ABSTRACT

Most archaeological sites such as Saqqara have numerous damaged pottery which needs conservation. This study presents a comprehensive study of one pottery sarcophagus extracted from the excavation of the Faculty of Archaeology, Cairo University at Saqqara (Season 2016-2017). The studied sarcophagus sherds were found approximately in forty-one sherds in large and small parts. The manufacturing process, mineral and chemical composition have been estimated by different examination and analytical methods such as the digital microscope, polarizing microscope, scanning electron microscope (SEM-EDX), X-ray diffraction (XRD) and differential thermal analysis (DTA). The microscopic investigation revealed that there are some cracks, color change in the coating layer and roughness of the surface. The polarizing microscope revealed the presence of several minerals such as Quartz, Mica, Pyroxene, Microcline, Biotite, Plagioclase, Iron oxides, some phosphate fossils and grog. SEM-EDX showed the homogeneous appearance of grains. It also showed the presence of Calcium, Magnesium and Potassium oxides at high concentrations together with Chloride and Sulphate salts. XRD showed some main minerals such as Gypsum, Anhydrite, Quartz, Calcite, Illite, Orthoclase and Diopside. DTA proved that the sarcophagus was fired at 900°C.

KEYWORDS: Pottery, Sarcophagus, Saqqara, SEM, XRD, DTA, Mineralogical Analysis.
1. INTRODUCTION

Pottery artifacts are numerously found in archaeological excavation sites. Pottery is one of the most objects prone to damage in archeological sites due to a pressure of mechanical loads from the burial environment (Smith, 1998). These sherds are extremely important to the archaeologists studying the area, and provide a lot of different information. Archaeologists can date a stratum, simply based on the fragments found within it. Apart from dating, pottery sherds can also tell an archaeologist about technology, population movements. Since pottery fragments can tell an archaeologist so much about site and human history. It is extremely important that the finds are dealt with and treated properly (Kowalchuk, 2014). The examination will usually be an investigative stage such as reveal the causes of any deterioration, as well as determining the nature of the pottery body (Buys and Oakley, 1993). Scientific examination of archaeological pottery has gained increasing consideration in recent years. It allows a diagnosis of the mechanisms of decay, necessary prior to any conservation treatment (Mirti, 2000).

Pottery fragments of the studied sarcophagus suffered from different deterioration aspects. Mainly, we observed salt crystallization, roughness of the surface due to bad polishing during manufacturing. As well as the presence of different gaps and holes filled with soil from burial environment. On the other hand, the coating layer suffered from separation, brittleness and soil remains adhered to the object body. It is clear from the broken edges of the sarcophagus that there is a large black area in the core of its body. The surface area of the sarcophagus has more hardness than the friable black core. Furthermore, much variant white spots were spread all over the surface of the sarcophagus (Saleh et al, 1992).

The excavation mission of the Faculty of Archeology, Cairo University began its work at the south of the ascending road of (Onas) pyramid, Saqqara under the supervision of Prof. Dr. Ola El-Augizi. This site is located just 28 km south of Cairo city, and its geographical coordinates are 29° north and 31° east (fig. 1). At the season of 2016-2017, during the restoration of (p3. sr) tomb and removing the accumulated soil layers from the external wall of the tomb, a burial well was found next to the northern wall. In that well, we found several fragments of pottery which required analysis before conservation processes. This study aims to identify the chemical and mineral composition of the studied pottery sarcophagus.

Figure 1. Google Earth maps. (A) Shows Egypt map, (B) Saqqara archaeological site, (C) Excavation sites and (D) Burial well.

2. MATERIAL AND METHODS

2.1. Archaeological samples

Some pottery fragments (Fig. 2), representing a late pottery sarcophagus extracted from excavations of the Faculty of Archeology, Cairo University at Saqqara, were chosen for this study. These fragments suffer from different deterioration aspects, such as separation of the external coating layer, fading and color change in some parts of the coating layer, erosion in the edges, and salt crystallization on the surface of some parts of the body. Moreover, weakness and brittleness of some parts of the body were observed. The archaeological samples were coded to facilitate the discussion (Table 1).
Table. 1. Shows different sample.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>Includes all parts of the body</td>
</tr>
<tr>
<td>G2</td>
<td>Outer coating layer with a part of the body</td>
</tr>
<tr>
<td>G3</td>
<td>White coating</td>
</tr>
<tr>
<td>G4</td>
<td>Black core</td>
</tr>
<tr>
<td>G5</td>
<td>Red coating</td>
</tr>
<tr>
<td>G6</td>
<td>Outer white coating with color change</td>
</tr>
<tr>
<td>G7</td>
<td>White sealing of sarcophagus cover</td>
</tr>
</tbody>
</table>

Figure 2. Shows the various pot sherds of the sarcophagus in varied colors and sizes.

2.2 Methods

2.2.1. Digital Microscope

USB 2.0 interface, Linux, Mac OS & above 10.5.5, from (10X-500X), Model: PZ01.

2.2.2. Polarized Microscope

• Type of polarized microscope: Nikon ECLIPSE LV100POL (DS-F11) MADE IN JAPAN-
• Place: Micro analytical center, Faculty of Science, Cairo University, Egypt

2.2.3. Scanning electron microscope with EDX

• Using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyzes), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolutions for Gun.1n). FEI Company, Netherlands
• Place: General Authority for Mineral Resources in Dokki - Egypt

2.2.4. Analysis of x-ray diffraction

• Type of X-ray analysis device used: Diffractometer-PW 1480-Netherland. Philips analytical x-ray b.v.
• Place: X-ray laboratory, Department of restoration, Faculty of Archeology, Cairo University, Egypt.

2.2.5. Differential thermal analysis

• Place: Micro analytical center, Faculty of Science, Cairo University, Egypt.

3. RESULTS AND DISCUSSION

3.1. Digital Microscope

The results of the examination using the digital microscope revealed the presence of various damage forms such as color change in many parts of the sarcophagus body, peeling of the coating layer and pits caused by poor manufacture, in addition to the presence of cracks in several parts of the body (fig. 3).
Figure 3. Shows the damage present on the pot sherds of sarcophagus. (A) Shows a black area between the red body and white coating, (B) shows the separation of the outer coating layer and appearance of black spots, (C) shows cracks in the inner surface of the body, (D) shows cavities in the core of sarcophagus, (E) shows black spots attached to the surface with a clear color change in the body and (F) shows pits and removal of white coating.

3.2. Polarized Microscope

Several samples were studied, which include the outer coating layer with a part of the body of the sarcophagus as well as the black core. These samples are generally composed of different grain sizes and shapes of quartz, in addition to the presence of pyroxene and mica, which confirms that the clay used in the manufacture of the coffin is Nile Clay (Wodzińska, 2009). We observed some phosphate fossils with a small amount of iron oxides and calcite as one of the additives to improve the characteristics of the clay (López et al., 2013). As shown in (Fig. 4) samples (G1, G2) contain quartz, fossils, and granules of grog and carbonate as fillers (Balliranoa, 2014). The presence of plagioclase feldspar mineral and biotite in the middle of the sample, and a large granule of quartz, crystalline quartz where the color of quartz is different as the sample stage are rotated (Reedy, 1994).
3.3. Scanning electron microscope with elemental analysis unit (SEM-EDX)

The SEM micrograph of sample G3 revealed the homogeneity in the granules size. Additionally, some gaps, micro-cracks and remains of the soil on the surface were also observed (Fig. 5A). Sample G4 revealed a relative heterogeneity in the granules size (Fig. 5B). Sample G5 shows homogeneity in the granules size, with some small gaps in the surface (Fig. 5C). Sample G6 shows a color change in the white coating layer (Fig. 5D) (Cultrone, 2001).
Figure 5. Shows the results of the SEM-EDX. (A) Represents sample G3 which shows cracks, (B) represents sample G4, which shows the presence of gaps and residues of some organic substances, (C) represents sample G5 which shows the homogeneity of the particle size and (D) represents sample G6 which shows roughness of the surface.

As shown in (Table. 2) and (fig. 6-7), the result of SEM-EDX analysis indicates that sample G3 has a high percentage of calcium oxide. The observed point represents the outer layer of white coating. Sample G4 shows an increase in the percentage of iron oxide, aluminum, and silica. Sample G5 shows the increase in the proportion of salts of chlorides and sulfate which may have migrate from the soil surrounding the sarcophagus (Adrian, 2007). This indicates that the sarcophagus deteriorated by the crystallization of these salts (Madkour and Khallaf, 2012). Sample G6 has an increase in the percentage of magnesium and potassium oxides, it indicates that the clay used in the manufacture of the sarcophagus is mainly a mixture of clays consists of Illite and Montmorillonite minerals (Almon and Davis, 1981).

Table. 2. Shows concentration of elements % in different samples.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Fe</th>
<th>Ca</th>
<th>K</th>
<th>Cl</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Na</th>
<th>O</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3</td>
<td>7.80</td>
<td>16.96</td>
<td>0.56</td>
<td>0.61</td>
<td>4.06</td>
<td>19.36</td>
<td>6.63</td>
<td>2.16</td>
<td>1.13</td>
<td>34.26</td>
</tr>
<tr>
<td>G4</td>
<td>11.04</td>
<td>3.07</td>
<td>2.85</td>
<td>1.16</td>
<td>0.00</td>
<td>30.57</td>
<td>10.03</td>
<td>2.24</td>
<td>2.33</td>
<td>34.13</td>
</tr>
<tr>
<td>G5</td>
<td>7.06</td>
<td>9.43</td>
<td>3.73</td>
<td>1.62</td>
<td>6.08</td>
<td>13.89</td>
<td>5.17</td>
<td>2.56</td>
<td>2.00</td>
<td>33.35</td>
</tr>
<tr>
<td>G6</td>
<td>6.33</td>
<td>11.48</td>
<td>4.10</td>
<td>0.73</td>
<td>2.73</td>
<td>16.28</td>
<td>5.97</td>
<td>2.94</td>
<td>1.40</td>
<td>36.40</td>
</tr>
</tbody>
</table>
Figure 6. Shows the concentration % of elements in different samples.

Figure 7. Shows results of SEM – EDX of samples; (A) Sample G3, (B) sample G4, (C) sample G5 and (D) sample G6.

3.4. X-ray diffraction analysis (XRD)

XRD provides the information about the major minerals present in the material (Venkatachalapathy et al, 2002) and to define firing temperatures could be critically considered (Riccardi et al, 1999). The X-ray data for the samples are given in (Table 3) and (Fig. 8). Sample G7 is composed of anhydrite, gypsum, quartz and calcite (Fig. 8A). Gypsum was used as a mortar for sarcophagus cover fixation. Anhydrite is altered mineral from Gypsum as a result of exposure to high-temperature. Quartz is also identified by XRD to be one of the components of mortar which plays a vital role as filler. Calcite is identified to be part of Gypsum mortar components, but a minor component (Madkour and Khallaf, 2012; Tennent et al, 1992).

Sample G4 is part of pottery composed of quartz, illite, halite, diopside, muscovite, gypsum, orthoclase and calcite (Fig. 8B). Quartz is a basic component of the sample (Castro and Carbó, 1992). Illite is part of
the surrounding burial soil. Halite is one of the soluble salts resulting from the effect of the burial environment. Diopside is a result of the transformation of carbonate compounds and indicates that the firing temperature is about 850°C (Ricci et al, 2017). Muscovite and Orthoclase are basic components in the sample. Gypsum is impurity component from the used mortar. A content of calcite indicates that the potteries were fired at temperature below 900 °C (the temperature of complete decomposition of calcite) or for a short time that did not allow the completed composition (Balliranoa et al, 2014).

Sample G5 shows the presence of several components such as diopside, biotite, quartz, dolomite, hematite, calcite and magnetite (Fig. 8C) (Rasmussen et al, 2012; Scarpelli et al, 2014). Diopside is formed in high temperature between 800 - 850°C and this gives us an excellent indication of the firing temperature degree of the sarcophagus (Shoval, 1994; Gajic-Kvascev et al, 2018). Quartz and biotite are a basic component of the clay minerals. Dolomite is an additive to the coating layer. Hematite is the main component of the red wash layer exists in some parts of sarcophagus body. Calcite is an additive to the coating layer together with the red sediment. Magnetite is one of the oxides associated with the red ochre.

The sample G3 is a white wash composed of anorthite, diopside, quartz and calcite (Fig. 8D). The main component of the white color is calcite that mixed with quartz as filler. The presence of anorthite and diopside is an indication of the firing temperature which is approximately 850°C (Cultrone et al, 2001). It also points out the application of white wash before firing the sarcophagus.

Table 3. Results of identified minerals % by XRD analysis of pot sherds.

<table>
<thead>
<tr>
<th>Component</th>
<th>G7</th>
<th>G4</th>
<th>G5</th>
<th>G3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>9.4</td>
<td>23.8</td>
<td>10.8</td>
<td>10.7</td>
</tr>
<tr>
<td>Gypsum</td>
<td>28.5</td>
<td>7.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>53.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcite</td>
<td>9.0</td>
<td>3.7</td>
<td>6.1</td>
<td>7.6</td>
</tr>
<tr>
<td>Illite</td>
<td>-</td>
<td>17.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diopside</td>
<td>-</td>
<td>15.5</td>
<td>38.1</td>
<td>31.2</td>
</tr>
<tr>
<td>Muscovite</td>
<td>-</td>
<td>8.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>-</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Biotite</td>
<td>-</td>
<td>-</td>
<td>21.4</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite</td>
<td>-</td>
<td>-</td>
<td>10.2</td>
<td>-</td>
</tr>
<tr>
<td>Hematite</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
<td>-</td>
</tr>
<tr>
<td>Magnetite</td>
<td>-</td>
<td>-</td>
<td>5.4</td>
<td>-</td>
</tr>
<tr>
<td>Anorthite</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50.5</td>
</tr>
<tr>
<td>Halite</td>
<td>-</td>
<td>16.8</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 8. Shows the results of the XRD of samples; (A) Sample G7, (B) sample G4, (C) sample G5 and (D) sample G3.
3.5. Differential thermal analysis (DTA)

The following observations were obtained from the thermal curve of sample G4 (Fig. 9):

- An exothermic reaction occurred at 450°C, where the water is dehydrated and some physiochemical changes were done due to the beginning of the decomposition process.
- Between 550 °C and 650 °C, the clay displayed dehydroxylation process of transformation of kaolinite to metakaolin (Chin et al, 2017; Moropoulou et al, 1995).
- Quartz is transformed from the alpha phase to beta phase at 573°C.
- An exothermic reaction occurs at 902.34°C.
- An endothermic reaction occurs at 946.29°C, where the decomposition of pure carbonates at 920°C (Roy, 2014).
- From the exothermic and endothermic reactions, it was found that the firing temperature of pottery sarcophagus was less than 900°C.

![Figure 9. Shows DTA curve of pottery sample from the sarcophagus body.](image)

4. CONCLUSION

The following conclusions can be drawn from the data we obtained:

Examination by digital microscope shows a channel gap in the body due to defects during the manufacture. It shows a black area between the red body and white paint, caused by insufficient firing together with cavities in the core of the coffin. The examination of the polarized microscopy shows that the samples are generally composed of different grain sizes and shapes of quartz which is considered the main component of clay. Pyroxene, mica, phosphate fossils, calcite and grog which are added to improve the characteristics of the used clay, were also detected. The presence of mica refers to the source of clay as Nile Clay.

The SEM micrograph of the sample's surface revealed the homogeneity in the granules size. The results of SEM-EDX analysis indicate that the samples have a high percentage of calcium oxide. It represents white coating; hence the lime mortar is used as a whitewash to beautify that surface. Additionally, an increasing percentage of salts of chlorides and sulfate as contamination from soil were detected. There is also an increase in the proportion of magnesium and potassium oxides, which may indicate the use of clay consisting of Illite and Montmorillonite minerals.

X-ray diffraction results of the samples of sarcophagus pottery showed that it consists mainly of Quartz, Illite, Diopside, Muscovite, Orthoclase and biotite. The mortar is mainly composed of Anhydrite, Gypsum, Quartz and Calcite. Red wash is composed of diopside, quartz, dolomite, hematite, calcite and magnetite. White wash is composed of anorthite, diopside, quartz and calcite. The presence of diopside shows that the firing temperature was over 850°C. Differential thermal analysis shows that the firing temperature of pottery sarcophagus was less than 900°C.
REFERENCES


