

Article

Fingerprinting Ceramics from the Chalcolithic Santa Vitória Enclosure (SW Iberia)

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Abstract: The Santa Vitória Chalcolithic site (southern Portugal) prompts several questions related to the provenance and production technology of artefacts. Archaeological ceramics from two sections of Ditch 1 of the Santa Vitória site were studied by neutron activation analysis and X-ray diffraction for the first time, with the main goal of contributing to the contextualization of the artefacts and better understanding their production processes/technologies and the provenance of raw materials. The results point to a local production of ceramics, since their mineral phases reflect the geological contexts around the archaeological site. The mineralogical assemblage indicates a firing temperature below 850 °C. Iron is the better discriminator of ceramics from both sections, which could be related to the addition of different proportions of temper grains during the ceramics' production. Although trace elements do not serve as discriminating geochemical indicators for the analyzed samples, they do imply a slightly higher heterogeneity in the composition of the ceramic paste from section 2. The negative Eu anomaly found in two samples is in accordance with the lower contents of Na₂O, related to plagioclase weathering. Detailed studies on ceramics and potential raw materials are foreseen to assist in discussing the role of this Chalcolithic archaeological site at a regional level.

Keywords: Chalcolithic ditched enclosures; archaeological ceramics; Santa Vitória site; mineralogy; geochemistry; NAA; southern Portugal

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1. Introduction

The characterization of ditched enclosures has a crucial relevance for the understanding of the Chalcolithic period in SW Iberia. Several Chalcolithic ditched enclosures have been identified in Spain [1–3] and in Portugal [4,5]. Knowledge regarding this type of site in the Portuguese territory has suffered a revolutionary increase in recent decades, resulting in different research projects and publications [5,6]. In Portugal, particularly in the interior of Alentejo, the ditched enclosures have a chronology that goes from the middle of the 4th to the end of the 3rd millennium BC, even though the presence of ditches (not necessarily of enclosures) has been occasionally referenced in the Early

Neolithic, with the vast majority of those currently known falling between the Late Neolithic and the Late Chalcolithic/transition to the Bronze Age [7]. This phenomenon cannot be seen as homogeneous, but it has generated intense debates about the nature of different contexts, with some authors referring to them as settlements [8–11], while others focus on their performance as centers for reunion, managing identities, and the social and political order [12,13]. In these enclosures, a strong cosmogenic connection can be observed [14], in particular a privileged orientation of various enclosures, the landscape relationships they establish, and the social practices they embrace. In some sites, deeper studies were performed focusing on remarkable artefacts and ceramics, and on the fill materials of the ditches, in order to characterize and understand their provenance and circulation issues in Chalcolithic Iberia [15–20].

The archaeological site of Santa Vitória is located near Campo Maior (Alentejo, southern Portugal). This Chalcolithic site can be described as a ceremonial enclosure of circular tendency forming sequences of contiguous semi-circular lobules defined by two concentric ditches (Figure 1). The inner enclosure of Santa Vitória has an entrance facing the summer solstice. The ditches reveal natural processes of infill, but anthropic ones were also registered. In other words, they were mainly filled with what seemed to be intentional depositions [21].

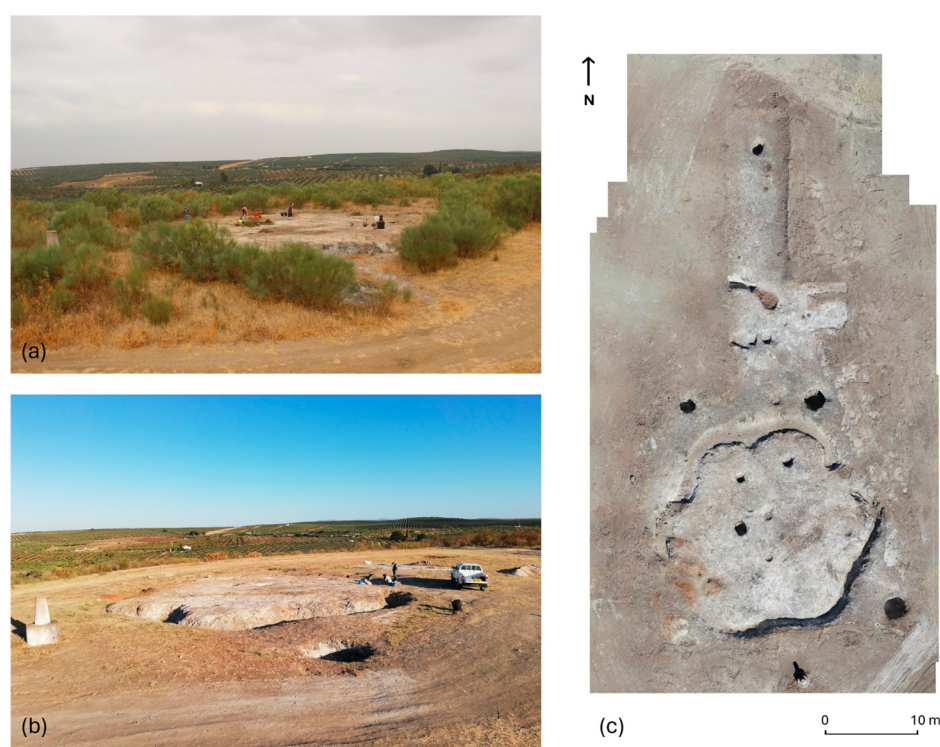


Figure 1. Santa Vitória enclosure, near Campo Maior (Portugal) (adapted from [21]): (a) start of the archaeological excavation (cleaning work in 2018); (b) Ditch 1 excavation in 2021; and (c) aerial view.

A research project has been developed on the Santa Vitória enclosure, by ERA Arqueologia, SA, aiming to allow for a more adequate characterization of the site, obtaining information about its architecture, and a comparison with the social dynamics and temporalities of a small ditch enclosure [21]. The Santa Vitória archaeological site is in an early stage of the work, and there is still a gap in the studies of the materials found in the excavations previous to the 1990s. Ceramic artefacts, an important expression of humanity since Prehistory, constitute one of the most important remains and always raise many questions, particularly related to provenance, raw materials, production technologies, as well as the social meaning and distribution networks of objects and/or ideas [22].

The study of ceramic artefacts of different typologies (bowls, beads, sherds, etc.), without decoration, collected in the Chalcolithic archaeological site of Santa Vitória (southern Portugal) is of great importance for the understanding of provenance and production technology issues as well as for the discussion of the role of the Santa Vitória site at a regional level. Ceramics typologies provide chronological information, since they vary over time, and could be used as indirect indicators of commensality practices and rituals associated with these communities. Since artefact provenance is intimately linked to the capability to gather far-flung communities, the assessment of the ceramic source (local, short, or long distance) is crucial to understanding the mobility of people and/or goods, or at least the communication with external communities, promoting the establishment of networks for the dissemination of practices, ideas, and the materials themselves. Archaeological and compositional studies offer significant results that are very useful in answering some of these questions.

In this work, analytical approaches were applied for the first time, which include the chemical and mineralogical characterization of ceramic paste, on 25 ceramic fragments collected at the Santa Vitória site, with the main purpose of identifying and quantifying the chemical elements present in the ceramic paste as well as identifying the mineral phases where they may be incorporated. With this compositional characterization of the ceramic materials, the aim is to contribute to a better understanding of their production processes or technologies, provenance, and mobility and to, on a broader scope, better knowledge of the prehistorical communities from the Santa Vitória site.

2. Archaeological and Geological Context

The Santa Vitória enclosure has different filling phases between the two structures found, and based on radiocarbon, they are dated from the second half of the 3rd millennium BC (Ditch 1: 2556–2040 cal BC; Ditch 2: 2460–2200 cal BC) [21]. Inside, no positive structures were found, only some pits. Structured depositions were recorded inside the ditches, together with recuttings filled by elongated stone agglomerations [21]. This site has been classified as a National Public interest.

The site is composed of two sinuous circular ditches with well-standardized lobes in sequence, with no spaces between them (Figure 2). The internal ditch (Ditch 1, defining Enclosure 1) has a plan with six lobes, a maximum diameter of 20 m inside, and an entrance oriented toward the summer solstice [21], with a width of 2 m. The ditch has a perimeter of 69 m, delimiting an area of 283 m². The external ditch (Ditch 2, defining Enclosure 2) develops 10 or 12.5 m (depending on whether we consider the innermost or outermost curvature of the sinuosity) from Ditch 1, with a maximum diameter of around 50 m. Here, ten lobules were identified (probably there are 12), which develop continuously without spaces between them, as in the lobes of Ditch 1. We can only identify one door, which is around 2.50 m wide and is oriented to the north. The ditch has an estimated perimeter of 178 m, which will delimit an area of 2036 m². Regarding other types of structures, nineteen pits were identified through archaeological excavations (Figure 2), eighteen of which were intervened in campaigns carried out in the 20th century. Of these nineteen pits, eight are inside Enclosure 1, nine in the space between Enclosures 1 and 2, and only two are outside Enclosure 2.

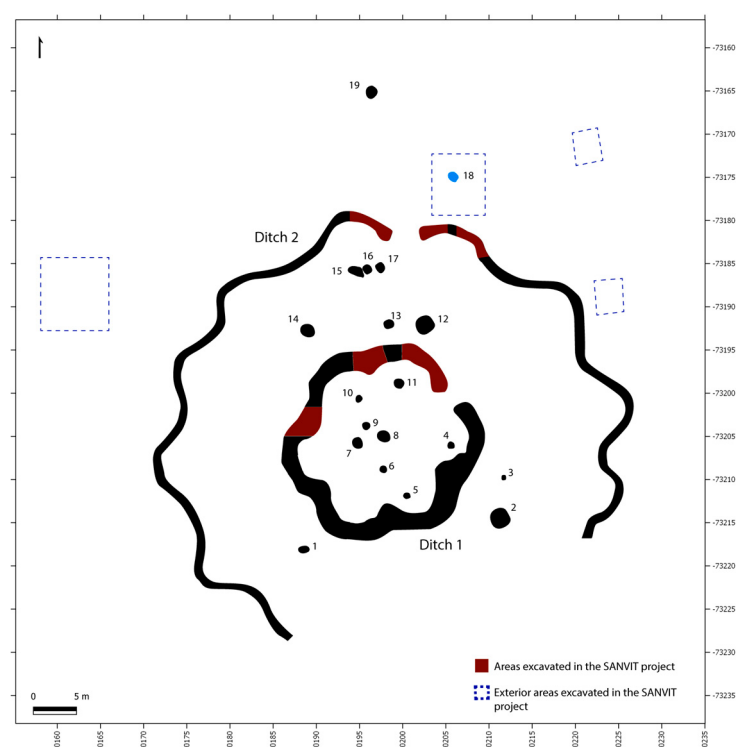


Figure 2. General plan of the Santa Vitória enclosure with ditch locations (and excavated areas), near Campo Maior (Portugal) (adapted from [21]).

The geology of the area is characterized by magmatic rocks and migmatites, with charnockite rocks that constitute an elongated outcrop in the NW/SE direction in the Campo Maior area. This is crossed by several veins and by an incomplete peripheral ring of gabbros, diorites, and hybrid rocks (soft rocks) that extend to Santa Vitória, constituting its geological substrate. Quartziferous diorites and amphiboles can also be identified, with the most common being hornblende with a greenish hue. It is also worth highlighting the existence of clayey soils in the areas surrounding Santa Vitória. The substrate presents high levels of alteration, appearing in vast areas in the form of a calcrete or with very fissured rock, factors that facilitated the excavation of the negative structures of the site [23].

3. Materials and Methods

3.1. Samples Collection

A set of 25 fragments of ceramic artefacts were collected in Ditch 1 (Sector 1) of the Santa Vitória enclosure, in two distinct sections and in different sampling campaigns (Figures 2 and 3). Section 1, located on the west side, appeared not to have undergone any intervention in its filling [21]. The 10 ceramic fragments collected in 2018 in this section were found in the upper part of the ditch in different stratigraphic units (SU 101, 105, 106, 107, and 108) (Figure 3a). The remaining 15 ceramic samples were collected in Section 2, to the north. It should be noted that only the lower part of the fill was excavated in this section, and the ceramics correspond to the 1st phase of the infill and were found in SU 137, 138, 139, and 140 (Figure 3b). The ceramic samples correspond to plates and bowls, and their description (types and sub-types) and shapes are shown in Table 1 and Figure 4.

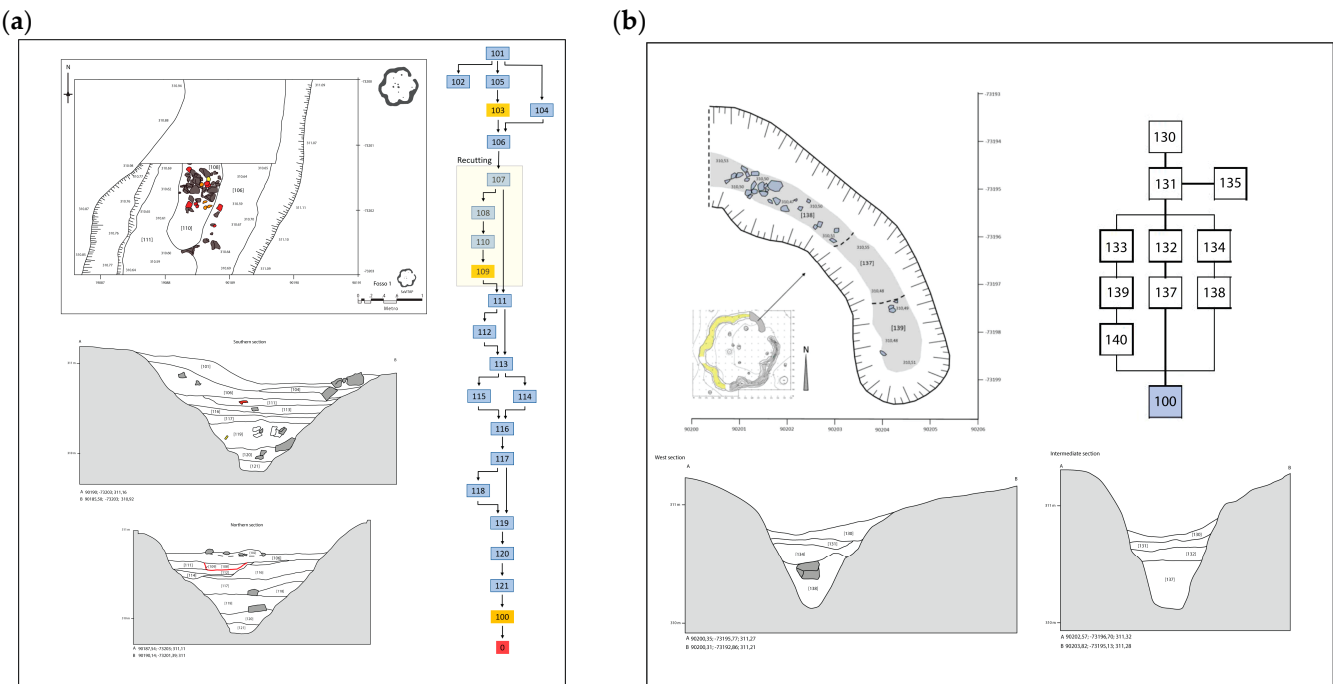


Figure 3. Representation of profiles from Ditch 1 of Santa Vitória archaeological site (Portugal): (a) plan of deposits of Section 1; and (b) plan of deposits of Section 2 (adapted from [21]).

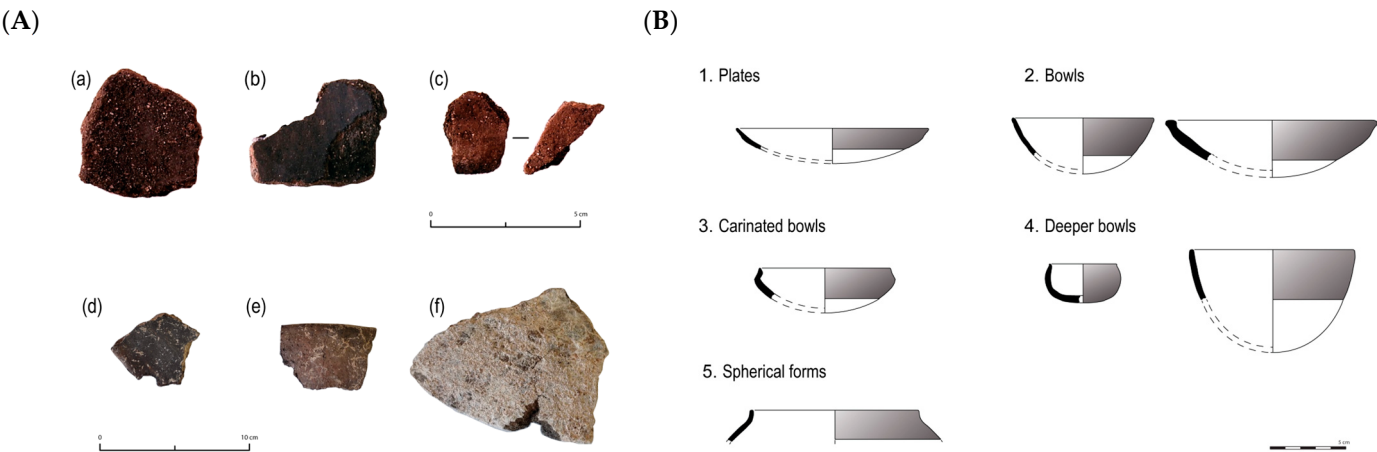


Figure 4. Ceramic artefacts from Santa Vitória Chalcolithic enclosure. (A) photographs of ceramic fragments collected in Ditch 1: Section 1—(a) sample 21 (type 2), (b) sample 38 (type 7), (c) sample 45 (type 2); and Section 2—(d) sample 163 (type 4), (e) sample 183 (type 4), (f) sample 188 (type 1); (B) representation of the ceramic forms: 1—plates; 2—Bowls; 3—Carinated bowls; 4—Deeper bowls; and 5—Spherical forms.

Table 1. Reference and description of ceramic artefact samples collected in Ditch 1 of the Santa Vitória enclosure (Portugal).

Sample Reference	SU	Section	Type	Sub-Type
21	101	1	1—plate	1.1
22	101	1	5—spherical	5.1
29	105	1	2—bowl	2.1
38	106	1	7—bag-type vessel	
45	106	1	2—bowl	2.3

52	107	1	4—deeper bowl	4.2
53	107	1	4—bowl	4.2
65	107	1	3—carinated bowl	3.1
101	108	1	1—plate	1.3
102	108	1	4—deeper bowl	4.1
163	138	2	4—bowl	4.1
172	139	2	1—plate	1.3
174	138	2	1—plate	1.3
182	137	2	4—bowl	4.2
183	137	2	4—bowl	4.1
187	139	2	1—plate	1.1
188	139	2	1—plate	1.1
191	139	2	1—plate	1.1
192	139	2	1—plate	1.1
200	140	2	1—plate	1.3
201	140	2	undet.	
202	140	2	2—bowl	2.4
203	140	2	4—bowl	4.2
204	140	2	4—bowl	4.2
205	140	2	2—bowl	2.1

undet.—undetermined.

3.2. Methods

The compositional characterization of the ceramic artefacts is based on chemical and mineralogical analysis. All samples were subjected to previous laboratory procedures in order to reduce or eliminate any contaminants resulting from processes that may have occurred during use and burial. Therefore, a small fragment is removed from each ceramic sample, and the surface is cleaned using a pure tungsten carbide chisel, in order to eliminate all external contaminants to which the sample was subjected during its burial. Once cleaned, the fragments are placed in glasses with distilled water for 24 h and then boiled for better cleaning. The fragments are then dried in an oven at 80 °C for one week. After drying, the samples are ground in agate mills.

The mineralogical composition was obtained by X-ray diffraction (XRD), using a Bruker D2 Phaser K α Cu radiation equipment ($\lambda = 1.5406 \text{ \AA}$), operating at 30 kV and 10 mA, in non-oriented aggregates of ceramic powders. The powder diffractograms were obtained by scanning an area from 4–70° 2 θ , using a divergence slit of 1°, and a goniometer speed of 1° 2 θ /min. The identification of the mineral phases was carried out [24], and the mineral proportions in the ceramic fragments were estimated by semi-quantification, based on peak areas according to [25,26]. Peak areas of the specific reflections were calculated and weighted by empirically estimated factors according to [27,28]. Given the uncertainties involved in the semi-quantification method, the results obtained should only be taken as rough estimates of mineral percentages.

The chemical analysis of the ceramic paste was carried out by means of Neutron Activation Analysis (NAA), using the K $_0$ method, performed at the Budapest Neutron Center (Hungary). With this method, it was possible to determine the concentration of 24 chemical elements. Around 100–150 mg of powder from the ceramic samples was placed in quartz ampoules and irradiated in the Budapest Research reactor, with a thermal neutron flux of $1.86 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ and an $f \approx 45$. Gamma spectrometry measurements were then performed using ORTEC PopTop 55195-P HPGe, Canberra GC3618 HPGe, and Canberra GC1318 HPGe gamma detectors (ORTEC, Oak Ridge, TN, USA) with an FWHM of 800–900 eV at 59.5 keV and 1750–1800 eV at 1332 keV. More details of the analysis method can be found in previous works [29–31].

The chemical elements' concentrations obtained in this work were normalized to a conservative chemical element (Sc) [32], prior to any statistical approach. This normalization is important to compensate for the influence of natural (geological, granulometric, mineralogical, and ceramic burial time) and anthropogenic (technology of production) processes on the variability of the chemical composition of the samples. Also, Sc is determined with good precision and accuracy by NAA. Multivariate statistical clustering analysis was carried out using the Statistica software (Version 13) [33], namely, the joining tree-clustering (hierarchical) method, using the concentrations of chemical elements as variables. The amalgamation rule employed in the joining tree-clustering was the unweighted pair group average. The Pearson correlation coefficient to evaluate similarities/dissimilarities between the different ceramic samples was used.

4. Results

The macroscopic observation of the ceramic fragments collected in the two sections of Ditch 1 provides evidence of a difference related to the texture of the paste, with the samples from Section 1 having a higher proportion of and larger temper grains than the ones from Section 2. The results obtained for the chemical and mineralogical composition emphasized, in a clearer and more detailed way, the main similarities/dissimilarities found among the different ceramic paste.

4.1. Mineralogical Composition

The mineralogical composition of the ceramic artefacts obtained by XRD and the semi-quantification of the mineral phases are shown in Table 2.

Table 2. Semi-quantitative mineralogical composition (%) of ceramic artefact samples collected in Ditch 1 (Sections 1 and 2) of the Santa Vitória enclosure (Portugal) (traces correspond to $\leq 1\%$).

	Sample	Plagioclase	Quartz	Amphibole	Phyllosilicates	K-Feldspar	Hematite
Section 1	21	37	24	9	25	3	2
	22	33	25	10	24	3	5
	29	34	34	10	18	2	2
	38	11	26	7	53	3	-
	45	26	22	8	40	2	2
	52	34	21	12	23	6	4
	53	38	22	15	17	5	3
	65	38	26	10	20	2	4
	101	43	25	9	16	5	2
	102	34	22	12	27	4	traces
Section 2	163	4	76	-	8	12	-
	172	39	16	21	20	3	traces
	174	30	21	17	27	3	2
	182	33	21	19	22	3	2
	183	49	20	19	8	3	traces
	187	40	18	18	18	5	traces
	188	35	18	18	24	3	2
	191	43	14	20	19	3	traces
	192	20	30	25	20	4	traces
	200	29	19	17	28	5	2
	201	10	48	13	22	6	traces
	202	20	34	14	22	9	traces
	203	17	48	10	15	9	traces
	204	37	19	28	13	2	traces
	205	40	16	21	19	3	traces

In general, the paste of the ceramics collected in Section 1 is essentially composed of plagioclases, associated with quartz, phyllosilicates, and amphiboles in different proportions. Alkali feldspars and hematite also occur, but in low quantities. Two samples (38 and 45) collected in SU106 show a different mineralogical assemblage, with phyllosilicates as the main mineral. No hematite was detected in sample 38. It is also noted that the only sample collected in SU105 (sample 29) has plagioclase and quartz in equal proportions as the main minerals.

Regarding the ceramic fragments from Section 2, the mineralogical association of the paste is identical to that found for the ceramics from Section 1, with plagioclases being dominant in most of the samples. However, there is a higher proportion of amphiboles in samples from Section 2. Quartz is the most abundant mineral in only four samples. Sample 183 differs from the others, showing lower proportions of phyllosilicates and a higher proportion of plagioclase. A completely different mineralogical composition is observed in sample 163, with quartz as the main mineral phase, associated with K-feldspars. Phyllosilicates and plagioclase were also detected in minor proportions. Neither amphibole nor hematite were detected in this sample.

4.2. Chemical Composition

The results of the chemical analysis of the 25 ceramic fragments (10 ceramics from Section 1 and 15 ceramics from Section 2) obtained by NAA are given in Table 3.

All samples show a similar chemical composition for most of the chemical elements studied. A general tendency for lower contents of Na, K, Fe, Rb, and Cs and higher rare earth elements (REE) contents in ceramics from Section 1 is observed. It should be noted that Br was detected in the majority of samples collected in Section 1, while in Section 2, it was only detected in sample 163. Calcium was only detected in eight samples from Section 2.

After Sc normalization, the chemical composition of the ceramic fragments from Section 1 is distinguished by the lowest Fe and Na concentration relative to the fragments from Section 2 (Figure 5). It is also observed that sample 163 (Section 2) has the highest contents of K, As, Rb, Cs, Ba, Hf, Ta, and Th and the lowest contents of Na, Cr, and Co. The ceramic fragment 183 (Section 2) was also identified with the highest Na and the lowest Cr concentrations (Table 3).

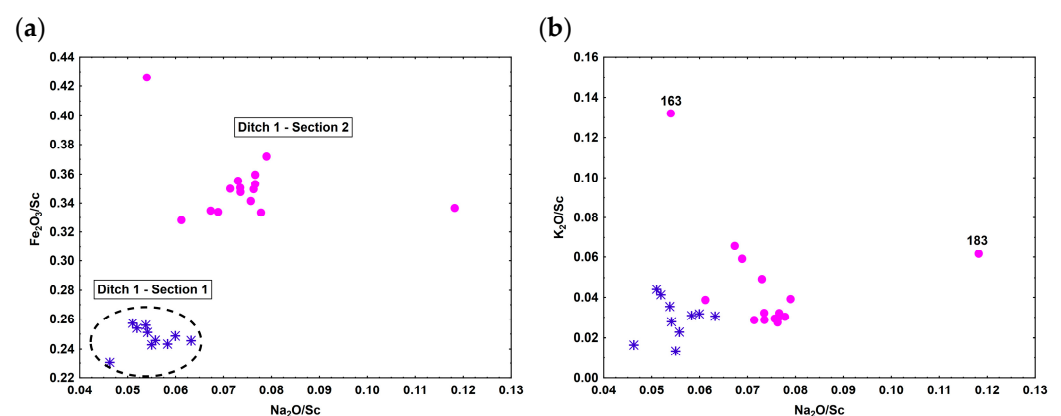


Figure 5. Graphical representation of Fe (a) and K (b) concentration *vs.* Na concentration (normalized to Sc) in ceramic samples from Ditch 1 of the Santa Vitória enclosure (Portugal).

Table 3. Chemical contents of major (%) and trace elements (mg/kg) in ceramic artefact samples collected in Ditch 1 of the Santa Vitória enclosure (Portugal). * normalized to chondrites. $\text{Eu}/\text{Eu}^* = 3 \times \text{Eu}^*/(2 \times \text{Sm}^* + \text{Tb}^*)$. $\text{Ce}/\text{Ce}^* = 3 \times \text{Ce}^*/(2 \times \text{La}^* + \text{Nd}^*)$.

	21	22	29	38	45	52	53	65	101	102	163	172	174	182	183	187	188	191	192	200	201	202	203	204	205
Na ₂ O	1.45	1.37	1.58	1.11	1.32	1.31	1.46	1.37	1.45	1.33	0.631	2.04	1.74	2.12	2.87	1.87	1.87	1.95	1.82	1.73	1.48	1.56	1.59	1.81	1.84
K ₂ O	0.768	0.706	0.763	0.397	0.868	1.13	0.772	0.334	0.592	1.06	1.54	0.735	0.859	0.826	1.50	0.725	0.818	0.761	0.717	0.696	1.27	0.988	1.55	1.23	0.774
Fe ₂ O ₃	6.01	6.37	6.13	5.55	6.27	6.59	6.07	6.04	6.40	6.49	4.98	9.35	8.17	9.10	8.18	8.42	8.90	9.22	8.40	8.50	7.16	8.37	7.88	8.83	8.66
CaO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.66	4.53	4.61	3.96	n.d.	n.d.	4.57	4.48	n.d.	n.d.	2.97	2.30	n.d.	n.d.
Sc	24.2	25.4	24.9	24.1	24.5	25.6	25.0	24.8	26.0	25.5	11.7	26.8	22.0	27.3	24.3	24.7	25.4	26.5	23.8	24.3	21.4	25.5	23.5	24.9	24.1
Cr	456	484	476	652	479	488	465	631	492	485	108	506	412	505	108	452	471	495	448	454	454	834	516	465	451
Co	36.2	43.4	33.6	35.8	38.1	39.6	37.6	38.2	41.7	43.7	14.4	41.2	33.6	35.1	31.2	40.3	42.0	41.2	37.9	35.3	29.8	38.4	32.8	41.2	40.7
Zn	107	103	92.8	64.1	112	99.6	103	104	99.1	98.6	55.4	106	95.9	104	63.4	78.1	100	86.8	83.2	81.7	74.7	82.4	66.5	91.9	216
As	23.5	9.64	12.3	8.43	7.51	6.79	9.20	9.61	8.09	8.39	17.0	6.40	6.76	5.34	8.23	6.93	7.50	5.99	5.65	5.45	6.85	3.73	8.55	6.22	6.32
Br	6.17	5.82	n.d.	n.d.	7.53	4.18	7.57	6.25	3.44	5.85	5.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rb	46.0	45.2	41.7	30.6	54.0	59.3	50.4	26.7	33.3	53.3	98.0	10.0	55.7	47.7	70.5	43.7	37.1	39.6	40.0	37.0	70.4	59.1	76.3	61.6	46.8
Cs	2.83	2.71	2.18	2.55	3.14	3.29	2.25	2.17	2.17	3.07	6.17	3.38	3.33	3.33	2.36	2.65	2.35	2.94	2.71	2.75	3.77	3.12	4.46	3.21	2.61
Ba	n.d.	709	587	854	848	531	952	454	459	441	897	702	705	660	782	659	663	526	574	561	583	468	374	557	744
La	21.1	22.6	19.4	18.9	23.2	22.6	20.2	16.9	18.8	21.7	28.0	20.5	20.4	20.5	23.1	21.3	19.71	20.1	17.7	18.5	16.8	17.0	18.9	22.3	20.3
Ce	47.2	51.2	47.9	48.0	53.2	52.6	46.3	39.1	46.9	54.5	61.3	47.4	46.5	46.7	52.7	49.1	47.2	46.0	41.5	44.7	36.7	39.2	41.3	51.7	47.0
Nd	25.0	24.0	26.4	23.0	27.0	31.0	25.3	19.0	25.9	25.2	29.1	24.2	5.00	23.1	27.8	5.0	5.00	24.6	5.00	5.00	5.0	20.4	22.0	27.2	5.00
Sm	4.56	4.84	4.67	4.88	4.64	4.99	4.61	3.64	4.35	4.84	5.07	3.52	4.35	3.62	5.35	4.49	4.41	4.80	3.96	4.13	3.52	4.21	4.08	4.62	4.21
Eu	1.40	1.44	1.40	1.14	1.42	1.41	1.40	1.11	1.39	1.41	1.09	1.32	1.25	1.35	1.36	1.32	1.33	1.29	1.23	1.22	1.00	1.00	1.02	1.34	1.26
Tb	0.633	0.696	0.681	0.761	0.652	0.730	0.704	0.512	0.659	0.719	0.811	0.699	0.649	0.718	0.841	0.700	0.657	0.708	0.620	0.585	0.518	0.627	0.595	0.693	0.647
Yb	2.32	2.18	2.20	2.50	2.06	2.16	2.15	1.88	2.06	2.10	2.72	2.04	2.09	2.08	2.26	2.44	2.10	1.83	2.02	1.96	1.60	2.01	1.84	2.05	2.24
Lu	0.315	0.325	0.359	0.367	0.050	0.311	0.350	0.286	0.334	0.343	0.444	0.050	0.315	0.050	0.354	0.323	0.267	0.327	0.245	0.253	0.271	0.290	0.298	0.301	0.050
Hf	3.17	2.73	3.42	4.38	2.88	3.49	2.80	2.90	3.28	3.20	7.59	2.77	2.80	3.64	5.07	3.38	3.72	2.97	2.61	3.13	3.99	4.21	4.22	2.96	3.39
Ta	0.554	0.635	0.658	0.553	0.644	0.757	0.591	0.507	0.642	0.694	0.931	0.623	0.636	0.627	0.731	0.583	0.647	0.574	0.597	0.590	0.641	0.618	0.669	0.650	0.650
Th	4.96	4.83	4.40	6.91	4.72	5.04	4.18	4.63	4.04	6.69	9.58	4.31	5.48	6.12	7.13	4.77	4.56	5.44	3.69	4.86	6.32	6.12	5.95	10.6	7.85
Eu/Eu*	1.16	1.12	1.13	0.88	1.15	1.07	1.14	1.15	1.20	1.10	0.81	1.40	1.08	1.38	0.96	1.10	1.13	1.01	1.17	1.11	1.07	0.90	0.95	1.10	1.13
Ce/Ce*	0.83	0.83	0.88	0.89	0.84	0.85	0.84	0.85	0.88	0.89	0.82	0.84	0.84	0.83	0.84	0.84	0.86	0.84	0.85	0.87	0.81	0.84	0.81	0.84	0.84
(La/Yb)	6.30	7.17	6.11	5.25	7.80	7.24	6.49	6.21	6.33	7.15	7.14	6.94	6.77	6.82	7.08	6.05	6.49	7.59	6.07	6.55	7.28	5.86	7.09	7.55	6.27
ΣREE	103	107	103	99.6	112	116	101	82.4	100	111	129	99.7	75.5	98.0	114	79.6	75.7	99.6	67.2	71.3	60.4	84.7	89.9	110.2	75.7

Regarding the REE, the patterns were obtained by normalization relative to chondrites [34–36]. The distribution patterns have a similar trend for all samples, and the following is observed: (i) Section 1—sample 65 has a different behavior, presenting the lowest REE contents ($\Sigma\text{REE} = 60.4$); and (ii) Section 2—sample 163 presents the highest contents of these elements ($\Sigma\text{REE} = 128.5$). Furthermore, a small fractionation between light REE (LREE) and heavy REE (HREE) is found in samples from both sections ($(\text{La}/\text{Yb})^* = 5.25\text{--}7.80$). A slight positive Eu anomaly ($\text{Eu}/\text{Eu}^* = 1.01\text{--}1.39$) is also observed in most of the ceramics, with the exception of samples 38 (Section 1) and 163 (Section 2), where a slight negative Eu anomaly was found ($\text{Eu}/\text{Eu}^* = 0.88$ and 0.81 , respectively).

5. Discussion

The compositional results obtained in this work confirm that the higher concentration of Na_2O in sample 183 is certainly related to the higher proportions of plagioclase detected, and the high contents of K_2O in sample 163 are in accordance with a higher proportion of alkali feldspars relative to plagioclase. A correlation between the higher amounts of Fe observed in the ceramics of Section 2 and the high amounts of amphiboles found in these samples also occurs.

It is important to notice that the presence of plagioclase and amphibole in the ceramic paste points to the idea of local production, since these mineral phases reflect the geological contexts around the archaeological site (gabbros and diorite). The evidence of local production was already observed for most of the Chalcolithic ceramics studied, even for more peculiar ones like bell beakers, from archaeological sites in the Lisbon region and other sites in central and southern Portugal (Penedo do Lexim, Espargueira, Baútas, Fraga da Pena, Porto Torrão, Cardim, Carrascal, Monte do Tosco, and Perdigões) [16,20,37]. However, in some of the archaeological sites previously mentioned, some cases of exogenous provenance were also identified (e.g., Fraga da Pena, Tomb 1 of the Perdigões site) [20]. So, an exogenous provenance cannot be disregarded in the Santa Vitória site.

The presence of phyllosilicates in high amounts in almost all the samples analyzed in this work, and the absence of high-temperature mineral phases, points to a firing temperature of production below $850\text{ }^\circ\text{C}$ [38]. A similar range of temperatures was indicated in previous works on Chalcolithic ceramics from the Lisbon region [37] and in the Perdigões archaeological site [20].

Based on the trace elements' concentrations, although these elements are not discriminating geochemical indicators for the analyzed samples, there seems to be a trend for a higher heterogeneity in the composition of the ceramic paste from Section 2. Considering Br, it was previously reported that, in non-calcareous clays, the Br content decreased rapidly up to $600\text{ }^\circ\text{C}$ and then decreased more gradually up to $800\text{--}900\text{ }^\circ\text{C}$ [39]. In this study, the presence of bromine in most of the ceramic paste from Section 1 could be related to organic matter deposition, associated with ceramics' utilization or post-depositional processes during burial.

Considering the REE, although no significant variations were observed in their concentrations in the Ditch 1 samples (either for Section 1 or Section 2), a small negative Eu anomaly was found in two samples. This Eu anomaly is in accordance with the lower Na_2O contents, suggesting that it is mainly due to plagioclase weathering, where Eu is mostly hosted [20,40,41].

Cluster analysis is a swift and efficient technique for evaluating relationships among a significant number of samples. The joining tree-clustering resulting from the cluster analysis of ceramic samples from Santa Vitória, using the chemical elements normalized to Sc as variables and the average Euclidean distance as a similarity coefficient, emphasizes that sample 163 is chemically distinct from the others, behaving as an "outlier" (Figure 6a). Removing this sample from the data matrix and using the same statistical method of analysis, it is observed that sample 183 also behaves as an "outlier" (Figure 6b), confirming the previous results (different mineralogical assemblages) and some different chemical behavior.

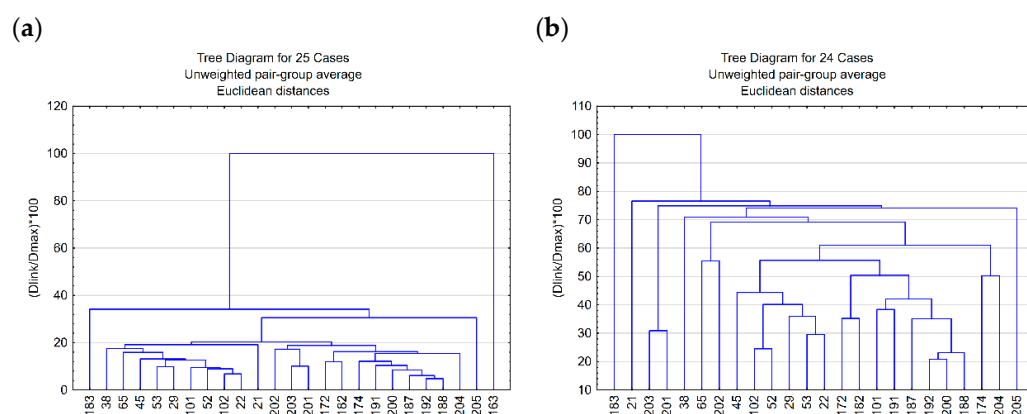


Figure 6. Joining tree-clustering resulting from hierarchical group analysis for ceramic samples from Ditch 1 of the Santa Vitória enclosure using the average Euclidean distance: (a) sample 163 as “outlier”; and (b) sample 183 as “outlier”.

According to the results obtained, these two samples must be disregarded from the matrix results for subsequent classification and grouping of samples, in order to make a better comparison between the remaining ceramics and to better understand their similarities or dissimilarities.

In this way, for the remaining 23 ceramic samples, the group analysis was carried out using Pearson’s correlation coefficient to evaluate correlations between variables. Two main groups were formed: one composed of ceramics from Section 1 and the other composed of ceramics from Section 2 (Figure 7). This result agrees with the observations made above from a textural, mineralogical, and geochemical point of view.

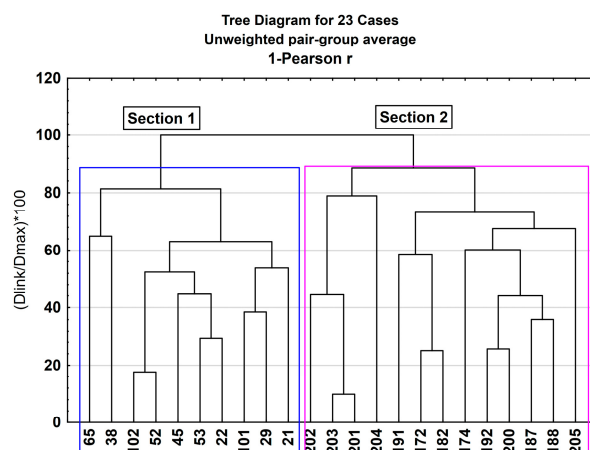


Figure 7. Dendrogram resulting from the hierarchical group analysis of the 23 ceramics from the Santa Vitória enclosure using Pearson’s correlation coefficient (without samples 163 and 183) (blue box—ceramics from Section 1; pink box—ceramics from Section 2).

In this work, a challenge in establishing geochemical patterns to distinguish between different ceramics typologies occurs. The discrepancy in the representation of each ceramic typology analyzed hinders the ability to identify consistent patterns based on geochemical characteristics.

The mineralogy and geochemistry of ceramic paste point to the use of local raw materials resulting from the weathering of basic rocks (such as the dioritic gabbro complex). The distinction observed in the ceramics retrieved from the two sections of Ditch 1, primarily characterized by major elements, may reflect the addition of different proportions and sizes of temper grains (non-plastic) during the ceramics’ production, which points to slight differences in the production technology and/or the presence of

communities with distinct identities and social practices over the time period relevant to the Santa Vitória enclosure.

6. Conclusions

This first study of Chalcolithic ceramics collected at the Santa Vitória archaeological site provides evidence of a distinction between the ceramic fragments collected in the two sections of Ditch 1, particularly the different infill phases, texture, and granulometry of the paste, with those in Section 1, having higher proportions and/or coarser temper grains.

The mineralogical composition of the ceramic fragments from Ditch 1 is similar, with plagioclase as the main mineral, in most of the samples. A higher proportion of amphiboles in the samples from Section 2 is observed and related to the higher contents of Fe. The presence of phyllosilicates in different proportions in all samples, and the absence of high-temperature minerals, indicate that the ceramics' production/use conditions will not have exceeded 850°C. Two ceramics were identified as "outliers", due to a distinct mineralogical and chemical composition, namely, in the K and Na concentrations, and the proportions of alkaline feldspars and plagioclases, respectively.

Despite the inability to use trace elements as geochemical fingerprints for these samples, there seems to be an observed tendency toward higher heterogeneity in the ceramics of Section 2. Also, the presence of bromine in most of the ceramic paste from Section 1 could be associated with ceramics' utilization or post-depositional processes during burial.

Even though potential raw materials were not analyzed in this first study, it can be inferred that local raw materials were used to manufacture these ceramics, based on the compositional study and the geological context of the Santa Vitória region. Nevertheless, addressing this challenge may require a more comprehensive and standardized approach to confirm local productions and identify potential imported materials. A study with a higher number of ceramic samples (from different typologies) and the compositional analysis of local/regional raw materials, establishing reference groups of local production, could contribute to greater knowledge of the impact of the Santa Vitória site on different local and regional Chalcolithic communities.

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