



# MATERIAL CHAINS IN LATE PREHISTORIC EUROPE AND THE MEDITERRANEAN

## TIME, SPACE AND TECHNOLOGIES OF PRODUCTION

textes réunis et édités par  
**Alexis Gorgues,**  
**Katharina Rebay-Salisbury,**  
**Roderick B. Salisbury**

**MATERIAL CHAINS IN LATE PREHISTORIC  
EUROPE AND THE MEDITERRANEAN**



- AUSONIUS ÉDITIONS -

— Mémoires 48 —

**MATERIAL CHAINS IN LATE PREHISTORIC  
EUROPE AND THE MEDITERRANEAN**  
Time, Space and Technologies of Production

*Edited by*

*Alexis Gorgues, Katharina Rebay-Salisbury, Roderick B. Salisbury*

*Published with the support of the Région Nouvelle Aquitaine*

— Bordeaux 2017 —



Notice catalographique

Gorgues, A., Rebay-Salisbury, K. and Salisbury, B. R., eds (2017): *Material Chains in Late Prehistoric Europe and the Mediterranean: Time, Space and Technologies of Production*, Ausonius Mémoires 48, Bordeaux.

Keywords :

Archeology, Protohistory, craftsmanship, techniques, Bronze Age, Iron Age, Mediterranean, Europe

AUSONIUS

Maison de l'Archéologie

Université de Bordeaux - Montaigne

F - 33607 Pessac Cedex

<http://ausoniuseditions.u-bordeaux-montaigne.fr>



Directeur des Publications : Olivier DEVILLERS

Secrétaire des Publications : Nathalie PEXOTO

Couverture : Stéphanie VINCENT PÉREZ

© AUSONIUS 2017

ISSN : 1283-2995

ISBN : 978-2-35613-194-2

Achévé d'imprimer sur les presses  
de l'imprimerie Gráficas calima, S.A.  
Avda Candina, s/n  
E - 39011 Santander - Cantabria- Espagne

15 septembre 2017

# Table of Contents

Authors.....	7
Alexis Gorgues, Katharina Rebay-Salisbury, Roderick B. Salisbury, <i>Material chains in late prehistoric Europe and the Mediterranean: time, space, and technologies of production. An Introduction</i> .....	9
Roderick B. Salisbury, Katharina Rebay-Salisbury, <i>Processes of theory: from production sequences and process to chaînes opératoires and object biographies</i> .....	15
Estelle Gauthier, Pierre Pétrequin and Maréva Gabillot in collaboration with Olivier Weller, Jessica Giraud and Robin Brigand, <i>A method of data structuring for the study of diffusion processes of raw materials and manufactured objects</i> .....	31
Roderick B. Salisbury, <i>Links in the chain: evidence for crafting and activity areas in late prehistoric cultural landscapes</i> .....	47
Alexis Gorgues, with collaboration of Florent Comte, <i>Wherever I lay my tools. Workspace morphology and temporality in the Northern Iberian world (sixth-first centuries BC)</i> .....	67
Ann Brysbaert, <i>Where are they? Buried, wasted, half-done and left-over: in search of creative artisans among their ‘rubbish’ in Late Bronze Age Tiryns, Greece</i> .....	97
Ziad El Morr, <i>Metal and society in Middle Bronze Age Byblos</i> .....	121
Tomaso Di Fraia, <i>Tablet weaving in prehistory and proto-history: the contribution of the Italian record</i> .....	139
Nicolas Frèrebeau, Charlotte Sacilotto, <i>On some Iberian unfired pottery sherds from the Late Iron Age (second century BC)</i> .....	157
Juan Jesús Padilla Fernández, <i>Romanization is coming! The appearance of the potter working class in Iberia at the end of the Second Iron Age</i> .....	171
Alexandre Bertaud, <i>Iron Age weapons in western Europe: from the biography of a weapon to the warrior’s interactions during the last centuries BC</i> .....	183
Index.....	195



# On some Iberian unfired pottery sherds from the Late Iron Age (second century BC)

*Nicolas Frèrebeau, Charlotte Sacilotto*

## CERAMIC MATERIAL PRODUCTION: TRANSFORMATIONS AND LOSS OF INFORMATION

Ceramic firing, by giving artefacts both their mechanical properties and part of the final aesthetic features, appears to be a critical stage in pottery production. Several stages of production can be restored from finished products or structures found in archaeological context, but firing can alter or delete clues about previous steps. The firing of pottery into ceramic material brings about a transformation in the solid state of a clayey material, so that the transformation process tends toward thermodynamic equilibrium, but never achieves it<sup>2</sup>. While some of these changes are reversible (dehydration or some phase transitions:  $\alpha$ -quartz/ $\beta$ -quartz for example), others involve the disappearance of certain minerals in proportion to heat inputs during firing.

Thus, the mineralogical composition of the final product differs from that of the initial raw material<sup>3</sup>. Clay minerals are the first to disappear from the first moments of heating: the loss of structural water (deshydroxylation – starting from 500 °C for some phyllosilicates<sup>4</sup>) leads to the destruction of crystal lattices and thus to the formation of amorphous compounds, gradually consumed by further reactions. Therefore, mineralogical analysis of ceramic materials, except for special cases, does not allow the identification of the clayey materials used. This loss partially compromises any reconstruction related to the selection and preparation of raw materials. This first step, however, is a source of information on ancient economic systems, providing information on access to natural resources and how members of a society had an impact on nature, both in their choices of raw material and in the techniques used.

Indeed, clay minerals condition for a large part the mechanical properties of the raw material. Their particular structure of superimposed sheets, between which molecules (water, organic molecules) and different chemical elements (cations) can be intercalated, ensures the plasticity of clays. The choice of the temper can also have a significant influence on the behaviour of artefacts during firing and throughout their use (mechanical and thermal resistance, etc.).

The significance of the unfired sherds of the Mas de Moreno lies in the unusual and privileged access they provide to these early stages of ceramic production, in an Iberian workshop of the Late Iron Age.

## THE POTTERY WORKSHOP OF THE MAS DE MORENO

### Location and environmental data

The pottery workshop of the Mas de Moreno was discovered at the beginning of the 1980s and since 2005 excavations have been undertaken by a Franco-Spanish team<sup>5</sup>. The workshop is located in the north of the province of Teruel, in the

1. This investigation received the support of the French government, through the program ANR-10-LABX-52 of the Agence Nationale de la Recherche.
2. Grapes 2006, 19; Heimann 1989, 123; Velde & Druc 1999.
3. On reactions during ceramic firing, see Duminuco *et al.* 1998, Riccardi *et al.* 1999, Rathossi & Pontikes 2010a, 2010b.
4. Yeskis *et al.* 1985.
5. Gorgues & Benavente Serrano 2007, 2012.



autonomous community of Aragón, near the city of Foz-Calanda. The Mas de Moreno belongs to the Bajo Aragón sierra, a northern expansion of the Iberian Cordillera, and overlooks the Ebro valley on the north side. The Ebro valley is a foreland basin to the south Pyrenees formed by the Cenozoic orogeny<sup>6</sup>. Prior to the Eocene, marine carbonates deposits accumulated, while the basin was below the sea level. During Tertiary times, the basin underwent changes of the drainage type from exorheic<sup>7</sup> as the sea level decreased (Eocene-early Oligocene) to endorheic<sup>8</sup> due to tectonic topography generation (late Oligocene-Miocene)<sup>9</sup>. Finally, the Ebro River cut through the barrier and, from the late Miocene, flows into the Mediterranean<sup>10</sup>. Today, due to this particular geology and semi-arid climate, the whole region consists of calcisols<sup>11</sup>.

The excavated area is located at the bottom of a dale and is flanked on the north by a series of small hills and on the south by the Guadalopillo, a secondary tributary of the Ebro River. The dale infilling is composed of Neogene (Oligocene) deposits (alternating clays, marls and limestone conglomerates) and is surrounded by Mesozoic ranges (oolitic limestones)<sup>12</sup>.

### Pottery production and the unfired pottery sherds

The earliest significant evidence for pottery production at the Mas de Moreno dates around 225/200 BC. Activity ends c. 40/30 BC. The workshop produces only Iberian type artefacts until 50/40 BC, when Roman tradition artefacts and Latin epigraphy appear<sup>13</sup>. Except for some imports or imitations of Italic elements, the ceramic material of the workshop consists only of products known as *Iberian painted wares*<sup>14</sup>. These are wheel thrown pottery, with a pink (7.5YR 7.5/3.5) uniform colour and a dusky/dark red (10R 3/5) painted decor<sup>15</sup>. These ceramic products have compact pastes, with no temper visible to the naked eye.



**Fig. 1.** unfired sherds found in the fill of the firing chamber of Kiln 5 of the Mas de Moreno (courtesy of A. Gorgues). The base of a pot is visible on the left.

Since the first discoveries in 2010, more than 700 fragments of unfired pots have been found (about 5 kg; table 1). In the field, these items are easily identified, due to the colour contrast with the sediment (fig. 1). Most of these unfired sherds consist of body fragments that could be confused with natural clay. However, several fragments of rim, handle and base were identified together with two painted sherds (fig. 2). Few forms are identifiable; they are similar to those of the Iberian productions from the 1<sup>st</sup> century BC in Aragón: small (painted) cups, *kalathos*, storage jars and loom weights were found (table 1). The unfired sherds were found in the infill of the stoking pit (stratigraphic unit 15205) and of the firing chamber (unit 15312) of Kiln 5, which was operative at the end of the wholly Iberian phase of the workshop (c. 75/50 BC)<sup>16</sup>. From a stylistic point of view, the likeness of the unfired sherds to the fired ones is obvious. However, these results were obtained on pieces in low quantity and with limited stratigraphic extent.

6. Gibbons & Moreno 2002, 1.
7. Lake or basin that drains through one or more outlets.
8. Lake or basin that has no outlet.
9. Casas-Sainz & de Vicente 2009, 217.
10. Garcia-Castellanos *et al.* 2003, 16.
11. For the soil map, see Jones *et al.* 2005, 65.
12. IGME 1977.
13. Gorgues & Benavente Serrano 2012, 275-279. On the epigraphy in the Mas de Moreno, see Gorgues 2009.
14. Coll Conesa 2000, 192; Mata Parreño & Bonet Rosado 1992, 119; Maestro Zaldívar 1989, 19.
15. Munsell Color 2009.
16. Gorgues & Benavente Serrano 2012, 279.

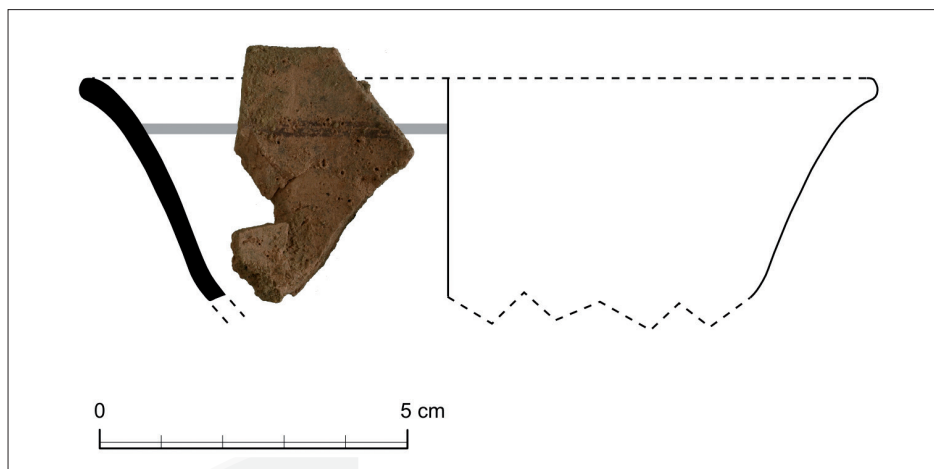


Fig. 2. a small unfired painted cup (BDX14722). Not to scale.

Éléments sous droit d'auteur - © Ausonius Éditions septembre 2017

Stratigraphic unit	Ceramic category*	Parts of pot	Mass (g)	NFR	MNI
15205	COM-IB	rim	1	1	1
		body	1518	276	
		handle	8	1	
	IB-PEINTE	rim	4	1	1
		body	3	2	
	IB-FINE	rim	2	1	1
		body	43	20	
		base	16	2	
	storage	rim	33	1	1
		body	447	38	
base		41	1		
handle		29	1		
loom weights	-	1021	14	-	
15312	COM-IB	rim	33	6	6
		body	1200	382	
		base	11	3	
		handle	32	4	
	IB-FINE	body	1	1	-
	storage	body	188	12	-
	loom weights	-	199	5	-
<b>Total</b>			<b>4830</b>	<b>772</b>	<b>10</b>

Table 1. the unfired sherds of the Mas de Moreno. COM-IB and IB-PEINTE categories refer to Adroher *et al.* (1993) classification. NFR: number of fragments; MNI: minimum number of individuals.

A first series of questions focuses on the motive for the rejection of these unfired objects, since such material would have been easily recycled in the workshop. Two points must be considered:

The deposition of these elements is a limited event in time because the conservation of certain forms implies a rapid burial.

The discovery of sherds in the stoking area indicates that they cannot correspond to the last kiln load left *in situ*. On the contrary, the position of the artefacts within the kiln and the heterogeneity of archaeological remains associated with the unfired sherds suggest that the kiln was filled with waste from the workshop after its abandonment. It is unlikely that these unfired fragments fell from the firing chamber since the excavations did not reveal any hollow space within the kiln.

During ceramic production, painting is generally applied soon after the forming stage, at the beginning of drying, to ensure adhesion. Moreover, the shaping of edges and bases as well as the addition of handles usually occurs after an initial phase of drying<sup>17</sup>. Since these elements were found within the unfired sherds, the selection process was probably achieved during the last stages of drying and before a possible firing. The following assumptions concerning the reasons for this rejection may be dismissed:

The rejection is not related to a particular category of object: the main forms identified on the workshop are present among the unfired sherds.

It is not related to paint defects, especially since pots with imperfect decorations were found among the finished ceramics.

Production defects were studied among the ceramics and led to the identification of strong qualitative requirements on the workshop<sup>18</sup>. The drying process is a critical step, as faults could appear, mostly cracks due to paste contraction. Calcareous and ferruginous inclusions were noticed on the slice of some ceramic sherds and fragments from stratigraphic unit (SU) 15312. These imperfections can be a factor in the formation of flaws before and during the firing process. It seems reasonable to assume that these unfired fragments belonged to the same fire load and were rejected due to defects of this kind. This last assumption was tested during this study. This point leads to the idea of a selection before the firing process, based on specific standards.

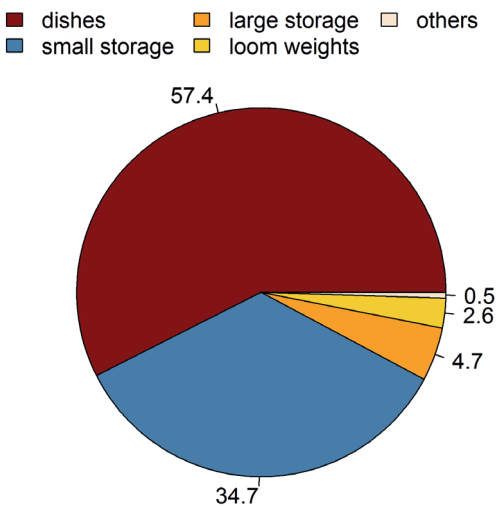


Fig. 3. categories of objects identified among the unfired sherds.

Before the discovery of the unfired sherds, it was possible to assess the composition of a kiln load through the content of the firing chamber of Kiln 5 (SU 15227). The low level of fragmentation (202 minimum individuals with 1614 fragments) and the presence of many pieces used to separate pots during firing, suggest that this unit consists of a unique set of material directly discarded after firing, and abandoned in the infill of the firing chamber<sup>19</sup>.

Thus, the unfired sherds from unit 15205 and the ceramic material from SU 15227 correspond to rejects before and after firing, respectively. These two stratigraphic units consist of several categories of objects with different functions: small, medium and large storage vessels, dishes, loom weights, etc. According to the minimum number of individuals, dishes (small cups) are the most represented artefacts, followed by small and medium storage vessels (*kalathoi*, cups and medium size jars), while large storage vessels are not very present (fig. 3). Accordingly, the kiln would be filled with a heterogeneous set of artefacts, mostly dishes – probably easily stackable in a firing chamber of relatively small size (less than 2 m<sup>3</sup>) – in connection with the organization of workshop production and its regional integration<sup>20</sup>.

17. Roux 1994, 83.

18. Sacilotto 2011; Frèrebeau, N. and Sacilotto, C., unpublished communication during the EAA meeting in 2013 in Pilsen, entitled "In the heat of kilns: assessing the technology of Iberian potters at the end of the Iron Age", session organized by Laure Salanova (CNRS, France) and Alison Sheridan (National Museums Scotland, UK).

19. Sacilotto 2011.

20. Gorgues 2009.

## THE PRE-FIRING STEPS OF THE POTTERY *CHAÎNE OPÉRATOIRE*

### Material and methods

23 unfired sherds were investigated, ensuring that the same individual (artefact) was not sampled more than once. All the studied samples are described in table 2.

Particle size distributions of 15 samples were measured by laser diffraction using a HORIBA LA-950V2 analyser. All the samples were pre-treated with hydrogen peroxide to remove organic material. Dispersion was carried out in aqueous medium using sodium hexametaphosphate and ultrasonification<sup>21</sup> for one minute. Calculation of the particle size distribution was achieved with the Mie solution to Maxwell's equation, using 1.33 as the refractive index of water and 1.55-0.1i for the sediment.

Five thin sections perpendicular to the surface of our samples were prepared.

Fifteen sherds were analyzed by X-ray diffraction (XRD) and wavelength dispersive X-ray fluorescence (WDS-XRF). A D8 Advance (Bruker) diffractometer equipped with a copper anode source ( $k_{\alpha 1}=1.5406 \text{ \AA}$ ) and a LynxEye© CCD detector was used in Bragg-Brentano configuration:

Fifteen samples were powdered in an agate mortar to define the complete mineralogical composition. The explored area covered the  $3-70^\circ$  ( $2\theta$ ) range, with angle step of  $0.02^\circ$  and a time step of two seconds.

Eight oriented aggregate mounts were prepared with the less than  $10 \mu\text{m}$  particle size fractions; the explored area covered the  $3-30^\circ$  ( $2\theta$ ) range, with angle step of  $0.02^\circ$  and a time step of four seconds. Each preparation was analysed after air drying, glycolation with ethylene glycol vapour, and heating to  $110^\circ\text{C}$ ,  $350^\circ\text{C}$  and  $550^\circ\text{C}$  in order to identify clay minerals<sup>22</sup>.

A SRS 3400 (Bruker) spectrometer, calibrated on 40 international standards, was used for elemental composition. 10 major and minor elements and 14 trace elements were measured. Loss on ignition (LOI) was calculated prior to XRF analyses, by firing the samples at  $950^\circ\text{C}$  for one hour after 24 hours drying at  $50^\circ\text{C}$ . XRF results are closed to 100% (LOI-free).

These analyses were completed by Raman spectrometry on the two painted sherds. A Renishaw RM 2000 Raman spectrometer equipped with a CCD detector and coupled to a confocal Leica DM LM microscope was used. The  $520.5 \text{ cm}^{-1}$  line of silicon was used for calibration and the laser source (wavelength 633 nm) was reduced (less than 5 mW) to avoid thermal degradation of the samples under illumination<sup>23</sup>. Spectra were acquired with the 50x objective, from 100 to  $2000 \text{ cm}^{-1}$  at  $2 \text{ cm}^{-1}$  resolution ( $1800 \text{ lignes.mm}^{-1}$  grating).

In addition, 30 ceramic sherds from stratigraphic units 15205 and 15227 were analysed by WDS-XRF under the same conditions.

All statistical treatments were performed with the R software v.3.0.0<sup>24</sup> and the packages "compositions"<sup>25</sup> and "FactoMineR"<sup>26</sup>.

Sample	Stratigraphic unit	Ceramic category	Ceramic type	Part of the pot	Painted decor	Analysis*
BDX14722	15205	IB-PEINTE	cup	rim	yes	LG, R
BDX14723	15205	IB-PEINTE	cup	body	yes	LG, R
BDX14724	15205	?	?	rim	-	LG
BDX14725	15205	-	?	handle	-	LG

21. The use of ultrasound, or high-intensity sound waves to change or mix materials.

22. Moore & Reynolds 1989; Bouchet *et al.* 2000.

23. de Faria *et al.* 1997, 875.

24. R Core Team 2013.

25. van den Boogaart *et al.* 2013.

26. Husson *et al.* 2013.



Sample	Stratigraphic unit	Ceramic category	Ceramic type	Part of the pot	Painted decor	Analysis*
BDX14726	15205	?	cup	base	-	LG
BDX14727	15205	?	storage jar	base	-	LG
BDX14728	15205	-	?	handle	-	LG
BDX14729	15205	?	storage jar	body	-	LG
BDX14914	15312	?	?	rim	-	LG, XRD (P, OM), XRF
BDX14915	15312	?	?	body	-	XRD (P), XRF
BDX14916	15312	?	?	rim	-	XRD (P), XRF
BDX14917	15312	?	kalathos	rim	-	LG, XRD (P, OM), XRF
BDX14918	15312	?	?	body	-	XRD (P), XRF
BDX14919	15312	-	-	handle	-	LG, XRD (P, OM), XRF
BDX14920	15312	?	?	body	-	XRD (P), XRF
BDX14921	15312	?	?	base	-	XRD (P), XRF
BDX14922	15312	-	-	handle	-	LG, XRD (P, OM), XRF
BDX14923	15312	?	?	body	-	LG, XRD (P, OM), XRF
BDX14924	15312	?	?	body	-	XRD (P), XRF
BDX14925	15312	?	?	body	-	LG, XRD (P, OM), XRF
BDX14926	15302	?	?	body	-	XRD (P), XRF
BDX15030	15205	-	loom weight	-	-	LG, XRD (P, OM), XRF
BDX15031	15205	-	loom weight	-	-	LG, XRD (P, OM), XRF

Table 2. list of the studied samples. \* performed analysis: TS = thin section petrography; LG = laser granulometry; R = Raman spectroscopy; XRD = X-Ray Diffraction (P: on powder, OA: on oriented mount); XRF = wavelength dispersive X-Ray Spectroscopy.

## Raw material selection and preparation

When dry, the unfired sherds have a homogenous brown colour with no inclusions (temper) visible to the naked eye. All the studied samples have a fine grain size; according to the EU Soil Map texture triangle (fig. 4), more than 90% of the particles are smaller than 50  $\mu\text{m}$  and none is bigger than 250  $\mu\text{m}$ <sup>27</sup>.

The unfired sherds allow us to identify the mineralogical composition of the pastes before firing. The non-plastic fraction, as identified by petrography and X-ray diffraction, is similar for all studied fragments. It consists of quartz, calcite (both in the form of isolated grains and in a crypto-crystalline form dispersed in the clay matrix), sporadic dolomite, calcium-feldspars and hematite; the presence of titanium oxides is strongly suspected. Moreover, oriented mounts allowed us to differentiate clay minerals: the unfired pottery sherds are composed of kaolinite, illite/muscovite, palygorskite, chlorites and smectites.

On the one hand, palygorskite appears as a promising marker of the origin of raw materials. This mineral is characteristic of inland lakes and lagoon palaeoenvironments, which is consistent with the past endorheic regime of the Ebro valley. Moreover, calcium carbonates (calcite, dolomite) and gypsum are the major part of the surrounding deposits, and clays associated with calcisols are magnesium swelling clays like palygorskite. These first results are consistent with a local supply of clay materials (mostly Cenozoic deposits)<sup>28</sup>.

27. Given the plethora of existing classifications (see Richer de Forges *et al.* 2008 for a review), we use the same triangle as the European Soil Bureau (Jones *et al.* 2005, 124). The triangle is constructed with the following classes: clay = ]0;2]  $\mu\text{m}$ , silt = ]2;50]  $\mu\text{m}$  and sand = ]50;2000]  $\mu\text{m}$ .

28. Meunier 2005, 289; Duchaufour 1997, 152-153.

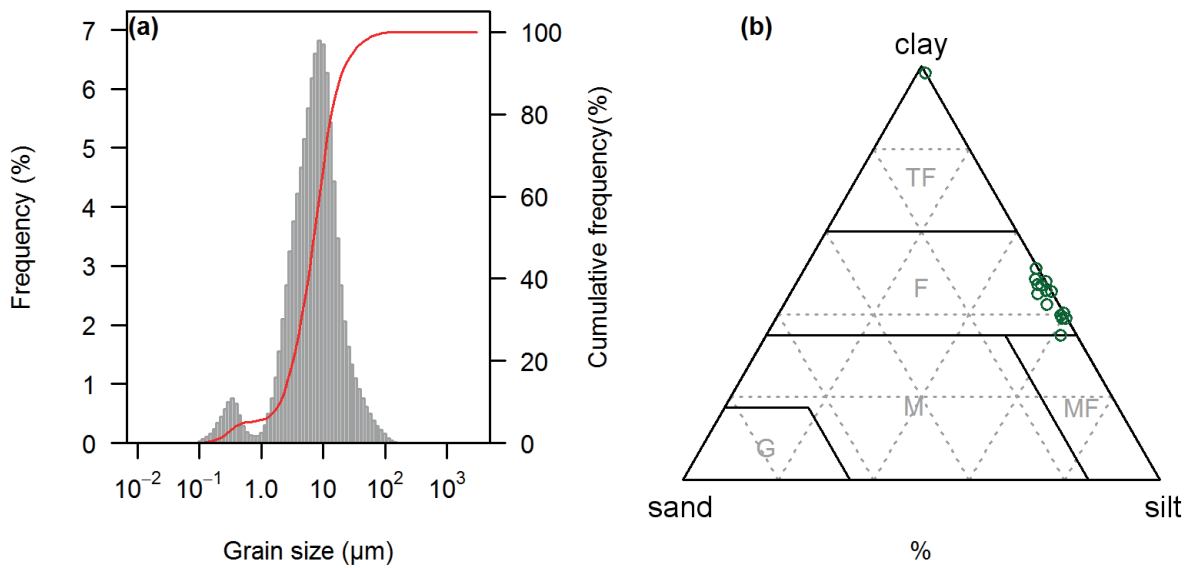


Fig. 4. (a) mean grain size distribution of the unfired pottery sherds; (b) FAO soil texture triangle: except one, the sherds can be described as fine texture.

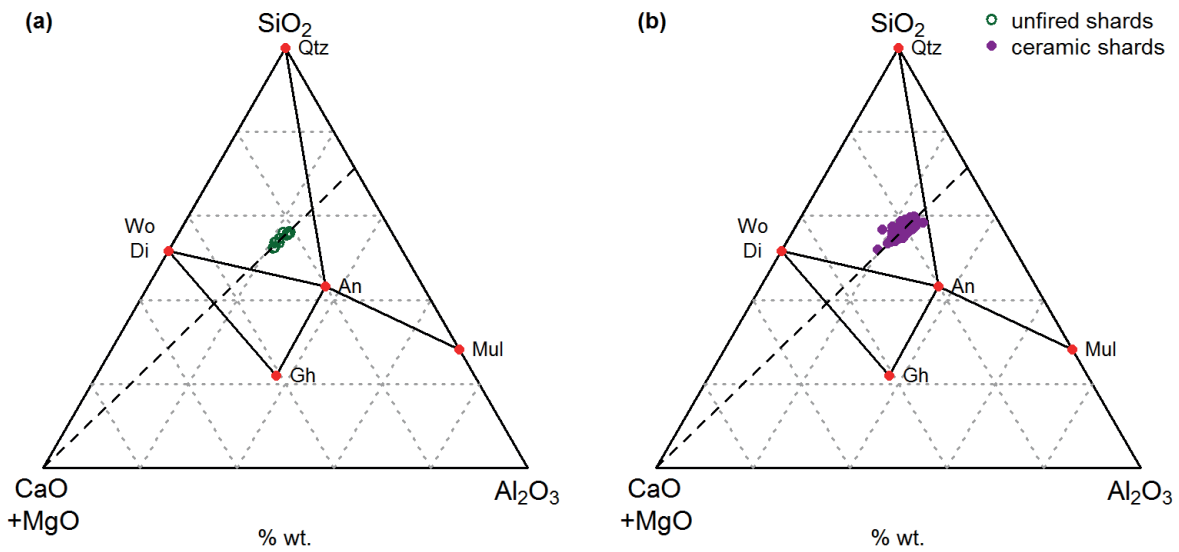


Fig. 5. compositions of the unfired (a) and ceramic sherds (b) in the (CaO+MgO)-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system.

On the other hand, the presence of the smectite group is quite unexpected in the context of ceramic production, since the use of swelling clays may be associated with strong volume changes during drying. Interestingly, this last point may – at least partially – explain the rejection of some of the unfired sherds, with regards to cracked or deformed pots.

These unfired sherds belong to the calcareous materials category, according to W. Noll's definition (fig. 5)<sup>29</sup>: the CaO value – relative to Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents (table 3) – allows the formation of calcium-rich minerals during firing. The colour

29. Noll 1991.

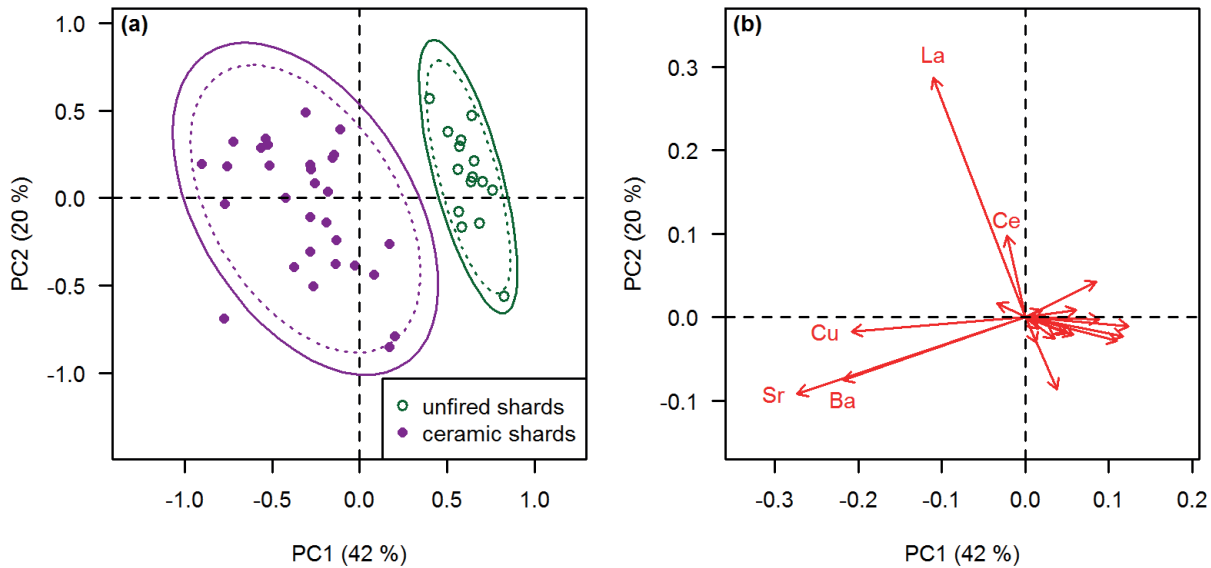


Fig. 6. PCA of the elementary compositions of the unfired sherds and contemporary ceramics. (a) Projection of the individuals on the first two components; (b) projection of the variables. 90% and 95% probability ellipses are drawn in dotted and solid lines, respectively.

of the ceramic materials produced in the Mas de Moreno is then the results of their particular chemistry: during firing,  $\text{Fe}^{3+}$  cations may be incorporated in pyroxenes or melilites instead of persisting as a chromogenic oxide, and lead to the formation of a creamy surface colour<sup>30</sup>.

Interestingly, a first comparison between the unfired sherds and contemporaneous ceramics highlights an unexpected difference based on chemistry. A Principal Component Analysis<sup>31</sup> was performed and shows that material category (ceramic vs. unfired clay) is a discriminant factor (fig. 6). Five hypotheses can be advanced to explain this difference: distinct sources of raw materials, distinct paste preparation, different uses, different post-depositional effects or a combination of the above<sup>32</sup>. This difference is mainly explained by the first two components (62% of the explained variance) for which cerium, lanthana, copper, barium and strontium have the highest loadings.

These elements have a strong attraction for water molecules and are therefore easily mobilized by water circulation. The workshop of the Mas de Moreno belongs to the semi-arid zone of Bajo Aragón where the strong seasonal contrasts and intense evaporation leads to the concentration of alkaline elements in soil and precipitation of various salts. Thus, the occurrence of post-depositional process is the preferred hypothesis since earth-alkaline elements contamination in ceramics is well documented and is currently the subject of a comprehensive study within the whole ceramic production of the workshop<sup>33</sup>.

30. Molera *et al.* 1998.

31. According to Aitchison (1986) developments, compositional data were transformed prior to PCA, using a centered log-ratio transformation.

32. Neff *et al.* 2003, 204.

33. Frèrebeau, forthcoming.

Sample	LOI (%)	(%)										(ppm)													
		CaO	Fe <sub>2</sub> O <sub>3,t</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	MnO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	Zr	Sr	Rb	Zn	Cr	Ni	La	Ba	V	Ce	Y	Th	Pb	Cu
BDX14914	19,5	17,23	4,75	1,00	1,72	51,35	20,74	2,86	0,04	< d.l.	0,17	244	252	106	52	88	36	56	299	127	105	34	< d.l.	29	14
BDX14915	18,9	17,21	5,03	0,99	1,63	51,50	19,78	3,51	0,04	< d.l.	0,17	240	239	94	41	91	47	52	293	123	116	33	< d.l.	24	11
BDX14916	20,6	21,01	4,31	0,92	1,67	48,78	19,96	2,98	0,03	< d.l.	0,19	217	274	96	45	88	53	24	294	124	149	31	< d.l.	< d.l.	13
BDX14917	18,8	17,17	4,64	1,01	1,71	51,34	20,89	2,88	0,04	< d.l.	0,19	242	254	104	58	85	28	57	286	114	99	37	< d.l.	37	13
BDX14918	18,9	17,39	4,58	1,00	1,70	51,29	20,77	2,87	0,04	< d.l.	0,22	241	258	104	58	86	30	75	300	120	115	37	< d.l.	34	12
BDX14919	20,1	19,58	4,42	0,95	1,73	49,76	20,27	2,96	0,04	< d.l.	0,15	231	272	108	52	83	19	60	284	116	106	32	15	33	12
BDX14920	18,5	16,51	4,80	1,02	1,74	51,63	21,08	2,87	0,04	< d.l.	0,17	244	242	106	53	89	22	65	312	121	114	34	< d.l.	32	16
BDX14921	18,3	16,49	4,66	1,02	1,72	51,87	20,96	2,88	0,04	< d.l.	0,23	246	247	106	56	92	22	45	313	122	109	38	15	32	16
BDX14922	20,7	21,43	4,32	0,93	1,70	48,56	19,80	2,95	0,03	< d.l.	0,14	225	273	105	55	81	20	39	301	113	99	29	15	31	14
BDX14923	18,6	16,58	4,83	1,02	1,73	51,63	20,94	2,89	0,03	< d.l.	0,20	248	249	106	57	89	30	49	287	123	106	35	16	36	14
BDX14924	18,6	16,77	4,64	1,01	1,73	51,64	20,84	2,92	0,03	< d.l.	0,27	244	257	111	58	85	27	55	295	120	84	35	< d.l.	52	19
BDX14925	18,5	16,72	4,83	1,02	1,71	51,50	20,91	2,88	0,04	< d.l.	0,25	246	284	105	57	90	16	34	332	128	87	35	15	27	17
BDX14926	19,9	19,71	4,90	0,94	1,76	49,60	19,43	3,30	0,04	< d.l.	0,16	223	299	103	52	83	22	75	260	137	158	31	16	37	17
BDX15030	20,0	19,38	4,02	0,95	1,70	50,75	19,99	2,89	0,04	< d.l.	0,13	247	239	108	52	85	23	60	273	112	101	36	15	35	15
BDX15031	20,6	20,66	4,01	0,92	1,72	50,00	19,41	2,96	0,04	< d.l.	0,14	240	246	106	54	82	27	34	277	114	133	33	< d.l.	30	15

Table 4: results of the WDXRF analysis. Data are normalized to 100% (LOI-free), < d.l. = below detection limit.



## Painted decor

Hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) belongs to the  $D_{3d}^6$  point group and has seven Raman active vibrational modes<sup>34</sup> (225, 245, 291, 299, 411, 498 and 611  $\text{cm}^{-1}$ ). The observation of these diagnostic bands allows the identification of this iron oxide as the main constituent of the painted decors, which is consistent with previous observations on Iberian painted wares<sup>35</sup>. The identification of hematite as the colouring material is also consistent with a local resource exploitation since this mineral regularly occurs in outcrops near the workshop (fig. 7).

In addition, in all our Raman spectra corresponding to hematite, two intense supplementary bands were observed at ca. 660 and 1320  $\text{cm}^{-1}$  with an additional shoulder at 710  $\text{cm}^{-1}$ . The 1320  $\text{cm}^{-1}$  band is interpreted as an overtone of a forbidden  $\sim 660$   $\text{cm}^{-1}$ , probably activated by disorder<sup>36</sup>. Indeed, this unexpected 660  $\text{cm}^{-1}$  band could be related to an imperfect structure of hematite<sup>37</sup> as Al- or Ti-bearing displays a broad band at ca. 660-670  $\text{cm}^{-1}$ <sup>38</sup>. The possibility of Al-for-Fe substitutions in hematite is inconsistent with our results, as Zoppi *et al.* observed a shoulder in the  $\sim 411$   $\text{cm}^{-1}$  area<sup>39</sup> (sensitive to the geometry of  $\text{FeO}_6$  octahedra) related with the development of a broad and weak band at 670  $\text{cm}^{-1}$ . Leon *et al.* suggest that Ti substitutions could explain the high intensity of the 670  $\text{cm}^{-1}$  band<sup>40</sup>: this area corresponds to the main band of several iron titanium oxides (ilmenite, ulvöspinel, pseudobrookite) and Ti-O bonds are prominent features in Raman spectra due to their higher polarizability. If this explanation appears in agreement with some of our results, it does not explain the presence of an additional shoulder at 710  $\text{cm}^{-1}$ . Maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) displays its strongest band at ca. 660 and a secondary one at 720  $\text{cm}^{-1}$ <sup>41</sup>. Thus, the ubiquity of the  $\sim 660/\sim 710$   $\text{cm}^{-1}$  pair of bands in our spectra could suggest a weak presence of maghemite. Interestingly, maghemite can form



Fig. 7. iron oxides outcrops near the village of Foz-Calanda (Teruel, Spain).

34. de Faria *et al.* 1997, 874; Oh *et al.* 1998, 63; Legodi & de Waal 2007, 164-166; Marshall & Marshall 2011, 135.
35. Parras *et al.* 2009; Ayora-Cañada *et al.* 2012.
36. Wang *et al.* 2009, 1001.
37. Wang *et al.* 2009.
38. Zoppi, *et al.* 2007; Leon *et al.* 2010, 1552-1554.
39. Zoppi *et al.* 2007.
40. Leon *et al.* 2010.
41. Oh *et al.* 1998; Legodi & de Waal 2007.

during iron oxide-hydroxide (namely lepidocrocite,  $\gamma\text{-FeO(OH)}$ ) heating at 200-280 °C, before transforming into hematite up to 370-600 °C<sup>42</sup>. As mentioned above, Iron oxide-hydroxides are naturally present around the workshop but were also found in archaeological context. Indeed, several limonite fragments were found that were certainly brought to the site intentionally, since their geological origin is incompatible with the immediate environment. This is probably a good indication of the use of these objects as pigments.

## CONCLUSION

The analysis of the unfired sherds of the Mas de Moreno allows a better description of the pre-firing stages of the ceramic *chaîne opératoire*. These first results highlight several technical choices and bring new data about the selection and preparation of natural resources in order to produce ceramic material, and about firing operations through the kiln load composition. Interestingly, the characterization of the clayey raw material brings out the use of material that is unexpected in terms of its mechanical properties, but the rejection of several artefacts indicates a good knowledge and control of ceramic production and highlights specific quality standards.

## ACKNOWLEDGEMENTS

This study received financial support from the Région Aquitaine through the research program “*Un artisanat en réseau: innovation et transferts de technologies dans le sud-ouest de l’Europe au I<sup>er</sup> millénaire av. n.è.*” This study received financial support by the state managed by the Agence Nationale de la Recherche (France) through the program “*Investissements d’avenir*” (ref. ANR-10-LABX-52).

The authors wish to thank A. Gorgues (Institut Ausonius, UMR 5607) and J. A. Benavente Serrano (Consortio Patrimonio Ibérico de Aragón) for their support and for providing the samples. N. Cantin (IRAMAT-CRP2A, UMR 5060), M. Pernot (IRAMAT-CRP2A, UMR 5060) and A. Ben Amara (IRAMAT-CRP2A, UMR 5060) are thanked for their help and reviews. Special thanks are offered to V. Merle (Laboratoire Archéologie et Archéométrie, UMR 5138) for the WDXRF analysis, A. Queffelec (Laboratoire PACEA, UMR 5199) for the laser diffraction and for particle size analysis and B. Martin (Laboratoire EPOC, UMR 5805) for preparing the thin sections.

42. Cornell & Schwertmann 2003, 373, 382.

## References

- Aitchison, J. (1986): *The Statistical Analysis of Compositional Data*, Monographs on Statistics and Applied Probability, London.
- Ayora-Cañada, M. J., Domínguez-Arranz, A. and Domínguez-Vidal, A. (2012): "Raman Microspectroscopic study of Iberian pottery from the La Vispesa archaeological site, Spain", *Journal of Raman Spectroscopy*, 43, 317-322.
- van den Boogaart, K. G., Tolosana, R. and Bren, M. (2013): *compositions: Compositional Data Analysis*, R package version 1.30-1. URL: <http://CRAN.R-project.org/package=compositions>.
- Belarte, M. C., Benavente, J. A., Diloli, J., Moret, P. and Noguera, J., eds (2012): *Iberos del Ebro. Actas del II Congreso Internacional (Alcaniz-Tivissa, 16-19 de noviembre de 2011)*, Tarragona.
- Bouchet, A., Meunier, A. and Sardini, P. (2000): *Minéraux argileux: structure cristalline, identification par diffraction de rayons X*. Bull. du centre de recherches Elf exploration production, Mémoire 23, Pau.
- Casas-Sainz, A. and de Vicente, G. (2009): "On the tectonic origin of Iberian topography", *Tectonophysics*, 474, 214-235.
- Coll Conesa, J. (2000): "Aspectos de tecnología de producción de la cerámica ibérica", in: Mata Parreño & Pérez Jordà 2000, 191-209.
- Cornell, R. M. and Schwertmann, U. (2003): *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, Weinheim.
- Duchauffour, P. (1997): *Abrégé de pédologie*, Paris.
- Duminuco, P., Messiga, B. and Riccardi, M. P. (1998): "Firing process of natural clays. Some microtextures and related phase compositions", *Thermochimica Acta*, 321, 185-190.
- de Faria, D. L. A., Venâncio Silva, S. and de Oliveira, M. T. (1997): "Raman microspectroscopy of some iron oxides and oxyhydroxides", *Journal of Raman Spectroscopy*, 28, 873-878.
- Frèrebeau, N. (2015): *Choix et trajectoires techniques en Péninsule ibérique à la fin de l'Âge du Fer: la cuisson des matériaux céramiques dans la vallée de l'Èbre (11<sup>e</sup>-1<sup>er</sup> s. av. J.-C.)*, Unpublished PhD Thesis, Université Bordeaux Montaigne, Pessac.
- García-Castellanos, D., Vergés, J., Gaspar-Escribano, J. and Cloetingh, S. (2003): "Interplay between tectonics, climate, and fluvial transport during the Cenozoic evolution of the Ebro Basin (NE Iberia)", *Journal of Geophysical Research*, 108, 1-18.
- Gibbons, W. and Moreno, T., eds (2002): *The geology of Spain*, The Geological Society, London.
- Gorgues, A. (2009): "L'épigraphie dans l'atelier de potiers du Mas de Moreno (Foz-Calanda, Teruel): la structure de la production à l'époque ibérique tardive (11<sup>e</sup>-1<sup>er</sup> s. AC)", *Palaeohispanica*, 9, 481-500.
- (2012): "Organisation du travail et technologie potière dans les ateliers ibériques tardifs du Mas de Moreno (Foz-Calanda, Teruel): bilan provisoire des recherches (2005-2011)", in: Belarte *et al.* 2012, 273-290.
- Gorgues, A. and Benavente Serrano, J. A. (2007): "Les ateliers de potiers de Foz-Calanda (Teruel, Espagne) aux 11<sup>e</sup> et 1<sup>er</sup> s. av. J.-C.", *Mélanges de la Casa de Velázquez*, 37, 295-312.
- Grapes, R. H. (2006): *Pyrometamorphism*, Springer, Berlin.
- Heimann, R. B. (1989): "Assessing the technology of ancient pottery: the use of ceramic phase diagrams", *Archaeomaterials*, 3, 123-148.
- Husson, F., Josse, J., Le, S. and Mazet, J. (2013): *FactoMineR: Multivariate Exploratory Data Analysis and Data Mining with R*, R package version 1.25. <http://CRAN.R-project.org/package=FactoMineR>.
- IGME (1977): *Mapa Geológico de España, E. 1:50.000, Calanda*. Ministerio de Industria, Servicio de Publicaciones, Madrid. Segunda serie – Primera edición.
- Jones, A., Montanarella, L. and Jones, R., eds (2005): *Soil atlas of Europe*. Luxembourg.
- Legodi, M. A. and de Waal, D. (2007): "The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste", *Dyes and Pigments*, 74, 161-168.
- Leon, Y., Lofrumento, C., Zoppi, A., Carles, R., Castelluccic, E. M. and Sciau, P. (2010): "Micro-Raman investigation of terra sigillata slips: a comparative study of central Italian and southern Gaul productions", *Journal of Raman Spectroscopy*, 41, 1550-1555.
- Maestro Zaldivar, E. (1989): *La cerámica ibérica decorada con figurada humana*, Monografías arqueológicas 31, Saragossa.
- Marshall, C. P. and Marshall, A. O. (2011): "Hematite and carbonaceous materials in geological samples: a cautionary tale", *Spectrochimica Acta*, 80, 133-137.
- Mata Parreño, C. and Pérez Jordà, G., eds (2000): *Ibers. Agricultors, artesans i comerciants, proceedings of the III Reunió sobre economia en el Món Ibèric, 1999*, València.
- Meunier, A. (2005): *Clays*, Berlin.
- Molera, J., Pradell, T. and Vendrell-Saz, M. (1998): "The colours of Ca-rich ceramic pastes: origin and characterization", *Applied Clay Science*, 13, 187-202.
- Moore, D. M. and Reynolds, R. C. J. (1989): *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*, Oxford.
- Neff, H., Cogswell, J. W. and Ross Jr., L. M. (2003): "Supplementing Bulk Chemistry in Archaeological Ceramic Provenance Investigations", in: Sayre & van Zelst 2003, 201-224.
- Oh, S. J., Cook, D. C. and Townsend, H. E. (1998): "Characterisation of iron oxides commonly formed as corrosion products on steel", *Hyperfine Interactions*, 112, 59-66.
- Parras, D., Vandenabeele, P., Sánchez, A., Montejo, M., Moens, L. and Ramos, N. (2009): "Micro-Raman spectroscopy of decorated pottery from the Iberian archaeological site of Puente Tablas (Jaen, Spain, 7th-4th century B.C.)", *Journal of Raman Spectroscopy*, 41, 68-73.
- Rathossi, C. and Pontikes, Y. (2010a): "Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part I: Reaction paths, crystalline phases, microstructure and colour", *Journal of the European Ceramic Society*, 30, 1841-1851.
- Rathossi, C. and Pontikes, Y. (2010b): "Effect of firing temperature and atmosphere on ceramics made of NW Peloponnese clay sediments. Part II: Chemistry of pyrometamorphic minerals and comparison with ancient ceramics", *Journal of the European Ceramic Society*, 30, 1853-1866.
- Core Team, R (2013): *R: A language and environment for statistical computing*, Vienna.
- Riccardi, M., Messiga, B. and Duminuco, P. (1999): "An approach to the dynamics of clay firing", *Applied Clay Science*, 15, 393-409.
- Richer de Forges, A., Feller, C., Jamagne, M. and Arrouays, D. (2008): "Perdu dans le triangle des textures", *Etude et Gestion des Sols*, 15, 97-111.
- Roux, V. (1994): "La technique du tournage: définition et reconnaissance par les macrotraces", *Terre cuite et société. La céramique, document technique, économique, culturel, Actes des XIV<sup>e</sup> rencontres*



- internationales d'archéologie et d'histoire d'Antibes*, APDCA, Juan-les-Pins, 45-58.
- Sacilotto, C. (2011): *De l'argile à la terre cuite, le traitement des productions sur un atelier de poterie ibérique à la fin de l'âge du Fer. Etude de l'atelier de potiers du Mas de Moreno (Foz-Calanda, Teruel, Espagne) des 1<sup>er</sup> et 1<sup>er</sup> siècles a.C.*, Unpublished Master dissertation, Université de Bordeaux Montaigne, Pessac.
- Sayre, E. V. and Van Zelst, L. (2003): *Patterns and process*, Smithsonian Center for Materials Research and Education, Washington.
- Velde, B. and Druc, I. C. (1999): *Archaeological ceramic materials*, Berlin.
- Wang, L., Zhu, J., Yan, Y., Xie, Y. and Wang, C. (2009): "Micro-structural characterization of red decorations of red and green color porcelain (Honglvcai) in China", *Journal of Raman Spectroscopy*, 40, 998-1003.
- Yeskis, D., van Groos, A.F.K. and Guggenheim, S. (1985): "The dehydroxylation of kaolinite", *American Mineralogist*, 70, 159-164.
- Zoppi, A., Lofrumento, C., Castellucci, E. M. and Sciau, P. (2007): "Al-for-Fe substitution in hematite: the effect of low Al concentrations in the Raman spectrum of Fe<sub>2</sub>O<sub>3</sub>", *Journal of Raman Spectroscopy*, 39, 40-46.





