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Archaeological Ceramic Fabric Attribution Through Material Characterisation—A Case-Study from Vale Pincel I (Sines, Portugal)

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Abstract: Defining groups of ceramic objects from archaeological excavations is a crucial and primary practice in the study of settlements, providing information related to ceramic technology, provenance, and interactions, among others. This process begins with a macroscopic analysis of each fragment, identifying common features to define ceramic fabrics. Regularly, this procedure requires further analytical techniques to refine the attribution of each ceramic object to the corresponding fabric. The Early Neolithic site of Vale Pincel I in Sines, Portugal, dates to the second and third quarters of the sixth millennium BC. The earliest examples of *ceramica impressa*, described by patterned impressions on the surface (impresso pottery), in Portugal were found here. These artifacts are indicative of the Western Mediterranean Basin cycle pre-Cardial ceramic tradition. From the numerous Neolithic ceramic fragments discovered at Vale Pincel I, archaeologists identified 42 fragments, categorizing them into 2 main groups (A and B) through visual analysis, while a third group (C) remained unclassified. Group A, thick ceramic body with reddish hues and very friable surfaces; Group B, thin ceramic body with greyish to black shades and a cohesive appearance. With the aim to resolve the classification of group C ceramics, this study uses a multi-analytical methodology, combining Optical Microscopy (OM), Wavelength Dispersive X-Ray Fluorescence Spectroscopy (WD-XRF), and X-Ray Diffraction (XRD). Integrating the analytical data with previously obtained archaeological information, Group C fragments were attributed to Groups A and B, demonstrating the absence of a distinct third group in Vale Pincel I, highlighting the effectiveness of analytical techniques in ceramic studies, and contributing to a deeper understanding of Neolithic ceramic technology in the Western Mediterranean Basin.

Keywords: archaeological ceramic; early neolithic; ceramic fabric; archaeometry; chemometric analysis

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1. Introduction

In the field of archaeology, the term "fabric" refers to the assortment of materials that make up ceramic objects and is also employed to categorize ceramics sharing specific material properties [1–3]. Grouping and describing ceramic fabric types is a common and important practice, as it helps archaeologists understand the cultural, technological, economic, and social aspects of past societies through ceramic production and use [1–4]. This process begins with a macroscopic analysis of retrieved objects, often through hand specimen examination, to determine ceramic characteristics like colour, hardness, texture, and visible inclusions' size, shape, and frequency [1,2]. When more detailed analyses are necessary, commonly, thin sections of the fragments are prepared and examined under a petrographic microscope [1,2,5]. This process allows the identification of most minerals present in a sample, and the quantification of voids and non-plastic elements' relative frequency [4,6]. However, certain limitations must be taken into account: as a multi-step preparation process, it is time-consuming, demands a significant sample size, and requires specialized expertise and experience from the user with the added risk of sample loss, particularly when working with highly friable specimens [3,4,6–8]. Additionally, the large majority of clay minerals are not visible using this technique, allowing only the identification of non-plastic inclusions [9]. Some concerns about the representativeness of thin sections also arise, leading to questions about whether these minerals and voids are truly quantifiable and representative of the entire ceramic object [3].

To address these challenges, various analytical techniques are available for studying ceramic archaeological materials. Among these, X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) are commonly employed. While they cannot replace petrographic analysis, their combined use provides valuable insights for defining ceramic fabrics. The main advantages of these techniques include reduced analysis time, smaller samples, quantifiable data output, and less reliance on the user's interpretation.

1.1. Neolithic Archaeometric Studies Conducted in Current Portuguese Territory

The onset of the Neolithic period marks a fundamental shift in human history, characterised by innovative approaches to regulating and developing natural sources of food through agriculture and livestock breeding. This shift allowed the transition from nomadic lifestyles to the sedentarisation of previous Mesolithic communities, with the consequent increase in social complexity [10,11]. The timescale and duration of the Neolithic period cannot be defined globally as it varies significantly across different regions [10]. Various forms of evidence contribute to our understanding of this transformation, including socioeconomic, demographic, environmental, and cultural, among others. While not a key marker of the Neolithic per se, pottery is a major indicator of the Neolithisation process, particularly when analysed in conjunction with the archaeological context and other associated materials (especially lithic artefacts) [10,11].

The Neolithisation process in the Iberian Peninsula has been a topic of extensive debate in recent years, especially concerning West Mediterranean areas [12–14], with two main paradigms appearing: the Model of Maritime Pioneer Colonization and the Dual Model [13,15]. The first, primarily associated with J. Zilhão [16,17], argues that Neolithic communities arrived in the Iberian Peninsula primarily through maritime routes, resulting in the fast Neolithisation of the coastal areas before spreading inland [13,15,16]. On the other side, the Dual Model, defended by J. Bernabeu-Aubán and others [18–21], integrates both maritime and terrestrial influences in the Neolithisation process, suggesting that while some Neolithic communities arrived via maritime routes, there were also significant movements of people and ideas through land routes. This model highlights the complexity of the Neolithisation process, acknowledging the contributions of both coastal and inland populations in the spread of Neolithic practices and emphasising the interactions between different groups [13,18].

In the context of Portuguese territory, recent models for the Neolithisation process propose a mixed approach, recognizing the coexistence and interaction between indigenous Mesolithic communities and incoming Neolithic groups, signifying that the Neolithisation process involved both local adaptations and external influences [13,14]. This model highlights the coexistence of Neolithic and Mesolithic communitieswho occupied different territories and interacted over several centuries, leading to a gradual transition rather than a complete cultural replacement. It emphasises the active participation of indigenous Mesolithic populations in adopting and adapting Neolithic practices, rather than being passive recipients of external influences. Additionally, the process involved various colonisation phenomena, including maritime and overland movements, indicating that diverse groups contributed to the spread of Neolithic practices across the region [13].

This ongoing debate has led to the appearance of archaeometric studies of Neolithic findings from different locations, in the hope of shedding some light and providing solid clues to the debate [12]. In current Portugal, archaeometric studies of Neolithic ceramics, apart from those analyses aimed at dating archaeological sites, are still limited. Until now, only the ceramic remains originating from the limestone Massif of Estremadura (eight archaeological sites) [22], the western Algarve (six sites) [22], Mondego Plateau (three sites) [23], Almada (one site) [24], and Coruche (one site) [25] were studied with an archaeometric approach (Figure 1).

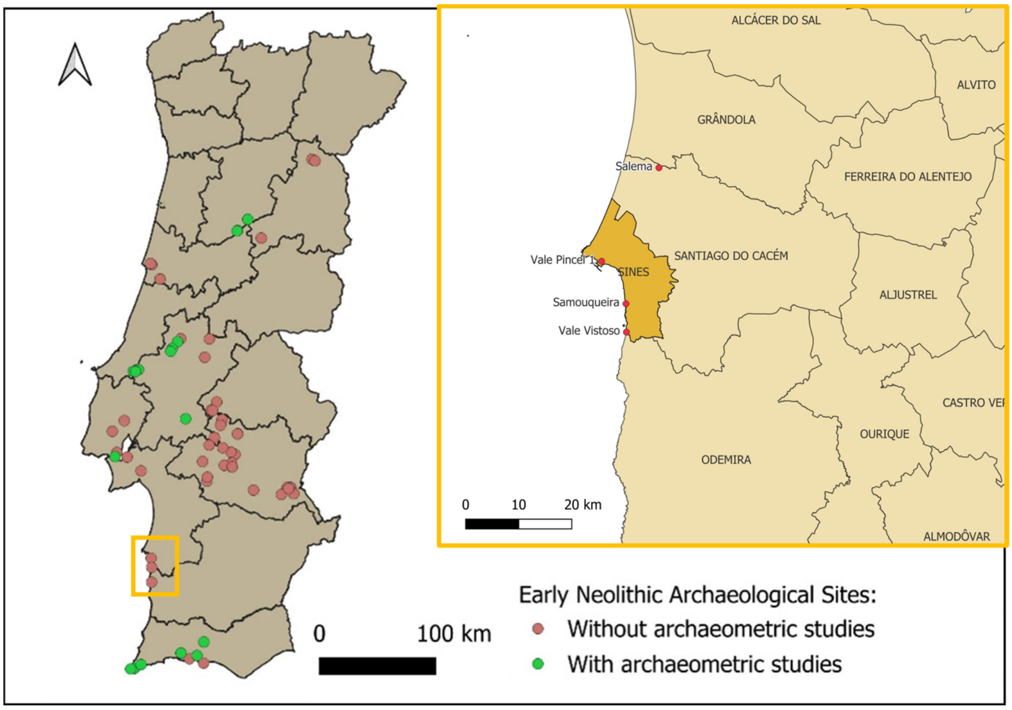

Figure 1. Location of 66 Early Neolithic archaeological sites in Portuguese territory, with identification of the sites where archaeometric studies were conducted. The detailed map shows the location of the Early Neolithic and/or Early evolved Neolithic sites of Southwest Portugal mentioned in the present work.

These studies used different analytical tools and techniques depending on the research questions to be answered and include a wide range of materials characterisation techniques such as Optical Microscopy (OM) [22,23,25], Raman Spectroscopy [24], X-ray diffraction (XRD) [24], X-ray fluorescence (XRF) [24], and Instrumental neutron activation analysis (INAA) [22,23,26]. These techniques provide data regarding the textural, chemical, and crystallographic characteristics of each fragment and allow us to better understand the technological development within ancient societies, offering important clues about the raw materials employed and manufacturing procedures [27]. Findings from these studies have revealed that Neolithic ceramics across different regions often reflect the use of diverse raw materials and manufacturing techniques, predominantly relying on locally available resources and knowledge. This underscores the effectiveness of archaeometric approaches in elucidating the Neolithisation process and its regional variations.

1.2. Archaeological Context of Vale Pincel I

The archaeological open-air site of Vale Pincel I, situated in Sines (Alentejo, Portugal) (Google Earth DMS Coordinates: 37°56′32.7″ N 8°50′47.9″ W), was discovered in the late 1970s, reigniting interest in the study of the Portuguese Early Neolithic period. Alongside other archaeological sites, such as Samouqueira, Vale Vistoso, and Salema, Vale Pincel I revealed the first known domestic structures from the Early Neolithic and/or Early evolved Neolithic in Portugal (Figure 1) [28]. The locations of the Early Ancient Neolithic settlements in the southwest coast of Portugal (dated from the sixth millennium cal BP) are coincident with the previously existent Mesolithic settlements [21]. The continuity in settlement sites, coupled with the societal and mobility patterns, suggests a significant persistence of Mesolithic cultural behaviours into the Early Neolithic way of life.

Located on the southeastern outskirts of the Sines Eruptive Massif, Vale Pincel lies on a complex geological setting. Directly above an area with contact metamorphic rocks, characterized by the presence of pelitic hornfels, it is in close proximity to the gabbros and diorites of Sines and to the Plio-Pleistocene sands from the coastal plain [29,30]. These deposits are largely composed of reddish and orange sands with small pebbles of quartz, shist, and red sandstones. Mudstones, carbonate concretions, and ferruginous pisolites can also be found in these deposits [30]. The emerged part of the Sines Eruptive Massif is composed of granular rocks, consistent in gabbro-diorites with posterior sienites, and is characterized by a dense lode network with high lithological variability (silica contents vary between 39% and 72%) [30]. It is worth noting the occurrence of small concentrations of ilmenite and magnetite in the sands S. Torpes beach (6 km southeast of Vale Pincel I) [30]. The ilmenite found here presents TiO_2 content close to 50% while the magnetite presents up to 90% of FeO^t [30].

Vale Pincel I is the largest archaeological site in the context of the Portuguese Neolithic, c. 10 ha. Located at 30 m of altitude, it is implanted, as with the other mentioned archaeological sites, on sandy areas, without natural conditions of defence and near cliffs along the coastline, adjacent to water courses [28,29,31,32]. Chronologically, Vale Pincel I was radiocarbon dated between the first quarter and the third quarter of the sixth millennium cal BP, with a greater probability density occupation in the interval between ca. 5640–5380 cal BP. This situates it among the "pioneer" locations with pre-Cardial occupation in the Iberian Peninsula [28,32]. The excavations conducted at this site uncovered multiple clustered habitat structures, characterized by large depressions in the ground (up to 10 m) and fireplaces both inside and outside the cabins [28,32]. The site's stratigraphy revealed a single Neolithic occupation layer, which was further divided into two phases, each containing abundant lithic and ceramic artifacts [29]. The reading of the stratigraphic survey revealed an extremely uniform five-layer stratigraphy in all of Vale Pincel's extension (Figure 2) [28]. The most superficial layer has 0.25 m thickness, presents a greyish sandy texture with few large dimension elements, and has a loose structure. The following layer has 0.2 m thickness, a yellowish colouration, and a sandy structure. Layer C.3's thickness varies between 0.15 m and 0.2 m, has a brownish colouration, and a sandy texture with scarce coarse elements. Subsequently, layer C.4 has 0.6 m light grey colour and a sandy structure without coarse elements. The final layer is composed of ferruginous sandstones with red and yellow stains [28].

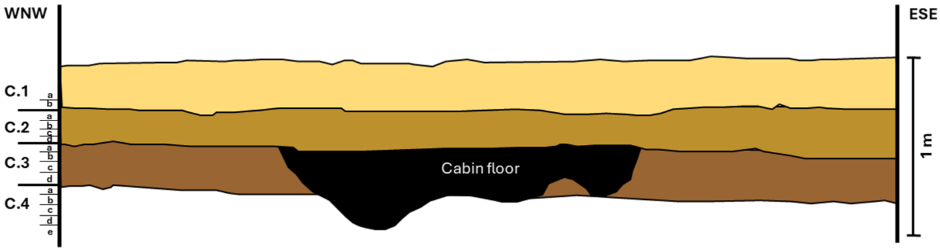

Figure 2. Vale Pincel I stratigraphy (image adapted by Ana S. Saraiva from the survey cut excavated in Vale Pincel I, available at [28]).

Early Neolithic Mediterranean ceramics from the sixth millennium BC can be largely categorized into two main traditions: the Cardial Ware Culture, characterised by decorative patterns made with cockle shells (Cardium), and the Impressed Ware Culture, marked by decoration crafted by pressing objects into the clay before firing. Besides these, it is worth mentioning that other local traditions existed, with each region adapting pottery styles based on their local resources, environments, and cultural practices. While the Cardial Ware Culture was particularly found in the western Mediterranean (southern France [33,34], Iberian Peninsula [35,36], Italy [37]), in the Mediterranean areas between Liguria and Southern Spain, several archaeological sites have also provided ceramic artifacts with impressed decorations, frameable in the Impressed Ware tradition [34,38–42].

The majority of Vale Pincel's ceramic findings show characteristics closer to the Impressed tradition, being Cardial characteristics found only in a small percentage of Vale Pincel's findings [28,32,43]. It can be argued that the Neolithic phase of Vale Pincel is part of the broader central-western Mediterranean tradition of impressed ceramics, preceding the emergence of the Franco-Iberian Cardial Ware culture [43]. The characteristics of Vale Pincel ceramics have parallels with archaeological sites found in Hérault and Provence in France and with Ligurian and south Italian sites [43–45]. Furthermore, the proportions of Impressed/Cardial ceramics found in Vale Pincel have equivalents in other settlements in the regions of Orão (North Africa) and Eastern Andalusia [28,46,47].

Vale Pincel's ceramic findings are not only the earliest Neolithic examples of ceramica impressa in Portugal attributed to the Western Mediterranean Basin cycle but also proved to be very important for understanding the Neolithisation process of the Western Mediterranean Basin. The ceramic findings at this location are characterised by simple forms, typically highly spherical objects or cups with a dome-shaped base, adorned with plastic or impressed decorations (occasionally Cardial) [28,29]. The discovery, in this location, of both *ceramica impressa* (predominantly non-Cardial) and artefacts belonging to a Mesolithic traditional lithic industry challenges the conventional diffusionist perspective of the "Cardial culture" and supports the possibility of the existence of multiple Early Neolithic cultures, not necessarily synchronous, emerging from the evolution of regional Mesolithic groups [28,32,43]. This finding contributes to the thesis of the process of Neolithisation of the Portuguese coast by cultural osmosis [21,32].

From the extensive number of ceramic findings excavated at Vale Pincel I (over 1200 fragments), two groups were defined based on macroscopic analysis [28]:

- Group A presents a ceramic body with low compaction and high number of irregularly distributed non-plastic elements, usually quartz of large dimensions (>1 mm, reaching 5 mm). They present irregular and very friable surfaces of reddish colours, with a greyish to black fracture. All fragments present thick walls (sometimes > 20 mm). The fragments from this group are typically from globular pots with impressed decoration [28].

- Group B ceramics have compact ceramic bodies with numerous non-plastic elements of reduced dimensions (<0.5 mm), irregularly distributed, and a few bigger, between 0.5 and 1 mm. Its surfaces are well smoothed and of greyish-brown colours, with fractures of uniform colour, identic to the surface, or with greyish-black areas. The thickness of the walls rarely surpasses 7 mm. The ceramic from this group usually corresponds to spherical vessels and bowls of reduced dimensions [28].

Group A ceramics are predominant in layers C.3a-2d (base of the archaeological strata) whereas group B, despite also being sporadically found in the lower layers, prevails in layers 2b and 2c (corresponding to the later and final occupation of the site). The upper layers might represent the transition from the Early Neolithic to the Evolved Early Neolithic, which was found in archaeological sites in the proximity of Vale Pincel I, such as Vale Vistoso and Salema (Figure 1) [28].

A third ceramic group, referred to as Group C, is composed ambiguous ceramic objects, presenting intermediate characteristics of groups A and B. These include thick ceramic fragments with dark grey colourations and friable surfaces, as well as thin, bright red fragments with compact surfaces. Due to their small size and undefined shapes, these fragments were typologically unidentifiable. The 15 ceramic fragments from Group C were retrieved from the archaeological layers C.3a-2d in different sectors of the excavation and, through an exclusively macroscopic analysis, could not be confidently attributed to either Groups A or B, nor did they present enough similar characteristics among each other to safely determine the existence of a third group.

The present study aims to explore the combined use of three analytical methods, as an alternative to the petrographic microscope, for grouping and defining ceramic fabric groups. For this, we will explore the combined strategic use of reflected light optical microscopy (OM), X-ray Fluorescence spectrometry (XRF), and X-ray diffraction (XRD) analysis for defining the ceramic fabric groups existent in a collection of Neolithic ceramic objects retrieved from Vale Pincel I. Through this integrated material's characterisation of each ceramic group, we propose to safely determine the major characteristics of the defined ceramic groups and classify the unassigned Group C samples. Subsequently, we intend to be able to contribute to existing reference listings for this archaeological period and geographical setting.

2. Materials and Methods

2.1. Samples

A total of 42 ceramic fragments from the extensive collection unearthed at Vale Pincel I were selected for this study. These were categorised as follows: 14 fragments from Group A, 13 from Group B, and 15 previously unattributed fragments, referred to as Group C (Figure 3).

The detailed information on the location where each ceramic fabric was recovered and its macroscopic characteristics are presented in Table 1. The obtainment of this data was performed before the present study by the responsible archaeologists through hand specimen analysis. Additional information regarding the archaeological work performed in Vale Pincel I is available at [28,32,43].

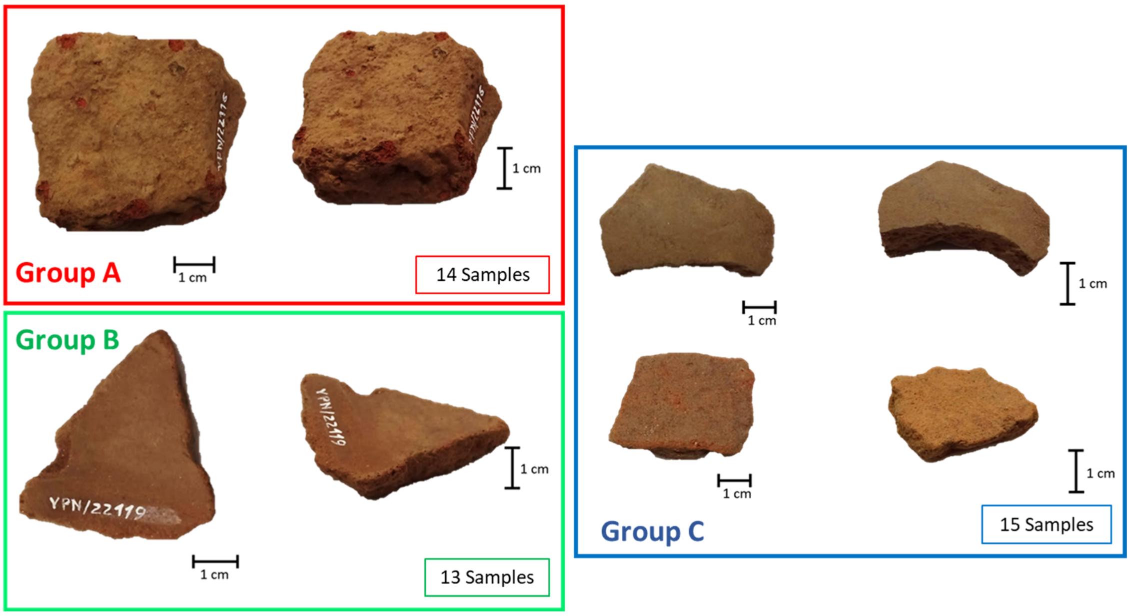

Figure 3. Photographs of representative samples from group A, upper left (VPN 22116), group B, lower left (VPN 22119) and group C, right (VPN 22145, up, and VPN 22147, down).

Table 1. Macroscopic characteristics and archaeological context of each ceramic fragment selected to be analysed in the present work.

	Sample	Sector	Square	Stratigraphy	Colour		Friability
					Surface	Core	
Group A	VPN 8532	XXVI	T16	2d	Light brown	Bright red	Friable
	VPN 22101	XXVI	S17	2b	Brown	Reddish	Friable
	VPN 22107	-	-	Surface	Brown	Bright red	Very friable
	VPN 22116	XXVII	O14	2b	Light brown	Bright red	Very friable
	VPN 22122	XXVI	S8	2a	Light brown	Dark red	Compact
	VPN 22123	XXVI	G7	2c	Brown	Reddish	Friable
	VPN 22124	XXVII	E15	2c	Light brown	Bright red	Very friable
	VPN 22125	XVII	I14	2c	Brown	Reddish	Friable
	VPN 22126	XVII	P11	2c	Light brown	Brown	Friable
	VPN 22127	XVII	I8	2d	Light brown	Bright red	Friable
	VPN 22128	XVII	O6	2c	Brown	Bright red	Very friable
	VPN 22129	XXVI	E15	2c	Dark brown	Dark red	Very friable
	VPN 22130	XVII	P10	2d	Light brown	Light red	Compact
	VPN 22131	XVII	R11	2c	Dark brown	Dark red	Compact
Group B	VPN 1981	XVII	F4	2c	Brown	Dark brown	Compact
	VPN 22098	XXVI	H14	2b	Grey	Dark grey	Compact
	VPN 22119	XXVI	I13	2a	Brown	Brown	Compact
	VPN 22132	XXVI	E15	2c	Light brown	Reddish	Friable
	VPN 22133	XVIII	E7	2b	Light brown	Brown	Compact
	VPN 22134	XVII	O8	2d	Brown	Dark brown	Compact
	VPN 22135	XXVI	E13	2c	Light brown	Brown	Compact
	VPN 22136	XVII	R12	2b	Grey	Dark grey	Friable
	VPN 22137	XVII	E12	2c	Light brown	Dark grey	Compact
	VPN 22138	XVI	G10	2c	Brown	Black	Compact
	VPN 22139	VIII	F16	2a	Light brown	Reddish	Friable
	VPN 22140	XVI	O17	2c	Light brown	Dark grey	Friable
	VPN 22141	XVII	F15	2d	Brown	Dark grey	Compact

Table 1. *Cont.*

	Sample	Sector	Square	Stratigraphy	Colour		Friability
					Surface	Core	
Group C	VPN 22148	XVII	D9	2b	Light brown	Bright red	Very friable
	VPN 22109	XXVI	I18	2a	Light brown	Light brown	Friable
	VPN 22117	XVII	S16	2a	Light brown	Reddish	Very friable
	VPN 22142	XVI	P4	2a	Light brown	Brown	Very compact
	VPN 22143	VIII	I16	2a	Light grey	Grey	Compact
	VPN 22144	XVII	E13	2b	Light brown	Reddish	Friable
	VPN 22145	XXVII	T6	2b	Brown	Dark grey	Friable
	VPN 22146	XXVII	I13	2c	Light brown	Light red	Friable
	VPN 22147	XVI	G13	2b	Light brown	Brown	Compact
	VPN 22149	XXVII	G14	2c	Light grey	Brown	Friable
	VPN 22150	XXVII	E14	2c	Grey	Dark brown	Compact
	VPN 22151	XVI	T3	2c	Light brown	Reddish	Very friable
	VPN 22152	XVII	G2	2d	Light grey	Brown	Compact
	VPN 22153	XVI	T3	2c	Light grey	Dark grey	Compact
	VPN 22154	XVII	D9	2b	Light brown	Reddish	Very compact

2.2. Sample Preparation and Analytical Techniques

All fragments underwent a series of textural, chemical, and mineralogical analyses for a comprehensive material characterisation. The choice of analytical methods employed in the present study was driven by a combination of the desired data, availability, cost, and time requirements, as well as the simplified sample preparation procedure involved and the potential for its reuse in further studies, if needed.

2.2.1. Microscopic Analysis

The main goal of the conducted microscopic analysis was to obtain the distribution, size, and shape of the non-plastic elements present in the ceramic fabrics, not being concerned with the identification of the minerals present in the ceramic body [3]. As in the present work we aim primarily to distinguish and classify each of the previously described ceramic groups to be able to interpret samples from group C, a reflected light Optical Microscope was chosen due to its reduced analysis and sample preparation time. Contrary to the very commonly employed Petrographic Microscope, this technique does not allow the identification of the minerals present, but it can perform a high-quality textural analysis and has a more accessible sample preparation, especially when dealing with very friable and rare objects [3]. Furthermore, the resulting prepared samples can be further studied with numerous other techniques, if necessary, such as Raman Spectroscopy, Scanning Electron Microscopy (SEM), and Fourier-transform Infrared Spectroscopy (FTIR), among others.

Optical Microscopy (OM) observations were performed using a Leica DMI5000M microscope (Leica Camera, Wetzlar, Germany) coupled with a Leica DFC295 digital camera. These instruments are interfaced with a computer running Leica Application Suite (LAS V4.9) software with multifocus functionality [48]. OM images were measured and quantified using ImageJ®1.53h software to obtain frequency, quantifications, and measurements of the non-plastic elements within the ceramic pastes. ImageJ® quantifications were performed using the 'Measure' functionality, obtaining the total number of pixels of each image. Then, the areas with the desired objects to quantify were selected using the 'magic wand' after image contrast enhancement through the 'threshold' tool. Following the selection of all non-plastic elements in the micrograph, the 'Measure' functionality was reapplied, now obtaining the total number of pixels in the desired areas. With the obtained data, the percentage of non-plastic elements was calculated. For the size of the inclusions, the 'set scale' functionality was employed to define the scale of the image. Then, the major axis of the visible non-plastic elements in the image were measured and, finally, the average size and standard deviation was calculated. The analysed sample area with this technique is approximately 4.2 mm^2.

2.2.2. Elemental Analysis

The elemental chemical composition was determined using a PANalytical–Axios 4.0 wavelength dispersive X-ray fluorescence (WDXRF) sequential spectrometer with a rhodium X-ray tube (20.21 keV), in conditions optimised for element quantification using the SuperQ v.5.3A software package (PANalytical B.V., Almelo, The Netherlands). The analysing crystals of LiF220, LiF200, Ge, PE, and PX1 were used for the separation of fluorescent X-ray peaks covering all measurable ranges. Measurements were performed under helium (He) flow and spectra deconvolution was achieved using the iterative least-squares method and semiquantitative analysis based on the fundamental parameter approach with the SuperQ IQ+ v.5.3A software package (PANalytical B.V., Almelo, The Netherlands). The statistical analysis of XRF data was performed with SOLO® 9.2 and Chemoface® 1.71 software [49] for the chemometric approach. For these analyses, the chosen preprocessing method was autoscale.

2.2.3. Mineralogical Analysis

X-ray Diffraction (XRD) analysis was conducted with a Bruker D8 Discover X-Ray diffractometer equipped with a LINXEYE detector and a germanium monochromator providing Cu Kα_1 radiation with 40 kV voltage and 40 mA current. The diffraction patterns were collected in the 2θ between 5° and 75°, with a step size of 0.05° and a count time of 0.7 s per step. The obtained spectra were processed using the Diffrac.EVA 5.0 software (Bruker, Mannheim, Germany).

2.2.4. Sample Preparation

For Optical Microscopy, a small sample from each fragment ($\approx$1 cm^3) was cut using a pair of pliers, embedded in acrylic resin [1], and then polished with silicon carbide (SiC) abrasive papers with decreasing granulometries (P320, P600, P1200, P2500, P4000), resorting to a polishing machine and using water for lubrification. For WDXRF and XRD analysis, a small portion ($\approx$6 g) of each fragment was cut using a nipper and was manually ground into powder using an agate mortar and pestle. For WDXRF analyses, each powder was placed in a plastic sample cup with Mylar®. For quantification purposes, an empty sample cup was measured and quantified with the same specifications, and the obtained results were subtracted from all sample's spectra. For XRD analyses, the same powdered sample was employed. Each sample was set in the powder sample holder and pressed with glass to obtain the flattest and most homogeneous possible powder. All samples were analysed through all the referred analytical techniques and underwent the same processes.

3. Results and Discussion

3.1. Textural Analysis

OM observations of the cross-sections of all fragments allowed us to establish the textural characteristics of the ceramic bodies for each group, detailing the distribution, size, and geometry of the major inclusions (Table 2). The ceramic bodies from each group exhibit distinguishable characteristics, observable in the Optical Microscope images (Figure 4).

Table 2. Summary of each group's average textural characteristics (NPE—Non-plastic elements).

Group	Area of NPE (%)	NPE Size Range
A	18.3 ± 2.4	(0.5 ± 0.1) mm–(1.5 ± 0.3) mm
B	15.9 ± 2.5	(0.3 ± 0.1) mm–(0.7 ± 0.2) mm
C	14.6 ± 4.1	(0.3 ± 0.1) mm–(1 ± 0.2) mm

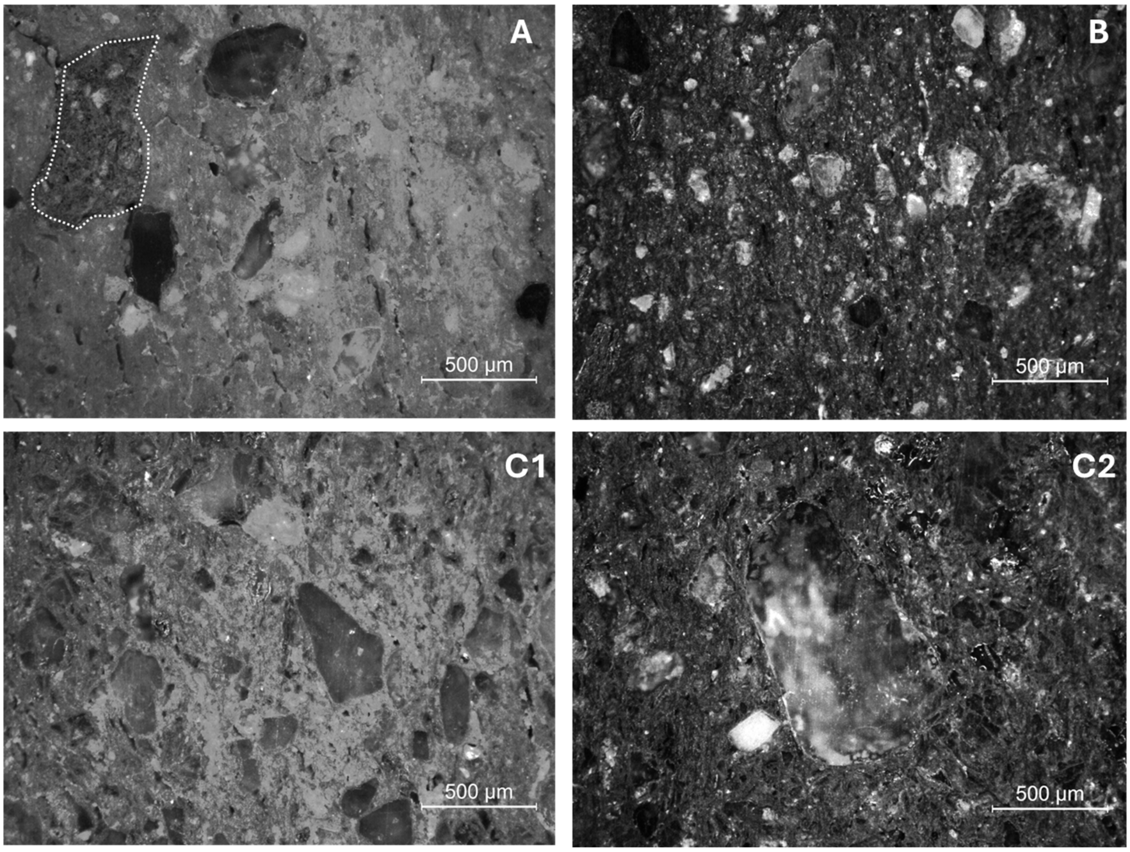

Figure 4. OM photographs of representative samples from each group: (**A**)—VPN 22107 (Group A), the area marked in the photograph shows a distinct typology of non-plastic elements visible in Group A's samples; (**B**)—VPN 22140 (Group B); (**C1**)—VPN 22117 and (**C2**)—VPN 22143 (Group C).Group A cross-sections show reddish hues closer to the surface of the fragments, transitioning abruptly into greyish/black colours in the centre of the fragment, resulting in a sandwich-like structure with a dark core and reddish exteriors. Group B fragments show homogeneous ceramic bodies, displaying greyish to black colours. The observed differences between groups in the ceramic paste's colours indicate different firing environments, a topic that will be later assessed in the analysis.

Focusing on the non-plastic elements (NPE) of the ceramic fabrics, all samples contain significant quantities of these constituents (>15%), irregularly distributed and without a preferred orientation within the matrix. It is also perceivable that samples from Group A (almost all) and none from Group B showed a distinct type of inclusion that can suggest the addition of grog or be a poorly diluted different clay within the ceramic body (area marked in Figure 4A). On average, for all Group A samples, these distinct inclusions correspond to c. 5% of the ceramic body texture. Grog improves the final ceramic object's properties by strengthening its walls, enhancing scratch and impact resistance, and increasing its ability to withstand thermal changes, making it ideal for cooking ware [50,51]. The mixing of different clay raw materials was a common practice to improve workability and firing behaviour [52]. The technological innovation of adding variated tempers and/or different clay raw materials could also have been a method to modify the available clay plasticity, making it more suitable for ceramic manufacture [50,51]. The use of grog in Neolithic ceramics, both Cardial and pre-Cardial, has already been documented at other Western Mediterranean archaeological sites in Spain and Southern France [22,53–55]. Nevertheless, the fact that these inclusions were found in Vale Pincel I Early Neolithic ceramic is particularly noteworthy as it represents a significant technological advancement in ceramic manufacturing and remarkable expertise.

Comparatively, fragments from Group A contained, on average, a higher amount and larger granulometry of non-plastic elements than those from Group B. These samples correspond to ceramic fragments of objects with bigger dimensions, opening the possibility of being an intended addition to the clay materials to provide better stability to the final object. Conversely, samples from group B similarly present substantial amounts of non-plastic elements, however significantly finer than the ones in group A. Concerning group C ceramic fragments, they exhibited intermediate characteristics: some with larger inclusions in a greyish clay matrix and others with numerous smaller inclusions within a reddish matrix. The averaged values for group C's samples were closer to group B. Nonetheless, this textural analysis alone is insufficient for definitive attribution of these fragments to either group, prompting the need for additional analyses.

3.2. Chemical Elemental Analysis

The WDXRF analysis allowed us to ascertain the chemical composition of the pre-established ceramic groups. All obtained data is available as Supplementary Material Table S1. The major oxides identified were SiO_2, Al_2O_3, and Fe_2O_3 (each with concentrations exceeding 15 wt.%). The minor oxides included TiO_2, P_2O_5, K_2O, CaO, MgO, and Na_2O with concentrations between 0.3 and 3 wt.%. Trace oxides V_2O_5, Cr_2O_3, ZnO, Ga_2O_3, Br, Rb_2O, SrO, ZrO_2, Nb_2O_5, CeO_2, and PbO were found at levels below 0.01 wt.% (Figure 5). Initial analysis of the WDXRF results suggested that all fragments were derived from non-calcareous clays. A correlation was observed between SiO_2, Al_2O_3, and Fe_2O_3 contents: Group A exhibited lower SiO_2 but higher Al_2O_3 and Fe_2O_3 amounts compared to groups B and C, with group C presenting intermediate averaged values of these oxides when compared to groups A and B.

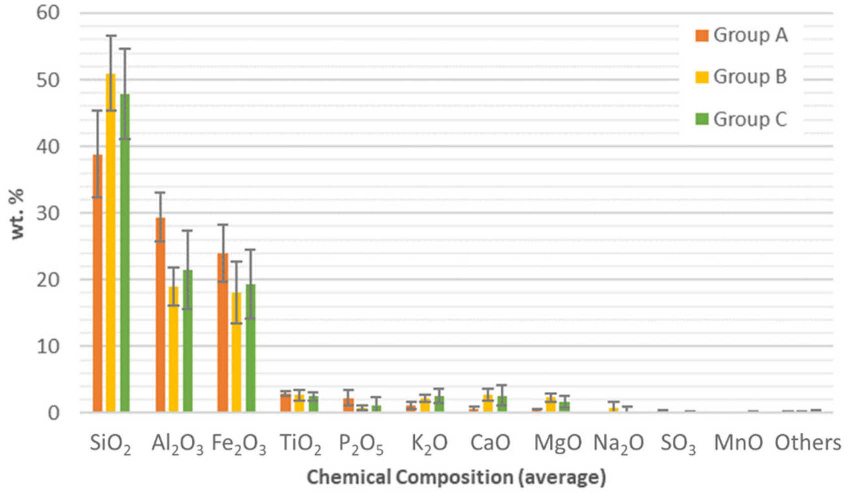

Figure 5. Graphical representation of the obtained average composition from the major and minor oxides of each group samples and its respective standard deviation.

The significant concentrations observed for iron and titanium oxides can be related with Vale Pincel's proximity to S. Torpes beach, where high concentrations of iron and titanium in the ilmenite and magnetite-rich sands occur. Further investigations resorting to petrographic analysis and the study of local raw materials sources are needed to deepen this question.

Phosphorus is an element present in all living organisms [56]. Fostered by the action of phosphoric acid, a typical product of organic substance decomposition, it easily reacts with soil compounds and forms not very soluble phosphates with strong bonds [56]. Due to this, an enrichment in its content is commonly associated with anthropogenic activity [56–58] and is generally considered soil contamination, resulting from its adsorption from the soils where the objects were discarded [58]. However, in some cases, particularly when Fe-bearing solutions exist, the presence of phosphates does not represent contamination occurring after burial, but it can be the result of bone fragments already present in the ceramic object pre-burial [57]. Other studies suggest that phosphorus presence is associated with the everyday use of the original objects for cooking [56,58,59]. As the obtained results show, higher phosphorus concentrations are associated with Group A's fragments, which correspond to large vessels with thick walls. This suggests that these may be cooking wares, and the higher phosphorus content could be a result of their use.

To better refine group differentiation based solely on WDXRF results, a chemometric analysis was conducted, focusing on the major and minor oxide quantifications obtained for each sample. The chosen statistical approach to the data was Principal Component Analysis (PCA) [60,61]. A PCA multivariate analysis converts an original set of unrelated variables into a new set of intercorrelated variables, the Principal Components, which are linear combinations of the original data. This data simplification allows a graphical, rapid, and visual interpretation of large information sets [61]. Initially, this method was applied to verify Groups A and B distinguishability based solely on the obtained elemental analysis, using only the major and minor oxides identified in the ceramic composition. These oxides correspond to the main constituents of clay minerals and typical tempers used. Phosphorus content was included in the PCA as it can be a potential help in the differentiation of the referred ceramic groups. The results (Figure 6) displayed a significant distinction between Groups A and B, showing that these data can be used to perform a supervised model to predict the classification of Group C's samples.

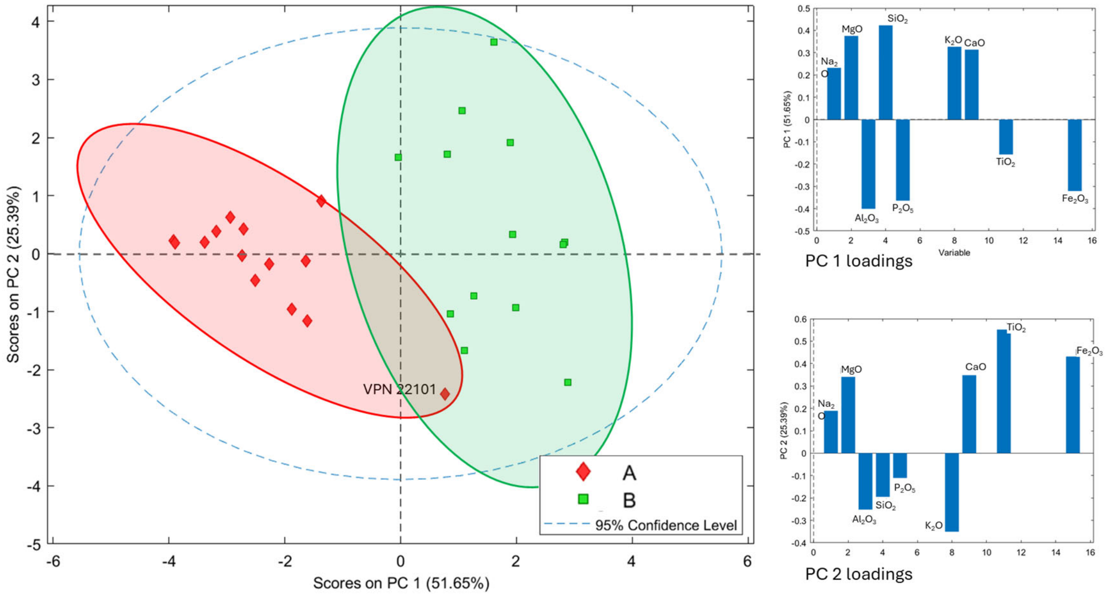

Figure 6. Principal Component Analysis biplot of Principal Component 1 versus Principal Component 2 considering major and minor oxides contents in the ceramics from groups A and B of Vale Pincel I. The represented ellipsis show the 95% confidence interval of each group. Loadings of PC1 (upper right) and PC2 (lower right).

In parallel, the PCA chemometrics results also indicate a potential previous misclassification of sample VPN 22101, originally assigned to Group A, given that this sample's composition more closely aligns with that of Group B compositions. Crossing the chemical elemental results of this fragment with the previously conducted textural analysis, it displays a darker ceramic body and a tendency to smaller inclusions, adding to its strong probability of belonging to Group B.

Focusing on the obtained loadings correlations (Figure 6), the following positive relationships are observable:

- Ti and Fe elements, probably associated with the nearby beach of S. Torpes, whose sands could be used as temper;
- Al and P, which can be associated with the presence of bones and/or cooking ware, or with aluminum phosphates;
- Na, Mg, and Ca that might be associated with local dolomite deposits and Na-feldspars;
- Si and K, probably indicating the simultaneous use of quartz and K-rich feldspars.

Observing these correlations and the PCA plot, Group A's fragments are more strongly associated with higher contents of Ti and Fe, as well as Al and P, while Group B's remains are more associated with Si, K, Na, Mg, and Ca. As group A is associated with large vases and group B with smaller vases and bowls, this variation can point to the purposeful addition of different tempers following each object's function. Further studies are required to deepen and explore these possibilities.

Following the PCA approach, and given the distinct separation between Groups A and B, a Partial Least Squares Discriminant Analysis (PLSDA) method was employed for classifying samples from Group C. PLSDA is a multivariate dimensionality-reduction tool that takes into account pre-established labels for each sample, making it a supervised chemometric method [62] that is able to consider Groups A and B data to build the model and then test Group C samples, resulting in a prediction of the probability of group's C samples belonging to either one of the pre-established models.

The results (Figure 7) show that samples VPN 22146 and VPN 22151 have a strong probability of belonging to group A and that the remaining 13 samples are mostlikely part of group B.

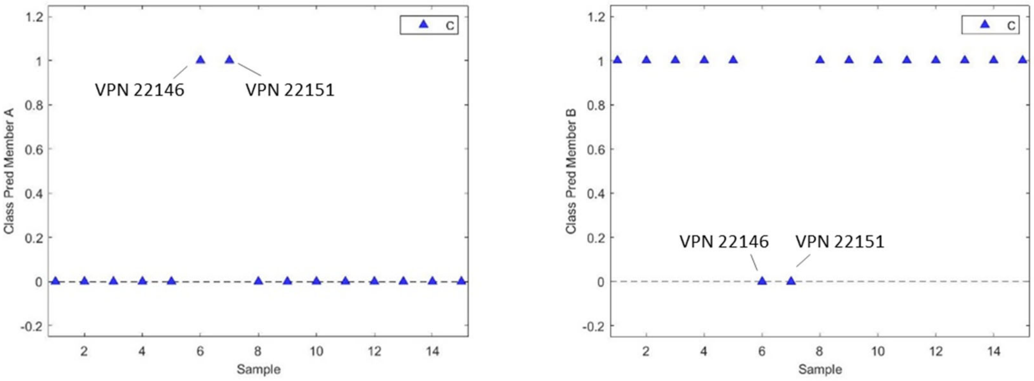

Figure 7. PLSDA class prediction of group C samples belonging to group A (**left**) and group B (**right**).

After this attribution, to better visualize the distinction between the groups and to clarify the inexistence of a separate Group C, a new PCA analysis was performedusing the data from the three groups (Figure 8).

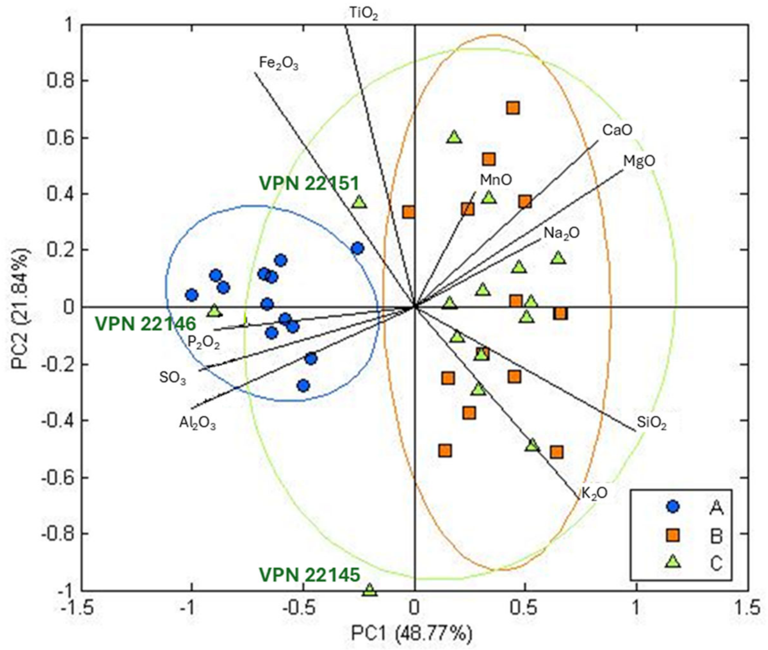

Figure 8. Principal Component Analysis biplot of Principal Component 1 versus Principal Component 2 considering major and minor oxides contents in the ceramics from all ceramic groups of Vale Pincel I. The represented ellipsis show the 95% confidence interval of each group.

The results showed a strong distinction between the two ceramic fabrics A and B, confirming that Group C's samples do not constitute a separate fabric and reaffirm the previous attributions.

3.3. Mineralogical Analysis

X-Ray Diffraction was used for the mineralogical analysis, which highlighted the differences between the studied groups and aided in the classification of group C fragments (Figure 9). Samples from Group A were characterised by the presence of quartz, iron and/or titanium oxides and aluminium phosphates. In contrast, samples from Group B, while also containing quartz, did not display iron or titanium oxides and instead displayed diverse feldspars and pyroxenes. The obtained mineralogical results can indicate the possible use of at least two local sources of raw materials, as the geological characteristics of Vale Pincel I's surroundings, studied in detail by [30], correspond to the mineralogical characteristics of the studied samples. Nevertheless, further studies resorting to thin sections, petrographic microscope analyses of the samples, and local raw materials are crucial to further advance in provenance studies.

The two samples chemometrically identified as belonging to group A (VPN 22151 and VPN 22146) present XRD spectra consistent with the other Group A samples. The samples from group C that were preliminarily attributed to Group B demonstrated mineralogical similarities with Group B samples.

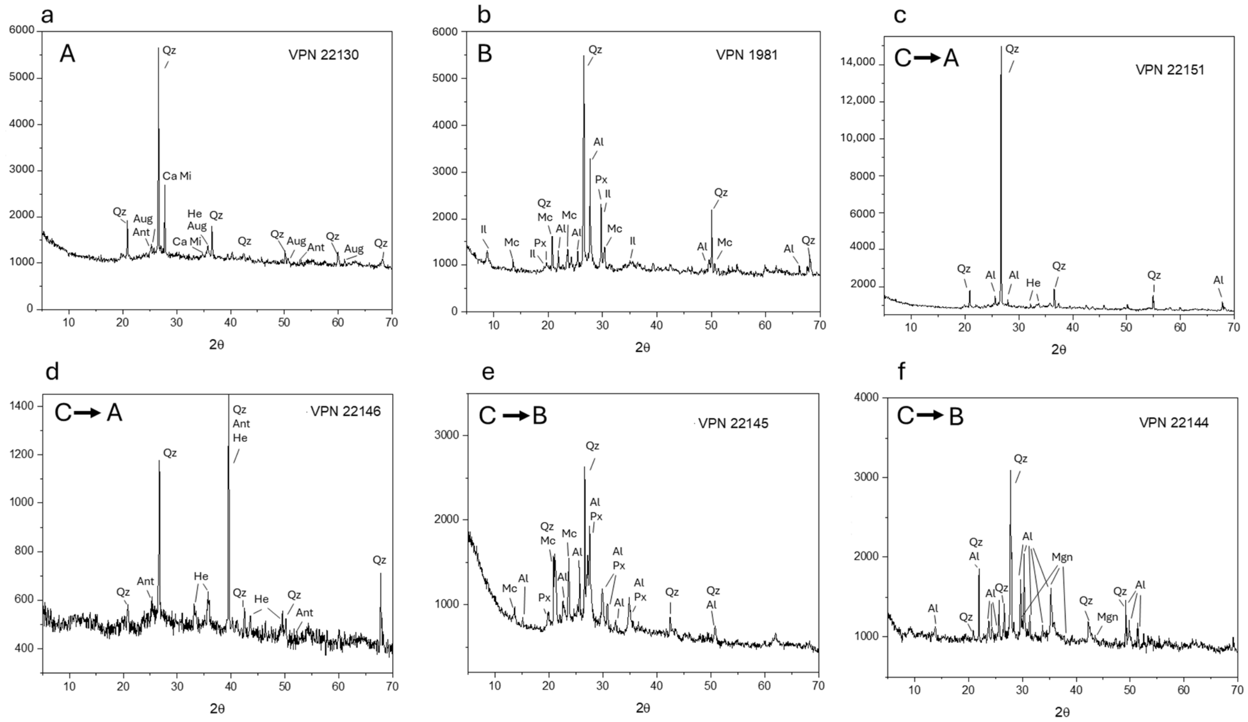

Figure 9. XRD spectra of representative samples from groups A (image **a**, sample VPN 22130) and B (image **b**, sample VPN 1981) and 4 spectra from group C samples: VPN 22151 (image **c**), VPN 22148 (image **d**), both attributed to group A, VPN 22144 (image **e**), attributed to group B and VPN 22145 (image **f**), previously unattributed. (Qz—Quartz; Aug—Augelite; Ant—Anatase; Al—Albite; Ca Mi—Calcium mica; He—Hematite; Mgn—Magnetite; Px—Pyroxene; Il—Illite; Mc—Microcline).

3.4. Attribution of Group C Ceramics

While WDXRF data, complemented by chemometric analysis, proved to be an important tool in the attribution of the ceramic fragments, not all samples from Group C could be confidently assigned using this technique alone. Consequently, the final attributions were made only after crossing results obtained from all the different characterisation techniques.

Cross-referencing the chemometric data with the OM images, it was possible to verify that sample VPN 22146, similarly to Group A fragments, presents a distinct inclusion typology, possibly grog or poorly diluted clay (Figure 10A). Conversely, the remaining samples from Groups C did not show these inclusions, aligning them more closely with Group B. Sample VPN 22146 and VPN 22151 (Figure 10A,B) show reddish colourations characteristic of Group A ceramics. In addition, it was established through XRD analysis that these two samples share mineralogical characteristics with Group A, while the remaining Group C samples show greater resemblance to Group B.

Unifying all collected information, it is possible to ascertain with confidence that group C samples belong either to Group A or Group B, and do not constitute a separate ceramic group. The attributions for each of Group C's ceramic fragments, based on the obtained results, are presented in Table 3.

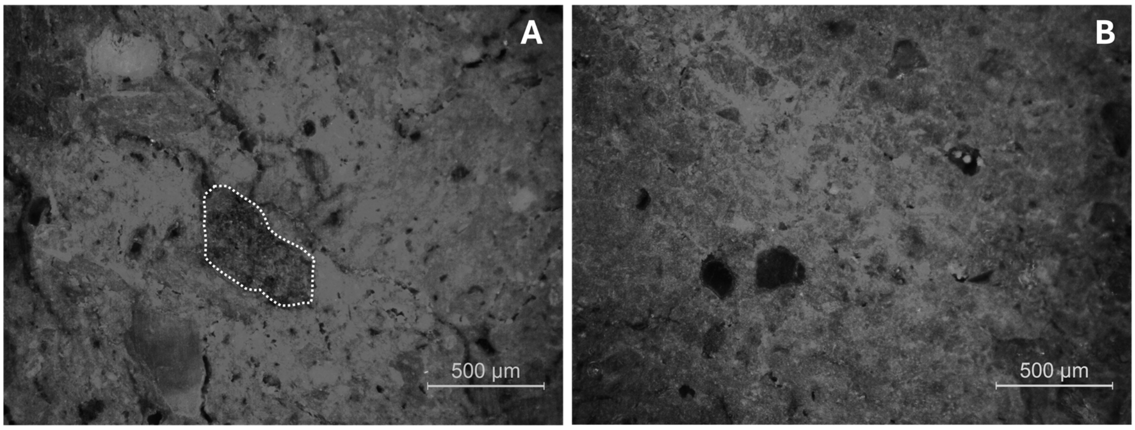

Figure 10. OM DF photographs of samples VPN 22146, magnification of 50× (**A**), and VPN 22151, magnification of 50× (**B**). The marked area in image A shows the distinct non-plastic element already described and present in fragments from Group A.

Table 3. Attributions made to group C samples after archaeometric analysis.

Group C Samples	Attribution After Analysis
VPN 22148	Group B
VPN 22109	Group B
VPN 22117	Group B
VPN 22142	Group B
VPN 22143	Group B
VPN 22144	Group B
VPN 22145	Group B
VPN 22146	Group A
VPN 22147	Group B
VPN 22149	Group B
VPN 22150	Group B
VPN 22151	Group A
VPN 22152	Group B
VPN 22153	Group B
VPN 22154	Group B

3.5. Ceramic Fabric Groups in Vale Pincel I

The conducted analyses permitted us to verify the presence of two distinct ceramic groups coexisting in Vale Pincel I, as shown in Table 4. The existence of two chemically distinguishable compositions indicates the most probable use of distinct raw materials sources. This may be linked to typological requirements of the final pieces or with raw materials availability at specific times. However, it must be noted that all the described differences cannot be fully explained simply by the usage of two distinct raw materials sources. The addition of temper, as well as changes in firing conditions and environment, also display a role in the previously reported differences between ceramic Groups A and B.

As group B ceramics were mostly found in higher levels of occupation (corresponding to more recent times), the observed differences can point to a possible technological evolution occurring within the same settlement. Yet this change could also be a result of existent trade routes, different raw materials sources available over time, and/or the possibility that each manufacturing technique was chosen to suit the functional requirements of the final object. To establish the social significance of this fact, further studies are required.

Table 4. Summary of material characterisation of each ceramic group from Vale Pincel Norte after archaeometric analysis, with the inclusion of the previously group C's ceramic fragments (NPE—non-plastic elements).

Vale Pincel Norte I Ceramic Fabrics	**Group A**	**Group B**
	Macroscopic analysis	
Ceramic matrix colour:	Reddish surfaces and brownish core—sandwich structure	Black to brown
Object typology:	Tall spherical vases with impress decoration	Spherical vases and bowls of reduced dimensions
Friability:	Very friable	Compact
	Microscopic analysis	
NPE frequency (%):	17.5 ± 3.2	15.5 ± 3.4
NPE distribution:	Random	Random
NPE size (mm):	0.5–1.5	0.3–0.6
NPE shape:	Sub-rounded and sub-angular	Majorly sub-angular
	Chemical analysis	
	Higher Al_2O_3 and Fe_2O_3 wt.%	Higher SiO_2 wt.%
	Mineralogical analysis	
	Quartz, Iron and/or Titanium oxides and Aluminum phosphates	Quartz, diverse Feldspars and Pyroxenes

4. Conclusions

The integration of exact sciences' analytical methodologies and chemometric analysis in this study proved to be an important and helpful tool for archaeological investigations, particularly in the important archaeological procedure of ceramic grouping, before conducting further studies and interpretations. The employed methodology allowed the attainment of more informed conclusions and unveiled data that would otherwise remain undiscovered.

With the samples from Vale Pincel Norte I, it was possible to allocate all Group C's fragments to the established Groups A and B, according to the material characteristics of each analysed ceramic fragment. Simultaneously enriching the reference collection data from the Early Neolithic Western Mediterranean Basin. The coexistence in the same settlement of two distinct ceramic fabrics with differentiable manufacturing processes opens new interpretations for the understanding of early Neolithic societies' practices and their evolution in the Western Mediterranean Basin. Further research will investigate representative samples of each, now defined, ceramic fabric group, aiming to compare the results obtained from Vale Pincel I with other archaeometric studies of Neolithic ceramics from different locations. The analysis of local raw materials will be critical in the possible establishment of a connection between the ceramic objects and the source of their materials.

The combined application of Reflective Optical Microscopy, X-Ray Fluorescence, and X-Ray Diffraction techniques, further supplemented by statistical analysis, proved to be an efficient alternative method when petrographic microscope analysis is not viable and/or there is the need for faster results. Moreover, it provided clarity in the classification and grouping of the analysed objects and simultaneously allowed to obtain chemical and mineralogical data that can be further explored to answer other questions related to the ceramic manufacture technology and provenance, and the selection of representative samples for future analyses.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage8030084/s1, Table S1: Chemical composition of all samples obtained by WDXRF analysis.

Author Contributions: Conceptualization, A.S.S., M.L.C., C.T.d.S., J.S., S.D. and J.P.V.; Data curation, A.S.S.; Formal analysis, A.S.S.; Investigation, A.S.S., M.L.C. and J.P.V.; Methodology, A.S.S., M.L.C. and J.P.V.; Project administration, J.P.V.; Resources, M.L.C., C.T.d.S., J.S., S.D. and J.P.V.; Supervision, J.P.V.; Visualization, A.S.S.; Writing—original draft, A.S.S.; Writing—review and editing, A.S.S., M.L.C., C.T.d.S., J.S., S.D. and J.P.V. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding authors.

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Conflicts of Interest: The authors declare no conflict of interest.

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