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CHARACTERIZATION TECHNIQUES OF CLAYS FOR THE ARCHAEOMETRIC STUDY OF ANCIENT CERAMICS: A REVIEW

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ABSTRACT

The provenance of ceramic artefacts is one of the fundamental issues in ceramic analysis and is related to the location a ceramic object was produced or manufactured. This, in turn, refers to the clay source from where the ancient potter exploited their ceramic raw material. Being aware of the local geology is crucial to the identification of potential raw materials for the ceramic manufacturing. Thorough examination of clays in terms of composition, plastic behavior, shrinkage and particle size, is necessary for the evaluation of their suitability for ceramic production. A combination of several analytical techniques can contribute to the identification and characterization of a ceramic raw material. The choice of the proper ones depends on different factors, such as precision, cost, time, expertise, availability and the way a researcher would combine them. The present study aims to unfold the criteria of clay sampling and investigate the appropriateness of the most relevant analytical techniques for the fully characterization of ceramic raw materials and thereafter provenance of ceramics made from them.

KEYWORDS: ceramic raw material, clays, physical properties, mineralogy, analytical techniques

1. INTRODUCTION

The physical sciences applied to study of ancient ceramics aim to contribute to the reconstruction of their life cycle from production through distribution to use, and then to help in the interpretation of the processing cycle. The reconstruction of the production technology of ceramics involves determining, a) what raw materials were used and how they were prepared and, b) how the ceramics were formed, surface treated and decorated, and fired (Tite, 2008).

Since only a few decades the archaeometric research regarding investigation of potential choice of raw (clay) materials for the ceramic manufacturing and the identification of provenance, has progressed considerably providing significant data and information employing analytical techniques. The groundbreaking treatise by Anna O. Shepard in 1956, entitled "Ceramics for the Archaeologists" brought a breakthrough in archaeometric research. The principles set by Shepard for the integration of Archaeology and Archaeometry have been a key topic in many conferences, books, and articles (Rice, 1987).

In modern archaeological methodology and practice, the ceramic analysis includes the (archaeological) typological classification and the stylistic analysis, the dating of the artefact and the technological investigation. The archaeometric approaches refer to: (a) the characterization and sourcing of the ceramic raw material, (b) the manufacturing technology, (c) the content of the vessels (ie. their capacity load and their eventual residues), and, (d) the absolute dating of the artefacts (Hodges, 1976; Liritzis *et al.*, 2002, 2013, 2020; Koh *et al.*, 2017).

Technological analyses and characterization can be strongly benefited by simple and low-cost methods of characterisation of the raw materials, such as colour and hardness or plastic behaviour. These are easy and straightforward to be obtained especially when an extensive collection of materials is considered. Furthermore, the range of variability of the samples studied can be quickly assessed based upon certain performance characteristics. If a more detailed characterization of the material is needed, then the use of several instrumental techniques is necessary.

As far as the ceramic analysis is concerned, since the middle of the last century (Shepard, 1956; Peacock, 1977), the petrographic study has been regarded as a particularly low-cost method and a valuable tool as well, because its use, especially for coarse specimens, can provide answers to critical archaeological queries. Their aplastic inclusions (ie. inert material added naturally or intentionally by the pot-

ters) often include fragments of minerals and rocks, as well as fragments of re-used ceramics sherds (grog), bones, fossils and plant residues. This content can offer valuable information through which the researcher can unravel provenance issues, commercial transactions and cultural exchanges; thus can enable archaeologists to infer about social organization of ancient cultures at the local level and their interaction with each other. The determination of the chemical composition and the microstructural characterisation of ceramic artifacts can lead to the definition of criteria that will assist in the reconstruction of their technology (Baziotis *et al.*, 2020). The combination of petrographic ceramic analysis and geological field survey to identify and sample raw materials suitable for ceramic manufacture, their processing and study provide important information about the possible interaction between ancient potters and the landscape. However, petrography via thin sections is not always adequate for provenancing pottery. Thus an integrated approach by using a series of analytical (spectroscopic) techniques, such as X-ray powder diffraction, scanning electron microscopy, geochemical analyses, and several others, is indispensable (Wiseman and Williams *eds*, 1996; Xanthopoulou, 2019; Liritzis *et al.*, 2020).

2. SEEKING SUITABLE RAW MATERIALS FOR CERAMIC PRODUCTION

In archaeometric studies which deal with the ceramic technology and the provenance of ancient artefacts such as pottery or ceramic building materials, the analysis of the raw materials is particularly important. Ceramic fabrics are often composed of various types of rocks and/or minerals among other constituents, which occasionally are extraneous to the geolithology of the area where the ceramic artifact was unearthed. It is similarly possible that these ceramic fabrics are the result of various admixtures involving more than one clays and temper. The variability of rock fragments and minerals employed as temper can be indicative of the lithologies encountered in the area of origin of the ceramic artifact.

Ethnographic studies suggest that the potters do not collect their materials at random, but select the portion having the most appropriate properties and the least variation (Rye, 1981). Additionally to the clay exploitation, potters collect also other materials for using them as temper and pigment, diluent agent, fuel and shaping tools. Regarding the clay sources, they could be both easily accessible and widely shared or were "secret" locations and not disclosed to outsiders or competitors, as seen in Bangkok, Thailand (Graham, 1922). In other cases, individual

pottery, workshops, families or communities had the rights to mine or sell clay. Ceramic workshops may own specific deposits that are inherited along family lines (e.g. Bailén, Spain; Curtis, 1962). The clay may be exploited by the potter or his/her assistant, or traded and purchased, depending on the cultural context.

The exploitation of clay sometimes was influenced by traditions, taboos or rituals. In Papua, New Guinea, for example, only married women without children could collect clay (May and Tuckson, 1982). They must wear traditional dress during the clay selection, and they could not smoke, chew betel, or speak pidgin, whilst no outsider was allowed to be a witness.

Another issue of concern in the ethnographic studies was the distance the potters were travelling to obtain the clays. Arnold (1980, 1985), after an investigation among the ethnographic literature, tried to quantify the areas within which potters moved to acquire their clays, tempers, slips and pigments. From a dataset of 110 different cases, he found that for the clay collection, the distance from the potting location to the clay source varied from less than 1 km to 50 km. In 31 cases, he found for the temper procurement the range was from less than 1 km to 24 km, for slips and paints the distance could reach up to 800 km.

The selection of the raw material may be limited by different external factors, i.e. the land ownership and its control, seasonal access, the depth of the overland and as mentioned above the distance of transport. As the distance increased, so the costs of production and of transport made the process proportionally less viable economically, except for specialized materials required in small quantities. The raw materials were usually transferred without any previous treatment, except for the removal of large stones or other impurities.

The choice and the procurement of the clay and temper can be examined through analysis, based on the identification of the geology of the sources. Knowledge of the regional or the local geology is crucial when a researcher seeks for ceramic raw materials and especially in studies of provenance. Geological maps illustrate the surface geology giving a picture of the various lithologies which contain evidence of the mineralogy and therefore of the composition. However geological maps can be complex and

contain various geological formations which are not always relevant with the specific studies. Furthermore sediments are usually described in a general way, such as conglomerates or silty clays, or sands whereas detailed description of small-scale deposits are lacking. In those cases the searching in literature or in geological reports is necessary. Nevertheless the study of the geological maps before a sampling campaign remains crucial and may assist to a great extent in the choice of the sampling locations.

Moreover, potential deposits exploited during ancient times are either exhausted or obscured due to geomorphological changes or urbanisation, and are usually not accessible anymore. Vice versa, some of the more recent clay deposits may not have been exposed during the ancient times. Archaeological structures which give evidence of ceramic production, such as kilns or workshop ruins may offer clues for the local provenance of clay through kiln wasters and tools. In regions where the ceramic activity is currently ongoing, personal communication with the local potters and ethnographic studies could provide information about the location of the more recent ceramic raw material sources.

Thus, bearing in mind the aforementioned criteria and factors which may affect the efficiency of a sampling campaign, seeking suitable ceramic raw material could be enhanced by the following:

- Knowledge of archaeological sites, which were ceramic production centers during antiquity. It would complement the research, the communication with modern traditional potters, who have a sense of the landscape and the available resources.
- Study of the geological formation using geological maps and literature research including various geological reports of the investigated region.
- Direct observation of the outcrops in the field and traveling across the landscape.
- Use of the appropriate equipment, such as a topographic map, a global positioning system (GPS) device, the Munsell color chart, a geological hammer, bailer, sample bags, a camera, notebook and indelible pen marker and a water container (Fig.1a)
- Testing the potential raw material in the field by molding the clay and evaluating their plasticity (Fig.1b).

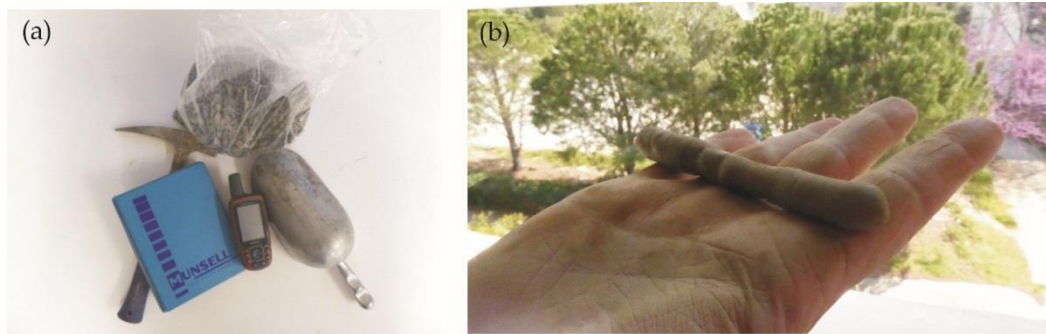


Figure 1 (a) Useful equipments for a sampling campaign; (b) on-site testing of the potential raw material.

3. COLOR DETERMINATION

The colour and hues of the final object are directly related to the chemical composition of the raw material, the preparatory stage (fillers, clay body, formation and drying) and the firing conditions (temperature and atmosphere inside the kiln), as well as, the geometry of the ceramic artifact (Molera *et al.*, 1998). In some cases the archaeological ceramics may sustain color degradation due to weathering conditions during the burial period (Pradell *et al.*, 1995; Molera *et al.*, 1998).

Earth materials found in various geological formations, such as Red Desert Soils in California, Arizona, and Nevada; the White Sands in New Mexico; the Yellow River (Hwang Ho) in China which carries yellow sediments *etc.*; were among many others which were often used as coloring agents in the development of human cultures since prehistoric times. As earth materials were modified for the vessels construction, the color was inherited to them. The Soil Color can be contributed to distinguish and identify horizons and eventually to classify them. The weathering of the rocks usually affect the soil color, since various oxides, such as iron and manganese oxides as well as organic matter change the primary soil color.

The color of the clayey sediments, the experimental ceramic briquettes and the ceramic samples are usually determined using the Munsell Soil Color Chart (2000). The chart of Munsell is considered the most common practice in the determination of colour because it can give a first assessment of the ceramic material and is simple, easy, and free of cost method. However, due to the time consuming and the error-prone of the subjectivity of the observer, alternative improved methods have been proposed. Those include the Photoshop RGB (Red, Green, Blue) indexes, using stereoscopic images as well as the use of digital micro USB microscope (Bratitsi *et al.*, 2018). Moreover, Visible Near Infrared spectroscopy (VNIR) contributed to a more accurate determination of colour, since tristimulus values from visible

region can be obtained. NIR spectrometer may provide results not only for colour coordinates but also about the reflectance spectra, which contain more information about mineral identification (Karoutzou *et al.*, 2019; Xanthopoulou *et al.*, 2019).

4. TECHNOLOGICAL AND PHYSICAL PROPERTIES OF THE CERAMIC RAW MATERIALS

Ceramics were the first composite material humans created by combining the four basic elements: earth, water, fire and air. Seeking the most suitable earth material for the ceramic production, they reached to the clay. Clay is a naturally occurring, earthy, fine-grained material that forms a coherent, sticky mass when mixed with a limited amount of water. The added water makes the clay plastic, a property that allows it to be deformed by applying a force and to retain the new shape when the force is removed. Another significant property of clay is its hardness and durability after its firing (under various temperatures and conditions).

The term 'clay' refers to a particular group of minerals, a category of rocks and soils in which these minerals predominate and a specific particle size that constitutes the major fraction of those minerals, rocks and, soils. The main factors controlling the properties of clays have been described by Grim (1962) as follows:

- Depositional context: primary or secondary clays.
- Texture: particle size and grain size distribution.
- Clay mineral composition: the identity, the abundance and the nature of crystallinity of the clay minerals present.
- Organic content: the kind and the amount of plant remain or organic molecules absorbed on the surface of clay-minerals particles.
- Presence of exchangeable ions or salts.
- Non-clay minerals: relative abundance, identity, shape, particle size and distribution.

Ceramic raw materials are sedimentary deposits and comparatively recent products of the weathering of the parent and, consequently older rocks. The depositional context refers to the location of the disintegrated material relative to the parent rock. By this criterion clays are either considered primary (residual) or secondary (transported or sedimentary).

Primary or residual clays are those deposits remaining in more or less the same location as the parent rock from which they came from. Since the alteration and decomposition of the parent rock (depending on the composition) is not always complete, residual clays usually contain coarse, unaltered and angular fragments of the parent material. The inclu-

sions which may form the constituents, most commonly, are quartz, feldspar and clay minerals. They can also comprise low organic content (less than 1%) and are often coarse and low plastic.

Secondary or transported clays are found in deposits or beds some distance from the parent rock, having been moved by streams, tides, waves, erosion, glaciation, wind or other forces (Fig. 2a; b and c). Secondary clays are more abundant than primary, more homogeneous and finer, as a result of sorting and redeposition. Depending on the conditions and the transport, secondary clays may be subdivided into marine clays, fluvial clays, lacustrine clays, volcanic clays, aeolian clays and glacial clays.

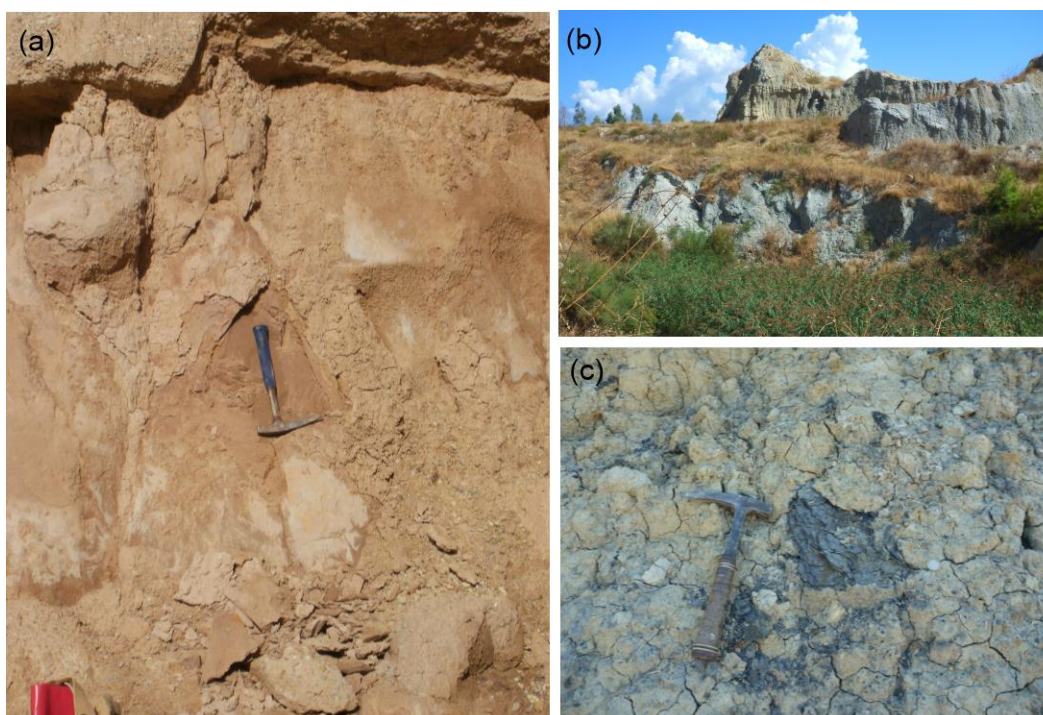


Figure 2 Outcrop of Pleistocene deposits in Trapeza village of Achaia in Greece; (b) and (c) Pliocene marly-clay deposits of a yellowish to white and a light grey to blueish color, which occasionally bear ample lignite beds in Solomos village of Corinth in Greece (Xanthopoulou, 2019).

Marine clays are probably the largest clay deposits and are found in coastal locations around the world. They are formed when very fine clay particles are carried by rivers to their ultimate marine destination and are settled out after contact with and adsorption of the ions in brackish seawater. Glacial clays are generally coarse and unsorted, high in impurities and useful for structural products or earthenwares. Lacustrine clays are exposed usually in lenticular deposits and they are often abundant in organic matter. Flint clays are stiff, organic-rich, low plasticity clays deposited in swamps.

The process of formation and its extent comprise the factors which determine the specific clay assemblages. Primary clays have usually more uniform

compositions, whereas secondary ones, being transported, have generally more complex compositions, owing to the mixing of minerals during transport.

The availability of primary and secondary clay sources determines to some degree the types of pottery that can be produced. White-bodied and high-fired wares, such as stoneware, require specialized raw material, whilst low-fired earthenwares can be produced from a variety of clays that can be found anywhere (Rye, 1981).

The principal groups of clay minerals include a number of types, which are kaolinites, halloysites, allophanes, illites, chlorites, montmorillonites, vermiculites and attapulgite-palygorskite-sepiolites. Below the most important clay minerals containing

in clay rich sediments used for making pottery are summarized as well as how they attribute to the properties of them (Grim, 1962; 1968):

- *Chlorites* have generally poor workability and fire to dark colors.
- *Halloysites* have a similar chemical composition with kaolinite, but a distinct crystal morphology. They may have poor workability, which results in cracking during molding and shaping; they must be fired in slow steps, to avoid fracture.
- *Illites* have varied compositions. Their crystal structure usually contains potassium, iron. The vitrification of illitic clays begins at a relatively high temperature (< 1000°C).
- *Kaolinite*, due to its crystal structure, does not readily allow fusion in the crystal lattice. Therefore kaolinitic clays are often refractory and withstand high temperatures. They are stable and can be fired rapidly, without damaging the vessel. Certain kinds of kaolinitic clays are relatively free of impurities such as iron or other colorants, and they fire to a white color. Their plasticity varies with the particle size and shape.
- *Montmorillonites* have fine particle size and allow a range of combinations in the fusible elements composing the crystal lattice. They have a very high plasticity and shrinkage during drying. Thus, in order to prevent cracking montmorillonites cannot be used alone. A low proportion (less 10%) of them in a mix may be useful because it improves the workability. Their fired color usually is brown, red or gray. Their strength during drying and their capacity to form films, make them suitable as constituents for pigments, slips and decorative coatings.

4.1 Plasticity

Plasticity of the clay-rich sediments is a fundamental property, since it defines the technical parameters to convert a ceramic mass into a given shape by application of pressure (Norton, 1938; 1974; Moore, 1963; 1965; Astbury *et al.*, 1966; Singer and Singer, 1979). In clay minerals system, plasticity is defined as *“the property of a material which allows it to be force repeatedly deformed without rupture when acted upon by a force sufficient to cause deformation and which allows it to retain its shape after the applied force has been removed”* (Perkins, 1995). There is direct link between plasticity of clays and the morphology of clay mineral particles. Their plate-like particles slip each other with the addition of water. As water is added, plasticity increases up to a maximum value, depend-

ing on the clay type. Clay workers are keen to call “fat” a highly plastic clay such as ball clay and “lean” clay the relatively non-plastic clay like kaolin, but it is very difficult to express these terms in measurable quantities. In the industry, plasticity is also referred to as “extrudability”, “ductility”, “workability” or “consistency” (Handle, 2007). The latter term relates to states of the raw materials, such as dry powder, granules, plastic body, paste and slip, which are dependent on the liquid content (Reed, 1995). Adding water to dry clay, will first increase the cohesion, which tends to a maximum when the water has almost filled the pores between the particles. The minimum amount of water to make a clay paste is called the “plastic limit” (PL). As the water increases, the clay body changes to another condition and becomes paste. In this state the yield strength reduces, the clay body becomes wet and sticky to the finger and cannot maintain a molded shape. The water content at which the behavior of clayey soil changes from plastic to liquid, is defined as the “liquid limit” (LL). The difference in the water amount at these limiting points is expressed as the “plasticity index” (PI) and is related to the dry mass of the clay.

In the ceramic manufacture, the measurement and control of the plasticity of the clay are necessary for the optimization of the processing conditions. The plasticity can be influenced either by the clay itself or the molding process (Henry, 1943; Carman, 1949; Marshall, 1955). As far as it concerns the clay, factors such as moisture content, mineralogical composition, grain size, type of exchangeable cations, the presence of salts and organic material, can affect the clay plasticity (Talwalkar and Parmelee, 1927; Wilson, 1936; Whitaker, 1939; Lawrence, 1958; West and Lawrence, 1959; Dumbleton and West, 1966; Barna, 1967; Onoda, 1996; Schmitz *et al.*, 2004; Bergaya *et al.*, 2006). Process-related factors are the application of pressure, temperature and characteristics of the water and additives used (Jefferson and Rogers, 1998; Malkawi *et al.*, 1999; Ribeiro *et al.*, 2004; Uz *et al.*, 2009; Zentar *et al.*, 2009).

Several techniques have used for the measurement and characterization of the plasticity of a clay body. Atterberg’s method is the most widely used technique for plasticity determination. The Atterberg’s limits (Atterberg, 1911) express the water contents at certain limiting or critical stages in soil behavior and they are used additionally as mean of soil classification and they are useful to the correlation of fine-grained soils. Casagrande (1958) standardized Atterberg test limits through the development of a liquid limit device rendering the method operative and independent. The determination of liquid and

plastic limits, as well as of the plasticity index is usually conducted following the ASTM (American Society for Testing and Materials) testing proce-

dures. Fig. 3 shows the case of Corinthian samples and how are distributed according to the liquid limits (LL) and plasticity index (PI).

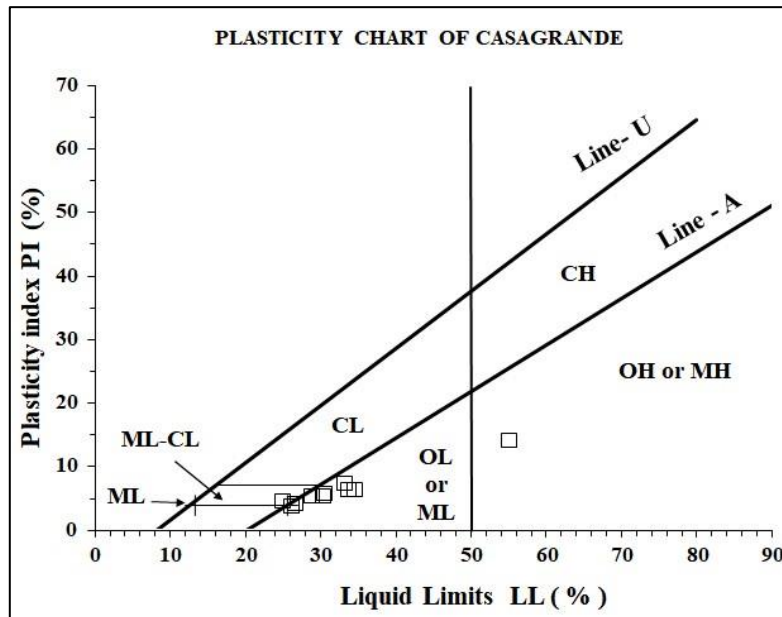


Figure 3 Plot on Casagrande's plasticity chart (after Casagrande, 1958) of Achaean clayey samples. Abbreviations: ML-CL= Soils of clay and silt, ML=Silt of low plasticity, OL or ML= Organic silt or silt of low plasticity, OH or MH= Organic silt or silt of high plasticity, CL= Clay of low plasticity or lean clay, CH= Clay of high plasticity or fat clay. The vertical line represents the liquid limit 50% that divides the chart into four main fields.

Another well-established classification chart is proposed by Marsigli and Dondi (1997) and is related to the molding behavior of materials basing on their variability of plastic limits and plasticity index. In Fig. 4 cases of raw materials collected from different areas in Greece (Achaea, Corinth and Xylokastro)

and Sicily are projected on Marsigli's and Dondi's chart. Sicilian samples seem to be plastic enough and suitable for pottery; whereas the greater number of the rest samples are more suitable for brick production.

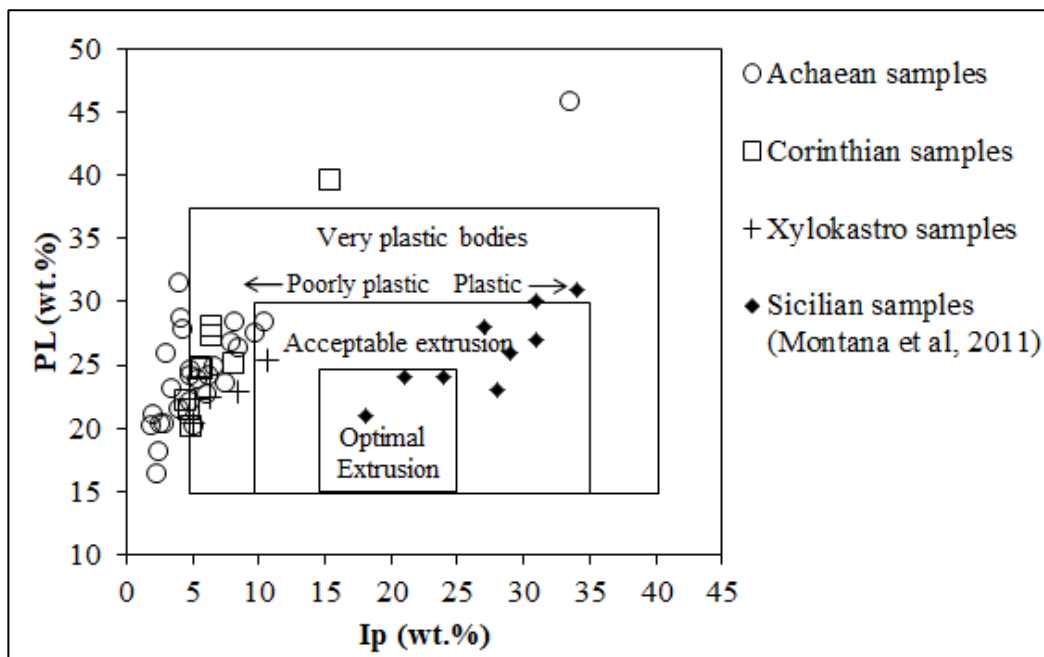


Figure 4 Classification chart of molding behavior using plastic limits (PL) and plasticity index (Ip) values (after Marsigli and Dondi, 1997)

4.2 Particle size analysis

The grain size of raw materials influences many properties of the finished products as well as the behavior of the ceramic body during its manufacturing. Specifically the grain-size distribution affects the behavior of the material during the shaping and drying procedures. In the fields of geology, soil science, agriculture, engineering and construction, clay is defined as the earth material having particles finer than 2 micrometers (μm). The extremely small particle size of clays gives them the properties and behavior of colloids, i.e. the ability of fine particles to disperse or suspend in another material (solid, liquid or gas).

The process of formation and its extent comprise the factors which determine the specific clay assemblages. Primary clays have usually more uniform compositions, whereas secondary ones, being transported, have generally more complex compositions, owing to the mixing of minerals during transport.

There are several proposed methods in literature that can be used in the determination and description of particle size of sediments. These methods are differentiated concerning the grade of precision and each method defines the particle size in a different way, measuring different properties of the same material (Konert and Vandenberghe, 1997; Iatrou, 2007). The most accepted and classical technique is the pipette, sieve and aerometer methods. The pipette method is based on Stokes' law and is suitable for finer particles (Iatrou, 2007). The sieve method defines the diameter of the particle size as the length of the hole through a particle passes. This method is suitable for the determination of sand and gravel-sized sediments. The aerometer method is also widely used and is based upon certain time and periodic density measurements (Centeri *et al*, 2015). Pipette method was considered more accurate, whereas the aerometer method was simplest. Both practices were time-consuming, carrying with errors and demanding a large quantity of sample. Last decades, new methods, such as laser diffraction, are proposed for fast and accurate measurement of the particle size, whereas needs a very small quantity of sediment.

The obtained data from particle size analysis could be plotted in grain-size scales depending on the boundaries of grain-size scales. J.A. Udden's scale is widely proposed and is based on a constant ratio of two between successive class boundaries together with terms for the classes by C.K. Wentworth (Tucker 2012). According to Wentworth grade scale gravel-sized particles have a diameter of >2 mm; sand-sized particles have diameters from <2 mm to >62.5 μm ; silt-sized particles have diameters

from <62.5 μm to >4 μm ; and clay is <4 μm . Sedimentologists use mostly the systems described either by Shepard (1954) or Folk (1954, 1974). Both classification charts comprise triangular diagrams that allow the description of the sediments based upon the field they are projected in.

Figures 5a and b display the distribution of the particle size for the same samples which were collected by sedimentary deposits in Corinth, Greece (Xanthopoulou, 2019). In this research, samples were examined in terms of particle size, using a laser diffraction system. The first diagram (on the left) is based on Folk's system, which uses the term mud (silt plus clay) and classifies the class of clay sediments under $2\mu\text{m}$. On the contrary, Shepard's diagram (on the right) divides mud in clay, silt and sand and defines the class of clay under $4\mu\text{m}$. The Folk's ternary plot was obtained after the calculations of the Gradistat software wherein the clay size scale adopted is under $2\mu\text{m}$ (Blott and Pye, 2001), in contrast to Shepard's scheme, where clay size is defined under $4\mu\text{m}$ (Shepard, 1954). Based upon the choice of the chart, it is observed that the Corinthian samples are classified into various fields that are differentiated through their clay content.

4.3 Mineralogical determination

Several analytical techniques are used to characterize compositionally the ceramic raw materials. Their mineralogical content is commonly determined through X-ray powder diffraction (XRPD), which can successfully identify the crystalline phases present in a material, even when these are too fine to be discernible through other techniques, such as, for example, the optical microscopy. Consequently, it is considered a very useful analytical tool in the study of ceramic raw material analysis since it permits to gain significant information not only for their coarser constituents but also for their finer, i.e. the clay minerals. The presence of the latter imparts to the clay paste various properties on which potters are usually based for selecting the clay that is most appropriate for the typology of their end ceramic product. The determination of clay minerals through XRPD is achieved through the analysis of multiple oriented preparations using the clay fraction (<2 μm) of the raw material after separating it employing gravitational sedimentation procedures, minimizing the non-clay constituents. The clay fraction water solution is poured on three glass slides and let to dry over night under laboratory conditions. After drying, the one of them is subsequently saturated with ethylene glycol or magnesium or glycerol solvation and the second one is heated to 490°C or 550°C , depending on the type of the clay mineral, such as the

smectite or the kaolinite, which collapse in heating (Moore and Reynolds, 1997). This procedure assists to mount the clay minerals as oriented aggregates on glass slides, namely to force the clay particles to lie flat. In this way the reflections of the clay minerals

and specifically those which are traced in about the same degrees 2θ are significantly enhanced. Figure 6 displays an example of XRD patterns obtained after three different treatments for aliquotes of the same sample (Xanthopoulou, 2019).

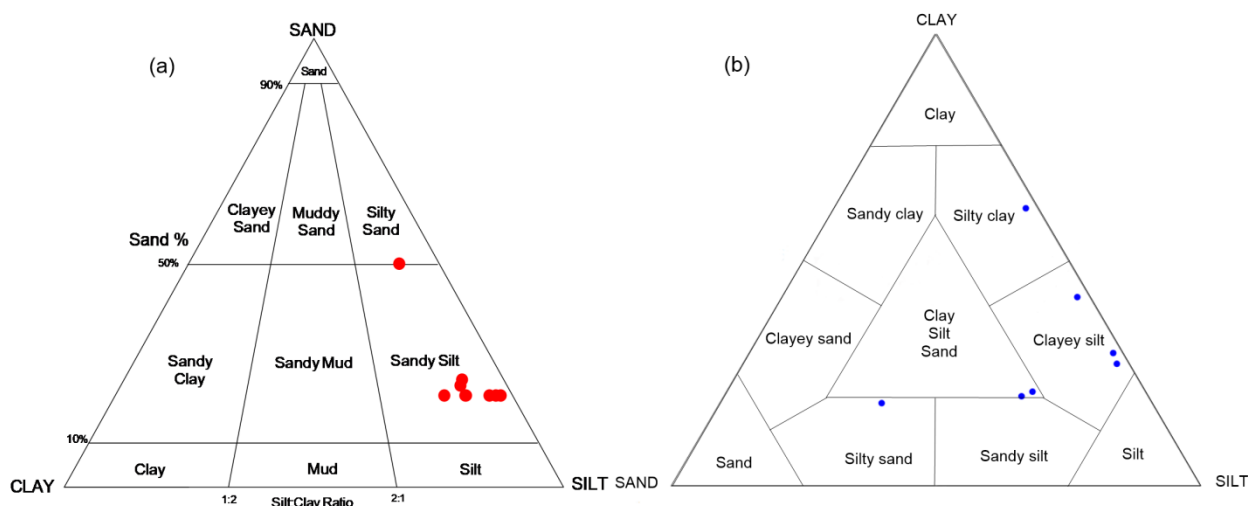


Figure 5 Distribution of Corinthian clay samples on (a) Folk's and (b) Shepard's classification chart, based upon their particle size (Xanthopoulou, 2019)

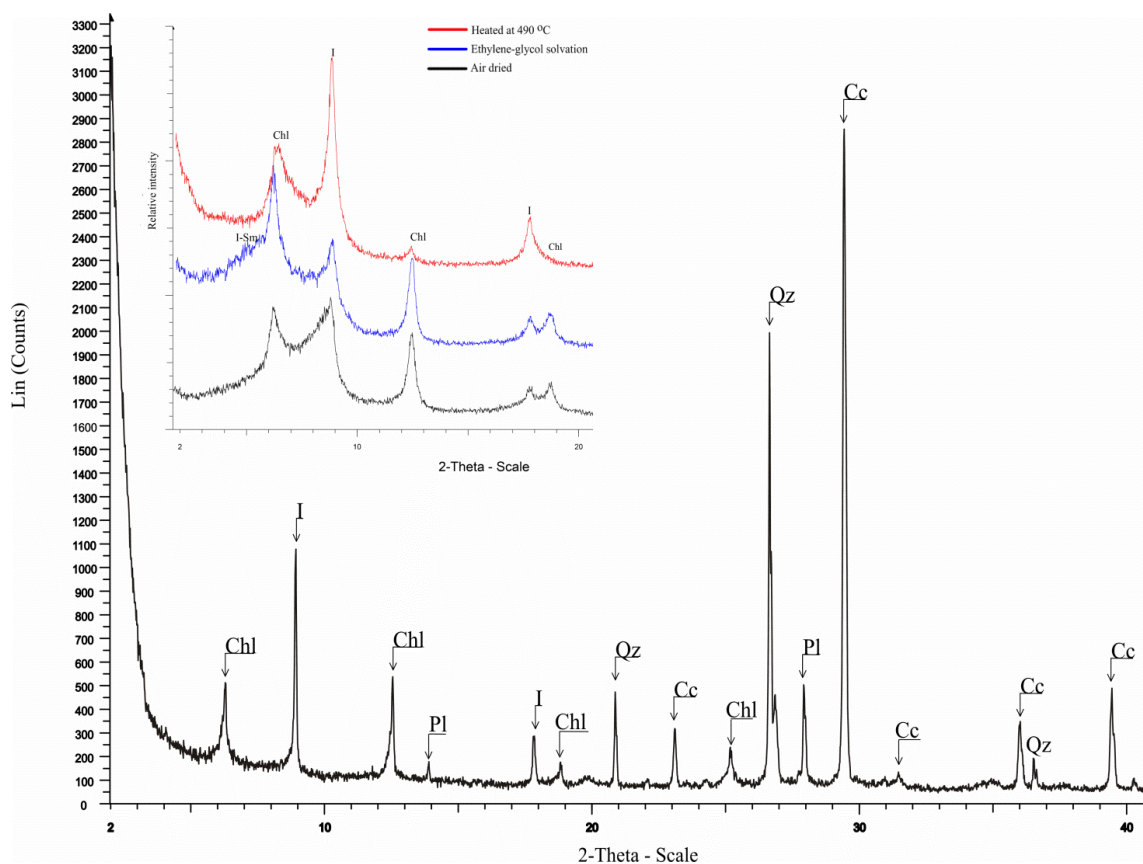


Figure 6 X-ray diffractogram of a clayey sample from Corinth, Greece. The embedded picture shows a composite diffractogram established according to the clay minerals content revealed from the $<2\mu\text{m}$ fraction. The diffraction pattern of each preparation is intentionally equally displaced in respect to Y axis for obtaining a better visual. Abbreviations: I= Illite, Chl= Chlorite, Qz= Quartz, Cc= Calcite, I-Sm= Illite-smectite.

Electron microscopy techniques, such as Scanning Electron Microscopy (SEM), Electron Microprobe Analysis (EMPA) and High Resolution-Transmitted Electron Microscopy (HR-TEM) are also adequate for the identification and study of the clay minerals (Fig. 7a-d). Scanning electron microscopes are usually equipped with energy or wavelength dispersive spectrometers or cathodoluminescence attachment, which offer not only a rapid qualitative analysis, but also quantitative chemical analysis and elemental distribution maps as well. The choice of the electron microscopy technique depends on several factors, such as the quantity, the size and the morphology of the material available, the precision

of the microanalysis, the potential and limitations of the instruments.

Infrared spectroscopy (IR) is also a widespread method of mineral determination. It is considered a rapid, economical and non-destructive technique and is usually applicable to structural analysis (Russel and Fraser, 1995). Similarly, Raman spectroscopy is widely used and provides information about the chemical structure and physical form of a material. It is a very useful tool in the examination of inorganic and organic substances since it can contribute to the recognition of mineral types, such as the minerals of iron oxides, which is not always feasible with other techniques.

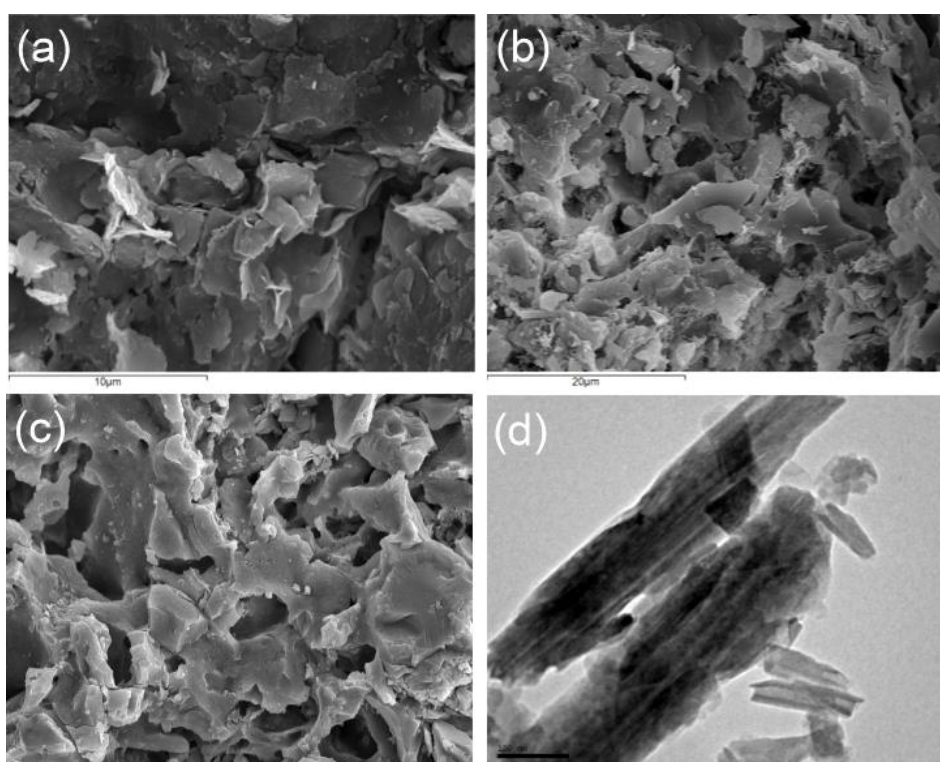


Figure 7(a-c) Secondary electron micrographs of fresh fractures of ceramic experimental briquettes fired at 700, 900 and 1050°C respectively. (a) It shows the maintenance of the plate-like structure of chlorite; (b) It displays the sintering of the particles and (c) shows the extensive vitrification of clay matrix (Xanthopoulou, 2019); (d) Transmitted Electron Microscope (TEM) micrograph in which the clay mineral halloysite recognized (Gianni, 2019).

5. CHEMICAL ANALYSES

Chemical analysis has emerged as a corner stone for the provenance studies of ceramics, since pottery which produced in a particular area carry a specific geochemical fingerprint. The firing process during ceramic manufacture resembles fairly well the isochemical processes encountered during pyrometamorphism in natural systems and therefore the chemical composition of the fired ceramic products can be assumed as indicative of the ceramic raw material composition (Pollard and Heron 1996). However, human involvement in the overall process of

the transformation of clay paste into fired ceramic material usually increases the complexity of the system and should be taken under consideration during ceramic studies. These may involve several factors that can influence the final composition of the pottery such as the natural variability of the clays themselves, the mixing of clays from different sources, the levigation or settling, the firing cycles and the possible post depositional alteration of the ceramics.

There are many analytical techniques which could be applied to the study of ceramics (either pottery or building materials) and raw materials. The

elements of interest usually prescribe the choice of the analytical technique. Chemical constituents are often categorized in major, minor and trace elements. Major elements generally comprise those constituting the earth crust and their content in ceramic raw materials is usually greater than 1% wt. (as element oxides) depending on their mineralogical assemblage and frequently include the light elements, such as silicon, aluminum, sodium, potassium, calcium etc. Minor and trace elements (including rare earth elements) are present in lower quantities and are usually measured in parts per million (ppm). The amounts and the types of minor and trace elements are usually characteristic of individual clays and are inherited from parent rocks, thus providing important clues for their source area.

Each analytical technique has a different ability to detect and measure certain constituents. Factors such as sensitivity, precision and accuracy are among those determining the selection of the proper method. Sensitivity refers to the lower detection limits of the instruments. Precision is a term that refers to the reproducibility of the procedure, whereas accuracy describes how close is the results to the true values. Their constructive combination implies the efficiency of the method selected.

Depending mainly on the aforementioned criteria the chemical characterization of the ceramic raw materials is often based upon spectroscopic or spectrometric techniques because they analyze the electromagnetic spectrum of radiant. X-ray fluorescence (XRF), optical emission spectroscopy (OES), inductive plasma coupled mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), neutron activation analysis (NAA), mössbauer spectroscopy etc. are among those routinely used (Maggetti, 2001; Munita et al., 2003; Prudêncio et al., 2008).

Taking into account the aforementioned processes for the characterization techniques of clays and provenance of ancient ceramics, an effective result is the making of simulated ceramics from the potential clay sources. The firing temperature and preparation

of clays for making briquettes would benefit from SEM or EPMA investigations of possible firing temperature in the antiquity and, in case of seeking production from local clay sources, the mixing scenario must be properly investigated.

6. CONCLUSIONS

The present article reviews the main analytical techniques which should be carried out during the characterization of clayey raw materials in terms of their suitability for ceramic production (provenance). The characterization of clays should begin with a systematic field prospection of the areas of interest and sampling of potential ceramic raw materials following some well established criteria. Thereinafter the selection of the most appropriate techniques from a variety of instrumental physicochemical techniques for mineralogical, chemical and technological characterization allows a thorough investigation of the specimens under study.

Colour determination allows to assess the material in a preliminary analysis regarding their composition. It also provides a sensitive marker for discriminating different geological formations during the fieldwork. The technological properties (granulometry and plasticity) of a material offer important information concerning their behavior during molding and ultimately in classifying it based upon its suitability for ceramic manufacturing. Concerning the mineralogical and chemical techniques the combination of the most efficient instrumentation and methods constitutes a crucial step towards avoiding complex methods of analysis which lead to difficulties in the interpretation of the results.

Last but not least, in the depth characterization of the clayey raw materials, the manufacturing of experimental briquettes using this selected clay source (s), would further complement a local origin clay investigation and could provide useful data for a comparative study with archaeological ceramics.

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