Multi-analytical approach for the study of Neolithic pottery from the Great Dolmen of Zambujeiro (Évora, Portugal) – a preliminary study

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ABSTRACT

The chemical and mineralogical composition of the Zambujeiro Dolmen ceramics was analyzed using stereomicroscopy (SM), X-ray diffraction (XRD), in-situ X-ray fluorescence spectroscopy (XRF) and scanning electron microscopy with X-Ray energy dispersive spectroscopy detection (SEM-EDS). Analysis have shown that quartz is the most abundant mineral in the ceramics, with feldspars, especially alkali feldspars (Na, K), being also present in the majority of the samples. Titanium-iron oxide minerals, like ilmenite, were also detected in some samples. The nature of the clay minerals varies among the samples, but it was possible to identify illite/smectite which can help approximate the firing temperature of the ceramics. Overall, the ceramics' composition is consistent with the geology of the area, confirming the local provenance of the materials used for its production. Analysis of the organic content was done using gas chromatography coupled with mass spectrometry (GC-MS). The ceramic organic content is likely from vegetable origin, which can be inferred from the presence of a high content of unsaturated fatty acids, various steroids of vegetable origin (campesterol, stigmasterol and beta-sitosterol), absence of cholesterol (steroid of animal origin) and a ratio of fatty acid C16:C18 > 1. Biomarkers for the presence of resins from the genus Pinus, the diterpenoid derivatives such as dihydroabietic and isopimaric acids, were identified in some samples. The reason for the use of resinous materials can be attributed to their sealing or gluing properties, but they could also bring a characteristic flavour to the materials stored in the ceramic vessels.

1. Introduction

The Great Dolmen of Zambujeiro (GDZ), built between the 4th and mid-3rd millennium BC, between the late Neolithic and Chalcolithic periods, is located on the right bank of Peramanca riverside, in Valverde, municipality of Évora (Portugal), and is one of the largest megalithic monuments on the Iberian Peninsula. The Zambujeiro Dolmen was identified and excavated between 1964 and 1968 and is classified as a National Monument since 1974. During the 1980s, due to the monument degradation, some conservation works and archaeological research were carried out [1]. The Zambujeiro Dolmen still preserves the grave (burial chamber and hall), much of the tomb hill, and on its periphery two large stelae-menhirs can be found. Collective inhumation was practiced there, accompanied by the deposit of articles of great quality, indicating that they were most likely a group of distinguished individuals. The collection of materials found in GDZ is large and includes several lithics such as arrows, axes and schist plates, as well as a large collection of pottery. Despite the lack of important information that should have been collected during the initial

Figure 1. The Great Dolmen of Zambujeiro.

excavations in this archaeologic site, the architectural monumentality of GDZ and the extent and variety of its spoil are sufficient reasons to try new types of studies that can bring more information about the life of people who were buried in this location (Figure 1).

The study of ceramics in archaeology is mostly concerned with the vessels provenance, manufacture and usage. The recent development of very sensitive and non-destructive analytical techniques can provide information at the microscopic level that can elucidate and complement the archaeological inventory of the spoil. Through the use of different physical and chemical techniques, it is possible to identify the mineralogical and chemical composition of the ceramics, and thus to obtain information on its provenance (eg., to distinguish the local ceramic from imported) and the production technology used (eg., identify kiln temperature) [2-4].

The chemical and mineralogical composition of the paste is partially inherited from the clay raw material. The clay is a secondary earth material and the clay deposit geochemistry depends on its parent rock, and the degree of physical and chemical weathering [5]. Thus, its composition reproduces the composition of the initial rock, modulated by climate that controls the weathering processes. The chemical and mineralogical data, therefore, can be used as fingerprints for provenance studies [6].

The precise identification of the mineralogical composition of the ceramic requires X-Ray Diffraction (XRD) and thermoanalytical experiments [7]. Chemical composition can be obtained by Scanning Electron Microscopy coupled with Energy Dispersion X-ray Spectrometry (SEM-EDS), X-ray fluorescence (XRF) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). The interpretation of data must be careful because mineralogical

and elemental composition of clay from a singular source and the pottery made from it can differ considerably. For instance, because the stability field of the minerals is dependent of the firing temperature, the pottery mineralogical composition might not correspond directly to the clay mineralogy since clay is a low temperature mineral.

Temper is added to a clay material in order to change its properties and improve its workability. Raw materials like sands, shell, micas, crushed rocks or grog can be used as temper. The mineralogical composition of temper can be assessed by stereomicroscopy and polarizing microscopy with data acquisition. The size of each temper unit is adequate to microscope analysis [8].

SEM-EDS analysis allows a further insight on the paste texture and the textural interrelationships of the mineral phases present that are too small to observe by optical microscopy. EDS spectra can provide elemental analysis of the paste and temper components, complemented with in-situ XRF. Although the major element composition stays constant during the firing, the possibility of chemical element inward or outward diffusion during the firing or the buried, inducing also mineralogical and textural transformations, must be considered. The analysis of the inner part of ceramics by XRF can provide information about this aspect.

With XRD it is possible to distinguish the minerals within the clay group [9]. Also, since it is known that the original clay components alter its original structure when subjected to certain intensity and heating rate [10, 11], it is possible to infer the approximate temperature ranges [12].

The preservation of organic molecules inside the porous structure of the ceramic, which can serve as biomarkers, allows the identification of certain food products or others that can provide information on the type of the ceramics use.

The study of vessel usage using the recovered organic compounds from the porous ceramic is based on the archaeological biomarker concept which relies upon matching the chemical structures of the organic materials and their distribution on the archaeological samples, the 'chemical fingerprinting', with the presence of chemicals in organisms known to have been exploited in the past. The archaeological biomarker concept can be applied to any class of biomolecules, such as ancient DNA, proteins, carbohydrates, and fats, even if, in most cases, these are only present in a degraded form [14]. In fact, the application of the archaeological biomarker concept requires not only knowledge of the biochemical compositions of the organic commodities exploited by humans in the past but also information on how these materials can be altered by processing and/or burial. Many of the mechanisms and pathways of molecular structural change resulting from degradation and decay are predictable and, thus, can enhance the interpretative framework [13].

Fats are one of the most stable biomarkers, and both animal and plant fats are composed mainly by triglycerides in which three fatty acids are attached to a glycerol by ester bonds. Triglycerides (TGA) from plant and fish origin are richer in unsaturated fatty acids, while saturated fatty acids are predominant in TGAs from animal origin. During burial, the ester bonds in the triglycerides can be broken by hydrolysis with the release of the fatty acids. TAGs can degrade forming diacylglycerols (DAGs), when only one fatty acid hydrolyzes, or monoacylglycerols (MAGs), when two fatty acids hydrolyze. Only the most well preserved archaeological fats still contain TAGs, while MAGs are most often detected.

Once released from the triglyceride, the short-chain fatty acids are more water-soluble and volatile than the long-chain fatty acids. The released unsaturated fatty acids are also more susceptible for degradation (the double C-C bond is more reactive) when compared to the saturated fatty acids. Usually, archaeological degraded fats have a larger amount of long chain saturated fatty acids like the palmitic and stearic acids, when compared to all other fatty acids. The presence of unsaturated fatty acids can be related to fish or plant origin, being the presence of long chain alcohols and alkanes a further confirmation for the plant origin of the fat residues. Sometimes the unsaturated fatty acids are no longer present, but their degradation products can provide further insight into the nature and the ways fats were processed.

Steroids can further assist in the identification of the fat origin since the presence of cholesterol in the organic residue extracted from ceramics indicate possible animal origin, while plant origin can be attributed when plant sterols, like campesterol or stigmasterol, are identified.

The application of the archaeological biomarker concept requires that the total extract recovered from the ceramic be separated into individual compounds, and that these compounds be identified. This requires that the analytical techniques employed be able to provide molecular-level resolution, achievable by the combination of chromatographic techniques (gas or liquid chromatography, GC or LC) with mass spectrometry detection (GC-MS or LC-MS).

In 1997, Evershed *et al.* [14] showed that the stable carbon isotopic composition of the main fatty acids preserved in the pottery appeared unaffected by diagenetic alteration during burial. Thus, by using on-line gas chromatography–

combustion–isotope ratio mass spectrometry (GC–C–IRMS) and by comparison with modern reference fats, researchers can now distinguish different animal fats (dairy and several ruminant and non-ruminant species) by plotting the $\delta^{13}C$ value for palmitic acid against that for stearic acid [15,16]. Using the available analytical methodologies, researchers have identified several commodities used during the Neolithic period in different parts of the world, including milk [17-23], animal fat [24, 25], fish [26], and resins [27, 28].

2. Methods

Seven ceramic samples recovered from GDZ were selected from the Évora Museum collection, and the study was divided in two parts: chemical and mineralogical composition of the ceramic paste that can be used as a fingerprint for provenance and production studies; and organic residue analysis that can provide data on the containers usage.

2.1. Ceramics' Chemical and Mineralogical Composition

The chemical and mineralogical composition of the ceramics paste was obtained using different analytical techniques that provide complementary information about the samples.

The samples were observed in a binocular microscope Leica M205C using magnifications between x65 and x110. The stereomicroscope (SM) was equipped with a Leica DFC 205 camera allowing image acquisition of resin mounted samples for the subsequent analysis by SEM-EDS.

Using SEM-EDS analysis, a high resolution image can be obtained and it can provide rapid qualitative or quantitative analysis of elemental composition with a sampling depth of 1-2 microns. Charac-

teristics X-rays may also be used to form maps or line profiles, showing the elemental distribution in a sample surface. A Hitachi S3700N SEM coupled to a Bruker Xflash 5010 SDD energy dispersive spectrophotometer was used in variable pressure mode, using a voltage of 20 KeV for spectra acquisition and image acquisition in backscattered electron mode.

In-situ XRF provides information about the elemental composition of the samples. The information obtained can be used complementary with SEM-EDS data. A portable XRF spectrophotometer Bruker Tracer III-IV SD was used for in-situ analysis. Spectra were recorded using a voltage of 40.0 kV and current intensity of 30.0 µA.

XRD can be used to determine the mineral composition of the ceramic paste. XRD patterns were recorded with a Bruker D8 Discover, using Cu K radiation, operating at a 2θ angular range of 3-75°, step size of 0.05° and a step time of 1 sec.

2.2. Organic Residue Analysis

The organic residues analysis was performed by gas chromatography coupled to mass spectrometry (GC-MS). GC-MS is a separation technique that allows the identification of the organic compounds present in the ceramic samples. The sample preparation included the previous cleaning of the ceramic to eliminate handling contamination, sample collection, extraction with a chloroform/methanol mixture, derivatization with N,O-Bis(trimethylsilyl) trifluoroacetamide + 1% trimethylchlorosilane (BSTFA) [28] and further injection in the GC-MS system.

A Shimadzu GC2010 gas chromatographer coupled to a GCMS-QP2010 Plus Mass Spectrometer was used with a Phenomenex Zebron ZB-5HT capillary column (15m length, 0.25mm I.D., 0.10 µm film thickness) to perform the analysis.

3. Results and Discussion

Traditional methods of pottery analysis by archaeologists rely on typological or stylistic criteria/features to provide information relating to the means and place of manufacture of individual vessels, their relative dates, and possible functions. Nowadays, advanced analytical techniques enable more detailed information on provenance and technology of fabrication and possible usages of the pottery materials.

The studies that have been published on the organic content of Neolithic ceramics have been done on materials excavated in settlement sites [17-28], while the Zambujeiro ceramics come from a funerary context.

Three methods were used to assess the composition of the ceramics: XRD for mineralogical composition, XRF for chemical composition, and SEM/EDS for chemical composition and spatial distribution of the elements, through elemental mapping. Optical microscopy was used to evaluate the size, form and orientation of clasts or minerals (Figure 2).

Figure 3 presents the X-Ray diffractograms for two of the studied samples. Quartz is the most common non-clay mineral found in ceramics, and it was found in all samples. Muscovite, a type of mica, was found in some samples. Amphibole, an inossilicate, was also found in some samples. Feldspars, especially alkali feldspars (Na, K) were also found in the majority of the samples.

The nature of the clay minerals varies from sample to sample and it was possible to identify
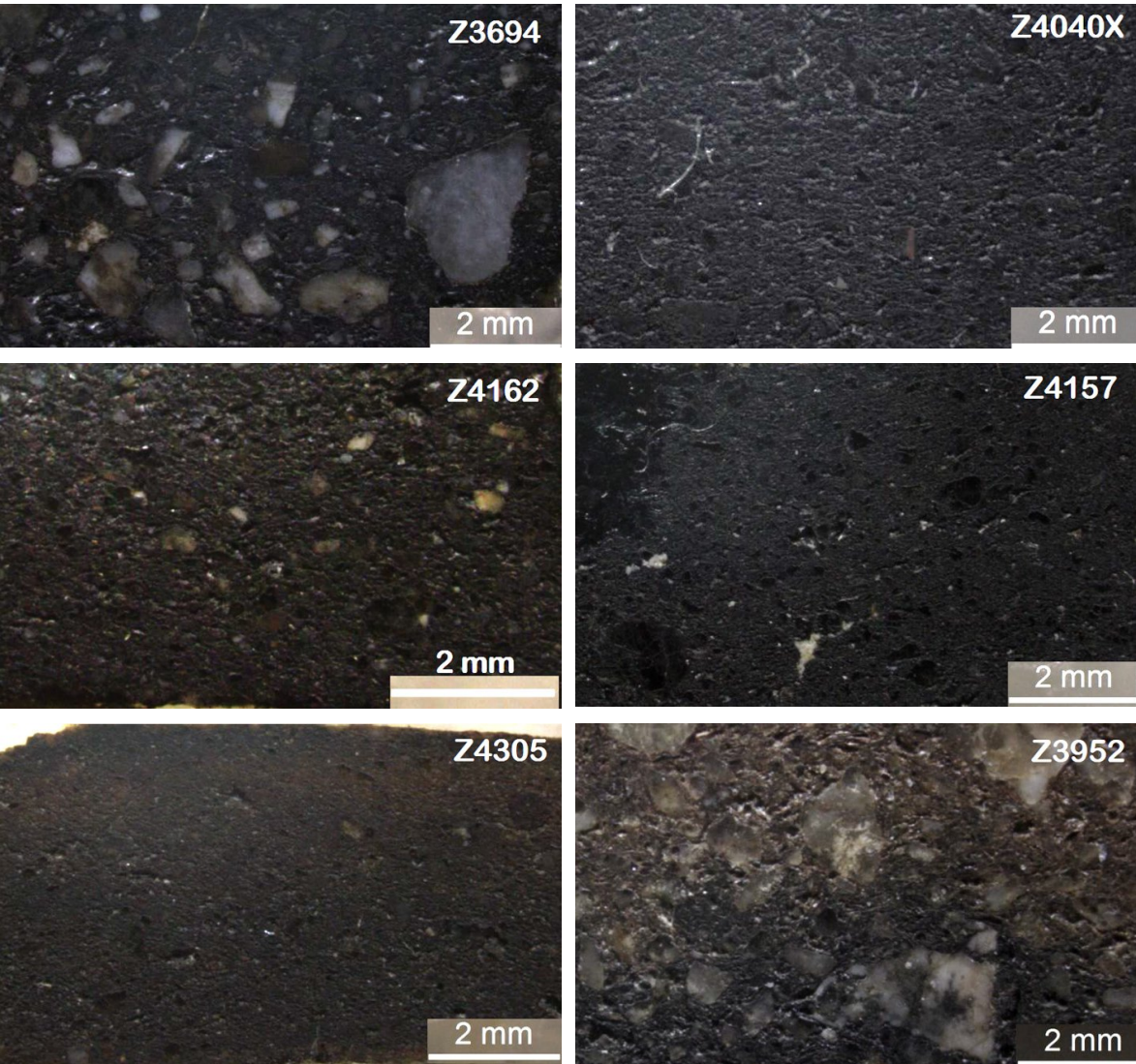
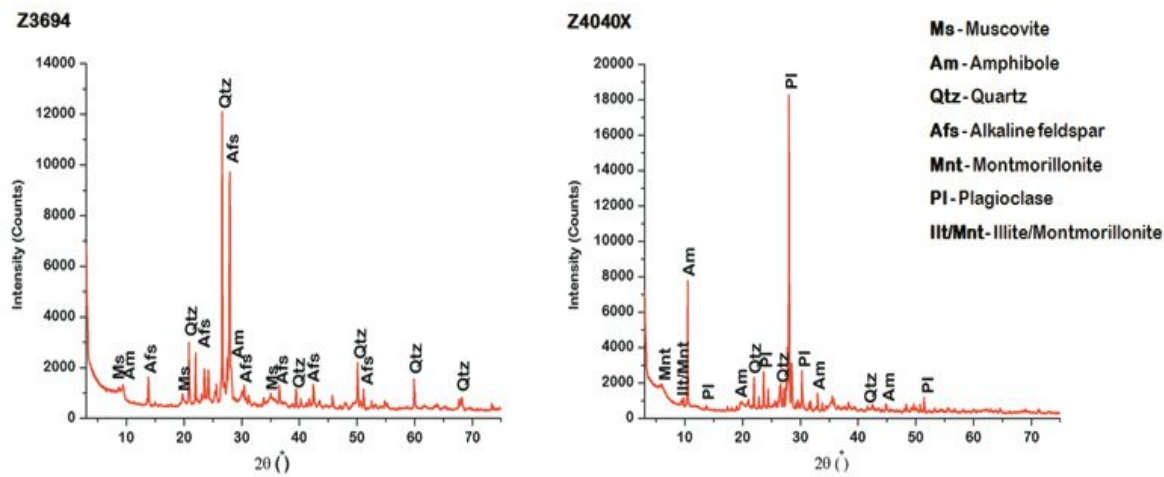Figure 2. Optical microscopy images of the studied samples.

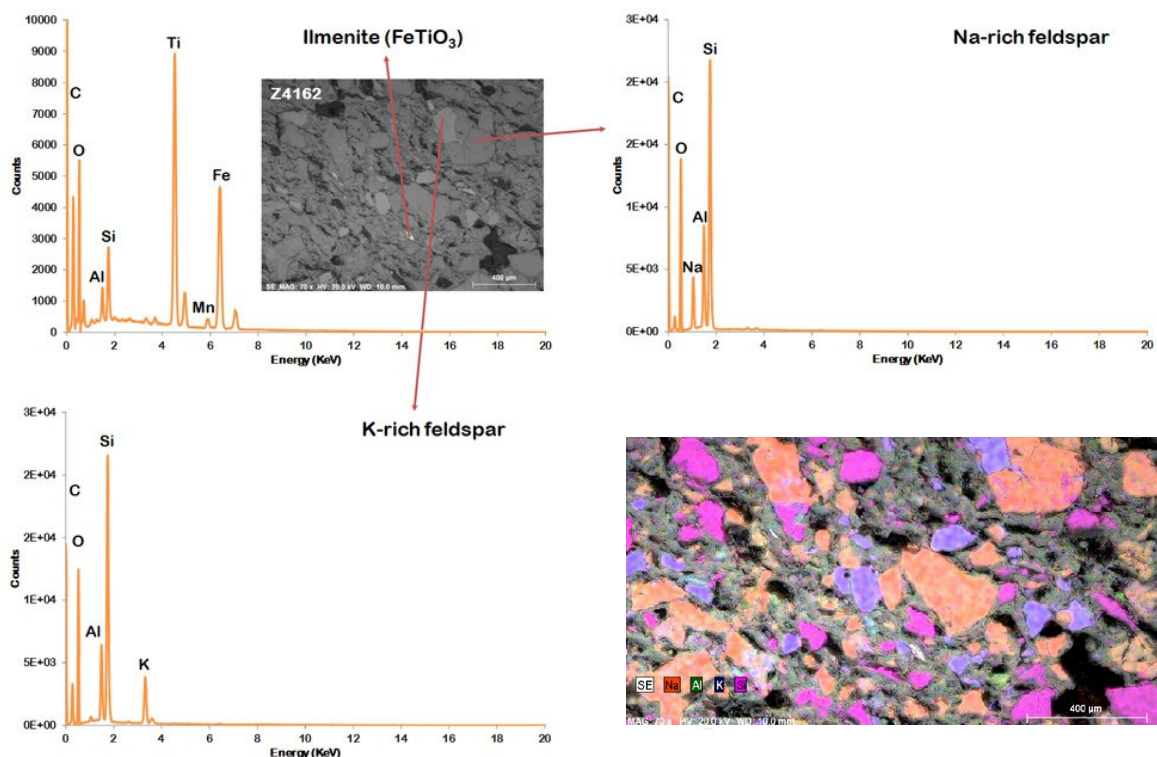Figure 3. X-Ray diffractograms for two of the studied samples..

Figure 4. SEM-EDS results for sample Z4162.

Figure 5. XRF results for sample Z41624.

illite/smectite. Clay minerals crystallize to other minerals, starting at 600 °C, so their presence in ceramics gives an estimate of the temperature used for firing.

The results for SEM-EDS (Figure 4) and XRF (Figure 5) complement the information given by XRD, confirming the presence of alkali feldspars and titanium-iron oxide minerals, like ilmenite. Figures 4 and 5 show examples of the SEM-EDS and XRF results for one of the samples (Z4162).

In Figure 6 two chromatograms are presented that are illustrative for the studied samples and in table I the corresponding peak identification are shown.

Overall, the samples exhibit good preservation as several unsaturated fatty acids (C18:1 and C18:2) and mono-acyl-glycerols (MAGs) were detected
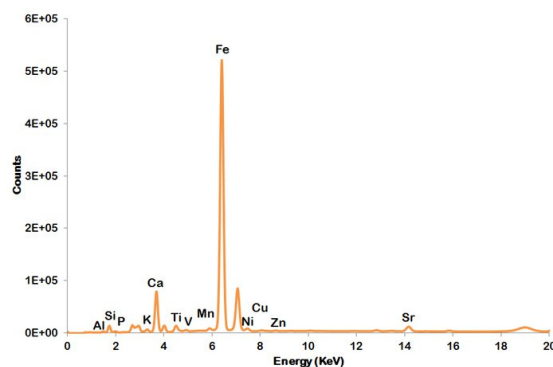
in most samples. The presence of unsaturated fatty acids in the original content of the vessels was further confirmed by the detection of azelaic acid, a degradation product of unsaturated fatty acids. The presence of polyunsaturated fatty acids, and in particular C18:2, is surprising in samples from this period. In archaeological environments, polyunsaturated fatty acids easily undergo oxidation processes localized at the double bonds via radical reactions with the inclusion of oxygen in
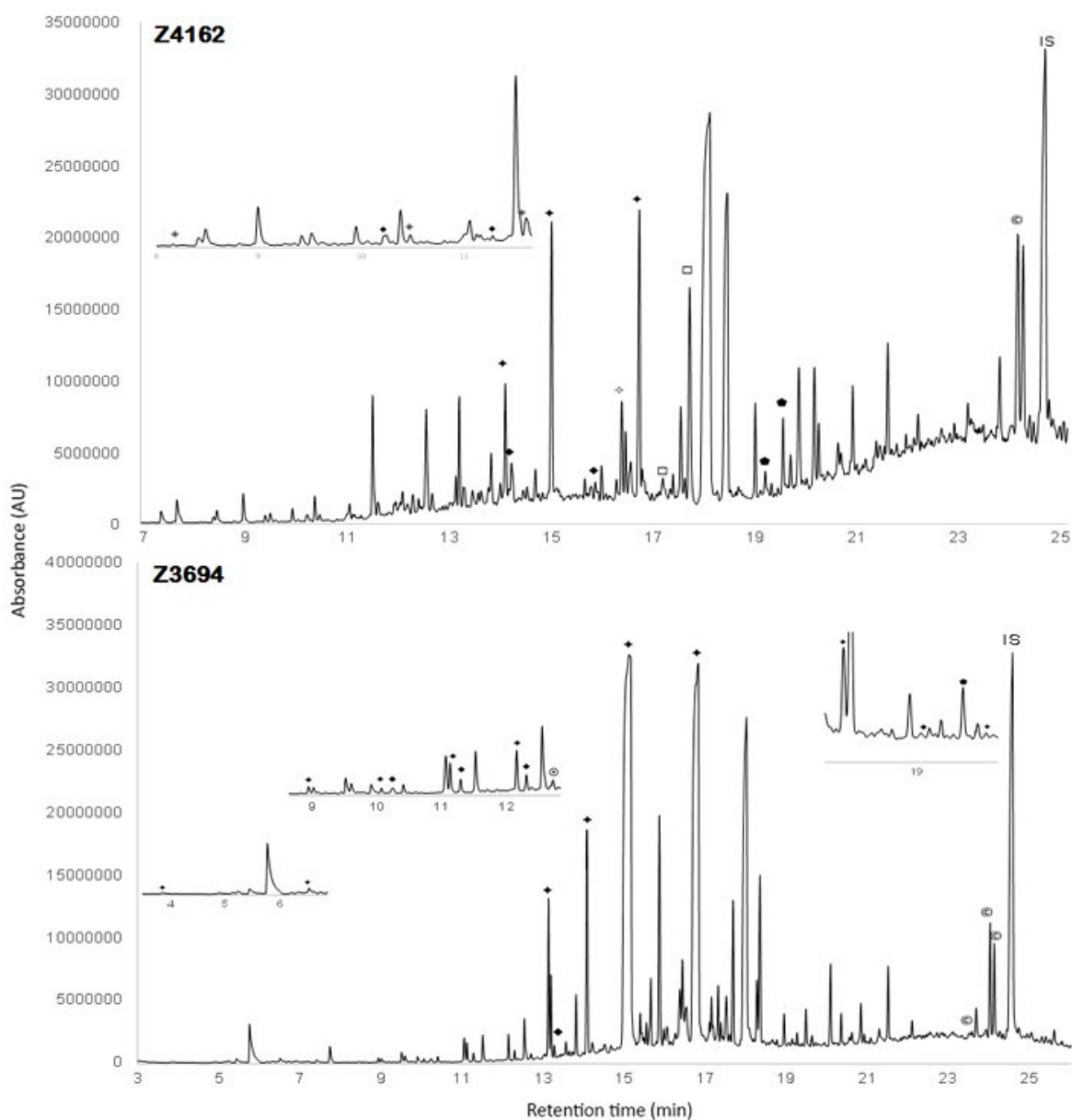
Figure6. GC-MS chromatograms of samples Z4162 and Z3694. Peak identification is shown in table I.

the carbon chain, carbon–carbon bond cleavage, and formation of lower molecular weight species, such as azelaic acid (also detected in the samples) [13].

The chromatographic profiles suggest that the ceramics were previously used for materials of vegetable origin: high content of unsaturated fatty acids, presence of various steroids of vegetable

origin (campesterol, stigmasterol and beta-sitosterol), absence of cholesterol (steroid of animal origin) and a ratio of fatty acid C16:C18 > 1 [13]. Despite the evidence for a vegetable origin of the fats stored in the studied fragments it is not possible to establish its botanical origin.

Another information gathered from the chemical analysis of the lipid extract is the absence of

Table I. Peak identification of the compounds present in the GC-MS chromatograms of samples Z4162 and Z3694.

Peak #	Rt (min.)	Possible identification	MW	Peak #	Rt (min.)	Possible identification	MW
	3,856	Caproic acid, TMS ester (C6:0)	188		14,203	1-Hexadecanol, O-TMS (C16)	314
	6,514	Octadecanoic acid, TMS ester (C8)	216		15,040	Palmitic acid, TMS ester (C16:0)	328
	8,162	Tetradecane (C14)	198		15,609	Margaric acid, TMS ester (C17:0)	342
	8,933	Decanoic acid, TMS ester (C10:0)	244		15,957	1-Octadecanol, O-TMS (C18)	342
	10,057	Undecanoic acid TMS ester (C11:0)	258		16,366	Linoleic acid, TMS ester (C18:2)	352
	10,222	1-Dodecanol, O-TMS (C12)	258		16,727	Stearic acid, TMS ester (C18:0)	356
	10,475	Hexadecane (C16)	226		17,222	Dehydroabietic acid Methyl ester	314
	11,117	Lauric acid, TMS ester (C12)	272		17,669	Dehydroabietic acid TMS	372
	11,278	1-Tridecanol, O-TMS (C13)	272		18,261	Arachidic acid, TMS ester (C20:0)	384
	11,547	Heptadecane (C17)	240		19,071	1-Docosanol, O-TMS (C22)	398
	12,141	Tridecanoic acid, TMS ester (C13)	286		19,258	2-Monopalmitin,TMS ether	474
	12,293	1-Tetradecanol, O-TMS (C14)	286		19,473	1-Monopalmitin TMS ether	474
	12,701	Azelaic acid, di-TMS (C9)	332		19,707	Behenic acid, TMS ester (C22:0)	412
	13,128	Tetradecanoic acid, TMS ester (C14)	300	©	23,476	Campesterol, TMS ether	472
	13,268	1-Pentadecanol, O-TMS (C15)	300	©	24,014	β-sitoesterol, TMS ether	482
	14,066	Pentadecanoic acid, TMS ester (C15:0)	314	©	24,116	Stigmasterol, TMS ether	484

long-chain ketones; these compounds are usually present when animal or vegetable fats are heated above 300 ºC [13], suggesting that the pots were not used for frying, but usage for boiling foodstuffs of vegetable origin cannot be excluded. However, food materials of plant origin (except the oils) have a small content of fats, leaving few residues in the ceramics when just boiled in water [13]. The large fat residue content of some of the analysed samples suggests that the ceramic vessels were likely used for storage of materials based on a vegetable fat.

One of the most interesting results of these analyses was the identification of diterpenoid derivatives such as dihidroabietic and isopimaric acids, in some samples. These compounds are known to be biomarkers for the presence of resins from Pinaceae family, and in particular from genus *Pinus*. So far, the use of pine resins in the Neolithic

period is rare, being more common the detection of resins derived from birch bark (genus Betula) [29]. The reason for the use of resinous materials can be attributed to their sealing or gluing properties. Resins can also impart a characteristic flavour to any material storage inside the vessels. The studied ceramics had no visual signs of the resin and it is not obvious why they were used in the first place. Pinaceae resins were widely used by the Romans to seal their amphorae, used to transport different food products throughout their empire [30].

4. Conclusions

Mineralogical composition of the ceramics, determined by XRD, showed quartz as the most abundant mineral in most samples. Feldspars, especially alkali feldspars (Na, K) were also found in the

majority of the samples. The nature of the clay minerals varies from sample to sample and it was possible to identify illite/smectite. This gives an approximation to the firing temperature of the ceramics, since illite decomposes above 950/1000 ºC, and smectite decomposes at lower temperatures However, this is not enough to determine the firing temperature of the ceramics, and further examination of the sherds using thermal analysis will be performed in a near future. SEM-EDS and XRF results corroborate the information given by XRD, confirming the presence of alkali feldspars and titanium-iron oxide minerals, like ilmenite. Results for the ceramics' composition are consistent with the geology of the area and confirm the local provenance of the materials used for the ceramics' production. The presence of a high content of unsaturated fatty acids, various steroids of vegetable origin (campesterol, stigmasterol and beta-sitosterol), absence of cholesterol (sterol of animal origin) and a ratio of fatty acids C16:C18 > 1, suggests that the fat content on the ceramics is likely from a vegetable source. Biomarkers for the presence of resins from the Pinus genus, dihydroabietic and isopimaric acids, were identified in some samples. Pinus resin could have been used for their sealing or adhesive properties, but they would also bring a characteristic flavour to the materials stored in the ceramic vessels.

5. References

[1] J. Soares, C.T. Silva, *Anta Grande do Zambujeiro – arquitectura e poder. Intervenção arqueológica do MAEDS, 1985-87*, MUSA, museus, arqueologia & outros patrimónios 3, FIDS/MAEDS, Setúbal, 2010, pp. 83-129

[2] S. Kramar, J. Lux, A. Mladenovi , H. Pristacz, M. Mirti , M. Sagadin, N. Rogan-Šmuc, *Mineralogical and geochemical characteristics of Roman pottery from an archaeological site near Mošnje (Slovenia)*, Applied Clay Science 57, 2012, pp. 39–48, doi: 10.1016/j.clay.2011.12.008

[3] L. Maritan, C. Mazzoli, L. Nodari, U. Russo, *Second Iron Age grey pottery from Este (north-eastern Italy): study of provenance and technology*, Applied Clay Science 29(1), 2005, pp. 31–44, doi: 10.1016/j.clay.2004.09.003

[4] R. Ravisankar, S. Kiruba, C. Shamira, A. Naseerutheen, P.D. Balaji, M. Seran, *Spectroscopic techniques applied to the characterization of recently excavated ancient potteries from Thiruverkadu Tamilnadu, India*, Microchemical Journal 99 (2), 2011, pp. 370–375, doi: 10.1016/j.microc.2011. 06.012

[5] A. M. Pollard, C. Heron, *Archaeological Chemistry*, Royal Society of Chemistry, Cambridge, 1987

[6] P. Mirti, L. Appolonia, A. Casoli, *Technological Features of Roman Terra Sigillata from Gallic and Italian Centres of Production*, Journal of Archaeological Science 26 (12), 1999, pp. 1427-1435, doi: 10.1006/jasc.1999.0435

[7] A. Moropoulou, A. Bakolas, K. Bisbikou, *Thermal analysis as a method of characterizing ancient ceramic technologies*, Thermochimica acta 269, 1995, pp. 743-753, doi: 10.1016/0040-6031(95)02570-7

[8] C. Belfiore, P.M. Day, A. Hein, V. Kilikoglou, V. La Rosa, P. Mazzoleni and A. Pezzino, *Petrographic and Chemical Characterisation of pottery production of the Late Minoan I Kiln at Haghia Triada, Crete*, Archaeometry 49(4), 2006, pp. 621–653, doi: 10.1111/j.1475-4754.2007.00324.x

[9] C.K. Wentworth, *A scale of grade and class terms for clastic sediments*, Journal Geology 30(5), 1922, pp. 377-392, doi: 10.1086/622910

[10] P.M. Rice, *Pottery analysis. A sourcebook*, University of Chicago Press, Chicago and London, 1987

[11] J.M. Vazquez Varela, *Aproximación etnoarqueológica a la temperatura de cocción de la cerâmica*, Gallaecia 22, 2003, pp. 407-411

[12] V. Schuster, *Diferentes tecnicas para el mismo problema: el estudio tecnologico de un conjunto ceramico fragmentário (Costa Nordeste Del Chubut, Patagonia, Argentina)*, Comechingonia Virtual 4(1), 2010, pp. 1-26

[13] R. P. Evershed, *Organic residue analysis in archaeology: the archaeological biomarker revolution*, Archaeometry 50(6), 2008, pp. 895–924, doi: 10.1111/j.1475-4754.2008.00446.x

[14] R.P. Evershed, H. R. Mottram, S. N. Dudd, S. Charters, A.W. Stott, G. J. Lawrence, *New Criteria for the Identification of Animal Fats Preserved in Archaeological Pottery*, Naturwissenschaften 84, 1997, pp. 402–406

[15] H.R. Mottram, S.N. Dudd, G.J. Lawrence, A.W. Stott, R.P. Evershed, *New chromatographic, mass spectrometric and stable isotope approaches to the classification of degraded animal fats preserved in archaeological pottery*, Journal of Chromatography A 833(2), 1999, pp. 209–221, doi: 10.1016/S0021-9673(98)01041-3

[16] R.P. Evershed, S.N. Dudd, M.S. Copley, R. Berstan, A.W. Stott, H. Mottram, S.A. Buckley, Z. Crossman, *Chemistry of Archaeological Animal Fats*, Accounts of Chemical Research 35(8), 2002, pp. 660-668, doi: 10.1021/ar000200f

[17] M.S. Copleya, R. Berstana, A.J. Mukherjeea, S.N. Dudda, V. Strakerb, S. Paynec, R.P. Evershed, *Dairying in antiquity. III. Evidence from absorbed lipid residues dating to the British Neolithic*, Journal of Archaeological Science 32, 2005, pp. 523–546, doi: 10.1016/j.jas.2004.08.006

[18] J. Dunne, R. P. Evershed, M. Salque, L. Cramp, S. Bruni, K. Ryan, S. Biagetti, S. di Lernia, *First dairying in green Saharan Africa in the fifth millennium BC*, Nature 486, 2012, doi:10.1038/nature11186

[19] M. S. Copley, R. Berstan, S. N. Dudd, G. Docherty, A. J. Mukherjee, V. Straker, S. Payne, R.P. Evershed, *Direct chemical evidence for widespread dairying in prehistoric Britain*, PNAS 100(4), 2003, pp. 1524–1529, doi: 10.1073/pnas.0335955100

[20] J. E. Spangenberga, I. Matuschikb, S. Jacometc, J. Schiblerc, *Direct evidence for the existence of dairying farms in prehistoric Central Europe (4th millennium BC)*, Isotopes in Environmental and Health Studies 44(2), 2008, pp. 189–200, doi: 10.1080/10256010802066349

[21] J. E. Spangenberg, S. Jacomet, J. Schibler, *Chemical analyses of organic residues in archaeological pottery from Arbon Bleiche 3, Switzerland evidence for dairying in the late Neolithic*, Journal of Archaeological Science 33, 2006, pp. 1-13, doi: 10.1016/j.jas.2005.05.013

[22] S. Isaksson, F. Hallgren, *Lipid residue analyses of Early Neolithic funnel-beaker pottery from Skogsmossen, eastern Central Sweden, and the earliest evidence of dairying in Sweden*, Journal of Archaeological Science 39, 2012, pp. 3600-3609, doi: 10.1016/j.jas.2012.06.018

[23] H.A. Hoekman-Sites, J.I. Giblin, *Prehistoric animal use on the Great Hungarian Plain: A synthesis of isotope and residue analyses from the Neolithic and Copper Age*, Journal of Anthropological Archaeology 31, 2012, pp.515–527, doi: 10.1016/j.jaa.2012.05.002

[24] M.W. Gregg, E.B. Banning, K. Gibbs, G.F. Slater, *Subsistence practices and pottery use in Neolithic Jordan: molecular and isotopic evidence*, Journal of Archaeological Science 36, 2009, pp. 937–946, doi: 10.1016/j.jas.2008.09.009

[25] A.J. Mukherjee, A.M. Gibson, R.P. Evershed, *Trends in pig product processing at British Neolithic Grooved Ware sites traced through organic residues in potsherds*, Journal of Archaeological Science 35, 2008, pp. 2059-2073, doi: 10.1016/j.jas.2008.01.010

[26] O.E. Craiga, V.J. Steeleb, A. Fischerb, S. Hartzd, S.H. Andersene, P. Donohoef, A. Glykoug, H. Saula, D.M. Jonesf, E. Kochh, C.P. Heronb, *Ancient lipids reveal continuity in culinary practices across the transition to agriculture in Northern Europe*, PNAS 108(44), 2011, pp.17910-17915, doi: 10.1073/pnas.1107202108

[27] A. Lucquin, R. J. March, S. Cassen, *Analysis of adhering organic residues of two "coupes-a-socles" from the Neolithic funerary site "La Hougue Bie" in Jersey: evidences of birch bark tar utilization*, Journal of Archaeological Science 34, 2007, pp. 704-710, doi: 10.1016/j.jas.2006.07.006

[28] S. Mitkidou, E. Dimitrakoudi, D. Urem-Kotsou, D. Papadopoulou, K. Kotsakis, J.A. Stratis, I. Stephanidou-Stephanatou, *Organic residue analysis of Neolithic pottery from North Greece*, Microchimica Acta 160, 2008, pp. 493–498, doi: 10.1007/s00604-007-0811-2

[29] M. Regert, *Investigating the history of prehistoric glues by gas chromatography–mass spectrometry*, Journal of Separation Science 27, 2004, pp. 244 – 254, doi: 10.1002/jssc.200301608

[30] F.C. Izzo, E. Zendri, A. Bernardi, E. Balliana, M. Sgobbi, *The study of pitch via gas chromatography–mass spectrometry and Fourier-transformed infrared spectroscopy: the case of the Roman amphoras from Monte Poro, Calabria (Italy)*, Journal of Archaeological Science 40(1), pp. 595–600, doi: 10.1016/j.jas.2012.06.017

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