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PhD Supervisors :
Prof. Univ. Dr. Ing. Mărioara ABRUDEANU
Prof. Univ.Dr. Rémy CHAPOULIE

PhD Student :
Ing. Laura TEODORESCU

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Scientific material related to this thesis

Articles:

1. **Teodorescu, Laura**, Ben Amara, A., Cantin, N., Chapoulie, R., Ducu, C., Ciucă, S., Tulugea, C., Terteci, C., Abrudeanu, M., 2021. Characterization of Archaeological Artefacts Using Methods Specific to Materials Science: The Case Study of Dacian Ceramics from 2nd c. BC to 1st c. AD. Materials 14, 3908. https://doi.org/10.3390/ma14143908

2. **Teodorescu, Laura**, Cantin, N., Ben Amara, A., Chapoulie, R., Roux, V., 2022. Mineralogical transformations due to salt whitening agent in modern Hebron ceramics. Journal of Archaeological Science: Reports 41, 103303. https://doi.org/10.1016/j.jasrep.2021.103303

PREFACE

Ceramic artefacts are one of the most studied objects by the archaeologist, since they can be found in big amounts in the majority of archaeological sites, dating from the Neolithic period onwards (Tite, 2008). Therefore, the study of these objects has been essential to the archeological interpretation of a site, a region and a period. The analytical techniques that have been developed in the field of materials science are widely applied to the study of the ancient objects of art and archaeology, in order to obtain information about the composition and the structure of the material used (Montana et al., 2011; Sciau and Goudeau, 2015).

To obtain the needed data, a multi-level approach is required to analyze the materials. The areas to be examined must be chosen according to objectives. An appropriate selection of techniques allows the study of the composition and structure of specific components. Several methods are specially applied to study different types of pottery from the past.

One of the main subjects of this thesis is the identification and fine characterisation of ceramics produced in Romania during the Dacian period, using the methods and techniques of engineering sciences. This research requires the mastery of methods and, above all, the definition of an adequate methodology for each type of ceramic according to the archaeological issue.

The complexity of studying the ceramic materials will be put into evidence, as well in providing information regarding of the use of raw materials, the manufacturing process, the firing conditions and the provenance of the objects.

Thus, the thesis encompasses **two important aims** such as:

1. Creating a suitable methodological approach in the study of Dacian potteries and to promote their study since archaeometry is a field in continuous development in Romania.
2. Answering to the question: which analytical technical methods of materials science can provide an answer to different archaeological questions?

In order to respond to these challenges, to explore the applicability of traditional and innovative techniques, and creating a constructive methodology in the analysis of the ceramics, during this thesis research, we established our methodology starting with a case study of Dacian ceramic from Ocnița-Buridava, and other two defined corpuses with a problematic clearly exposed:

- One case concerns the diffusion of Adriatic oil amphorae in the Danube region in Roman times,
- The other case deals with a particular ceramic manufacturing process in Palestine today. This case aims to understand the role of salt as a bleaching agent and to better understand the transformations of the ceramic material during its manufacture.

This implementation allowed us to know more about ceramics and to apply the right methods and methodology to study ceramics from Romania, whose archaeological issues were less well defined but whose study is so promising.

The manuscript of this thesis is divided in **six chapters.**

Chapter I - GENERAL INTRODUCTION

In the last part of the XXth century, a scientific discipline emerged, broadly defined as the application of physical, chemical, biological, geological or mathematical principles and methods for the characterization of archaeological objects and materials related to cultural heritage. The term widely used for this discipline is "Archaeometry", which has been used since the founding of the international research journal "Archaeometry" in 1958 in Oxford, England. Archaeometry is largely used as an alternative term for "Archaeological Science" or "Science in Archeology" (Artioli, 2010).

A main aspect in approaching the study of archaeological materials and objects is the correct identification of the type of material investigated, being the first step in interpreting how it was made, its field of use, its origin and other cultural information related to the human community. The archaeological materials discovered from excavations, in terms of their attributions, can be grouped into artifacts, structures and articles associated with human activities (Renfrew and Bahn, 2016).

Artifacts are objects made or modified by man at a specific time and place. They can provide various evidence of how the ancient population incorporated different types of materials into everyday life, as well as the techniques used in their manufacture. Their analysis requires an interaction between specialists such as archaeologists, curators, art historians and scientists from different fields.

The ceramic artifacts have been studied from various points of view: mineralogical and chemical aspects, artistic, aesthetic and use. In particular, a lot of archaeological research has been devoted to the study of the chemical and mineral composition of ancient pottery to identify, origin, raw material and manufacturing process, dating, and to gain a perspective on human history and culture (Stefan and Mazare, 2001). It is important to emphasize that each analytical technique offers advantages as well as limitations, so a broad understanding of the techniques available is necessary to take advantage of the full spectrum of modern analytical tools (Edwards and Vandenabeele, 2016).

The study of artefacts requires the integration of a multitude of sciences, in particular physics, chemistry and materials science (**Fig.1**), known also as archaeometric methods.

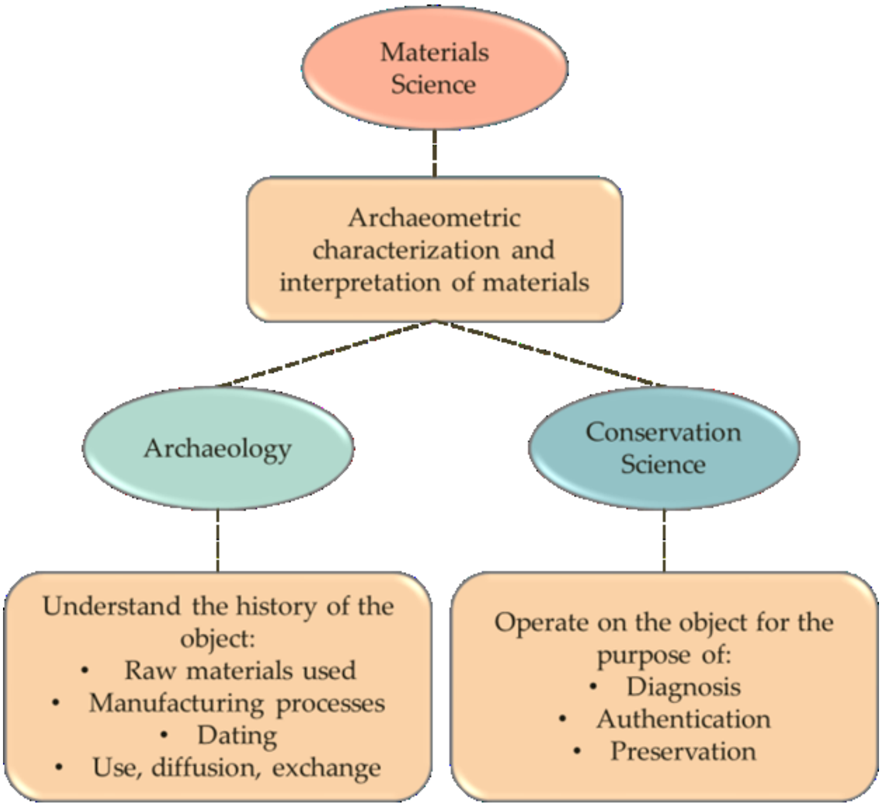


Fig. 1 Fields of application of archaeometric analyzes (modified after Artioli, 2010)

Ceramic archeomaterials

Among the archaeological discoveries, ceramics, and in general ceramic artifacts are the most studied objects by the community of archaeologists, people of art and science related to this field (Sciau and Goudeau, 2015). The oldest pottery (a statuette called Venus from the Western Dolni, discovered in the Czech Republic) dates to the approx. 25th century BC, but the ceramic vessel technology had independent origins in East Asia around the 12^{th} century BC, which indicates that pottery was a well-known activity at that time (Vandiver et al., 1989; Bougard, 2011).
In the study of ceramics, the most important aspects are:

- Identification of the raw materials used (as well as their geological origin)
- Shaping process
- Firing conditions
- Glazing and coloring (if present)
- Chronology
- Field of use

Techniques for investigation and characterisation of ceramic artifacts

Archaeometry refers to each application that uses physico-chemical characterization methods to understand the nature and changes over time of art and archaeological materials.
The object under investigation must necessarily be a physical material, either artistic or archaeological, and no matter how unclear or debatable the origin of the object, regardless of its size or complexity, the object is related to human activity.
Therefore, understanding the nature of the object is to discover not only the physico-chemical nature, but to reveal the human process that produced it, the social context. For this purpose, archaeometry uses all available techniques and methods, developed in the most diverse and specialized scientific disciplines (Tykot, 2004).
The bridge between ancient ceramics and materials science and engineering (defined as an interdisciplinary field focused on the discovery and design of new materials), would seem that it doesn't exist. However, the basis of materials science involves the study of the microstructure, crystallographic phases and defects of materials in relation to their properties, which can be applied directly to heritage materials (Sciau and Goudeau, 2015).
After defining the questions, the decisions specifically involved in the archaeometric analysis of the archaeological materials are:

- sample's preparation
- selection of analysis techniques and methods
- duration and cost of investigations
- interpretation of results and drawing conclusions

Several principles are needed to understand the operations and limitations of available analytical techniques. Most analytical techniques use a sample to investigate the material of interest, whether it is a natural mineral, or a synthetic compound, present in different states: liquid, gaseous, solid, amorphous, and crystalline (Greene and Moore, 2010; Tian, 2016).
Thus there are different ways to analyse the ceramic bodies. For example some **methods for elemental analysis** employed for the ceramic characterisations are: Inductively Coupled Plasma Mass Spectrometry (IPC-MS), Energy Dispersive X-ray Spectroscopy (EDX/EDS) and X-Ray Fluorescence spectroscopy (XRF). These methods are broadly used in order to determinate the major and minor elements in the ceramic matrix.
The chemical analyses for major, minor and trace elements help in grouping together the pottery made from the same raw material. They can also enable to distinguish the groups by studying the ceramic bodies made from different raw materials. Since there is a variability in the chemical composition of the different sources, for provenance studies the analysis needs to be performed on a large number of samples, which are then grouped together using statistical methods (Tite, 2008). However, in this thesis it was used another way to determine a ceramic provenance by comparing discovered ceramic samples from different places with other ceramics coming from a certain production site, as reference group (see Chapter IV - The Case Study Of Istrian Olive Oil Amphorae Workshop To The Danube Provinces In The Roman Period) (Maritan, 2004; Ricci, 2016).
The chemical and mineralogical composition of the minerals present in the ceramic matrix also makes it possible to determine characteristics such as firing conditions and raw materials used, to characterize a certain workshop with regard to time and origin and to examine the manufacturing

technology. Knowledge of the manufacturing process helps to reconstruct the technical history of ancient potters and assesses their ability to produce and craft specialization as well as cultural exchange (Ricci, 2016).

The field of **ethnoarchaeology** (see Chapter V - THE ACTION OF SALT IN THE MANUFACTURING PROCESS IN HEBRON'S CERAMIC) is defined as a sub-discipline of archaeology combined with anthropology, offering in a comprehensive way a direct observation of the manufacture, form, use and meaning of the artifacts made by people. Thus, with the help of ethnographic methods, improves the interpretation of archaeological data by providing more information and explanations (Stiles, 1977; Cantin and Mayor, 2018).

Most of the times, these studies are more focused on the determination of the firing conditions than the forming methods, making possible to estimate the original firing temperature with the help of the detection of different mineralogical phases.

The ceramic mineralogy is usually investigated with the help of optical microscope (OM – petrographic analysis), X-Ray Diffraction (XRD), Scanning Electron Microscope with Energy-Dispersive X-ray Spectroscopy (SEM-EDX), thermogravimetric analysis (TGA/DSG), Fourier-Transform InfraRed spectroscopy (FT-IR) and Raman spectroscopy. The effects of the firing conditions can be also analysed and observed on the morphology and microstructure of the final product. These features are examined using SEM, petrographic microscopy and porosity analysis (Shepard, 1985; Duminuco et al., 1998; Cultrone et al., 2001; Maritan et al., 2006; Ricci, 2016).

Specific objectives of the thesis

As mentioned before, archaeometry is a field in continuous development in Romania. Thus, the objectives of the thesis work are:

- Characterization of the artifacts by using specific materials engineering techniques
- Establishing the composition of the ceramic objects, their structure and to associate their manufacturing technologies used.

At the beginning, the research was focused in answering to the questions regarding the choice (or selection) of the raw materials and the manufacturing technique of the ancient Dacian potters and to create a first archaeometric database regarding the area of Buridava. Since the corpus was limited, a second case study was added regarding the provenance of ceramic vessels, the amphorae Dressel 6B from Istria. The case study is focused in developing the analytical methodology for amphorae analysis, using a portable XRF.

Beyond the methodological approach, the archaological objective was to study the export of the amphoras Dressel 6B from the initial production Center (Loron) to other sites following the Danube region.

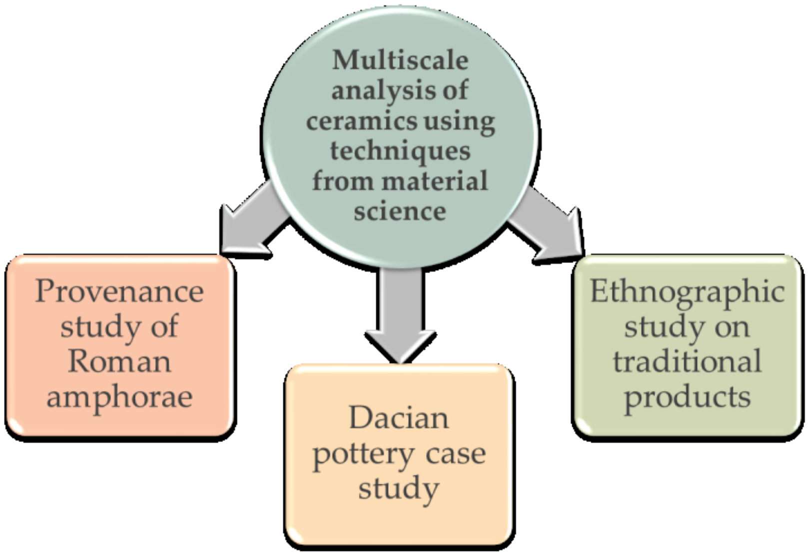


Fig. 2 Plan of the research thesis

In the end, in order to formulate a suitable methodology for understanding the complexity of the ceramic material, a last case was added is based on an ethnographic study (**Fig.2**). This last case concerns modern ceramic production. It is based on an ethnographic study; the aim of our research was to develop a multi-approach methodology in order to answer to the questions of the archaeologist, such as: how salt is influencing the colour of a ceramic body? What kind of physico-chemical changes occur in the ceramic bodies from Hebron? In order to widen our knowledge, eighteen experimental bricks have been manufactured in the laboratory, varying the percentage of salt and the firing temperatures.

Experimental research plan

After the preliminary steps, the ceramics were analyzed with a variety of methods available in the laboratory. The choice of the methods used depended on the specific problematic or question, of each series of corpus samples.
The defined milestones for the experimental program were chosen in order to obtain the desired information of the ceramic (**Fig.**), such as:

- the measurement of colour
- the study of texture
- the analysis of the various components of the ceramics
- the study of the mineralogical changes during firing, inside of a ceramic body.

The principle of the devices will be briefly presented in the following chapter (Chapter II Chapter II - A MULTI-SCALE **ANALYTICAL APPROACH**) as well with the corresponding experimental parameters (since are always the same). The study of the texture of the ceramic bodies will be carried out mainly on polished sections.

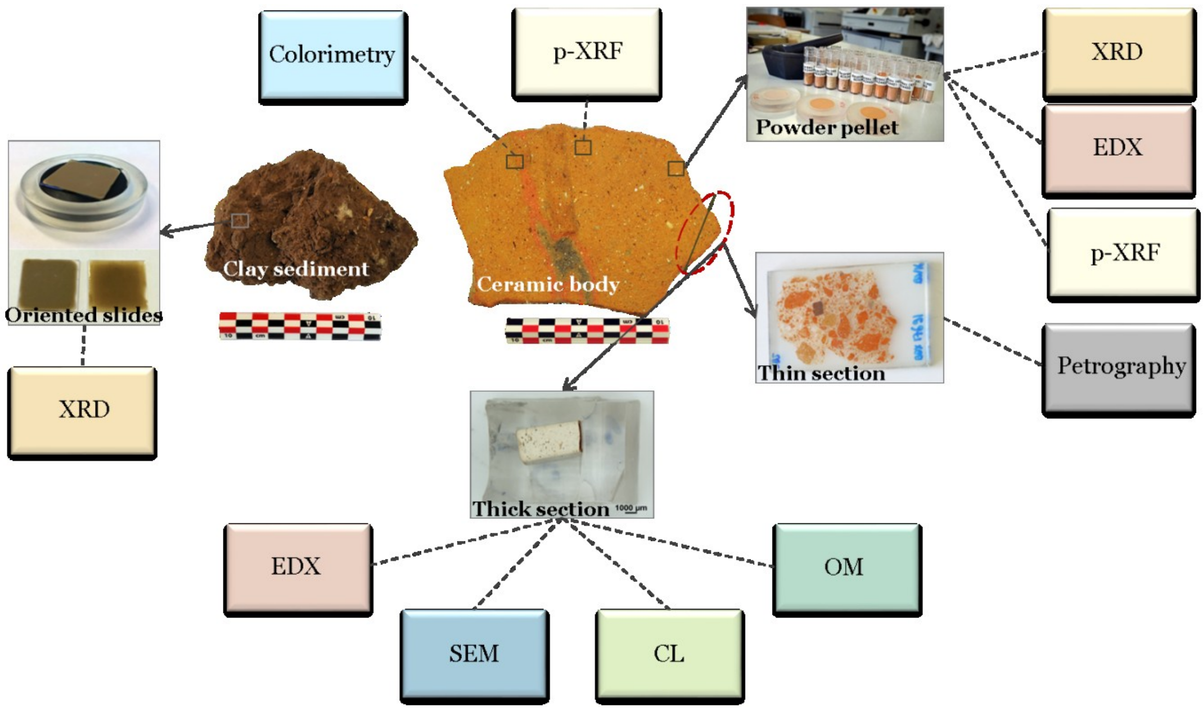


Fig. 3 Multi-scale analysis employed for this thesis research and their sample preparation

Chapter II - A MULTI-SCALE ANALYTICAL APPROACH

As generally indicated in the previous chapter, the field of ceramic studies is wide and complex, allowing obtaining information about: a certain territory and its geo-sources, the production technology, the morphological-style evolution of the ceramic bodies, and the socio-economics dynamics related to the exchange (or trading) goods. Thus, for responding to these different problematics, generally three conditions three conditions must be considered in order to proceed to sampling:

- conclusion of the archaeological study of the territory and / or the archaeological site and completion of the morphological-stylistic analysis of the ceramic collection,
- formulation and implementation of the archaeometric research questions,
- choosing the experimental procedure (Gliozzo, 2020).

In addition, for suitable sampling criteria it should be taken into account the following conditions:

- Is the sample collection *representative*, being linked to chronology, raw material and the manufacturing technologies used
- Another requirement should ensure the *functionality* of the sampling strategy. For example, sampling should always remain flexible enough in allowing the research to be expanded if new questions can appear in the analysis process.
- The last prerequisite for a sampling strategy is that the *suitability* between the types of samples taken and the analytical techniques used, should be taken into account.

These techniques can be **non-destructive**, **micro-destructive**, or **destructive** (Gliozzo, 2020).

Furthermore, the sample preparation is one of the most important point in order to obtain a quality data. A first aspect is to focus on the zone of the interest which will be after analyzed. A second aspect is to be aware that some analysis methods require different shape of sample.
Most of the preparation of the samples is divided in two types: the "thick" samples which are used for reflection observations and the "thin" samples; which are used for the transmission observations (Tian, 2016).
Before studying any sample in the laboratory, a reference number has to be assigned. This consisted in the case of Bordeaux laboratory, of attributing a reference starting by BDX (BorDeauX) prefix and followed by an inventory number. The samples were then photographed in order to preserve, in the form of an image, the state of the object at the time of its entry into the laboratory. As mentioned above, it should be considered that in order to accede to different analysis, different sample preparations are needed.
For instance, **the thick sections** are suited to study the texture of the ceramic body and to specify the chemical composition, thanks to the use of SEM-EDX (Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy), CL (CathodoLuminescence) and OM (Optical Microscopy).
For petrography analysis, **thin sections** are needed, since the polarized light should cross the section in order to determinate the mineralogical composition due to the optical properties of the minerals.
As sherds are generally heterogeneous, powder can be prepared. Then, the **powder pellets** are produced in order to face the heterogeneity of the samples by homogenizing them after grinding them, and setting them as pellets for p-XRF and SEM-EDX measurements. In addition, **the oriented slides** prepared for the clay minerals, allow the precise identification of the clay minerals by XRD.

Chapter III – THE CASE OF DACIAN POTERY

This chapter deals with the main topic of this thesis, presenting a case study of Dacian ceramics. The aim of this research was to explore the relation between the ceramic composition and the manufacturing process. For that, we characterized chemical and mineralogical potteries selected in archaeological context, a corpus of ceramics samples was provided for laboratory (for archaeometrical studies), by the Museums of Argeş County Museum and from "Aurel Sacerdoțeanu" Vâlcea County Museum.
The archaeological discoveries have highlighted the role and status of the Dacian settlement in trade with the Roman world, as well as the existence of a possible center of dynastic power. The area was well known for its richness in salt since prehistory.
The Latin inscriptions, the numerous Roman artifacts and the chronology, give Buridava a special status, even during the 1st century BC (Berciu, 1967, 1981; Berciu and Iosifaru, 1980).
Even though the Dacian city was of a great importance to the region; however, after the Roman conquest, the Dacian city began to lose its prestige (Crişan, 1993).
In this thesis research, ten different ceramic fragments were selected (**Table 1**).

They come from incomplete vessels, discovered during the excavations, dating from the La Tène culture. The dating of the ceramics was made by the archaeologist, by typological and stratigraphic dating methods.

Five wheel-made vessels and five hand-made vessels were provided for investigation by the archaeologists (**Fig. 4**).

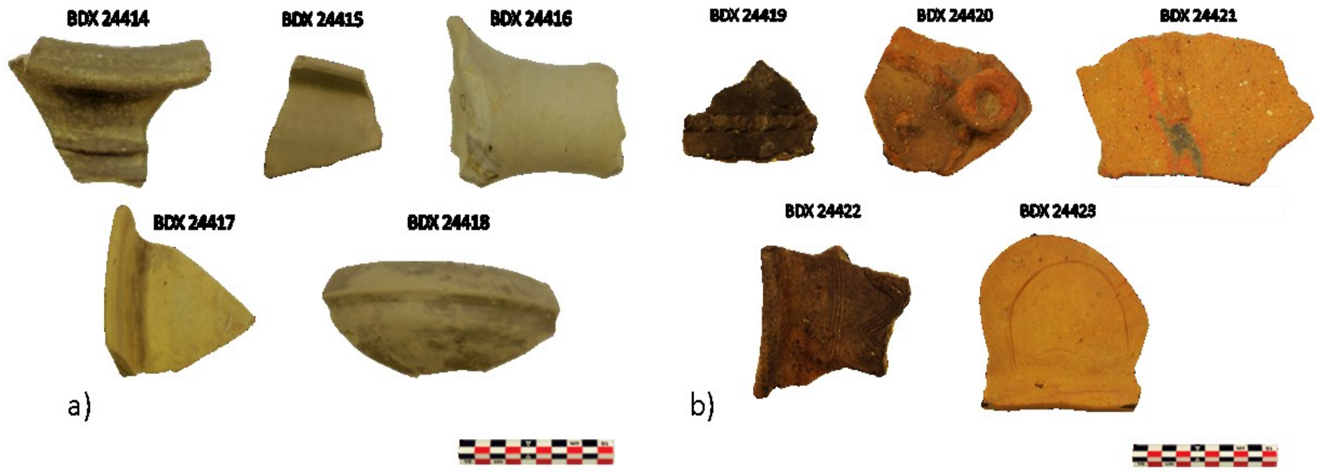


Fig. 4 Fragments of wheel-made ceramics (a) and fragments of hand-made ceramics (b), donated by the Museum of Rm. Vâlcea "Aurelian Sacerdoțeanu", County Museum of History Vâlcea.

They samples were sorted based on macroscopic observations (morphology and topography of the surface and fresh fractures), the colour of the ceramic body, the granulometry and the proportion of inclusions according to their manufacturing technique (Teodorescu et al., 2021).

Table 1 Detailed context and features of potsherds studied in this research (YD - Year of Discovery, Tr.- Trench number)

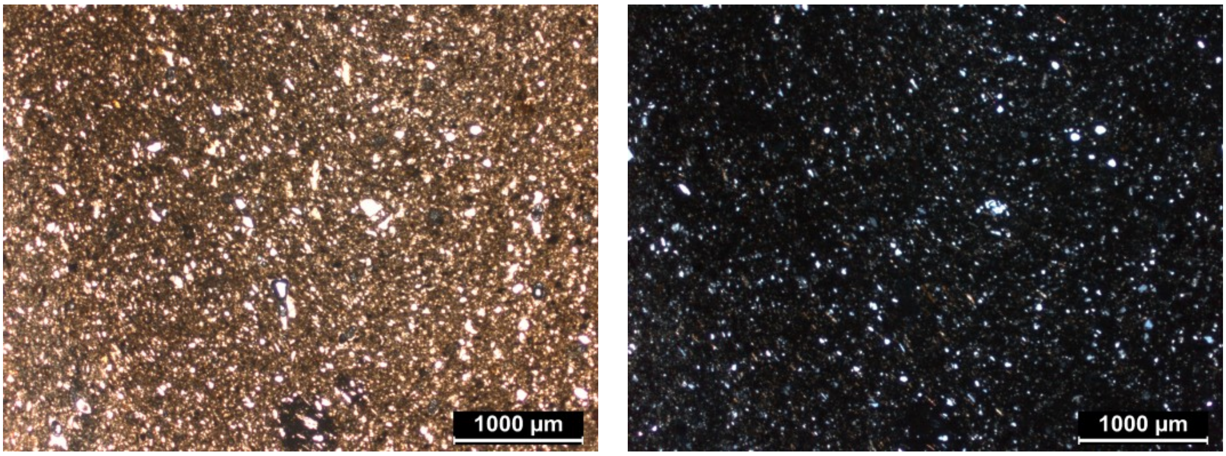
Technology group	Sample ID	Archaeological Context	Category	Object Type
Wheel-made	BDX 24414	YD. 1975, Tr. XXVE	Fine	Pitcher
	BDX 24415	YD. 1976, Tr. XXIX		Fruit bowl
	BDX 24416	YD. 1975, Tr. XXVF		Fruit bowl
	BDX 24417	YD. 1968, Tr. Xa		Bowl
	BDX 24418	YD. 1974, Tr. XXVD		Bowl
Hand-made	BDX 24419	YD. 1975, Tr. XXVF	Coarse	Bowl
	BDX 24420	YD. 1974, Tr. XXVD		Bowl
	BDX 24421	YD. 1968, Tr. Xa		Bowl
	BDX 24422	YD. 1974, Tr. XXVD		Bowl
	BDX 24423	YD. 1975, Tr. XXVF		Bowl

We indexed the samples in the laboratory, from BDX 24414 to BDX 24423. Two types of sampling were carried out for each ceramic fragment, for the preparation of the powder on the one hand and the thick and thin sections on the other hand.

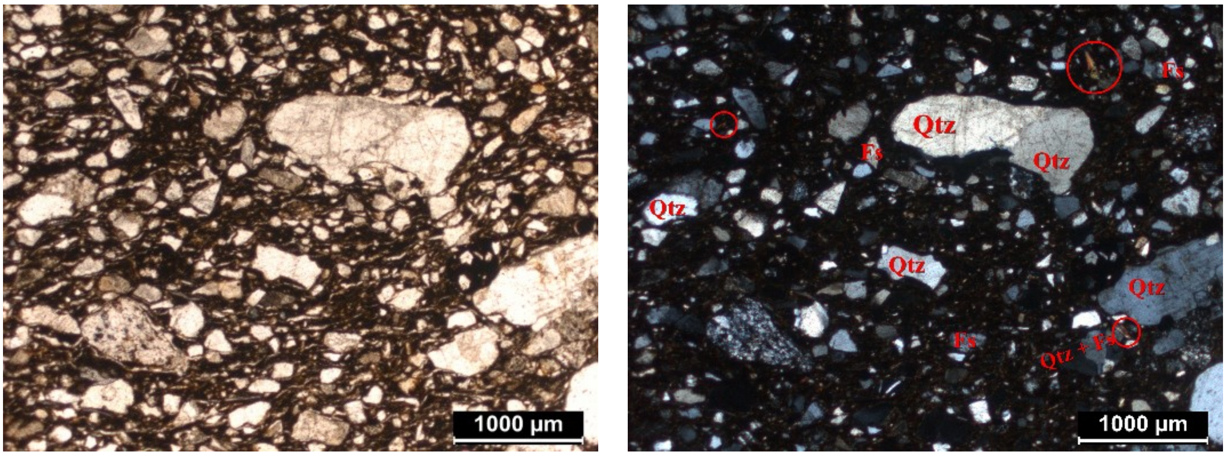
The information about the microstructure of ceramics is first obtained by analysis under a polarizing microscope. Petrographic analyses were performed on all 10 thin sections.

The petrographic analysis made possible to observe the granulometry and the distribution of the inclusions, allowing us to make the initial assumptions about the manufacturing techniques. Microscopically, all ceramic bodies are mainly composed of quartz, feldspars, micas (biotite and muscovite), amphiboles and voids (pores).

The wheel-made samples (from BDX 24414 to BDX 24418) show a fine and compact matrix. All these samples are very rich in very fine inclusions, which do not exceed 40 µm in size (**Fig.** , a - b). The size distribution of the non-plastic components presents unimodal texture. It can be assumed that the clay raw material has been specially purified or selected. The presence of voids is low, demonstrating the compactness of the ceramic. The porosity seen under the microscope indicates a controlled and slow burning in special furnaces, such a two-chamber furnace being discovered at Buridava Dacică (Anghel, 2002, 2011). In contrast, hand-made samples also contain metamorphic rocks and acid plutonic rocks. They present a coarse matrix, with inclusions whose granulometry reaches approximately 2 mm (**Fig.** , c – d). The size distribution of the present inclusions presents a trimodal texture and the porosity observed is mainly represented by elongated voids. Usually, these voids are the primary pores, randomly distributed in the ceramic body. They are formed during the modelling process, when thin layers of water and/or air are trapped between the layers of clay. Then, after drying and burning of the ceramic, the pore size primarily increases (Ionescu et al., 2007).



(**a**) (**b**)



(c) (d)

Fig. 5 Petrographic observations: observation on matrix of BDX 24418 ((**a**) plane-polarized light; (**b**) cross-polarized light); observation of matrix of BDX 24419 ((**c**) plane-polarized light; (**d**) cross-polarized light). The identified minerals are mainly quartz (Q), altered feldspars (Fs) and mica (indicated by the circle)

Cathodoluminescence (CL) allowed having an overall view for all the ceramics. The CL imagery obtained on large surfaces of cross-sections, helped in discriminating minerals and in providing clues of the heat treatment applied.

The **X-ray diffraction analysis** revealed differences due to the deficiency or abundance of some mineralogical phases (**Table 2**).

Table 2 Mineralogical content (wt%) using X-ray diffraction analysis by Rietveld method. (SD: standard deviation). Hematite detected with a value of <1%

Technology group	Sample ID	Illite-Muscovite	Biotite	Quartz	Microcline	Orthoclase	Albite	Anorthite	Hornblende
Wheel-made	BDX 24414	22	3	36	6	5	18	9	1
	BDX 24415	11	4	35	20	1	35	14	3
	BDX 24416	11	3	32	16	5	32	14	5
	BDX 24417	31	8	23	9	5	23	12	5
	BDX 24418	21	7	29	17	1	29	11	4
Hand-made	BDX 24419	19	6	43	3	5	13	7	4
	BDX 24420	14	4	55	7	1	9	7	2
	BDX 24421	16	5	43	2	6	20	6	3
	BDX 24422	25	5	37	14	1	6	7	4
	BDX 24423	20	8	35	8	3	13	10	4

Muscovite/illite reflections were recorded in all samples, even though two of the wheel-made samples (BDX 24415 and BDX 24416) reported lower values than the rest. The content of quartz is generally higher in handmade ceramics. Slightly higher values of microcline and anorthite were recorded in the wheel-made samples compared to the hand-made samples **(Table 2).**

It should be pointed out that illite-muscovite can be used as a thermal guideline. In previous investigations, Rodriguez-Navarro (Rodriguez-Navarro et al., 2003) described that the crystals of muscovite can undergo a noticeable change upon heating at temperatures over 350°C. In addition, the previous investigations showed that illite (muscovite) decomposes entirely at approximately 900°C (Bohor, 1963; Holakooei et al., 2014).

SEM imagery highlighted the microtexture of the ceramic sherds, wheel-made and hand-made. Additionally, SEM-EDX analyses were carried out ceramic powder pellets and thick sections.

The SEM images have outlined a compacted matrix and the presence of fine inclusions present in the wheel-made pots, confirming the observations made by petrography and cathodoluminescence. Moreover, in terms of the dimension of the inclusions, a clear difference corresponding to the two groups of manufacturing techniques was observed (**Fig. 6**).

Based on SEM-EDX, the values acquired for the powder pellets samples were expressed in percent oxides, choosing the average value of the spectrum.

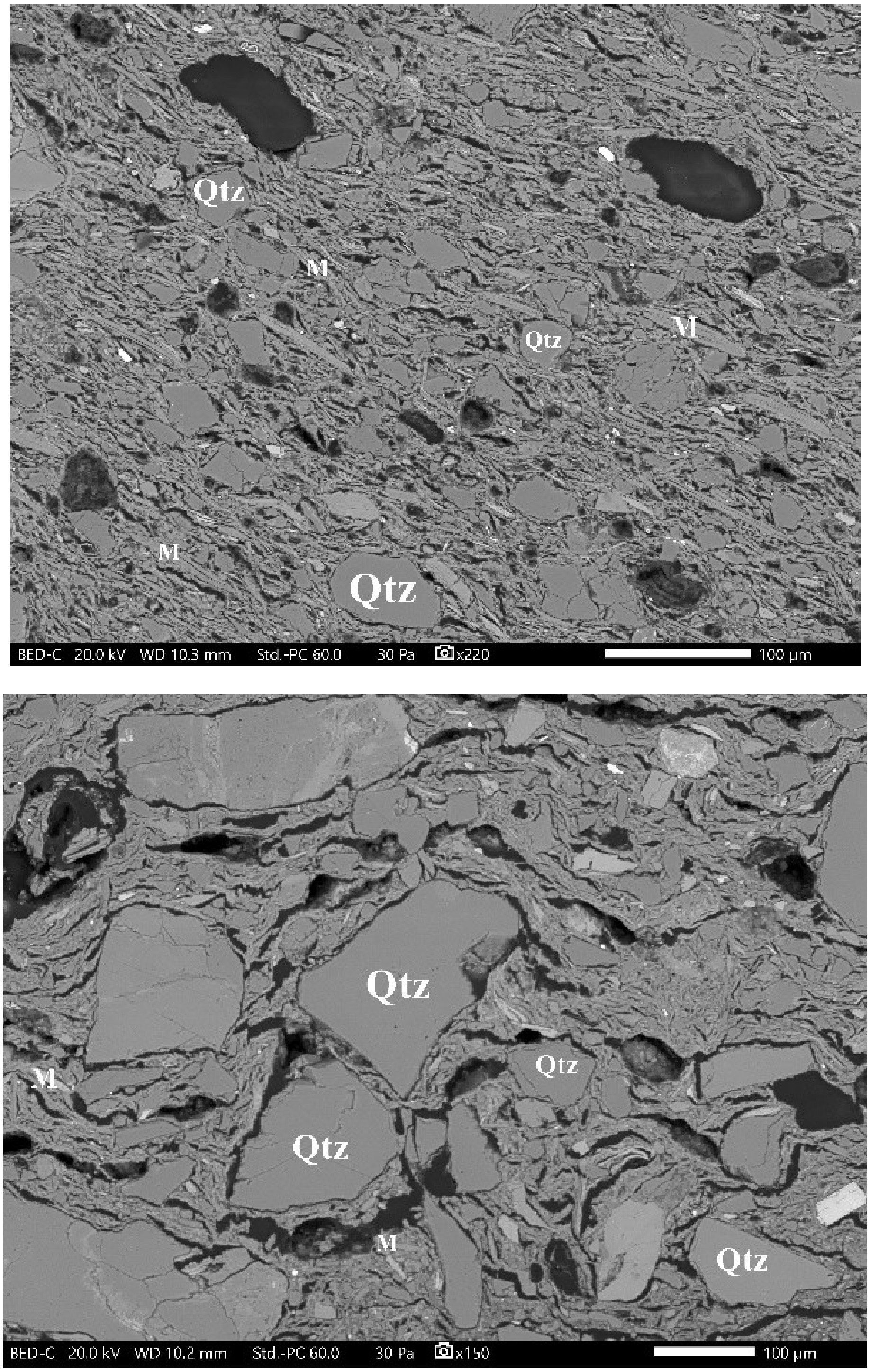


Fig. 6 BSE SEM-images showing quartz (Qtz) and mica (M) inclusions, (**a**) sample BDX 24414 and (**b**) sample BDX 24421; scale 100 µm

Multi-scale analysis methods allowed differentiating two types of ceramic manufacture in ten Dacian vessels, excavated from the archaeological site of "Ocnița-Buridava", Romania.

In the manufacture of all pottery, non-calcareous clay sediments were used. We noticed a significant difference in grain size among the ceramic fragments, where the hand-made ones are coarser. Petrographic analysis, cathodoluminescence imaging and SEM revealed that the proportion of inclusions (mainly quartz, muscovite and albite) is relatively higher in this group.
These initial investigations have generated archaeometric data that will enable the formation of an initial database for future comparisons when other additional data will be collected.

Chapter IV - THE CASE STUDY OF ISTRIAN OLIVE OIL AMPHORAE WORKSHOP TO THE DANUBE PROVINCES IN THE ROMAN PERIOD

The study of amphorae on northern Adriatic during the Roman period awakened a special interest of different researches such as archaeologists, historians and archaeometers. The past of several decades of research on the production and consumption sites of Dressel 6B amphorae made possible nowadays to access to a wide database and bibliography.
In Istria (nowadays Croatia) a general picture was drawn regarding the production and distribution of Dressel 6B from Fažana and Loron (Bulić, 2020; Cipriano, 2020; Machut et al., 2020; Marion and Tassaux, 2020; Szakmány, 2020).
Thus, the present study aimed to develop an analytical methodology of portable X-ray Fluorescence (VANTA-OLYMPUS - C Series), in order to provide answers regarding the questioning of Istrian oil amphorae diffusion.
Beyond the methodological approach, the archaeological objective was to study the export of the amphorae Dressel 6B from the initial production Center (Loron, in present Croatia) to other sites following the Danube region (**Fig.**).

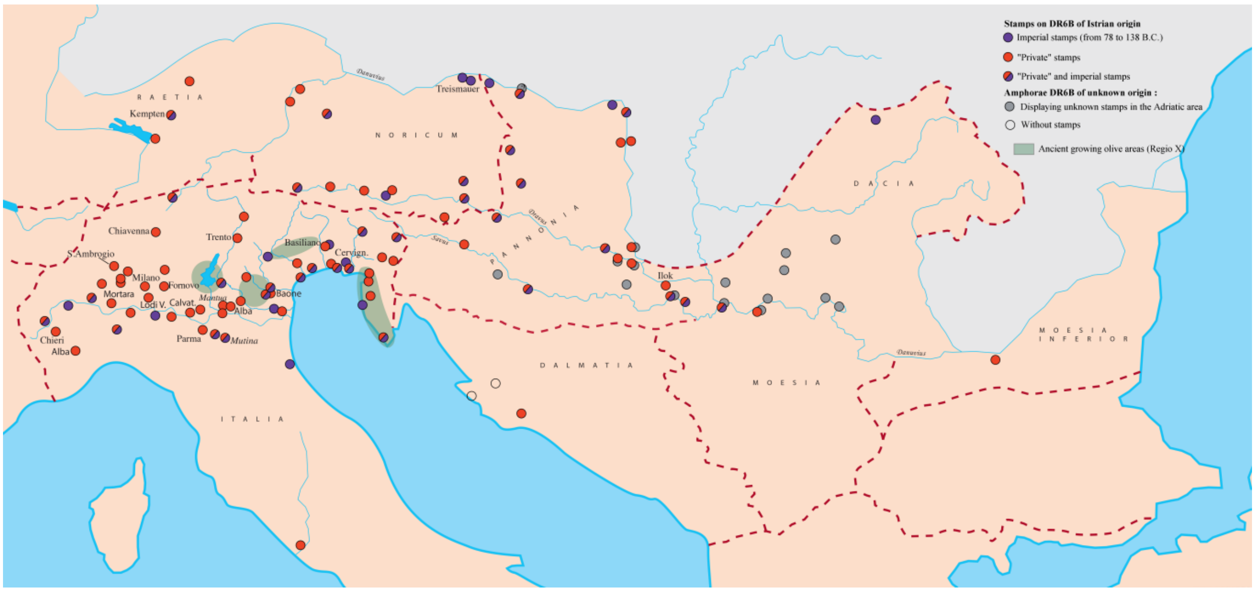


Fig. 7 Diffusion of Dr 6B Istrian oil amphorae. Map designed by Y. Marion (Marion and Tassaux, 2020)

A selection of thirty-three samples by Yolande Marion (Associate researcher at the Ausonius Center - Bordeaux), was analyzed representing the Dr 6B amphora type (**Fig.**). They were sampled from different sites in order to compare their compositions and estimate their origin production (Istria or not?) and to establish a trading route. The amphorae could have been circulating either by river either by land.

Fig. 8 Amphora Dressel 6B type (Machut, 2013)

Thus, a list with thirty three amphorae sampling was made, inclosing different locations: eighteen samples which were donated by the National Museum of Zagreb (Croatia), five samples from Museum of Sisak (Croatia), two samples from Museum of Sirmium (Serbia) and eight samples from Viminacium Study Center (Serbia).

The sampled amphorae, few of them, according their stamp, were produced in Istria (in the atelier of Loron: Crispinill…, Calvia Crispinilla and IMP.AVG. GER– title of the emperor Domitian and in the atelier of Fažana: LAEK B and LESBI and another one TRAVL ET CRIS on the Tergeste’s territory). The others were produced in North-Eastern Italy – APIC and, probably, COSTINI and L. TRE OPTA. The other stamps (OFF (Hedera?) Cl, DAP.AT.P.F, ANT. (Hedera?) MAERIS, M.MAESII, T. FLA. TALANI, COCCEIVSII, TI SECANDIDVS) are unknown in the Adriatic area.

First we began in testing all the parameters of the device. For doing so, we selected few standard samples which allowed us to have a reference value and to test the reliability of the device, as well the measurement accuracy.

Each sample was analyzed on crossed sections (soft polished to 35 μm) on a test surface of 10 mm diameter. For very thin samples a collimation to 3 mm diameter beam spot was necessary to be used.

In addition, each sherd was fresh polished, in order to avoid any external pollution and to obtain a flat surface for better measurements.

It should be however noted that the XRF incident radiation normally has limited penetration, so the elements that are more abundant on the surface are predominantly detected, which may be significantly different from the bulk composition of a sample (Ceccarelli et al., 2016).
When using sample powder, pellets were obtained using the Carver 4350 L pelletizer, from 95% powder mixed with 5% Hoecht C wax.
The accuracy of the results was estimated from measurements carried out on international standard SARM69 (MINTEK, certified) powder and as well on our internal laboratory standards represented by three different types of ceramic bodies, which were previously analyzed with ICP-AES method (in Caen laboratory), with various concentrations of major elements, expressed as oxides percentage (MgO, Al_2O_3, SiO_2, K_2O, CaO, TiO_2, MnO, Fe_2O_3) and trace elements (Ba, Sr, V, Zr, Rb, Y, Zn, Cr, Ni) expressed in parts per million:

- one very homogeneous earthenware (BDX 21063),
- one amphora with very few inclusions (BDX 16854),
- one Ethiopian ethnographic pottery with many inclusions homogeneously distributed (BDX 17729).

All the reference values of these used standards are represented in **Table**

Table 3 Reference values of three laboratory standards and one international standard. Major and minor elements are given in mass percentages and expressed as oxides; trace elements are given in parts per million normalized to 100% (<l.d. – inferior to limit of detection)

Sample ID	Type	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	MnO
BDX 21063	ICP-AES	70.75	26.32	0.78	0.38	0.61	0.22	<l.d.	0.88	0.01
BDX 16854	ICP-AES	60.46	15.37	7.04	0.93	9.8	2.38	1.04	2.81	0.18
BDX 17729	ICP-AES	65.78	18.14	10.61	1.04	0.58	0.87	<l.d.	2.44	0.35
SARM69	MINTEK	69.23	14.97	7.46	0.81	2.46	1.92	0.82	2.04	0.13

-

Sample ID	Type	Ba	Sr	V	Zr	Rb	Y	Zn	Cr	Ni
BDX 21063	ICP-AES	143	65	61	42	114	22	98	31	35
BDX 16854	ICP-AES	383	246	145	145	148	28	n.d	n.d	n.d
BDX 17729	ICP-AES	262	56	90	1171	112	115	n.d	n.d	n.d
SARM69	MINTEK	583	113	163	282	69	30	71	232	55

Furthermore, the tests were followed by other steps such as selecting the time measurements for the samples, the reproducibility of the measurements and of course deciding making the measurements using GeoChem mode, which is an internal calibration of the device from the factory. The calibration was assured with the help of dozens of SARMs from a wide geochemical range (Frahm, 2018).
In addition, the methodology was applied on the amphorae samples, on soft polished fractures. With the help of PCA it was possible to create groups and to observe better the distribution of the samples (**Fig.**).

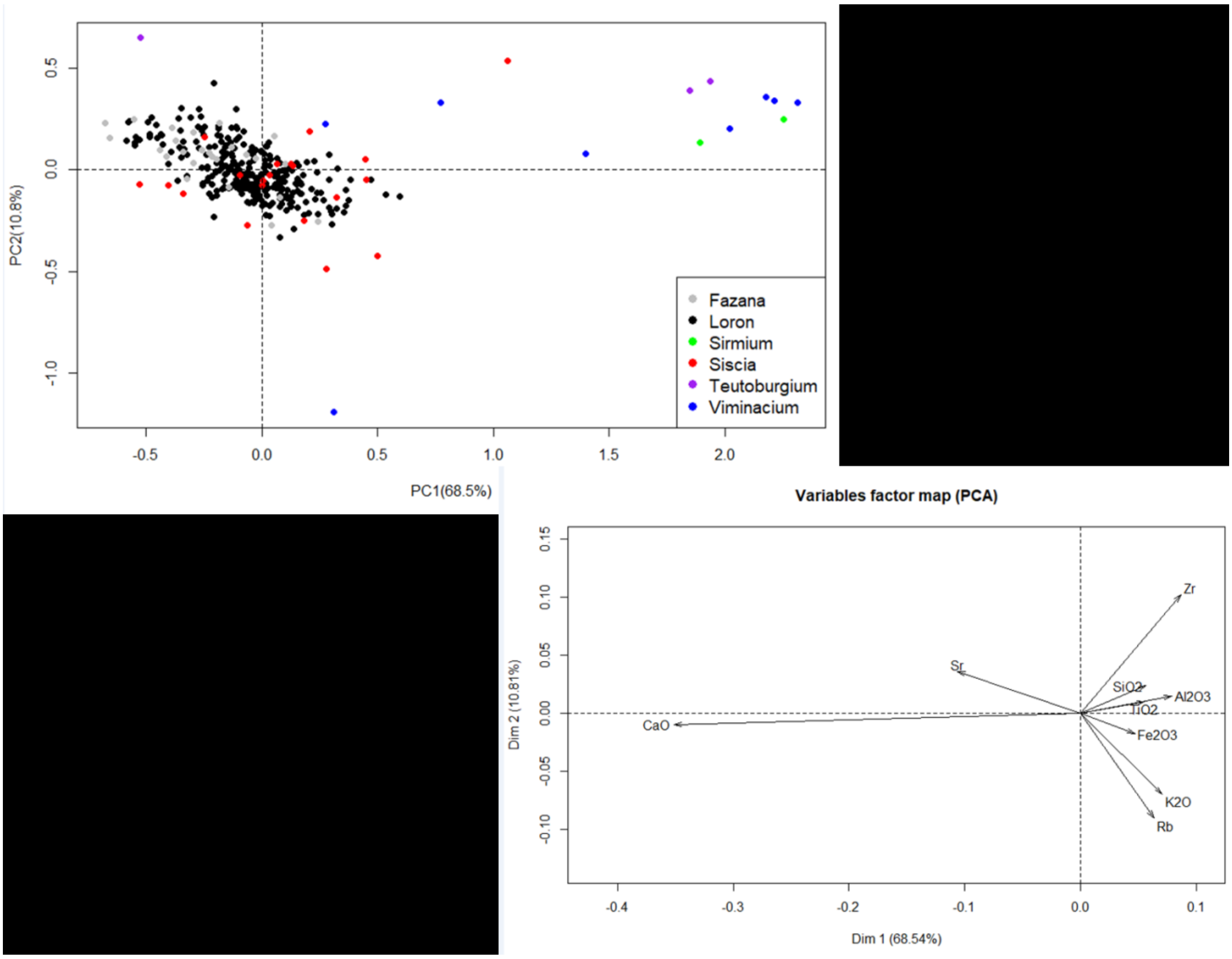


Fig. 9 Scatter-plot and multivariate diagram comparing the obtained data, from each archaeological site

Moreover, since in our case we had a provenance study with and reference group where we could compare our results with it, we applied the outlier detection in the multivariate space, using a statistical method named Mahalanobis Distance (MD), using R program. Thus, the statistical approach that we used allowed us to answer to the question regarding the provenance of the amphora bodies. Only one sample (BDX 25423) out of thirty-three, could correspond to the Loron production (**Table 4**).

Table 3 Calculated Mahalanobis distance between the archaeological reference group and each individual sample

Sample ID	Mahalanobis Distance	Sample ID	Mahalanobis Distance
BDX25412	24,94	BDX25429	6,99
BDX25413	9,92	BDX25431	13,09
BDX25414	23,62	BDX25432	10,06
BDX25415	9,98	BDX25433	20,73
BDX25416	9,49	BDX25434	9,43
BDX25417	6,99	BDX25435	12,56
BDX25418	6,90	BDX25436	25,74
BDX25419	6,88	BDX25437	18,04
BDX25420	9,91	BDX25438	26,06
BDX25421	7,67	BDX25439	22,25
BDX25422	4,31	BDX25440	15,39
BDX25423	**2,70**	BDX25441	15,44
BDX25424	6,43	BDX25442	32,09
BDX25425	7,25	BDX25443	20,78
BDX25426	8,36	BDX25444	20,98
BDX25427	8,02	BDX25445	19,81
BDX25428	7,03		

The same approach was made using the Fažana corpus. However, in this case, all the samples were observed as outliers.

Altogether, the present case study shows that p-XRF can be a powerful tool for preliminary analytical approach in the case of amphorae samplings and can provide an initial classification based on elemental composition, helping to refine and prioritize the sample selection.
Nevertheless, it should be underlined the fact that in order to have a better view of the data and to link better all these information, additional analysis and measurements should be taken into account such as petrography, XRD and SEM-EDX.

Chapter V - THE ACTION OF SALT IN THE MANUFACTURING PROCESS IN HEBRON'S CERAMIC

This chapter shows the complexity regarding the study of the ceramic materials, underlining better the physico-chemical changes that can occur into a ceramic body. For this a case study on Hebron potteries was chosen, showing the effects and influence of salt (NaCl) on the colour and the mineralogical transformations especially in Ca-rich ceramic bodies. In order to conduct this research, raw clay material and pot sherds were collected from the modern production at Hebron (**Fig.**).

Fig. 10 Potsherds collected by the archaeologist V. Roux (Préhistoire et Technologie, UMR 7055, CNRS, University of Paris Nanterre) representing the "pink" sherds (image on left) and "white" sherds (image on right)

Salt has long been used by potters in various forms because they knew the different effects produced on their ceramics, especially a whitening effect (Brooks et al., 1974). The question of the physico-chemical properties induced by the presence of salt continue to intrigue, as several scientific studies have been conducted to better understand the effect of halite in ceramic production, from an analytical point of view. For example, Rye (1976) highlighted conspicuous cubic voids in thin sections, which were interpreted as pseudomorphs of salt crystals. The effects produced during firing by the presence of sodium chloride in a Ca-rich ceramic body (obtained from a carbonate-rich clayey material) are numerous and wide-ranging (Combès and Louis, 1967; Bearat et al., 1989)

An ethnographic survey was recently conducted in Hebron (Palestinian territories) by Valentine Roux (French Director of Research at the CNRS, member of the Prehistory and Technology Laboratory UMR 7055). She observed and described the potters traditions using salt as an adjuvant in the making process. Hebron potters explain the addition of salt in the clay paste for a whitening effect. She described the Hebron's ceramic tradition meaning the manufacturing process shared by the potters, the variety between the workshops and the finished products. In addition, V. Roux observed the same effect of whitening of water jars in the Jodhpur region (India). The potters from India are using directly salted clay, adding sawdust and crushed granite or gravel. In the end, they will obtain a white jar with high porosity. Apparently, the secret of the potters to obtain a jar that keeps water fresh is to prepare a paste, which is porous and permeable, so that the water will percolate through the clay walls (Roux, 2015).

In her study, she found that potters used four raw materials for producing utilitarian vessels: yellow clay sediment (noted as YC), red clay sediment (terra rossa) (noted as RC), sand and salt (**Fig.**). The volumic proportion used in the preparation between yellow clay and red clay is 2/3 part for 1/3. The sand is 1/6 of the total volume. The potters believe that the addition of the red clay, gives more plasticity to the mixture in order to prevent the clay from shrinking too fast while drying and to avoid the accidents during the firing process

Fig. 11 Raw materials: yellow and red clay sediments and sand (left image); wedging the clay with a pug mill (right image). At this stage the salt is added to the clay material (photographs by V. Roux)

In this study, the samples consist in four modern potsherds and four raw materials (which are used by the Hebron potters in their manufacture), collected in Hebron. In addition, for enlarging our understanding of the whitening effect and the parameters involved in the mechanism of the firing process, eighteen experimental samples were prepared, using the same clays used by Hebron's potters. These samples were placed on an aluminium container and allowed to air-dry at room temperature for 48 hours. Each of them was composed of 20 g of clay sediment (previously desegregated), to which salt was added in different proportions: 0%, 2% and 5% of total clay by weight. Due to the absorption effect, the red sediment was mixed with 10 ml of water, and the yellow sediment, with 15 ml.

Before analyzing the potsherds and the experimental bricks, the **grain size** distribution of the raw materials was first measured using a Laser Diffraction particle size analyser (Horiba LA-950) device in order to characterize their properties and evaluate clay plasticity. The raw material-samples were treated with oxygenated water and sodium hexametaphosphate. They were diluted before pipetting to 300 ml, and placed in the grain size sampler.

The **colour of the ceramic bodies** was studied and monitored using a Konica Minolta CM-2600D portable spectrophotometer (360-740 nm) with a spectral resolution of 10 nm and a diameter analytical area of 10 mm. The standard illuminator was D65 using CIE 1964 10° standard observer. The calibration was performed with a black and white reference set to SCI (spectral reflection included) mode.

Cathodoluminescence (CL) was then utilized to provide data on the shape and size of inclusions, grain size/distribution and pore spaces in polished section of the fired samples.

The XRD measurements were performed on powdered samples to identify the mineral constituents of both raw materials and fired briquettes and for the orientation of deposits to discriminate the clay mineral species. In addition, a Rietveld refinement was applied by using TOPAS software, to quantify the mineral phases. For analyzing clay minerals on oriented slides,

it was first necessary to eliminate the carbonates without attacking the clay phases. For this, a weak acid solution with a buffer at pH 5 was used. The oriented slides were then submitted to ethylene glycol and heat treatments (at 350°C and 550°C) according to Bouchet et al. (2000).
SEM imagery (JEOL - IT500 HR) facilitated the observations of the micro-texture of the modern potsherds and briquettes in thick sections, as well as the progress of the mineral transformations upon firing. The acquisition of the spectra (**SEM-EDX**) was done on thick polished sections of the ceramic bodies and on pressed pellets obtained from the powder of the samples. All results were expressed in wt% oxides (normalized to 100%), making possible to quantify the major and minor elements (Na_2O, MgO, Al_2O_3, SiO_2, SO_3, K_2O, CaO, TiO_2 and Fe_2O_3), while Cl was expressed in simple wt%.
In the end, the study confirmed the role of halite in the bleaching of ceramics with a high CaO content. Indeed, colorimetric measurements carried out on experimental bricks with different salt contents, showed a significant loss of the red component as the salt concentration increased, as well as a loss of the yellow component to a lower degree (**Fig.**). These colorimetric losses are associated with a decrease of their saturation. At the same time, the clarity has significantly increased.

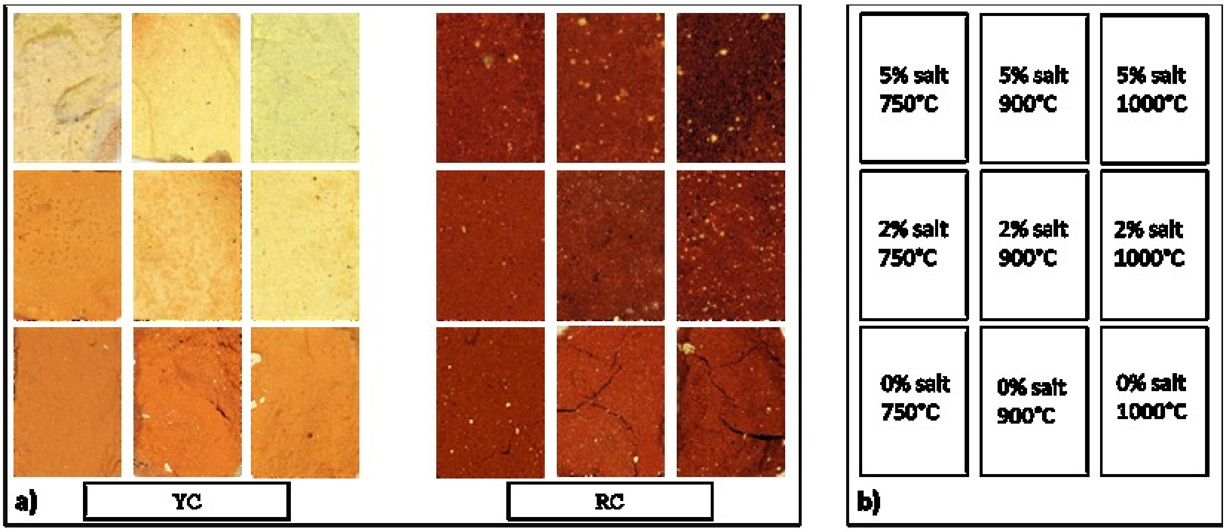


Fig. 12 a) Colour surface of experimental samples made from yellow (YC) and red clay (RC) sediments; (b) the protocol used per sample (salt content and firing temperature)

These factors allow for the empirical characterization of the whitening effect observed visually and confirm the main role of salt in this process, beyond the effect of temperature alone.
The mineralogical phase changes recorded in the experimental bricks have also been highlighted by different methods.
Cathodoluminescence images showed these changes in the material. Qualitative and quantitative XRD results allowed for the documentation of the evolving proportions for these different phases, relatively to the increases of salt content and firing temperature. In fact, the process of alteration of clay minerals to form new calcium silicates appears to take place at a lower temperature in the presence of salt than has been generally thought. In this regard, significant

differences in the microstructure of the calcareous clays with 5% salt are observed with the appearance of Ca-silicates (gehlenite, wollastonite) as early as 750°C.
Furthermore, the colour changes, due to the trapping of Fe ions in the crystal lattice can now be explained (Nodari et al., 2007). Although Mossbauer measurements – which could be the best method to apply in such cases - have not yet been carried out, Chevalier et al. (1976) have shown that gehlenite, anorthite or wollastonite crystals can trap Fe ions in their lattice, by substitution of Al^{3+} and Ca^{2+}. They pointed out that ferric oxide is known to be produced when biotite reaches high temperatures, such as 900°C, and that crystallization improves at 1000°C. In addition, R. Noller and H. Knoll (1983) conducted investigations by making possible the insertion of Fe^{3+} into the lattices of Ca-Mg-Al silicates. They observed that the difference in coloration could be explained for synthetic silicates by a polarized binding of Fe^{3+} ions in a disordered matrix. Therefore, the experimental data presented here provides significant explanatory evidence for the action of NaCl on the whitening of calcareous clays. By lowering the temperature at which calcium silicates are formed, NaCl serves to reduce the necessary temperature at which the bleaching effect commences.
Moreover, the result obtained by the SEM-imagery has made it possible to more accurately describe and assign the presence of rhombohedral voids (**Fig. 2**).
Results show that they are due to the dissolution of the carbonates, contrary to what has been put forth previously in the scientific literature where voids were attributed to the dissolution of salts (Rye, 1976).
Returning to the Hebron ceramics specifically, it is clear from the experimental results that the two colorations obtained (pink and white) can in fact be explained primarily by a difference in salt concentration in the initial mixture rather than other factors.
Other measurements currently underway will further consider the effect of salt on the porosity of ceramics. These observations will be compared with ceramics produced elsewhere at other sites (notably in India) where similar practices with salt addition, have been reported.

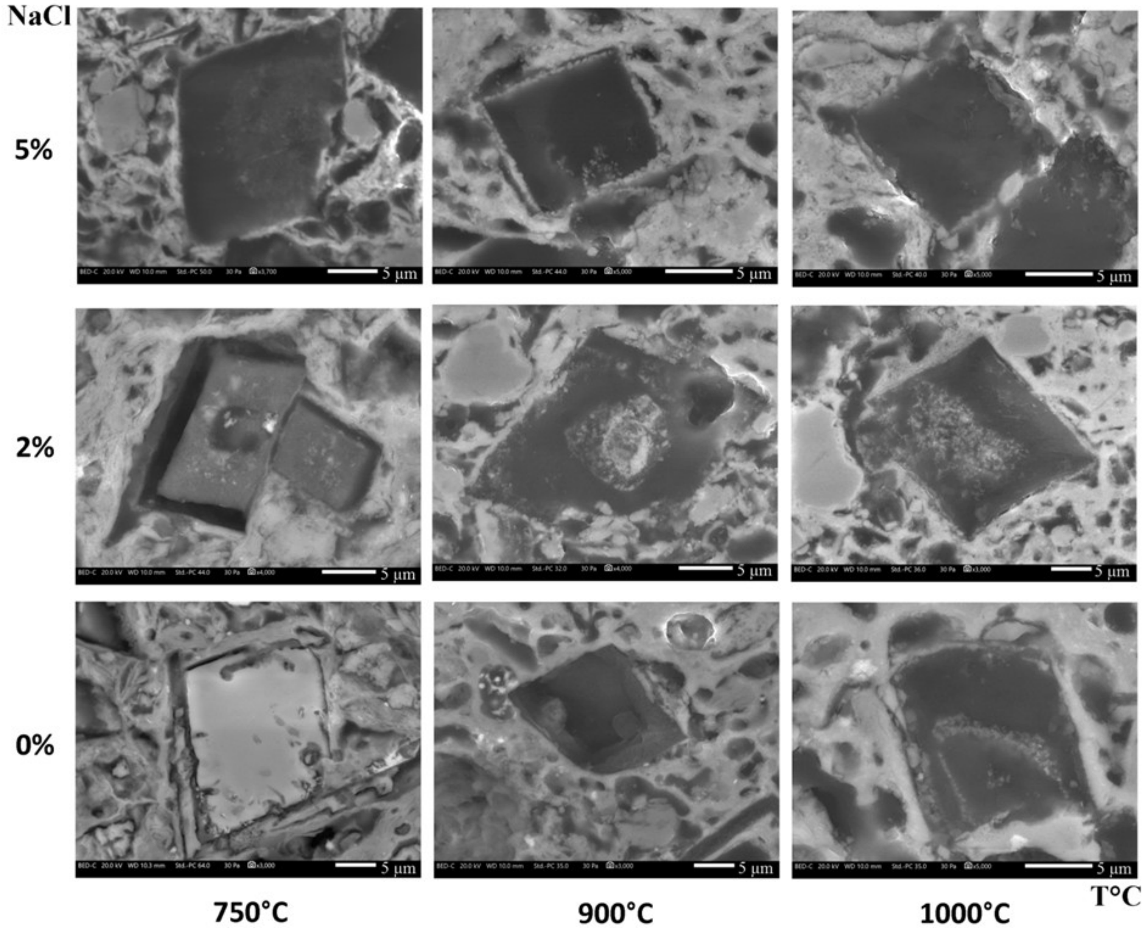


Fig. 2 SEM-BSE images of calcite or rhombohedral voids present in the matrix of the experimental brick

The study confirmed the role of halite in the bleaching of ceramics with a high CaO content. Indeed, colorimetric measurements carried out on experimental bricks with different salt contents, showed a significant loss of the red component as the salt concentration increased, as well as a loss of the yellow component to a lower degree. These colorimetric losses are associated with a decrease of their saturation.

At the same time, the clarity has significantly increased. These factors allow for the empirical characterization of the whitening effect observed visually and confirm the main role of salt in this process, beyond the effect of temperature alone. The mineralogical phase changes recorded in the experimental bricks have also been highlighted by different methods. Cathodoluminescence images showed these changes in the material. Qualitative and quantitative XRD results allowed for the documentation of the evolving proportions for these different phases, relatively to the increases of salt content and firing temperature. In fact, the process of alteration of clay minerals to form new calcium silicates appears to take place at a lower temperature in the presence of salt than has been generally thought. In this regard, significant differences in the microstructure of the calcareous clays with 5% salt are observed with the appearance of Ca-silicates (gehlenite, wollastonite) as early as 750°C.

Chapter VI – GENERAL CONCLUSIONS, PERSONAL CONTRIBUTIONS AND FUTURE PERSPECTIVES

Conclusions

The multiscale approach carried out in this thesis research was efficient to investigate the complex and heterogeneous structure of ceramic materials, with the help of three different case studies.

The first case concerned the Dacian ancient ceramics, from La Tène culture where, the main aim was to determine the chemical and mineralogical characteristics of ceramics, making possible to discriminate the ceramic artefacts according to their manufacturing.

The applied methodology made possible to analyze ten Dacian pottery sherds that were found in the archaeological site of Ocnița-Buridava, Romania. The study made possible to discover the presence of non-calcareous ceramic bodies. In addition, we observed a large difference in grain size between the ceramic sherds, as for example, the ones made by hand being coarser.

The research started with the petrographic analyzes where we observed that all ceramic bodies were mainly composed of quartz, feldspars, micas (biotite and muscovite), amphiboles and voids. With the help of cathodoluminescence and SEM images, we noticed that the proportion of inclusions was higher in the handmade ceramic group. Furthermore, the granulometric distribution suggested that these non-plastic inclusions were originally present in the clay and not added by the potter. The XRD analysis highlighted the presence of illite-muscovite in our samples, which we used as a thermal guide (Rodriguez-Navarro et al., 2003). Therefore, the results showed that the firing temperature of the Dacian ceramic sherds was relatively low (below 900°C). Hence, this research made possible to notice the differences in texture, in chemical and mineralogical composition between the ceramics according to their manufacturing technique.

The second case we focused on a provenance study of Adriatic amphorae in the Danube's region, with the help of a new device, which was bought at the beginning of the year 2021 in the laboratory of Archéosciences Bordeaux, a p-XRF VANTA-OLYMPUS (C Series).

Following all the processes for setting parameters and calibration, the methodology was applied on the amphorae samples, on soft polished fractures. With the help of PCA it was possible to create groups and to better observe the distribution of the samples. Moreover, since in our case we had a provenance study with a reference group, we could compare our results with it. We applied the outlier detection method in the multivariate space, using a statistical calculus named Mahalanobis Distance (MD), using R program. Thus, the statistical approach allowed us to make a hypothesis regarding the provenance of the amphora bodies. Only one sample (BDX 25423) out of thirty-three, could correspond to the Loron production.

This study made possible to clarify the reliability of p-XRF, by making the analysis without any special preparation and demonstrating the practicability of this device (without special preparation of the samples).

The last case was focused on the ceramic manufacturing process in Hebron nowadays, by implementing another strategy, which is defined as ethno-archaeometry. This research helped us to understand the role of salt as a bleaching agent and to better understand the transformations of the ceramic material during its manufacture. Furthermore, ceramic analyzes on experimental

bricks were made, in order to reconstruct the production processes from the selection of raw materials to the firing of the vessel (Cantin and Mayor, 2018). First we analyzed four modern potsherds and four raw materials (used by the Hebron potters in their manufacture), collected in Hebron. For enlarging our understanding of the whitening effect, eighteen experimental samples were prepared, using the same clays used by Hebron's potters. The study confirmed that the role of salt in the bleaching of ceramics was visible only on the samples with a high CaO content. The mineralogical phase changes in the experimental bricks have been observed and recorded with the help of cathodoluminescence, of qualitative and quantitative XRD analysis and SEM-EDX analysis. The results allowed the observation of the evolving proportions of different phases, relatively to the increases of salt content and firing temperature. We observed that the process of transformation of clay minerals to form new calcium silicates appeared to take place at a lower temperature in the presence of salt than what was been generally expected. Moreover, we managed to accurately describe and assign the presence of rhombohedral voids discovered in the experimental brick with SEM imagery. Results showed that they are due to the dissolution of the carbonates, contrary to what has been put forth previously in the scientific literature where voids were attributed to the dissolution of salts (Rye, 1976).
By studying these three case studies, this thesis achieved to answer to the main challenges such as employing a suitable methodological approach for the study of Dacian potsherds (creating a database which can be used for future projects) and as well in applying different analytical technical methods of materials science which provided an answer to different archaeological and ethnographical questionings.

Personal Contributions

These years of research, I could attend many trainings and sessions offered by the laboratories teams. These scientific internships enabled me to implement and finally be autonomous with the use of the techno-analytical methods specific to materials science, required to analyze the ancient ceramic materials, thus contributing to solve archaeological questions.
Furthermore, I achieved to:

1. Understand the archaeologist's questions and contribute to solve its tipping points: identification of raw material and their provenance thanks to physico-chemical characterisation, knowledge of production technics and trading routes
2. Take into account the complex nature of the ancient ceramics:
   - 2.1. Define and discuss the chronology thanks to the stratigraphic data and the typological information when they are known.
   - 2.2. Observe and take into account the alteration state of the sherds.
   - 2.3. Prepare the samples according to the different types of analysis to be performed.
   - 2.4. Define the best methodology for analyzing ceramics depending on the questioning.
3. Build an archaeometric database of Dacian ceramics from the southern of Carpathians, that will be increased by new incoming data, to enable comparative studies
4. Observe the differences regarding the texture, chemical and mineralogical compositions among ceramics, depending on their manufacturing technique and confirm the role of salt as a bleaching agent in ceramics with a high CaO content.

5. Provide data regarding the provenance of amphora bodies, from the East, making a link between the present countries France, Italy, Croatia and Romania.
6. Demonstrate that portable equipment (pXRF) can be a powerful tool for a preliminary analytical approach (based on elemental composition in this case) that can provide a first classification of ceramics, thus helping for the selection of samples which will undergo further and full laboratory analyses.

<u>Perspectives</u>

Since different cases have been investigated and presented in this work, some challenges have inevitably appeared during research and some issues need to be further studied.

For example, in the case of Dacian ceramics it's important for future studies to raise an archaeological/ethno-archaeological question/enquiry in order to be able to select the pottery that can answer the questions posed by archaeologists.

In addition, Dressel 6B amphorae have also been discovered in Romania. It would be interesting to approach the Romanian museums that can provide us the needed samples for study and add the obtained results to the existing database.

Regarding the last case of research, where salt is playing an important role in the manufacturing process in Hebron's ceramic and other ongoing measurements will further investigate the influence of salt on the porosity of ceramics. These observations will be compared to ceramics made in Jodhpur (India) where similar salt addition practices have been reported. In addition, this study will allow to use this implemented methodology and to explore other corpuses where salt was used in the manufacture of ancient archaeological ceramics.

However, in all the case studies above, it should be underlined the fact that the key point in having a successful research, consists in defining archaeological issues or questionings, thus selecting an appropriate corpus of samples to be analyzed. Of course, all these steps require a multidisciplinary collaboration, which begins in the field, continues in the laboratory, and in the end can be valuable for publications and/or museum exhibitions (Gliozzo, 2020).

In addition, possibility to develop intense archaeometric research in Romania in the future are very high since there is a large opportunity to use efficient equipment from several research teams (such as the laboratory from Pitesti, CRC&D AUTO) working on modern materials. It is sufficient to put into practice the skills acquired in the framework of this thesis and to strengthen the links with archaeologists and museum curators.

Thus for the future studies it should be enlarged the number of samples from the present studied corpuses, but also adding other ceramic collections (as mentioned, from closed areas) and to take advantage of the knowledge of the presented methods in this thesis, to use them to other types of materials (such as glass and metals), even if maybe other different methods should then be included (specially for metals).

The project of the thesis was made between the University of Pitesti and the University Bordeaux Montaigne, making possible in obtaining a double diploma in materials science and in physics of archeomaterials. The thesis research was focused on three case studies, thus each of them has benefited different financial support:

- Characterisation of heritage materials using material engineering techniques, from archaeological excavations at south of Carpathians – a collaboration between Argeş County Museum, Vâlcea "Aurelian Sacerdoțeanu" Museum and University of Pitesti. The research funded by a doctoral grant from University of Pitesti and an ERASMUS mobility support between University of Pitesti and University Bordeaux Montaigne.
- The case study of the diffusion of Istrian olive oil amphorae workshops to the Danube provinces in the Roman period – research based on a previous program of a collaboration between Ausonius and Archéosciences Bordeaux. The work on this thesis is part of the continuation concerning the questions of circulation and diffusion of amphorae towards the Danube areas. The research has been funded by a grant obtained from the Institut Français de Roumanie (IFR) - Bucarest and a LabEx Science Archeologiques de Bordeaux grant (ANR-10-LABX-52).
- Mineralogical transformations due to salt whitening agent in Hebron ceramics – This research is part of the project "Traditional knowledge of the Hebron's potters and Heritage Resilience (Palestinian Territories)" in collaboration with the archaeologist V. Roux (Préhistoire et Technologie, UMR 7055, CNRS, University of Paris Nanterre), which will allow to discover the challenges of an ethnographic corpus with ceramic traditions, making possible to test our interpretive methods in archaeometry.

During the 3 years of research (2019-2021), I was employed as a scientific research assistant at the Regional Research and Development Centre for Innovative Materials, Processes and Products for the Automotive Industry (CRC&D-Auto), at University of Pitesti, under the guidance of Prof. Conf. Cătălin Ducu.

Most of the investigations presented in this thesis have been carried out in the laboratory of Centre de Recherche en Physique Appliquée à l'Archéologie de l'Institut de Recherche sur les Archéomatériaux (IRAMAT-CRP2A, UMR 5060 Université Bordeaux Montaigne – CNRS) in Bordeaux, France, nowadays under the name of Archéosciences Bordeaux UMR 6034.

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