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THERMOANALYTICAL ANALYSIS OF SACIDAVA CERAMICS

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Abstract: *The present paper is a brief review of the techniques based on thermal analysis applied in the context of the characterization of art and archaeological objects, exemplified by various case studies. Thermal analysis methods as TGA correlated with scanning electron microscopy and energy dispersive X-ray microanalysis (SEM-EDS) and porosity measurements were used to investigate the thermal behavior and surface morphology of some ceramic pieces taken from the archaeological site of Sacidava. Upon progressive heating in a static air atmosphere and in the temperature range 20-800 °C, all investigated materials present three main successive processes, associated with dehydration and thermo-oxidative degradations. Clay minerals, as the main material for the production of ceramics and pottery, exhibit some characteristic reactions (dihydroxylation, decomposition, transformation) during firing (heating effects) and several thermoanalytical criteria can be used to reconstruct the previous production conditions.*

Keywords*: Material damage; Cultural heritage; thermal analysis; TGA; SEM-EDX*

1. INTRODUCTION

The conservation and restoration of the artifacts and monuments go beyond just preservation. Identifying the raw materials used in artifacts and monuments helps create a full picture of past civilizations. The presence of an artifact in one region contains materials that only exist hundreds of miles away, that suggests trade, migration, or cultural exchange [1].
Understanding how materials have broken down over time helps conservators know what environmental factors to protect against or reverse. In this context, the analytical methods can map the distribution of elements within an artifact, they also help distinguish between original components and later restorations or contaminants [2,3].
Thermogravimetric Analysis (TGA) is another powerful analytical technique often used in conservation science.
TGA measures the change in a material's mass as it is heated over time. This is useful for understanding thermal stability, composition, and decomposition patterns of materials, especially organic compounds or materials with binders, resins, or additives [4-6].
In conservation, TGA can be used to identify organic vs. inorganic content, to determine moisture or volatile content, and analyze binders and coatings, such as waxes, resins, or glues used historically. Also, by this technique is possible to detect decomposition temperatures, which can guide safe cleaning or restoration methods [7, 8].
Under such context, in this paper some TGA analysis correlated with scanning electron microscopy and energy dispersive X-ray microanalysis (SEM-EDS) and porosity measurements will be used to investigate the thermal behavior and surface morphology of some ceramic pieces taken from the archaeological site of Sacidava.

2. EXPERIMENTAL PART

The samples (Fig.1) have been collected from the ruins of Sacidava.

S1 S2 S3

Figure 1. The samples collected from Sacidava archaeological site

Thermogravimetric analyses (TGA) were carried out using two different instruments to assess the thermal stability and compositional characteristics of the samples. The first analysis was performed with a Pyris 1 TGA analyzer (Perkin-Elmer TGA-7, Waltham, MA, USA) in a temperature range 50 - 700 °C, with 10 °C/min as heating rate, under inert nitrogen atmosphere to maintain an inert environment.
The second analysis was conducted using a TA Q5000 TGA system (TA Instruments), where the samples were heated in a temperature range of 20 - 1000 °C at a rate of 10 °C/min, also under nitrogen atmosphere with a rate of 50 mL/min. These conditions ensured thermal decomposition occurred in an inert atmosphere, allowing for precise monitoring of mass loss associated with

volatile components, degradation processes, and thermal transitions.

The nitrogen adsorption–desorption isotherms were measured at 77.35 K over a relative pressure range (p/p_0) of 0.005 to 1.0 using a NOVA 2200e Gas Sorption Analyzer (Quantachrome Instruments). Data acquisition and processing were conducted using NovaWin software (version 11.03). Before the measurements, the samples were degassed 4 hours under vacuum at 160 °C in order to remove moisture and other adsorbed contaminants.

The main parameters: specific surface area, the pore size distribution and mesopore volume were determined by he Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) model, respectively.

Surface morphology and chemical composition of the analyzed samples were examined using a field emission scanning electron microscope equipped with a focused ion beam (FESEM-FIB), model Auriga (Carl Zeiss SMT, Germany). Topographical and morphological features were visualized in the sample chamber using the secondary electron/ion detector (SESI). Elemental analysis was performed using an energy-dispersive X-ray spectroscopy (EDS) system integrated into the FESEM-FIB workstation, utilizing the X-MaxN detector (Oxford Instruments, UK) and Aztec acquisition and processing software. EDS measurements were conducted at an acceleration voltage of 10 kV to verify the chemical composition of the sample surface.

3. RESULTS AND DISCUSSION

The conservation and restoration of artifacts and monuments play a vital role in understanding their origins and the raw materials from which they were made [9]. Identifying the source materials not only aids in selecting the most appropriate conservation methods but also provides crucial insights into ancient trade routes, production techniques, and the ways in which prehistoric societies utilized natural resources.

The thermal behavior of the investigated ceramic samples is illustrated in Figure 1. Thermal analysis within the 100–250 °C range indicates the removal of absorbed water, which is characteristic of each specific clay deposit. The loss of chemically bound water occurred near 400 °C. Controlled heating is crucial beyond these thresholds, as a rapid rise in temperature can lead to vitrification and potential deformation of the ceramic bodies. Color-based estimations, such as the attribution of a light brown hue to firing temperatures around 600 °C, underscore the importance of precise temperature regulation during the ceramic manufacturing process [10].

The presence of low calcium levels suggests firing at lower temperatures, aligning with the findings from mineralogical and chemical analyses. Iron oxides were found to be a critical factor influencing ceramic coloration during firing. Depending on concentration and atmospheric conditions, these oxides can produce color changing from red to dark brown or even black. Oxidizing atmospheres typically result in lighter colors due to the refractory nature of iron oxides, whereas reducing atmospheres yield darker tones by facilitating the fluxing behavior of these compounds [11].

Calcite detection in ceramic samples suggests firing temperatures between 650–800 °C, typically associated with a reducing environment. The presence or absence of specific iron oxide phases (hematite (α-Fe_2O_3) and magnetite (Fe_3O_4)) favour the reversible change of magnetite to hematite under oxidizing conditions [12].

The analysis identified three key temperature ranges for thermal decomposition: RT–220 °C, 220–600 °C, and 600–700 °C. Total mass loss (ML) ranged from 2.8955 mg in sample S1 to 41.13 mg in sample P2, to 5.624 mg in sample S3.

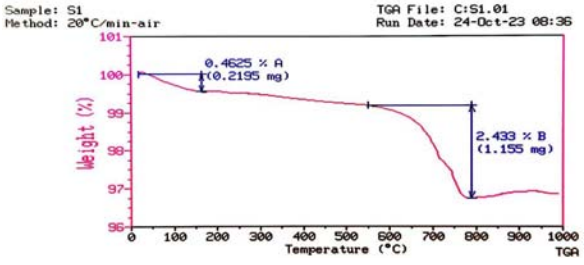
RT to 160 °C: Dehydration of phyllosilicate minerals took place, confirming the release of structurally bound water.

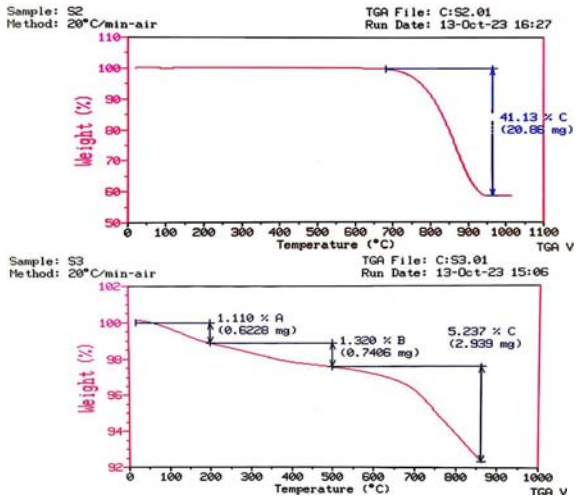
220 to 600 °C: Organic matter decomposition, producing water, CO_2, and other by-products.

In the final stage (600–800 °C), dehydroxylation of phyllosilicates caused significant structural changes, resulting in the formation of chemically active phases. This process affects several mineral properties, including specific heat capacity, phase transitions, and the coordination environment of silicon and aluminum atoms.

The microstructure of ceramics, particularly in the 850–1000 °C range, tends to be stable, allowing for analysis of both primary minerals and newly formed phases. This stability makes ancient ceramics a valuable resource for: distinguishing technological traditions, assessing firing techniques and atmosphere, understanding the degree of vitrification, which affects the ceramic's mechanical strength, porosity, and overall quality [13 - 15].

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability and composition of the samples. The first stage of mass loss, observed up to approximately 150 °C, corresponds to the evaporation of physically adsorbed water. Between 150 °C and 500 °C, one or more decomposition steps may occur, typically associated with the degradation of organic components or structural water loss. At temperatures exceeding 720 °C, further mass loss is generally attributed to the decomposition of inorganic constituents such as carbonates or silicates. The TGA results, expressed as weight loss (%) over the corresponding temperature ranges, are presented in Figure 2.





A = 20 -160ºC; B= 160-600ºC; C=600-1000ºC

Figure 2. TGA diagramms for Sacidava samples

The Ca-rich ceramic fragments exhibit a CaO content exceeding 5%, as inferred from the weight loss attributed to CO_2 release during thermal decomposition. These samples show a hygroscopic water content of approximately 2%, with mass loss occurring around 80 °C. Distinct peaks observed between 580 °C and 640 °C correspond to the thermal decomposition of common clay minerals such as kaolinite, illite, and chlorite.

Under SEM an extended vitrification is registered, due to the firing temperature at over 850°C, and a glassy phase is visible by a lower porosity [16].

The Ca-poor samples (Figure 2) display a characteristic DTG profile with a prominent peak around 640 °C, indicative of the decomposition of clay minerals such as kaolinite, illite, and chlorite.

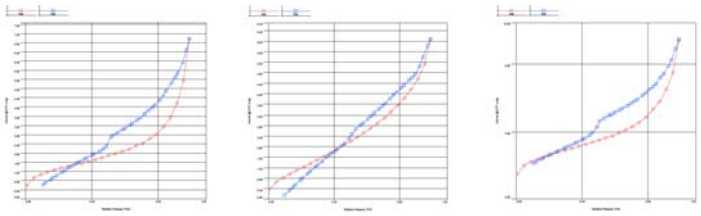
According to recent studies [17–20], the composition and microstructural texture of crystalline phases—particularly calcite and various calcium aluminosilicate compounds play a crucial role in explaining the differences observed in vitrification behavior. Based on the assumed firing temperatures (as shown in Fig. 2) and the SEM micrographs (Fig. 4 S1-S3), an advanced to extensive stage of vitrification can be inferred, particularly in the case of Ca-rich clays.

Ceramics rich in calcium typically exhibit the formation of high-temperature crystalline phases such as anorthite, diopside, and plagioclase, which result from solid-state reactions between calcium-bearing compounds and silicates during firing. These phases contribute to a more glassy matrix and denser microstructure, consistent with high levels of vitrification.

In contrast, Ca-poor ceramics generally display limited phase transformation. They tend to preserve a greater proportion of primary minerals such as quartz, feldspar, and mica, due to the lower fluxing potential and restricted formation of new crystalline phases in the typical firing range of 700–1000 °C, whioch is not the case in our samples.

Additionally, the presence of hematite in red-firing ceramic bodies is indicative of oxidizing firing conditions, which influence both the coloration and mineralogical composition of the final product.

For a materials characterization, could also mention how SEM-EDX supported the identification of these phases, or how microstructure affects mechanical strength and porosity, Fig.3.



Isotherm curves

BJH method Desorption dV(d) results:

S1	S2	S3
Surface area: 4.728 m2/g	Surface area: 5.229 m2/g	Surface area: 9.002 m2/g
Pore volume: 0.0108 cc/g	Pore volume: 0.0094 cc/g	Pore volume: 0.0147 cc/g
Pore Diameter Dv(d): 9.132 nm	Pore Diameter Dv(d): 7.201 nm	Pore Diameter Dv(d): 6.522 nm

Figure 3. Porosity and textural properties of the samples

The dV/d(log d) plot derived from BJH analysis provides a detailed representation of how pore volume is distributed across different pore diameters. In ceramic materials, this distribution reflects both the raw clay mineralogy and the thermal history of the artifact:

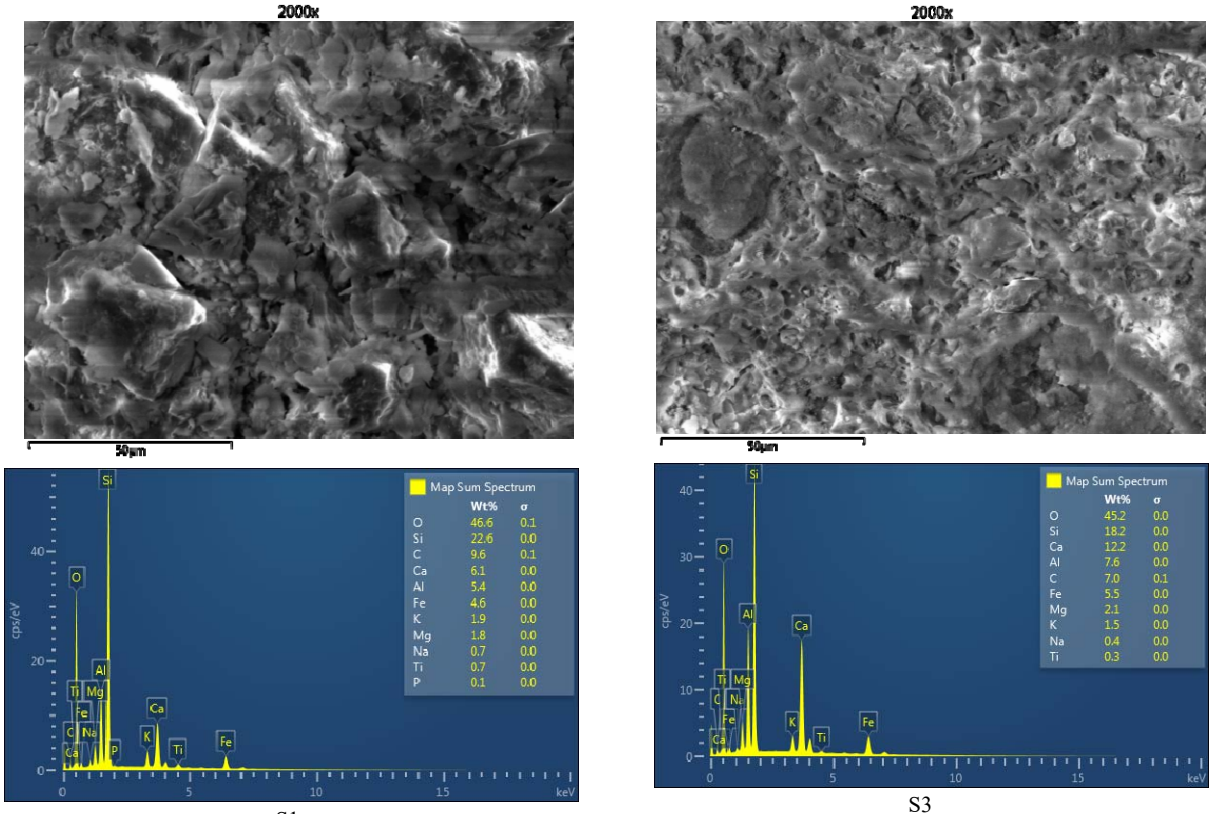
Ca-poor ceramics, which undergo limited vitrification, typically exhibit higher total pore volume and a broader distribution of mesopores, due to incomplete sintering and retention of relict clay microstructure.

Ca-rich ceramics, especially those subjected to higher firing temperatures, show narrower pore size distributions with lower total pore volumes, indicating enhanced vitrification and glass phase formation that seals or collapses fine pores.

A shift in the dominant pore size toward smaller diameters may suggest partial sintering, while a shift toward larger diameters may indicate particle coarsening, bloating, or the presence of inclusions or leached phases.

The BJH desorption dV/d(log d) profile thus acts as a microstructural “signature” of the ceramic body, helping to distinguish between firing regimes, raw material compositions, and even post-depositional alteration.

EM-EDX (Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy) further confirmed the elemental composition of these phases, identifying high concentrations of Ca, Si, Al, and Mg, consistent with the presence of calcium-rich silicates and aluminosilicates. The distribution of elements also revealed localized areas of vitrification and melt phases, especially in samples fired at higher temperatures, Fig.4.



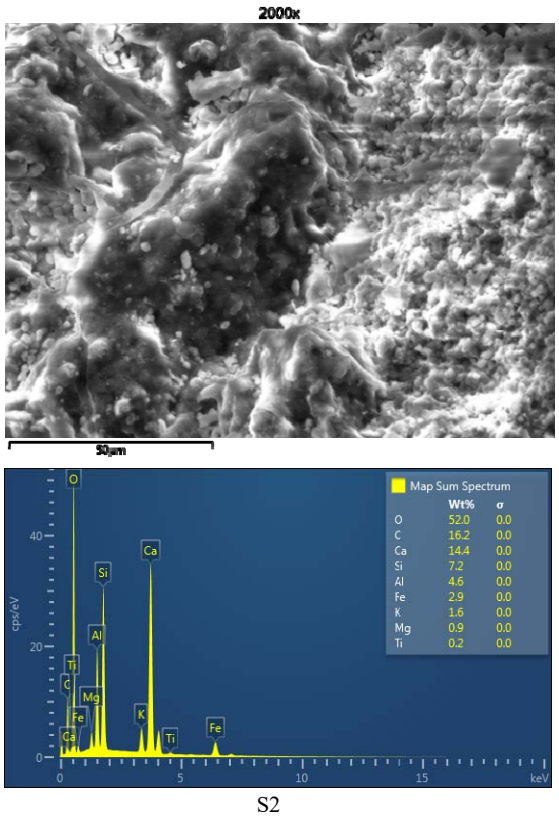


Fig.4. SEM-EDX for Sacidava samples (S1-S3)

Scanning Electron Microscopy (SEM), combined with Energy-Dispersive X-ray Spectroscopy (EDX or EDS), provides valuable insight into both the morphology and elemental composition of ceramic materials at the microscale. This technique is particularly useful for examining firing behavior, phase development, and micro-textural features, all of which are essential for understanding the technological processes used in ancient ceramic production.

The EDX detector enabled semi-quantitative elemental analysis of specific regions within the ceramic matrix. Spot analyses and elemental mapping were performed to determine the distribution of different elements, including Si, Al, Ca, Mg, K, Na, Fe, and Ti. These elements are indicative of the original clay composition as well as the secondary phases formed during firing.

High calcium concentrations in vitrified regions, supporting the formation of Ca-rich silicates such as anorthite, diopside, and augite.

The presence of Fe and Ti correlating with inclusions or colorant phases such as hematite, particularly in red-firing ceramics.

4. CONCLUSIONS

Thermal modifications in the microstructure and texture of the ceramic, heko to understand the manufacturing techniques employed in the production of ancient clay artifacts. The development of the ceramic during firing and depend on the mineralogical and chemical

composition of the raw clay material. As firing temperatures increase, which can be effectively analyzed through scanning electron microscopy (SEM).

The evolution of ceramic technology reflects a continuous and deliberate improvement of manufacturing practices over time. The solid-state phases formed during firing—whether stable or metastable—act as mineralogical fingerprints of the production process. These phase assemblages reveal not only the firing conditions, but also provide clues about the source and selection of raw materials, firing atmosphere, and technological choices.

One of the key discriminators in ceramic mineralogy is the carbonate content of the clay—ranging from Ca-rich, Ca-poor, to marly clays with intermediate calcium levels. This variable strongly influences the paragenesis (mineral formation sequence) within the ceramic body. Specifically, the behavior and transformation pathways of calcium oxide (CaO) during firing play a pivotal role in either enhancing or inhibiting vitrification, largely depending on whether augite ($Ca(Mg,Fe)Si_2O_6$) or other silicate phases are formed.

In Ca-rich clays, the decomposition of calcite ($CaCO_3$) leads to reactive CaO, which can promote the formation of vitrifying silicates such as diopside and augite, resulting in a denser and more cohesive matrix. Conversely, in Ca-poor ceramics, vitrification is less pronounced, and the original clay minerals often remain partially intact, resulting in a more porous and granular microstructure.

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