invaded rocks and the acidity of the vapours from the magma.

Importantly, the character of the clays depends on the original source material and the effects of wall-rock contamination. As described briefly in Chapter 2.2.3.1, the basic components of a clayey deposit not only contain clay fractions but also coarser fractions such as silt and sand. Each one of these fractions may contain sedimentary, metamorphic or volcanic and/or igneous rock fragments, depending on the sediment’s geological character. These fractions also contain associated minerals, most commonly: phyllosilicates (micas and feldspar), plagioclase, quartz and calcite (for calcareous sediments).

During firing, the raw material minerals undergo partial decomposition, dihydroxylation and phase transformation during firing, a complex mineralogical composition is always formed, which creates the accurate determination of the firing temperature an inherently complicated task. The description of a ‘firing temperature’ is in itself an ambiguously termed definition, since the heating rate and soaking time of clay materials are not strictly correlative: an estimated firing temperature at 960°C with a heating rate of 800°C/hr followed by rapid cooling, produces the same effects on vitrification as obtained from a firing at 900°C, with a slow heating rate of 200°C/hr and a 1 hour soaking time. Therefore, in this dissertation, the ‘equivalent firing temperature’ (or EFT) will be evaluated using XRD
and SEM, in order to observe the mineral’s crystalline phases and secondary phases present in the samples and estimate the degree of vitrification, in conjunction with the determination of the chemical composition of the sample set.\cite{4}\cite{5}\cite{6}\cite{29}\cite{30}

The mineralogical evolution of a calcium-rich clay which underwent firing in oxidizing conditions was conducted by Benghezal in 1989, and it is with this type of analysis with which this present dissertation will base its indexing of minerals such as illite and quartz under, in context with the predicted EFT (Fig. 4).\cite{31}\cite{32}

As seen in Fig.4, certain mineral compositions are only observed within a certain range of predicted EFT’s: for example, the presence of gehlenite suggests an EFT of a Ca-rich fired clay to be at least around 850°C and above. As mentioned in Chapter 2.2.3.2, the chemical orientation of quartz has an influence on the predicted EFT; nevertheless, quartz is not an uncommon mineral to be found across the range of EFTs described in the dissertation, from 500°C and above 1000°C. Additionally, diopside and hematite are minerals which are most commonly seen to only be present for predicted EFTs equal to or above 850°C.

Figure 4- Mineral composition stability (x-axis) vs. EFT (y-axis) comparison for Ca- rich clays\cite{31}\cite{32}
2.3 ARCHAEOMETRIC TECHNIQUES UTILISED

2.3.2 X-RAY FLUORESCENCE (XRF)

2.3.2.1 WAVE DISPERSIVE XRF (WD-XRF)

XRF is an analytical elemental technique which has been used for several archaeometric studies in order to evaluate the chemical composition of archaeological artefacts. A stable atom is constituted of a central nucleus (made of protons and neutrons) which are bound by electrons in orbit around it. These electron orbitals are arranged in terms of their different energy levels, and each energy level is called an “electron shell”, as first proposed by Niels Bohr in 1913 [33]. In XRF, characteristic X-rays (i.e. an element-specific radiation) are produced when a high energy incident primary X-ray interacts with an atom and disturbs the atom’s equilibrium, such that an electron is ejected from one of the lower electron shells closest to the atom and consequently creating an electron vacancy. In order for the atom to attain a stabilised state from this current unstable configuration, a higher energy electron ‘drops’ into this lower electron shell vacancy. This event causes the release of a characteristic X-ray radiation (or an X-ray photonic fluorescence) specific to each element. This aforementioned WD-XRF process is shown in Fig. 6 below, using Sulphur (S) solely to depict an example atom interaction.

![XRF process example using Sulphur 'S'](image)

It is this final step which is vital in permitting researchers to determine the elemental characterization of a material, since it provides quantitative information about the sample measured. Furthermore, each electron shell has a complimentarily assigned shell name, starting at the most strongly bound K
shell and moving to higher energy shells L, M, N, etc. In terms of X-ray transitions, the most probable vacancy to be occupied by another electron (and therefore release a characteristic X-ray radiation) is between adjacent shells, i.e. if the ejected electron is from the K shell, then the most likely transition is a higher energy level electron from the L shell to replace the vacant K shell electron vacancy, since these shells are adjacent. XRF is capable of identifying both primary (Na, Mg, Si, P, Al, K, Fe, Mn, Ca, Ti) elements and certain trace elements (Rb, Y, Zr, Ni, Zn, Ba, Th, U, Pb, Ga, Cu, Cr, Nb, Sr).

In this dissertation, a Panalytical-Axis PW 4400/40 spectrometer was used for WD-XRF analysis. Each sample from the sample set underwent individual fragment homogenization after being powdered in a tungsten-carbide mill and dried for 24 hours at 100°C. The ‘lower limit of detectability’ is defined as a net intensity of counts equal to the minimum number of three standard counting errors from the background intensity- under the current experimental conditions, the ‘LLD’ given by the manufacturer was 0.1ppm. Similarly, the regression limits of a detector are defined by the ability of the machine in detecting an element, above or below which an element is considered undetected. These values are shown in Appendix 1 for the experimentation machine used in this dissertation.

In order to provide an accurate result, primary and trace elements were determined through fused-bead duplicate reference standards (Fe₂O₃, Al₂O₃, MnO, P₂O₅, TiO₂, MgO, CaO, Na₂O, K₂O and SiO₂) beforehand, using 0.3g of the specimen in an alkaline solution with lithium tetraborate (1:20 solution).

2.3.2.2 VARIABILITY AND CONTAMINATION

Provenance and origin are terms which are often interlinked in archaeometry, but their definitions hold an important value when describing an archaeologically-based material structure. The provenance postulate states that “there exists differences in chemical composition between different natural sources that exceed, in some recognizable way, the differences observed within a given source.” In archaeometry, the study of provenance begins with the sample in its ‘received state’- it is then analysed to understand the fabric and paste, and therefore the raw materials used, which is related to a geographical area.

Difficulties in analysis arises when a provenance study needs to verify whether a technological process has had an effect on the compositional characteristics of raw materials or not. In 1976, Bieber et al. established an equation to model the different sources of variation, shown in Eq. 1 below.

\[ S_T^2 = S_N^2 + S_S^2 + S_A^2 \]

Here, \( S_T^2 \) is the observed overall variance of one group of samples made from a given clay source, \( S_N^2 \) is the natural variance in the raw material source, \( S_S^2 \) is the sample variability (i.e. the variability
introduced in the data due to sampling, such as including errors in sample inhomogeneity), and $S_A^2$ is the analytical variability (measured by repeating an unknown sample’s composition, for example). In order to address these variability issues in data analysis, Equation 1 was altered in order to also consider other types of variability, such as variability introduced by technology, ceramic use due to contamination and/or alteration processes. Therefore, a methodological approach which takes into account the contamination of ancient ceramics was used in the statistical treatment of compositional data, described by a logarithmic transformation first proposed by Aitchison in 1992. The type of graphical analysis utilised in archaeometry has a large influence on the dominating or correlating features shown in terms of data representation, and in order to best interpret and assess the data, there are many types of variate analysis available.

Univariate graphical analysis, such as box-and-whisker plots and histogram related plots, represent a type of preliminary analysis of statistical data and are readily available as software packages, such as MINITAB or S-Plus 2000. They are useful in order to determine distinct groups in a dataset (for boxplots), and results may suggest the need for a logarithmic transformation. Histograms, for example, are only useful when there is a small dataset, which is not the common case for ceramic artefact analysis. Bi-variate plots is a type of two-dimensional data analysis, which is especially useful for archaeometric interpretation when there are two variables which are interlinked, which may be incorrectly identified as independent of one another. For example, for tin and arsenic in bronzes, it much more useful to see clustering or structural effects if these elements were plotted against each other on an X-Y bivariate plot, instead of considering these elements as independent of each other (since they are chemically related to one another).

Multi-dimensional (or multi-variate) analysis is a type of analysis which uses a matrix in order to describe large compound datasets (larger than two observations/variables per specimen), regardless of the number of observations made relating to each sample. In such cases, an $n \times p$ matrix, where $n =$ number of archaeological specimens (rows) and $p =$ observations made from specimens, often oxides (columnar), is represented by $\mathbb{X}$. If the data from the sample is from a multivariate normal type distribution, in order for the data in $\mathbb{X}$ to have accurate properties, specific mathematical functions i.e. transformations, must be completed, such that the data in matrix $\mathbb{X}$ is transformed into matrix $\mathbb{Y}$. For the typical element in matrix $\mathbb{X}$, $x_{ij}$ is the measurement in the $i$th row and $j$th column in matrix $\mathbb{X}$, $y_{ij}$ is the measurement in the $i$th row and $j$th column matrix $\mathbb{Y}$.

In this dissertation, a comprehensive chemistry-based analysis is completed, in order to interpret results into well-defined groups, initially ignoring information about the archaeological aspects, such as the production centre (since the kiln site is unknown). Using this approach, both Principal
Component Analysis (PCA analysis) and Cluster Analysis provides techniques in order to achieve this goal. A pre-statistical treatment must be completed, in order to provide a reasoning for further statistical analysis. In scaling, raw data may be standardised\textsuperscript{[41]}, or may undergo logarithmic transformations\textsuperscript{[42],[43]}. In order to keep a description of pre-statistical treatment brief, only logarithmic transformations are described in the following paragraph. There are two types of logarithmic transformations in pre-statistical treatment of data, either through ‘log centering’ or ‘log additive ratio (alr)’ transformations. In ‘log centering’, the denominator inside the log component in Eq. 2 ($x_{ij\rho}$) is replaced by $g(x) = \sum(x_{ij\rho})^{1/\rho}$, the sum of all elements in the raw data including contaminating elements (assuming that $\sum_j(x_{ij}) = 100\%$). This proves problematic in statistical analysis, since every element which involves this denominator will thereon provide inaccurate results, by including a perturbating contamination term. In this dissertation, the approach used is to transform the data to logarithmic base 10 (as seen in Eq.2) and for this transformed data to lie within an unconstrained ($\rho -1$) dimensional subspace, for which standard statistical methods apply\textsuperscript{[44],[43]}.\textbf{Equation 2}

$$y_{ij} = \log \left( \frac{x_{ij}}{x_{ij\rho}} \right)$$

In Eq.2\textsuperscript{[43]}, $j = 1,2 \ldots (\rho -1)$. Elements which may introduce contamination in the dataset are removed, and the $x_{ij\rho}$ value is described as the least varying element in the data. Therefore, by using alr transformation, the perturbations only effect the logarithms of the perturbated elements. This alr transformation is done in order to have more nearly equal variances and a more nearly equal weight in an unstandardized analysis. It is also believed that trace elements are naturally log-normally distributed, therefore their logarithms will be normally distributed as a consequence.

PCA attempts to reduce large datasets by adjusting data, hypothesizing that leading components (leading index variables) will account for most of the total variance (i.e. the sum of the variances of the individual variances), from a larger set of measured variables. In order to optimise this process, PCA determines the optimal quantity of components, choice of measured variables for each component and optimal weights. Therefore, PCA gives an initial step into chemically related components within a sample group\textsuperscript{[41]}. In order to complement PCA analysis results, a cluster analysis was also performed.

A cluster analysis of data points is completed in order to better understand chemical compositions which are related to one another. These groups may then be further sub-divided into sub-groups, such than all samples within a group are chemically similar to one another, as well as chemically distinct
from other groups. Cluster analysis may be achieved through various types of mathematical algorithms, such as: single-linkage clustering, complete-linkage clustering, average-linkage clustering, Ward’s method, centroid clustering, etc. Additionally, these groups may be unified using ultra-metric distances, which can be calculated in various ways, such as: Euclidian, Euclidian Square, Mahalanobis, Penrose, etc.

The type of cluster analysis used in this dissertation was hierarchical centroid clustering, using a squared Euclidian distance. For PCA analysis, a squared Euclidean distance is also utilised. Therefore, in order to establish a first step study to study material distribution, a chemical and mineralogical analysis was conducted, by defining chemical groups (CGs) within the sample dataset.

### 2.3.3 X-RAY DIFFRACTION (XRD)

In XRD, the main crystalline phases of minerals are identified, which is an especially useful archaeometric technique used in this dissertation in order to determine equivalent firing temperatures of the water jar samples (as described in Chapter 2.2.3.3), as well as any secondary minerals which may have formed. X-rays are released from a source (e.g. from an X-ray tube, which releases electrons from a cathode filament) and interact with the sample, altering the incident X-ray path (i.e. diffraction). The wavelength of the X-ray ($\lambda$), the distance between the internal planes of the crystal lattice ($d$), and the angle of diffraction ($\theta$) are measured using Bragg’s law\(^{[45]}\) (shown in Eq. 3 below) which holds true for when there is a constructive interference pattern produced after sample interaction (i.e. when the positive peaks of the two X-ray waves are aligned, and therefore amplified).

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} \textbf{Equation 3}

A circle of film is used in order to record the diffraction pattern produced from the diffracted X-ray beams after sample interaction, as each cone intersects the film giving diffraction lines. Since these diffraction lines are characteristic of the inter-atomic spacing distance in the crystal lattice, the minerals in the sample can be well identified and are seen as peaks on a diffractogram, which usually has $2\theta$ peak position (dependant on Bragg’s law Eq. 3) and peak intensity (based on X-ray counts detected) The setup of the photographic film used in the Debye Scherrer camera setup is seen in Figure 7\(^{[46]}\) below.
For the XRD analysis in this dissertation, a *Panalytical X’Pert Pro MPD Alpha-1 scanning diffractometer* was used, in conjunction with *High Score Plus* (by *Panalytical*) and the *Joint Committee of Powder Diffraction Standards (JCPDS)* data bank, in order to evaluate the mineral phases present. The *PW3113/60 Incident Beam Monochromator* was mounted onto a bracket with two *PreFiX* positions on the X-ray tube. The radiation used was a Cu-Kα radiation (λ= 1.5406 Å) and the spectra was recorded using an angle of diffraction ranging from $\theta = 5^\circ$ to $\theta = 80^\circ$, with a step time and step-size of 47.5s and 0.026$^\circ$2$\theta$, respectively.

**2.3.4 SCANNING ELECTRON MICROSCOPY (SEM)**

In order to further complement the previously described archaeometric techniques used in this dissertation, SEM is a non-destructive technique which allows the user to identify crystalline structures and microstructures, morphology and the elemental composition of each sample. The *FEI Quanta 200 Scanning Electron Microscope* was used in this dissertation, in a HiVac (High vacuum between $10^{-6}$ and $10^{-7}$ Torr) operating mode with *EDAX Genesis* software in order to analyse data points produced and generate diffractograms. In conjunction, a *JSM-7100F Field Emission Scanning Electron Microscope*, with a *Mag690-100 Three-Axis Mag. Field Sensor* was used, with *INCA* software, in order to analyse data points.
Fig. 8[47] above shows a simplified general schematic for a SEM, with its main instrument parts highlighted. The electron gun is generated by a tungsten wire filament supplied with an applied current, in order to produce a primary electron beam which is manipulated through the system towards the sample through various electromagnetic and objective lenses. In order to avoid astigmatism-related distortions in the sample, stigmator coils are used to zero focus and fine focus sample images. Finally, apertures are micron-sized holes on metal disks, which can be used to control and narrow the beam path by reducing the focal spot diameter.

2.3.4.1 SECONDARY ELECTRONS (SE)

The manipulated electron beam interacts through the atom dense sample, creating detectable scattering events. In SEM beam-sample interaction, the two main detection signals are secondary electrons and backscattered electrons.[48] Both of these detection parameters utilise the particle-like nature of electrons. Secondary electrons (SEs) are generated by the transfer of energy to the atom by the initial electron beam (and other SEs). This creates the expulsion of an electron from the atom known as the ‘secondary electron’. This is an inelastic event (Fig. 9), and the energy of this SE must be below 50eV, in its definition.[49]
Due to this lower energy level, SEs are only detectable at the surface sample. High resolution topographical information is therefore evaluated from the specimen, as the SE radiation is firstly collected by a positive electrical bias detector, called the ‘Everhart-Thornley’ detector. The signal then hits a phosphor scintillator, which emits light to promote photoelectric electron production in a photomultiplier tube, and repeated (i.e. signal is amplified). The signal is displayed on a computer monitor to produce a surface image. Any secondary electrons which were generated within the sample’s core had its low energies absorbed.

The characteristic X-ray energy transitions produced from the vacancy of an electron in SE production (Fig. 9) have clear, definitive values specific to each elemental shell, allowing for clear peaks to be displayed, dependent on the energy of the X-ray detected and the X-ray intensity (in counts per second). Additionally, the XRD machine was configured to utilise automated peak identification in its graphical analysis in this dissertation.

2.3.4.2 BACKSCATTERED ELECTRONS (BSE)

In elastic backscattered electron (BSE) interaction, there are no significant changes in electron beam energy, as the primary beam of electrons are scattered such that they scatter without interacting directly with sample nuclei or sample electrons (Fig. 10). Therefore, BSEs typically have high energy particles with similar energies as that to the initial electron beam. BSEs use in SEM’s is in detection of atomic number contrast and configuration of sample topography. The heavier an element (i.e. the larger its atomic number ‘Z’ is), the greater the primary electron’s elastic scattering.
effect (and number of returning backscattered electrons) will be, resulting in a brighter image resolution. BSEs signals may arrive to the detector from both reflection from the sample surface or from deep within the sample.

As shown in Fig. 10, BSE interaction is based on electrons travelling in straight lines (elastic collisions), therefore a sample with uneven topographical features may change the tilt angle of returning BSEs, giving a poor detection image. In order to control the detection image, the contrast and brightness of the final image produced was varied accordingly.

RESULTS, DISCUSSION & INTERPRETATION

3.1 WD-XRF ANALYSIS

In order to provide a first step into the archaeometric analysis of the twenty-one water-jar samples, a chemical statistical analysis was performed using the data collected from WD-XRF experimentation. In order to do this, all major and trace elements were imported onto Microsoft Excel software and statistically treated using S-Plus 2000. Since the trace elements were received as ppm, these were firstly converted into weight percentage (wt. %) values.
Secondly, some traces which were deemed to be below the regression limits of the XRF machine (or in some cases deemed to be irrelevant values due to the contamination from the mill or ground) were removed, including: Sn, Co (mill contamination), Mo, W (mill contamination), P and Pb (soil contamination). In order to first understand which elements would introduce the most variability in the chemical data, a compositional symmetrical variation matrix was created using *S-Plus 2000*, describing the total variability in the dataset (as seen in *Chapter 2.3.2.2*) and represented graphically below in *Graph 1* the log transformed symmetric matrix (*Appendix 2*).

![Graph 1- Variance of major and minor elements found in XRF](image)

As seen in *Graph 1*, the element which is the most stable (or the least variable) is Nb, with a variance of 0.69%; conversely, Ni is an element in the dataset which has the largest variability of 3%. This allows us to progress from a first-step idea of which elements should be considered in a multi-variate statistical analysis. The chemical results showed that all samples were of calcareous material, and the wt % of CaO ranged from 12.96% to 27.07%.

The standard deviation of all major and minor elements was found to be low in all samples, considering the standard deviations within each chemical group. If considering standard deviation in terms of elements, the standard deviations are large, especially elements which are the most variable, such as CaO and SiO₂. All elemental mean, maximum and minimum wt %, standard deviations and sample type is shown in *Table 1*. 

![Table 1](image)
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CHEMICAL GROUP</th>
<th>TYPE</th>
<th>Fe₂O₃</th>
<th>MnO</th>
<th>TiO₂</th>
<th>CaO</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>MIN</th>
<th>MAX</th>
<th>MEAN</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>POL028</td>
<td>CG-1</td>
<td>IM  OF  DECORATED JAR</td>
<td>5.95</td>
<td>0.0762</td>
<td>0.86</td>
<td>20.61</td>
<td>2.40</td>
<td>0.26</td>
<td>42.22</td>
<td>12.57</td>
<td>3.03</td>
<td>0.44</td>
<td>3.50</td>
<td>7.50</td>
<td>6.67</td>
<td>0.58</td>
</tr>
<tr>
<td>POL030</td>
<td>CG-1</td>
<td>IM  OF  DECORATED JAR</td>
<td>6.81</td>
<td>0.0646</td>
<td>0.97</td>
<td>15.19</td>
<td>3.15</td>
<td>0.53</td>
<td>47.03</td>
<td>15.79</td>
<td>2.72</td>
<td>0.42</td>
<td>3.86</td>
<td>7.41</td>
<td>6.38</td>
<td>0.68</td>
</tr>
<tr>
<td>POL039</td>
<td>CG-1</td>
<td>UNDECORATED COMMON WEAR</td>
<td>7.19</td>
<td>0.0832</td>
<td>1.08</td>
<td>15.51</td>
<td>2.93</td>
<td>0.54</td>
<td>49.73</td>
<td>17.37</td>
<td>3.06</td>
<td>0.45</td>
<td>3.86</td>
<td>7.37</td>
<td>6.33</td>
<td>0.68</td>
</tr>
<tr>
<td>POL040</td>
<td>CG-1</td>
<td>UNDECORATED COMMON WEAR</td>
<td>6.81</td>
<td>0.0646</td>
<td>0.97</td>
<td>15.19</td>
<td>3.15</td>
<td>0.53</td>
<td>47.03</td>
<td>15.79</td>
<td>2.72</td>
<td>0.42</td>
<td>3.86</td>
<td>7.41</td>
<td>6.38</td>
<td>0.68</td>
</tr>
<tr>
<td>POL042</td>
<td>CG-1</td>
<td>UNDECORATED COMMON WEAR</td>
<td>7.19</td>
<td>0.0832</td>
<td>1.08</td>
<td>15.51</td>
<td>2.93</td>
<td>0.54</td>
<td>49.73</td>
<td>17.37</td>
<td>3.06</td>
<td>0.45</td>
<td>3.86</td>
<td>7.37</td>
<td>6.33</td>
<td>0.68</td>
</tr>
<tr>
<td>POL043</td>
<td>CG-1</td>
<td>UNDECORATED COMMON WEAR</td>
<td>6.81</td>
<td>0.0646</td>
<td>0.97</td>
<td>15.19</td>
<td>3.15</td>
<td>0.53</td>
<td>47.03</td>
<td>15.79</td>
<td>2.72</td>
<td>0.42</td>
<td>3.86</td>
<td>7.41</td>
<td>6.38</td>
<td>0.68</td>
</tr>
<tr>
<td>POL047</td>
<td>CG-1</td>
<td>UNDECORATED COMMON WEAR</td>
<td>7.19</td>
<td>0.0832</td>
<td>1.08</td>
<td>15.51</td>
<td>2.93</td>
<td>0.54</td>
<td>49.73</td>
<td>17.37</td>
<td>3.06</td>
<td>0.45</td>
<td>3.86</td>
<td>7.37</td>
<td>6.33</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 1: Standard deviation and mean elemental composition of samples
In order to undergo multivariate statistical analysis of the XRF chemical data, an additive log-ratio transformation (alr) of the dataset, using Nb as the divisor (since it is the least variable element in the sample set) was completed. The centroid agglomerative method was used for a hierarchical-type clustering analysis, which was scaled with a squared Euclidean distance, in order to plot the cluster tree. Additionally, in order to provide a more complete analysis, a principal component analysis (PCA) was obtained in conjunction with cluster analysis, such that a clearer chemical difference between chemical groups (CGs) could be obtained: these results can be seen in Graph 2 and Graph 3 below.

As seen in Graph 2 above, the cluster dendrogram above represents a clear chemical distinction between samples, in accordance to their ultra-metric distance (y-axis represents Euclidian square distance). The height of each node in Graph 2 is in proportion with the intergroup dissimilarity between its daughter nodes. It can be seen that POL048 was found to be a clear outlier in our sample-set and can therefore be separated into its own CG (CG-3). CG-1 shows clear similarities between sample POL028, POL040, POL039, POL047, POL043, POL030 and POL042. CG-2 presents a correlation.
between two sets of samples in the same chemical group: POL032, POL029 and POL036 were found to have similarities with all other samples in CG-2, however there is an indication of a chemical difference between these samples (CG-2B) and the rest of CG-2 (CG-2A). This difference may be due to a particular elemental presence, which is further investigated using PCA analysis (Graph 3).

In Graph 3, the PCA scatter plot of the first two principal components shows a clear distinction between CGs. The total variability of the scatter plot is the sum of variability between PC 1 (50.28%) and PC2 (22.01%), and is therefore 72.29%. The outlier POL048 in CG-3 implies its chemical difference may be due to a higher presence of Rb and K2O in this particular sample. It must be noted, that since there is a low Na presence (below 1%) in the samples, the presence of K2O is accredited to not being
The separation of CG-1 and CG-2 is deemed to be due to a larger presence of Ni, Na₂O, Fe₂O₃, TiO₂ and K₂O (in terms of major elements) for CG-1 than CG-2, and is skewed towards more negative PC 1 and positive PC 2 values. This is seen more evidently numerically in Table 1; by identifying the chemical content of Fe₂O₃ in the sample-set which defines the clay matrix composition for example, it is seen that for CG-1 the mean value for Fe₂O₃ is 6.67 wt.%, compared to 4.13 wt.% for CG-2 (which is 2.54 wt.% lower overall), whereas for the outlier, the Fe₂O₃ content is 5.4 wt.%.

Additionally, the mean TiO₂ content for CG-1 (0.97 wt.%) is 0.29 wt. % larger than for CG-2 (0.68 wt. %), which further provides reasoning for the division of CGs.

As seen in Graph 3 (and identified in Graph 2), the subgroup CG-2B represents a separate chemical compositional variability in comparison with CG-2A, which is due to the presence of CaO. Table 1 highlights these chemical weight % of CaO for samples POL029, POL032 and POL036, which ranges from 26.21 wt.% to 27.07 wt. % CaO. The mean CaO of these three CG-2B samples is 26.85 wt. %, in comparison the CG-2A, which has an overall mean of 17.9 wt. %. To further highlight the differences in CaO content within CG-2, the maximum wt. % CaO sample in CG-2B, POL041, has a CaO content of 20.7 wt.% (which is 5.51wt. % lower than any samples in CG-2A). Additionally, a larger SiO₂ presence (between 32.08 wt. % and 35. 58 wt. %) is found for CG-2B, in comparison to a SiO₂ abundance for CG-2A, which ranges from 39.21 wt. % to 48.75 wt. % (also seen numerically in Table 1 and graphically in Graph 3). In order to show a clearer graphical representation of the CG-2A sub group within the sample-set, as well as provide further evidence for the formation of CGs, bivariate plots were analysed (Graph 4, Graph 5).

The bi-variate plot in Graph 4 shows a clear positively linear correlation (r Pearson= 0.92) between Fe₂O₃ and TiO₂, which suggests a more ferruginous clay for CG-1, when compared with CG-2. Additionally, CG-1, CG-2 and the outlier CG-3 can clearly be seen as independent of one another, as defined by the Fe₂O₃ and TiO₂ content. It must be noted, however, that this particular bi-variate plot does not present an ideal reasoning for a distinction between sub groups CG-2A and CG-2B, since the elements which are defined in the x-y axis are not representative in reasoning the need for a sub-group classification. In Graph 5, the bi-variate plot was created comparing Ni and SiO₂ values shows that CG-2A is separated from CG-2B due to SiO₂ abundance in the material.

Furthermore, the Ni content provides an insight into the chemical differences in CGs, since there is a clear separation between CG-1 (<1 wt. % Ni), with CG-2 and CG-3 (both > 1 wt. % Ni). In this reasoning therefore, Graph 5 also suggests that CG-3 has a stronger positive correlation with CG-2, if strictly considering the elemental abundances of SiO₂ and Ni content only. In reference to CG-3, POL048 is
characterised by low CaO and MgO content, as well as higher Fe₂O₃, Al₂O₃ and K₂O wt. %, when compared to CG-2 (as seen in Table 1, Graph 3, Graph 4).
3.2 XRD ANALYSIS

Using XRD, the mineral crystalline phase analysis can be further developed, in relation to the equivalent firing temperatures (EFT) for every sample in all CGs (as described in Chapter 2.2.3.3). These results are shown in Table 2 below. It can be seen that for CG-1, samples POL030, POL039 and POL042 contained the primary phases of quartz, calcite, illite-muscovite and alkali feldspar, which suggests an EFT < 800 °C-850°C. As temperature increases, the decomposition of the phyllosilicates (illite muscovite and alkali feldspar) and calcite present a primary indication that there is an increase of the EFT. This can clearly be seen across all CGs in Table 2, as when EFTs are described to be < 800 °C-850°C, illite-muscovite is an always present mineral phase (e.g. POL030, POL031, POL048), whereas for EFT > 850°C, illite-muscovite is only seen in traces as EFTs increase above 900°C (e.g. POL032, POL043). Furthermore, for CG-1 there is a clear increase in the presence of pyroxene such as diopside, as trace peaks (POL040) become more prominent (POL047, POL043) as EFT increases from 850°C to the EFT range between 900°C and 1000°C.

<table>
<thead>
<tr>
<th>Chemical Group</th>
<th>EFT (°C)</th>
<th>Mineral phases present (XRD)</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG-1</td>
<td>≤800/850</td>
<td>Quartz, calcite, illite-muscovite, alkali feldspar, hematite (trace)</td>
<td>POL030, POL039, POL042</td>
</tr>
<tr>
<td></td>
<td>850-950</td>
<td>Quartz, calcite, illite-muscovite, gehlenite, plagioclase, diopside (trace)</td>
<td>POL040</td>
</tr>
<tr>
<td></td>
<td>900-1000</td>
<td>Quartz, calcite, plagioclase, gehlenite, diopside, alkali feldspar, illite-muscovite (trace), hematite (trace)</td>
<td>POL043, POL047</td>
</tr>
<tr>
<td>CG-2</td>
<td>≤800/850</td>
<td>Quartz, calcite, illite-muscovite (lower in POL029), hematite (trace; absent in POL029 and POL034)</td>
<td>POL029, POL031, POL034, POL035, POL038, POL041, POL046</td>
</tr>
<tr>
<td></td>
<td>850-950</td>
<td>Quartz, calcite, gehlenite, plagioclase, illite-muscovite, hematite (trace; absent in POL044)</td>
<td>POL037, POL044</td>
</tr>
<tr>
<td></td>
<td>850-950 (most likely 900-950)</td>
<td>Quartz, calcite, gehlenite, illite-muscovite (low)</td>
<td>POL036</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quartz, calcite, gehlenite, plagioclase, illite-muscovite (low), diopside (trace), hematite (trace)</td>
<td>POL033, POL045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quartz, calcite, gehlenite, illite-muscovite (trace), diopside (trace)</td>
<td>POL032</td>
</tr>
<tr>
<td>CG-3</td>
<td>≤800/850</td>
<td>Quartz, calcite, illite-muscovite, plagioclase, alkali feldspar (low), hematite (trace)</td>
<td>POL048</td>
</tr>
</tbody>
</table>

The presence of plagioclase, pyroxene and gehlenite also provides further evidence in order to define the clay’s firing temperatures. In order to provide an example progression of minerals (Graph 6) with increasing EFTs, CG-2 is analysed graphically below.
KEY
ill-musc. = illite muscovite
qtz = quartz
cal = calcite
geh = gehlenite
kfs = alkali feldspar
px = pyroxene
pg = plagioclase

Graph 6- XRD mineral-defined spectrographs in CG-2, (for all) x-axis: Position (2θ of Cu detector); y-axis: counts
a) (Top) POL029, EFT <800°C - 850°C; b) (Middle) POL037, EFT 850-950°C; c) (Bottom) POL033, EFT 900°C - 950°C
As described, it is clear that illite muscovite begins to decompose as the EFT increases, as the peaks for illite-muscovite only appears more than once in Graph 6a (identified four times), when compared with Graph 6b and Graph 6c. For all samples POL029, POL037 and POL033 seen in Graph 6a, Graph 6b and Graph 6c, respectively, the highest peaks are for the presence of quartz and calcite, since the material being analysed is clay-based. It can be seen in Graph 6b and Graph 6c, that the counts of plagioclase between $2\theta = 27^\circ-28^\circ$ increases as the EFT increases from $850^\circ C$ to $950^\circ C$. Plagioclase are not expected to be seen below $850^\circ C$, which is evident by Graph 6a, which does not identify a plagioclase peak.

Additionally, another clear indicator for firing temperatures is the relative abundance of gehlenite (as seen in Fig. 4). It is clear that the strong peak for gehlenite, at $2\theta = 31.5^\circ$ increases in counts as the EFT increases. In Graph 6a, gehlenite does not appear in any counts, though as EFT increases to between $850^\circ C$-$950^\circ C$, this peak begins to increase, as seen in Graph 6b. In Graph 6c this peak is at its highest count, which signifies its higher abundance in the material and therefore implies that the EFT for POL033 is more indicative of being between $900^\circ C$-$950^\circ C$. Furthermore, the presence of pyroxene for both Graph 6b and Graph 6c further provides evidence of a higher EFT, signifying an EFT between $900^\circ C$-$950^\circ C$.

For CG- 2, the XRD patterns for CG- 2B (POL029, POL032, POL036) showed low peaks for illite-muscovite, even for the low-fired sample POL029 (as seen in Graph 6a). Additionally, trace peaks for hematite appeared for CG- 2B, however hematite was completely absent for CG- 2A. Finally, no plagioclase were observed for any samples in CG- 2A, however for CG- 2B, the plagioclase which are present includes diopside (POL032) and gehlenite (POL032, POL036). Therefore, the mineralogical differences described provide an additional indication for the existence of two separate sub-groups in CG- 2 seen in the WD-XRF chemical analysis in this dissertation (Chapter 3.1). Mineralogically for CG- 3, the outlier POL048 was found to contain primary crystalline phases of: quartz, calcite, illite-muscovite, plagioclase, alkali feldspar (low) and hematite (trace). Since there is no peaks for gehlenite or diopside indicated by the XRD analysis for this sample, it is therefore suggested that the EFT for POL048 is estimated to be below $800^\circ C$-$850^\circ C$.

3.3 SEM ANALYSIS

3.3.1 VITRIFICATION

In order to further develop the basis of evolving EFTs for the samples described and distinguished by CGs in this dissertation, the rate of vitrification in varying estimated EFT samples were analysed using SEM. For a low-firing temperature material, sample POL042 was investigated in order
to complement the XRD results indicating its EFT to be between 800°C and 850°C (as seen in Table 2). Fig. 11 below various SEM images of the clay matrix for POL042, in order to describe the geometrical disposition of the sample, at varying magnifications, as well as identify vitrification densities.

In order to not have ‘tilt effects’ to disproportion BSE images, the clay-based samples were polished before being introduced into the SEM for analysis. In addition, in order to observe the vitrification and sintering states (as opposed to high atomic number mineral analysis), fresh fractures provided an ideal analysis state for SEM, therefore no polishing was required. In Fig. 11a, POL042 has a magnification level of x1000, is at 20kV and is at a working distance (WD) of 14mm. The blue dashed line indicates an inhomogeneous clay-matrix structure, defined by a bimodal-type distribution. The left-hand side
of the image shows a finer grain structure, whereas the right-hand side shows a less fine structure. Additionally, there are also natural inclusions of large rock fragments within the material, suggesting a tempering. For larger EFTs, it is common to find rock fragments intact since the increase in temperature transfers energy to the material and the inclusion fragmentates further. Therefore, the presence of these rock fragments in Fig. 11a suggests a lower firing temperature. Fig. 11b and Fig. 11c indicates a further magnification of x5000 into the clay matrix near the boundary, as well as the chemical characterization of the sample at this location, respectively. Fig. 11b shows clay pellets beginning to fuse together, and the image shows a clear initially vitrified glassy phase filament structure. Additionally, Fig. 11c shows that the clay matrix in POL042 is characterised by predominantly calcite, silicates and alumina-based compounds (much like all other samples used in this dissertation), with some K and Fe related inclusions. Vitrification provides a more definitive description of a lower EFT, and therefore POL042 agrees with previous XRD results (Table 2) in being a material with an EFT < 800°C-850°C, and the vitrification structures shows the EFT to more likely be between 700°C and 750°C.

POL044 in this part of the dissertation is used in an example to analyse a medium-temperature fired sample (850°C-950°C) for vitrification effects (Fig. 12, Table 2), as well as a chemical characterization and POL043 provides an indication of vitrification for high-temperature fired clay samples, between 900°C-1000°C (Table 2, Fig. 13).
As seen in Fig. 12 above, compared to Fig. 11b, there is clearly a larger vitrification density, as more clay pellets fuse together as the predicted EFT increases. Additionally, since the clay matrix is orientated in a preferred direction, it can be hypothesised that this is due to the fabrication of clay through the use of a wheel (as described in Chapter 2.2.3.1), as opposed to a hand-made material fabrication.

The darker black spots seen in Fig. 11, Fig. 12 and Fig. 13 shows the swelling effects of liberated CO$_2$ gas from the fabric present, due to carbon burning in the material, producing microcellular structures with large bloating pores. Since an extended compact vitrification is seen for POL044, it is described as having an EFT being above 750°C, agreeing with previous XRD results (Table 2) identifying EFTs for POL044 as between 850°C-950°C (the extent of vitrification suggests an EFT between 900°C-950°C).

Much like Fig. 12, and unlike Fig. 11b, the vitrification in Fig. 13a shows an extended compact vitrification, which is indicative of high EFTs, much greater than 750°C. Fig. 13a (mag x2000) shows a large similarity in the fusing of clay pellets as Fig. 12, suggesting that the EFTs for both POL043 and POL044 are close to one another. Fig. 13b shows a larger magnification of the clay matrix vitrification effects in POL043, at x5000 magnification. Here, the microcellular glassy phase filament structures are clearly identified, and the liberated CO$_2$ bloating points are well defined (seen as dark spots in Fig. 13b). Therefore, in terms of vitrification, the SEM results for POL044 also agree with previously predicted XRD results (Table 2) in identifying the EFT to be between 900°C-1000°C (though more likely to be 900°C, since a total vitrification is not directly seen).
3.3.2 MINERAL INCLUSIONS

Since secondary minerals precipitate into fired ceramics after cooling down, several types of mineral inclusions were identified in this dissertation using SEM. Secondary calcites (from the decomposition of primary calcites) may be formed from gehlenite for calcareous-fired pottery between 850°C and 950°C. There are three main types of secondary calcites: spherical, micritic and hexagonal secondary calcites. All of these types of secondary calcites were observed in this dissertation using SEM, and can be seen in Fig. 14 above. Fig. 14d may represent a fossil which has not totally decomposed in the material, as seen by the whiter, micritic secondary calcites.

![Figure 14- BSE SEM secondary calcite types; a) (top left) POL043, hexagonal, mag x2000, 20kV, WD= 13.7mm; b) (top right) POL042, spherical, mag x2000, 20kV, WD= 13.1mm, c) (bottom left) POL044, micritic, mag x5000, WD= 10.7mm; d) (bottom right) POL044, micritic and hexagonal, mag x1000, 20kV, WD= 10.6mm](image-url)
All secondary calcites were characterised chemically through SEM by its large presence of Ca in the spectra. As an example, the spectra for Fig. 14a is shown in Fig. 15 above, for sample POL043. In addition to secondary calcites, other post-depositional secondary minerals such as potassium chloride was identified near the surface of POL036, showing a highly definitive cubic microstructure, as seen in Fig. 16 for varying magnifications.

Figure 15- SEM spectra showing voltage (keV, x-axis) against counts (y-axis) with elemental labels for POL043 in Fig 14a

Figure 16- SEM BSE image of Potassium Chloride on POL036 surface; a) (left) mag x2000, 20kV, WD= 9.8mm; b) (right) mag x5000, 20kV, WD= 14.1mm
3.3.3 HEAVY MINERALS

Higher atomic number elements appear much brighter in SEM BSE images, since more backscattered electrons are collected at the SEM detector for heavier elements. A small number of heavy minerals were found in the clay-matrices, and they were all extremely finite in size and abundance within all samples. Zirconite, \( \text{Zr(SiO}_4\text{)} \), pyrite, \( \text{FeS}_2\) and monazite \( (\text{Ce, La, Nd, Th})\text{PO}_4\) are identified in Fig. 17 below as examples, for POL033 (Fig. 17a), POL042 (Fig. 17a) and POL048 (Fig. 17b), respectively.

![Figure 17: BSE SEM images of heavy minerals in clay matrix in, a) (left) POL033, mag x2000, 20kV, WD = 13.8mm; b) (middle) POL042, mag x2000, 20kV, WD = 12.9mm; c) (right) POL048, mag x4000, 20kV, WD = 12.5mm](image)

It is common to find heavy minerals in calcareous clay-based artefacts, since heavy elements are found as trace elements in most ground soils, especially Fe-based heavy minerals. Minerals in clay fractions play a vital role in chemical and physical properties, especially if found in larger-than-trace quantities, though are generally regarded as major impurities for ancient ceramics. Heavy minerals may be explained due to the breakdown of primary minerals (such as plagioclase and feldspar), though may also be due to the formation of clay minerals from rocks (such as Fe, Zr, Al and Ti), which are found in these calcareous clay samples, since they are strongly resistant to weathering effects. The presence of Zi and Ti may also suggest the relation of the sample to be related to a volcanic fabric.

3.3.4 SLIP AND GLAZE

In this sample-set, fragment POL032 located on the rim of the jar (Table 1), was found to contain a type of slip on its surface. This slip can be seen in Fig. 18 below, as a darker contrasted section along the border of the sample. In order to analyse the slip, a chemical characterization was completed along the slip at a magnification of x2000, to produce a more reliable quantitative result for slip composition. The SEM spectra for Area 1, indicated in Fig. 18 below, can be seen in Fig. 18a. INCA software produced automated peak identification in Fig. 18a, and it can be seen that the main
elements present in the slip includes Si, Ca, Al and Fe. The Fe in the slip may be produced from disassociated raw clay materials under firing, which produces Fe-oxides and Fe-hydroxides. In calcareous clays, Ca-Fe-aluminosilicate minerals are formed under oxidizing conditions, as CaO reacts with these Fe-oxides.[53] A quantitative description of the spectra in Fig. 18a is seen in addition to Table 3 below. As seen in Table 3, the slip found in POL032 was found to be a Ca-Fe-aluminosilicate material, compositionally containing (in order of highest wt. % presence): 25.76% Si, 21.27% Ca, 3.69% Al and 3.34% Fe.

Table 3- Elemental composition and weight % of chemical characterization shown in Fig. 18a, of POL032 glaze

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<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight% Sigma</th>
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</table>

Figure 18- SEM BSE image for POL032, indicating points of characterization analysis along slip surface, mag x100, 20kV, WD= 10mm
Alkali glazes are usually characterised by the presence of copper and/or iron, and variations in MgO and K$_2$O content is commonly corresponded to plant ash glass for production.\cite{54,55} In Fig. 19 below, a clear glaze is identified in the sample POL033, where the SE image in Fig. 19b indicates a finer textured coating on the surface, with no obvious porosity.

In terms of the elemental composition (Appendix 3), it was found that the glaze was (much like the slip in Fig. 18a), predominately a Ca-Si based material, with distinct peaks for Al, Cl and K, and trace elements of Ti and Fe. The influence of K$_2$O in the glaze composition therefore suggests an alkali glaze, where it is likely that alkali oxides were used as fluxes and a plant ash glass source of flux. Since glazes were not found for all a large enough range of samples in the dataset, more research must be done in order to correlate provenance with glaze characterization.
CONCLUSION

In this investigation, an archaeometric study was carried out in order to analyse ancient calcareous-based Islamic water-jar ceramic fragments, dated to around the 10th and 11th century, discovered in the town of Pollentia in the Balearic Islands. Through multivariate statistical analysis with XRF chemical data, an additive log-ratio transformation (alr) of the dataset was performed in order to create chemical groups (CGs) through the adjunction of principal component analysis (PCA), and a hierarchical-type clustering analysis using the centroid agglomerative method.

Three definitive chemical groups (CGs) were found (Graph 3, 4) for the sample-set, with dissimilarities in chemical composition creating a sub-group (CG-2B) within CG-2. POL048 (CG-3) was found to be an outlier in this dissertation, and was characterised by a low CaO and MgO content, as well as higher Fe$_2$O$_3$, Al$_2$O$_3$ and K$_2$O wt. %, when compared to CG-1 (POL028, POL040, POL039, POL047, POL043, POL030, POL042) and CG-2 (POL032, POL029, POL036, POL044, POL041, POL033, POL031, POL034, POL045, POL038, POL035, POL037, POL046), seen in Table 1, Graph 3 and Graph 4. The defining chemical differences between CG-1 and CG-2 was due to a larger presence of Ni, Na$_2$O, Fe$_2$O$_3$, TiO$_2$ and K$_2$O (in terms of major elements) for CG-1, than for CG-2. The subgroup CG-2B was found to have a higher CaO mean wt. % content of 26.85%, in comparison with CG-2A, which had an overall CaO mean of 17.9%. Additionally, a larger SiO$_2$ presence (between 32.08 wt. % and 35.58 wt. %) was found for CG-2B, in comparison to CG-2A (between 39.21 wt. % to 48.75 wt. %).

Using XRD and SEM, mineral crystalline phase analysis and vitrification microstructural compositions provided an equivalent firing temperature (EFT) analysis for the sample-set, as well as supported evidence for defining CGs determined by WD-XRF. The EFT range in the sample-set ranged from < 800°C-850°C up to between 900°C-1000°C (Table 2). As firing temperature increased, the decomposition of the phyllosilicates (illite-muscovite and alkali feldspar) and calcite also increased. For the low-fired ceramics (e.g. POL030, POL031, POL048, POL039) were all found to contain clear definitive peaks for illite-muscovite, whereas for almost all other samples above 850°C, illite-muscovite was only seen in traces (e.g. POL032, POL043). Plagioclase were not expected to be seen below 850°C, which is evidenced by Graph 6a.

Furthermore, for CG-1 there is a clear increase in the presence of pyroxene such as diopside, as trace peaks (POL040) became more prominent (POL047, POL043) as EFT increased from 850°C to an EFT range between 900°C and 1000°C. Additionally, the peak for gehlenite (Fig. 4), at 2θ = 31.5° increased in counts as the EFT increases, as Graph 6 sees the highest peak of gehlenite for sample POL033 (Graph 6c), which was predicted to have a high EFT of above 850°C (between 900°C-900°C).
For CG-2, the XRD patterns showed trace peaks for hematite in CG-2B samples, however hematite was completely absent for CG-2A. Additionally, no plagioclase were observed for any samples in CG-2A, however for CG-2B, plagioclase were present due to diopside (POL032) and gehlenite (POL032, POL036). The mineralogical differences described provided an additional indication for the existence of two separate sub-groups in CG-2 seen in the WD-XRF chemical analysis in this dissertation (Chapter 3.1). Mineralogically for CG-3, the outlier POL048 was found to contain primary crystalline phases of: quartz, calcite, illite-muscovite, plagioclase, alkali feldspar (low) and hematite (trace). Since there were no peaks for gehlenite or diopside indicated by the XRD analysis for this sample, it was suggested that the EFT for POL048 was estimated to be <800°C-850°C.

SEM was used in this dissertation in order to correlate the changes in vitrification with EFTs of the selected samples in different estimated EFTs, complementing previous XRD results. For low-firing temperatures (<800°C-850°C), sample POL042 showed an inhomogeneous clay matrix structure with a bimodal-type of distribution for fine grain structures, which could be related to a volcanic fabric production. Large rock fragments, as well as an initial vitrification glassy phase filament structure in POL042 (agreeing with XRD results) suggested its EFT to be <800°C-850°C, most likely in the 700°C-750°C range. For the medium-fired and high-fired ceramics fragments, POL044 and POL043 were selected, respectively. These clay matrices were found to have an extensive compact vitrification of a similar nature in terms of microcellular grain structure, as well as definitive bloating points due to CO₂ gas liberation during firing. This suggested that both POL044 and POL043 agreed with previously predicted XRD results (Table 2) in identifying the EFTs to be above 750°C, between 900°C-1000°C (though more likely to be 900°C, since a total vitrification was not directly seen). In addition to this, SEM was capable in identifying all three main types of secondary calcites: spherical, micritic and hexagonal secondary calcites, as well as post-depositional cubic potassium chloride and heavy minerals such as: zirconite, monazite and pyrite (Fig. 17). Finally, a slip on the sample surface was characterised in POL032 as containing a Ca-Fe-aluminosilicate based composition (Fig. 18), and an alkali glaze found for POL033 (Fig. 19) suggested a plant ash glass glaze production due to a distinct K₂O peak. [55]

To take this project further and improve on the results found, a mercury intrusion porosimeter (MIP) or bubble point experiment may be used, in order to further improve the understanding of the pore-size distribution and total porosity in the ceramics on the firing temperatures. In addition, a more complete petrographic analysis may be used in order to determine fabric composition and provide a strong provenance relation for the samples.
BIBLIOGRAPHY


## Appendix

### Appendix 1

XRF machine manual, including regression limits and X-ray operating modes

| Element | %     | 0.15-59.20 | 0.01-15.70 | 0.05-12.81 | 0.04-49.00 | 1.13-90.40 | 0.01-2.71 | 0.01-0.35 | 0.07-23.65 | 0.12-43.51 | 0.12-43.51 | 0.8-5.27 | 0.7-8.00 | 7.13-18.00 | 20.13-13.00 | 10.36-60.00 | 3.37-10.00 | 0.37-10.00 | 3.37-10.00 | 0.37-10.00 | 0.37-10.00 | 2.37-10.00 | 20.37-52.00 | 5.95-17.00 | 10.17-20.00 | 7.49-9.00 | 4.12-3.00 | 5.11-6.00 | 4.23-8.00 | 5.31-10.00 |
|---------|-------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|--------|--------|------------|------------|--------------|-----------|------------|------------|------------|------------|------------|----------|------------|----------|------------|----------|------------|----------|------------|
| U       | 0.21  | 0.21       | 0.01       | 0.08       | 0.45       | 0.45       | 0.05       | 0.01       | 0.31       | 0.13       | 0.13       | 5       | 16     | 11        | 16        | 16          | 9         | 10         | 7          | 8          | 8          | 6         | 22         | 22        | 30         | 30        | 30         |
| R       | 0.40  | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40     | 0.40    | 0.40      | 0.40      | 0.40         | 0.40      | 0.40       | 0.40       | 0.40       | 0.40       | 0.40       | 0.40     | 0.40       | 0.40      | 0.40       | 0.40      |
| L       | 0.70  | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70     | 0.70    | 0.70      | 0.70      | 0.70         | 0.70      | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70     | 0.70       | 0.70      | 0.70       | 0.70      |
| C       | 0.30  | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30     | 0.30    | 0.30      | 0.30      | 0.30         | 0.30      | 0.30       | 0.30       | 0.30       | 0.30       | 0.30       | 0.30     | 0.30       | 0.30      | 0.30       | 0.30      |
| D       | 0.05  | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05    | 0.05      | 0.05      | 0.05         | 0.05      | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05       | 0.05      | 0.05       | 0.05      |
| X       | 0.15  | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15     | 0.15    | 0.15      | 0.15      | 0.15         | 0.15      | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15     | 0.15       | 0.15      | 0.15       | 0.15      |
| kV      | 0.70  | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70     | 0.70    | 0.70      | 0.70      | 0.70         | 0.70      | 0.70       | 0.70       | 0.70       | 0.70       | 0.70       | 0.70     | 0.70       | 0.70      | 0.70       | 0.70      |
| mA      | 0.50  | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50     | 0.50    | 0.50      | 0.50      | 0.50         | 0.50      | 0.50       | 0.50       | 0.50       | 0.50       | 0.50       | 0.50     | 0.50       | 0.50      | 0.50       | 0.50      |
| A       | 0.15  | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15     | 0.15    | 0.15      | 0.15      | 0.15         | 0.15      | 0.15       | 0.15       | 0.15       | 0.15       | 0.15       | 0.15     | 0.15       | 0.15      | 0.15       | 0.15      |
| F+      | 0.05  | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05    | 0.05      | 0.05      | 0.05         | 0.05      | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05       | 0.05      | 0.05       | 0.05      |
| F-      | 0.05  | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05    | 0.05      | 0.05      | 0.05         | 0.05      | 0.05       | 0.05       | 0.05       | 0.05       | 0.05       | 0.05     | 0.05       | 0.05      | 0.05       | 0.05      |
## Appendix 2

Log transformed 16x16 Y matrix, for major elements detected in XRF

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## Appendix 3

SEM graph, indicating elemental composition of POL033 glaze, taken from Fig. 19b