

# Probing Beneath the Surface: A Study of Ancient Egyptian Faience

By

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Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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Michelle Whitford



# Statement of Attainment

My thesis involved collaborative work with many people. This work enriched the project and was greatly appreciated. The help of others will be detailed below.

In Chapter 2, Nicole Leong provided me with the citations relating to the discussion on Ibi's tomb. Miss Leong provided both the hieroglyphic translation and transliteration for the first faience word, and also confirmed my translation and transliteration of the second faience word.

In Chapter 3, destructive analysis modelling using the pico-second laser was conducted by Alex Stokes while I observed on site. The microscope images and analysis of this experiment is all my own work.

In Chapter 4, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) samples were prepared by Alex Stokes, who introduced and taught me how to use the system. Mister Stokes also cross-sectionally polished several samples for myself to analyse using the system. All SEM/EDX experiments presented in this thesis are my own work. SEM/EDX analysis used in this thesis were also conducted by myself.

Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) was conducted with the assistance of Dr Will Powell. Dr Powell prepared the samples for study, introduced, and taught me how to use the system. The LA-ICP-MS data, plots, and analysis are all my own work.

In Chapters 5 and 6, Time-Of-Flight Secondary Ion Mass Spectrometry was completed on site at La Trobe University, Melbourne. Dr Robert Jones prepared the samples and conducted the TOF-SIMS experiments while I observed on site. I decided which beads should be scanned by discussing with Dr Jones the output parameters of the TOF-SIMS experiment. Dr Jones introduced the TOF-SIMS system to me and I was able to control the software, but Dr Jones was ultimately in control of the machine at all times. All analysis of the TOF-SIMS data is my own work.

Principal Components Analysis (PCA) was introduced to me by Professor Paul Pigram, Nicholas Welch, and Robert Madiona. Mister Welch and Mister Madiona taught me how to conduct PCA using the *Eigenvector PLS MATLAB toolbox*. Initial analysis tests were conducted by Mister Welch and Mister Madiona to show me how best to analyse my data. The PCA elemental matrices, plots, and analysis presented in this thesis are all my own work.

*Research is what I'm doing when  
I don't know what I'm doing.*

Wernher von Braun

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# Abstract

Ancient Egyptian faience is a material of many mysteries. There is limited knowledge on the recipes and manufacturing processes used to craft it. This unfortunately has led to a lack of information about faience, unsatisfactory conservation methods, and confusion about the provenance of artefacts. This thesis focuses on developing a rigorous understanding of three sets of faience artefacts. Analysis into the chemical composition of faience reveals that there are key elements used to produce different coloured artefacts. These elements are then matched to potential minerals and mineral sources, and also linked to specific time periods throughout Ancient Egypt. All three artefact sets are dated to an historical period. Next, the ageing processes of faience are investigated. Ageing in the form of alkali and alkaline leaching is observed in two of the three sets of artefacts, prompting a discussion about fraudulent artefacts. These results provide the first known investigation into the authentication of faience artefacts. A vast majority of Ancient Egyptian artefacts are displaced and have no historical context. Using TOF-SIMS analysis, all three artefact sets were shown to appear distinct when categorised by origin. This is the first time determining the origin of faience has been demonstrated to be possible.



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*Many physicists these days  
sound like the Delphic oracle -  
with equations.*

John Twelve Hawks

# 1

## Introduction

Egyptian faience is a beautiful material associated with Ancient Egyptian artefacts, and yet it is very poorly understood. The poor historical context of faience means that it is an erroneously defined material - it is frequently cited as a ceramic [1, 2], a glaze [3], or even a frit [4]. Unsatisfactory definitions have resulted in uncertain and often inappropriate conservation procedures as there is limited knowledge about faience recipes, and therefore its deterioration process.

Egyptologists have been studying faience since the early nineteenth century [5]. Unfortunately, early ‘excavators’ were no more than treasure seekers and had little regard for an artefact’s provenance or context [6]. This has led to a vast amount of unprovenanced artefacts, leaving faience poorly understood from an historical context. Further problems include the limited epigraphical and archaeological evidence about faience including the sources of its material, production recipes, and manufacture.

Recently, there has been a renaissance in the study of ancient glass. While advances have been made in understanding ancient glass deterioration by studying leaching processes in replica glass [7–9], there has been no deterioration analysis completed on faience. Current techniques used to study ancient glass involve destructive analysis which is not well received by conservators and historians. While some work is being conducted using non-destructive or micro-destructive techniques, such research is still in its infancy. A new micro-destructive method applied to ancient glass analysis is Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). While TOF-SIMS has proven to be a successful technique for understanding the mechanisms of ancient glass deterioration [10], faience has yet to receive the same study.

This thesis focuses on applying known methods used for ancient glass analysis to Egyptian faience. This will involve using both non-destructive and micro-destructive techniques on real faience artefacts, including Scanning Electron Microscopy, Energy-Dispersive X-Ray Spectroscopy, Laser Ablation Inductively Coupled Plasma Mass Spectrometry, and Time-Of-Flight Secondary Ion Mass Spectrometry. First the chemical composition of sample faience artefacts will be analysed to both observe the elemental homogeneity of faience artefacts, and to begin to understand the ingredients and recipes for faience manufacturing. Understanding the chemical composition will reveal major elemental inclusions that are consistent through all faience artefacts, as well as the appearance of any elements relating to the colour of the artefacts. Secondly, a study on the similarities and differences between the elements and molecules found in three sets of faience artefacts from different sources will be conducted. This study will highlight whether there are any chemical signatures due the source of these artefacts, demonstrating the possibility to provenance faience. Finally, the deterioration mechanisms of faience artefacts will be examined. A comparison to ancient glass deterioration will be necessary to understand the ageing behaviours observed. These behaviours will generate a discussion about the appearance, and non-appearance, of ageing effects and what implications the lack of ageing effects have on the authenticity of artefacts. Overall this study will develop both non-destructive and acceptable micro-destructive methods for analysing Ancient Egyptian faience.

*Even the finest sword plunged  
into salt water will eventually  
rust.*

Sun Tzu

## 2

# Perspectives on Egyptian Faience

Egyptian faience is defined by the British Museum as “*a ceramic material composed of crushed quartz, or quartz sand, with small amounts of lime and plant ash or natron. This body material is usually coated with a bright blue or green glaze of soda-lime-silica type*” [1]. Egyptologists have observed faience artefacts in Egypt from the Predynastic Period to the Roman Period (see Appendix B for the chronology of Ancient Egypt). Faience was ubiquitously used for beads, amulets, and shabtis (funerary figurines) (see Figure 2.1) - all artefacts associated with the funerary culture of the Ancient Egyptians. In particular, beads are commonly found artefacts throughout Egyptian excavations; “*The Egyptians were passionately fond of beads, and it is by no means exceptional to find upon a single mummy an equipment consisting of a number of necklaces, two or three [beaded] collars, a [beaded] girdle of two, and a full set of [beaded] bracelets and anklets.*” [11]

Funerary customs in Ancient Egypt were elaborate [12], so the extent of faience use



Figure 2.1: Three examples of faience artefacts. A) Collar necklace of Hapiankhtifi, a Middle Kingdom steward whose tomb was located at Meir (image credit: The Metropolitan Museum). B) Shabti of Nesi-ta-nebet-Isheru, whose tomb was possibly at Deir el-Bahri (image credit: The Brooklyn Museum). C) Amulet of the falcon god Horus from the Late Period, found at Naukratis. Note the extensive damage and ageing on the amulet in the form of discolouration and a change in lustre - almost none of the original colour is visible. (image credit: The British Museum).

within this context was significant. Figure 2.1 shows a small portion of the variety of artefacts found in Egyptian tombs. Faience artefacts are overwhelmingly, but not exclusively, coloured blue, green, and aqua. Other colours observed include yellow, black and red [13]. The blue and green colours are important in the funerary context because of their association with the god Osiris, god of the Underworld, directly linked to death and resurrection. Osiris is an anthropomorphic god whose skin is often illustrated either blue or green [14]. Green was symbolic of resurrection in Egyptian mythology associated with the continual rebirth and regrowth of crops along the Nile [15], whereas blue could either be associated with death due to cyanosis, or with lapis lazuli [14]. Thus it is clear that both blue and green have strong links to funerary associations.


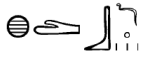
Unfortunately, the role of faience in daily life cannot be fairly assessed. There are limited examples of settlement archaeology, especially during the dynastic periods. This is because ancient towns and cities in Upper Egypt (in the south) are almost always located underneath modern cities, whereas towns and cities in Lower Egypt (in the Nile Delta) are often displaced due to the shifting river patterns. Therefore Egyptian archaeology predominately focuses on funerary and religious contexts because there is an abundance of tombs located on the outskirts of the modern Egyptian cities. The results and conclusions presented in this thesis



will therefore relate to funerary contexts rather than the daily life context.

## 2.1 Etymology and Nomenclature

The term ‘faience’ was originally used to describe medieval tin-based pottery from Faenza, Italy. Medieval faience artefacts are ceramic based and glazed with blue and green colours. These artefacts are now called majolica. Egyptian faience was named ‘faience’ by early Egyptian excavators [16] due to its physical appearance and similarity in colour to majolica wares. The problem with this attribution is that Egyptian faience shares no similarities in production, manufacturing methods, or composition to majolica. This has led to a misunderstanding of Egyptian faience resulting in confusion over its definition. For the purpose of this thesis, the Ancient Egyptian material will be called faience to distinguish it from majolica.

The Ancient Egyptians had their own names for faience. A common name used was , transliterated as *thn.t* which translates as “that which is brilliant or shines” [2]. Faience was also occasionally referred to as , transliterated as *bsbd* which translated as ‘lapis lazuli’ [2]. These ancient names can be seen in honorific titles, for example, the funerary papyrus of Qn-hr states his title as *imy-r irw bsbd*, which translates as “overseer of faience makers” [17]. These Egyptian names are based on a simple appraisal of the material, showing a basic understanding of different material types [18].

## 2.2 The Context of Faience

There is limited evidence of the manufacturing methods of faience both epigraphically and archaeologically. The evidence that is available is contentious in nature with no explicit connections to faience, only implicit ones.

The Ancient Egyptians produced a vast amount of texts such as writings on papyri, carved inscriptions, and pictorial wall paintings in tombs. These texts reveal much about religious ideologies as well as a perspective into daily life, largely from the upper classes of society. In particular, texts in tombs often illustrate aspects of practical activities, like farming and crafting, but do not offer any detailed insight into the processes involved in such activities.

The descriptions of these texts are limited, as *“la fonction de ces écrits est d’ordre administratif et littéraire et leur contenu n’a que peu de rapport avec un savoir-faire pratique”* [19]<sup>1</sup>. There are no texts about the recipes used when making faience artefacts, and very little about the manufacturing processes.

One possible reference to the manufacturing processes of faience is a wall painting from the tomb of Ibi, the chief steward of the Twenty-Sixth Dynasty pharaoh Psamtik I [20] (see Figure 2.2). Ibi’s tomb is located in Thebes and contains many well preserved wall paintings. It was first excavated by Champollion in 1844 [21], but he did not provide any deep analysis on the wall paintings in the tomb. Ibi’s tomb was further explored by Scheil in 1894 [22], who described one of the scenes (see Figure 2.2) as *“un ouvrier lave du métal dans une terrine, un autre travaille une fleur”* [22]<sup>2</sup>. However, the most cited interpretation of this wall scene is Davies’ 1902 comparison of Ibi’s tomb with a similar tomb dated to the Sixth Dynasty. Davies states that this scene shows *“the mass which is being mixed in the dish is the paste which is used in the manufacture of shabti figures and other small objects and afterwards glazed. His companion is moulding or fitting together an elaborate coloured ornament, the chief part of which is in the form of a lily with water drops hanging from it”* [23]. This interpretation has proliferated the literature as evidence of faience manufacturing.

It is unlikely that Davies’ interpretation is correct. It is also unlikely that the object being moulded and glazed is a lily, but instead a New Kingdom motif of a papyrus umbrel [24]. The umbrel design is not found in faience artefacts. With this wall scene now believed to be unrelated to faience manufacturing, we cannot rely on epigraphical evidence to understand faience.

Unfortunately similar results are found when analysing the archaeological sources. While there are a huge number of objects made from faience in the archaeological record, there is limited archaeological evidence of the process of faience manufacturing. The earliest possible evidence of a faience workshop is the Middle Kingdom settlement of Abydos [18]. Large pits lined with fire affected brick were interpreted as kilns for baking faience [18]. There

<sup>1</sup>Translation provided by Professor Yann Tristant: *“The function of these writings is administrative and literary; their content has little to do with practical know-how.”*

<sup>2</sup>Translation provided by Professor Yann Tristant: *“A worker is cleaning metal in a basin, another is working the chemical preparation.”*

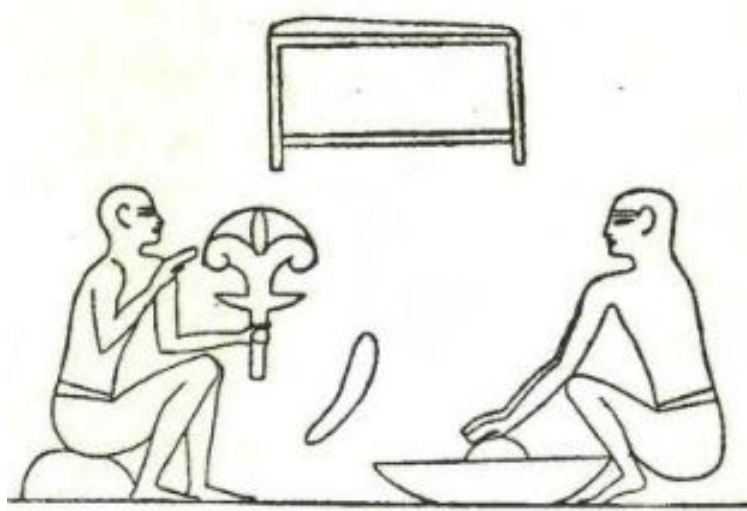


Figure 2.2: A drawing of the wall scene in the tomb of Ibi, as produced by Scheill [22]. The image shows two men working; the man of the right is mixing something in a bowl and the man on the left is moulding a floral object.

is no excavation report for this dig yet, so it is impossible to confirm the initial speculation about this site being used as a faience workshop.

Faience workshops have also been suggested at Lisht during the Middle Kingdom. The Metropolitan Museum of Art excavations at the pyramid of Amenemhet I report evidence of a house described as a “*glaze factory*” [25]. A sunken floor in one room was suggested as a place for kneading materials, while another room had a poorly preserved kiln. [25] Unfortunately the excavation report does not substantiate these claims. There is no evidence of the “*powdered limestone and water*” [25] claimed to be used in the sunken floor. Similar sunken floors found at Lisht are not associated with glaze making. For example, the tomb of Wosret is said to have “*a square cavity in the center of the tiny chamber’s floor*” [26] but there is no suggestion this is for glaze making. Nicholson and Peltenburg suggest that the kiln found at Lisht could easily be a grain silo [18]. It seems that the initial claims of discoveries of faience workshops can be discounted and cannot be used as evidence for manufacturing methods.

## 2.3 The Manufacturing Methods of Faience

The lack of clear epigraphical and archaeological evidence for the manufacturing process of faience means that scientific analysis must be relied upon to understand these processes. Three methods for manufacturing have been proposed: efflorescence, cementation, and application. Efflorescence involves mixing the glazing materials with the core material so that the glazing salts move towards the surface as the binding water evaporates during the firing process [18, 27]. In the cementation process (also called the Qom technique), the artefact is made and then surrounded in a glaze powder during the firing process [28]. Finally, the application technique involves either painting or dipping the artefact into a glaze slurry or powder and then firing it [3].

Observing the surface of artefacts does not produce any indication of the manufacturing method of an artefact. Inspection of surface microstructures was conducted by Vandiver in 1983 with limited success [29]. In the same year, Tite *et al.* compared laboratory-made artefacts using the efflorescence and cementation methods, to real artefacts thought to be made from the same techniques [30]. They discovered that both the efflorescence and cementation methods present very different microstructures in their glaze layers when their cross-sections were observed using a Scanning Electron Microscope (SEM). This was expanded by Tite *et al.* in 1986 using an SEM to look at the glaze layers of replica faience made from the application method [31]. Evidence of variations between different manufacturing methods was observed when looking at the interaction between the surface and core layers within the replica artefacts [31]. Tite *et al.* then analysed a range of glazed steatite (also known as soapstone) artefacts dated between the Badarian Period and Roman Period using an SEM to observe microstructures. They determined different manufacturing methods based on the physical indicators seen in their earlier experiments, and also demonstrated the differences between the relative percentage of magnesium and copper between artefacts made from the different manufacturing methods [32].

Recently, Tite *et al.* further expanded their study by analysing 35 faience artefacts spanning from the Middle Kingdom to the Third Intermediate Period. They compared the artefact microstructures to replica faience made from either the efflorescence method or the cementation method [33]. They found that both the modern efflorescence and cementation

methods result in similar glaze layers to ancient artefacts. All of these studies suggest that SEM is a useful technology for observing microstructures in faience materials.

## 2.4 The Composition of Faience

With no known chemical recipes for faience, scientific analysis has also been utilised to elucidate the chemical composition of faience artefacts. The first comprehensive compositional study on faience artefacts was conducted by Kaczmarczyk and Hedges in 1983, who studied a collection of faience artefacts ranging from the Predynastic Period to the Roman Period [34]. They used X-Ray Fluorescence Spectroscopy (XRF) to determine the individual chemical constituents of the surface of their faience samples. XRF is widely used to analyse the chemical composition of the surface of an artefact [35]. Importantly, portable XRF has been adapted to analyse artefacts *in situ* and on artefacts or architectural features which cannot be moved. While such technology is highly useful for initial studies, XRF is a surface analysis tool, and therefore cannot penetrate below the surface layer. This can result in a biased reading based on contaminants found on the surface of artefacts.

More recently, spectroscopy and mass spectrometry have been used with great success to identify major and minor elemental compositions of ancient artefacts. Energy Dispersive X-Ray Spectroscopy (EDX) is a non-destructive method for determining major elemental compositions in a range of materials [35]. EDX works by penetrating the sample with an electron beam, resulting in the emission of a characteristic X-Ray which can be analysed to determine the elements present on the surface of the artefact. This results in no damage to the material and has been widely used in ancient glass studies [36, 37]. While EDX is useful in determining the chemical composition, it is not sensitive enough to determine trace elements present below 0.1% which are often crucial in elemental analysis [35]. Hence EDX is often used as an initial test to determine elements of interest for further studies.

Both XRF and EDX are not sensitive enough to successfully complete a full elemental trace analysis of an artefact. With both methods it is difficult to distinguish trace amounts of heavier elements from experimental uncertainties, as the trace elements can disappear within the noise of the system. Two different types of mass spectrometry have been used for trace

analysis in ancient glass with great success: Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), and Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). LA-ICP-MS methods have proven to be suitable for trace analysis due to their high sensitivity, precision, and accuracy [38]. LA-ICP-MS has been used to study trace elements in ancient glass as well as isotopic information about ancient materials [39, 40]. An important function of LA-ICP-MS is its ability to depth profile samples [41, 42]. Depth profiling involves ablating and analysing the sample over several thin layers. By analysing a sample layer by layer, one can distinguish between surface contaminants and bulk material. One major disadvantage of LA-ICP-MS is that it is “*quasi-destructive*”[43] because the process involves removing small amounts of material to analyse. LA-ICP-MS is therefore best suited to material of low value, or chips and flakes from larger more important pieces.

The other spectrometry method which has proven highly successful in ancient glass is TOF-SIMS, a highly sensitive analytical tool with high resolution that can be used for elemental trace analysis [44, 45]. TOF-SIMS involves bombarding a sample with primary ions that ionize and eject material from the sample. The ionised ejected material are called secondary ions. The secondary ions are then processed by a mass spectrometer to determine their chemical and isotopic composition. It was successfully shown by Fearn *et al.* that TOF-SIMS could observe corrosion in replica ancient glass [46–48]. Research of this type has not yet been applied to faience. It is therefore clear that both LA-ICP-MS and TOF-SIMS are successful in analysing ancient materials, indicating that they would be appropriate methods for studying faience. In particular, LA-ICP-MS and TOF-SIMS are very good at analysing metals, which are an important feature in the material culture of faience.

*Every act of creation is first an  
act of destruction.*

Pablo Picasso

# 3

## Experimental Method

A variety of methods were used for analysing the Egyptian faience. Initially, non-destructive analysis was completed to determine rudimentary material parameters. This was done by using Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy at low energies. Next, simulations of micro-destructive testing was completed on replica faience to determine the extent of damage expected upon real artefacts. Once micro-destructive testing was deemed appropriate, Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Time-Of-Flight Secondary Ion Mass Spectrometry were conducted on three different sets of real faience artefacts.

### **3.1 Artefact Selection**

It was decided that small and invaluable artefacts would be the most appropriate samples for this project. All four experimental methods used required small sample sizes, so items approximately 1 cm<sup>3</sup> or smaller were used. The most readily available and suitable artefacts

were beads as these objects are small in size and ubiquitously found in Ancient Egyptian excavations. Three sets of beads were chosen to maximise the amount of information that could be gained. Each bead set came from a different source:

1. Museum of Ancient Cultures, Sydney,
2. The Australian Institute of Archaeology, Melbourne, and
3. Private Collector, London.

All three bead sets have no provenance and were dated to the Late Period without good evidence. The proposed artefact dates were not determined scientifically but based on appearance and thus cannot be assumed as correct. All three sets contain beads of either toroidal or cylindrical shapes (see Figure 3.1). Only the toroidal beads were scanned as the cylindrical beads were too bevelled to produce accurate results. The three sets contained a variety of different faience colours. The Museum of Ancient Cultures set contained beads that were blue, green, red, yellow and black. The Australian Institute of Archaeology set contained beads that were green, blue, brown and yellow. The Private Collector set contained only blue beads. Each bead was colour matched using a *CAPSURE X-Rite* colour matching tool and then cross-checked with the Munsell chart to determine a Munsell colour. They were grouped into colours visually for their name designations (see Appendix A for a table of information about each artefact).

It must be noted that there is no knowledge as to whether the artefacts were cleaned before they were received for these experiments. Extra cleaning was not conducted before analysis so that the surface material was not compromised by cleaning agents. There was also a desire to observe surface contaminants, which cleaning would have removed.



## 3.2 Non-Destructive Analysis

### 3.2.1 Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy

Initial experiments were focused on non-destructive analysis. Samples of different colours and visual appearance from the Museum of Ancient Cultures were mounted onto a platform with carbon tape to minimise the effects of charging. The samples were first viewed using the Scanning Electron Microscope (SEM) to find regions of interest under the highest vacuum conditions. Such regions included clean and optically uniform surfaces as well as surfaces which contained patches of darker material. Some of the beads scanned were still joined together (see Figure 3.1), so special interest was taken into looking at the cavity between the two joined beads to see if there were any signs of the manufacturing processes used.



Figure 3.1: A group of blue beads from the Museum of Ancient Cultures. The beads are still joined together as they would have been at the time of manufacture. It is proposed that such beads are made by rolling the raw material and slurry mix onto a rod or reed. The raw mixture would then be notched at even points to create smaller beads. Upon firing, the rod or reed would burn away and a long tube of notched beads could be produced, and snapped to make smaller beads. Methods similar to this have been discussed by Lucas and Harris [4].

Three areas were selected for compositional analysis using the Energy Dispersive X-Ray Spectrometer (EDX) to see if there was compositional consistency within each bead. Areas

were chosen based on the clean and optically uniform surfaces found using the SEM. The regions of interest were chosen to produce an EDX detector reading between 2-12 kcps (kilo-counts per second). This ensured that the detector was angled to the surface of the bead such that it had the highest reading of backscattered electrons as possible. The samples were viewed using the 15 kV acceleration voltage mode to reveal a backscattered electron image with good contrast.

The EDX results were loaded and viewed on *Bruker Quantax 70 EDS* software where a spectrum was produced over a 60 second detection period. The software suggested key elements due to the production of peaks over a normalised weight percentage of 0.01. Some manual peak selections were necessary due to broad peaks blending in with smaller peaks, and some small peaks not being registered. There can be high confidence in the accuracy of the spectrum, as the software is first calibrated with a copper stub with known k-alpha and k-beta X-Ray emissions. The software then produces an Excel document with the intensity in arbitrary units and the energy levels in keV that can be replotted and analysed.

### 3.3 Modelling Destructive Analysis

Archaeological analysis is focused on maximising information while minimising damage [49]. Non-destructive analysis is always preferred over destructive analysis, but the information gained by non-destructive analysis is limited. Destructive analysis is any such analysis where an artefact loses material or is altered in some way. This includes events such as removing material from the artefact like paint or glaze, ablating surface material via various methods, or cleaving and grinding material into a powder for easier analysis. It is often the case that destructive analysis will yield much more information than non-destructive analysis such as non-invasive spectroscopy, visual inspections, or X-Ray imaging.

Before conducting any destructive analysis, it was paramount ascertain whether regions of material removed, measuring up to a few hundreds of microns in diameter, would significantly alter the visible appearance of the artefacts. Tests were conducted on a modern replica of faience (see Figure 3.2) using a pico-second laser. The pico-second laser was chosen because

it best simulated the destructive analytical techniques outlined in the next section. The pico-second laser is ultra-fast and has a long wavelength, thus reducing the heat-affected zone. A single pulse with duration between 8-10 ps was used on the replica sample, with a repetition rate of 20 kHz, fluence of 11.657 and pulse energy of  $2 \times 10^{-5}$  J. The target area had a size of 500  $\mu\text{m}$  comprising a collection of 25 nested rings. This area was chosen as it is the upper limit of target areas of the destructive methods described below.

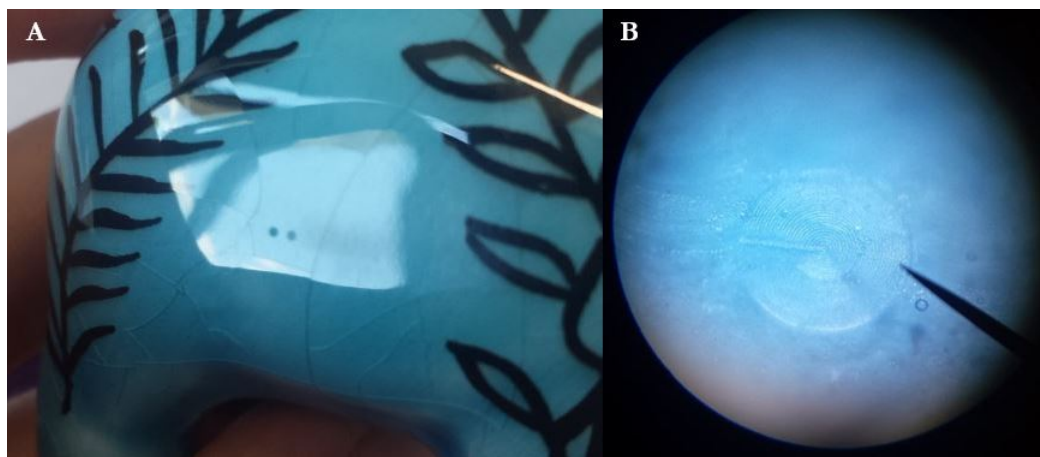


Figure 3.2: A) An image of the replica faience with two tested regions. The diameter of the target areas is 500  $\mu\text{m}$ . A change in lustre can be observed at this level. B) A close-up of the damaged area on the replica faience. The concentric ring pattern can be observed but there is no obvious heat-affected zone or signs of heat damage.

The damaged area was then viewed under a microscope to observe the extent of the damage (see Figure 3.2). It was observed that there were minimal heating effects experienced by the glaze on the sample artefact, and no obvious heat-affected zone. The nested rings are clearly visible, suggesting that the heat produced by the laser is quickly dissipated and does not effect regions outside of the target area. It was also observed that the shiny surface of the replica glaze changed its lustre and appeared more matte.

This result demonstrated minimal damage to replica faience, suggesting that similar results would be achieved with real faience artefacts. Three blue faience beads provided by the Museum of Ancient Cultures were tested using the pico-second laser. Two of the three beads already presented signs of ageing where the blue colour was changing to green and yellow hues. Each bead was targeted with the same laser parameters as above.

After the beads were exposed to the pico-second laser, they were observed under a

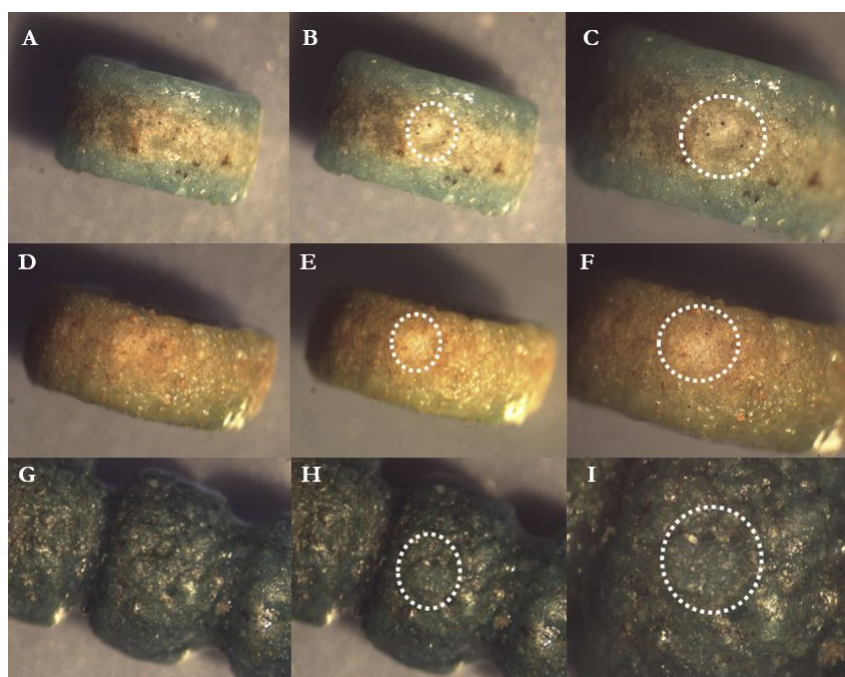


Figure 3.3: Before and after images of the three Museum of Ancient Cultures beads viewed under a microscope. A) The aqua bead before exposure. B) The aqua bead after being exposed to the pico-second laser. The damaged region has been circled, highlighting the slight change in colour. C) A closer image of the damage region in the aqua bead. D) The green bead before exposure. E) The green bead after being exposed to the pico-second laser. The damage region has been circled, revealing a slight change in colour which appears to be due to surface dirt ablation. F) A closer image of the damaged region in the green bead. G) The dark blue bead before exposure. H) The dark blue bead after being exposed to the pico-second laser. The damaged region has been circled, showing minimal colour changes. I) A closer image of the damaged region in the dark blue bead.

microscope to assess the damage. Figure 3.3 shows the before, after, and close-up images of the damaged area of the beads. Visually, the damage due to the pico-second laser is minimal. The damage primarily takes the form of discolouration because target areas appear a shade lighter than their initial colours. The target areas also appear cleaner because of the surface ablation. This suggests that pico-second laser has ablated the surface material and exposed some of the core material. This is further supported with the change in lustre, as the target area appears more matte than initial observations. It is likely that there are some minimal changes to the topology of the target area, but due to the coarseness of the surface of artefacts such damage is negligible.

## 3.4 Micro-Destructive Analysis

### 3.4.1 Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Samples were mounted onto a flat platform and levelled to ensure that the top faces of the beads were at the same height. Analysis was conducted using a *Photon Machines* Laser Ablation Inductively Coupled Plasma Mass Spectrometer Microprobe (LA-ICP-MS) at the Geochemical Analysis Unit at Macquarie University. The machine has a 193 nm excimer laser with a frequency of 5 Hz and an output pulse energy of 4 mJ. The ejected material was then transported to the spectrometer by argon carrier gas flowing at 1.02 L/minute. Surface spectra was taken with a 50  $\mu\text{m}$  circular raster analysis area and scanned for 118 seconds. Depth profiles were taken with a 50  $\mu\text{m}$  spot area with 30 seconds of background scanning and 90 seconds of analysis scanning.

For the LA-ICP-MS experiment, one bead of each colour was selected from the Museum of Ancient Cultures set to test for uniformity within the beads. Each bead was scanned three times with the depth scan at different places along the bead. Analysis areas were chosen with bias to optically smooth surfaces as viewed through the finder camera in the machine. Areas with large regions of different colours were not scanned. All the beads were depth profiled three times, but raster scanned only once. The results were regarded as accurate as they were calibrated against two different standards, STD610 and BCR2, of known elemental composition. These standards were scanned at the beginning and end of the experiment so that the data could be averaged over any equipment error experienced by the spectrometer.

### 3.4.2 Time-Of-Flight Secondary Ion Mass Spectrometry

Samples were mounted on a circular mask (see Figure 3.4). Analysis was completed using an *ION-TOF TOF.SIMS 5* Time of Flight Secondary Ion Mass Spectrometer (TOF-SIMS) machine at the Centre for Materials and Surface Science (CMSS), La Trobe University, Victoria. The machine has a bismuth manganese (Bi/Mn) liquid metal ion gun source, but only the bismuth source was used for this experiment. Surface spectra were taken with an analysis area of 100  $\mu\text{m}$  x 100  $\mu\text{m}$  with the  $\text{Bi}_+^1$  source at 30 keV and with target current of 1.0 pA. Depth profile were taken with a sputter area of 350  $\mu\text{m}$  x 350  $\mu\text{m}$  with an  $\text{O}_+^1$  source at 1 keV and beam current of 250 nA. Profiles had a mass resolution of >6000 at  $^{29}\text{Si}$ . The



chamber was flooded with low energy electrons to compensate for charging.

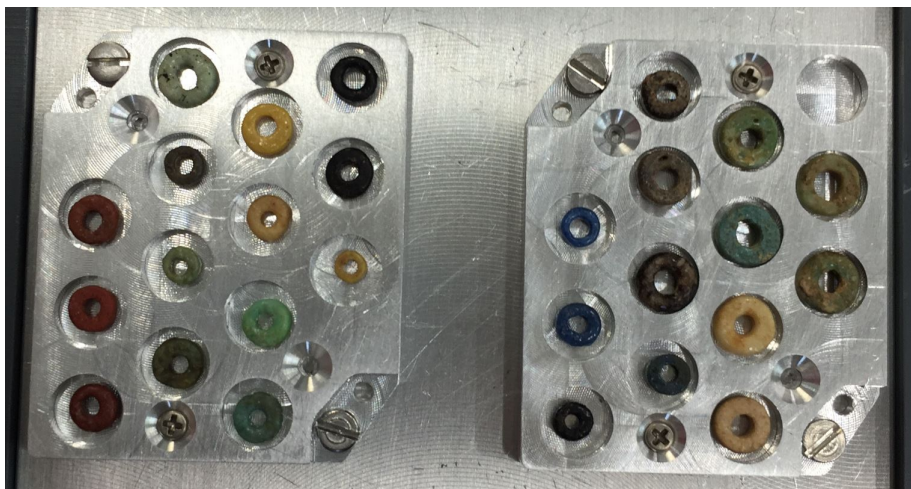


Figure 3.4: The Museum of Ancient Cultures and Australian Institute of Archaeology beads that were analysed by the TOF-SIMS. While only two beads of each colour for each set were scanned, multiples of each colour were chosen to find the optimal surfaces to scan. The Private Collector beads were scanned using a different mount due to their size.

Areas chosen for analysis were selected based on the topology and charging aspects of individual beads. Flat surfaces with minimal surface roughness were chosen to achieve the highest signal. This was difficult to achieve as the beads had a naturally bevelled topology making it difficult to find a  $350\text{ }\mu\text{m} \times 350\text{ }\mu\text{m}$  flat surface. Therefore while three of each colour bead from the Museum of Ancient Cultures set were mounted, only two were scanned because it was noted that one out of every three beads was often unsuitable for scanning.

*There are always flowers for  
those who want to see them.*

Henri Matisse

# 4

## An Artefact of Any Colour would Look as Sweet

One of the first set of questions posed in this thesis were what are the recipes for faience, and what elements are responsible for the variety of colours and shades of the faience beads? Before even looking at the elemental composition of a variety of beads, the homogeneity of faience beads first needed to be established. After this was done, analysis of the major and minor elemental constituents was carried out. Broad analysis was supported with methods of higher resolution to determine the impact of trace elements. Following these procedural methods, there is a discussion of the probable elements and minerals that appear to influence the different colours seen in faience.

## 4.1 Homogenous Beads

Determining whether faience artefacts are chemically homogeneous is an important aspect of understanding their manufacture. Uniformity would suggest a recipe where artisans skilfully crushed up their raw ingredients into a mixture which is the matrix of the whole artefact. If there is a divergence between the surface composition and the core composition, this could imply that a glaze of different composition was applied to the core of the material (implying that the cementation or application method of manufacture was undertaken). However large inclusions of elements would suggest a simple, unrefined mixing method.

Homogeneity was explored using Energy Dispersive X-Ray Spectroscopy (EDX). EDX scans the surface of an artefact and provides an elemental spectrum of the characteristic X-Rays received by a detector. EDX can provide an image of the target region highlighting where elements are detected (see Figure 4.1). This is analytically useful for identifying the morphology of the homogeneity of faience in a visual format. It gives a broad compositional view where it is easy to see deposits of individual elements.

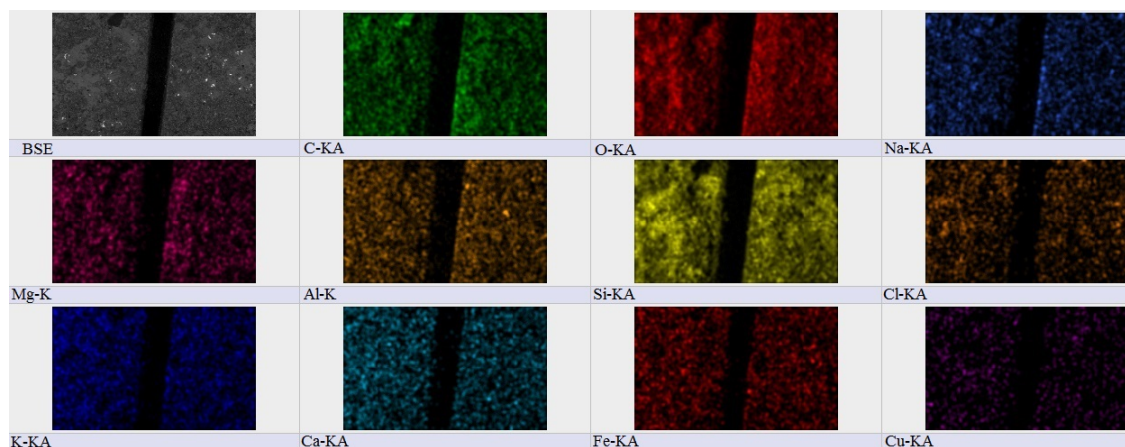


Figure 4.1: A 500  $\mu\text{m}$  EDX scan of a red bead from the Museum of Ancient Cultures. This bead demonstrates good uniformity of elements as there are no elemental hotspots present. The images from left to right show the backscattered electrons, carbon, oxygen, sodium, magnesium, aluminium, silicon, chlorine, potassium, calcium, iron, and copper.

Homogeneity was observed for all surface scans. There was some variability in the normalised weight percentages of elements for beads of the same colour, but such differences were minimal. To develop an average elemental composition from the EDX, a red and blue



bead from the Museum of Ancient Cultures were scanned in four different locations and then averaged to produce the elemental composition (see Section 4.2 for analysis).

Nonuniformity in the chemical composition was first observed when a cleaved bead was examined using the EDX. The beads were cross-sectionally polished based on material removal via an argon ion beam. This form of cross-sectional polishing was undertaken to ensure that all subsurface features would be preserved and not contaminated with the abrasive compounds used in traditional polishing methods. Figure 4.2 shows a large iron inclusion which presents as a void in the silicon image. This demonstrated that while perhaps on the surface homogeneity was apparent, this could not be guaranteed below the surface.

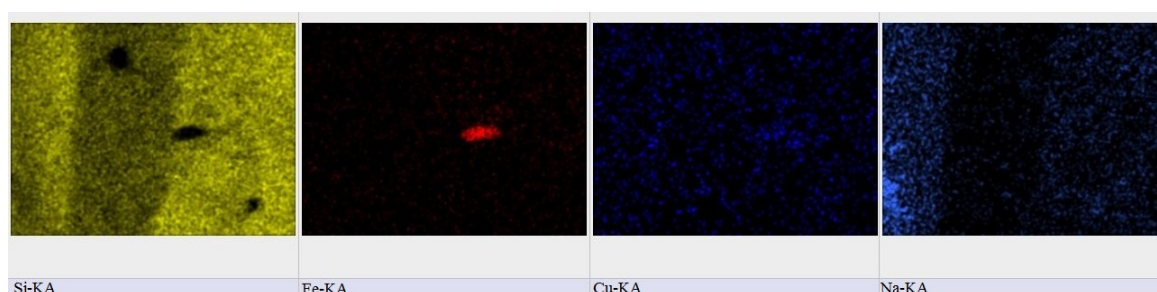


Figure 4.2: A 200  $\mu\text{m}$  EDX scan of a sample red bead. This bead was cross-sectionally polished before scanning so the target region was the core material. The images from left to right show silicon, iron, copper, and sodium. An iron inclusion was clearly visible, and corresponded to a silicon void.

Further testing on homogeneity was conducted using a Laser Ablation Inductively Coupled Plasma Mass Spectrometer Microprobe (LA-ICP-MS). LA-ICP-MS was first conducted in the depth profile mode, where one target region was pulsed for 90 seconds. This was completed for all beads, at three different locations for each bead. The elemental concentration for one bead was plotted for the three different scanning regions to see if the LA-ICP-MS demonstrated nonuniformity in the subsurface. Figure 4.3 shows the consistency of elements in one aqua bead. Results suggest that the three target regions are mostly homogeneous, with the exception of some metals for the target site for 'Aqua 2'. The 'Aqua 2' site demonstrates a stronger presence of aluminium, titanium and iron. This could be explained by this region having large inclusions, or a stronger percentage, of iron. Minerals such as hematite and ilmenite are a possibility because they are iron oxide minerals that are associated with both aluminium and titanium [50], thus explaining the increase in aluminium and titanium. These results imply that there is a degree of homogeneity with some mineral inclusions apparent in

the faience beads.

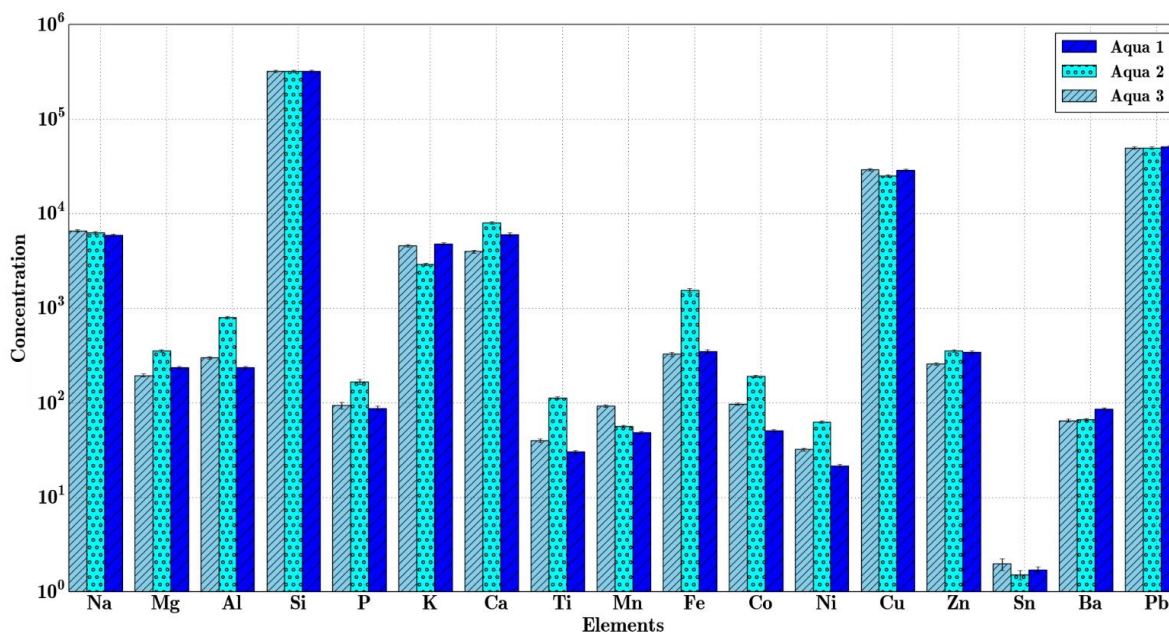


Figure 4.3: An LA-ICP-MS log plot of the major elements in the composition of a single aqua bead scanned in three different places. Good consistency was found across most elements, with the exception of aluminium, titanium and iron. The errors are one sigma.

## 4.2 Elemental Composition

Knowing that faience artefacts can be nonuniform in nature, averaging methods were conducted to determine the elemental composition of different coloured faience artefacts. EDX was used to determine a rudimentary analysis of major elements. Analysis was conducted by scanning two beads of each colour from the Museum of Ancient Cultures in four different locations. The average of the results helped to remove any differences due to nonuniformity. The results of this experiment are presented in Table 4.1.

The EDX results presented several interesting results. Firstly, all beads revealed a strong presence of silicon, calcium, and sodium while secondly there are some differences in metal concentration linked to specific colours. In particular, lead present in relatively strong concentrations in the yellow beads, copper appears high in the blue, green and aqua beads, and finally iron is strong in the black beads. Before further analysis was conducted on the connection between metals and colours, a second elemental test was conducted to confirm the

EDX results. LA-ICP-MS was used on beads from the Museum of Ancient Cultures. Both surface and depth scans were conducted using the LA-ICP-MS. Only the depth results are presented in this thesis (see Figure 4.4), as the surface results only showed small variability to the depth results which could be explained by fluctuations in the homogeneity as discussed above. To further avoid variations, two beads of each colour were scanned, with each bead scanned three times to achieve an average value.

Bead Colours by Normalised Weight Percentage						
	Red	Black	Yellow	Blue	Aqua	Green
<b>Oxygen (O)</b>	42.96	39.07	40.89	47.39	42.30	47.64
<b>Carbon (C)</b>	28.65	32.28	21.09	17.92	27.24	20.40
<b>Silicon (Si)</b>	<b>21.73</b>	<b>19.66</b>	<b>27.45</b>	<b>27.03</b>	<b>22.92</b>	<b>24.38</b>
<b>Sodium (Na)</b>	<b>1.55</b>	<b>1.20</b>	<b>1.73</b>	<b>1.69</b>	<b>1.15</b>	<b>1.13</b>
<b>Magnesium (Mg)</b>	1.09	0.90	1.40	0.26	0.69	0.51
<b>Calcium (Ca)</b>	<b>1.58</b>	<b>1.59</b>	<b>1.17</b>	<b>1.07</b>	<b>2.05</b>	<b>2.67</b>
<b>Iron (Fe)</b>	<b>0.78</b>	<b>2.39</b>	0.38	0.08	0.56	0.35
<b>Aluminium (Al)</b>	0.49	0.66	0.39	0.41	0.77	0.18
<b>Manganese (Mn)</b>	0.54	0.70	0.00	0.00	0.00	0.00
<b>Phosphorus (P)</b>	0.33	0.13	0.21	0.03	0.21	0.03
<b>Chlorine (Cl)</b>	0.31	0.37	0.49	0.67	0.45	0.47
<b>Potassium (K)</b>	0.11	0.26	0.14	0.39	0.20	0.19
<b>Sulfur (S)</b>	0.18	0.05	0.00	0.06	0.12	0.08
<b>Copper (Cu)</b>	0.00	0.48	0.00	<b>2.09</b>	<b>1.49</b>	<b>1.90</b>
<b>Lead (Pb)</b>	0.00	0.00	<b>4.09</b>	0.84	0.00	0.30

Table 4.1: The average normalised weight percentages of elements present in the Macquarie University Museum of Ancient Cultures faience beads. The results presented are the average value for two beads, each scanned at four different locations. The total weights do not sum to 100 due to the variability in the averaging process. Highlighted values are indicative of interesting results which will be discussed below.

The LA-ICP-MS results demonstrated a much higher sensitivity than those presented in Table 4.1. This is due to the presence of many more elements, including trace elements. Trace elements are important when understanding ancient materials because they may indicate

certain minerals chosen by the ancient artisans. Elements which appear in the LA-ICP-MS results that did not present in significant quantities in the EDX data are cobalt, nickel, zinc and tin.

To explore the impact of elemental concentration and colour, the concentration of each element was plotted for faience artefacts of different colours (see Figure 4.4). These results again show a strong presence of silicon, calcium, and sodium in all colours as revealed by the EDX. Furthermore, the LA-ICP-MS also corroborated the EDX results for lead (with the aqua bead also having a high concentration of lead), copper and iron. An element which was not flagged by the EDX that may indicate colour was cobalt which was strong in the blue and aqua beads. Using deduction, it is possible to make suggestions as to the probable minerals supplying these elements.

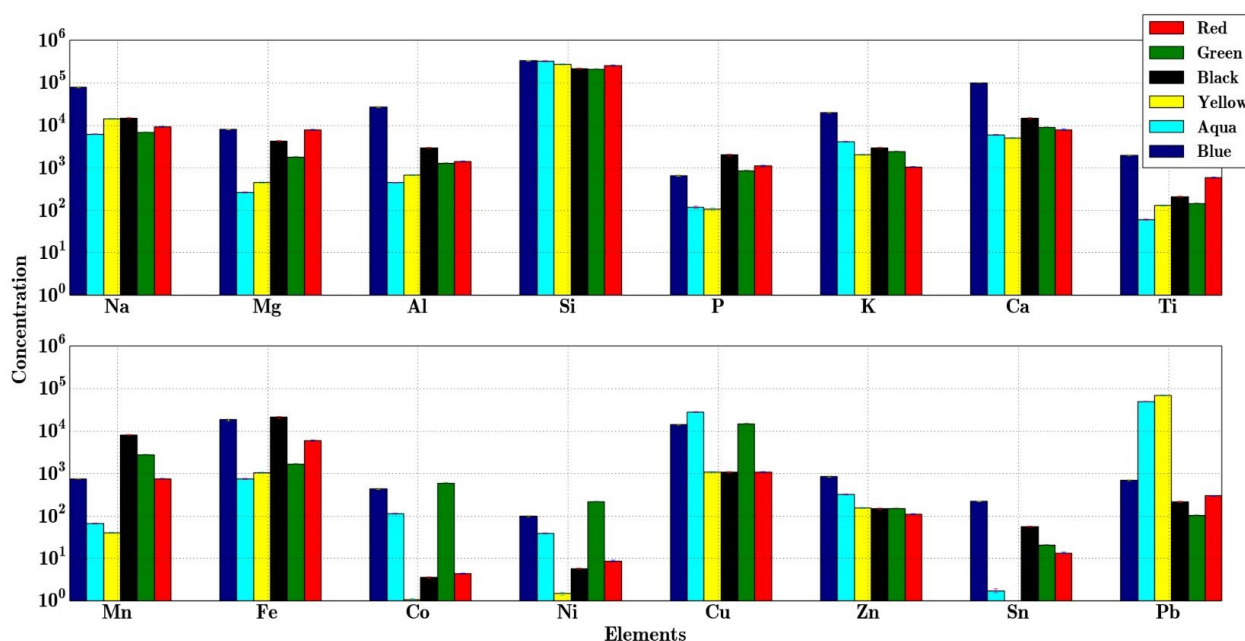


Figure 4.4: An LA-ICP-MS log plot of the concentration of selected elements over a depth profile of different coloured faience beads.

#### 4.2.1 Mineral Suspects

There were three main elements that appeared strongly in all beads in both the EDX and the LA-ICP-MS: silicon, calcium, and sodium. The silicon content can be explained by sand, one of the fundamental raw materials used in faience production. Sand is abundant in Egypt, making silica the likely source for the high silicon content in faience. It has also been

suggested that quartz is a potential source for the silicon content [51, 52]. However this is disputed by Lucas and Harris, and Kaczmarczyk and Hedges, who claim that there is not enough quartz in Egypt to have manufactured the extensive quantity of faience artefacts found [4, 34].

Calcium has also been recorded to be present in Ancient Egyptian sand [53]. While calcium is present in Egyptian sand, the main source is likely to be from limestone (calcium carbonate), used since the First Dynasty [54]. Major limestone quarries are located throughout Egypt, but in particular at Tura, Masara and Mo'alla [54]. Calcium is therefore an easily accessible element for use in the core material of faience.

The presence of sodium is important in the manufacturing of faience. The most likely source of sodium is natron (sodium carbonate and sodium bicarbonate compound). Natron was a widely used material in Ancient Egypt, most notably, as an embalming salt for mummification [53]. Currently there are three known sites for natron in Egypt: Wadi Natrun, Beheira, and El Kab [13]. Sodium, in the form of sodium carbonate, was used as a flux for silica, lowering the melting point of silicon to produce faience [4]. Hence it is not surprising to find sodium in significant quantities in all three sets of beads, and in all studied faience artefacts [34].

### **But what makes faience the colour it is?**

There were several elemental indicators believed to be linked to colour. Firstly, there is a high concentration of lead in the yellow beads (see Table 4.1 and Figure 4.4). It is thought that the source of the yellow colour is from lead monoxide. Lead monoxide can be found in the naturally occurring mineral litharge, which forms from oxidized galena (lead sulfide) ores. Galena was abundant throughout Ancient Egypt [4], and was mined from sites such as Gebel Rosa that was active in the Twenty-Sixth Dynasty [55]. Galena was commonly used in Egypt both makeup [56] and faience [4].

While not strongly apparent in the EDX, lead was present in high quantities in aqua in the LA-ICP-MS results (see Figure 4.4). This potentially indicates how ancient artisans developed a lighter blue colour, since lead appears as a major difference between the blue and aqua beads. Lead oxide has been reported in some Eighteenth, Nineteenth, Twenty-Sixth

and Thirtieth Dynasty blue faience artefacts [57]. It therefore seems probable that lead was added to blue faience in small amounts to lighten the colour.

Copper and cobalt appear strongly in blue, aqua, and green faience beads. It has long been thought that copper is the inclusion which causes faience to be blue [4, 58, 59]. Copper was in production from the Predynastic Period [60] and was readily available throughout Ancient Egypt. In particular, the regions Wadi Dara [61] and El-Urf [62] show evidence of mining from as early as the Early Dynastic Period. Naturally occurring minerals such as malachite (a copper carbonate hydroxide), azurite (a form of copper carbonate) and chrysocolla (a hydrated copper silicate) have all been listed as potential sources of copper used by the Ancient Egyptians [4]. There is also the possibility that copper was mined as cuprite (copper oxide), a bright red mineral that is often found in association with the other named minerals as well as iron oxide. This may explain the presence of copper in red beads and may even be a major factor in colouring them red.

The other element often associated with blue, aqua and green faience artefacts is cobalt, and cobalt-oxide. There are no large cobalt deposits found in Egypt, meaning that most, if not all, cobalt was imported except for the trace amounts found associated with copper. Cobalt in significant quantities (above 0.075% [34]) isn't found in ancient artefacts until the Eighteenth Dynasty [63]. The consequence of this is that it is possible to date artefacts containing large quantities of cobalt to at least the New Kingdom, but not before. The duration between New Kingdom and the Late Period represents a large range of time, but this first use of cobalt provides a *terminus post quem* (the limit after which), where cobalt is present in the compositional analysis.

Iron is another major element present in all beads, but particularly so in black beads (evident in both Table 4.1 and Figure 4.4). As mentioned in Section 4.1, both hematite and ilmenite are potential sources of iron. There is an abundance of iron mines in Egypt, particularly along the Sinai [64]. Both minerals can be black or red in colour which explains why iron is strongest in the red and black beads in Table 4.4.

## 4.3 Determining Dates

Ancient Egypt's metal ages were distinct, and the chronology of metal use is well documented [4]. These distinctions makes it possible to use the concentration of certain metals as a method of dating an artefact. Iron is one such metal which can be used as a dating indicator. Ancient Egypt entered the iron age very late compared to other ancient cultures. Before the Late Period, the only source of iron was from meteorites [1, 4] because the Ancient Egyptians had not yet developed adequate technology to extract iron by smelting iron ore. Recent research has shown that Predynastic iron beads [65] and Tutankhamun's dagger [66] were manufactured using meteoric iron rather than terrestrial iron. This strongly suggests that iron, like cobalt, can be used as a *terminus post quem* to date artefacts containing meteoric iron. Such iron is distinguished by a high percentage of nickel relative to terrestrial iron.

All three set of beads analysed in this thesis contain iron. To determine the source of the iron, the relative percentages of iron and nickel were taken from the LA-ICP-MS data, and later confirmed by the TOF-SIMS analysis, for a comparison of the content. Lucas and Harris stated that meteoric iron contains a high percentage of nickel, within the ranges of 6 - 14% [4]. The nickel content for all beads was well below one percent when compared to the iron content. This implies that all three sets of beads can thus be dated to at least the Late Period with high degree of confidence since the low percentage of nickel suggest these beads contain terrestrial iron rather than meteoric iron ore.

This indication is further corroborated by the presence of cobalt-oxide in concentrations above trace values (see Figure 4.5). As discussed in Section 4.2.1, cobalt only began to be found in significant quantities in artefacts from the New Kingdom onwards. This corroborates with the percentages of iron and nickel, suggesting that all three sets of beads were manufactured late in Egypt's history. This result provides a new method for historians to determine approximate dates for unprovenanced faience artefacts containing metals.

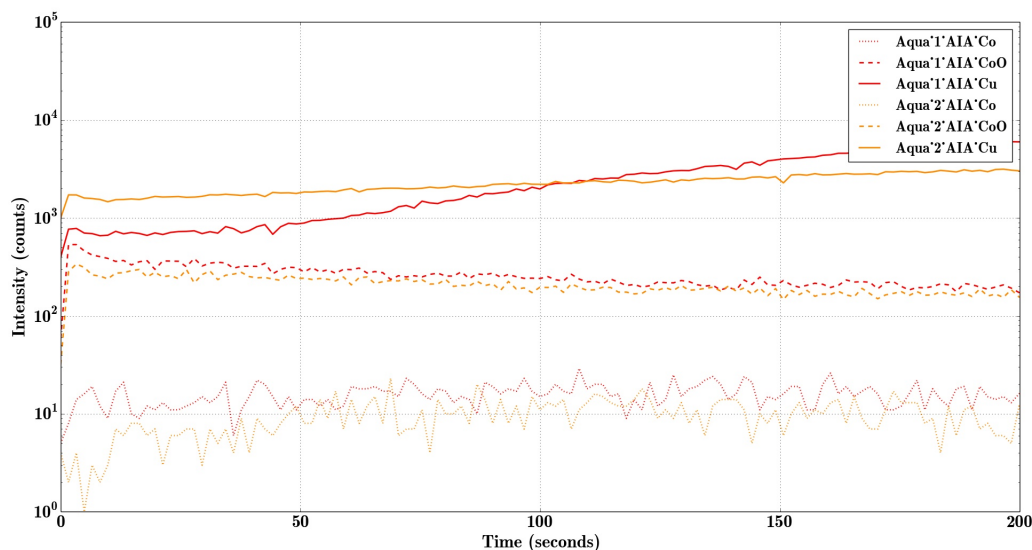


Figure 4.5: A TOF-SIMS plot of the copper, cobalt, and cobalt-oxide values found in the aqua AIA beads. These trends were similarly observed for all blue beads.

## 4.4 Summary

In this chapter, the homogeneity of faience beads was discussed. It was decided that it is possible to find areas of nonuniformity in faience due to an iron inclusion observed in the subsurface of a bead. Therefore, when the elemental composition of faience is analysed, averaging techniques must be completed. EDX and LA-ICP-MS results showed that all beads exhibit a strong presence of silicon, calcium, and sodium. The source of these three elements were discussed in depth. The EDX and LA-ICP-MS also showed varying differences between metal content corresponding to different colours. The key elements associated with colours are lead which was strong in yellow and aqua; copper and cobalt which are strongest in blue, aqua and green beads; and iron which is prominent in black and red beads. Iron is also interesting, as depending on the relative percentage of iron to nickel, one can classify whether the source of iron was meteoric or terrestrial. This classification then allows for a *terminus post quem* to identify a probable date for the manufacture of faience artefacts.



*Aut inveniam viam aut faciam.*

I will either find a way, or make  
one.

Hannibal Barca

# 5

## The Recent or Entire History of an Artefact?

Provenance is one of the most important aspects for understanding the historical background and veracity of an artefact. Provenance provides the age and origin of an artefact. Without provenance there is no historical context so the meaning of an artefact is more difficult to ascertain. Unfortunately, treasure hunters for hundreds of years have excavated, removed, and displaced a large quantity of ancient materials [6], including faience. As a consequence, many faience artefacts in museums have no provenance rendering their physical appearance the only source of information about those artefacts. Without additional information, it is impossible to determine the origin of unprovenanced faience. This chapter presents a new approach for differentiating the faience beads supplied from different sources.

### 5.1 The Same, Only Different

It is proposed that ancient faience artefacts made by the same artisan, using the same ingredients, and at the same time, should share a chemical signature. Despite the variation in metals

concentrations due to desired colour choices (as discussed in Chapter 4), fundamental raw materials like silicon, calcium, and sodium, and environmental elements like hydrocarbons, should present similarly in sets of beads. The similarities and differences of any faience object should become obvious when artefacts from different sources are compared.

Depth profiling was conducted using the TOF-SIMS method (see Section 3.4.2), where each sample was kept in a static position with respect to the TOF-SIMS beam over the course of the scan. The samples were exposed to the TOF-SIMS beam for two hundred seconds, which resulted in a scanned depth of some hundreds of nanometres. Exact measurements of depth were not achievable in this thesis due to the rough topography of the surface layer of the faience beads. Simple measuring techniques were therefore not feasible, and a more highly specialised photometric device would be required. Such equipment was not available at the time of experimentation. Despite this, an estimation of the depth can be given based on the TOF-SIMS analysis carried out on replica ancient glass. Fearn *et al.* replicated ancient glass through accelerated ageing by exposing their glass to high humidities [46]. They then depth profiled their glass using Secondary Ion Mass Spectrometry (SIMS) to observe any changes in elemental composition. By comparing their data to the results presented below, an estimated range of 100 - 200 nm is believed to be a representative range for the scanning depth for the artefact samples presented in this thesis.

## 5.2 A Curious Case of Hydrocarbons

The hydrocarbon group was subject to analysis because some interesting trends were observed during the TOF-SIMS experiment. Notably, the hydrocarbons appeared unique to each set of beads (see Figure 5.1). The hydrocarbons in the Museum of Ancient Culture beads start at a maximum value and decrease very slowly to an approximately constant value, well above the level of noise. Occasionally, anomalous spikes were observed in these beads (see Figure 5.1). This is in contrast to the Australian Institute of Archaeology beads, where the hydrocarbon values started at a maximum and dropped rapidly to a negligible value compared to the major chemical constituents. Finally, the Private Collector beads decrease in a fashion similar to the Museum of Ancient Cultures beads, but eventually drop to negligible values as well.

Before any comparative analysis was conducted, the appearance of the hydrocarbons was subjected to further research. The hydrocarbons in the Australian Institute of Archaeology and the Private Collector beads can be explained as surface containments because they both decrease to negligible levels, indicating that they are only present in significant amounts on the surface of the beads. However, the Museum of Ancient Cultures beads demonstrated differing behaviours. They showed slow decay of the hydrocarbons that plateau to a non-negligible amount. This potentially indicates that the hydrocarbons are ingrained into the material in addition to being present as surface contaminants.

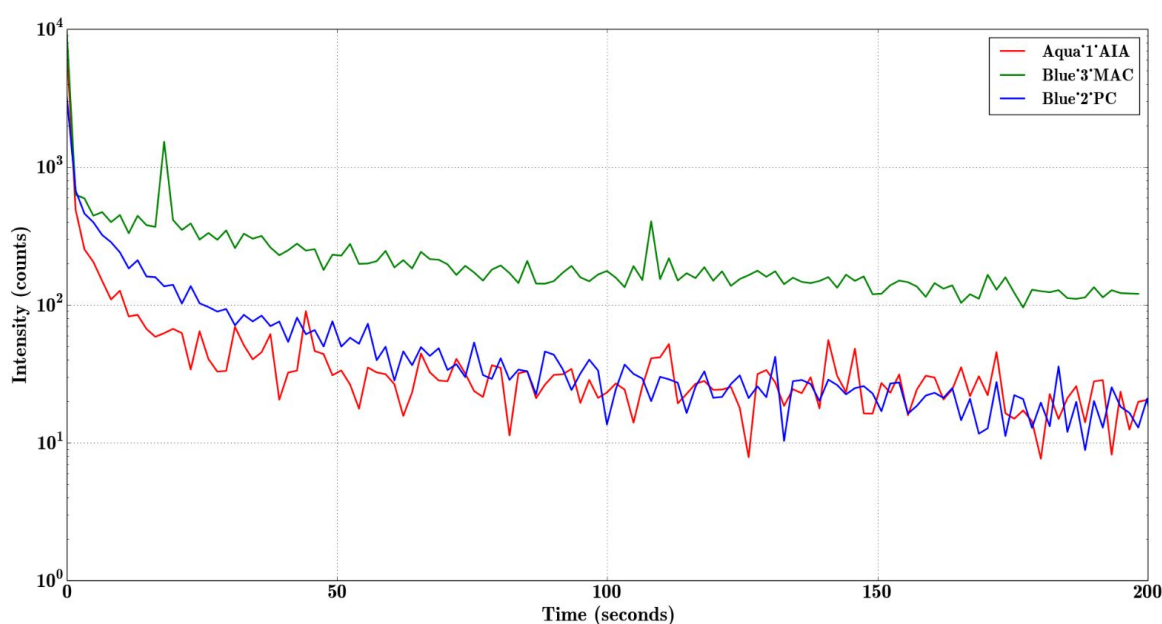


Figure 5.1: A log plot of the TOF-SIMS depth analysis of the hydrocarbon  $C_2H_3$  for all three sets of beads. Note the variation in exponential decay. These trends were similar regardless of colour. Further notice anomalous peaks observable in the MAC bead. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

It was proposed that the anomalous peaks observed in the Museum of Ancient Cultures beads could be the result of trapped organic material in the subsurface material. This proposition is supported by the higher background levels measured in the subsurface region of all Museum of Ancient Cultures beads. A red bead and a blue bead from the Museum of Ancient Cultures were cleaved and cross-sectionally polished (as described in Section 4.1). Using an SEM, the two beads were viewed to look for any significant features in the subsurface material.

These SEM results demonstrated significant subsurface features (see Figure 5.2). This

implies that it would be likely that any region subject to depth related analysis would intercept these subsurface features. Using the SEM, these features were identified as holes due to observed shadowing effects. The appearance of these holes may explain the depth dependent evolution in hydrocarbon content, and could further explain the peaking behaviours shown in the Museum of Ancient Cultures beads. Thus, for this set, the hydrocarbons are not just surface effects, but believed to also be ingrained into the material. Similar results were produced by both Dutkiewicz *et al.* [67] and Volk *et al.* [68] when they observed subsurface hydrocarbon pockets in naturally occurring crystals. For the faience artefacts, the process of how the hydrocarbons became ingrained into the material was not clear. Further, analysis into the specific hydrocarbon chains was not completed in this thesis due to time constraints. Both the mechanism and specific nature of these hydrocarbons will be investigated in the future.

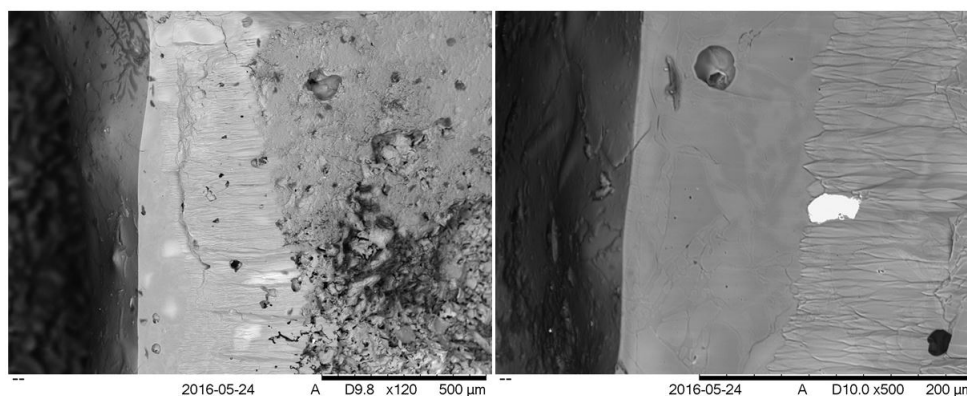


Figure 5.2: A 500  $\mu\text{m}$  SEM images of a blue bead (left) and a 200  $\mu\text{m}$  SEM image of a red bead (right) demonstrating subsurface much less than 50  $\mu\text{m}$  from the surface. Note that the left bead presents many small holes whereas the right bead shows infrequent large holes.

### 5.3 Looking for Similarities and Differences

Two matrices were constructed and analysed: hydrocarbons and metals. The hydrocarbon matrix consists of any C-H chain, long or short, present within the faience beads. The metals matrix included any major elemental peak that contained any metallic element. These matrices were then processed using the *Eigenvector PLS MATLAB toolbox* where the artefacts were categorised according to the source of the beads: Museum of Ancient Cultures, Australian Institute of Archaeology, or Private Collector. There is no guarantee that the beads in each

of the three sets are from the same maker, the same geographical location, or the same time period. The two matrices were then analysed via Principal Component Analysis to look for the chemical similarities and differences between the three sets.

### 5.3.1 A Short Introduction to Principal Components Analysis

Principal Component Analysis (PCA) is a method for understanding variance and similarities between data. The data are plotted initially on a Cartesian plane. A line is then constructed that represents the region of the most variance in the plane, and then the most variance perpendicular to that line (see Figure 5.3). These two lines of variances are called the Principal Components Axis 1 (PC1) and the Principal Components Axis 2 (PC2). PC1 and PC2 become the new axes for the plane. Data points are reformulated and rescaled to assess how much they influence the PC1 and PC2 lines. Rescaled data should then begin to reflect either the variance within, or more importantly, any similarities within these data points. This will result in clustering regions in the PCA plot.

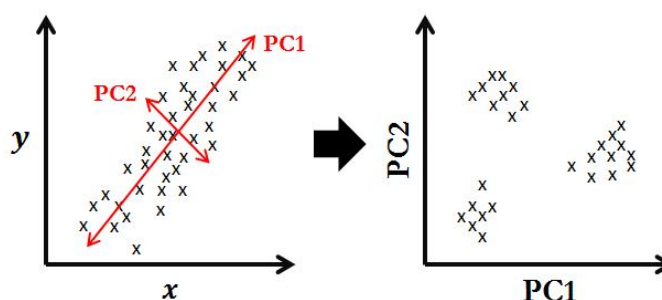


Figure 5.3: An image on how PCA works. Data points are plotted, and then the two lines of most variance are determined. The plot on the right shows the PCA plot, where data points are plotted based on how much they influence the PC1 and PC2 lines. Clustering should be observed for points that show similarity.

### 5.3.2 Hydrocarbon PCA Results

The PCA results for the hydrocarbons demonstrated variability between all three sets of beads (see Figure 5.4). PC1 demonstrated a weighting of 79.66% of the elemental matrix. The main features in PC1 vary from moderately long chain hydrocarbons dominating the negative PC1 axis ( $C_2H_5$ ,  $C_3H_5$ ,  $C_3H_7$ ,  $C_4H_7$ ,  $C_4H_9$ , and  $C_5H_9$ ), to organic compounds focused in the positive PC1 axis ( $CH$ ,  $C_2H_2Cl$ ,  $CAI_2$ , and  $CH_2SOMn$ ). PC2 had a much smaller weighting

than PC1, representing a weighting of only 13.07%. The main features in PC2 vary from moderately long chain hydrocarbons dominating the negative PC2 axis ( $C_3H_7$ ,  $C_4H_7$ ,  $C_4H_9$ ,  $CAI_2$ ,  $C_5H_9$ ,  $C_5H_{11}$ ,  $C_6H_9$ ,  $C_6H_{11}$ ), to short chain hydrocarbons dominating the positive PC2 axis ( $C_2H_3$ ,  $C_3H_3$ ,  $C_3H_5$ ,  $C_4H_3$ , and  $C_2H_2Cl$ ).

The Museum of Ancient Cultures and the Private Collector beads exhibit significant concentrations of pure hydrocarbons, whereas the Australian Institute of Archaeology beads exhibit a propensity for organic hydrocarbon compounds. One Australian Institute of Archaeology bead also exhibited a pure hydrocarbon chemical ‘fingerprint’. With respect to short and long chain hydrocarbons, the Museum of Ancient Culture beads appear to have a variance based on both types. The Australian Institute of Archaeology beads appear near the zero line, suggesting that they have less variance of this type. The Private Collector beads show an extreme preference for short chain hydrocarbons.

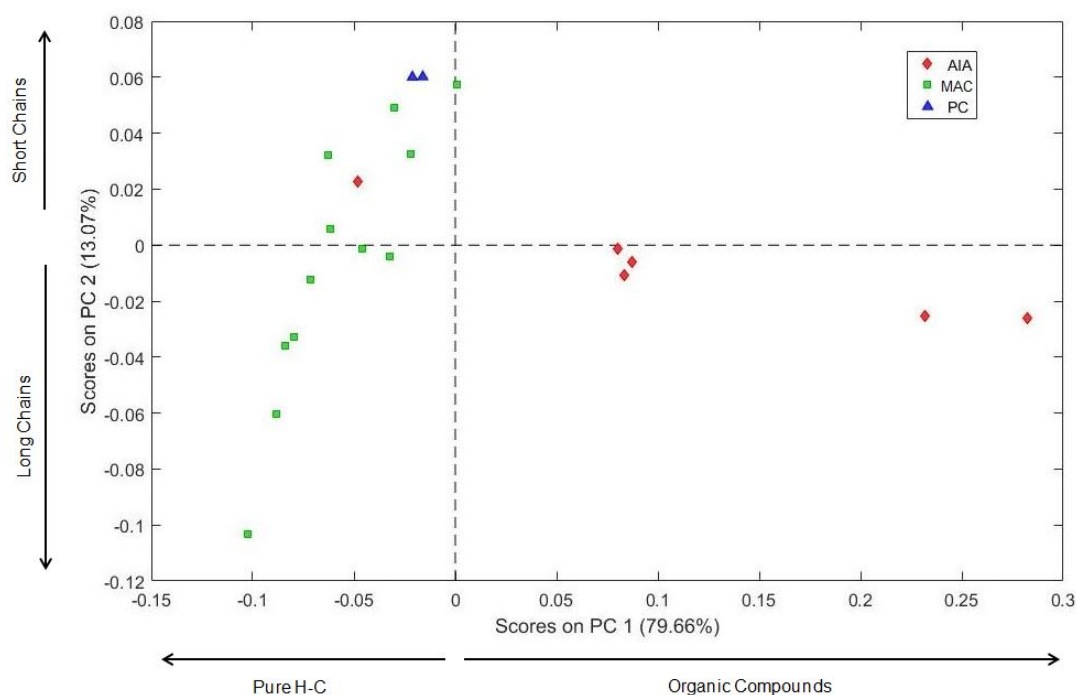


Figure 5.4: A PCA plot of the TOF-SIMS hydrocarbon data for all three sets of beads. The corresponding colour plot can be found in Section 6.2.2, Figure 6.5. The arrows indicate the elements most prominent in each section of the plot. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

### 5.3.3 Metals PCA Results

After the hydrocarbons were processed using PCA, a metal matrix was created and analysed. The metal matrix excluded the hydrocarbons, and consisted of major elemental peaks up to a maximum weight of lead oxide. It must be noted that silicon and sodium were excluded as they were common in large concentrations in all beads. The metals matrix was also processed using the *Eigenvector PLS MATLAB toolbox* to create a PCA plot.

Less clustering was observed in the metal PCA plot when compared to the hydrocarbon PCA plot (see Figure 5.5). PC1 demonstrated a substantial weighting of 70.29% of the elemental matrix. The main features in PC1 are potassium and aluminium dominating the negative PC1 axis (Al, K) and magnesium focused in the positive PC1 axis (Mg,  $^{25}\text{Mg}$ , and  $^{26}\text{Mg}$ ). PC2 had a much smaller weighting than PC1 of only 18.44%. The main features in PC2 vary from potassium and copper isotopes dominating the negative PC2 axis (K,  $^{41}\text{K}$ , Mn, Cu, and  $^{65}\text{Cu}$ ), to aluminium, magnesium and iron dominating the positive PC2 axis (Mg, Al, Fe).

Both the Museum of Ancient Cultures and the Australian Institute of Archaeology beads appeared to have a similar compositional form based on aluminium, potassium, and magnesium. However the Private Collector beads show the greatest swing towards elemental aluminium and potassium. The Museum of Ancient Cultures beads are almost exclusively influenced by potassium, manganese and copper. Both the Australian Institute of Archaeology and the Private Collector beads are exclusively influenced by magnesium, aluminium and iron.

## 5.4 Is it Possible to Distinguish Different Sets of Beads?

The results presented for both the hydrocarbons and the metals matrices suggest that it is possible to separate faience artefacts according to their source. Each set appears in a unique region of the hydrocarbon PCA plot based on the hydrocarbons most dominant in each set (see Figure 5.4). The Museum of Ancient Culture beads were most influenced by pure hydrocarbon chains with no variance for long or short chains, whereas the Private Collector

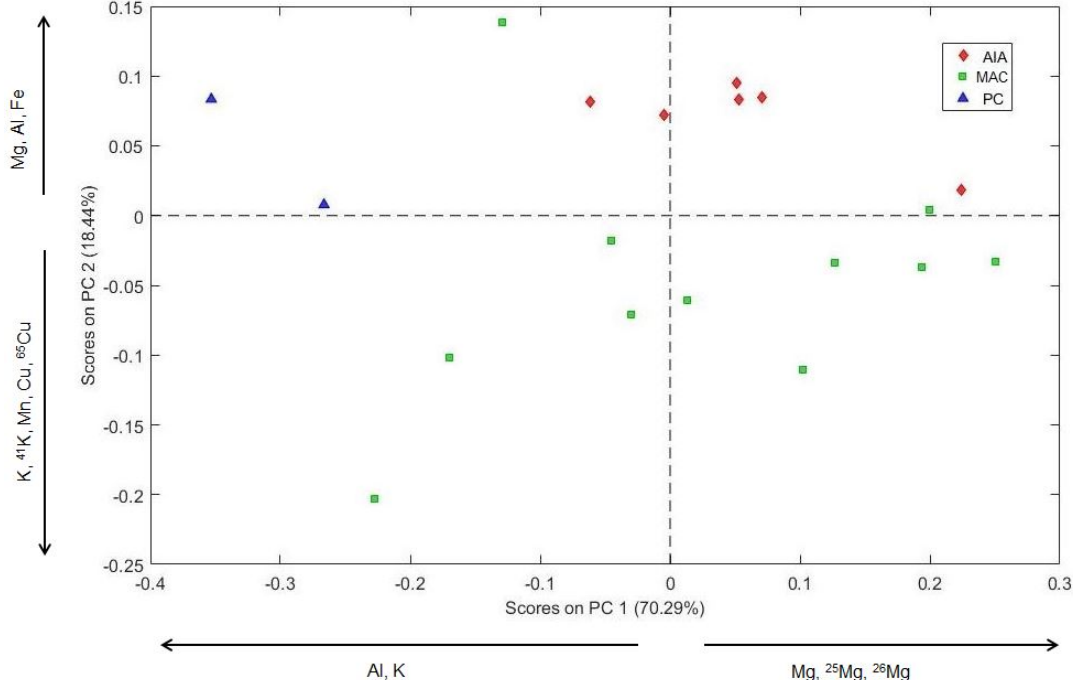


Figure 5.5: A PCA plot of the TOF-SIMS metals data for all three sets of beads categorised by origin. The arrows indicate the elements most prominent in each section of the plot. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

beads appeared in the extreme values for short chain hydrocarbons. In contrast, the Australian Institute of Archaeology beads appeared to exhibit organic hydrocarbon compounds the most, with equal weighting to both short and long chains. These differences make each set of faience beads easily identifiable by source.

For the metals matrix (see Figure 5.5), each set is still distinct but the distribution is much broader than in the hydrocarbons plot. The Museum of Ancient Cultures are most defined by a preference of potassium, manganese, copper and magnesium. The Australian Institute of Archaeology beads have been most influenced by magnesium, aluminium and iron, with minimal influence by potassium, manganese and copper. Finally, the Private Collector beads appear extremely influenced by aluminium and potassium, with some exhibition of magnesium, aluminium and iron.

The clustering for both the hydrocarbon and metals matrices show that all three bead



sets are distinguished by source. The hydrocarbon PCA plot (see Figure 5.4) shows obvious clustering related to source whereas the metals PCA plot (see Figure 5.5) shows a broader distribution, but still some distinctness relating to source. It is possible that both the hydrocarbon and the metals PCA distributions reflect similarities and differences based on geographical location, or by different manufacturers. More analysis will be conducted to confirm this hypothesis, but could potentially result in a useful diagnostic tool for historians.

For the first time it has been demonstrated that faience artefacts from different sources can be distinguished from each other. While research of this type has not been conducted on faience, some analysis has been conducted on distinguishing the origins of ancient glass. Rutten *et al.* present results showing the elemental differences between ancient glass from Egypt and Jordan [45]. They conclude that Egyptian glass is chemically different to Jordanian glass and thus can be distinguishable. This supports the hypothesis that the beads in this thesis may be distinguishable by origin, however the initial results presented indicate for the first time that it is also possible to distinguish faience artefacts based on their source.

It must be noted that the differences observed in the hydrocarbons PCA plot could potentially be due to modern conservation methods. Due to the unknown history of the sample artefacts, it is not known whether the faience beads were treated with any cleaning agents. Cleaning agents may potentially change the surface and subsurface elemental composition of faience due to the porous nature of faience. For example, common soaps contain alkyl carboxylates contain hydrocarbons, and it is possible that all three bead sets could have been cleaned in soapy water. The differences in hydrocarbons could then reflect alkyl carboxylates and their constituent hydrocarbons being absorbed by the beads. Therefore the hydrocarbon PCA analysis alone is not conclusive. But the hydrocarbon and the metals PCA results together imply that beads can be grouped in terms of source.

It is therefore likely that the differences observed in the PCA analysis in this chapter based on both the hydrocarbon and metals analyses reflect differences in elemental composition based on source. A larger sample size with materials of good provenance would be able to confirm whether the reason behind the differentiation is due to chemical signatures based on geographical location, or perhaps based on individual faience manufacturers. Extending

the research presented in this chapter may lead to the ability to provenance unprovenanced artefacts, which would be of immense benefit to historians.

## 5.5 Summary

In this chapter, two main elemental groups were analysed: hydrocarbons and metals. The hydrocarbon group was first validated by comparing observed spectrum peaks to the likeliness of finding significant features in the subsurface material of the artefacts. SEM images illustrated hole structures with a high chance of targeting a region with holes when conducting depth analysis. This result led to the conclusion that hydrocarbons may be ingrained into faience via subsurface hydrocarbon pockets rather than just be containments on the surface of the artefact. After this validation, PCA was conducted on both the hydrocarbon and metals groups to observe variance. When categorised by source, all three artefact sets were distinguishable. The hydrocarbons plot showed tighter clustering than the metals plot (see Figure 5.4 and Figure 5.5). This result is the first instance of faience being distinguished on the basis of source.

*Denial ain't just a river in Egypt.*

Mark Twain

# 6

## When is an Egyptian Artefact not an Egyptian Artefact?

Authenticity is paramount when working with artefacts. Genuine artefacts provide a wealth of information to historians. Artefacts are bought and sold for very large sums of money to collectors and museums. Consequently, a large number of fakes have appeared through black market trading. With many faience artefacts unprovenanced, it is very easy for black market traders to produce fake faience artefacts, and very difficult for historians and museum curators to determine the legitimacy of their artefacts. Current methods for determining the authenticity of faience is solely based upon the appearance of the artefact. Evidence of discolouration, anachronistic materials, or a lack of ageing effects, like rust, are all indicators that an artefact may be fake. Some success has been achieved using scientific methods to probe the elemental composition of artefacts in the search for anachronistic materials. However, this has been overcome by black market traders who source ancient materials to incorporate into their modern fakes. A classic example is the use of period correct canvases

for fake paintings to give false readings when the artwork is analysed [69]. This chapter investigates new methods for determining the authenticity of faience artefacts based on new state-of-the-art diagnostic tools. Observations of alkali and alkaline leaching and elemental clustering are used together to highlight potentially fraudulent material.

## 6.1 Alkali and Alkaline Leaching

Ancient artefacts are affected by ageing processes. Materials, particularly those with a metallic component, undergo various destructive processes like discolouration [70, 71] and corrosion [46, 72] as they age and are exposed to the environment. While these effects can be devastating to the structural integrity of artefacts, these ageing processes may be the key to determining the authenticity for faience artefacts. Evidence of age should be reflected in the deterioration mechanisms observable in artefacts.

TOF-SIMS depth profiling was again used in the same manner as described in Section 5.1. The intensity of elements was observed over time (which is equivalent to depth as described in Section 5.1) to observe the initial trends in intensity for a selection of alkali and alkaline elements.

### 6.1.1 TOF-SIMS Depth Results

The blue and aqua beads from the Museum of Ancient Cultures and the Australian Institute of Archaeology show very similar trends for the intensity over time for lithium, sodium, potassium, and calcium. For the alkali elements, the blue and aqua beads rapidly increase to a maximum value (see lithium in Figure 6.1, sodium in Figure 6.2, and potassium in Figure 6.3). The general trend after that is to either see the values drop to an approximate plateau (like the trends in Figure 6.3), or slowly decrease to a constant value consistently higher than the initial value (like the trends in Figure 6.1 and Figure 6.2). The alkaline plot in Figure 6.4 illustrates a more gradual increase for both the blue and aqua beads from the Museum of Ancient Cultures and the Australian Institute of Archaeology. The lower intensity beads plateau within the 10 seconds plotted, whereas the higher intensity beads continue to increase. It must be noted that one of the Museum of Ancient Cultures beads (Blue '3' MAC) demonstrates much lower intensity values in both the alkali and alkaline plots. While its intensity values

appear similar to the Private Collector beads, Blue '3' MAC still demonstrates a trend similar to the other Museum of Ancient Cultures and Australian Institute of Archaeology beads.

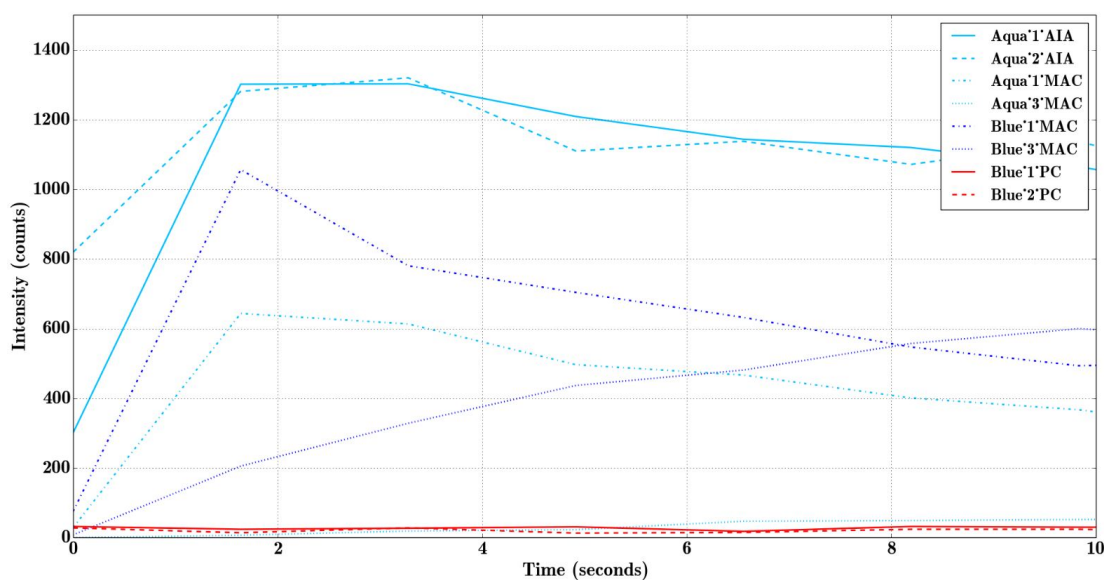


Figure 6.1: A TOF-SIMS profile for lithium in blue and aqua beads. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

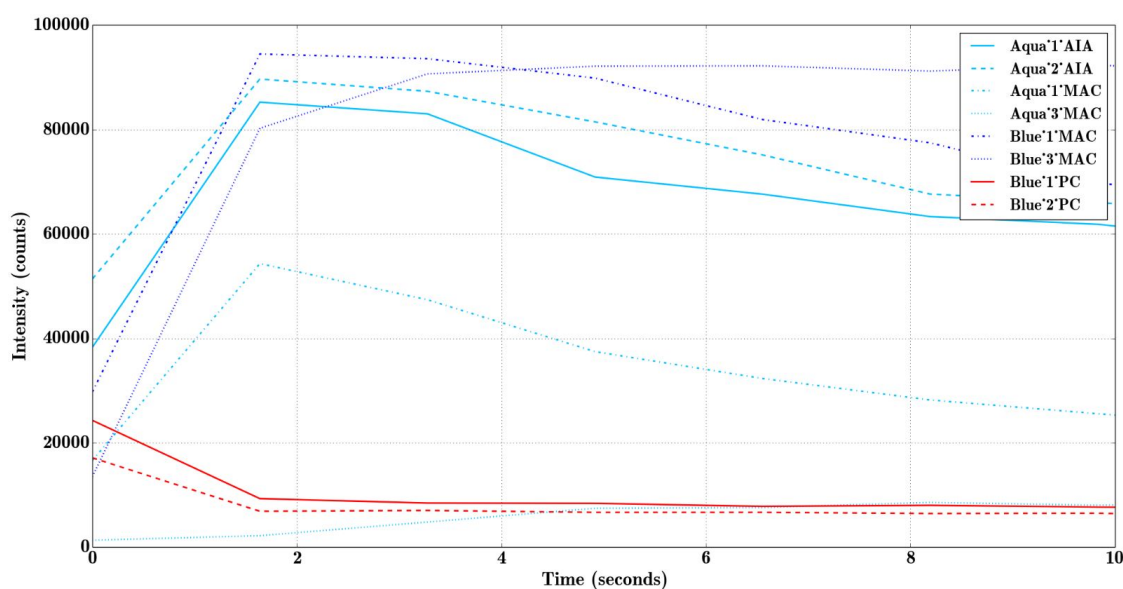


Figure 6.2: A TOF-SIMS profile for sodium in blue and aqua beads. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

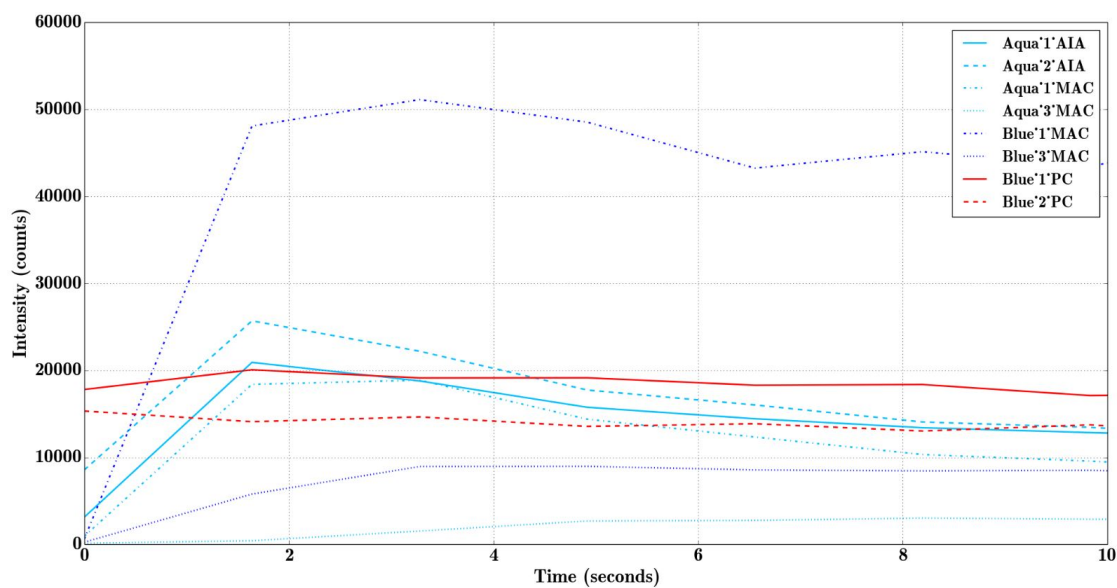


Figure 6.3: A TOF-SIMS profile for potassium in blue and aqua beads. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

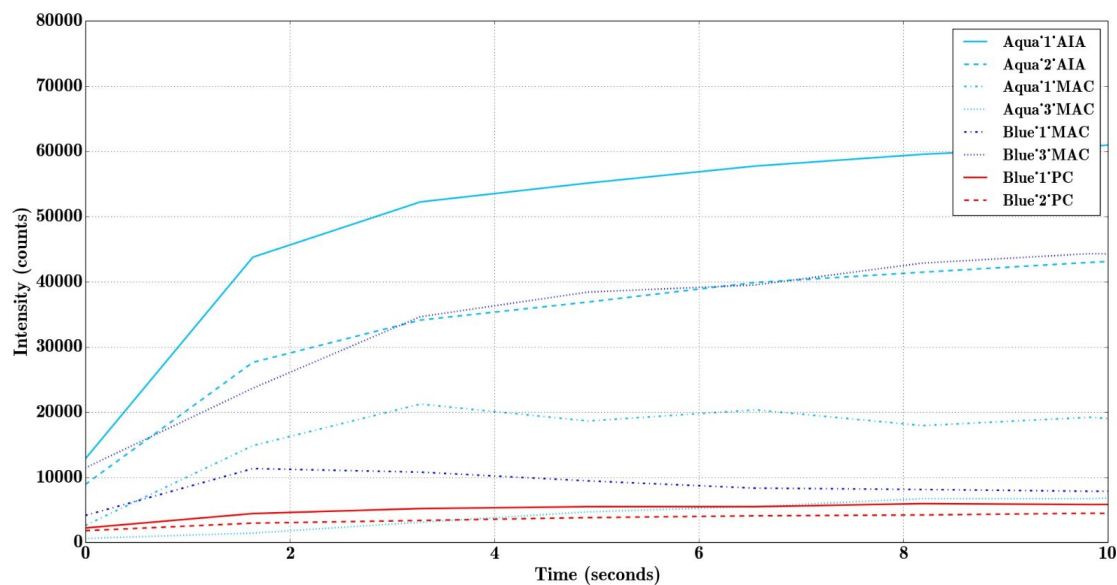


Figure 6.4: A TOF-SIMS profile for calcium in blue and aqua beads. In the legend, AIA = Australian Institute of Archaeology, MAC = Museum of Ancient Cultures, and PC = Private Collector.

The Private Collector beads in both the alkali and alkaline plots demonstrate different trends to the other beads. The potassium and calcium plots (Figure 6.3 and Figure 6.4) show contrasting behaviours as the Private Collector beads show minimal divergence from a constant value across the graph. In the sodium plot (Figure 6.2), the Private Collector beads

start at a maximum value and then decrease to a plateaued value. It must be noted that the lithium and calcium are low in intensities for the Private Collector beads.

### 6.1.2 Discussion

The major ageing event that is proposed to be observed by the TOF-SIMS is leaching. Leaching is a deterioration event where elements are drawn out of the material due to the materials' interaction with the environment. Longer exposures to humidity have resulted in larger leaching trends for sodium and potassium in replica glass [10], so it seems that ancient artefacts should indeed show signs of leaching.

Only two of the three sets of artefacts demonstrated the proposed leaching trends for the alkali elements lithium, sodium, and potassium, and the alkaline element calcium. This is clearly observable for both alkali and alkaline elements where the blue beads from the Museum of Ancient Cultures and the Australian Institute of Archaeology show a depletion zone, which is where an element has been leached out of the material leaving an elemental void. This depletion zone often rises to a peak where there is a build-up of material and then plateaux to the core value of the element. This is observed in the major alkali elements lithium, sodium and potassium (see Figure 6.3). These trends are consistent with the results presented by Fearn *et al.* with their replica ancient glass [46]. This thesis appears to be the first report of ancient faience artefacts demonstrating leaching. This shows that faience seem to behave and age in a similar fashion to ancient glass.

One puzzling anomaly in the above results is that there is no evidence of the proposed alkali or alkaline leaching in the Private Collector beads (see Figure 6.1, Figure 6.2, Figure 6.3 and Figure 6.4 highlighted in red). These two beads either maintain a relatively constant position along the graph, where slight fluctuations can be explained by experimental perturbations in the profiling, or because of the rough topology of the artefacts. In the sodium plot, the Private Collector beads demonstrate an initial maximum value which slightly decreases to a plateau. These trends are directly opposite to the leaching presented by the Museum of Ancient Cultures and the Australian Institute of Archaeology beads, as well as reported leaching observed in ancient glass [8, 46]. The other alkali metals exhibit similar behaviour. While the Museum of Ancient Cultures and the Australian Institute of Archaeology beads

show calcium leaching, the Private Collector beads appear to have no leaching at all but maintain a constant value along the graph (see Figure 6.4).

These results suggest that the Private Collector beads have not experienced ageing effects. One possible explanation for the lack of leaching is to suggest that the Private Collector beads have been cared for so well that they have been protected from adverse environmental conditions such as humidity. However, such care only stretches as far back as the excavation of these beads and thus leaching should still be observable for the thousands of years preceding their discovery. The alternative opinion is to see these beads as modern replicas or fakes. Before drawing this conclusion, however, a second test was conducted to seek further evidence of their veracity.

## **6.2 Perfect Clustering**

Suspecting that the two Private Collector beads were not genuine, the PCA results were re-examined in the context of authenticity.

### **6.2.1 PCA Results and Discussion**

PCA was conducted on two different matrices: a hydrocarbon peak list, and a metals peak list. In both matrices it was observed that there was a general lack of clustering, especially when categorising the artefacts by colour. This may indicate that due to the variability within the beads as discussed in Chapter 4, only broad distributions are observable. Surprisingly, the data points that show the closest clustering are the Private Collector beads (see Figure 6.5), suggesting that there is very little variation in the chemical composition of these two beads. The implication is that they appear too tightly manufactured, perhaps made by the same artisan, at the same time, with the same ingredients with little to no variation in homogeneity. This would then imply that because the other two sets do not show tight clustering that they are diverse in their age and maker. However due to the similarity in shape, style and lustre of the Museum of Ancient Cultures and Australian Institute of Archaeology beads, it is likely that these two groups are in fact sets sharing common traits. This result, along with the lack of lithium, sodium, potassium or calcium leaching clearly shows a major difference between the Private Collector beads and the other two sets. Such divergence can be explained by



questioning the authenticity of the Private Collector beads, suggesting that these beads may be fraudulent.

It must be noted that only two beads that showed visual similarity were received and analysed from the Private Collector. Broad distribution may indeed be observable with a larger sample size, and therefore the clustering observed in this experiment may be an experimental anomaly. It is due to this that the PCA cannot be used for conclusive testing of authenticity, and that multiple approaches to this study have been undertaken to provide a more holistic approach. Future experiments will include much larger sample sets to determine the usefulness of PCA as an authenticating diagnostic tool.

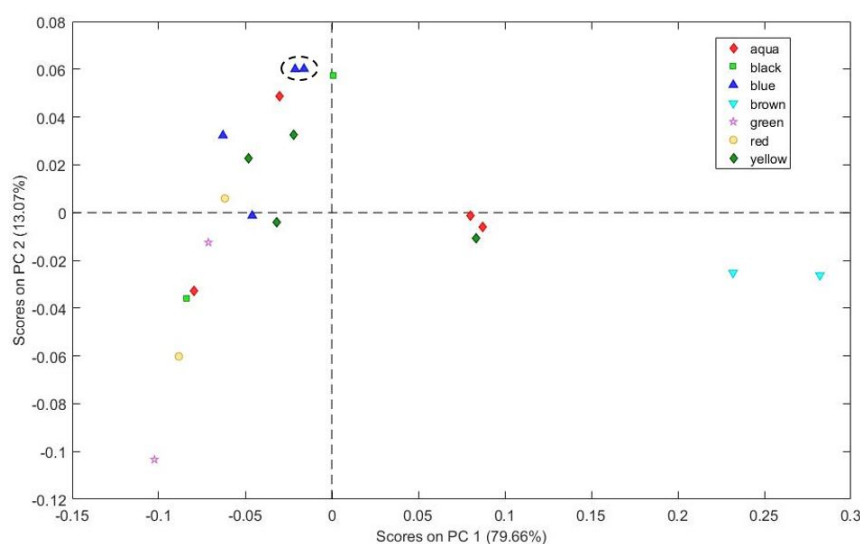


Figure 6.5: A PCA plot of the TOF-SIMS data from all three sets of beads. The two Private Collector beads have been circled to show their strong clustering.

## 6.3 Summary

In this chapter the results of TOF-SIMS and PCA demonstrated strong evidence of a proposed leaching trend in the beads from the Museum of Ancient Cultures and Australian Institute of Archaeology beads. The Private Collector beads however, show no signs of this trend which raises concerns about their ancient authenticity. It is highly unlikely that ancient beads would show no signs of leaching because in theory they have been exposed to environmental humidities for thousands of years. A second test using PCA was conducted to review the

compositional performance of the beads. This resulted in a general lack of clustering when the artefacts were categorised by colour, except for the Private Collector beads which showed tight clustering. While this may indicate that the Private Collector beads were made together from the same materials and at the same time, it would also imply that all the other beads are diverse in age and maker. Due to the evidence of a lack of leaching for the Private Collector beads, it is more likely that the PCA result actually points towards a modern manufacture with relatively homogeneous materials. These two results indicate that the Private Collector beads are suspicious in nature, and potentially fraudulent. This approach has the potential to form a new method for authenticating ancient faience artefacts.

*Look deep into nature, and then  
you will understand everything  
better.*

Albert Einstein

# 7

## Conclusions and Future Work

In this thesis, faience was indeed probed beneath the surface. By using a variety of diagnostic tools, a deeper understanding of faience has been achieved. Firstly, the chemical composition of three sets of faience beads was established using Energy Dispersive X-Ray Spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry. The EDX was most useful for determining the significant elemental inclusions, whereas the LA-ICP-MS was suitable for indicating the trace elements present. As discussed, trace elements are an important feature in faience artefacts, as it is the trace elements which appeared to influence the colour of the artefact.

Elements that appeared universal to all faience artefacts analysed were silicon, calcium, and sodium. These findings corroborate with the basic ingredients listed in most scholarly recipes lists of faience. Significant trace elements that were observed are lead, copper, cobalt, and iron. The association of these trace elements with particular colours implies the use of certain minerals. An understanding of the minerals used in Ancient Egypt can reveal

information about the technological skills of the Ancient Egyptians. Furthermore, concepts such as trade can further be developed, as elements such as cobalt are not found naturally in Egypt. This means that during the Eighteenth Dynasty a trade route was developed whereby Egypt could now receive and use cobalt in their faience objects.

The dating of beads was explored by looking at specific appearances and ratios of elements. Importantly, the ratio of iron and nickel indicated that all beads analysed were dated *terminus post quem* to the Late Period. This was due to the low percentage of nickel compared to iron, indicating that the source of iron was from terrestrial iron ore, rather than meteoric iron ore. This was further corroborated by the presence of cobalt in high concentrations, giving a *terminus post quem* to at least the Eighteenth Dynasty. This method of dating provides a new way for historians to date any artefacts that contains the presence of certain elements. This is especially useful if there are no other ways to date the artefact, which is a common occurrence for faience artefacts.

The similarities and differences between the chemical compositions of each three sets of beads was then explored. The hydrocarbon and metal elemental results from the Time-Of-Flight Secondary Ion Mass Spectrometer were used for Principal Components Analysis to highlight variance between the three sets. Both the hydrocarbon and metal PCA plots showed that it is possible to distinguish sets based on their source; the Museum of Ancient Cultures, the Australian Institute of Archaeology, and a Private Collector. There were various reasons proposed to cause this effect. Firstly, the presence of cleaning agents on the faience artefacts may divide each group based on the type and how long the artefact was exposed to the agents. Secondly, specific manufacturers and manufacturing methods may influence the hydrocarbon and metal contents of faience artefacts. Finally, it is possible that the similarities and differences observed in the PCA plots are due to a geographical signature.

Future work will involve exploring this concept in a much greater depth. Accelerated ageing tests will be conducted to determine the exact effect various cleaning agents have on replica faience artefacts. Water, soap, alcohols, acids, and humidity will all be tested. The replica faience will then be analysed by the TOF-SIMS to demonstrate the effect each agent has on the hydrocarbons, metals, and the leaching of faience when compared to a control

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model. Replica faience created by different manufacturing methods will also be tested to determine the effect manufacturing has on the hydrocarbon and metals content as a function of depth. Finally, real faience artefacts of known provenances will be studied to determine whether the same distributions are observed when the hydrocarbon and metal contents are analysed using PCA.

The last experiment described in this thesis involved exploring the concept of authenticity in faience artefacts. Alkali and alkaline leaching was observed for two of the three artefact sets. The Private Collector beads demonstrated no leaching, and in some instances showed directly opposite trends to the leaching curves observed in the Museum of Ancient Cultures and the Australian Institute of Archaeology beads. This presented as an anomalous result because it is impossible for ancient artefacts to be immune to the effects of humidity over thousands of years. It was proposed that these beads may potentially be modern fakes. A second test to confirm this was based on the PCA results of the hydrocarbons for the two beads. Extreme clustering was observed for the Private Collector beads, whereas the other two beads sets demonstrated a broad distribution. The combination of the tight clustering and the lack of leaching suggested that the Private Collector beads are suspicious in nature. These results present the first possible method for authenticating faience beads.








Future work in this area will involve larger sample sets to determine whether the leaching trends observed for the Museum of Ancient Cultures and the Australian Institute of Archaeology are the general trend for all faience artefacts. An extension upon this will be again using replica faience artefacts to simulate the leaching observed. Upon doing this, it will be prudent to determine the best methods and environmental conditions for *preventing* the leaching. Such information would be vital for museum curators and historians and is currently unknown.

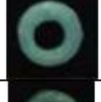
One of the most challenging aspects of this thesis was the small sample size and the lack of provenance of the artefacts. Unfortunately, these are issues encountered in all historical studies due to the nature and use of ancient artefacts. There is a strong preference for non-destructive analysis over any other type of analysis. This thesis will present a proof-of-concept to conservators and museum curators that EDX, LA-ICP-MS, and TOF-SIMS are minimally destructive, so much so that there is no damage visible by eye on faience artefacts after using

these methods. This study is therefore crucial for proving that micro-destructive analysis can provide suitable and appropriate diagnostic methods for understanding artefacts on a much deeper level, once suitable tests, like the ones shown in this thesis, have been conducted. The revolution in analysing Ancient Egyptian faience artefacts is beginning, and this thesis demonstrates that there is a wealth of exciting results to be achieved when one probes beneath the surface.












## Artefact Table

Artefact Code	Origin	Munsell Colour	Analysis	Image
red_MQ_1	Museum of Ancient Cultures	10R 4/4	EDX	
red_MQ_2	Museum of Ancient Cultures	10R 4/4	EDX, LAM	
red_MQ_3	Museum of Ancient Cultures	10R 3/4	TOF-SIMS	
red_MQ_4	Museum of Ancient Cultures	10R 4/4	TOF-SIMS	
red_MQ_5	Museum of Ancient Cultures	10R 4/4	TOF-SIMS	
green_MQ_1	Museum of Ancient Cultures	5GY 6/1	EDX, LAM	
green_MQ_2	Museum of Ancient Cultures	5G 5/2	EDX	

Artefact Code	Origin	Munsell Colour	Analysis	Image
green_MQ_3	Museum of Ancient Cultures	10GY 5/1	TOF-SIMS	
green_MQ_4	Museum of Ancient Cultures	10GY 6/1	TOF-SIMS	
aqua_MQ_1	Museum of Ancient Cultures	10GY 7/1	EDX, LAM	
aqua_MQ_2	Museum of Ancient Cultures	5G 6/2	EDX, LAM	
aqua_MQ_3	Museum of Ancient Cultures	5G 6/2	TOF-SIMS	
aqua_MQ_4	Museum of Ancient Cultures	5G 7/2	TOF-SIMS	
yellow_MQ_1	Museum of Ancient Cultures	2.5Y 8/8	EDX, LAM, TOF-SIMS	
yellow_MQ_2	Museum of Ancient Cultures	2.5Y 6/4	EDX	
yellow_MQ_3	Museum of Ancient Cultures	2.5Y 7/4	TOF-SIMS	
black_MQ_1	Museum of Ancient Cultures	10YR 2/1	EDX, LAM	
black_MQ_2	Museum of Ancient Cultures	N 2.5	EDX	
black_MQ_3	Museum of Ancient Cultures	N 2.5	TOF-SIMS	
black_MQ_4	Museum of Ancient Cultures	N 2.5	TOF-SIMS	
blue_MQ_1	Museum of Ancient Cultures	5PB 6/2	EDX, LAM, TOF-SIMS	
blue_MQ_2	Museum of Ancient Cultures	5PB 6/3	EDX, LAM, TOF-SIMS	
blue_PC_1	Private Collector	5G 7/1	TOF-SIMS	



Artefact Code	Origin	Munsell Colour	Analysis	Image
blue_PC_2	Private Collector	5G 8/1	TOF-SIMS	
brown_AIA_1	Australian Institute of Archaeology	2.5Y 3/1	TOF-SIMS	
brown_AIA_2	Australian Institute of Archaeology	10YR 4/1	TOF-SIMS	
yellow_AIA_1	Australian Institute of Archaeology	2.5Y 8/4	TOF-SIMS	
yellow_AIA_2	Australian Institute of Archaeology	2.5Y 7/3	TOF-SIMS	
aqua_AIA_1	Australian Institute of Archaeology	10BG 5/1	TOF-SIMS	
aqua_AIA_2	Australian Institute of Archaeology	5B 3/1	TOF-SIMS	
green_AIA_1	Australian Institute of Archaeology	10GY 5/1	TOF-SIMS	
green_AIA_2	Australian Institute of Archaeology	5GY 4/1	TOF-SIMS	





# The Chronology of Ancient Egypt

The chronology of Ancient Egypt is still one of contention. In this paper, we will use the dynasties as described by Manetho [73], with the dates defined by the Oxford History of Ancient Egypt [74].

<b>Paleolithic Period</b>	<b>700,000 - 7000 B.C.</b>
<b>Predynastic Period</b>	<b>5300 - 3000 B.C.</b>
<i>Lower Egypt</i>	<i>5300 - 3200 B. C.</i>
Neolithic	5300 - 4000 B.C.
Maadi Cultural Complex	4000 - 3200 B.C.
<i>Upper Egypt</i>	<i>4400 - 3000 B. C.</i>
Badarian Period	4400 - 4000 B.C.
Naqada I Period	4000 - 3500 B.C.
Naqada II Period	3500 - 3200 B.C.

Naqada III Period 3200 - 3000 B.C.

**Early Dynastic Period 3000 - 2686 B.C.**

First Dynasty 3000 - 2890 B.C.

Second Dynasty 2890 - 2686 B.C.

**Old Kingdom 2686 - 2160 B.C.**

Third Dynasty 2686 - 2613 B.C.

Fourth Dynasty 2613 - 2494 B.C.

*Pharaoh Khufu builds the Great Pyramid of Giza*

Fifth Dynasty 2494 - 2345 B.C.

Sixth Dynasty 2345 - 2181 B.C.

Seventh and Eighth Dynasty 2181 - 2160 B.C.

**First Intermediate Period 2160 - 2055 B.C.**

Ninth and Tenth Dynasties 2160 - 2025 B.C.

Eleventh Dynasty (Thebes Only) 2125 - 2055 B.C.

**Middle Kingdom 2055 - 1650 B.C.**

Eleventh Dynasty (all Egypt) 2055 - 1985 B.C.

Twelfth Dynasty 1985 - 1773 B.C.

Thirteenth Dynasty 1773 - 1650 B.C.

Fourteenth Dynasty 1773 - 1650 B.C.

**Second Intermediate Period 1650 - 1550 B.C.**

Fifteenth Dynasty (Hyksos) 1650 - 1550 B.C.

Sixteenth Dynasty 1650 - 1580 B.C.

Seventeenth Dynasty (Hyksos) 1580 - 1550 B.C.

**New Kingdom 1550 - 1295 B.C.**

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Eighteenth Dynasty 1055 - 1295 B.C.

*Akhenaten (and his wife Nefertiti) and Tutankhamun reign in this dynasty*

## **Ramessid Period 1295 - 1069 B.C.**

Nineteenth Dynasty 1295 - 1186 B.C.

*Rameses II builds the Ramesseum and Abu Simbel*

Twentieth Dynasty 1186 - 1069 B.C.

## **Third Intermediate Period 1069 - 656 B.C.**

Twenty First Dynasty 1069 - 945 B.C.

Twenty Second Dynasty 945 - 715 B.C.

Twenty Third Dynasty 818 - 715 B.C.

Twenty Fourth Dynasty 727 - 715 B.C.

Twenty Fifth Dynasty 747 - 656 B.C.

## **Late Period 664 - 332 B.C.**

Twenty Sixth Dynasty 664 - 525 B.C.

*Xerxes is successful at the Battle of Thermopylae against King Leonidas of Sparta*

Twenty Seventh Dynasty (First Persian Period) 525 - 404 B.C.

Twenty Eighth Dynasty 404 - 399 B.C.

Twenty Ninth Dynasty 399 - 380 B.C.

Thirtieth Dynasty 380 - 343 B.C.

Second Persian Period 343 - 332 B.C.

## **Ptolemaic Period 332 - 30 B.C.**

Macedonian Dynasty 332 - 305 B.C.

*Alexander the Great establishes the Macedonian Empire*

Ptolemaic Dynasty 305 - 30 B.C.

*Cleopatra reigns towards the end of this dynasty*

## **Roman Period 30 B.C. - A.D. 395**



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