PHYSICOCHEMICAL STUDY OF BYZANTINE CERAMICS IN ANCIENT SIKYONA

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Abstract

The technical construction and decoration of eleven ceramic shards from Ancient Sikyon are investigated in detail. The samples belong to the collection of Byzantine - Christian Museum of Athens and they derived from the excavation in the area of Ancient Sikyon conducted by archaeologist Anastasios Orlandos. The ceramics studied in this work are dated within Byzantine and Post-Byzantine Period, since they were manufactured in the representative Byzantine style. Optical microscopic and stereoscopic examination was carried out on the samples in order to view their layer build-up, while the combined use of μRaman and μFTIR spectroscopy led to the detection of the construction materials used.

KEYWORDS: Ancient Sikyon, Pottery, Optical Microscopy, RAMAN Spectroscopy, FTIR Spectroscopy.

Introduction

The ancient city of Sicyon founded in the 8th century. B.C. The area of ancient Sicyon is located in western Corinth. The urban area is approximately 2500 acres and it is about 3.5 km southwest of the Corinthian area. The Sikyon flourished during the Archaic period and its main representative was Cleisthenes. An ancient monarchy at the times of the Trojan War, the city was ruled by a number of tyrants during the Archaic and Classical period and became a democracy in the 3rd century BC. In Hellenistic times it was also the home of Aratus of Sicyon, the leader of the Achaean League. Sicyon was celebrated for its contributions to ancient Greek art, producing many famous painters and sculptors. This area was well known for the artistic workshops (mainly pottery) as well as for the architectural monuments. From the first excavations were conducted in ancient Sikyon, the historical richness of the region was revealed. First, the ancient theater came to light and followed the ancient market, the parliament, the stage, the aisled basilica, the Roman baths and the arena (Lolos 2011, Kissas 2013).

His successor Aeschines was expelled by the Spartans in 556 BC and Sicyon became an ally of the Lacedaemonians for more than a century. During this time, the Sicyonians developed the various industries for which they were known in antiquity. As the abode of the sculptors Dipoenus and Scyllisit gained pre-eminence in woodcarving and bronze work such as is still to be seen in the archaic metal facings found at Olympia. Its pottery, which resembled Corinthian ware, was exported with the latter as far as Etruria. In Sicyon also the art of painting was supposed to have been invented. After the fall of the tyrants their institutions survived until the end of the 6th century BC, when Dorian supremacy was re-established, perhaps by the agency of Sparta under the ephor Chilon, and the city was enrolled in the Peloponnesian League. Henceforth, its policy was usually determined either by Sparta or Corinth (Lolos 2011, Ραθώση 2005, Κυπραίου 2005).

During the 4th century BC, the city reached its zenith as a centre of art: its school of painting gained fame under Eupompusand attracted the great masters Pamphilus and Apelles as students, while Lysippus and his pupils raised the Sicyonian sculpture to a level hardly surpassed anywhere else in Greece. The tyrant Aristratus, a friend of the Macedonian royal family, had himself portrayed by the painter Melanthius aside the goddess of victory Nike on a chariot. In this period Sicyon was the undipusted center of Greek painting with its school attracting famous artists from all over Greece, including the celebrated Apelles and Pausias (Lolos 2011).

In this work, a systematic physicochemical investigation of eleven ceramic samples of the collection of Byzantine - Christian Museum of Athens derived from the excavation in the area of Ancient Sikyon conducted by Anastasios Orlandos have been studied in an attempt to clarify the characteristics of their technical construction and decoration style. These ceramics are dated within Byzantine and/or Post-Byzantine Period, since they were manufactured in the representative Byzantine style. (Παπανικολά 2005).

Finally, a very important reason for studying the above mentioned ceramics is the absence of systematic investigations for these great artistic ceramic workshops that belonged to a city-state that left its own particular mark not only in the history of Peloponnese, but also in the history of the ancient Greece as a whole.

Experimental Methods.

Following the approval of the Ministry of Culture, samples obtained from the ancient Sikyon shards of the Byzantine and Christian Museum of Athens and, then, they were suitably prepared for the application of analytical techniques.

Samples were extracted from already damaged, but highly representative, areas of each object. Then, the samples were placed in a special mold and pour with filling material that is transparent polyester resin with hardener material and, in the final stage, they were polished in the grinding wheel STRUERS LABOPOL - 21.

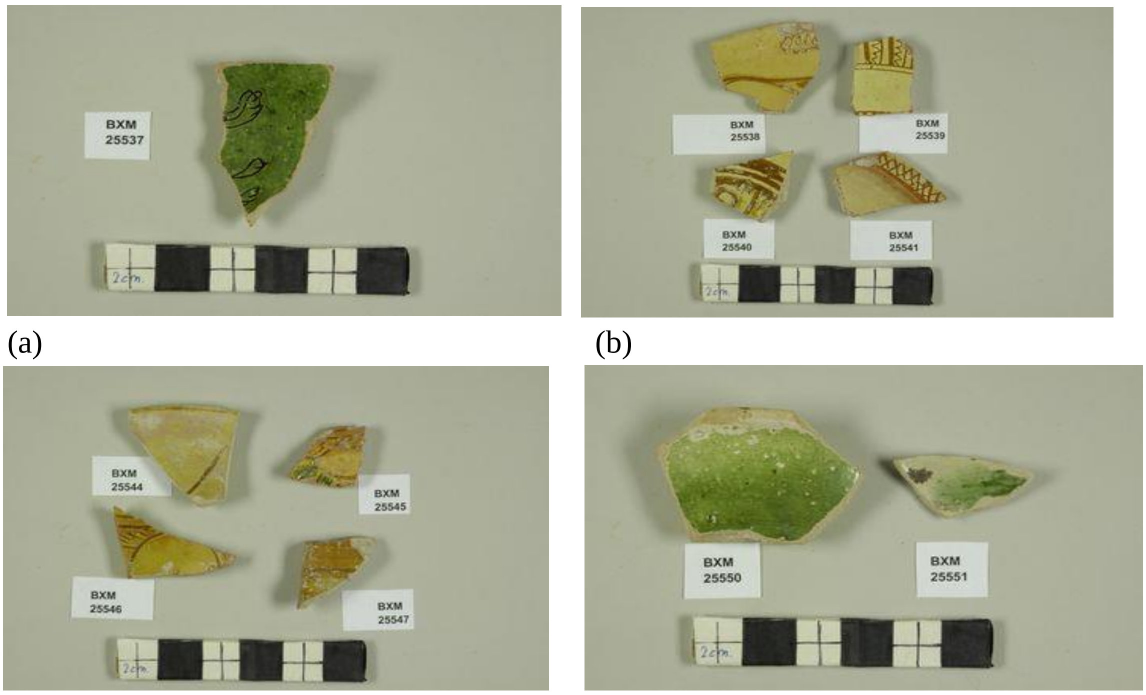
The initial visual examination of the samples cross sections was conducted using a LEICA M205 FA stereoscope, while for the samples observation in high magnification a LEICA DM 2500 M polarizing microscope, equipped with a quartz halogen lamp and an UV excitation light source (100 W), was used.

Raman measurements were performed on a Lab Ram (Jobin Yvon) spectrometer equipped with a confocal aperture. The samples were investigated in the backscattering geometry under the microscope (objective 100×). The green beam (λ=514 nm) of a Ar^+ laser was focused to a spot of diameter 1-3 μm. The instrument was calibrated just before and right after each measurement, by using the spectrum of a silicon wafer as a reference.

Micro-FTIR measurements were performed using a Nicolet 6700 spectrometer connected to a Nicolet microscope operated in reflectance mode. The spectra were obtained at a resolution of 4 cm^{-1}, using a gold plate as a background, while the OMNIC program was used for data handling.

Results

The study of the samples was performed using a series of techniques in order to identify the construction materials and certain characteristics of pottery originating from Ancient Sykion. The techniques that were applied to the samples were Stereoscopy, Optical Microscopy, Raman Spectroscopy and finally the Infrared Spectroscopy (FTIR). The purpose for the use of these techniques was the study of the structure, the chemical composition, their manufacturing technology, the origin of raw materials and stylistic influences from neighbouring areas.



(a) (b) (c) (d)

Figure 2: Typical photographs in the visible light of two green (a and d) and yellow (b and c) ceramic shards of Ancient Sikyon

Figure 2 presents the photographs in the visible light of four of the most representative ceramics shards studied in this work. The bright green (Fig. 2a and d) and yellow (Fig. 2b and c) colour can be observed. As well as, the decoration is seemed with the thick black outlines up the green colour and the thickness oulines up the yellow colours. All the sherds are glazed with a colourless glaze.

The use of Stereoscopy clearly showed the presence of three layers in ceramic shards, the clay, slip and glaze. Further, all the layers of the ceramics were observed in more detail by optical microscopy as well as the size of the particle size and the color hues of the layers. Also, a first estimate was made for the construction and decoration technology of these ceramics. More specifically, the pottery is characterized by two types of clays, the red (Fig. 3a) and white (Fig. 3b) clay. The slip layer is used both in red and white clay. The reason for using slip in the white clay is that the white clay has not high purity with embedded large size impurities with size from 5-30 μm. The size of grains in red clays varies from 1-10 μm. The slip is composed of similar materials as the clay but in higher purity and quality structure, since it is necessary to achieve a good quality white surface in order to stabilize the porous and this can be attributed to the best possible decorative theme. Finally, the ceramics are decorated with the decoration under the glaze

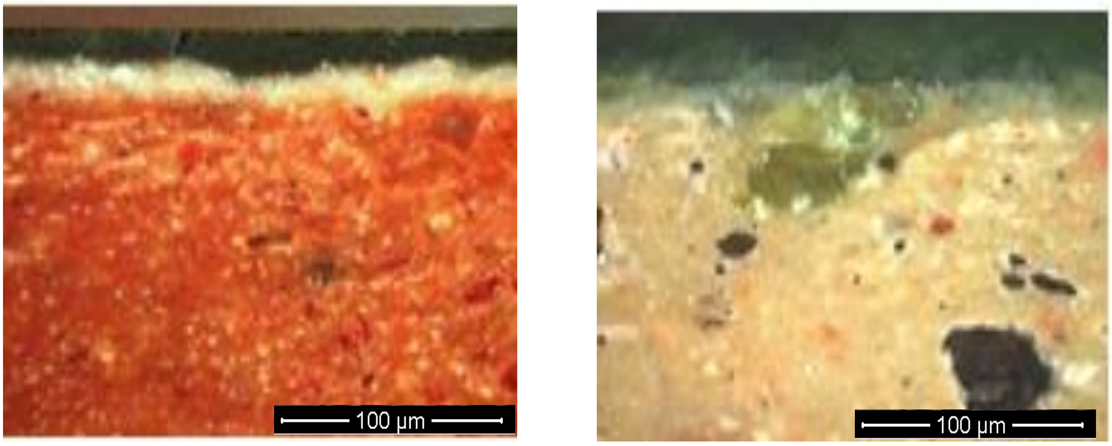


Figure 3: Microphotographs in reflected light of the cross-sections of samples collected from (a) red and (b) white clay shards The presence of three layers glaze, slip and clay can be observed: glaze, slip and clay.

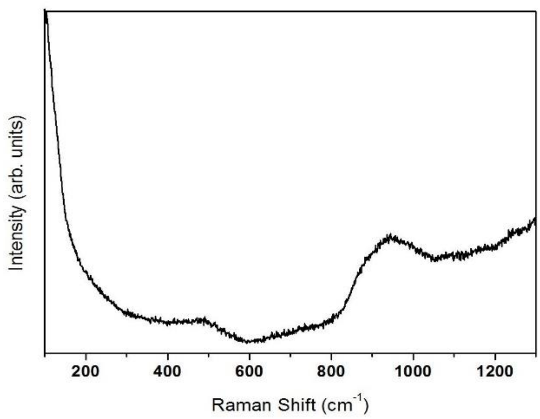


Figure 4: Typical μRaman spectrum of glaze of the s37 sample.

Figure 4 shows a typical μRaman spectrum of the glaze surface of the sample with code-name s37. The appearance of two broad bands denotes that the glaze consists mainly of amorphous material (glass). Similar spectra obtained for the glaze layers of all samples studied in this work.

The μRaman spectrum obtained from the slip layer of the sample with code-name s37 is shown in Fig. 5 and denotes the presence of Rutile (TiO_2), Anatase (TiO_2), a-Quartz, Bone white ($Ca_3(POA)_2$) and Lead White (Basic lead (II) carbonate). It should be noted that similar spectra obtained for the slip layers of all samples studied in this work.

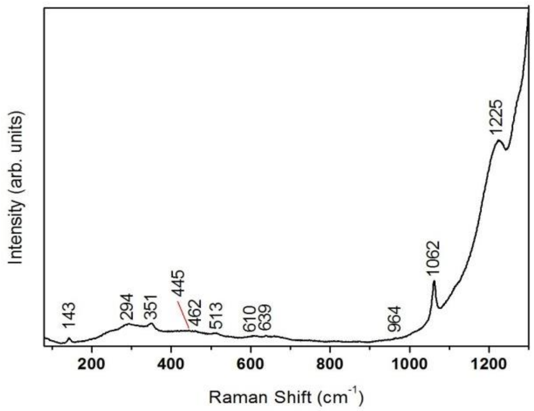
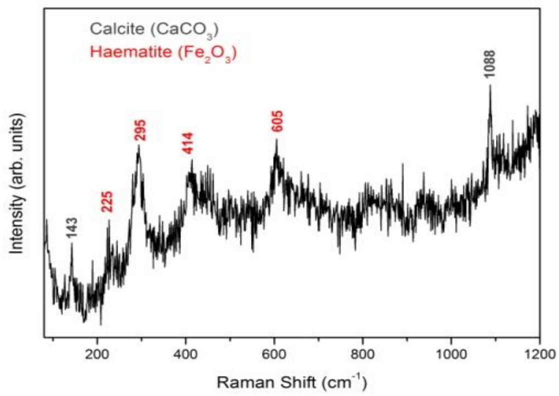


Figure 5: Typical μRaman spectrum of slip of the s37 sample.



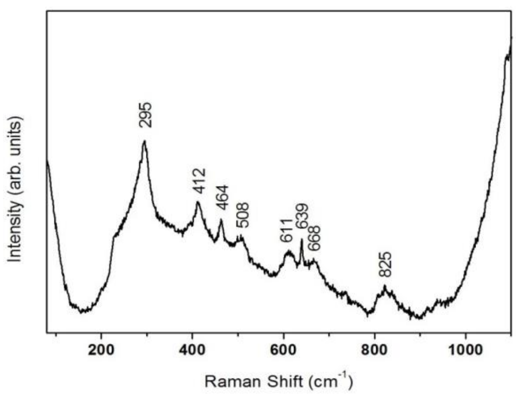


Figure 6: Typical μRaman spectra of (a) red s46 and (b) white type clays s51.

Concerning the red type bodies of the samples, the μRaman analysis (Fig. 6a) s46 showed that they consist maily of Hematite (Fe_2O_3) and Calcite ($CaCO_3$), while for the white type bodies s51 the analysis denotes the presence of Hematite (Fe_2O_3) in combination with Magnetite ($FeO.Fe_2O_3$), a-Quartz, Anatase (TiO_2) and an olivine type structure $Co_2(SiO_4)$ (Fig. 6b).
It should be noticed that, the Hematite content is high for the red type clays, while in the white clay structures Hematite is observed small percentage and, according to the images of optical microscopy, this material appears in grains form (a complete homogenization to impart a clear red color has not been observed).

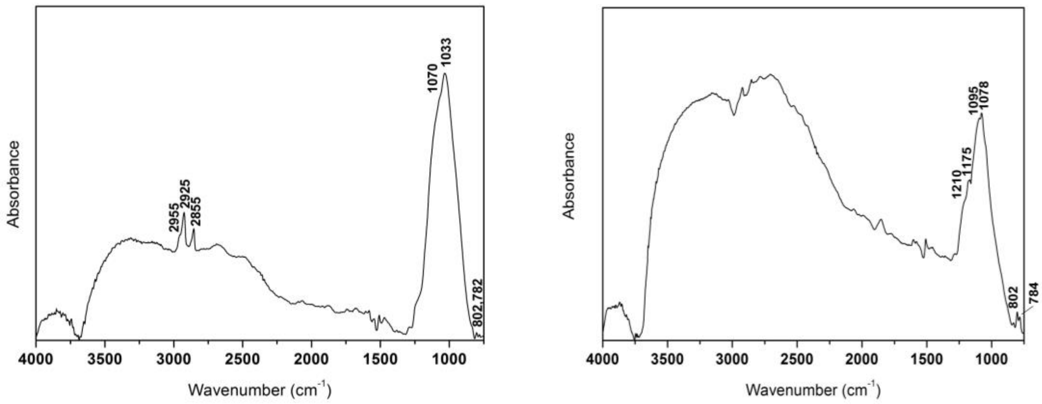


Figure 7: Typical μFTIR spectra of (a) glaze s37 and (b) and body s37.

Finally, μFTIR measurements of s37 showed that glaze consists mainly of Amorphous Al-Si, Kaolin, a-Quartz and Organic matter, probably oil (Fig. 7a), while the bodies of s37 with μFTIR spectra showed the presence of a-Quartz, Kaolin (red clay type) and traces of organic material.

Conclusions

The pottery of Ancient Sikyon characterized by two types of clays the red and white bulk. In the red clay oxides of iron (Fe_2O_3) are present in high percentage to impart this red hue. In contrast, small percentage of iron oxide (Fe_2O_3) is observed for the white ceramic structure and according to the images of optical microscopy the presence of this material is in the form of grains. A complete homogenization to impart a red hue has not been observed. The same slip is used for both red and the white type ceramics. The spectroscopic analysis showed that the slip is comprised of similar materials as the ceramic structure but of higher purity and quality. The reason is to achieve a good quality white surface in order to stabilize the porous and as much as possible the decorative theme can be attributed. Lastly, the ceramic is decorated with under glaze technique and it is believed to have been twice the process of firing.

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