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ANCIENT POTTERY ANALYSIS USING SEM IMAGE PROCESSING

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Abstract

The term ceramics suggests a group of materials capable of being designed so as to have particular physical and chemical properties and to fulfil a wide range of functions (that traditionally have often been accomplished by other types of materials). In archaeology, ceramics hold an important and varied role as a key to understand many aspects of the development of human civilizations. From long ago, the ancient art has been faked. Today there are fakes that look so convincingly real that they can deceive even the most experienced eye. Recently, scientific tests have been introduced to help us determine whether an object is ancient or not, but they all have shortcomings. This paper aims to explore some of the ways in which ceramics have been studied by physicist through Scanning Electron Microscope (SEM) analysis. We present a scientific analysis of the pore structure of ancient ceramic samples in order to establish a method that allows us to differentiate between the true and false ancient ceramic sample. This method is useful in the administration and tracking down the traffic with objects of patrimony.

Keywords: ancient ceramics, pore structure, SEM technique

1. Introduction

Archaeology may be defined as the study of human past based on the material remains of past human activity. In the case of ceramics there are some questions related to their date of manufacture, the technology of their manufacture, their origin (in terms of both the source of the raw materials and the place of manufacture), and their use.

The raw materials used in pottery (clay, water, and fuel) are widely distributed over the surface of the Earth. Clay has the property of being plastic even wet and thus it can be turned into the desired shape; but as it dries it becomes hard and when sufficiently heated its shape becomes permanent and cannot be made plastic again by the addition of water. Once fired, pottery is very durable. Pottery may be broken into shreds but it does not rot away and generally, it is not recycled.

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We try to demonstrate the potential of SEM technique for the characterization of ancient ceramics. This non-destructive analysis offers a means of getting information on the process and even sometimes on the date of ancient artefacts [1]. Finally, we explore the relationship between statistical pore distribution in wall thickness of ceramics and authenticity of ancient ceramic samples [2, 3]. Porous ceramics are produced within a wide range of porosities and pore sizes depending on the application intended. Porosity and pore size distribution can be carefully controlled by the choice of organic composite and the amount added. In addition, these parameters can give information about authenticity of ancient ceramic samples. Much information remains written in the microstructure of the ceramics bodies. Porosity signatures are specific to the technology applied to the manufacturing process.

2. Experimental

Ceramic fragments belonging to Cris 1 culture have been examined. Shreds from the pottery vessels have been found at Barbosi, Adancata – Imas1 site in southeastern Moldavia (Romania). The ceramic shreds are small, fragmentary and not decorated. Two main types of pottery were analyzed: the first group of samples consisted of 'true' ancient ceramic certified by experienced antiquity specialists (symbol GA). The second group of pottery samples consisted of 'false' ceramic (symbol GF) that appeared similar to first group, but could not be positively identified through archaeological characteristics. It was assumed that these samples might be imitations. This classification is made by professional archaeologists given the complex relationships between the physical objects/contexts/circumstance encountered in excavation. The authenticity of ceramic shreds is proved by the information based on archaeological indicators: repertory, period, ethnic group/culture, material/technique, dating and discovery area. An artefact is interesting to a professional archaeologist if it is know what other artefacts go with it, where the site was located, when it was occupied, what the people did there. All these data have allowed to professional archaeologist to discern between true GA and false GF ceramic

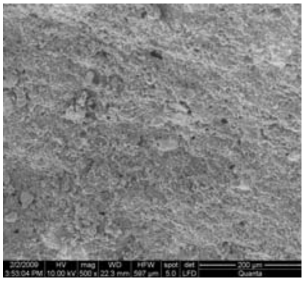
The samples were analyzed using SEM technique. SEM does not actually view a true image of the specimen, but rather produces an electronic map of the specimen that is displayed on a cathode ray tube. Electrons from a filament in an electron gun are beamed at the specimen in a vacuum chamber. The beam forms a line that continuously sweeps across the specimen at high speed. This beam irradiates the specimen that in turn produces a signal in the form of either X-ray fluorescence, secondary or backscattered electrons. The signal produced by the secondary electrons is detected and sent to a cathode ray tube (CRT) image. The scan rate for the electron beam can be increased so that a virtual 3-D image of the specimen can be viewed. The image can also be captured by standard photography. SEM used in our measurements is Quanta 200 FEI type and characterizes both conductive and non-conductive samples. The wide variety of signals generated in the SEM imaging process allows for the selection of an imaging mode that best fits the analytical task. Secondary electrons (SE) provide high resolution and emphasize topography. Backscattered electrons (BSE) bring out material contrast. SEM permits to obtain surface detail and perform statistical analysis to more fully characterized particle and/or pore size and shape distributions (statistically relevant data about particle size and shape with ability to view the actual image of the statistical outliers). For spherical particles and/or pores, size is defined by the diameter. However, for irregularly shaped constituents, characterization of size must also include information on the type of diameter measured as well as information on constituent shape. The samples must be clean, dry, vacuum compatible and electrically conductive. To avoid the samples contain any volatile components such as water, this will need to be removed by a drying process. The size of the specimens was around 6 mm in diameter and they can move 50 mm in the X and Y directions. SEM provides the necessary required sample space for the large and irregular specimens to navigate without requiring mechanical adjustments.

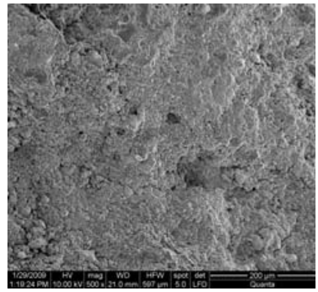
Figure 1 shows SEM pictures of the microstructure of the porous ceramic samples (true GA and false GF samples).

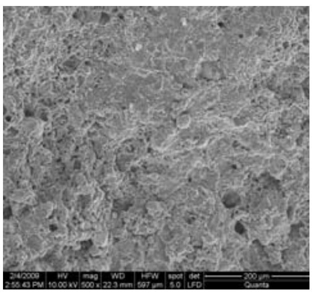
Analysis of the true and fake samples revealed discrepancies between their porosity structure, indicating that they were manufactured through different techniques and/or at different locations, despite their apparent similarity.

The files with the pictures obtained based on the SEM method (.TIFF format) are imported into the AutoCAD program, for digital scaling and measurement of the pores dimensions. The equivalent size of the pores is calculated considering the diameter d of a circle of spherical pores. For the pores analysis, at each sample 50 digital measurements have been made on a scattered randomly distribution in the sample picture field [4, 5]. Image analysis captures a 2-dimensional image of the 3D pore and calculates various size and shape parameters from this 2D image. One of the major diameters calculated is the circle equivalent diameter, which is the diameter of a circle having the same area as the 2D image of the particle. Of course, different shaped pores will have an influence on this circle equivalent diameter but, importantly, it is a single number that gets larger or smaller as the pore does and it is objective and repeatable. It is unlikely to be statistically significant as the single value depends upon which individual pore is chosen. A number of pores that are representative for the ceramic sample as a whole have to be measured and statistical parameters generated. Many real-world samples are broadly shaped like a 'Normal' or 'Gaussian' distribution. This allows us to apply statistical methods in order to evaluate confidence parameters and make recommendations on the minimum number of particles to analyze to achieve a reasonable level of statistical significance. We assumed the Gaussian distribution for ceramic samples in study.

Figure 2 shows the Gauss probability distribution of pore sizes of the ceramic samples versus diameter d of the pores.


GA001


GA002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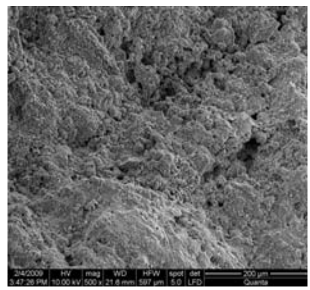
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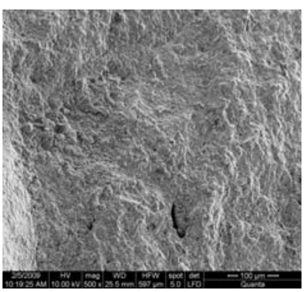
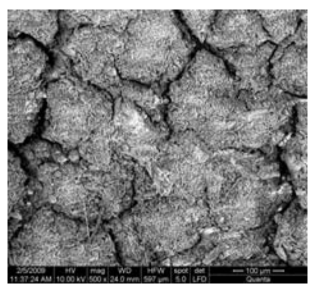
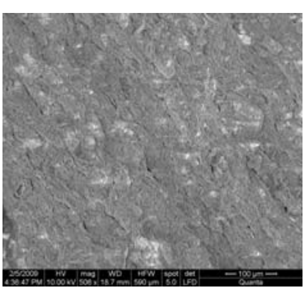

GA071


GA080


GF087

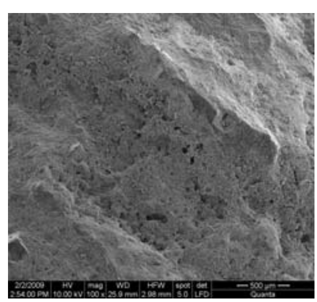

GF091

Figure 1. SEM pictures of true (GA) and false (GF) ceramic samples.

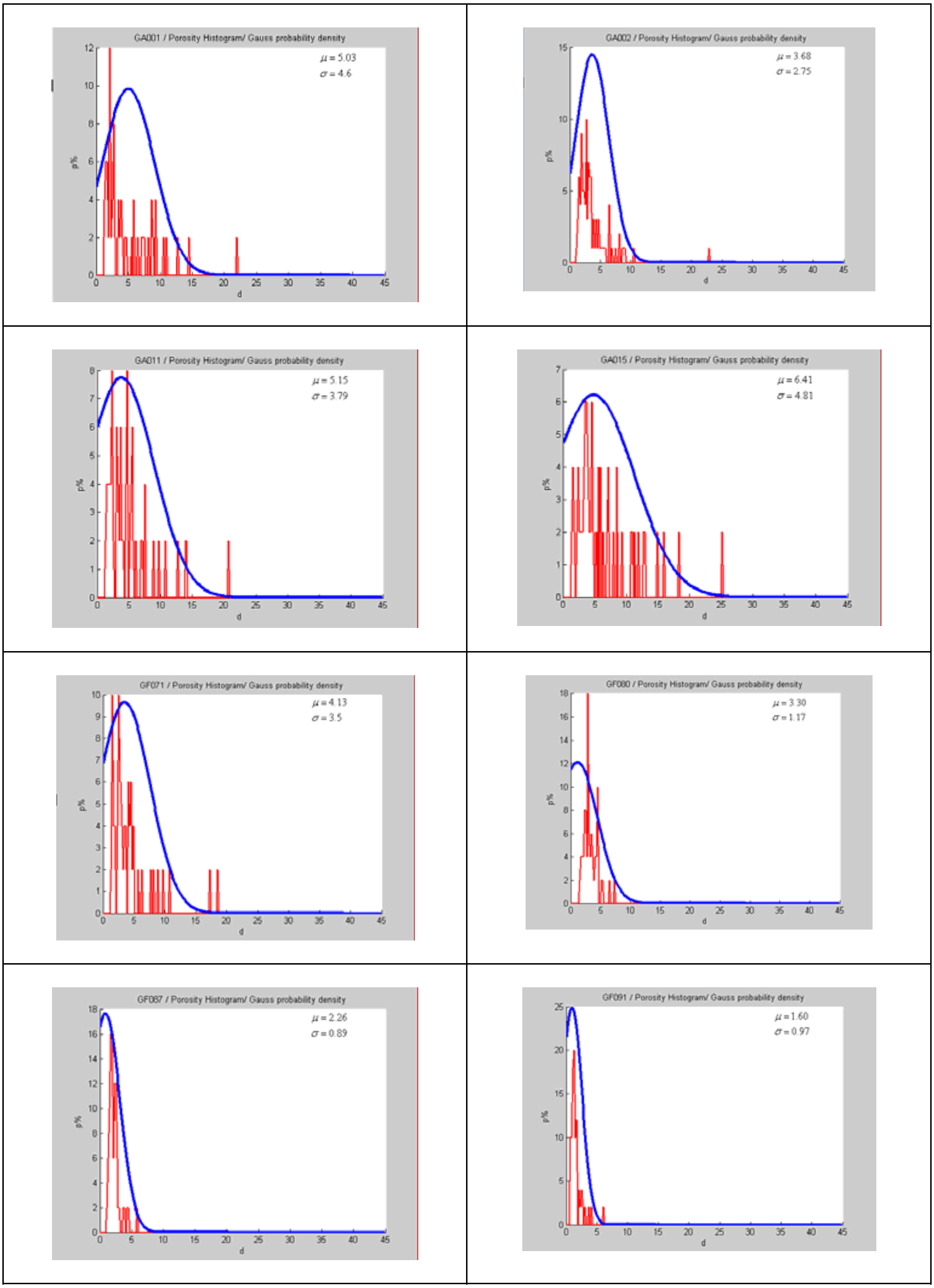


Figure 2. Gauss probability density p% versus diameter *d* [μm] of the pores (red line is histogram related with porosity size and sample distribution; blue line is Gauss probability density).

3. Statistical results for SEM analysis experimental data

Based on the SEM-scanning electron microscope [4, 5] a randomly scatter pores dimensions experimental data are obtained for each ceramic surface sample. For practical purpose the randomly pores dimension measurements have to be processed using a statistical analysis. The random variables for describing the samples are defined by a number of central grouping and variability parameters and by the probability density function (histogram). The central grouping tendencies parameters are: the mean value (mathematic average) and also other parameters rarely used in statistical analysis of chemical-analytical data, as the median and the module values [6, 7]. Those parameters are pointing out to the central tendency, the symmetry and the homogeneity of the statistical series values.

The variability parameters are: amplitude, dispersion or variance, the standard deviation or the quadratic average deviation. Those parameters are pointing out the variability, dispersion, the values scattering around the central tendencies [8].

The mean value (mathematic average) of x_1, x_2,....x_i,....,x_n values is equal to their sum divided by the total n number:

$$\mu = \frac{x_1 + x_2 + x_3 + ... + x_i + ... + x_n}{n} = \frac{\sum x_i}{n} \qquad (1)$$

The amplitude is the easiest form to characterize the scattering experimental data. It represents the difference between the highest value x_{max} and the smallest value x_{min} of a statistical data series:

$$\Delta x = x_{\max} - x_{\min} \qquad (2)$$

The selection dispersion is the main parameter of the scattering experimental data. The dispersion or the variation of a statistical series (selection) is the mathematical average of the quadratic deviation of the selection values towards their mathematic average:

$$\sigma^2 = \frac{\sum (x_i - \mu)^2}{n} \qquad (3)$$

The standard deviation or the selection quadratic average deviation σ is the square-root of the selection dispersion:

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{n}} \qquad (4)$$

The probability function and the probability density function (histogram) of the random variable $X \in \{x_i, i = \overline{1,n}\}$ are defined as following:

$$F_X(x) = P[X \le x];$$

$$f_X(x) = \frac{dF_X(x)}{dx} \quad \Rightarrow \quad f_X(x) \cdot \delta x = P[x < X \le x + \delta x] \qquad (5.a)$$

having a Gauss normal distribution with the following expression:

$$f_X(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (5.b)$$

where the distribution parameters are the mean value μ and the standard deviation σ from equations (1) and (4).

The full width at the half of the maximum of distribution is $\Gamma = 2.355\sigma$.

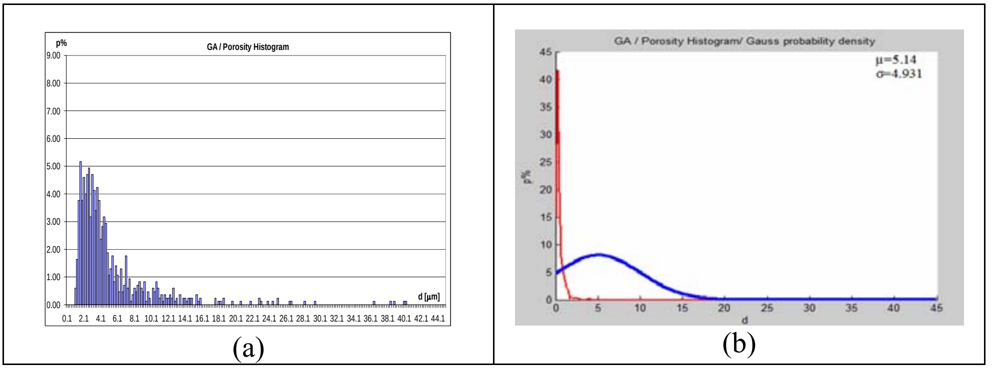
Tables 1 and 2 present the statistical mean value and standard deviation for the pore dimensions, based on SEM analysis, cumulated for all the 'true' and 'false' ceramic samples, as presented in Figures 1 and 2.

Table 1. The statistical mean value and standard deviation for the pore dimensions, based on SEM analysis, for all ‚true' ceramic samples (sampling resolution 0.2 μm).

Sample	GA 001	GA 002	GA 004	GA 011	GA 011x	GA 015	GA 019	GA 025	GA
Mean (μm)	5.03	3.68	3.85	5.15	5.06	6.41	6.26	3.95	**4.92**
Std.dev (μm)	4.06	2.75	3.01	3.79	3.48	4.81	5.65	3.04	**3.82**
Full width at the half of the maximum	10.83	6.47	6.61	8.92	8.64	11.32	10.57	9.89	**9.15**

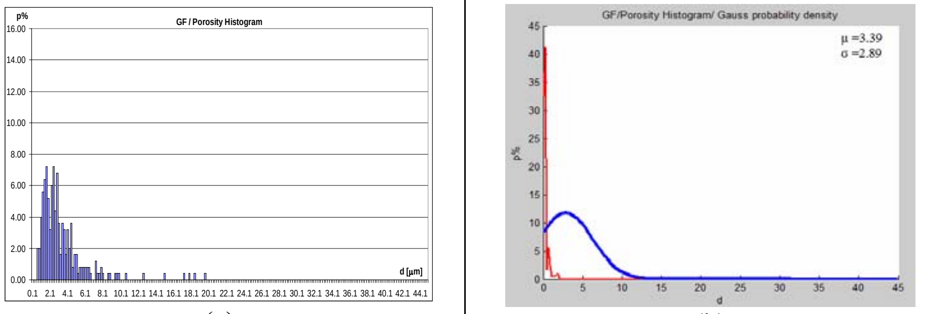
Table 2. The statistical mean value and standard deviation for the pore dimensions, based on SEM analysis, for all ‚false' ceramic samples (sampling resolution 0.2 μm).

Sample	GF071	GF080	GF087	GF091	GF
Mean (μm)	4.31	3.30	2.26	1.60	**2.84**
Std.dev (μm)	3.50	1.17	0.89	0.97	**1.38**
Full width at the half the maximum	8.24	2.75	2.09	2.28	**3.84**



(a) (b)

Figure 3. The pores dimension histogram cumulated for 'true' ceramic samples: (a) pores size, (b) Gauss probability density p% versus diameter *d* [μm].



(a) (b)

Figure 4. The pores dimension histogram cumulated for 'false' ceramic samples: (a) pores size, (b) Gauss probability density p% versus diameter *d* [µm].

Figures 3a and 4a present the pores dimension histogram cumulated for all the 'true' and 'false' ceramic samples. Figures 3b and 4b show the pores dimension Gauss normal distributions cumulated for all the 'true' and 'false' ceramic samples.

In the case of 'true' ceramic samples, the pores dimension distribution is extended on a wide significant values range 1 – 40 µm. The maximum of the Gauss distribution is around five µm.

In the case of 'false' ceramic samples, the pores dimension distribution is grouped around a narrow significant values range 1 – 15 µm. The maximum of the Gauss distribution is around 2.5 µm.

4. Discussion

SEM analysis reveals air bubbles in the walls, a finding that indicates poor handling of the clay. SEM profiles make it possible to test the theoretic explanation for pottery-making techniques. This can be carried out with each individual piece of ceramic. SEM has facilitated the study of ancient ceramics by providing more accurate, less time-consuming profiles of all types of pottery as well as new insights into pottery-making techniques.

The SEM pictures of the first group of samples (true samples symbol GA) differ from that of samples of the second group (false samples symbol GF) indicating different formation conditions. These experimental data were evaluated considering size distribution of the interconnected pores. The GA ancient ceramic samples present statistically bigger pores, which is an indication of poor handling of the clay. Bigger interconnected pores are seen due to release of the gases formed during burning of the organic material. The FA ancient ceramic samples present smaller pores and sample number GF080 shows a sort of needle shaped pore that indicates a better handling and burning of the clay.

When considering the Gauss probability distribution of group GF each of the samples presents different shapes of the pore size distribution curves in comparison with those of the first group GA. Except for one sample (GF-71, see

Figs. 1 and 2) all the other samples can be successfully identified as regards authenticity by their porosity, pore sizes and pore size distribution. This means that the groups of samples we have studied have different porosity statistically, which are determined by their manufacture materials and/or batch composition.

Until now, as far as ancient ceramic is concerned, there is a lack of information regarding porosity- material/technique and period/area relationship. One can always seek more effective empirical curve fitting to differentiate among the various artefacts. There are various models that fit porosity data, at least approximately, but these data are often variable in quality. The fundamental reason why these studies have been limited in their effectiveness of characterization of the ancient ceramic is that these models have been based on a single, fixed character of porosity (e.g. all bubbles, or all pores between particles of fixed shapes and stacking). In reality, both mixtures and changes of porosity need to be considered. In addition, these special categories of artefacts belonging to national patrimony limit the possibility of sampling.

5. Conclusions

We have shown the potential of SEM technique for the characterization of ancient ceramics belonging to Cris 1 culture. This non-destructive analysis offers a way to get information on the process and even sometimes on the date of ancient artefacts. SEM has facilitated the study of ancient ceramics by providing more accurate, less time-consuming profiles of all samples of pottery as well as new insights into pottery-making techniques. SEM profiles make possible to test the theoretic explanation for pottery-making techniques. This can be carried out with each individual piece of ceramic.

However, an extensive application of the technique still seems difficult. The main disadvantages are the need of a specific image treatment for each sample (image acquisition from SEM, digitalization, porosity volume fraction evaluation by specific surface area measurement in AutoCAD program). In the frame of the future database built for the Romanian cultural heritage, this SEM method could be a powerful tool for classification.

Acknowledgement

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