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Ancient Technologies: The Egyptian Sintered-Quartz Ceramics

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Abstract
To physicists and engineers, ceramics represent materials demonstrating excellent strength and hardness, materials that can serve as electrical insulators or conductors, some of them being able of a high-temperature superconductivity. To researchers working in archaeology and art history, ceramics mean objects such as figurines, tiles and tableware helping understanding cultures and technologies of the past. They are among the most common artifacts to be found in archaeological sites, because made of an imperishable material. Then, ceramics are for interdisciplinary studies the subjects by excellence. Here we will discuss the Egyptian faience, a ceramic based on sintered-quartz materials, an old high-tech material that allows creating objects which have glossy surfaces with lustre of various blue-green colours. This paper shows how faience had been produced and discusses some methods used for its analysis. Keywords are: Ceramics, Egyptian Faience, Ancient Technologies, Archaeometry, Scanning Electron Microscopy, Xeroradiography, Raman Spectroscopy, Synchrotron radiation micro-computed tomography.

Introduction
To researchers interested in physical properties and applications of materials, the study of ceramics, which are materials demonstrating excellent strength and hardness and serving both as electrical conductors and insulators, is very important. Such study requires basic investigations on their crystal structures, phase transitions, defects, and heat and charge transport properties; how ceramics interact with light and electro-magnetic fields and how respond to temperature is relevant for their several applications. Let us consider just one example showing the importance of ceramics. The Yttrium-Barium-Copper Oxide ceramic was discovered in the 1980s as the first member of the family of high temperature superconductors [1]. That is, it was the first material to become a superconductor at a temperature above the liquid nitrogen temperature. Its discovery was so stirring that revitalized the researches on superconductivity.

In archaeology and art history, the study of ceramics means the study of those objects such as figurines, tiles and tableware, which are made of inorganic solids, prepared by sintering some raw materials and by the action of heat. These artifacts have an important role in understanding cultures and technologies of the past; they are among the most common artifacts to be found in archaeological sites, because made of an imperishable material, generally in the form of fragments of broken pottery, called “sherds” or “potsherds”, that is, fragments of pottery. They are also known as ostraca (Figure 1).
Figure 1: A shred can be a small piece of art, as we can see in this ostracon of the Egyptian Museum of Turin.

The earliest ceramics made by humans were pottery objects, which were made from clay and hardened in fire. After, ceramics evolved in their composition and became glazed to have a coloured, brilliant and smooth surface. The Egyptian faience is one of these ceramics, based on sintered-quartz materials, which has a glossy surface with lustre of various blue-green colours.

To study ceramics, scholars can use two approaches: one is a traditional analysis which involves sorting artifacts into specific types based on style and morphology, the other is a more technical approach based on ceramic analysis, which needs an examination of the composition of artifacts and sherds. This analysis allows determining the source of the raw materials and, through this, the possible manufacturing site. Key criteria are, for pottery, the composition of the clay and the temper used in making the object under study. Let us remember that temper is a material added to clay during the initial production stage, and it is used to aid the subsequent drying process. After determining clay and temper compositions, the origin of raw materials can be proposed, if it is possible to identify a region where both are occurring.

The analysis of ceramic artifacts in therefore a large part of the multidisciplinary science, which is known as "archaeometry". This science consists of the application of scientific techniques to the analysis of archaeological materials. In fact, archaeometry is mainly based on physical and chemical methods, but it is also requiring studies on ancient environments, able to give information on past landscapes and climates, flora and fauna, as well as on the diet and health of people. In this paper, we will discuss the Egyptian ceramic, which is known as the Egyptian faience, aiming to show its importance as a material by excellence for interdisciplinary studies.

The Faience

The pre-dynastic Egypt produced several styles of pottery. From geometric subjects, the artists evolved in representing people and animals: during the Naqada II period, we find also
the ship theme that we can see in two images of Figure 2. Besides pottery, in the pre-dynastic graves, archaeologists found the first simple objects made of faience, some blue glazed beads that were used as substitute for precious materials such as turquoises [2]. After, faience was used for more complex artifacts.

Figure 2: Pre-dynastic pottery of the Egyptian Museum of Turin. During the Naqada II period, we have also the ship theme that we can see in the decoration of the two jars.

The Egyptian faience is a ceramic based on sintered-quartz materials. Let us note that the term “faience” is commonly referred to a glazed earthenware, the use of which spread in Europe during the Renaissance from France and Italy [3]. The term was derived from Faenza, the town in Italy, where the glazed earthenware was mainly produced. The other name often used for this earthenware is “majolica”. In fact, majolica itself had a long tradition in the North African and Near East Islamic production of ceramic. It was in the 19th century that European archaeologists used the misleading name of “Egyptian faience” to designate the siliceous ceramics produced in the ancient Egypt. The ancient faience was a completely different material, first created to imitate the gloss and colour of gems and precious stones. Let us stress again that this material started to be used in jewellery in Egypt about the fourth millennium BC [4], that is, during the pre-dynastic age.

As we will see in our discussion, the objects obtained from faience can be considered as old “high-tech” products, because of relative difficulties in giving them shape, lustre and colours. Probably invented in Egypt, during the processes associated with copper industry, this material was traded during the Bronze Age, as demonstrated by the faience objects that have
been found throughout the Bronze Age Mediterranean archaeological sites. Together with glass ingots, faïences have been recovered from the Uluburun shipwreck of 1300 BC, off the Turkish coast [5], a Late Bronze Age shipwreck then [6]. Ref.5 presents the results of elemental analyses of some deep blue and turquoise glass ingots from this shipwreck, showing that their composition is consistent with an Egyptian origin.

It seems that the production of faïence was older than that of glass, with which has in common the same raw materials. Egyptian faïence was made by grinding quartz or sand crystals and mixing them with various percentages of sodium, potassium, calcium, magnesium and, sometimes, copper oxides. Adding water, this mixture creates a thixotropic paste [7,8]. The paste is then shaped by hand in small objects, or poured into a mould. The objects were then exposed to heat. During the heating, the faïence creates its glaze, a thin hard layer of various glossy colours, depending on the particular recipe used for preparing the paste. Several researches who studied the Egyptian faïence technology indicate that this recipe changed over time and from place to place. Some of the changes involved the use of soda-rich ashes derived from halophytic plants as flux additives. Let us remember that a flux helps the materials to fuse at a lower temperature. Around the beginning of the first millennium BC, the ashes were replaced by the natural natron, which was the flux used in the glass production. Besides the changes of composition, also the techniques used in the production changed [9−11].

The natron is naturally occurring as a mixture of sodium carbonate decahydrate, which is a kind of soda ash, and of sodium bicarbonate, with small quantities of sodium chloride and sodium sulfate. The term “natron” is coming from the Ancient Egyptian. Let us note that the modern chemical symbol for sodium, Na, is coming from the Latin name “natrium”, which was referring to Wadi El Natrun, a valley in Egypt from which natron was mined in ancient Egypt.

As previously told, the mixture of the faïence could have copper oxides. The addition of copper produced the turquoise colours of faïence. The addition of manganese gives the black or purple colour. Around the beginning of glass production, during the second millennium BC, other colours had been created [12]. Using cobalt, the Egyptian obtained the blue colour, and with the addition of lead antimonite, the yellow. When glazed with blue-green hues, the faïence was considered as substitute for blue-green precious materials such as turquoise and lapis lazuli. In fact, in a funerary papyrus, we find that, to indicate the “faïence”, it was used the word “lapis lazuli” [13,14]. Ancient Egyptians knew the faïence as “tjehnet”, which meant “brilliant” or “dazzling”. And in fact, the objects made of faïence are shining with light. There is also a symbolism involved in the glazing of faïence: the blue could recall both the river Nile and the waters of heavens, the green could suggests images of vegetation, and then of regeneration and rebirth.

The objects created with faïence were amulets, beads, rings, scarabs, even beautiful bowls, and the funerary figurines known as shabtis (see some examples in Fig.3-5). The shabtis, also called ushabtis or shawabtis, were placed in tombs among the grave goods and were imagined as servants for the deceased, in the case that during afterlife, the owner of the grave had been called upon to do manual labor. The shabtis were the “answerers,” and therefore they usually carried inscriptions asserting they were prompt to answer the gods' summons to work [15]. The practice of using these servants originated in the Old Kingdom. Most shabtis were of small size, and many produced in multiples, such that they sometimes covered the floor around a sarcophagus [15]. Exceptional shabtis are of larger size, or produced as a one of-a-kind master work (see for instance, the head in the Figure 4).
Figure 3: Amulets representing the Eye of Horus, Egyptian Museum of Turin. This Eye is an ancient symbol of protection and good health. It is also known as the Eye of Ra.

Sometimes faience is considered as one of the earliest forms of glass making, and archaeologists suppose that faience, frit and glass were all made in the same workshop complexes. This was deduced from the marked similarity of the composition of faience and contemporary glasses. However, the technology of producing glass and faience is quite different. Let us briefly discuss the working of this ceramic, which is defined as the first human “high-tech” product [14]. Faience is, like our contemporary ceramic materials, an artificial medium; it is a non-clay based mixture, composed of quartz, small amounts of calcite, lime and alkalis. The faience wet mixture is, like the clay, thixotropic, but faience is a difficult material when it has to hold a shape. If pressed too much, it cracks, because of its limited plastic deformation. Therefore, to help its wet working performance, some archaeologists proposed that some binding agents, such as clay, egg white, Arabic gum or resin had been used. However, modern experiments to reproduce the faience suggest just the use of alkalis as binders, such as natron or plant ashes [11].
Figure 4: Upper images show faience bowls blue-glazed and decorated. One of the bowl, besides the decoration with lotus flowers and blossoms has two symmetric faces of the goddess Hathor. This decoration is therefore a symbol of rebirth. Unknown origin. New Kingdom, Dynasty XVIII-XX (1350-1070 B.C.), Egyptian Museum of Turin. Middle left: faience bowl decorated with lotus flowers and blossoms from the Kha’s Tomb, Egyptian Museum of Turin. Middle right: wonderful bowl of blue faience, unknown origin, decorated with lotus flowers and fishes. First period of XVIII, Dynasty (XV century BC), Aegyptisches Museum und Papyrussammling of Berlin. The decoration seems a work by Maurits Cornelis Escher. In the lower panel, we can see some funerary figurines known as shabtis of Sety I, from the Valley of the Kings, XIX Dynasty, Egyptian Museum of Turin.
Methods of shaping and glazing

Three methods had been hypothesized to shape the body of faience objects: modelling, moulding and abrasion. The last method was used in conjunction with the first two. Modelling was probably the first technique used, as we can see from the pre-dynastic bead manufacture: the object made of faience assumed its shape modelled by hand [2]. Moulding was the process of manufacturing objects by shaping the faience paste using a rigid frame.

Quite interesting are the glazing technologies employed to obtain the lustre. The glazing of a siliceous body employs various methods. Among them, the main three methods are application, efflorescence and cementation. Application glazing has been the most common glazing method in ceramic technology. The procedure is the following: a mixture of small particles of silica, lime and alkalis are mixed in water to form a slurry [2,16]. This slurry is brushed on the object to glaze, or the object is dipped in it. A coating of fine powders is then created on it that glazes upon firing [17]. The use of this technique is evidenced by the presence of brush markers, drips and glaze running lines [18]. The second glazing technique is the efflorescence. This is in fact a self-glazing process: the glazing materials, which are water-soluble alkali salts, are mixed with the particles of quartz of the core object [10]. Water evaporates and then the salts migrate from the body to the surface of the object. On surface, the salts crystallize, creating a thin superficial layer that, again, glazes upon firing [13].

As discussed in [18], the cementation method is another self-glazing technique. After the object has been formed and dried, it is buried in a glazing mixture (the cement) consisting of...
alkalis, copper compounds, calcium oxide or hydroxide, and/or quartz. Upon firing, at about 1000 °C, a glaze layer is formed on the faience surface, and, around the object, a capsule. In this method, the alkalis and copper vaporisation are crucial to the glaze formation. After firing, the cementation mixture can be crumbled away from the object, which is now coated with glaze (Fig. 6, and see also Figure 2 of Ref.18). Cementation glazing was appropriate for small objects such as beads.

Figure 6: In the cementation method, as explained in Ref.18, the object is formed and dried. Then, it is buried in a glazing mixture (the cement) consisting of alkalis, copper compounds, calcium oxide or hydroxide, and/or quartz. Upon firing, at about 1000 °C, a glaze layer is formed on the faience surface, and, around the object, a capsule. After firing, the cementation mixture can be crumbled away from the object, which is now coated with glaze.

Reference 18 is proposing a detailed discussion of some mechanisms of glazing. One of them is the Interface Glazing Mechanism (IGM). IGM involves the diffusion and migration of alkalis from the glazing powder to the siliceous faience body. Therefore, we have the production of a glass phase covering the object and a penetration into the bulk, which produces the buffer layer and some glass between the grains of quartz of the bulk (see Fig. 7). This mechanism depends on the direct contact between the glazing powder and the surfaces of siliceous objects. To characterize it, Ref.18 uses three major parameters: the object appearance, the microstructure and the glass phase composition. For what concerns the object appearance, the glaze coatings on the objects glazed are typically white or whitish blue. The microstructure of the glaze has a thickness, which is moderately thin. The glass phase compositions have essentially a high concentration of alkalis and a low concentration of copper. A comparison between the glaze, the buffer layer, that is the region between the glaze and the bulk, and the interparticle glasses reveals a decrease in copper content from the glaze layer to the bulk.

Figure 7: Two examples of how could appear some cross-sections, near the surface and in the bulk, of faience as observed by means of a Scanning Electron Microscope. The surface is covered by the glaze, which is glass. In the bulk, we can see the
grains of quartz, and, among them the glass gluing together these particles. Between the surface and the bulk there is the buffer layer. These images have been created using that of Reference18 as a model.

There is another technique, to have the glaze: this technique is the vapour glazing, based on the vaporization of salts. The salts are transported as vapours through the enveloping powder to the quartz body. Reference 18 calls this technique, the Chlorides Glazing Mechanism (CGM), because it is based on the vaporisation of alkali chlorides. As compared to objects glazed by the IGM-mechanism, the mechanical strength of objects glazed by CGM is considerably lower, and therefore they break easily. The microstructure of the body shows minimal interparticle glass. For what concerns the glass phase composition, in contrast to the objects glazed by the IGM-mechanism, the glass phases present in the glazes produced by the CGM mechanism are of the low alkalis - high copper type [18].

Interdisciplinary studies on faience

As discussed in Ref.18, the use of Scanning Electron Microscope (SEM) is able to distinguish the glass phase from the texture of the grains, giving information on the thickness of the glaze and of the buffer layer. Let us stress that SEM analyses are typically used for researches of chemistry, materials science and physics, and therefore the Scanning Electron Microscope is one of the most popular instruments in the laboratories of these research areas. However, to have a SEM analysis of faience, we need some cross-sections of it, turning this analysis in a destructive analysis.

In fact, non-destructive analyses exist able to give information on the employed technologies. The macro-photography or the use of optical microscopes can reveal some markers of the employed technique [18]. Another non-destructive method is the xeroradiography, capable of detecting subtle differences in the radiodensity of solid objects. As told in [19], xeroradiography has particular application in examining ceramics, because it produces images of greater contrast than conventional x-ray radiography. In this manner, many features of the ceramics such as its orientation in the bulk, joints, air bubbles and inclusions can be easily identified. Therefore, xeroradiography helps understanding the construction process of objects, because it allows distinguishing between modelling or moulding.

Another non-invasive analysis is the Raman spectroscopy, where a laser light interacts with molecular vibrations, reticular and other excitations of the material. This interaction shifts the energy of the laser photons. Therefore, the Raman spectroscopy, as the Infrared spectroscopy, provides information on the vibrational modes in the material. In the Raman analysis, a sample is illuminated with a laser beam. Scattered light from the laser spot is collected and the wavelengths close to the laser line removed to analyse only the light with shifted energy. Among the first results on faiences obtained using the Raman data, we have those proposed in Ref.20. The researchers studied the coloured glazed Egyptian faiences to evaluate the effectiveness of Raman microscopy as a tool for archaeometric analysis. They concluded that Raman microscopy was extremely effective for the analysis of red and yellow faience, but no so good for the analysis of green-blue faience.

After these first analyses, we can add FT-Raman spectroscopy and visible Raman microscopy to the non-destructive tools able to investigate the pigments of ancient artifacts. For instance, specimens excavated from Tell el Amarna by Flinders Petrie in the 1890s, have been studies by Raman techniques, providing information about the chemical composition of the materials used by the artists of the XVIIIth Dynasty, at the time of King Akhenaten
Moreover, as discussed in [22], where the Raman spectroscopy is used for the Roman Age mosaic glass tesserae, the Raman technique is useful to study the surface weathering. It is remarkable that the researchers were able to determine if a sample were original or a modern restoration [22]. Then, Raman spectroscopy, besides being important for pigments identification, can have a relevant role in the determination of fake faience too.

Recent researches on faience are also using the synchrotron radiation micro-computed tomography. This is a technique able to magnify images to be used as a non-invasive and non-destructive tests, in particular on biomedical samples [23]. In Ref.24, the synchrotron radiation micro-computed tomography (SR-micro-CT) was combined with the micro-probe energy dispersion X-ray fluorescence spectrometry (EDXRF) to have the microstructure and composition of beads made of Chinese faience. In China, faience suddenly appeared in the Western Zhou Dynasty (1046–771 BC), and its production is considered to be influenced by the West [24].

It is clear then, that any research project concerning the study of faience is necessarily involving archaeologists, historians, archaeometrists and researchers of materials science. In fact, the research needs a characterization of the material and a study of its provenance, and the determination of techniques of manufacture. We need also to know, about the production, some features like the firing temperature, the flux used, the pigments chosen for decoration, and so on. We can therefore conclude that ceramics, and in particular faience, can be the subjects of interdisciplinary projects by excellence.

References


