

Keysight Technologies

Potential of Low Voltage Scanning Electron Microscopy Use in Archaeology and History of Art: A Preliminary Study

Application Note

Introduction

Laboratory studies of artifacts have become increasingly common in the last few decades. Archaeologists (both excavators and curators), art historians and conservators have become aware of the importance of analytical studies of these objects for the interpretation, conservation, and restoration of such valuable cultural materials [1–10]. The materials studies usually span the range of metals (bronzes, ferrous alloys, lead, silver, gold), oxide ceramics (pottery, faience, stoneware, porcelain, vitrified materials

such as glass, glaze, pâte-de-verre), polymers, and composites. Hence, imaging of artifact microstructure provides invaluable insight for artifacts classification/characterization, better understanding of their manufacturing technologies, and the best conservation approach or treatment method for their preservation. What is particularly important in the study of archaeological and artistic samples is that not only the examination technique(s) have to be non-destructive, but also that, in most cases, a sample cannot be cut, fractured, or altered. This poses tremendous constraints on the analyst

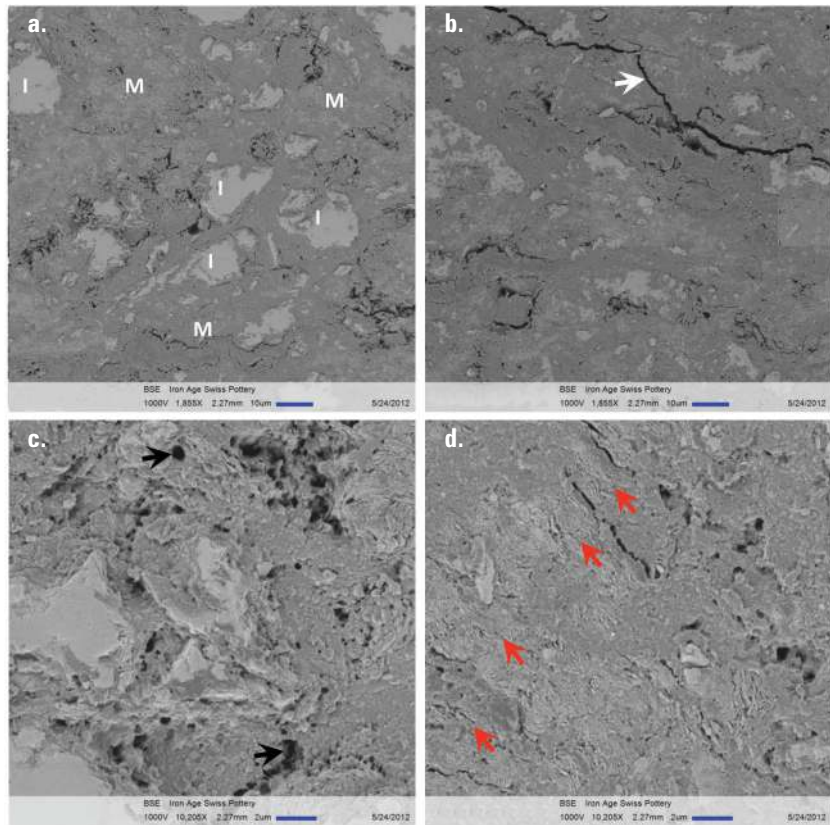
in sample choice, preparation, and examination, as illustrated by the example sample studied for these papers [9–10]. Therefore, size, shape, and state of the surface dictate the type of analytical technique and instrument chosen. In this application note a few cases are presented where the Keysight Technologies, Inc. 8500 Low Voltage Scanning Electron Microscope (LV-SEM) was used for a given type of artifact to answer specific questions of interest either to archaeology, art history, or conservation science. The samples included in this study are shown in Figure 1.



Figure 1. Samples studied in this application note: (i) petrographic thin section of an Iron Age pottery (Hallstatt culture) from Uetliberg, Switzerland; (ii) thin section of a Roman wall painting fragment from Avenches, Switzerland; (iii) Roman wall painting fragment from Pompeii, Italy; (iv) thin sections of glass vessel cores from Tel Amarna, New Kingdom Egypt; (v) and (vi) Egyptian blue and steatite scarabs from Middle Bronze Age Palestine.



Figure 2. BSE images taken with Keysight 8500 Low Voltage Scanning Electron Microscope (LV-SEM) of a petrographic thin section of Iron Age pottery sample from Uetliberg, Switzerland showing the main morphological features of the composite ceramic material: cementing clayey matrix (M); mineral or non-plastic inclusions (I), macro-cracks and pores (white and black arrows); nano-pores; and striation of the clayey matrix (red arrows). The latter is due to the preferred orientation of clay material during shaping/making of the pot.



Methodology

1. Samples

The artifacts imaged here are: (1) Iron Age pottery from Switzerland (6th–7th Century BC) [11]; (2) Roman wall painting fragment from Avenches (Aventicum), Switzerland (1st–2nd Century AD) [12]; (3) Roman wall painting fragment from Pompeii, Italy (1st Century AD) [13]; (4) unfired glass vessel ceramic core from Tel Amarna, New Kingdom Egypt (14th Century BC) [14]; (5) and (6) two scarabs from Middle Bronze Age Palestine (~18th Century BC) made of Egyptian blue and steatite, respectively (unpublished data).

2. Sample Preparation and Imaging

Samples were processed and prepared in different ways, but preparation for LV-SEM imaging was minimal. Specimens are simply examined either as-is samples mounted in special holders or as polished sections/ thin and adhered via carbon tape to aluminum stubs and loaded onto

microscope stage. Samples were prepared for imaging in different ways. Samples (1), (2) and (4) are thin sections prepared initially for petrographic analysis with polarized light optical microscopy; (3) hand specimen of wall painting fragment examined as is; (5) and (6) hand specimens of scarabs each examined as is and also a small amount was scratched and sprinkled on carbon tape. All samples were imaged in high resolution mode at 1000 V either in SE or BSE modes.

Results and Discussion

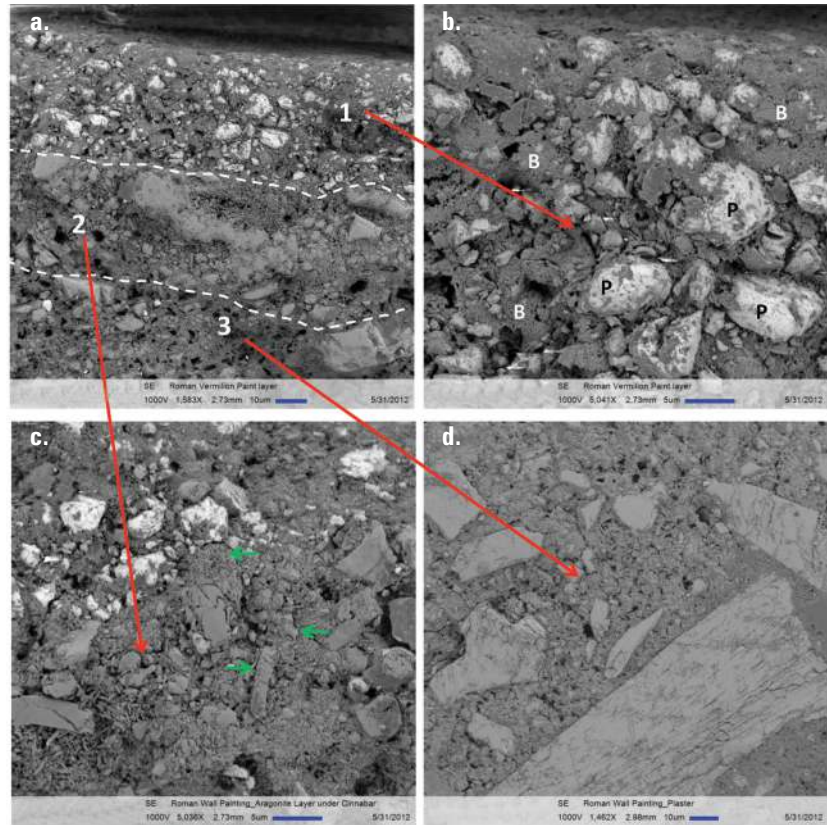
1. Iron Age pottery from Uetliberg, Switzerland

The sample imaged here is an uncovered petrographic thin section of a rare pottery shard from the site of Uetliberg, Switzerland. Many questions are of interest to the archaeologist/ archaeometrist when dealing with such rare artifacts. Analyses should provide sound evidence for classification, sourcing, and understanding of

fabrication technology. Microscopy has the potential to partly answer all three questions. Thus, LV-SEM is used here as non-destructive technique that needs minimal sample preparation while not requiring a coating of the sample. The attempt here is to infer information on the fabrication technology from SEM imaging. Figure 2 includes BSE images showing revealing features of interest. First, qualitative as well as quantitative assessment of naturally occurring non-plastic inclusions (or added temper) relative to the clayey matrix can be done easily on low magnification images. Second, macro- and micro cracks and pores as well as micro-striation or preferred orientation of the matrix certainly indicate less elaborate or skilled treatment of the clay material before shaping of the pot, which is consistent with hand-made vessel technology. However, nano pores are the result of mineral transformation of the clay material during firing, such as dehydroxylation/decarbonation that release gases such as H₂O and CO₂ causing expansion and evolution of the



Figure 3. SE images taken with Keysight 8500 (LV-SEM) of a petrographic thin section of a Roman wall painting fragment from Avenches, Switzerland. Image (a) shows three layers (1, 2, and 3) emphasized in detail in (b), (c) and (d), respectively. (b) Paint layer is composed of vermilion or cinnabar (indicated by P); (c) paint under-layer made of aragonite white pigment rich in micro-fossils, which was a common practice in Roman wall painting; (d) lime plaster made of slaked lime ($\text{Ca}[\text{OH}]_2$) as binder and calcite or limestone powder as aggregate material. Note the carbonate matrix (binder) in the paint layer (indicated by B) is evidence of a “fresco” painting technique, when the pigment is applied to a fresh layer of lime plaster that causes the lime to diffuse into the paint and carbonate with time thus cementing the paint layer permanently.



porous structure. The evolution of nano-porosity which is certainly a function of the firing temperature and atmosphere, and will be discussed in a separate note once the appropriate samples are ready. These remarks indicate a simpler ceramic technology associated with the Iron Age (Hallstatt) culture of pre-Celtic central Europe, compared with Mediterranean World during the same era.

2. Roman wall painting fragment from Avenches, Switzerland

Figure 3 shows SE images taken of a petrographic thin section of a Roman wall painting fragment from the famous site of Avenches (Aventicum) currently in southwestern Switzerland. Several layers are seen from the paint surface and inward (Fig.3a). The paint layer is composed of a pigment (red cinnabar or $\alpha\text{-HgS}$) and a lime binder. The pigment grains are well rounded, thus indicating that a ground natural pigment was most probably used. A thin layer (Fig. 3b) essentially composed of aragonite white pigment was applied under the

cinnabar. This was a very common practice in Roman painting to apply white aragonite or yellow ochre under cinnabar [8, 12]. The reasons for this technique, is that cinnabar was among the most expensive pigments that unfortunately can turn black under certain environmental conditions [7, 12]. Therefore, it is believed that Roman artists attempted to economize and stabilize the luxurious pigment by applying white or yellow buffering materials such as aragonite (CaCO_3) or yellow ochre (goethite- $\text{FeO}\cdot\text{OH}$). The aragonite layer imaged here contains numerous micro-fossils (green arrows in Fig. 3c), thus indicating a sedimentary (marine or lacustrine) origin of the white pigment. The third layer (Fig. 3d) is the final coat of lime plaster, which is composed of a carbonate matrix (lime binder) prepared with a carbonate aggregate. Vitruvius, the famous Roman engineer recommended in his “Ten Books of Architecture” for a long lasting construction a plaster made of lime and an aggregate of spathic calcite or

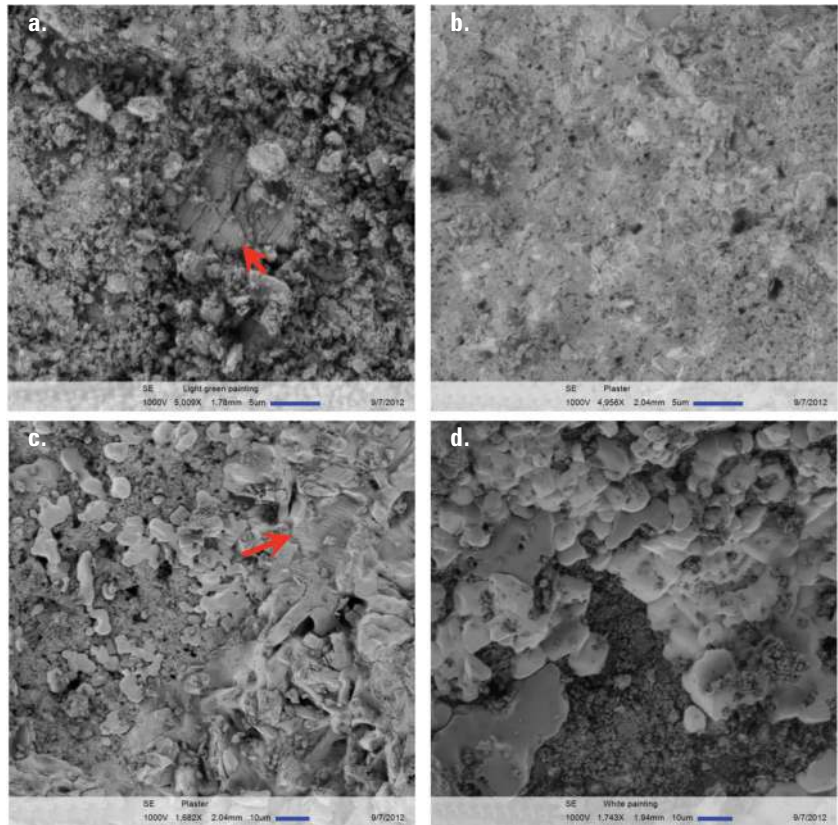
marble dust. The material used here is a powder of a local limestone as substitute.

3. Roman wall painting fragment from Pompeii, Italy

The sample examined here is a wall painting fragment from the house of Fabio Rufo in Pompeii, Italy [13]. The fragment has light green, white and red bands applied on a yellow background. Only the white area was examined for this study. The fragment shows signs of alteration in the form of deposition/formation of a patina on most of the paint surface. The patina is a coherent and smooth coat of material forming usually on external surface of archaeological materials (and in the pores) as a result of a strong and dynamic chemical interaction with the environment (atmosphere, soil, water). It is simply the product of the interaction between the intrinsic constituents of the sample with extrinsic factors through dissolution (leaching), precipitation, recrystallization on the surface and in



Figure 4. SE images taken with Keysight 8500 (LV-SEM) of the top surface of a Roman wall painting fragment from the house of Fabio Rufo in Pompeii, Italy. The paint layer shows both physical and chemical degradation. The former had led to disintegration of the pigment and exposure of the plaster applied underneath (images a and b). Chemical degradation is manifested by dissolution of calcium carbonate from the plaster (calcite) and the paint layer (here aragonite) during wet season and precipitation of calcite during dry season and/or area (images c and d). The high porosity of the plaster (image b) facilitates materials transport and crystallization, respectively. The neo-calcite smooth surface and rounded shape of grains and their coalescence indicates the process had continued over several seasons.



the pores and cracks. Therefore, this phenomenon is of great importance in archaeological conservation since it alters the physical appearance and integrity of the artifact, but also its chemical and/or mineral composition.

LV-SEM imaging of the white band shows the pigment is aragonite as manifested by the elongated form crystals, typical of aragonite. This is in agreement of XRD analysis [13]. Exposed areas of the fragment shows the plaster is porous and fine-grained (Fig. 4a,b), but occasionally with some large crystals of spathic calcite (red arrows in Fig. 4a,c). The paint layer shows both physical and chemical degradation. The former had led to disintegration of the pigment and exposure of the plaster applied underneath (Fig. 4a,b). Chemical degradation is manifested by dissolution of calcium carbonate from the plaster (calcite) and the paint layer

(here aragonite) during wet season and precipitation of calcite during dry season and/or area (Fig. 4 c,d). The high porosity of the plaster (Fig. 4b) facilitates materials transport and crystallization, respectively. The neo-formed calcite smooth surface and rounded shape of grains and their coalescence indicates a dynamic process that had continued over several seasons. The white paint band made of aragonite (Fig. 5a) has also suffered this alteration with different degrees and forms of degradation (Fig. 5b,c,d). Neo-formed calcite continues to grow at the expense of aragonite pigment (Fig. 5d) and plaster calcite (Fig. 4c). It is worth saying that this degradation process that takes place under specific environmental conditions pose serious challenges to art conservators and restorers, since transformation of aragonite to calcite is irreversible under such conditions.

4. Unfired glass vessel ceramic core from Tel Amarna, New Kingdom Egypt

Ancient Egyptian civilization and material culture in particular have not ceased to fascinate people and impress specialists. In the following examples, three cases of Egyptian pyrotechnology are presented. In the first example, unfired core samples were investigated. These are pastes shaped and dried before glass was applied to their surface. It has been debated for over a century about the constituents and preparation methods of these glass vessel cores. Sand and clay were proposed by archaeologists despite the inconvenient chemical and/or mechanical properties of the ceramic core produced if sand or clay had been used. In one case, the silica from the sand will melt at the interface with glass vessel wall and it would not have been removable. Use of clay material would have caused a shrinkage in the ceramic core and a misfit with

Figure 5. SE images taken with Keysight 8500 Low Voltage Scanning Electron Microscope (LV-SEM) of the surface of a white paint layer of the same sample in Figure 4. The paint layer is composed of aragonite pigment, as evidenced by the characteristic elongated crystals (image a and b). Image in (c) shows growth and coalescence of neo-formed, rounded, and smooth calcite crystals. Image in (d) shows the growth of these calcite crystals at the expense of aragonite pigment (red arrows). It is worthy saying that this degradation process that takes place under specific environmental conditions does pose serious challenges to art conservators and restorers, since transformation of aragonite to calcite is irreversible under these conditions.

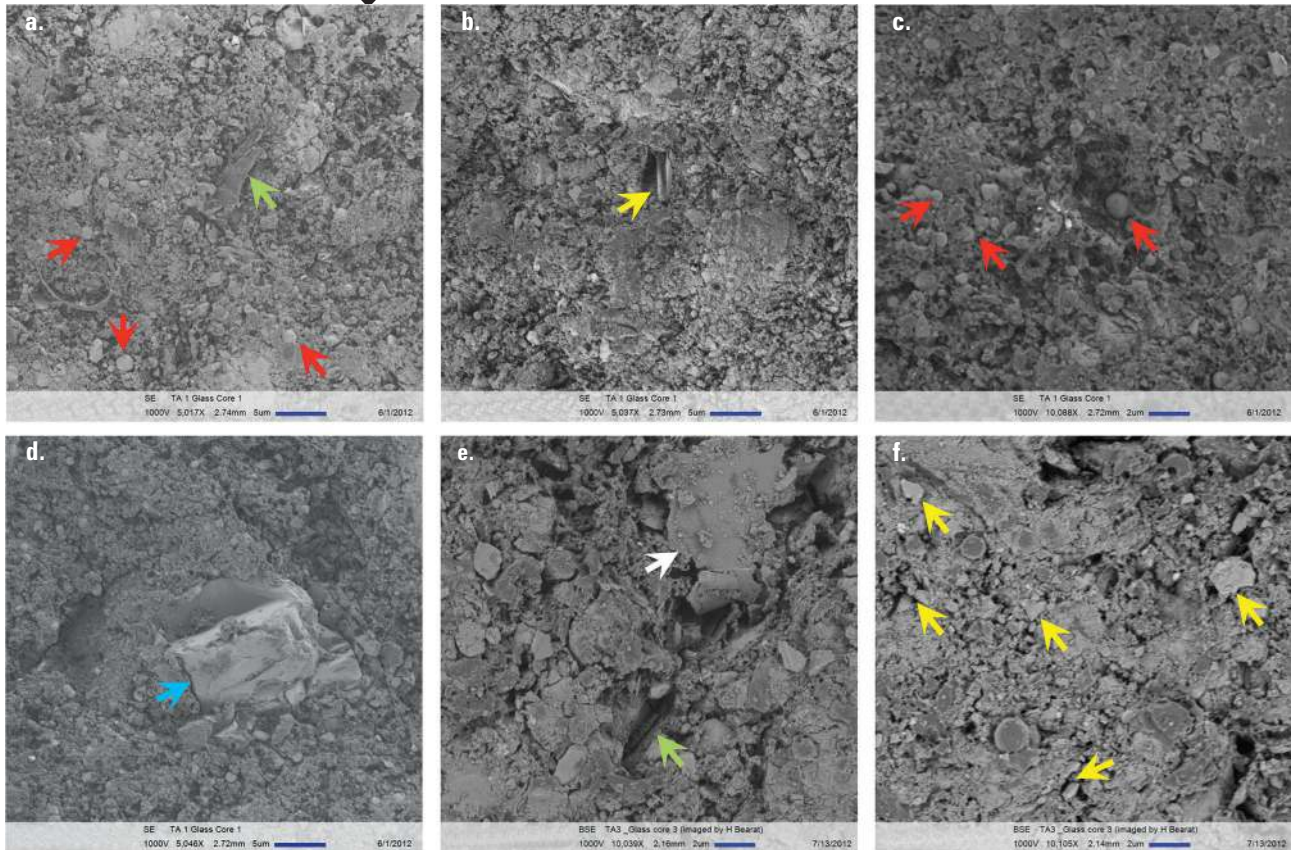
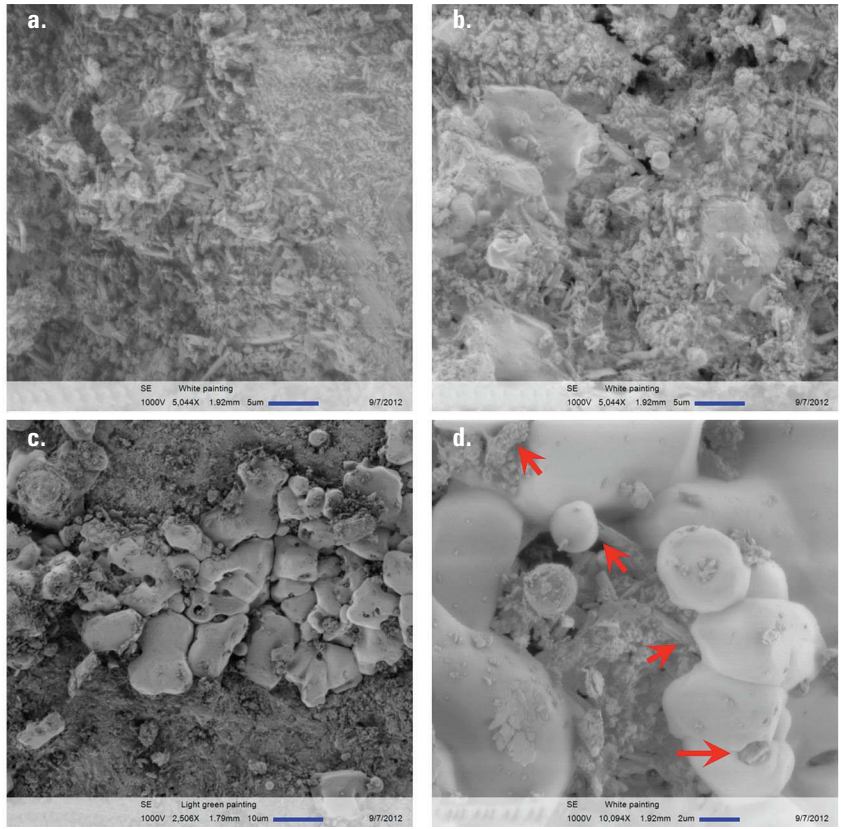
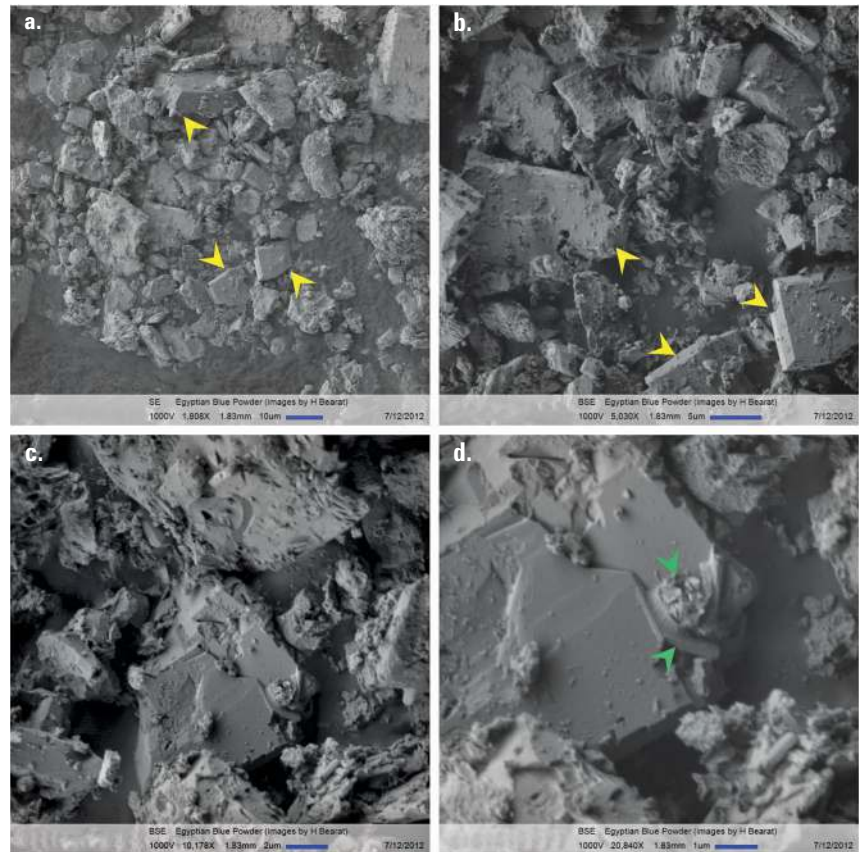


Figure 6. SE and BSE images taken with Keysight 8500 (LV-SEM) of glass vessel core material from Tel Amarna, New Kingdom, Egypt: core # 1 (a) through (d) and core # 2 (e) and (f). Recent analytical studies of three exceptional samples of unfired core material that was prepared for use in making glass vessels have brought new evidence on ancient glass technology. The images show that the core is a composite material prepared from: animal bone, animal dung, and clay. Yellow arrows indicate bone fragments; blue quartz which is associated with clay; white clay particles; brown relic of straw and barley grains from dung; red relics of bacteria from animal dung.



Figure 7. SE and BSE images taken with Keysight 8500 (LV-SEM) of a scarab made of Egyptian blue from Middle Bronze Age Palestine. Egyptian blue is the common name given to the synthetic blue pigment, which is equivalent to the tetragonal mineral cuprorivaite- $\text{CaCuSi}_4\text{O}_{10}$. It had been widely used in ancient Egypt both as a pigment in painting and gemstone imitation for inlaid, amulets, scarabs, statuettes, etc. It is widely believed that fabrication was conducted in two firing cycles separated by grinding, homogenizing and reshaping of the first frit. Second firing is performed to enhance the blue color and adhesion through crystal growth and sintering of the material. Green arrows show examples of crystal growth through solid state reaction.



the glass wall, which would cause its fracture in addition to the difficulty to remove the fired clay (ceramic) from the glass vessel afterward. Some exceptional samples found at Tel Amarna, new capital of King Akhnaten, where glass making workshops were found in the Pharaoh's palace complex were imaged. Two unfired samples, core 1 and core 3, already prepared in thin sections (Fig. 1, iv) were imaged to elucidate the nature, form, and distribution of its major constituents. Visual and optical microscopy examination have shown the samples were prepared from three major raw materials: animal bone, animal dung, and clay. The latter contained some quartz sand. Figure 5 includes SE and BSE images of the samples. The presence of straw (green arrows), barley grains (separated manually), and relics of bacteria (red arrows) indicate the use of animal dung, and most probably that of horses. Large grains (crystals) of quartz (blue arrow) and of clay minerals (white arrow) indicate the use of some clay as a plastic component to shape the core. However,

a larger component is powdered animal bone (yellow arrows), which was most probably that of birds (ducks and chicken). The combination of these ingredient is a fascinating invention, given the properties and availability of these materials. Each would have served different purposes. The animal dung would burn thus providing heat and leaving large pores that prevent shrinkage and ensure a friable product. The animal bone, would provide a refractory strong, but still friable, skeleton for the core. Moreover, it could have been recycled after removal from the glass vessel. The clay, if added as a minor component, would provide a plastic material to help shape the product and give enough strength after drying. Non-adherence to the glass wall was insured through application of a calcium carbonate-rich (marl) material as a slip on the core surface.

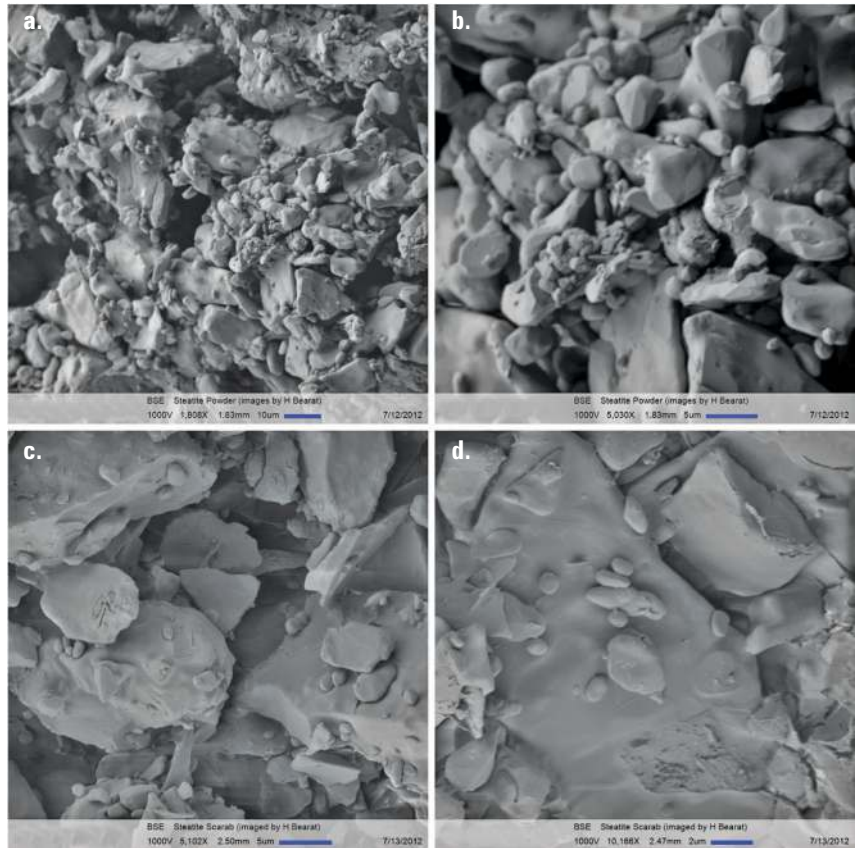
5. Egyptian blue scarab from Middle Bronze Age Palestine

Amulet, scarabs and small statuettes were very common in ancient Egypt and neighboring countries. They were made

in many different materials, whether natural or synthetic. In most cases, they served as seals with hieroglyphs that have historic and cultural significance. The first scarab examined here comes from a well dated archaeological site in Middle Bronze Age Palestine (corresponding roughly to the 18th Century BC). It is made of Egyptian blue and was imaged as is. The latter is a purely Egyptian invention known from pre-dynastic time through the Roman era. The material was made by mixing quartz, calcite, and copper ore roughly in the stoichiometric oxide composition of the equivalent mineral cuprorivaite ($\text{CaCuSi}_4\text{O}_{10}$), that is $\text{CaO}:\text{CuO}:\text{SiO}_2$ in the ratios of 1:1:4. As this stoichiometry was hard to control and the reactions take place in the solid state, where diffusion is controlling and limited, craftsmen used to grind the product finely, reshape it, and then refire it to enhance color and crystal (grain) growth. The scarab examined here is friable contrary to vitrified and coherent balls from the Roman times, where crystals with complete facets were seldom seen.



Figure 8. BSE images taken with Keysight 8500 (LV-SEM) of a scarab made of steatite from Middle Bronze Age Palestine. Steatite is the common name given to a metamorphic rock composed of talc (which is a hydrated magnesium silicate- $Mg_3Si_4O_{10}(OH)_2$, also called soapstone and soap rock. Due to its low hardness it can be carved and shaped easily and once fired, it acquires enough strength. Images show the grains to be rounded with a smooth surface; their size varies from submicron to above 10 microns. As the scarab was fired, the grain surface shows a thin coat of amorphous material produced by dehydroxylation of the talc mineral.



Here one sees clearly the tetragonal crystals that exceed 10 microns in dimension. Moreover, the blue color is homogeneous throughout the scarab. Hence, the crystal form and size, homogeneity of color, friability, evidence of crystal growth by diffusion (green arrows), all point to a refiring of the scarab. Another index to refiring is the fact that the inscription on the flat surface of the scarab (Fig. 1v). The inscription would have suffered from melting if it was applied before first firing.

6. Steatite scarab from Middle Bronze Age Palestine

This sample comes from the same context as the precedent one (Fig. 1vi) and was imaged as is. It is made of steatite or soapstone, which is composed essentially of talc ($Mg_3Si_4O_{10}[OH]_2$). This is a very convenient material to carve or shape, given its reduced hardness (1 on Moh's scale). The scripted flat surface shows traces of light green glaze rich in copper. Therefore, the scarab might have been fully glazed, but the glaze

has deteriorated as a result of use or burial. The steatite surface is rough and friable. Images obtained for this sample show well rounded grains with smooth surface. BSE images (Figure 8) show the grains to be rounded and have a smooth surface; their size vary from submicron to above 10 microns. As the scarab was fired, the grain surface shows a thin coat of amorphous material produced by dehydroxylation of the talc mineral. Cementing material is absent, which explains the friability of the sintered product. This in turn may explain the motivation of glazing the scarab to minimize its erosion and disintegration. A goal that was met at least in part, since the object has survived almost 4000 years of burial.

Conclusions

Using Keysight 8500 LV-SEM, it was quite possible to image, with high resolution and excellent contrast, several artifact samples that are too precious to alter, cut or fracture. Given

the fact that these insulating materials, whether inorganic or a mix of organic and inorganic, were quite easy to image without the need for a metal coating or radiation damage to the samples. For instance, a petrographic thin section cannot be coated for imaging, as this will jeopardize further examination with optical microscopy. Other samples such as wall painting fragments or scarabs of Egyptian blue and steatite were imaged as is, without the need for coating or taking a specimen. These analyses are otherwise not as feasible using other FE-SEMs: cold field emission SEM operating at low voltage and E-SEM, respectively. It is fair to say also that Keysight 8500 LV-SEM is proving more helpful in studying valuable archaeological and artistic samples such as painting and pigments, ceramic and sintered materials, textile, glasses and glazes, etc., when compared to other FE-SEMs currently available.

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