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An archaeometallurgical explanation for the disappearance of Egyptian and Near Eastern cobalt blue glass at the end of the Late Bronze Age.

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Abstract

A recent compositional study of Egyptian cobalt blue glass from museum collections in Japan (18th Dynasty) and from the site of Dahshur (18th and 19-20th Dynasties) concluded that a new source of cobalt was exploited for the later Dahshur glass, thereby suggesting that glass production continued into the Ramesside period (Abe et al., 2012). It is shown in the current article that some of this 18th Dynasty glass and the majority of the 19-20th Dynasty glass had been recycled, not only supporting the general consensus that glass production virtually disappeared by 1250 BC, but that the cobalt source did not necessarily change. It is further proposed, however, that the generally accepted cobalt source for Egyptian glass was not the alum deposits of Egypt's Western Desert, but derived from cobaltiferous siliceous ores, possibly from central Iran. Re-analysis of the compositions of cobalt blue glass frit found at Amarna, as well as Egyptian and Mesopotamian glass suggests that the cobalt colourant was a by-product of silver extraction from these ores and can therefore be considered as a concentrated cobalt glass slag, which travelled in the form of a frit to glass producers who added it to locally derived base glasses and/or their precursors. Experiments conducted on ore containing cobalt-nickel arsenides with native silver, demonstrate that not only can silver be extracted and that concentrated cobalt glass can be produced by simply adding a flux, but that some components of the ore partition preferentially into the silver or the glass slag, thereby weakening their associations with the other components in archaeological glass. Treating the cobalt blue colourant as a slag composed of the gangue of a smelting system, provides an explanation for the unique elevated levels of alumina and lower levels of potash found in cobalt blue glasses, as well as providing an explanation for the cessation of cobalt exploitation at the end of the Late Bronze Age. It is suggested that the exhaustion of native silver and siliceous silver ore deposits during the Bronze Age, with argentiferous lead ores becoming the main source of silver, depleted the amount of cobalt available, thereby reducing the amount of glass produced which, in turn, led to increases in recycling during the New Kingdom period.

Key words: ancient glass, cobalt, silver, glass frit, recycling, New Kingdom Egypt, Mesopotamia, lead isotopes, compositional analysis, Iran.

1. Introduction

The earliest known glass objects were beads, perhaps initially created as accidental by-products of metal-working (slags) or during the production of faience, a pre-glass vitreous material made by a process similar to glazing. Although there is evidence of glass since the 3rd millennium BC (Peltenburg, 1987: 5-30; Lilyquist and Brill, 1993: 5), the first significant finds of man-made glass are in Egypt and the Near East around the end of the 15th century and into the 14th century BC. The objects associated with glass at this time are mainly opaque and/or coloured. That some of the words for glass in the Amarna letters are Hurrian or Akkadian (Oppenheim, 1973) hints that early glass was imported to Egypt, perhaps brought over by Thutmosis III (1479-1425 BC) (Nicholson, 2006; Jackson, 2018).

Until recently, there was no clear physical evidence of Egyptian glass in Mesopotamia, nor Mesopotamian glass in Egypt (Walton et al., 2009; Rehren and Freestone, 2015). However, Varberg et al. (2015; 2016) have demonstrated that glass of Mesopotamian origin reached Egypt and Europe. Nonetheless, just as the innovation spread and became established throughout Egypt and the Near East, after around 1250 BC the number of glass finds dramatically drops, indicating that glass production had massively declined by the end of the 2ndmillennium (Moorey 1994:198; Shortland, 2012:169-173; Rehren, 2018). As Shortland (2016:95) highlights, 'There therefore remains a short flowering of this technology in the third quarter of the 2nd millennium BC, and then it disappears almost completely'.

Sudden transitions between material types in the archaeological record are often attributed to changes in the accessibility of the raw materials, or the material being replaced by other materials which are easier to process and/or provide better functional properties. However, issues surrounding accessibility are unlikely to be pertinent to glass *per se*, as all early glass appears to be of the same compositional type (soda-lime-silica), with glass only becoming only a truly utilitarian functional material after the invention of glass blowing (c. 50 BC). This could suggest that the low amounts of glass recovered after c. 1250 BC (Shortland, 2016: 95), with glass production not resuming for about five centuries, was because glass objects were no longer in demand. It is proposed here, however, that the disappearance of glass at the end of the LBA, was not because glass itself went out of fashion but because the raw material precursors required to render the glass opaque and produce the colour combinations desired from glass objects were no longer readily accessible. In particular, it is proposed that the disappearance of cobalt blue, a major colourant in early glasses, is directly related to the exhaustion of native silver and dry (also known as siliceous or quartzose) silver ores at the end of the LBA, affecting glass production across the ancient world.

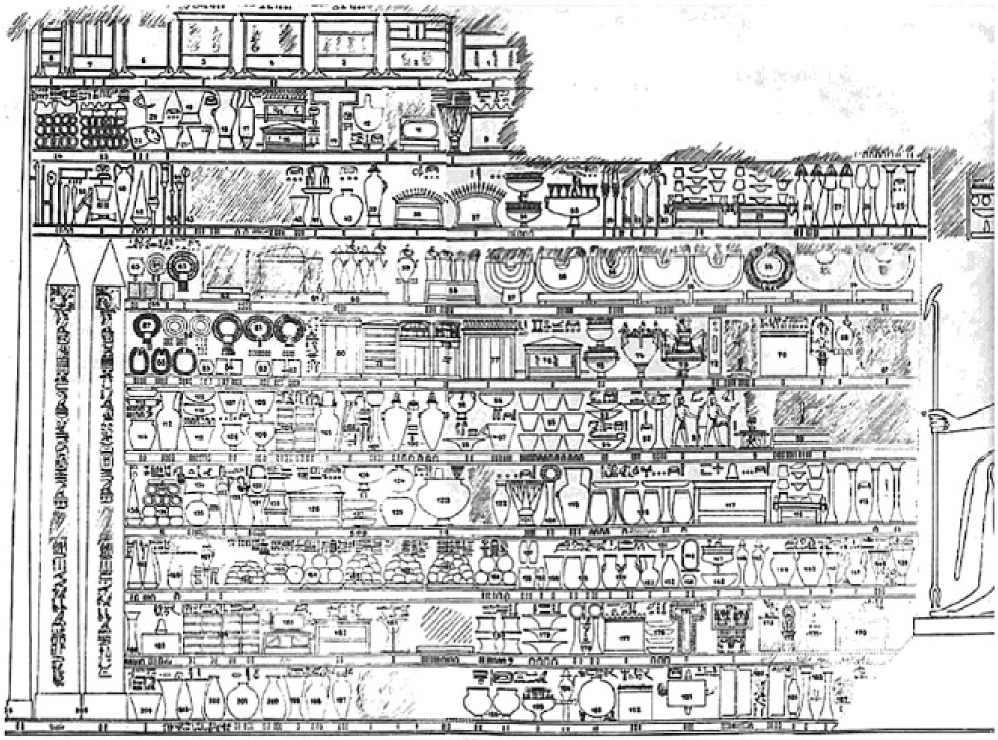
2. Provenancing Cobalt Blue Glass and Trade

There are several possibilities when considering the glass trade. Trade in:

- raw materials for glass making
- colourless glass ingots and colourants
- coloured glass ingots
- finished glass objects (e.g. beads, vessels etc.)

There is evidence of objects and coloured ingots being transported, e.g. Uluburun shipwreck (Jackson and Nicholson, 2010) but, so far, no colourless ingots (which fits well with the dearth of colourless glass prior to mid-1st millennium) implying that glass was pre-coloured before being transported. Since silica and fluxes were readily available in Egypt and the Near East, the colourant was potentially the more valuable commodity, which could suggest that it was the colourant that travelled and was added to locally derived base glass or its precursors before the ingots were transported.

In addition to Varberg et al.'s work (2015; 2016) there are some indications that coloured glass travelled to Egypt. The Hall of the Annals at the Temple at Karnak, in Thebes, has a scene on one wall depicting Thutmosis III's spoils from his successful campaigns in the Levant and Syria, including gold, silver and glass (Sherratt and Sherratt, 1991), with glass referred to as 'stones of casting' in the Amarna letters. Three baskets are dark-blue and their contents are depicted in two forms: one basket has 5 round objects, the other two are baskets of irregularly-shaped lumps. The round objects appear human-made and are potentially dark-blue glass ingots (Shortland, 2012: 140-145). Although one of the baskets with irregularly shaped lumps could be lapis lazuli, the second is denoted differently, which suggests that it is not lapis lazuli but is also dark-blue glass (Figure 1).



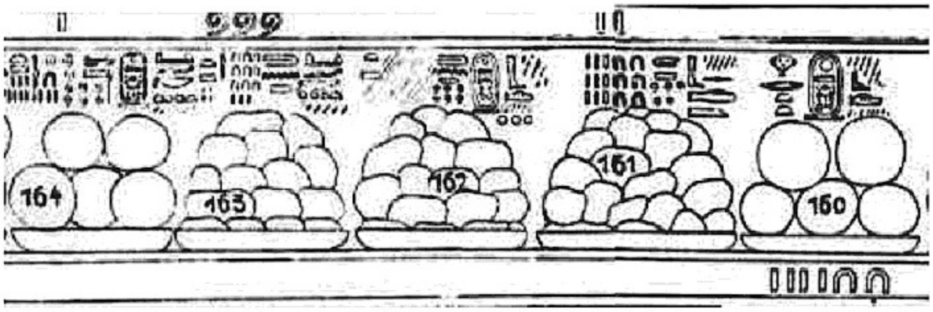


Figure 1 (upper) Depiction of the Hall of the Annals scene at Karnak showing the tribute given by Thutmosis III to the temple. (lower) Close up showing baskets of glass and precious stone. The scene reads right to left, so basket 1 with the five round objects is at the far right with two baskets of irregularly shaped lumps to its left. (adapted from a drawing by Wreszinski, 1922 – in Wreszinski, 1931).

Mycenaean blue glass was analysed in the 1970s using neutron activation analysis (NAA), indicating the Western Egyptian Desert as the origin for cobalt (Sayre and Smith, 1974: 47-70). Nikita and Henderson (2006), examining a larger sample, identified five additional cobalt compositional groups based on manganese, nickel and zinc levels as well as the presence or absence of the volatile arsenic, which they attributed to additional cobalt sources. According to Shortland (2012) these new groups may be a consequence of the detection limits of their microprobe analysis, a view supported by the LA-ICPMS work of Walton et al. (2009) which showed that (for the cobalt Mycenaean glass they analysed) the Western Egyptian Desert was the most likely origin for cobalt, with trace elements of chromium and lanthanum, which are not colour-derived but derive from the base glass raw materials, supporting an Egyptian source (Shortland et al., 2007).

LBA and early IA cobalt glass beads have been found in France, which have elevated levels of alumina, nickel, manganese and zinc, again suggesting an Egyptian Western Desert origin (Gratuze, 2006). This is interesting as the later IA glass was being made when the Egyptian oases sources were no longer being used. A similar conundrum can be found in IA Nimrud and Kaman-Kalehöyük in Turkey where cobalt blue glasses have been found which appear to have been made with cobalt alum from Egypt much later than when it was being exploited in Egypt (Brill, 1999; Henderson et al., 2018). This perhaps suggests another as yet undiscovered cobalt source with similar composition to that of the Western Desert oases. Furthermore, the absence of cobalt blue glass is notable at the late New Kingdom site of Lisht in Egypt (Smirnou et al., 2018).

Gratuze (2013) outlined the main chemical associations with cobalt pigments used in glass and glaze production in Western Europe and Mediterranean regions from the Bronze Age through to the 18th century AD. However, as with many of the provenance studies, there is a reliance on compositional anchors which rarely connect objects to specific mineral deposits, but generally associate objects with other objects which have been assumed to derive from specific mineral deposits. For example, the discovery of 175 glass ingots in the cargo of a late 14th century BC shipwreck off Uluburun, Turkey, suggests trade in glass. Their shape and size have clear parallels with Egyptian production sites, indicating that glass was being transported from Egypt to Mycenaean Greece. However, although the presence of cobalt blue glass on board the Uluburun is generally taken to be evidence of Egyptian provenance, this is based on the fact that these ingots have similar composition to Egyptian and Mycenaean cobalt blue glass. Therefore, unless it can be shown with certainty that cobalt in cobalt blue Egyptian glass comes from Egypt, thereby implicating an Egyptian source at least for the colourant, the similarity in chemical composition between cobalt blue glass from Egypt and the Uluburun shipwreck points to a common, but not necessarily an Egyptian origin. Another complicating factor is that different compositional signatures could also be a consequence of recycling.

3. Glass, Colour and the Source of Cobalt

The commonest source of cobalt oxide is the mineral asbolane (also known as asbolite) (Hodges, 1981: 45), an impure oxide of manganese. Less common is the sulphide, linnaeite. Cobalt introduced to a glass by linnaeite could therefore be expected to have low levels of manganese, while glasses coloured using cobalt from asbolane would contain a relatively high proportion of manganese (Hodges, 1981: 204). Sayre (1964: 1-25) distinguished between 'western' Roman cobalt-blue glass containing elevated manganese levels from those in Mesopotamia and south-west Iran which had significant levels of arsenic, with impurity levels of iron, nickel, copper, tin and lead oxides also supporting these regional provenances. Cobalt is also found associated with nickel, bismuth, arsenic and silver in what are somewhat confusingly known as five-element ores (Ag-Co-Ni-Bi-As +/- U), although only Co-Ni arsenides in association with native silver are generally pre-requisite for the classification (Kissin, 1992), often in the form of minerals such as skutterudite ($(Co, Ni, Fe) As_{2-3}$), cobaltite ($CoAsS$), safflorite ($CoAs_2$) and nickeline ($NiAs$). Occurrences of these ores are probably world-wide (Bastin, 1939; Kissin, 1992; Badham, 1976: 559-571; Ramdohr, 1969: 1174), with well-established examples found in North America, central Europe and more recently the Anarak district of Iran (Tarkian et al., 1983).

Cobalt has been found in association with manganese, zinc, nickel and alumina in Egyptian New Kingdom vitreous materials (Kaczmarczyk and Hedges, 1983) with elevated levels being present in cobalt-coloured glasses. Figure 2 shows the relationship between cobalt and nickel for Egyptian glasses (LBA Egyptian and 'early' 1st millennium BC) compared to Italian and Greek glass from the 10th to the 7th centuries BC and a few samples from Ur, Mesopotamia (10th-6th centuries BC) (Duckworth, 2011: 146). It can be seen that CoO increases almost linearly with NiO for Egyptian glasses (apart from one find - dated between the 8th-5th centuries BC), indicating that both have been introduced into the glasses from the same ore source. However, the turquoise, blue and black samples from Italy (10th-7th centuries BC), do not show the same correlation, indicating that the cobalt in these samples was from another source.

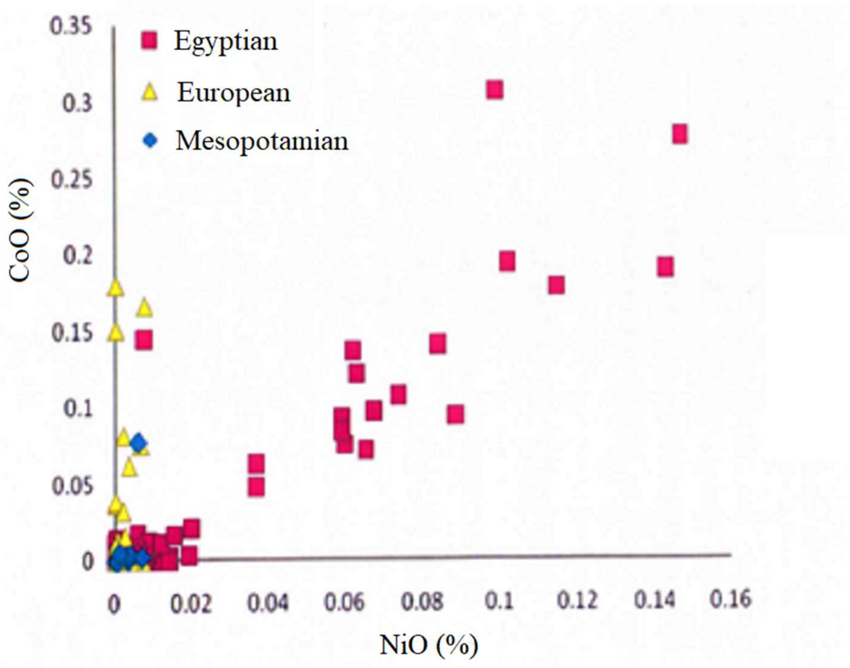


Figure 2. Bivariate plot of NiO vs. CoO in weight % for cobalt-coloured blue glass. The linearity of the relationship between NiO and CoO for the Egyptian glass has been considered consistent with the use of cobalt alum from the Western Desert of Egypt (adapted from Duckworth, 2011: 146; Fig. 5.14). Note that the slope of the Egyptian data is about 1.67 (i.e. ∆NiO/∆CoO = 0.6).

Figure 3. Map of Egypt showing the locations of the Kharga and Dakhla Oases as well as other places associated with glass mentioned in this text.

Cobalt-bearing alums found in the oases of the Western Desert of Egypt are thought the most likely source of the cobalt used to colour LBA Egyptian glass (Shortland, 2000) (Figure 3), despite these minerals being a dull pink colour and not the deep blue found in glass. Nevertheless, this source was initially proposed by Farnsworth and Ritchie (1938) who realised that cobalt was a deliberate additive to 18th Dynasty cobalt blue glass, thereby suggesting an Egyptian alum source might have been used as the source of the cobalt-bearing mineral. Garner (1956) also suggested that a cobalt bearing ore was used for the colouration of Egyptian glass. Lucas (1962) suggested a Persian source for a cobalt colourant, with Stern and Schlick-Nolte (1994) also endorsing a source in Iran or Asia minor. Dayton (1981; 1993) suggested a central European source, although this was rejected by Kaczmarczyck and Hedges (1983: 301-302) and Nikita and Henderson (2006). Kaczmarczyck (1986) and Rehren (2001) supported that cobalt-bearing alum from the Western Oases was source of Egyptian cobalt, with the

Kharga and Dakhla Oases considered to be the most likely source of the cobalt used to colour LBA Egyptian glass (Shortland, 2000).

Glass compositional signatures, however, are not entirely consistent with either oasis. The ED-XRF analyses on which Kaczmarczyk (1986: 369-376) based his interpretation, were to some extent questioned by Lilyquist and Brill (1993) as the relative levels of the impurities in the final glass were not consistent with this view. For example, the elevated levels of alumina which were assumed to be a consequence of the cobalt-bearing alum source, were found in all 21 cobalt-blue glasses (>1.2%Al_2O_3) they analysed but were also present in seven of the 43 Egyptian non-cobalt glasses. Furthermore, cobalt-blue glass has low potash levels (i.e. K_2O), something shared by both New Kingdom and cobalt-blue glass found at Nimrud (Reade et al., 2005: 23-27). Shortland and Tite (2000) argued that the low K_2O levels in the Egyptian glass indicated that the soda source derived from natron, as plant ash imparts a concentration well in excess of 1.5%K_2O. The high magnesium content of these glasses was considered to result from the cobalt alum. This view was challenged, however, by Rehren (2001) who advocated a plant ash source. Tite and Shortland (2003) modified their position suggesting that Egyptian cobalt glass contained both natron and plant ash. Reade et al. (2005: 23-27) considered the early 1st millennium BC Nimrud glass derived its soda from natron as its lime contents was much lower than that expected in glass where the alkali is added in the form of plant ash. This leaves an open question regarding the soda source in the Egyptian glass, as these glasses contain high lime. The alum sources of Egypt's Western desert contain effectively no lime.

Several ideas have been proposed to explain the disparities between these alum sources and New Kingdom cobalt glass compositions. These are based on the modification of the alum source material, such as roasting the ores (Henderson, 2013: 71), converting the alum into a sulphate (Kaczmarczyk 1986: 369-376; Noll, 1981: 143-154) or other methods which concentrate the alum prior to its addition in glass-making (Shortland et al., 2006[1]). However, although low concentrations of cobalt (Co^{2+}) are needed to colour glass (i.e. 0.05% cobalt oxide (CoO) is sufficient to produce a rich, deep blue

(Henderson, 2000), compared to 1-2% CuO), these alums have very low concentrations of cobalt, with CoO/Al_20_3 levels being around 4 times lower in the alums than in cobalt blue glass and frit (semi-reacted glass) (Tite and Shortland, 2003). Furthermore, experiments to concentrate the cobalt have failed to reproduce the ratios found in archaeological glass and frit, which suggests that large amounts of alum would have needed to be added or that alums from these sources were much richer in cobalt in the past (Shortland et al., 2006[1]). However, in order to accommodate the larger amounts of alum in the crucible required to attain the archaeologically attested amounts of cobalt, the amount of plant ash in the recipe would have to be decreased, thereby explaining the low levels of K_2O in the cobalt-blue glass but not the comparable levels of MgO found in non-cobalt glasses (Rehren, 2001). Alternatively, adopting Occam's razor, it is reasonable to suggest that the New Kingdom cobalt may not have derived from the alum deposits of the Western Desert. This is discussed in Section 4.

3.1 Colouring glass and frit

The way that cobalt, or any other colourant, was introduced to colour ancient glass has not yet been fully resolved. Early glass was made by heating a mixture of silica which acts as a network former, soda (plant ash or natron) as a flux to reduce the melting temperature of the silica, and lime, which acts a stabiliser preventing the glass product from dissolving in water, in a furnace to around 1000°C. Lime was introduced in the form of shell with the silica source, possibly inadvertently. Furnace temperatures were achieved by burning wood, or a waste product of some other process (e.g. pressed olive cakes from olive oil manufacturing), thereby introducing contaminants such as potash and phosphorus oxides into the system (Paynter, 2009). Furthermore, the presence of iron compounds, often associated with the silica source, caused glass to take on a blue-green hue, which along with entrapped bubbles, airborne carbon particles from the burning fuel and particulate material deriving from the furnace walls, crucibles, shaping utensils and workshop areas, potentially resulted in the production of a dirty, translucent glass.

These aesthetic problems can be alleviated by colouring and opacifying the glass, and by first making a glass frit. Opaque glass in New Kingdom Egypt was achieved by introducing antimony compounds into the base glass (Shortland, 2002). The making of a frit has been considered to be an intermediate step in the production of glass (Petrie, 1909: 124), allowing bubbles and any contamination to be removed before reheating the frit to make glass proper (Nicholson, 2007: 121). Most of the earliest glass was opaque and coloured and of sufficient quality to be used for luxury items. For example, during the 18th Dynasty in Egypt coloured containers were used for perfume or cosmetics (Shortland, 2000; Nicholson and Henderson, 2000: 195-205).

It is possible that both colourants and opacifiers were added during the frit forming process. A mechanism has been proposed in which it has been suggested that calcium antimonate crystals were mixed directly into a translucent glass (Lahlil et al., 2010). Semi-finished white opacified glass has been recovered from Amarna which suggests that that calcium antimonate had been added to a base glass to make a semi-reacted glass frit. Whether this frit was produced at Amarna or had arrived there through trade is uncertain (Smirnou and Rehren, 2011). White opaque glass would require the addition of cobalt (blue), lead (yellow) and copper (blue/green) compounds to attain the basic colour palette used for early glass vessels and beads (red requires different processing conditions). Renormalized compositions of yellow Roman glass from addition of lead antimonate (i.e. after subtraction of lead, antimony and iron oxides) were found to have elevated levels of silica (and lower values of lime, potash and magnesia, relative to the renormalized compositions for other colours). It was proposed that a yellow colourant was added to colourless glass in the form of a lead-antimony-silica mixture (called *anima* to suggest parallels with the Venetian production of yellow glass in the 18th and 19th centuries AD) (Freestone and Stapleton, 2013). Similarly, a calculation of reduced compositions from analytical data for 1st to 4th century AD Roman glass published by Mass et al. (1998) shows that, as compared to white and turquoise glasses, opaque yellow and green glasses, the latter coloured by a combination of lead antimonate and copper oxide, exhibit elevated silica contents. Yellow glass from the New Kingdom period does not exhibit the same reduced compositions

(Shortland and Eremin, 2006), suggesting that the pigment was added directly into the base glass. However, these results are not completely unambiguous, with three of the 19 samples tested having elevated levels of silica with respect to the main group (possibly indicating that the pigment was introduced in the form of a vitreous material). This could suggest that the other 16 yellow samples were prepared by introducing the pigment directly into the glass. Alternatively, it could suggest that if dilution of glass was conducted during recycling (i.e. broken yellow glass with high silica levels was added to glass with lower silica levels to produce a mixture), the three outliers could represent the original undiluted glass.

Addition of a colourant in the form of a vitreous material into a base glass (rather than adding a mineral or its precursors directly to a base glass) circumvents the difficulties surrounding the addition, mixing and even-distribution of low amounts of additive into larger volumes, i.e. the bulk base glass melt or the silica-soda-lime precursors. Streaking found in yellow Egyptian glass has been considered to be related to the relatively high viscosity and the resultant difficulty in mixing in the pigment (Molina Giralt, 2014: 47). This would be particularly pertinent for the addition of cobalt where only a few hundred ppm are required to colour the glass deep blue, as long as it is distributed homogenously. In effect, 1kg of glass (around the mass of a glass ingot) requires only around 0.05kg of CoO (assuming that cobalt was readily available in its oxide form), which would need to be distributed throughout the bulk. Using cobalt glass frit, such as that found at Amarna (see Figure 4 -top), would not only introduce a granular additive of a similar composition to the base glass solvent but also provide a much greater volume of material to distribute, thereby providing a larger area of interaction to colour the base glass evenly.

Traditionally assumed to represent the first stage of glass manufacture (Petrie, 1894: 25-6) (Petrie speaks of frit as a colourant and then goes on to place it in the context of glass manufacture), cobalt blue frit found at Amarna O45.1 has an unusual composition: high levels of silica (often with unreacted quartz pushing the silica concentration up to as high as 84% - i.e. greater than faience and glass found at the site), lower levels of soda (average 8.7%) and lime (average 0.7%) than found in glass, and levels of cobalt (average 0.21%) much higher than required to colour glass deep blue (Tite et al., 1998: 111-120; Tite and Shortland, 2003). Furthermore, cobalt blue frit was found in association with 'fritting pans' which have been interpreted as having multifunctional purposes as crucibles for fritting or melting glass and as moulds for glass ingots (Nicholson et al., 1997). These cylindrical vessels were also internally lined with a white slip containing high levels of CaO (probably applied as lime silicates or lime - Rehren and Pusch, 1997), perhaps to prevent glass from being contaminated by iron from the clay vessel, and/or to facilitate the release of glass after cooling. This not only suggests that crucibles/melting pots were being re-used rather than being deliberately broken to extract the glass, but also that the colourant, in the form of frit, may have been added during this melting process in these crucibles, thereby allowing the low-soda content vitreous colourant to be distributed evenly in the viscous base glass before melting. A fragment of cobalt-coloured semi-finished glass from Nicholson's excavations in Amarna (Jackson and Nicholson, 2007: 109, 115) supports that cobalt could have been introduced to a base glass in the form of a frit. Tite and Shortland (2003: 285, 305-306) now suggest that the frit was indeed used in glass colouring, stating 'the compositions of the cobalt-blue glass and frit are consistent with the hypothesis that the cobalt-blue glass was produced from a mixture of cobalt-blue frit with additional plant ash and quartz'. Figures 4 and 5 show examples of blue frit in fritting pans, glass rods and cobalt-blue glass objects recovered at Amarna (18th Dynasty).

In sum, higher levels of silica in some glasses could suggest that colourant was added to a base glass or its precursors at the fritting stage of glass manufacture in the form of a vitreous material. This stage not only allowed bubbles and any contamination to be removed and colourants to be introduced but also permitted the colourant to distribute throughout the base glass during reheating to make glass proper. The frit found in the fritting pans at Amarna O45.1, with its low levels of calcium stabiliser, was probably not used directly for making objects. In fact, its high cobalt concentration suggests that it could be a concentrated vitreous colourant, which only later would be mixed with a base glass. This would suggest that the frit at Amarna was placed in fritting pans for another reason. This is now examined with regard to cobalt blue glass and frit.

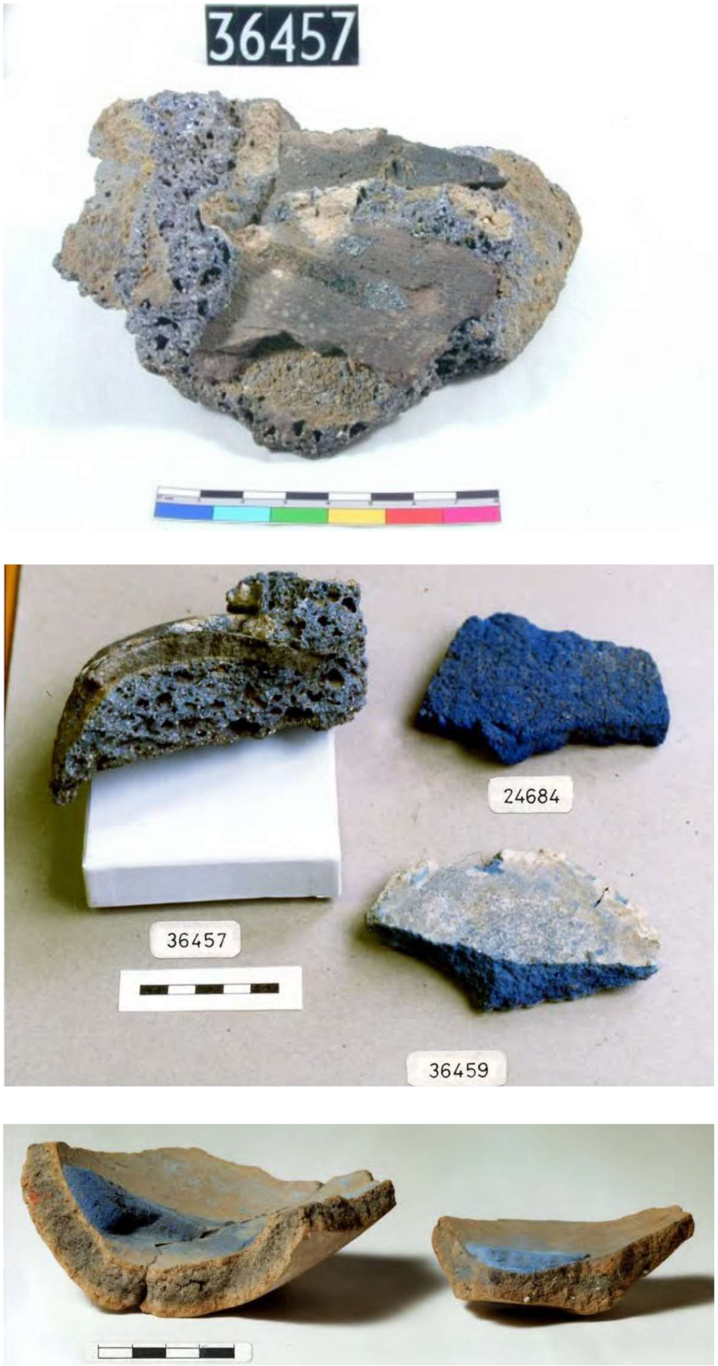


Figure 4. (top) Photograph from Petrie Museum (UCL) – Acc. no. UC36457 described as a fragment of broken pottery fritting pan enveloped by a mass of dark blue unfinished frit with visible chips of uncombined silica from crushed quartz pebbles and numerous air bubbles; shape of frit indicates pan profile. (middle) Images from Weatherhead and Buckley courtesy of Petrie Museum (UCL) (1989:220): On the left (UC 36457) is described as a spongy light-purple frit with small white inclusions, with attached sherd (possibly the remains of a fritting pan). UC24684 is described as a section from (circular?) cake of blue frit and UC36459 as a circular cake of blue frit. All are described as having a coarse texture. (bottom) Images from Weatherhead and Buckley courtesy of Liverpool Museum (1989:220): described as potsherds as containers of blue frit; left: Acc. No. 56.21.280.1; right: Acc. No. 56.21.281.

Figure 5. Photographs from Petrie Museum (UCL). All recovered from Amarna (18th Dynasty): (top) UC25042 – described as a fragment of dark blue glass; also described as raw glass. (middle) UC6524 – described as glass rods: turquoise, lapis blue and red. (bottom) UC6523 – described as a fragment of a cobalt-blue glass ring.

4. Re-analysing Glass Data

A recent compositional analysis of Egyptian cobalt-blue glass from museum collections in Japan (18th Dynasty, probably made at Malkata or Amarna), and from the site of Dahshur (18th and 19-20th Dynasties), measured using pXRF in a vacuum atmosphere, concluded that a new source of cobalt was exploited in Egypt after 1250 BC (Abe et al., 2012). These datasets were selected for re-analysis here as they are one of the only larger modern datasets which were measured by the same research group using the same instrument. Furthermore, the main colourant of these blue glasses was cobalt, exhibiting low copper concentrations (mean = 0.12%CuO; s = 0.16) for all apart from one sample, which had 2.28%CuO. These criteria (i.e. cobalt-coloured/low copper-concentration) were placed on all the data re-examined in this article (i.e. means of all samples: 0.19%CuO, s = 0.32; CoO = 0.15%, s = 0.1).

Figure 6 shows bivariate plots of the 18th Dynasty cobalt glass for CoO vs. NiO, MnO, ZnO and Al_2O_3. The linearity of these plots suggests that these components entered the system together and has been used to support that cobalt can be provenanced to the alum sources of the Western Desert Oases mentioned above (Figure 3).

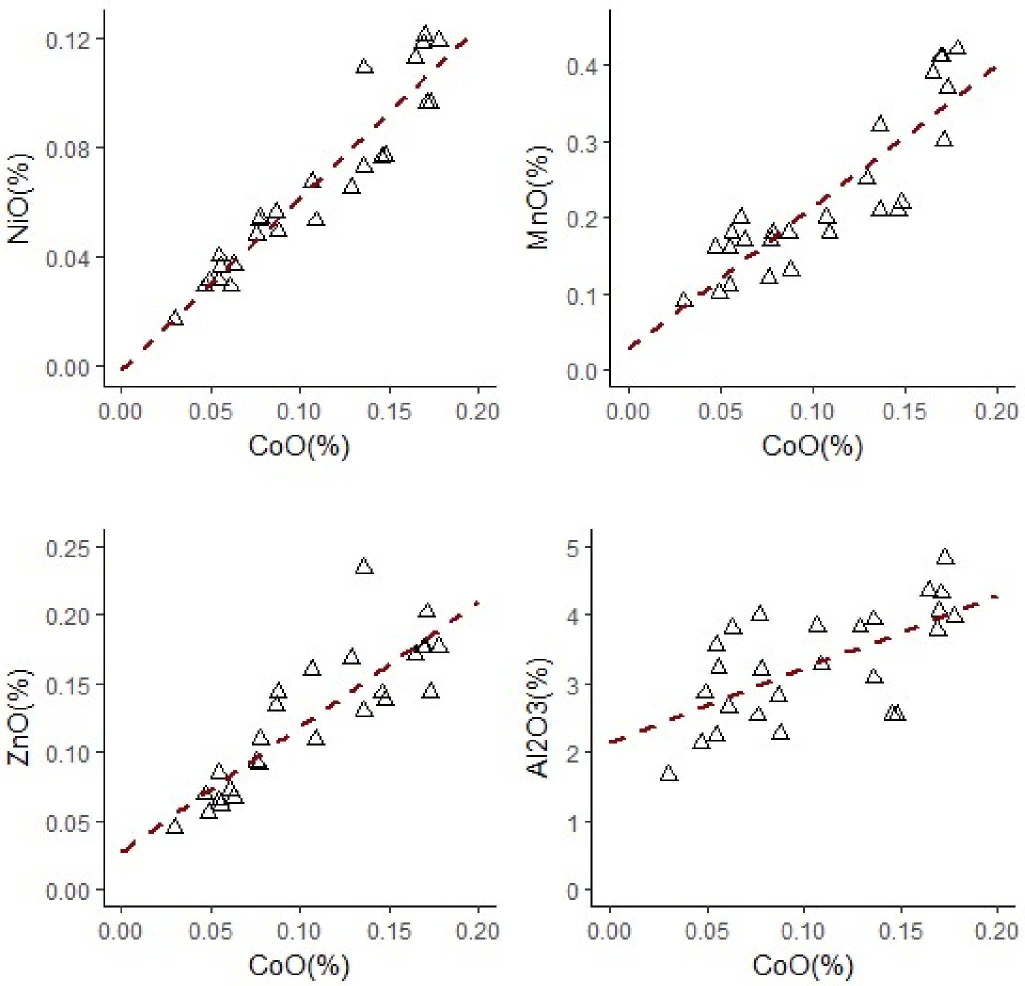


Figure 6. Bivariate plots of NiO, MnO, ZnO and Al_2O_3 vs. CoO in weight % for cobalt-coloured blue glass measured using pXRF. The relationships between NiO, MnO, ZnO and CoO show very linear interactions. Al_2O_3 shows more variation over the same concentration range (data from Abe et al., 2012).

The relationships between CoO and NiO, MnO and ZnO are remarkably linear, with the intercepts of the linear fits being close to the origin, supporting that these components not only entered the glass system together but derived from a common source. Ternary diagrams of these components were found to cluster tightly for these glasses along with an analysis from a faience object from the 18th Dynasty (Figure 4: Abe, et al., 2012). However, a linear relationship between cobalt oxide and alumina is less apparent. The variation is not only higher than the plots of NiO, MnO and ZnO, but the data also indicates a plateau. Figure 7 shows that a similar interaction is also apparent with laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) measurements on Egyptian cobalt blue glass from Malkata (green triangles) and Amarna (red triangles) (Shortland et al., 2007; Varberg et al., 2015, 2016). WDS measurements for the *same* Malkata samples (blue triangles) are also plotted (Shortland and Eremin, 2006), highlighting not only the differences found between the results from different techniques but also why a linear interaction between Al_2O_3 and CoO has gained so much traction in the academic literature. In essence, taken together, these results suggest that the interaction between cobalt oxide and alumina is not particularly linear, which in turn questions whether alumina entered the system with the cobalt, or at least whether alumina can be considered as diagnostic to provenance cobalt.

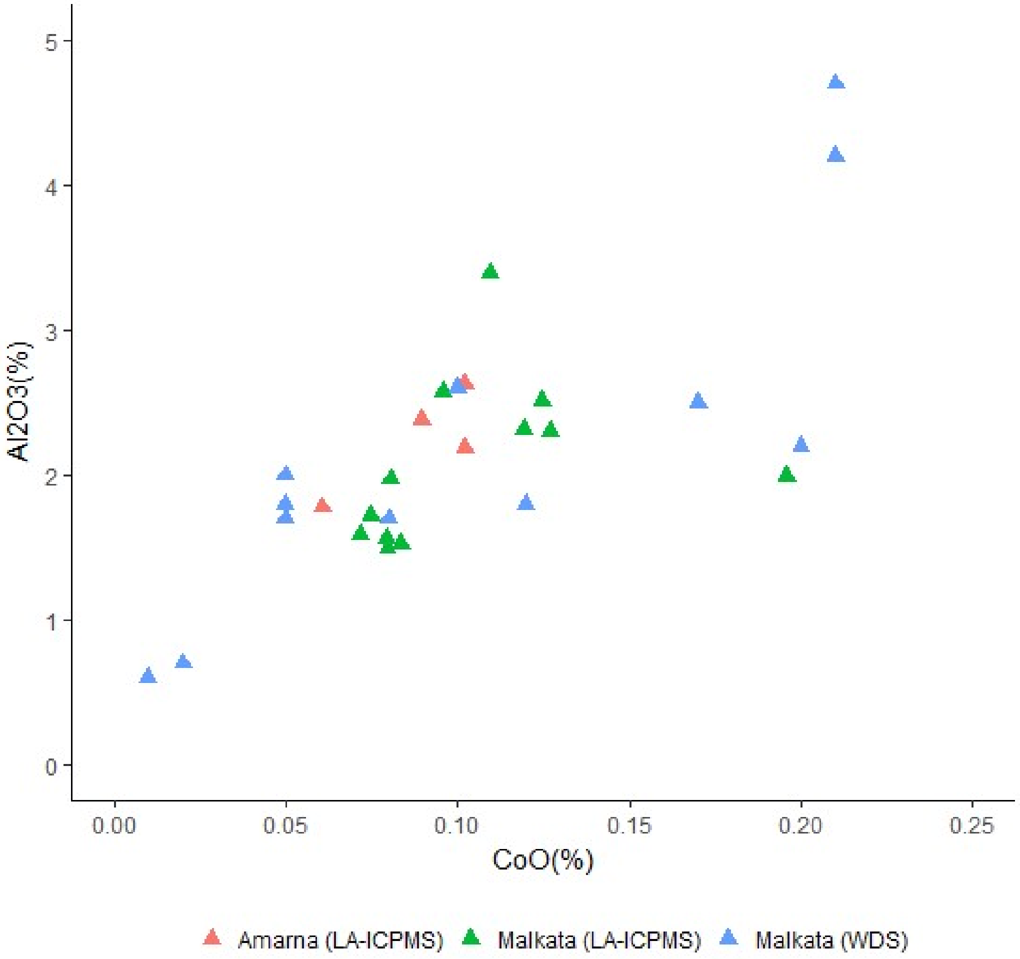


Figure 7. Bivariate plot of Al_2O_3 vs. CoO in weight % for cobalt-coloured blue glass from Amarna and Malkata measured using LA-ICPMS and WDS. WDS and LA-ICPMS was conducted on the same samples for the Malkata glass, highlighting the differences in concentration between these techniques, with WDS recording both lower and higher values than from LA-ICPMS. Note that sample UPP38 from Malkata is not included here because, although previously classified by WDS as a cobalt-blue glass (i.e. WDS: CoO = 0.05%), LA-ICPMS measured 0.0028%, suggesting that CoO was not the main colourant. As with the pXRF data in Figure 6, the interaction between Al_2O_3 vs CoO does not show a particularly good linear relationship. (Amarna: LA-ICPMS data from Varberg et al., 2015 and 2016; Malkata: WDS and LAICPMS data from Shortland and Eremin (2006) and Shortland et al., 2007, respectively).

A re-analysis of cobalt blue glass data has been conducted treating the system as a series of sub-compositional components, by transforming the data to a log-ratio scale (Aitchison, 1986; 2005). This approach removes the effects of the constant sum constraint (which compels the data to lay between 0 and 100%) in order to eliminate any 'spurious correlations' (Chayes, 1949). In essence, it considers from the outset that the interest lies in the *relative* magnitudes and variations of components, instead of in their absolute values. Multivariate analyses were performed using the 'Compositions' package in R created by van den Boogaart (2013), applying Aitchison's geometry (i.e. the centred log-ratio transformation) to the raw compositional data. The dendrograms and ternary diagrams presented use the association of variables from variation matrices in order to detect similar patterns of variation between them. The Ward algorithm was applied as the clustering criterion for the dendrograms (i.e. minimum variance), using the Euclidean distance method as the clustering option. The R package 'clustsig' (Whitaker and Christman, 2014) was used to determine which (if any) clusters were significantly different. The null hypothesis was that there was no *a priori* group structure. The alpha level at which to reject the null hypothesis was 0.05. Dendrograms for individual samples are also presented, derived using the same method.

The distributions of the concentrations of oxides in glasses and frit were investigated by plotting kernel density plots based on a gaussian function using a bandwidth equal to the standard deviation of the dataset. The y-axis was scaled so that the total area of the plot was unity. Y-axis values have not been included on these plots as it was the shapes of the plots (i.e. the density values add little to the understanding of the distribution profile) which were used to assess the compositional profiles of each component in the datasets examined.

4.1 Egyptian glass from museums in Japan (18th Dynasty) and Dahshur (18th and 19th-20th Dynasties)

A multivariate analysis was performed of the full chemical data set from Abe et al. (2012), apart from SnO2, which was below the detection limit for the majority of samples. The dendrogram in Figure 8 shows the 18th Dynasty glass from museum collections. As expected NiO, CoO, MnO and ZnO are closely associated, i.e. the cluster is based on their similar patterns of variation. As anticipated from the bivariate plots above (Figure 6), alumina has lower co-dependence and is less well associated with all these element oxides, being better associated with the refractory oxides, e.g. MgO and TiO_2. CuO and PbO are not well associated with the other components or with each other.

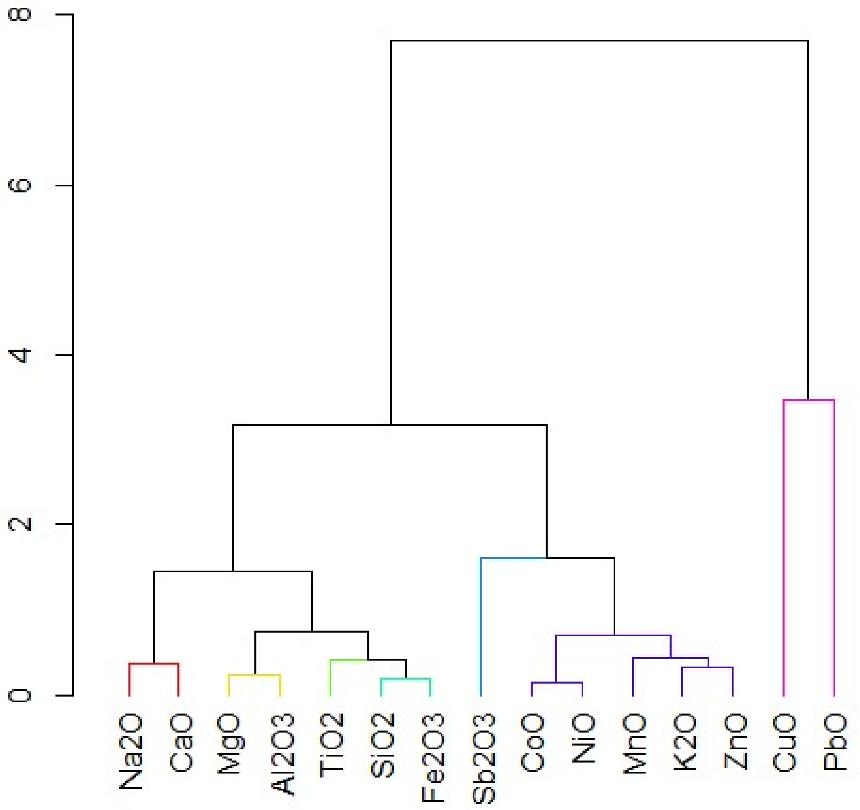


Figure 8 Dendrogram derived from the variation matrix of 26 samples of 18th Dynasty Egyptian glass from museum collections in Japan, probably originating from Amarna and Malkata (data from Abe et al., 2012). Note the close association between CoO, NiO, MnO and ZnO. K_2O and Na_2O are not well associated, as would be expected from a plant-ash fluxed glass. Al_2O_3 and MgO are closely associated with TiO_2, SiO_2 and Fe_2O_3. CuO and PbO are not well associated with the other components in the glasses or with each other.

Figure 9 shows the dendrogram for the 19-20th Dynasty glass from Dahshur. As with the 18th Dynasty museum pieces in Figure 8, NiO, MnO, CoO and ZnO are well associated. However, there are also differences between the two dendrograms: K_2O is better associated with Na_2O (discussed in Section 4.4) and, Al_2O_3 is less well associated with MgO and TiO_2 (discussed in 4.2) in the 19th-20th Dynasty glass from Dahshur than in the 18th Dynasty glass from museum collections.

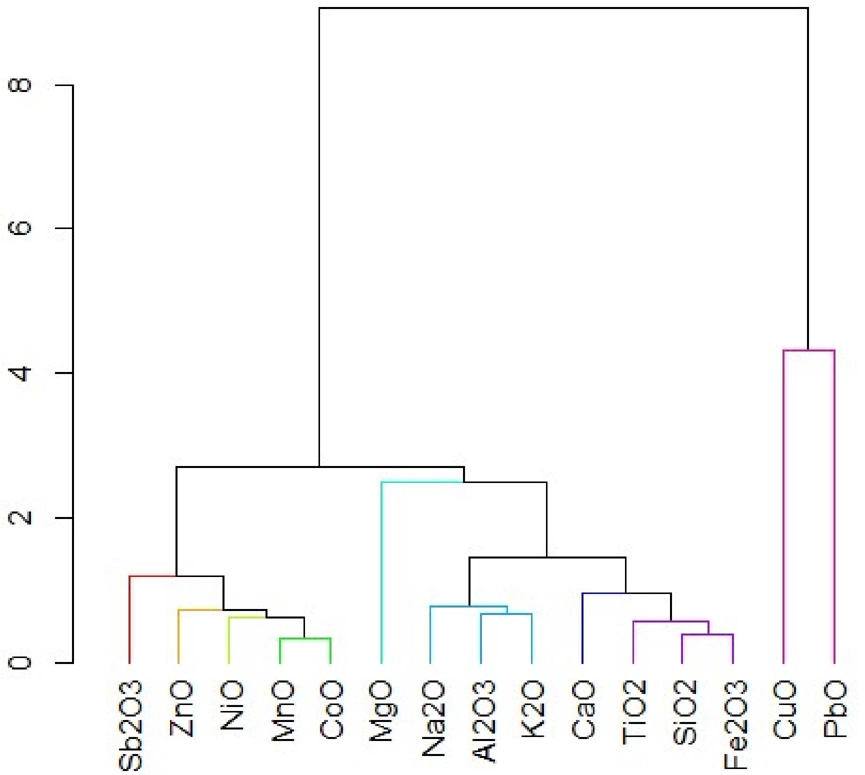


Figure 9 Dendrogram derived from the variation matrix of 20 samples of 19th-20th Dynasty Egyptian glass from Dahshur, (data from Abe et al., 2012). Note the close association between CoO, NiO, MnO and ZnO. K_2O and Na_2O are better associated and Al_2O_3 is less well associated with MgO, TiO_2, SiO_2 and Fe_2O_3 than in the 18th Dynasty glasses in Figure 8.

Using the variation matrix for each sample to construct a dendrogram shows that the 18th Dynasty glass and 19th-20th Dynasty glass fall into two distinct groups when the dendrogram is cut high (>10) (Figure 10), apart from one 19th-20th Dynasty and two 18th Dynasty samples. All the 18th Dynasty glass found at Dahshur falls within the main 18th Dynasty group. It will be shown that these groups are a consequence of recycling, rather than different recipes or practices and will be discussed in sections 4.2 and 4.3.

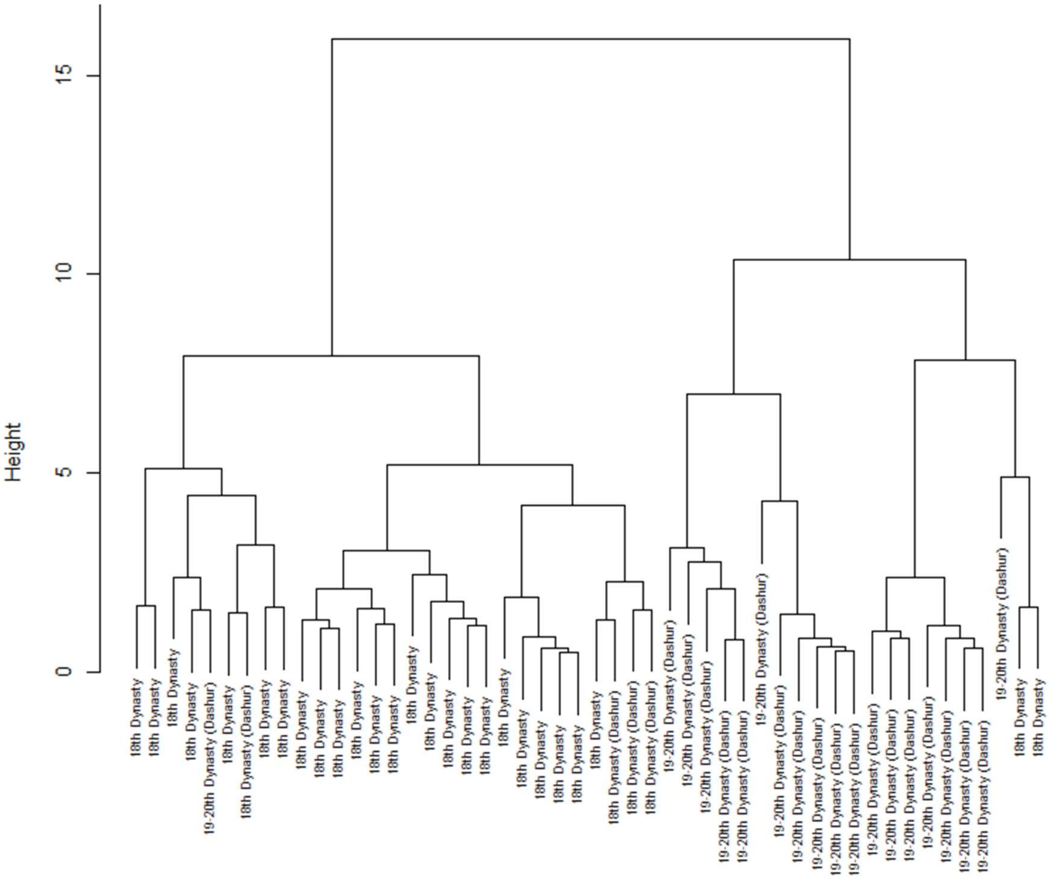


Figure 10. Dendrogram derived from the variation matrix of 50 samples of the 18th Dynasty glass from museum collections in Japan and the 18th and 19th-20th Dynasty Egyptian glass from Dahshur (data from Abe et al., 2012). When the dendrogram is cut high (>10), the 18th Dynasty glass forms 2 distinct groups, one main (24 samples) and one group (2 samples) associated with the 19th-20th Dynasty glass from Dashur. The 19th-20th Dynasty glass from Dahshur forms a distinct group (19 samples), with one sample falling within the main 18th Dynasty group. Two 18th Dynasty glasses are associated with the 19th-20th Dynasty group from Dahshur. All 18th Dynasty Dahshur glasses lie within the main 18th Dynasty group (4 samples).

To examine this dataset further, the following plot (Figure 11) shows the relationship between alumina and titania using the 18th Dynasty glass plotted above, alongside 18th Dynasty glass and glass from the Ramesside Period (19th-20th Dynasties) found at Dahshur.

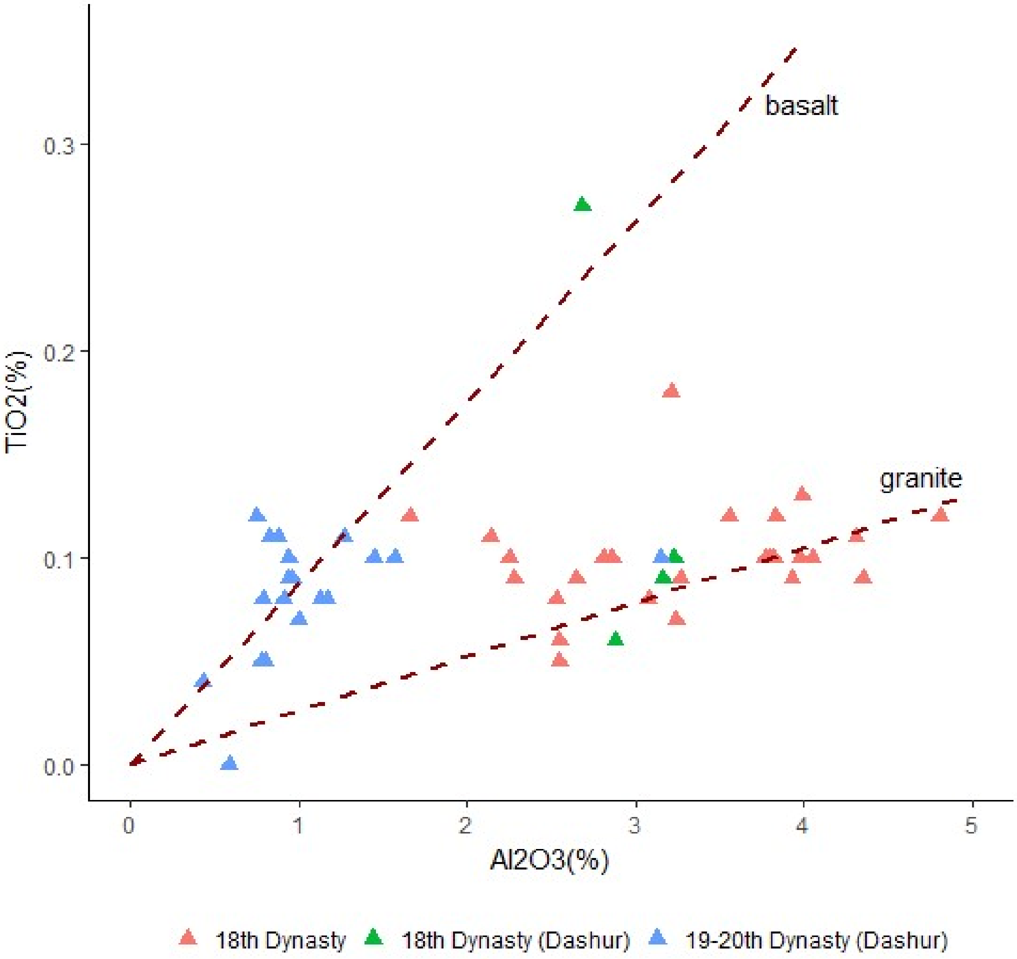


Figure 11 Bivariate plot of TiO_2 vs Al_2O_3 in weight % (data from Abe et al., 2012) for the Egyptian cobalt blue glasses. The dashed lines show relative amounts of TiO_2 and Al_2O_3 for granite and basalt determined from Daly (1914:563). Generally, the 19th-20th Dynasty glass from Dahshur fall on the basalt line, while the 18th Dynasty glass from museum collections in Japan and the 18th Dynasty glass from Dahshur generally fall on the granite line. Note that only one sample from Dashur (19th-20th Dynasty) appears to fall on the granite line, and one sample classified as 18th Dynasty Dashur falls on the basalt line. The three remaining 18th Dynasty Dashur samples fall with other 18th Dynasty samples, indicating that the chronology of these samples is more significant than their find site in terms of these compounds.

Both the 18th Dynasty data (red triangles) and Ramesside data from Dahshur (blue triangles) show interactions which are relatively linear and potentially converge at the origin. This could suggest that these two components enter the system together. Although a linear regression could have been used to represent these interactions, the lines on the plots are *not* linear regressions applied to the data but were derived from the average compositions of granite and basalt, the main components of igneous rocks (Table 1; Daly, 1914:169 in Parker, 1967). In other words, these dashed lines are independent measurements of igneous materials, determined from the average compositions of basalt and granite rocks (Table 1).

Table 1: Composition of granite, basalt and igneous rock calculated as a 1:1 ratio of granite and basalt (from Daly, 1914:563 in Parker, 1967).

%	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Granite	70.47	0.39	14.90	1.63	1.68	0.13	0.98	2.17*	3.31	4.10	0.24
Basalt	49.65	1.41	16.13	5.47	6.45	0.30	6.14	9.07	3.24	1.66	0.48
Igneous	60.06	0.90	15.52	3.55	4.06	0.21	3.56	5.62	3.28	2.88	0.36
* includes 0.06% BaO and 0.02% SrO. ratios of TiO_2/Al_2O_3: 0.026 (granite); 0.087 (basalt); 0.058 (average igneous rock - basalt:granite 1:1)											

The proximity of the 18th Dynasty dataset to the granite line could suggest that alumina and titania entered the glass system together, perhaps as a consequence of contamination from grinding tools. The proximity of the Ramesside data to the basalt line could suggest that grinding tools of different compositions were used at Dahshur compared to those at Malkata or Amarna. Granite and basalt are both common in Egypt. As hard, igneous rocks have compositions between granite and basalt (i.e. often in a ratio of 65:35, respectively (Mead, 1914 in Parker, 1967)), some variation would be expected between the two lines. However, the absolute levels of Al_2O_3 appear quite high (~ 0.5-5%Al_2O_3) to be explained by contamination from grinding tools alone (i.e. ~30-330g of igneous rock for a 1kg glass ingot), suggesting that another mechanism is responsible for igneous material entering the system.

Similar interactions between TiO_2 and Al_2O_3 are also found with another dataset for Egyptian cobalt blue glass from Malkata and Amarna measured using LA-ICPMS (Figure 12). Mesopotamian cobalt blues glass axes recovered from Nippur measured using the same method are also plotted. Both datasets show relatively linear interactions, which again indicates that these two components entered the glass system together. Most of the glass from Nippur falls very close to the granite line while most of the glass samples from Egypt lie mid-way between the basalt and granite lines, i.e. indicative of the average composition of igneous rocks.

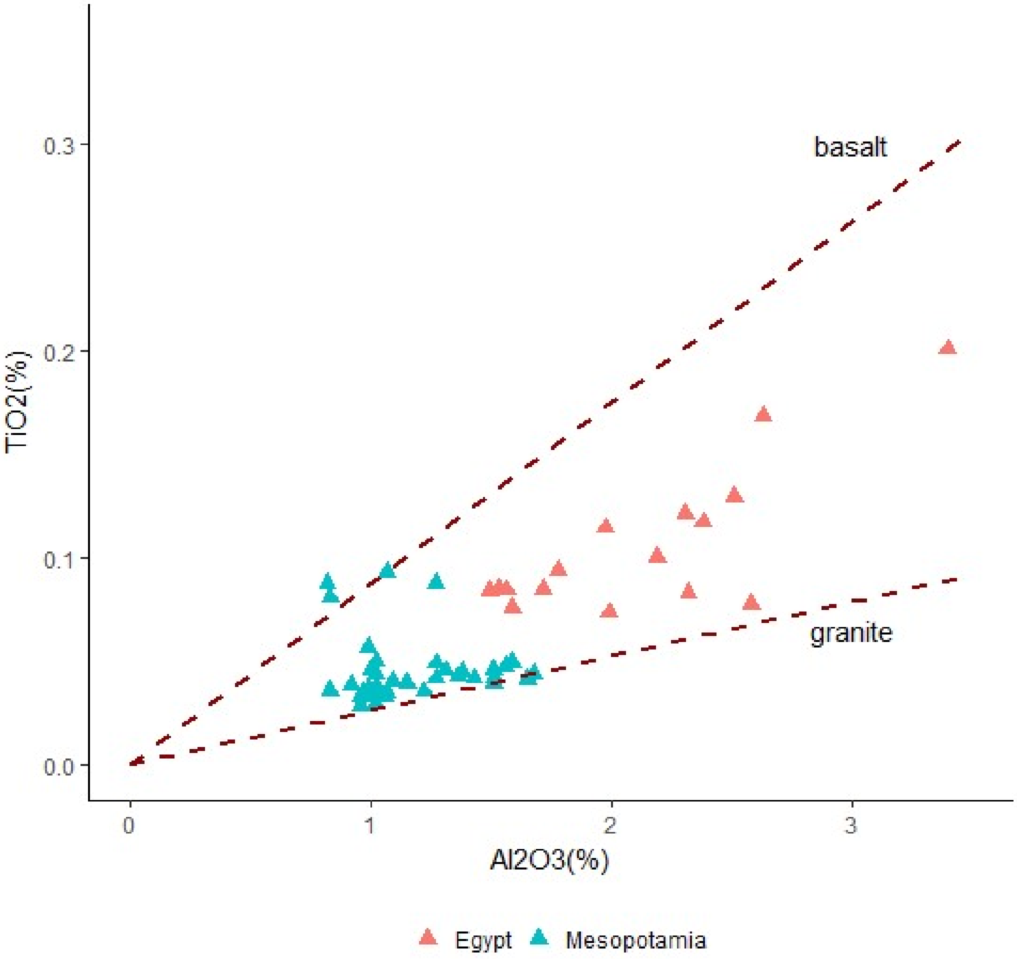


Figure 12 Bivariate plot of TiO_2 vs Al_2O_3 in weight % for the Egyptian cobalt blue glass from Amarna (Varberg et al., 2015, 2016) and Malkata (Shortland et al., 2007) and Mesopotamian cobalt blue glass from Nippur (Walton et al., 2012). The dashed lines show relative amounts of TiO_2 and Al_2O_3 for granite and basalt determined from Daly (1914). The Mesopotamian glass falls on the basalt line and the granites lines, while the Egyptian glass Amarna and Malkata falls between the basalt and granite lines.

As mentioned above, Egyptian cobalt blue glass has elevated levels of alumina compared to glasses of other colours, which has been attributed to the alum source. The question now arises as to, if titania and alumina entered the glass through contamination during grinding, why cobalt blue glass would generally have elevated levels of igneous material compared with glass not coloured by cobalt. This will be discussed in Section 4.4. However, regardless of whether grinding or some other mechanism resulted in the elevated levels of alumina and titania in these glass systems, what is apparent is that contamination by the elements found in igneous rocks is sufficient to explain the presence of alumina without recourse to the sophisticated chemistry required to extract cobalt from the cobaltiferous alums. Furthermore, since Mesopotamian cobalt blue glass is less likely to have been derived from the alum deposits in Egypt, the linearity of the plot supports that the alumina levels are related to contamination from igneous rocks, for both Egyptian and Mesopotamian glass. Essentially, there is no need to provenance the cobalt to alum mines in Egypt's Western Oases, which are sedimentary deposits with much higher levels of alumina and lower levels of cobalt than cobalt blue glass and have not been found to contain titania (Shortland et al., 2006[1]). Furthermore, without the need to accommodate alumina as part of the suite of elements used to identify the cobalt source, the number of potential sources from where the cobalt derived increases.

Discounting the alum sources of the Egypt's Western Desert, in effect, opens up the argument regarding where the cobalt originated. What is clear, however, is that cobalt is associated with Ni, Mn, and Zn, and this suite of elements and the minerals from which they derive is diagnostic of cobalt's source. Moreover, although alumina is probably not part of this mineralisation package, it must still be present in sufficiently high amounts to have entered the system along with these other components, in the same way as the components of gangue enter the slag when metals are extracted from ores.

4.2 Mixing glass

The different compositional signatures between the Ramesside (19th-20th Dynasty) and 18th Dynasty glass discussed above has been used to support that a different cobalt source was used in the later period at Dahshur (Abe et al., 2012), predominantly because the Al_2O_3 levels in the Ramesside glass were significantly lower than the empirical limit of 1.2%Al_2O_3 found in most cobalt glasses. Furthermore, and more significantly, the differences in alumina levels have been used to suggest that glass production continued after the New Kingdom period, i.e. a new cobalt source was exploited for this later glass.

The following density plots show the distribution of CoO, NiO, MnO and ZnO in the 18th Dynasty glass plotted in Figure 6. Figure 13 shows that the distribution of cobalt oxide concentration in the 18th Dynasty glass is bi-modal, with two distinct peaks around 0.07 and 0.16% cobalt, i.e. the lower peak having about half the CoO level of the higher peak. Both NiO and MnO show similar bimodal distributions (Figure 14). Furthermore, as with CoO, the peaks at lower concentrations for both NiO and MnO appear to be about a factor of 2 lower than the peaks at higher concentrations. Although more difficult to discern, Al_2O_3 and ZnO exhibit broad distributions commensurate with more than one peak. This suggests that the lower concentration peaks could simply represent a dilution of the higher concentration peaks, i.e. cobalt glass with 0.16wt% cobalt was mixed with a base glass (containing only trace levels of CoO, NiO, MnO and ZnO) in approximately a 1:1 ratio. ZnO is consistent with this interpretation, with its broader distribution perhaps reflecting that it can be reduced when heated to 950^{o}C (Greenwood and Earnshaw, 1997) in the presence of carbon, resulting in the volatile Zn metal. The lower concentration peak of the Al_2O_3 distribution, however, is less than a factor of 2 lower (2.8%) than the upper peak (3.9%), which could reflect additional grinding with the base glass before dilution resulting in further contamination, the use of a silica source with higher alumina levels for the base glass, or contamination from the crucible during re-melting. Again, regardless of the mechanism, the data is consistent with the proposition that that the 18th Dynasty glass had an initial average composition of around 0.16%CoO, 0.11%NiO, 0.38%MnO and about 0.15%ZnO and 3.9%Al_2O_3 (i.e. the higher peaks) prior to any dilution. Some of this composition of glass would have been used directly to make objects, while some was re-melted, potentially a consequence of recycling broken objects. In effect, these distributions would support that some of the cobalt blue glass was re-melted during the 18th Dynasty.

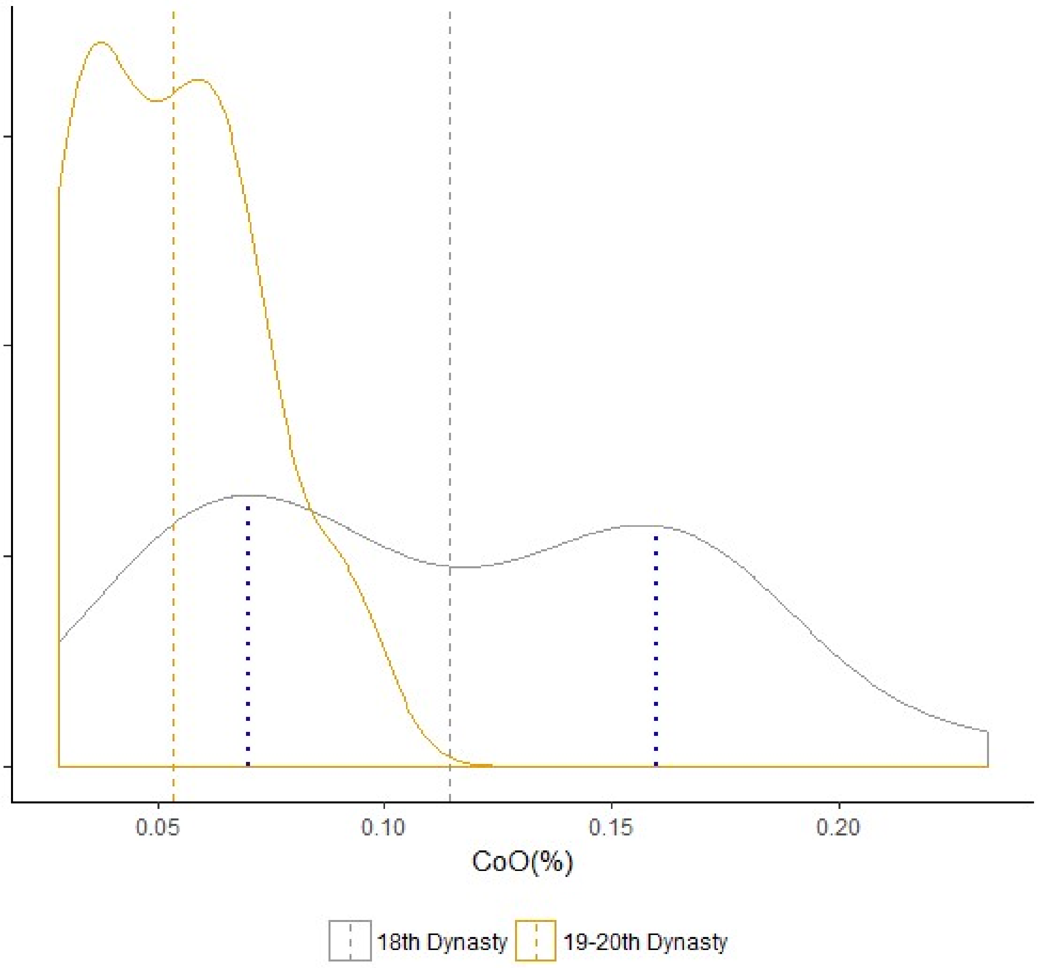


Figure 13 Density plot for the 18th Dynasty glass from museum collections in Japan and 19-20th Dynasty glass from Dahshur. The blue dotted lines show the peaks of the bimodal distribution of the 18th Dynasty glass. The dashed lines show the average CoO concentration in weight % for each dataset (data from Abe et al., 2012).

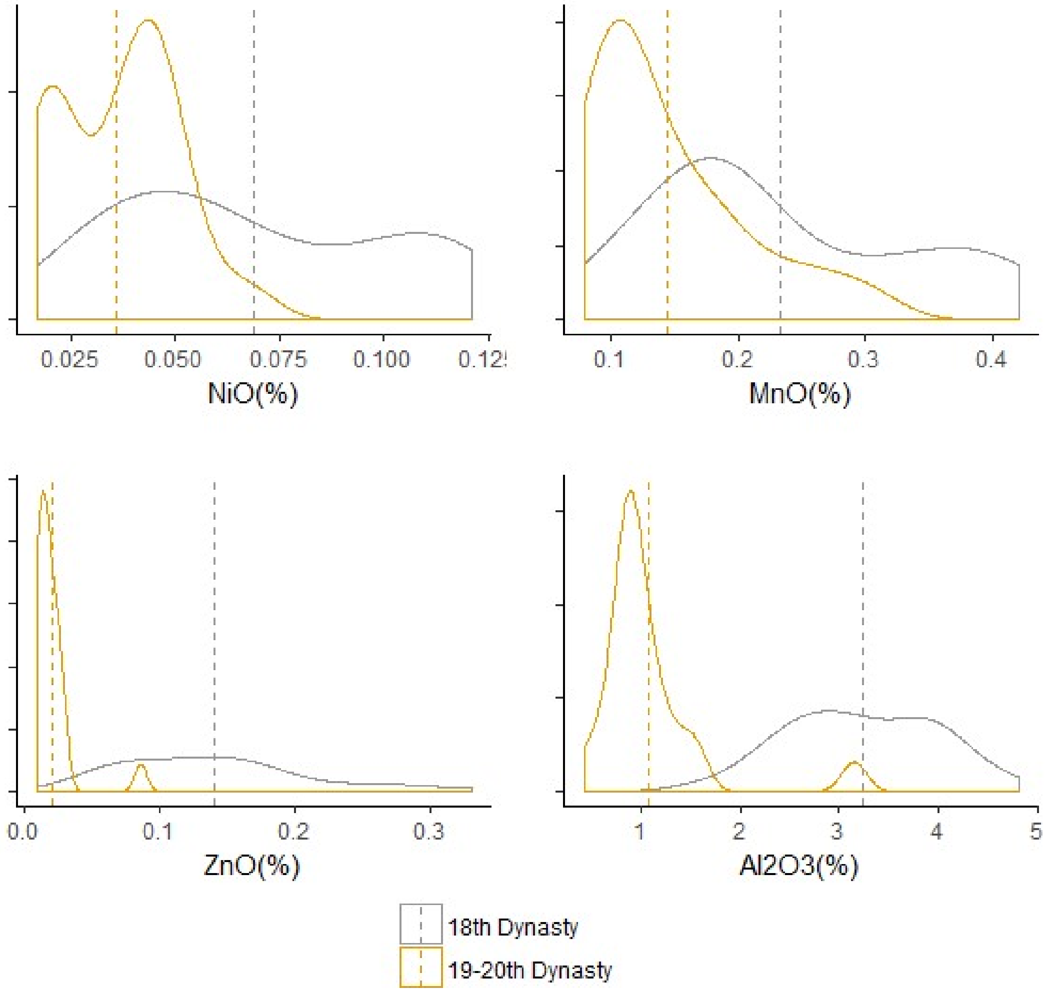


Figure 14 Density plots for the 18th Dynasty glass from museum collections in Japan and 19-20th Dynasty glass from Dahshur for NiO, MnO, ZnO and Al_2O_3. The dashed lines show the average concentrations in weight % for each dataset (data from Abe et al., 2012).

What is also apparent from the density plots is that the distribution of the glass from the Ramesside period at Dahshur is lower in concentration for all these oxides compared to the 18th Dynasty glass. Although it is difficult to state with certainty whether this is a consequence of further dilution of existing 18th Dynasty glass, this interpretation is supported to some degree by the average compositions (dashed vertical lines in Figures 13 and 14) for each oxide during both periods, i.e. CoO, NiO and MnO potentially show further dilution by a factor of about 2 for this later glass. In other words, the difference in the average concentrations could be interpreted as glass from both compositional distributions from the 18th Dynasty being further diluted with a base glass. This would suggest that the Ramesside (19-20th Dynasty) glass from Dahshur in Figure 11 derives from glass that originally fell on the granite line with the 18th Dynasty glass, before subsequently shifting to lower levels of alumina after dilution. If this is the case, then it would indicate that the Ramesside blue glass was not made with cobalt from a different source but derived from re-melting existing 18th Dynasty glass. This proposition is now further examined.

The dilution practice of re-melting 18th Dynasty glass in the 19th-20th Dynasties is to some degree revealed by examining the alumina and titania distributions. As noted above, the lower peak of the Al_2O_3 distribution for the 18th Dynasty glass is less than a factor of 2 lower (2.8%) than the upper peak (3.9%) (Figure 14). Furthermore, the average Al_2O_3 level of the whole 18th Dynasty distribution is more than twice as high as the average of the 19th-20th Dynasty glass (3.2% and 1.05%Al_2O_3, respectively). This suggests that the lower peak of the 18th Dynasty glass (and thereby the average level of the all the 18th Dynasty glass) is higher than expected from the first 1:1 dilution with a base glass. In other words, the higher alumina level is potentially due to contamination from the furnace lining or crucible during recycling which would increase both the alumina and titania concentrations (but not the ZnO, NiO, MnO or CoO concentrations), i.e. Nile silt has average Al_2O_3 and TiO_2 concentrations of about 15% and 2%, respectively (Shortland et al., 2006[2]). This glass was diluted again to produce the 19th-20th Dynasties glass. The range of the TiO_2/Al_2O_3 ratio for both Nile silt (Shortland, 2000), Ballas clay (from the edge of the Western Desert near Luxor) (Baba, 2009) and pottery found at Amarna and Malkata (Shortland, et al., 2006[2]) are plotted in Figure 15, which shows that decreasing cobalt oxide levels (i.e. more dilution) results in an increase in the TiO_2/Al_2O_3 ratio approaching a level consistent with materials used for the furnaces and crucibles. Figure 16 shows that the TiO_2/Al_2O_3 distribution is much narrower for high cobalt concentrations (i.e. 18th Dynasty glass) but covers a wider range at lower CoO concentrations resulting in a much wider distribution for the later Ramesside period glass, i.e. more mixing results in more contamination and, therefore, more variation.

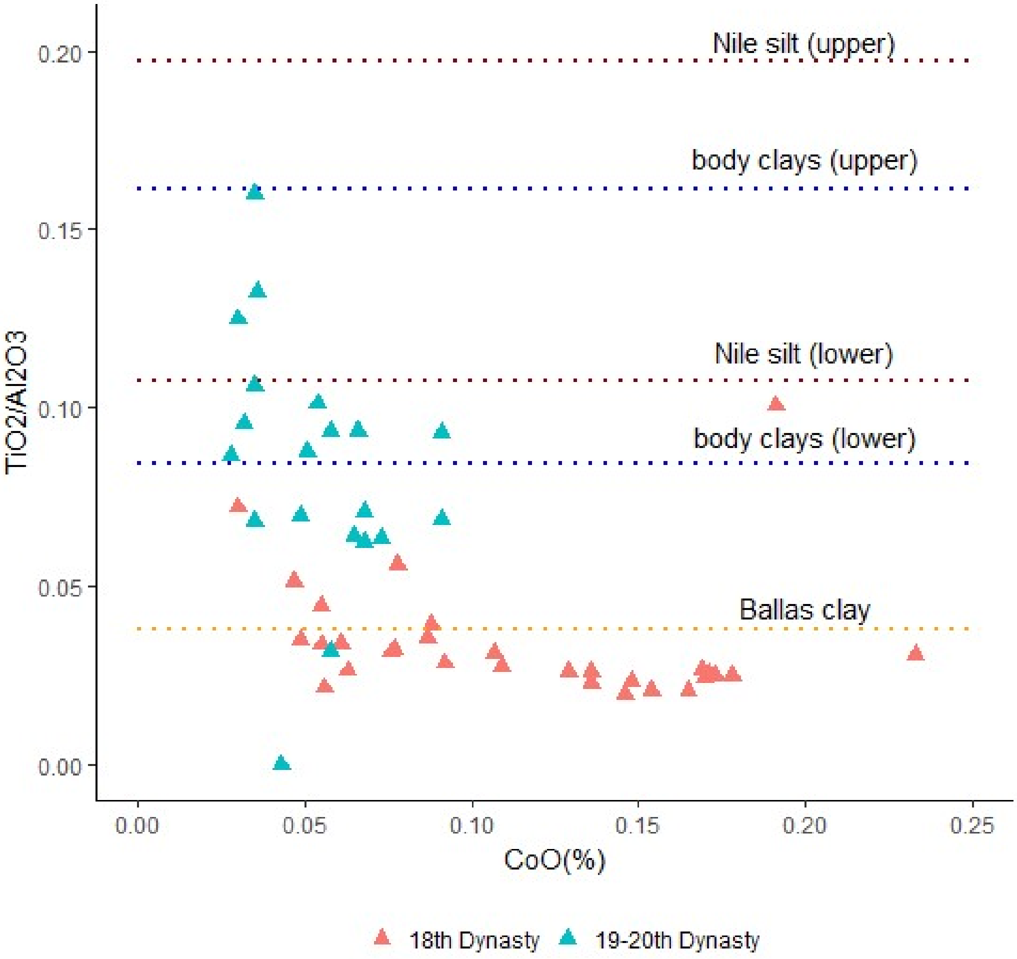


Figure 15 Plot of TiO_2/Al_2O_3 vs CoO for the 18th Dynasty glass and 19th-20th Dynasty glass from Dahshur (data from Abe et al., 2012). The horizontal dotted lines show the ratios of TiO_2/Al_2O_3 for Nile silt (Shortland, 2000), body clays from Amarna and Malkata (Shortland et al., 2006[2]) and Ballas clay found on the edge of the Western Desert near Luxor (Baba, 2009).

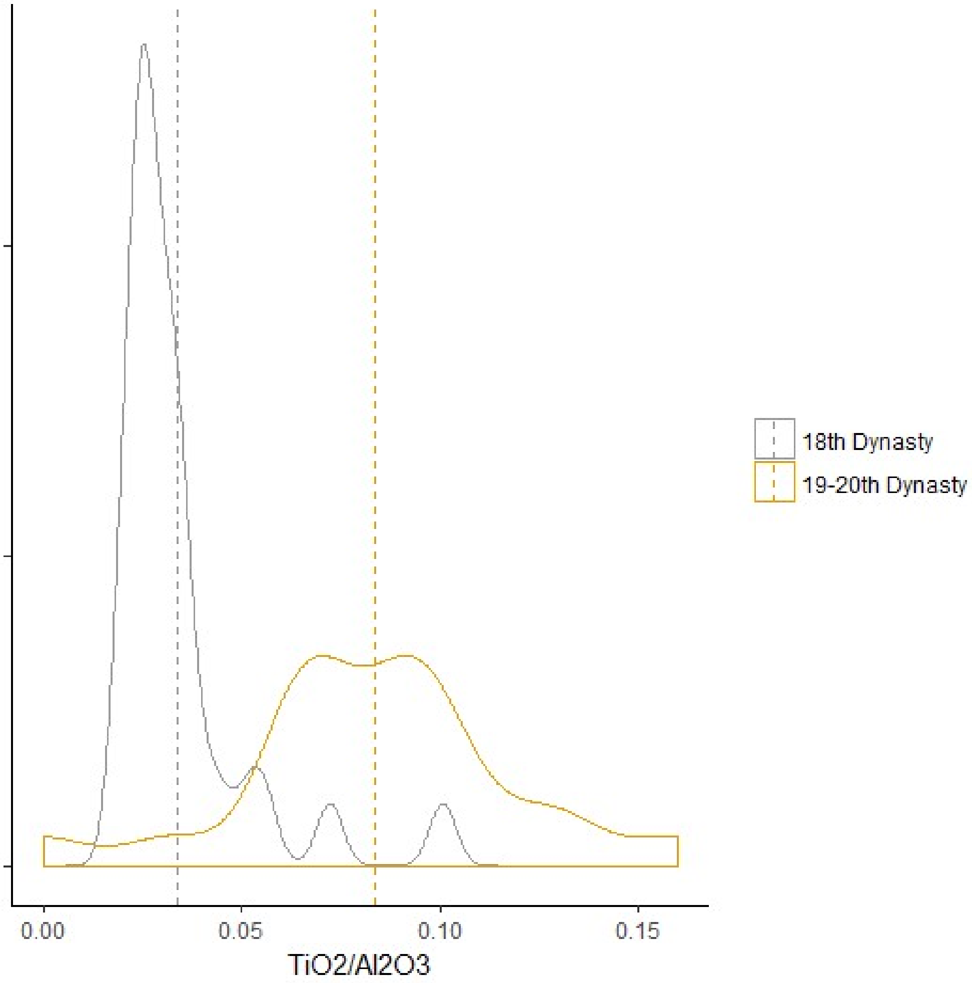


Figure 16 Density plot of TiO_2/Al_2O_3 for the 18th Dynasty glass from museum collections in Japan and 19-20th Dynasty glass from Dahshur. The 19th-20th Dynasty glass from Dahshur has a much broader distribution than the 18th Dynasty glass (data from Abe et al., 2012).

In essence, Figures 15 and 16 suggest that alumina and titania, derived from minerals found in the furnace or crucible materials (e.g. feldspar, rutile etc.), contaminated the 18th Dynasty glass, raising the alumina and titania levels to higher than expected from the first dilution, before subsequent dilution again in the Ramesside period. This is supported by the fact that alumina and titania are less well associated with further dilution (i.e. recycling) as evidenced by the differences in the dendrograms for the 18th Dynasty and 19th-20th Dynasty glass in Figures 8 and 9. In other words, alumina and titania initially entered the glass system together but contamination from re-melting and reworking affected the strength of this association.

Further support for mixing is found by examining possible contamination from lead. Recycling coloured glass requires that colours are separated prior to re-melting. This is unlikely to be a completely efficient process, with elements required to make other colours potentially contaminating the cobalt blue glass. Although an indirect measure, the fact that the 18th Dynasty glass from the museum collections has an average of 0.021%PbO while 19th-20th Dynasty glass from Dahshur has an average of 0.041%PbO strongly suggests that yellow glass (coloured by lead antimonate) entered the system. Furthermore, PbO is not well associated with the other components, clustering only with copper (Figures 8 and 9). The distribution (Figure 17) shows that most of the 18th Dynasty glass has low levels of PbO which is potentially the trace levels prior to any recycling (the peak in Figure 17 is about 0.01%PbO). Some 18th Dynasty glass has elevated levels of PbO, providing further support that recycling occurred during this period. The 19-20th Dynasty glass has a much broader distribution than the 18th Dynasty glass, suggesting that the majority of this glass has been contaminated with lead, which is consistent with recycled glass. The weak association of copper with the other components (Figures 8 and 9) is also indicative of contamination, from copper-blue glasses. Interestingly, Sb_2O_3 clusters with the other components than with PbO (Figure 8 and 9). This is possibly a consequence of contamination from white opaque glass, where antimony is associated with calcium thereby weakening its association with lead, i.e. calcium antimonate (white glass) and lead antimonate (yellow glass) both entered the system during the recycling process.

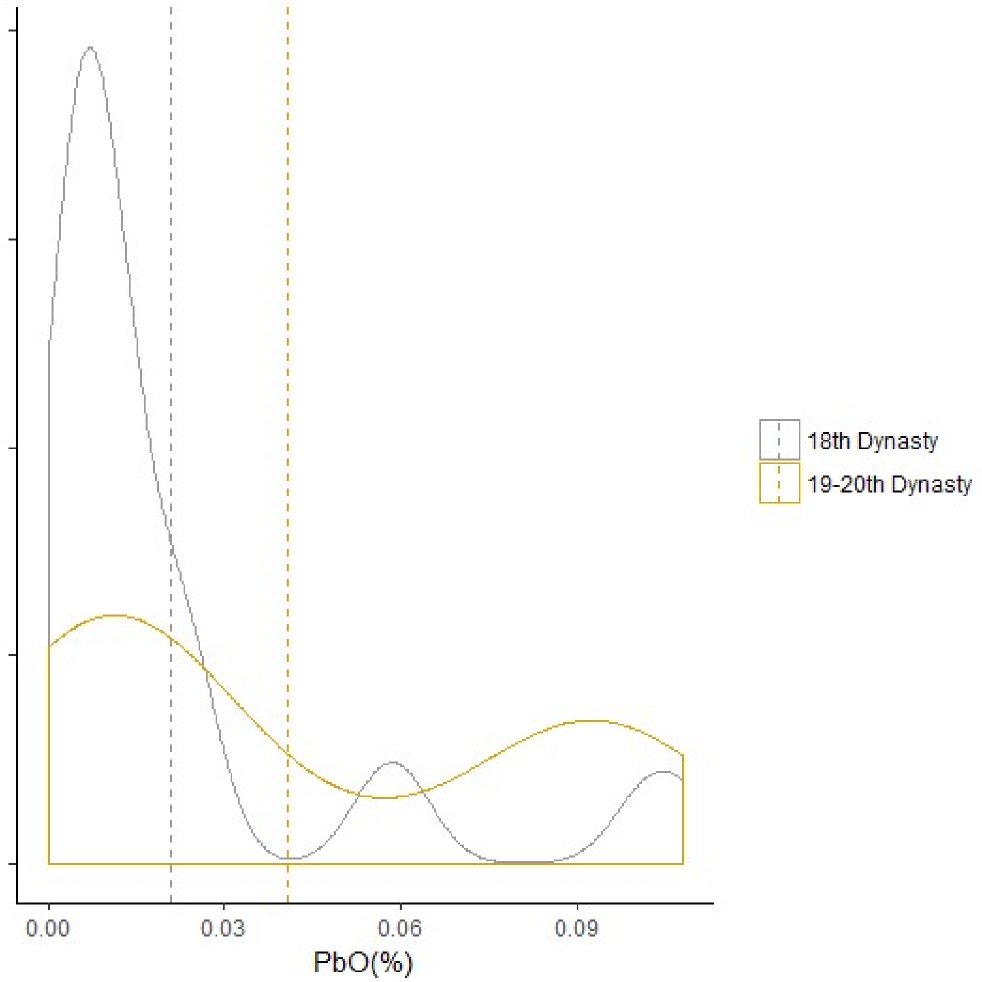


Figure 17 Density plot of PbO for the 18th Dynasty glass from museum collections in Japan and 19-20th Dynasty glass from Dahshur. The 19th-20th Dynasty glass from Dahshur has a much broader distribution than the 18th Dynasty glass (data from Abe et al., 2012).

In effect, the initial 18th Dynasty glass (the higher peak concentrations of CoO, NiO, MnO and Al_2O_3 in Figures 13 and 14) was diluted at least twice (by a factor of around 4) by the Ramesside period. From the distributions in Figures 13, 14, 16 and 17 it is also possible to infer that more than one dilution occurred during the Ramesside period. Although such dilutions were probably derived empirically, it is interesting to note that the cobalt level in the Ramesside glass (average CoO = 533ppm) was around the lower limit to maintain a rich, deep blue (Henderson, 2000). This fits well with the narrative that glass was not produced in significant amounts after c. 1250 BC, with glass-makers reducing the levels of cobalt through dilution with a base glass to the point where the colour was still effective.

This mixing mechanism means that there is no need to propose a new cobalt source during the Ramesside period to explain the different compositional signatures, nor to require the production of cobalt-blue glass to continue after the New Kingdom period. Furthermore, the relationship between TiO_2 and Al_2O_3, in similar proportions to those found in igneous rocks, is sufficient to suggest that the alum mines in Egypt's Western Oases were not the source of cobalt for either the 18th Dynasty or 19th-20th Dynasty cobalt blue glass. The repercussions regarding the provenance of cobalt glass will be discussed below. However, this proposition immediately resolves one archaeological issue surrounding the presence of cobalt in glass, in that it is no longer necessary to speculate on why such accessible sources as the Kharga and Dakhla oases, with their proximity to both Amarna and Malkata and even Dahshur (Figure 3), stopped being exploited by around 1250 BC: the claim being made here is that they had not been used for colouring glass before, and they remain unused. However, it raises several archaeological science issues with regard to how to provenance the cobalt and deal with glasses which have been mixed. First, alumina can no longer be considered a reliable indicator among the suite of oxides used to inform on the cobalt source, as igneous rocks are not unique to Egypt and contamination from furnaces and crucibles are probably inevitable. Moreover, it is much more difficult to make sense of groups clustering on bivariate plots if glass has been mixed, as some points will fail to cluster in a compositional group because of dilution, irrespective of provenance. For example, from the LA-ICPMS data for the Egyptian and Mesopotamian glasses, the average ZnO level of the Nippur axes is 0.015%, which is approaching an order of magnitude lower than the Egyptian cobalt glass (ZnO= 0.114%). Although this appears to be a useful discriminator to differentiate between groups, the low ZnO values for the Nippur axes could be indicative of dilution as well the loss of volatile zinc due to re-melting and re-working the glass. This implies that if the glass used for the Nippur axes was diluted more than once (or experienced higher temperatures or more reducing conditions during processing), the cobalt source may have been zinc-rich.

4.3 Mixing frit with a base glass

Smirnou and Rehren (2011) refer to the cobalt blue frit found by Petrie and studied by Shortland and Tite (Tite el al., 1998; Shortland, 2000; Shortland and Tite, 2000; Tite and Shortland, 2003; Shortland et al., 2006[1]) and Jackson and Nicholson (2007) as 'enigmatic', with its presence underlying 'the possible existence of local glass-making, but also the potentially complex nature of the materials and processes involved in LBA glass-making, as indicated by the cuneiform texts (Oppenheim *et al.* 1970)'. However, if we consider the cobalt blue frit found at Amarna O45.1 as a vitreous concentrated colourant to be added to base glasses or their precursor materials, we potentially have the key to discovering the complex nature of these materials and processes.

If the concentrated cobalt frit from Amarna and base glass mixture potentially provided the initial composition of the cobalt-blue glass that was used for some objects, any subsequent dilutions should be reflected in plots of the main compositional components of glass against the CoO concentration. The pXRF analyses on 26 blue glass samples from the 18th Dynasty plotted in Figure 6 present the opportunity to examine this. Although it is recognised that pXRF is a surface technique and that soluble species are more likely to be depleted at the surface (i.e. leaching of alkali oxides), the overall trends with CoO support the introduction of cobalt via a frit.

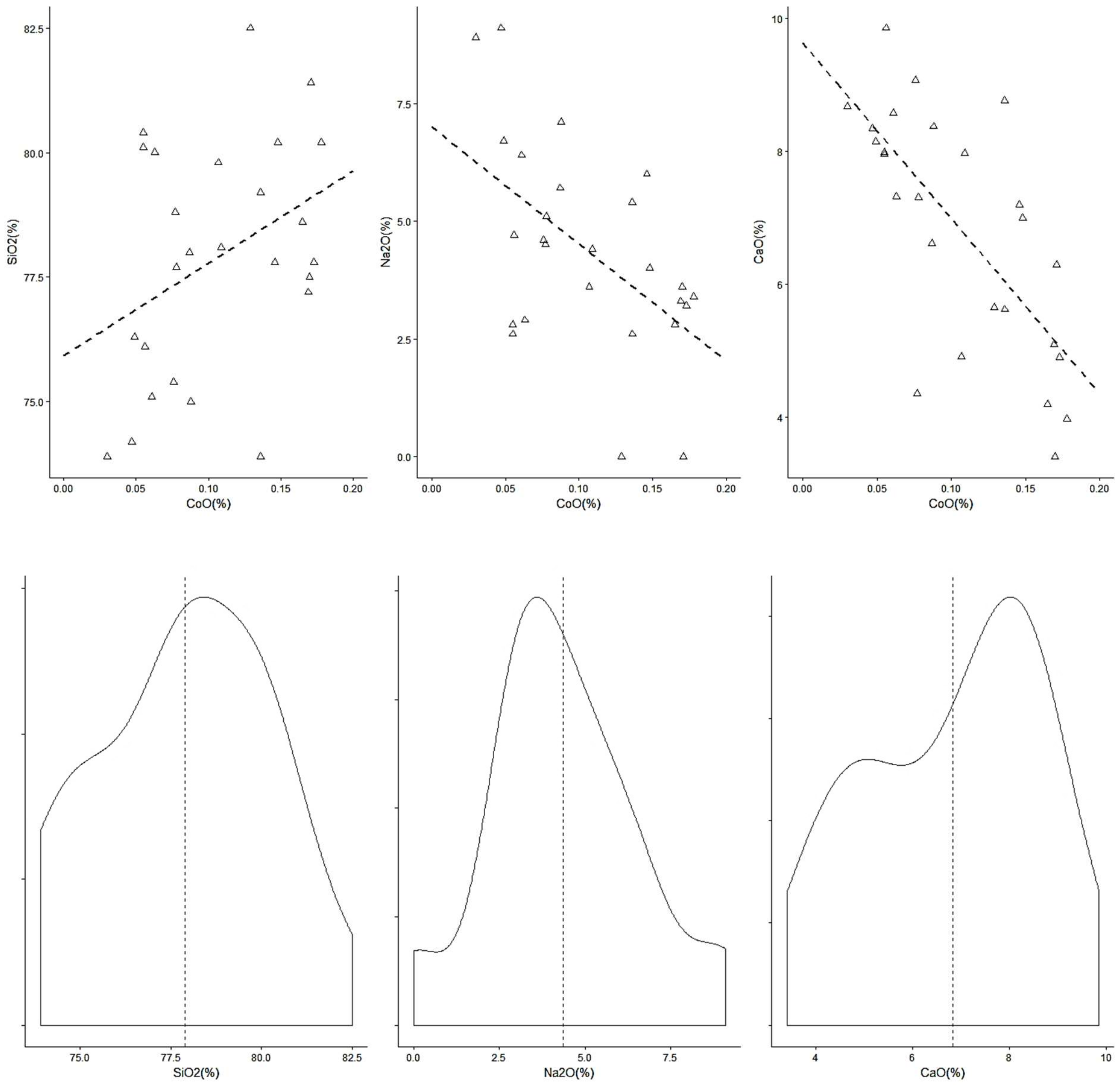


Figure 18 Bivariate plots and associated density plots of the major glass-forming oxides for the 18th Dynasty glass from museum collections in Japan. SiO_2 and CaO show bimodal distributions. Na_2O shows some evidence of a shoulder. Dashed lines on the bivariate plots are linear regressions applied to the data. The dotted lines on the density plots show the average concentrations of each component in weight % (data from Abe et al., 2012).

Despite the scatter in the data, Figure 18 shows that the silica concentration is lower at lower concentrations of CoO. Moreover, there is potentially a bimodal distribution, with the higher SiO_2 concentrations perhaps reflecting the presence of unreacted quartz from the frit entering the glass, as found in the cobalt blue frit at Amarna site 045.1 and the shoulder on the SiO_2 distribution potentially reflecting the subsequent dilution with a base glass of lower SiO_2 concentration. The CaO and Na_2O concentrations appear to increase with decreasing CoO concentration. The CaO also exhibits a bimodal distribution, which suggests that the initial glass (shoulder) had a lower CaO concentration because it was a mixture of frit (with low CaO) with a base glass, followed by dilution with a base glass with higher CaO concentration. The Na_2O level is quite low (Na_2O~ 3%) which is probably a consequence of the pXRF detecting leaching at the surface (or the limits of pXRF to detect sodium even under vacuum conditions). Na_2O also does not exhibit a bimodal distribution, although the peak is non-symmetrical and there is possible evidence of a shoulder. Nevertheless, the analysis is consistent with the hypothesis that the initial glass derived from mixing concentrated cobalt in the form of a frit (with low soda, low lime and high silica) to a base glass.

In essence, the plots in Figure 18 support the premise that a base glass was mixed with cobalt glass frit (with higher silica, lower soda, lower lime and concentrated cobalt) to produce the initial blue glass used for objects, which was later diluted with a base glass in the 18th Dynasty and again in the Ramesside period. Assuming that the 18th Dynasty dilution is the result of mixing blue glass with 5%CaO (shoulder) and 78%SiO_2 (upper peak) in a ratio of 1:1 with a base glass, suggests that the base glass would have had a CaO concentration of 11% and a SiO_2 concentration of 72%. These are reasonable values for a stable base glass. In summary, based on the pXRF data from Abe et al. (2012), 18th Dynasty cobalt blue glass had an initial average composition of around 78%SiO_2, 5%CaO, 0.16%CoO, 0.11%NiO, 0.38%MnO and about 0.15%ZnO and 3.9%Al_2O_3 (i.e. the higher peaks in Figures 13 and 14; the higher peak for SiO_2 and the shoulder for CaO in Figure 18) prior to any dilution.

The mixing of a cobalt-concentrated frit with a base glass opens up the possibility that although the base glass may have been made locally, the concentrated frit colourant may have derived from elsewhere. On first inspection this would appear to contradict the work of Shortland et al. (2007) and their use of Ti, Cr, Zr and La to discriminate between Egyptian and Mesopotamian sources of glass. However, as shown above in Figure 15, higher levels of Ti are associated with clays derived from Nile river silt. Similarly, elevated levels of La and Zr found in Egyptian glasses have been attributed to this

Nile source, while elevated Cr levels found in Mesopotamian glasses have been attributed to alluvial soils derived from the weathering of ultramafic rocks in Turkey at the head waters of the Tigris and Euphrates rivers (Shortland, 2007; Walton et al. 2009). Since these elements potentially enter the glass by the partial melting of the clay crucible (i.e. contaminating the glass in a similar way to Al_2O_3), they will yield a signature of the location where the colourant was added to the base glass, and not necessarily the location where the colourant derived. The same rationale can be applied to the Sr and Nd isotope analyses conducted on glasses from Egypt and the Near East by Degryse et al. (2010), which can identify the base glass precursors and not necessarily the additives. In other words, these studies do not rule out a Bronze Age trade network of a vitreous cobalt frit colourant, in a similar fashion to how smalt was traded to China from Europe in the Qing Dynasty period for porcelain (Giannini et al., 2017).

4.4 Frit composition

Although the re-analyses in Sections 4.1 and 4.2 have shown that differences in alumina concentrations between the 18th and 20th Dynasties are potentially related to glass recycling, this does not explain why the alumina levels are generally higher in cobalt glass (i.e. alumina >1.2%) compared to other colours, i.e. all colours were presumably re-melted and reworked and were therefore subject to similar amounts of contamination from crucibles and furnaces. This is now investigated through reanalysing compositional data from the cobalt blue frit recovered from Amarna O45.1.

The compositions of the cobalt frit found at Amarna are difficult to compare directly with the pXRF or LA-ICPMS data in Figures 6, 7, 11 and 12, because the frit samples were measured using a different technique (WDS). The compositional ranges from WDS were: CoO: 0.14-0.28% (average=0.2%); MnO: 0.1-0.4% (average=0.2%); Al_2O_3: 2.3-4.7% (average=3.1%) (Note: NiO and ZnO were not measured). Nonetheless, the highest cobalt level found in the 18th Dynasty cobalt glasses described was 0.18% (average 0.1%CoO), which is lower than the frit found at Amarna site 045.1 and is consistent with the addition of a concentrated colourant in the form of a glass frit to a base glass. In effect, the cobalt concentrations in the frit measured by WDS frit support that it can be considered as a vitreous concentrated cobalt additive.

Table 2 shows the full composition of the frit (n=11) which was recorded by Tite et al. (1998), as well as averages presented in later publications (e.g. Tite and Shortland, 2003). Despite differences in the average results (discussed below), the compositional data clearly shows that the frit found at Amarna has much lower soda and lime concentrations and as well as higher silica than the glass found at the same site. Moreover, the coefficient of variation is high for some of the compositional components measured, in contrast to the quite standardised recipes for making glass. However, the coefficient of variation for silica is quite low (CV: 3.8%).

Table 2: Composition of the cobalt blue frit from Amarna O45.1. The upper table shows the mean, standard deviation and coefficient of variation from the 11 measurements recorded in Tite et al. (1998). The lower table shows the average composition recorded in Tite and Shortland (2003) alongside the composition of glass from the same site. The differences between the mean values of the frit in the two tables is because some data was omitted in Tite and Shortland (2003) because of possible contamination from the lime lining found on the inside of the cylindrical vessels.

n=11	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO	SnO_2	PbO
mean (%)	8.57	1.44	3.14	83.21	0.04	0.38	2.10	0.12	0.24	0.46	0.2	0.02	0.02	0.02
st.dev.	2.13	0.52	0.76	3.15	0.05	0.21	1.66	0.10	0.09	0.22	0.05	0.01	0.06	0.04
CV (%)	24.8	36.5	24.1	3.8	138.7	56.0	79.1	83.1	39.1	46.5	24.4	67.4	331.7	222.5

mean (%)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO
Frit	8.7	1.4	3.3	84.4	0.4	0.7	0.14	0.28	0.5	0.21	0.00
Glass (n=24)	19.6	4.3	2.5	63.8	1.0	7.6	0.08	0.20	0.6	0.13	0.18

As a glass, frit has a very unusual composition. It neither contains significant amounts of magnesia nor potash which is generally the signature of the use of a soda-rich plant ash as a flux. Furthermore, the burning of halophytic plants (those adapted to growing in a saline environment) from the desert, or from a brackish water environment, generally produces ashes which are typically rich in both soda and lime (Brill 1970: 105-128; Verità 1985), neither of which are found in similar levels in the frit. To produce glass with low-magnesia and low-potash glass, a relatively pure inorganic or mineral soda source would be required, such as an evaporite, like natron from the Wadi Natrun in Egypt. However, such minerals are usually associated with high soda levels. It is therefore not possible to classify the frit as a variant of a known type of glass. Furthermore, with its low calcium level, it would not have been used directly as a glass as it would have probably been soluble in water (Freestone et al., 2008: 29-46).

In effect, the low amounts of potash in the frit tend to suggest that plant ash was not used to make the frit. This is supported by the compositional variation matrix (Table 3) and the dendrogram derived from it (Figure 20), which show that there is lower co-dependence (higher value) between K_2O and Na_2O (0.530) than between most components. Plotting the SiO_2-K_2O-Na_2O sub-composition on a ternary diagram (Figure 19) shows a narrow variance ellipse, with the data appearing to follow a one-dimensional pattern joining the vertices Na_2O and K_2O. Such a narrow ellipse suggests that the ratios involving SiO_2 have an almost constant value, and that most compositional variance is due to variation in Na_2O/K_2O. A similar ternary plot with CoO, which as a colourant is probably independent of the glass formers, shows a similar pattern. This suggests that the system was not fluxed using plant ash (or that a number of different types of plant ash were used at this site for these cobalt glasses). In other words, the system was most probably fluxed with a soda-based mineral, even though the soda levels are quite low. This suggests that Tite and Shortland's (2003) modified position is effectively supported– Egyptian cobalt blue glass contained both natron (or some type of soda mineral) and plant ash, the former from the frit and the latter from the base glass to which the frit was subsequently mixed.

Table 3: Variation matrix for the cobalt blue frit from Amarna O45.1. Note that SnO2, P2O5 and PbO are not included as they were at the lower limits of detection for WDS, with only a few samples having non-zero values. Note the strong co-dependence (low values - underlined) between CoO and MgO, Al_2O_3 and SiO_2, and between SiO_2 and Na_2O and Al_2O_3. The co-dependence between Na_2O and K_2O is not strong (0.530) suggesting that these two components are not associated. CaO has low co-dependence with all other components, presumably due to contamination from the lime coatings on the cylindrical vessels where the frit was found. Data from Tite et al., 1998.

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO	CoO	CuO
Na_2O	**0.000**	0.167	0.193	**0.077**	0.530	0.475	0.339	0.355	0.265	0.140	0.276
MgO	0.167	**0.000**	0.273	0.176	0.401	0.789	0.277	0.262	0.201	**0.091**	0.393
Al_2O_3	0.193	0.273	**0.000**	**0.043**	0.271	1.126	0.319	0.193	0.578	**0.078**	0.644
SiO_2	**0.077**	0.176	**0.043**	**0.000**	0.341	0.847	0.239	0.194	0.410	**0.059**	0.401
K_2O	0.530	0.401	0.271	0.341	**0.000**	1.631	0.409	0.561	0.842	0.271	0.856
CaO	0.475	0.789	1.126	0.847	1.631	**0.000**	0.879	1.204	0.438	0.919	0.636
TiO_2	0.339	0.277	0.319	0.239	0.409	0.879	**0.000**	0.314	0.422	0.240	0.534
MnO	0.355	0.262	0.193	0.194	0.561	1.204	0.314	**0.000**	0.450	0.126	0.600
FeO	0.265	0.201	0.578	0.410	0.842	0.438	0.422	0.450	**0.000**	0.279	0.314
CoO	0.140	**0.091**	**0.078**	**0.059**	0.271	0.919	0.240	0.126	0.279	**0.000**	0.420
CuO	0.276	0.393	0.644	0.401	0.856	0.636	0.534	0.600	0.314	0.420	**0.000**

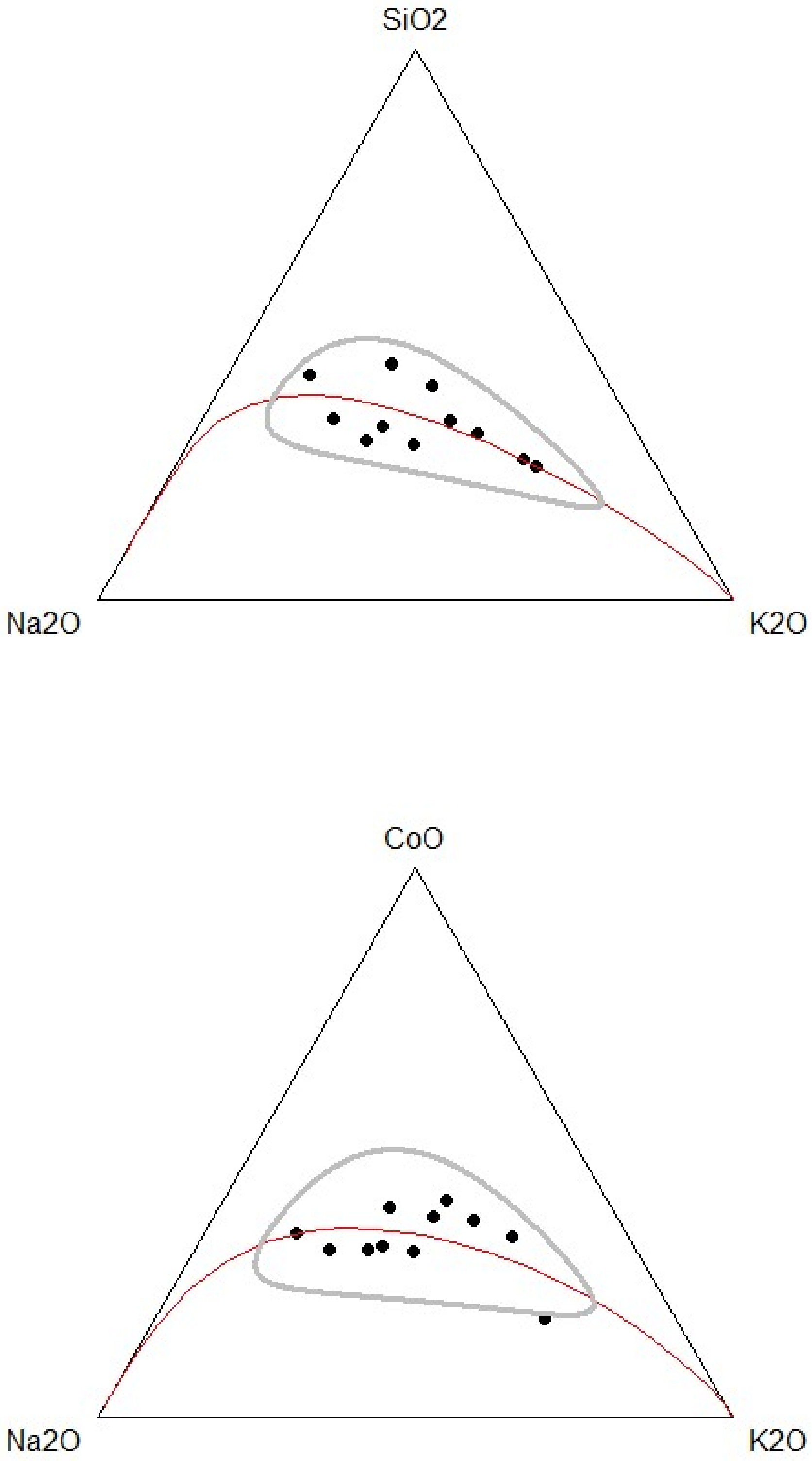


Figure 19 Ternary diagrams for the subcompositions SiO_2-Na_2O-K_2O and CoO-Na_2O-K_2O exhibiting one-dimensional patterns joining the vertices Na_2O and K_2O. The red lines display the direction of the principal component of the subcomposition. The ellipse shows the variance structures through 95% probability regions. Data from Tite et al., 1998.

The dendrogram for the frit (Figure 20) is quite different to those of the glasses in Figures 8 and 9, with most components falling in one significant cluster. Moreover, CoO is much better associated with the glass formers (SiO_2, Al_2O_3, MgO) than in the glasses. In fact, there is higher co-dependence between CoO and these oxides than with MnO (in contrast to its behaviour in glass). It should be noted that there is little co-dependence between lime and the other components in the frit system as evidenced by CaO failing to cluster with any other component. The probable reason is contamination from the lime lining of the cylindrical vessels recovered at Amarna O45.1 associated with the frit. The slight differences in average concentrations (apart from lime) presented by Tite and Shortland (2003) compared to the earlier paper (Tite et al., 1998) are a consequence of data being excluded, i.e. the authors have removed analyses where they believed the glass were contaminated by this coating. No data were removed in the current re-analysis. In essence, contamination has occurred making the variation in CaO an unreliable indicator in these samples. Nevertheless, its absolute level in the system is still remarkably low (average 0.7%CaO), which suggests that the silica source was not the same as that used to manufacture the base glass.

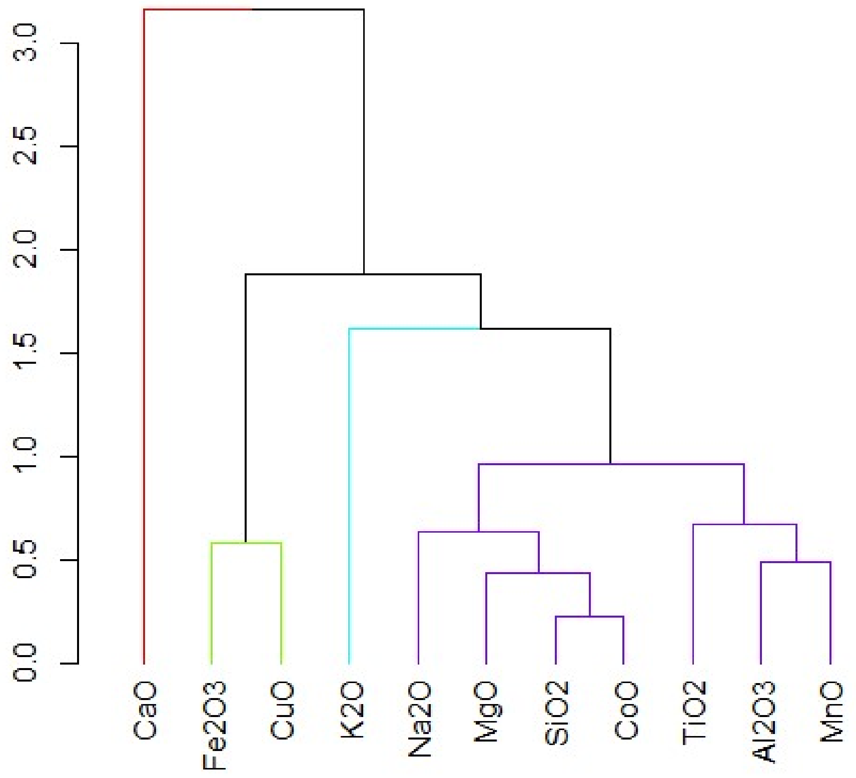


Figure 20 Dendrogram derived from the variation matrix of 11 samples of frit from Amarna O45.1. (data from Tite et al., 1998). Note the close association between CoO, SiO_2, MgO, Na_2O, TiO_2, Al_2O_3 and MnO. CaO is not well associated with any of the other components, presumably because of contamination from the lime coating on the cylindrical vessels where the frit was found.

The use of a soda-based flux for the frit (as evidenced by the variation between K_2O and Na_2O in Figure 19) may go some way to explaining why Egyptian cobalt glass has lower amounts of K_2O compared to glasses of other colours. K_2O concentrations for Egyptian cobalt glass generally lie below 2%K_2O (Lilyquist and Brill, 1993). Non-cobalt coloured glasses generally have K_2O levels which fall between 2-3%K_2O, which suggests that adding frit colourant to a base glass made using plant ash as a flux, would reduce the K_2O levels in the cobalt blue glass produced. A simple rule of mixture calculation for mixing frit (K_2O~0.4%) with a plant ash fluxed base glass (K_2O~2.5%) in a 1:1 proportion shows that the glass produced would have around 1.5%K_2O, as found in most Egyptian cobalt blue glass (Note a 1:1 proportion would produce a blue-coloured glass with about 0.1%CoO, which is about the average of cobalt blue glass from 18th Dynasty Egypt).

Figure 21 shows K_2O vs CoO for 18th Dynasty glass from Amarna and Malkata and frit from Amarna, measured using WDS and electron microprobe. The scatter in the data is somewhat expected as the consequence of the inevitable K_2O contamination from burning wood during recycling (Paynter, 2009). However, it can be seen, perhaps optimistically, that higher levels of cobalt appear to correspond to lower levels of potash, potentially converging on the levels of K_2O found in the frit. Such an interaction would support that frit made with a soda-based mineral (with low K_2O) was mixed with a base glass thereby lowering the K_2O level with respect to the base glass to make the initial glass. Subsequent dilution with a base glass, would decrease the CoO concentration and increase the K_2O levels. This is further supported by the two dendrograms for the 18th and 19th-20th Dynasty glasses in Figures 8 and 9: with more dilution, K_2O becomes more associated with Na_2O and clusters with MgO, as would be expected if a plant ash flux was used to make the base glass. Although the potential linear relation of the frit on the K_2O vs CoO plot (Figure 21) may be spurious (i.e. their co-dependence in the variation matrix is not high (0.271), predominantly a consequence of one possible outlier) it may indicate that these components have a common origin, which suggests that they derive from the same source.

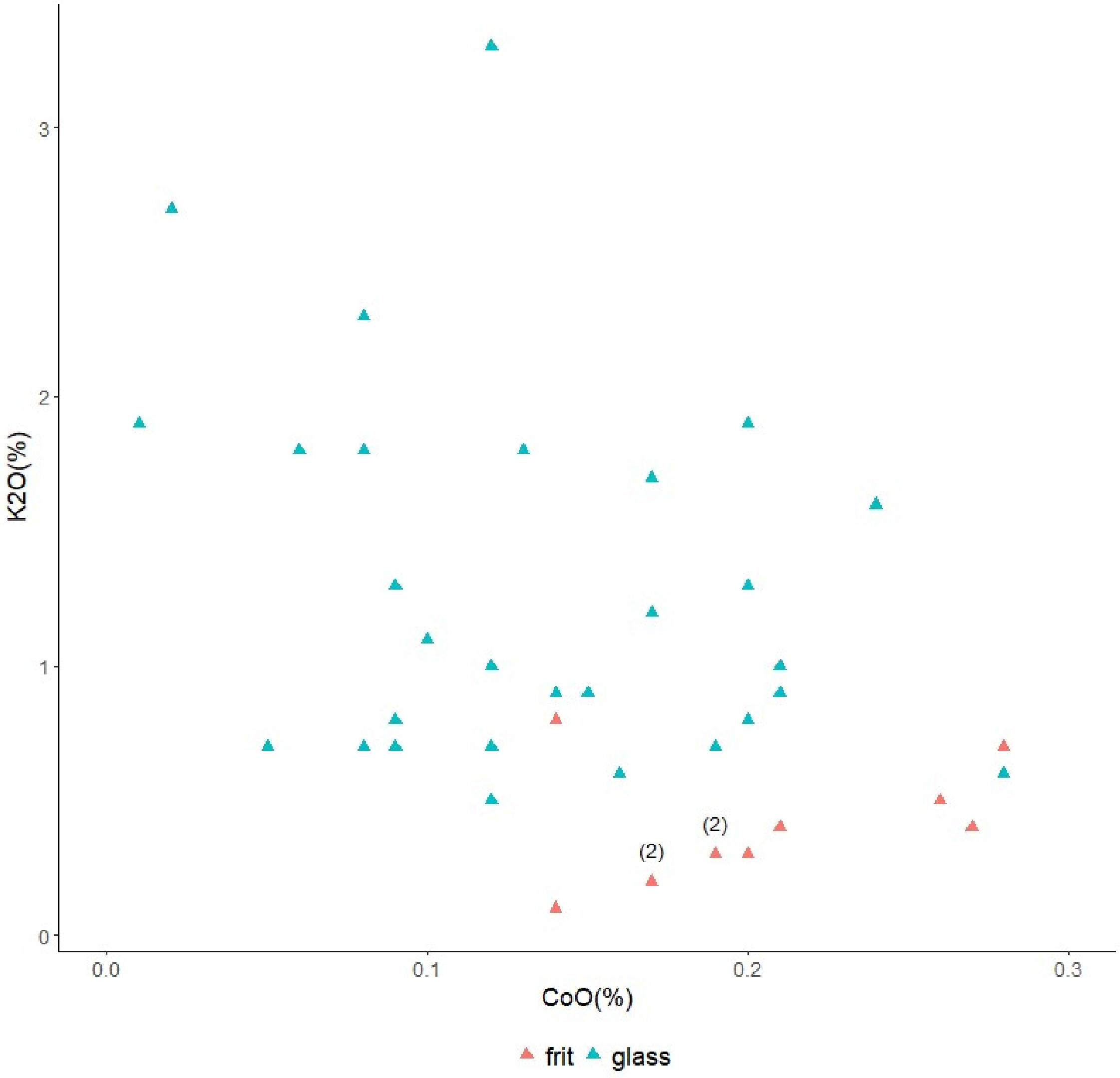


Figure 21 Bivariate plot of K_2O vs CoO in weight % for the frit found at Amarna O45.1 (Tite et al., 1998) using WDS, and for glass from Amarna (Nicholson and Henderson, 2000) using a probe, and Malkata (Shortland et al., 2007) and Amarna (Tite et al, 1998; Shortland and Eremin, 2006) using WDS. Higher levels of CoO appear commensurate with lower levels of K_2O, potentially converging on the composition of the frit. The scatter in the data is probably a consequence of contamination from burning wood during recycling, increasing the variation in the K_2O data. Note the possible positive linear relationship between K_2O and CoO for the frit measurements, suggesting that they entered the system together (two measurements overlap where indicated).

The higher levels and greater variation of K_2O for the Nippur cobalt blue axes (average=3.6%K_2O; range: 1.68-5.55%K_2O with one outlier at 8.59) suggests a different type of plant ash for the base glass, more contamination from processing, or possibly more recycling. However, these differences do not necessarily suggest a different colourant source. In other words, the cobalt-coloured soda-based frit may have been something that the glass makers of both Mesopotamia and Egypt needed to acquire in order to colour blue their glasses derived from their own local base glass precursors.

The variation matrix for the Amarna frit also shows that there is good co-dependence between CoO and MgO (0.091), Al_2O_3 (0.078) and SiO_2 (0.059). This could suggest that cobalt was added to a silica source containing high alumina and low magnesia in known proportions. However, the large variation in the cobalt levels in the frit suggests that this unlikely, i.e. CoO: 0.14-0.28% (average=0.2%). Furthermore, the low amounts of lime tend to discount the Nile River as the silica source for the frit, while the high alumina levels tend to discount its introduction through a silica source of quartz pebbles. Another possibility is that there was a common source for each of these pairs, a source with Co, Si, Al and Mg in the proportions required to produce a high silica, high alumina, low magnesia cobaltiferous frit. This could suggest that the silica source was a siliceous rock containing cobalt compounds and high alumina. Furthermore, although the co-dependence between CoO and MnO is not as high as that for SiO_2, Al_2O_3 and MgO, MnO still forms a significant group with these components, which, as with the glasses, suggests they entered the system together. This provides further support for an alternative to the alum deposits for the source of cobalt, in that it suggests that the cobalt was embedded in a siliceous rock - a rock which contained sufficient levels of alumina to elevate its concentration in the glass system. In other words, cobalt-blue glass had elevated alumina compared to other colours because it derived from a system where alumina was a natural component of a siliceous rock, such as an igneous rock, as mentioned previously (Figures 11 and 12).

This association between cobalt and the components found in igneous rocks is also supported by examining the absolute values of the concentrations in the frit and igneous rocks (i.e. Tables 1 and 2). The ratio of the average concentration of Al_2O_3 in the frit to its average composition in igneous rock is 3.3/15.52 (i.e. 0.21). Similar ratios are found with K_2O, TiO_2 and CaO, i.e. 0.14, 0.16 and 0.12, respectively. The similarity in these ratios suggests that these components, found in the cobalt blue frit from Amarna, not only entered the system together but were introduced directly by contamination from igneous material. In other words, the igneous rock was diluted by a factor of between 5 and 8 during the frit forming process. Conversely, the ratios for Na_2O and SiO_2 are 2.65 and 1.41, respectively, suggesting that these glass formers were added to the cobaltiferous igneous rock, adding to any silica and soda already present, thereby diluting the concentrations of Al_2O_3, K_2O, TiO_2 and CaO to the levels found in the frit. The presence of unreacted silica in the frit (average=29% unreacted quartz, from visual inspection - Tite and Shortland, 2003) supports that silica was added. Assuming that the host rock was igneous, and that its dilution calculated from the Al_2O_3, K_2O, TiO_2 and CaO can be used as a scaling factor for elements associated with the mineralisation within the rock, we derive that the concentrations of cobalt, manganese, nickel and zinc were 5-8 times higher in the rock than in the frit. This would suggest that the host rock contained 1-1.6% CoO and 4-6.4% MnO. Although ZnO and NiO were not measured in the frit from Amarna, assuming that a base glass was mixed with frit in a 1:1 ratio suggests that the concentrations of these components in undiluted glass (i.e. the higher peaks of Figures 14) can be used to estimate the concentrations of these components within the host rock, i.e. 1.1-1.75% NiO and 1.5-2.4% ZnO. Incidentally, the CoO calculated by this method would be 1.6-2.56%, which, considering that this is based on a distribution, is close to that calculated directly from the frit (1-1.6% CoO). In other words, the signature of the host rock from which the cobalt derived was potentially an igneous rock with CoO, NiO and ZnO of concentrations around 1% to 2.6%, and MnO between 4% and 6.5%. Despite the higher levels of MnO with respect to CoO, this is *not* the signature of asbolane (which has a ratio of MnO:CoO of about 14.2) but is more likely to be another ore system with NiO, MnO, CoO and ZnO. This is discussed in Section 4.5.

The remarkably good co-dependence between Na_2O and SiO_2 in the frit (0.077) also supports that silica and soda were added to cobaltiferous rock in that the association suggests SiO_2 and the Na_2O entered the system together, either from a common source or in measured proportions.

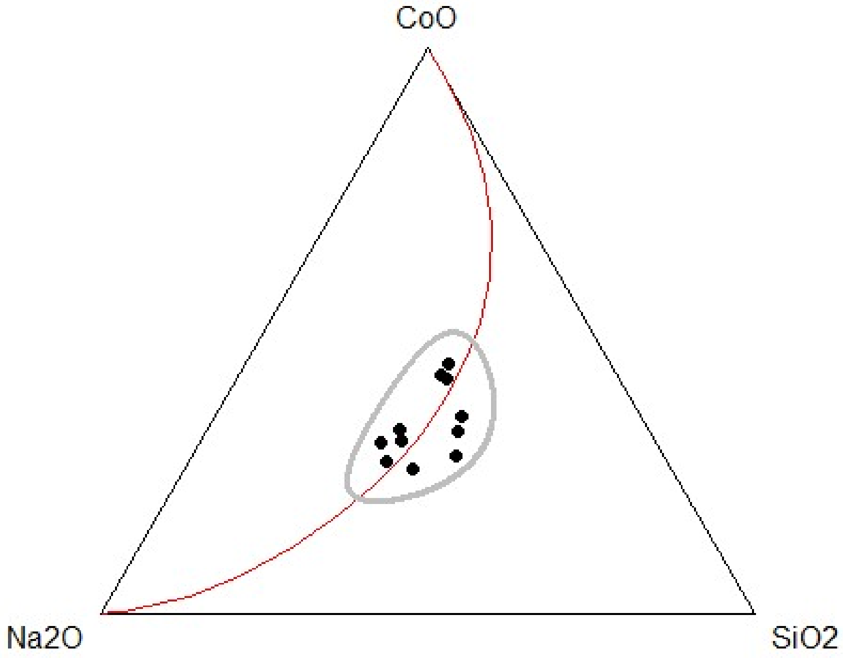


Figure 22 Ternary diagram for the subcomposition CoO-Na_2O-SiO_2. The red line displays the direction of the principal component of the subcomposition. The ellipse shows the variance structure through 95% probability regions. The tight clustering indicates the low compositional variability between these components.

The ternary diagram (Figure 22) does not demonstrate any obvious one-dimensional pattern for the CoO-Na_2O-SiO_2 sub-composition, suggesting that the variation is not dominated any of the component pairs. This is supported by the low coefficient of variation of SiO_2 (CV=3.8%) in the frit samples which indicates that a controlled (and probably fixed) amount of silica was used, with the most probable scenario being that it was placed in a vessel of fixed volume, i.e. a crucible. The coefficient of variation of Na_2O is also not high (24.8%). The relationship between Na_2O and SiO_2 can be seen on the bivariate plot (Figure 23), suggesting that higher amounts of silica are associated with lower amounts of Na_2O. This would seem contrary to what would be required, in that a higher silica content would suggest that more flux should be added. However, this interaction is exactly what would be expected if a vessel of fixed volume was used, i.e. in this case, the concept of compositions adding up to 100% may inform on the proportions of the silica and soda added to the cobaltiferous rock in a crucible.

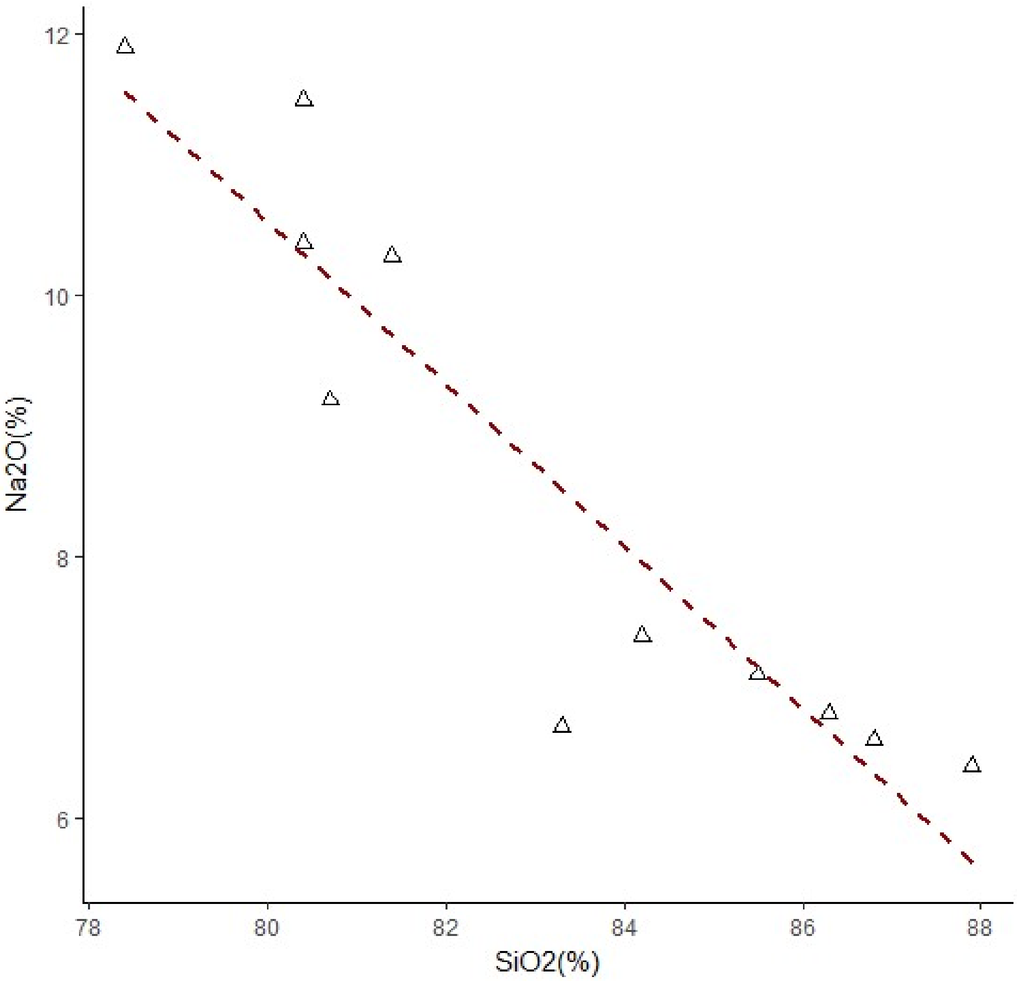


Figure 23 Bivariate plot potentially indicating that silica and soda were added in proportions relative the total volume of the system to form the frit. Data from Tite et al., 1998.

Furthermore, these added components must have been fairly pure, as there is low co-dependence between Fe_2O_3 and SiO_2 (0.410), the opposite to what would be expected if, say, sand had been added, i.e. iron is often present in the silica source, and would therefore be associated with silica. In other words, silica, probably sourced from quartz (possibly pebbles, but more likely quartz associated with the rock), and soda probably from an evaporite or a soda-based mineral, was added to a cobaltiferous rock which already contained Al_2O_3, K_2O, TiO_2, and CaO. Fe_2O_3 generally clusters with silica in the glasses (Figure 8 and 9). This is consistent with mixing of frit with a base glass, when it considered that the silica source used for the base glass was potentially associated with iron compounds, which would result in a closer association between iron and silica *after* the frit had been mixed with the base glass components.

CuO is also not particularly well associated with any component in the frit but it clusters with Fe_2O_3. Low co-dependence of CuO is also found in the glasses (Figures 8 and 9), which could be due to the deliberate addition of copper or bronze as a colourant (Mass et al., 2002). However, this is less likely for the frit, primarily because the levels of CuO in the frit (average: 0.02%CuO; range: 0-0.05%Cu) are much lower than would be expected for an additive, bearing in mind that 1-2%CuO is required to colour glass. In other words, copper probably entered the system as an impurity with the cobalt.

Despite the low concentration of CuO, which suggests that it is a natural component of the system, the low co-dependences and the clustering of CuO and Fe_2O_3 in the frit system would suggest that neither appear to be part of the mineralisation of the cobalt source. This could suggest their presence in the frit is due to contamination, such as from the fritting pans or from post-deposition. However, it is also possible that both were components of the cobalt source but their associations with the other components were weakened during the *formation* of the cobalt-rich colourant.

This leads to the inevitable question as to why anyone would deliberately mix a siliceous rock with additional silica and a soda flux and heat it up to about 1000^{o}C to make a glassy material unless they were trying to remove another component from the system. It is therefore proposed that cobalt frit colourant, such as that found at Amarna O.45, was not manufactured deliberately in order to produce a glass frit with low soda, low lime and high silica to which cobalt was added, but that this frit was a natural by-product of a metallurgical smelting system in which a soda-based mineral acted as a flux to melt cobaltiferous rock in order to remove a metal. By this rationale, the blue glass produced from melting the siliceous rock was, in essence, the slag of the system.

This may appear to be a nested argument in that the it rests on the three conclusions previously outlined:

a) A large proportion of 18th and 19th Dynasty glass was recycled.

b) Cobalt blue colourant derived from siliceous rocks and not from the alum deposits of Egypt's Western Desert.

c) This colourant was introduced into base glasses in a vitreous form.

Nevertheless, considering that the cobalt blue frit was a slag rather than a deliberately made glass, not only goes someway to explaining the variation in the concentrations and close associations of most components but also its unusual composition. This scenario would also provide a reason for the low co-dependences of CuO with the other components in the frit system and why they cluster - unlike refractory oxides, CuO would potentially partition during the extraction process, thereby reducing its co-dependences with the other components in the system. This is examined in the next section. Furthermore, if the colourant which arrived in Egypt was already a glassy slag (perhaps in the form of irregular shaped rocks – see Figure 1), then the purpose of melting this raw material in fritting pans could have been to remove contaminants and debris. In other words, the cobalt blue slag needed to be purified before it was subsequently added to a base glass.

Relating glass to metal production is not a new concept (e.g. Peltenburg, 1987: 5-29; Mass et al., 2002), with Dayton (1981; 1983) being the first person to claim that Egyptian and Mycenaean cobalt-blue glass derived from a silver ore, i.e. the silver-bearing cobalt ores of Erzgebirge on the Czech-Germany border. Although these studies had their detractors, it is proposed here that regardless of the archaeological veracity of the silver-cobalt ore source identified by Dayton (1981; 1983), re-examination of cobalt-blue frit is a potential window to view whether cobalt-blue glass and frit found at Amarna are related to the extraction of metal.

4.5 The origin of the frit

The compositional signature of the cobalt blue frit found at Amarna is probably significantly more indicative of cobalt's provenance than the composition of glass proper, which has not only been diluted but may have been contaminated during recycling. The compositional analysis of the cobalt blue frit shows that CoO is well associated with most of the components in the frit which, apart from MnO, is generally not observed in 18th Dynasty glass (see dendrograms Figure 8 and 9). This suggests that CoO derived from a siliceous rock which included Al, Ti, Mg, Co and Mn and possibly Fe and Cu. It is also probable that Ni and Zn were present, but at levels too low to be measured by the WDS technique, as observed generally in cobalt blue glass (e.g. Figure 6). Even the low concentrations of potash appear related to cobalt, as evidenced by the possible linear interaction between K_2O and CoO in Figure 21, suggesting they derive from a common source. In essence, it is these components which can be used to provenance cobalt. Furthermore, even the trace levels of P_2O_5, SnO_2 and PbO found in some of the frit samples (Table 2) may be diagnostic regarding the source of the cobalt, despite being at the limits of detection for WDS. Moreover, the presence of sulphur found in the cobalt blue Malkata glasses (n=12) at an average level of 0.35%SO_3 (range: 0.24-0.56%SO_3) using WDS, suggests that some of the components may have been initially in the form of sulphides or sulphates (Shortland and Eremin, 2006). Arsenic has been detected in Egyptian cobalt blue glasses from Malkata (n=12) which, despite the low concentrations and high variability, are higher than the concentrations in colourless glass (n=7) found at the same site (colourless=1.16ppm, s=0.97; cobalt blue=6.43ppm, s= 4.28) (Shortland et al., 2007). This could indicate that some of the components of the cobalt system were arsenides prior to any high temperature processing. These components and their associations are suggestive of a five-element mineralisation in which Ni, Co and As have a high degree of correlation with each other (Kissin, 1992). For the case of the Egyptian glasses, NiO and CoO are definitely well associated (Figures 2 and 6). A linear relationship is also found between these components in Mesopotamian glass from Nippur using LA-ICPMS data (Figure 24, data from Walton et al., 2012).

Any association with arsenic, however, is likely to be diminished during processing as it is volatile, especially if the ores were roasted (Yin et al., 2014; Wilson and Mikhail, 1989). Furthermore, arsenic losses from melt systems have been shown to increase on further re-melting, with fluctuations in temperature resulting in significant arsenic losses (Mödlinger et al., 2017). This could indicate that heating and cooling during processing (as would be expected in the working of glass into objects) as well as recycling, would result in large but unpredictable arsenic losses. For example, European cobalt-blue beads (17th century AD) were found to have arsenic levels of between 400 and 7000ppm, with concentrations potentially depending on the shape of bead produced (Hancock et al., 2000). These beads, which were provenanced to the cobalt-arsenide minerals found in the Hartz mountains of eastern Germany (i.e. high arsenic levels in the ores), not only demonstrate that low arsenic concentrations are found in cobalt-blue glasses but may also suggest that large variations in arsenic levels are related to times in the furnace (and the number of times the glass is heated and cooled) to form different types of bead, i.e. some shapes are presumably worked more than others. Section 5 investigates how arsenic levels vary on re-heating an arsenic-rich cobalt-blue glass. In essence, an absence of arsenic can still indicate a five-element ore provenance for cobalt-blue glass, a mineralisation which is also often associated with manganese, zinc, lead, copper and sulphur in a variety of host lithological environments (Kissin, 1992; Bagheri et al., 2006; Tarkian et al., 1983; Mazaheri Kuhanestani et al., 2014).

Five-element deposits are found in various locations around the world such as Cobalt in Ontario, Canada, the districts of Freiberg, Jachymov and Erzgebirge in Germany (Kissin, 1992) and the Anarak district in central Iran (Tarkian et al., 1983; Bagheri, et al., 2006). Records regarding the exploitation of these deposits dates back to the Middle Ages for Erzgebirge (Ore Mountains). The mines in the Cobalt district of Canada exploited silver and uranium in the 20th century (Kissin, 1992). No records are known of when the deposits in the Anarak district of central Iran began to be exploited but the Talmessi and Meskani mines have been dormant since 1960 (Bagheri et al., 2006). This type of mineral deposit contains a distinctive suite of minerals (Co, Ni, As, Ag and +/- Bi, U). However, such mineral deposits often show some variation and the entire suite is not always present. Moreover, in the Anarak district, copper arsenides also appear to be associated with this mineralisation (Bagheri et al., 2006; Mazaheri Kuhanestani et al., 2014). These deposits in central Iran are particularly relevant to the discussion here. Not only are they more likely to be associated with the glass production in Mesopotamia and Egypt – the Kashan deposit was suggested by Garner (1956) as a possible source for cobalt glass found at Eridu, Iraq c. 2300 BC - but Pb and Zn in these deposits are believed to have derived from schist while geochemical and petrography indicate that Ni, Co, Cu and As derived from ultramafic rocks (Mazaheri Kuhanestani, et al., 2014). This suggests that a greater co-dependence would be expected between Ni and Co (as parts of the mineralisation), than between Zn and Co. These associations are evident in Figures 8 and 9. Furthermore, the abundances of the major elements for rocks and veins from the vicinity of the Talmessi and Meskani mines in the Anarak district (Bagheri et al., 2006) have levels of SiO_2 (42.65-61.55%SiO_2), which are lower than the frit (84.4%SiO_2), and insufficient Na_2O (0.96-4.26%Na_2O) for the system to be self-fluxing. In other words, SiO_2 and Na_2O was potentially added to extract any metal from this system, as discussed in Section 4.4.

To examine this further, the linear relationship in the Egyptian 18th Dynasty glasses between NiO vs CoO (Figure 2 and 6) has a gradient of about 0.6 (0.56 for the elements). Figure 24 shows the interaction using the LA-ICPMS data for cobalt blue glass from Amarna and Malkata (from Varberg et al., 2015, 2016; Shortland et al., 2007) and Nippur (Walton et al., 2012).

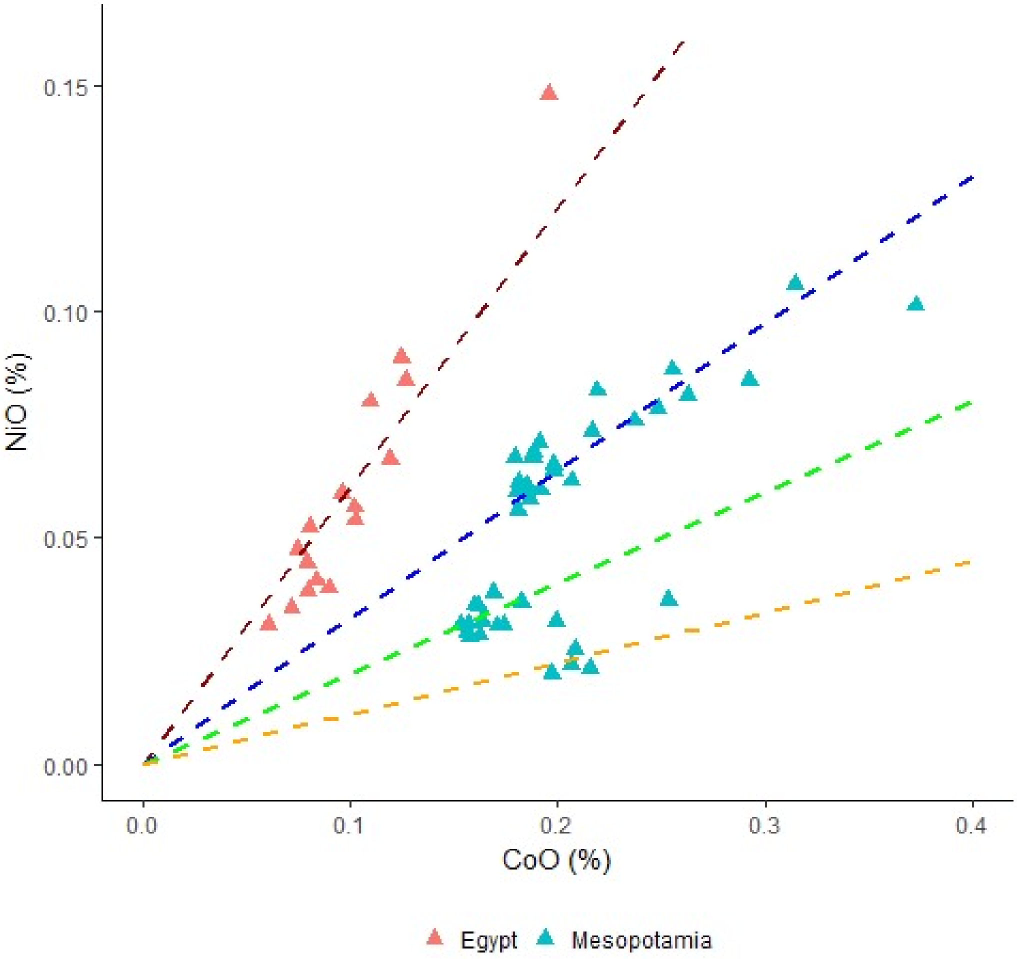


Figure 24 Bivariate plot of NiO vs CoO for glass from 18th Dynasty Egypt and Nippur in Mesopotamia using LA-ICPMS. The linear line for the Nippur axes (blue dashed line) shows that NiO and CoO potentially derived from skutterudite (gradient ~0.3). The gradient of the Egyptian glass data (dark red dashed line) is about twice high (gradient ~0.6), which could suggest that the five-element ore mineralisation is dominated more by a nickel mineral, such as nickeline. Although it is difficult to place the rest of the Nippur data on lines, they are still consistent with a five-element system which has variable levels of nickel and cobalt in the mineralisation. LA-ICPMS data for cobalt blue glass from Amarna and Malkata (from Varberg et al., 2015, 2016; Shortland et al., 2007) and Nippur (Walton et al., 2012).

In Figure 24, the gradient for the Amarna/Malkata LA-ICPMS glass is similar to the 18th Dynasty pXRF data in Figure 6, i.e. about 0.6, and passes through the origin (dark red dashed line). The glass from Nippur is more difficult to interpret. There appears to be an interaction with a gradient of about 0.3 (blue dashed line) which can pass through the origin. The Mesopotamian glass and the Egyptian glass appear to converge. There also appears to be lower groups from Nippur where it is difficult to apply linear lines.

Nonetheless, these interactions are consistent (or at least not inconsistent) with a five-element ore system which has variable levels of nickel and cobalt. The ratio of Co to Ni at Meskani and Talmessi deposits in the Anarak region of Iran range from 1:0.3 to 11:35.4 (Khoei et al., 1994, in Matin, 2015), i.e. Ni/Co: 0.3-3.22, respectively. This wide range would encompass both the Egyptian and Mesopotamian cobalt blue glasses. The fraction of nickel to cobalt in skutterudite (one of the main cobaltiferous minerals in these deposits (Tarkian, et al., 1983; Mazaheri Kuhanestani et al., 2014) is 0.33, i.e. empirical formula: $Co_{0.75}Ni_{0.25}As_{2.5}$; wt%: Co=17.95%, Ni=5.96%, As=76.09%). This is similar to the gradient for the Mesopotamian glass data, suggesting strongly that the cobalt in the Nippur glass was from an almost pure deposit of skutterudite. The higher gradient for the Egyptian data is potentially a consequence of variable amounts of nickel and iron replacing cobalt in this mineral, i.e. skutterudite has a variable formula ($(Co, Ni, Fe) As_{2-3}$)). Less cobalt could suggest more nickel, and therefore a higher slope on the NiO vs CoO plot. However, the presence of another nickel-based mineral (such as nickeline) in association with the cobalt mineral could also increase the gradient for the Egyptian glass, potentially suggesting less-rich cobalt ore was exploited for export. Nevertheless, the ratio of Ni to Co found in both Mesopotamian and 18th Dynasty glass is consistent with minerals found in five-element deposits in Iran and provides an explanation for the high association and linear relationship between CoO with NiO. On the other hand, although ZnO is clearly associated with CoO in Egyptian glass, it is better associated with MnO (e.g. Figure 8). In essence, whereas Ni and Co are potentially part of the five-element ore mineralisation, Zn and Mn are found in associated minerals (which may or may not be present). FeO in glass is likely to have a variable concentration, due to the iron associated with the silica used to make the base glass and is therefore difficult to relate to the ore. Figure 25, however, shows that FeO in the frit increases with CoO. Although the linearity is questionable, it is still consistent with the frit deriving iron from skutterudite, one of the main minerals in a five-element ore system.

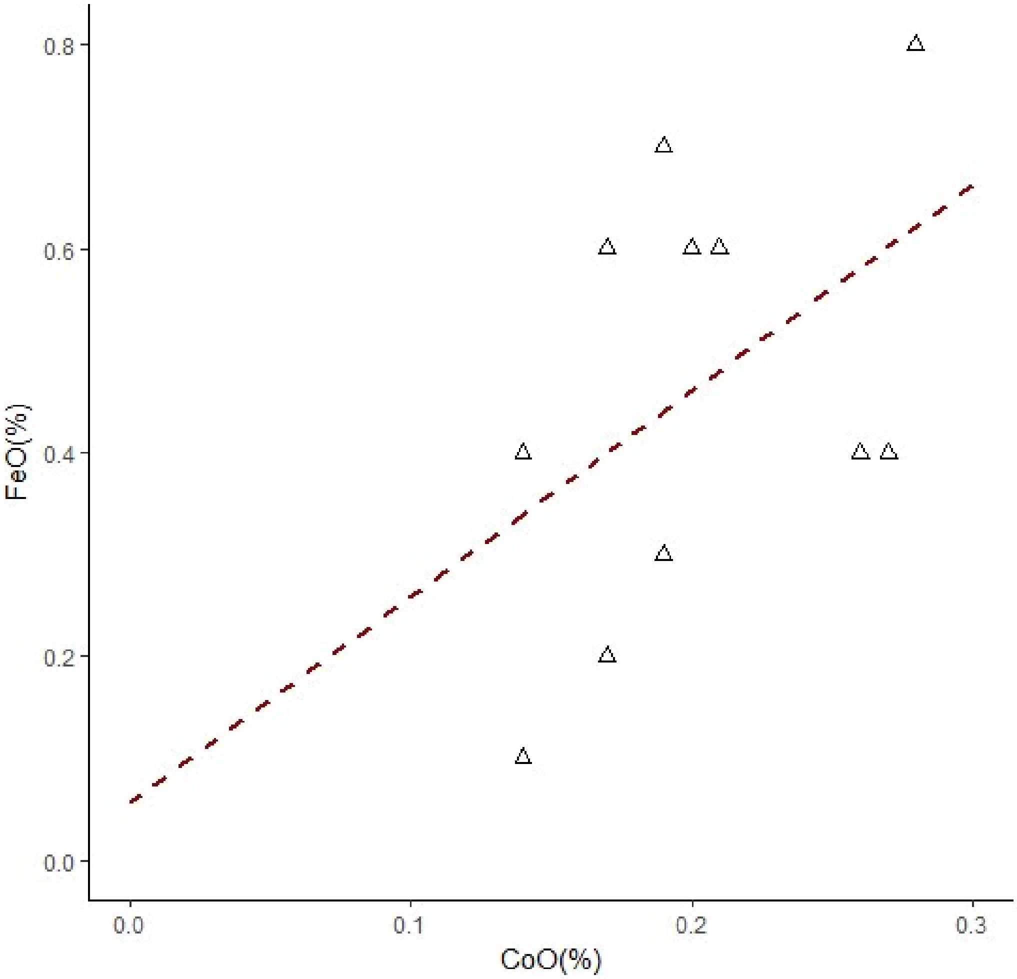


Figure 25 Bivariate plot potentially showing a possible linear relationship between FeO and CoO in the frit found at Amarna O45.1, supporting that cobalt entered the system from the mineral skutterudite ((Co, Ni, Fe) As_{2-3}) as suggested by the linear interaction between NiO and CoO in Figures 2,6 and 24. Data from Tite et al., 1998.

Differentiating the components which are integral to the five-element mineralisation (e.g. Co and Ni, Fe when the main cobalt mineral is skutterudite, and Cu in the case of the Anarak deposits) from those minerals which are associated with some deposits (e.g. Mn and Zn), such as in the post-ore stage, goes someway to explaining the differences between Egyptian and Mesopotamian glass. The Nippur axes, for example, have very little manganese or zinc and the interaction between MnO and ZnO with CoO is not linear (although the absence of linearity could be a limit of detection issue). However, the linear relationship prevails between NiO and CoO (Figure 24). Similarly, the early 1st millennium Nimrud blue glasses studied by Reade et al. (2005) also do not exhibit the relationship between Mn and Co, despite being elevated in the same suite of elements as the 2nd millennium Egyptian cobalt glasses. This could be (and has been) interpreted as different cobalt minerals being exploited (e.g. asbolane vs linnaeite). However, it could also indicate the variability and the variation in the associated minerals which are found in five-element deposits. Although from a different period, seven types of cobalt blue pigments used in Islamic ceramics and glass have been identified (Wen, 2012, 249-251). These pigments, which are considered to have an Iranian provenance, have various combinations of elements (Co, Fe, Zn, Cu, Pb, As, Ni, Sb, Mn and Bi) in variable proportions, often with some elements being absent. These variations potentially reflect the Iranian cobalt ore sources exploited (see Matin and Pollard, 2017).

Copper, although being well associated with the five-element ore mineralisation at mines in Anarak, is not well associated with cobalt in the frit or in glass. In glass, this lack of association is potentially due to contamination. In the case of the frit, although the compositional signature has yet to be influenced by dilution and its associated contamination from recycling, it has still undergone high temperature processing. As with any smelting system, the absolute amounts of each component in the frit would be dependent on how each component partitions (i.e. concentrates) between the metal being extracted and the glassy slag phase. For those elements which concentrate in the metal, associations with the elements in the glass slag would be diminished. This suggests that any component which partitions primarily with the extracted metal will have lower co-dependence in the glass with those components that partition with the glass. In other words, the low levels of copper in the frit (0-0.02%) and its low association with cobalt is because some proportion of it was extracted.

Plotting the CuO-FeO-CoO sub-composition on a ternary diagram (Figure 26) shows a broad variance ellipse. Such a broad ellipse suggests that the compositional variance is shared between each of the components in this sub-composition. In other words, although the variation is high between each component, none of these components dominates the compositional variance. This broader variance structure would be expected if the association of CuO and Fe_2O_3 with CoO was diminished due to partitioning.

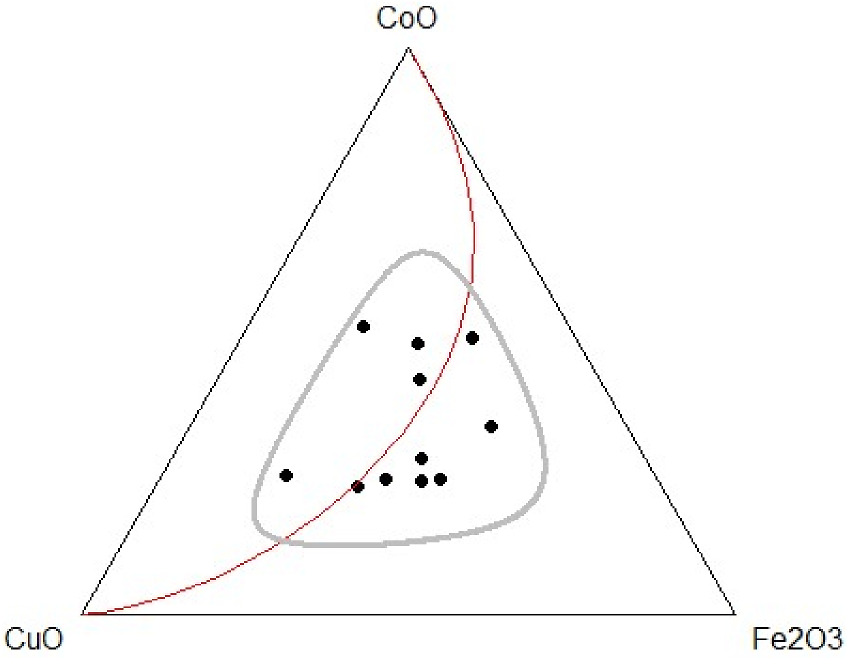


Figure 26 Ternary diagram for the sub-composition CuO-Fe_2O_3-CoO exhibiting a broad pattern suggesting that the compositional variance is shared between each of the components. The red line displays the direction of the principal component of the subcomposition. The ellipse shows the variance structure through 95% probability regions. Data from Tite et al., 1998.

This also suggests that the other two components generally associated with the five elements system (i.e. Ag and Bi) may also have partitioned with the metal during the extraction process. In fact, for these metals, which are found in their native form in the five element systems, it is quite probable that both bismuth and silver would not partition with the glass. Furthermore, any metal (or metal compound reduced to the metal) found in the glass would be in the form of entrapped prills, rather than dissolved in the glassy covalently-bonded matrix. In essence, this suggests that the extracted metal (and potentially the principal reason for processing the ore) would be absent, or present only as a rare discrete phase within the glassy slag, taking with it components that partition predominantly in the metal phase. Moreover, in terms of archaeology, considering that the cobalt frit was a by-product which was valued and traded, the metal which had been extracted may not even form part of any assemblage at the location where the frit was recovered.

There are indications that any metal removed from the system was not difficult to extract. Considering that the glass slag had value as a colourant, supports the previous suggestion that the process occurred in a crucible, in order to avoid contamination. The low levels of K_2O, MgO and P_2O_5 in the frit (Table 2) further suggest that it was produced in an environment where contamination from the products of burning wood to fire the furnace was minimised. This suggests that crucibles containing the ore minerals, the host rock and any soda-based flux additive were heated from the outside and that the main component for recovery was easily reduced, or was already in the metallic form, but embedded in the cobaltiferous siliceous rock.

As one of the main components of the five-element ore system, silver is a potential candidate for the metal which was extracted. Fahlore (a copper arsenic sulphosalt) has been found in association with significant silver and zinc contents at the Talmessi and Meskani mines in Anarak, with host rocks of dacite (an igneous volcanic rock containing plagioclase and quartz) and andesite (an intermediate between basalt and granite). Interestingly, the silver from Early Bronze Age silver objects recovered at Ur were interpreted to have originated from a fahlore, objects which suggested a silver, copper, lead and zinc mineralisation and contained trace levels (< 100-500ppm) of Co, As, Ni, Mn, Fe and Sn (Salzmann et al., 2016: 141-145; also see Pernicka and Bachmann (1983) for a similar interpretation at Laurion). Furthermore, of the element suite, only silver could be extracted without a strong reducing atmosphere. Cobalt, zinc, manganese, lead and nickel would require smelting with charcoal in intimate contact with the charge and, apart from lead, were not metals that were smelted deliberately in antiquity. Moreover, if copper was predominantly in the form of a sulphide, as is possible since SO_3 was measured in the Malkata samples, it would be very difficult to reduce to a metal using heat alone. It was also a metal that was being readily extracted from other sources.

Silver, when in association with Ni-Co-As ores, is in the form of native silver and would therefore, not need to be reduced. Even cerargyrite (i.e. silver chloride- AgCl), would be readily reduced to silver metal. Smith (1967) argued that the earliest silver objects were made of native metal or of cerargyrite, both of which form silver on melting under a cover of charcoal. Furthermore, despite the trace levels found in the LA-ICPMS studies, silver is not always found in low concentrations in cobalt blue glass. Figure 27 shows an energy dispersive X-ray spectrum of cobalt blue glass found at Amarna (Nicholson and Henderson, 2000). The fact that silver was detected with this analytical technique suggests that silver was present at levels greater than 0.1%, and probably higher. Moreover, it wasn’t detected in the white and yellow glasses investigated. However, although silver was detected in cobalt blue glass does not mean that it is was distributed homogenously throughout the glass matrix. As mentioned above, a metallic phase will not be soluble in glass but is more likely to be in the form of entrapped prills.

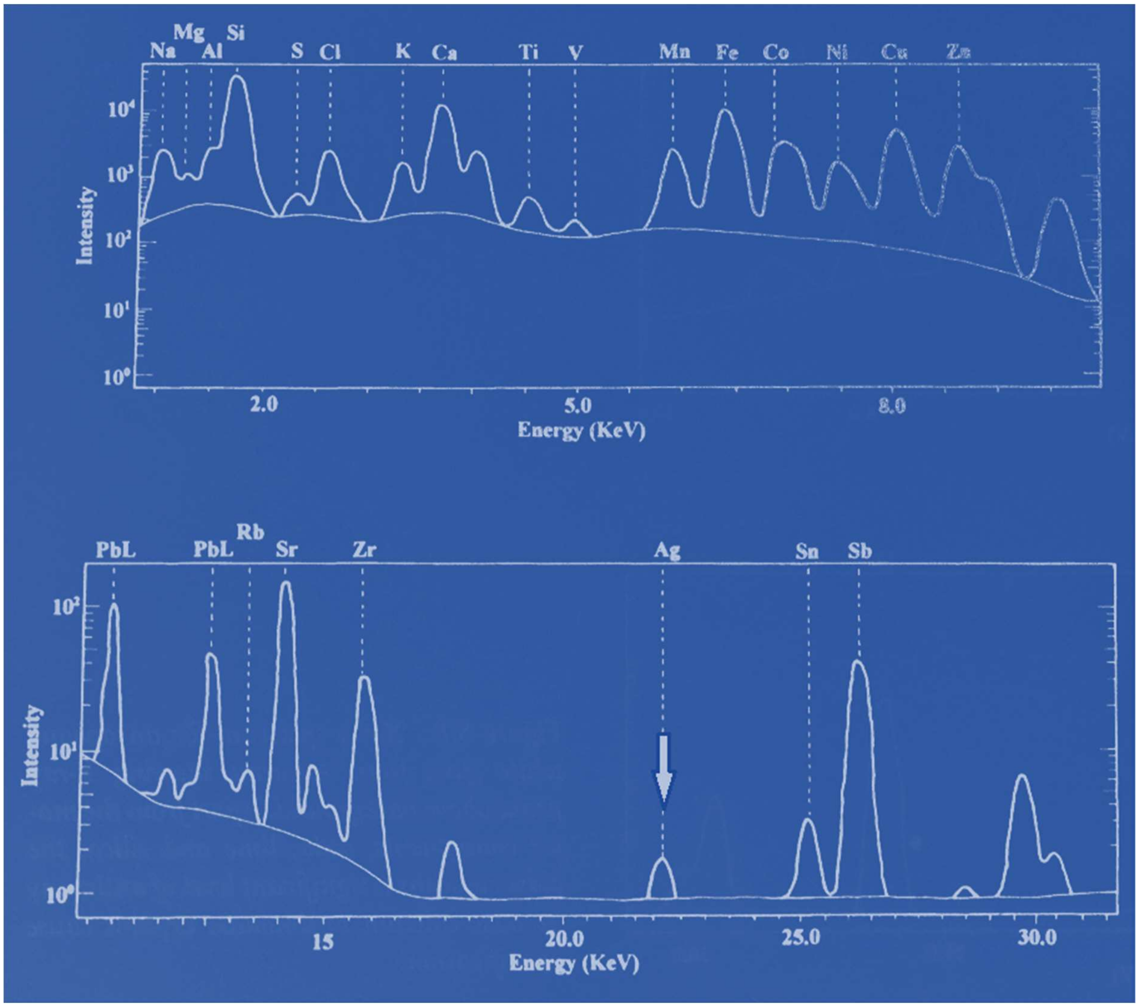
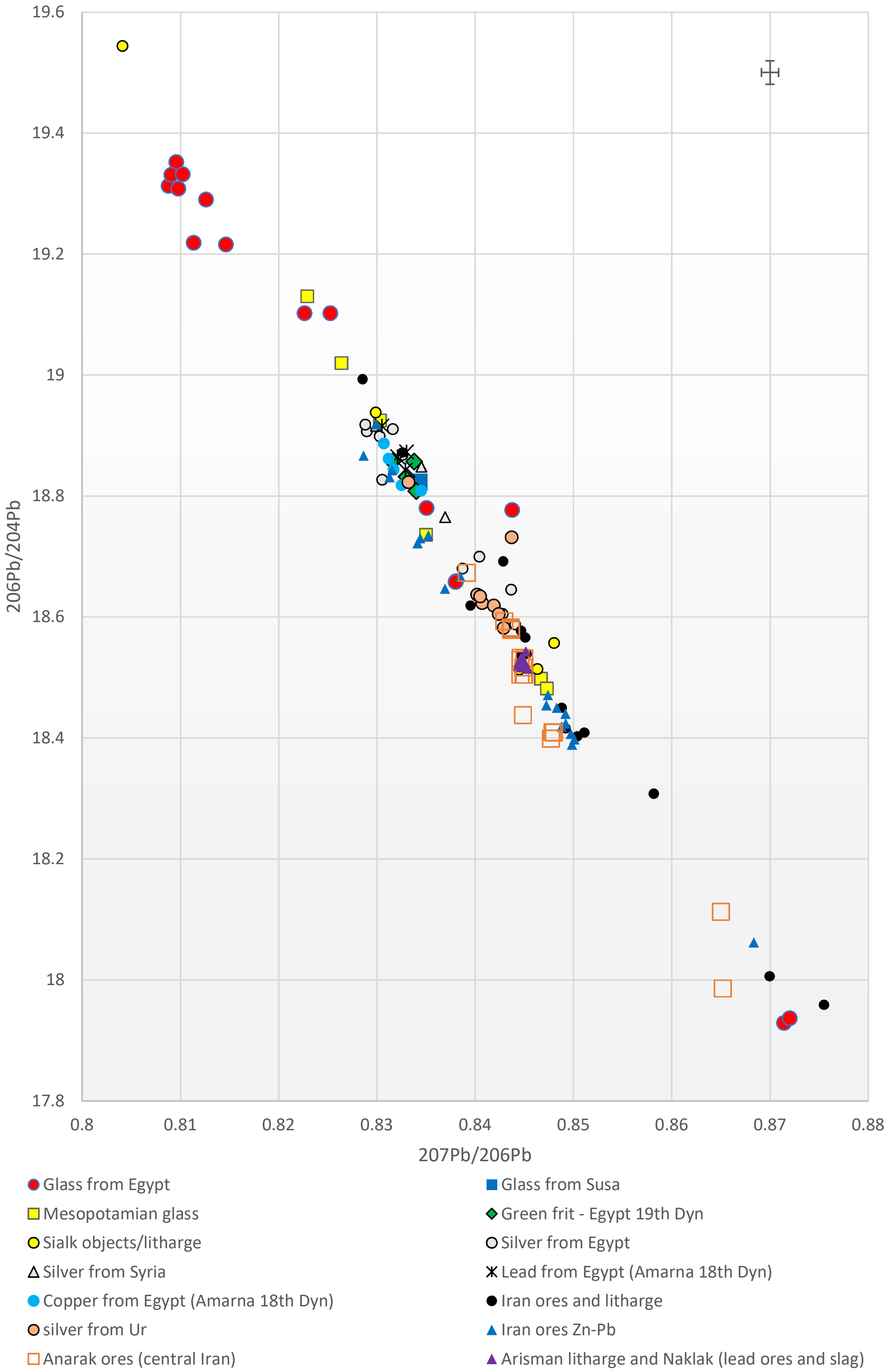


Figure 27 Energy dispersive X-ray spectrum for an opaque blue glass from Amarna showing X-Ray peaks above background. In addition to the major components of soda, lime and silica, the significant antimony peak reflects the presence of calcium antimonate as an opacifier. The presence of cobalt, silver and nickel is suggestive of a Ag-Ni-Co-As ore. As arsenic is volatile its absence is not unexpected. Any bismuth and uranium present are likely to have been below the detection limits. (adapted from Nicholson and Henderson, 2000).

The difference in measurement techniques used by different research teams is therefore significant. LA-ICPMS is generally used to determine the composition of the glass matrix. Spot or line ablations would be constructed to avoid any particulate phases and de-spiking of LA-ICPMS data would also result in any particulate phase being smoothed out of the data in order to determine a more representative composition for the glass matrix. In essence, LA-ICPMS has been used to determine major, minor and trace elements in the matrix, while methods such as SEM-EDS, WDS and EPMA provide bulk analyses on the major components of the matrix as well as the presence of major elements in specific particulate phases, albeit at higher (i.e. worse) detection limits. This would suggest that any silver prills present in the glass slag would generally be detected only by an instrument focussing on an area, or if specific phases were being investigated. Furthermore, assuming the main reason to smelt silver-bearing ores was to extract silver, any prills observable to the naked eye (around 50 microns in diameter) would have been removed from the glass (breaking the coloured glass frit up into small transportable 'stones of casting'). Moreover, considering that the cobalt glass slag is a concentrate which would have been diluted with a base glass to produce cobalt blue glass (probably in a 1:1 ratio) would explain not only the low amounts of silver found in cobalt glass in the archaeological record but also its high variation and low co-dependence with any other component. In essence, the EDS spectrum in Figure 27 is probably rare, as it suggests that this bulk measurement of the glass must have scanned a potentially isolated silver prill.

In summary, the reanalysis of the cobalt blue frit found at Amarna suggests that it was the slag of a smelting system. The components found in the frit are consistent with a five-element ore mineralisation in which Ni and Co are intimately associated. As these systems contain native silver dispersed and embedded within a rocky matrix, it is suggested that the silver was the main reason to process these ores, with the cobalt blue glassy slag being the by-product of the smelt. The five-element ore deposits of central Iran have the components that are found associated with the frit, suggesting that such deposits may have been exploited to extract silver and a cobalt-concentrated vitreous slag (frit). The fact that both Mesopotamia and Egyptian glass show linear relationships between CoO and NiO and also appear to have similar host rocks (i.e. the interaction in Figure 12) could suggest that they both derived from a five-element ore system but with different post-ore stage mineralisations. In essence, although it is not the purpose here to directly link the deposits at Anarak with all cobalt blue glass found in the archaeological record, there do appear to be some compositional similarities which may have so far been overlooked. Furthermore, the fact that cobalt glass has been found at Eridu with 0.15%CoO (Garner, 1956) and at Nippur with very high cobalt levels (0.93%CoO) (von Neumann, 1929), may also suggest that the use of a vitreous concentrated cobalt blue colourant was not confined to Egypt. It could also suggest that the frit exported to Egypt had already been diluted with a base glass.

There is also indirect evidence which supports that the cobalt blue frit from Amarna could have derived from the Near East. In addition to Varberg et al.'s (2015; 2016) evidence of movement of glass from the Near East to Egypt and Europe, some copper blue (turquoise) glasses opacified with calcium antimonate found in Egypt have no tin. Near Eastern glass is generally tin-free (Lilyquist and Brill, 1993:71). This suggests that the Egyptian turquoise glass may have derived from the Near East before being re-coloured during recycling in Egypt with bronze (perhaps after dilution), thereby introducing tin into the system. This would also provide a reason for the composition of some Egyptian blue glasses which have copper and cobalt as colourants (Smirnou and Rehren, 2013), where the presence of both are clearly redundant in terms of colouring the glass. Perhaps more significantly, is that lead antimonate yellow early glasses found in Egypt have higher lead isotope ratios than galena ore deposits from the lead mines in Gebel Zeit in Egypt's Eastern desert and are close to the few yellow glasses found in the Near East (Shortland et al., 2000), i.e. from Tell Brak and Tell Rimah (c. 13th century BC). Lilyquist and Brill (1993 :59-65) considered that there was a Mesopotamian ore field defined by glass. Figure 28 shows LIA mirror plots for these glasses and for glass from Egypt (yellow glass, one red) and from Susa (yellow glass) in Iran (Lilyquist and Brill, 1993), green glass frit from Egypt (19th Dynasty) (Shortland, 2006), objects and litharge recovered from Sialk in central Iran (Nezafati et al., 2008: 329-350) and from Arisman (Pernicka et al., 2011), lead ores and slag from Naklak (Pernicka et al., 2011), silver from Egypt and Syria (Oxalid, 2018) and the Royal Tombs at Ur (Klein et al. 2016: 89-97), copper and lead objects found at Amarna (Oxalid, 2018), and ores and litharge from Iran (Stos-Gale, 2001), ores specifically from the Anarak district (Pernicka et al., 2011; Nezafati et al., 2008: 329-350) and ores from Zn-Pb deposits (with sections associated with Ag) from the Urumieh-Dokhtar and Sanandaj-Sirjan zones extending from NW-SE Iran (Mirnejad et al., 2011). All archaeological samples are LBA or earlier. The 208Pb/206Pb vs 207Pb/206Pb also includes MBA silver from Sidon (Veron and Roux, 2004) which did not have Pb204 values.


19.6
19.4
19.2
19
18.8
18.6
18.4
18.2
18
17.8
206Pb/204Pb
0.8
0.81
0.82
0.83
0.84
0.85
0.86
0.87
0.88
207Pb/206Pb
● Glass from Egypt
■ Glass from Susa
□ Mesopotamian glass
◆ Green frit - Egypt 19th Dyn
● Sialk objects/litharge
○ Silver from Egypt
△ Silver from Syria
✱ Lead from Egypt (Amarna 18th Dyn)
● Copper from Egypt (Amarna 18th Dyn)
● Iran ores and litharge
● silver from Ur
▲ Iran ores Zn-Pb
□ Anarak ores (central Iran)
▲ Arisman litharge and Naklak (lead ores and slag)

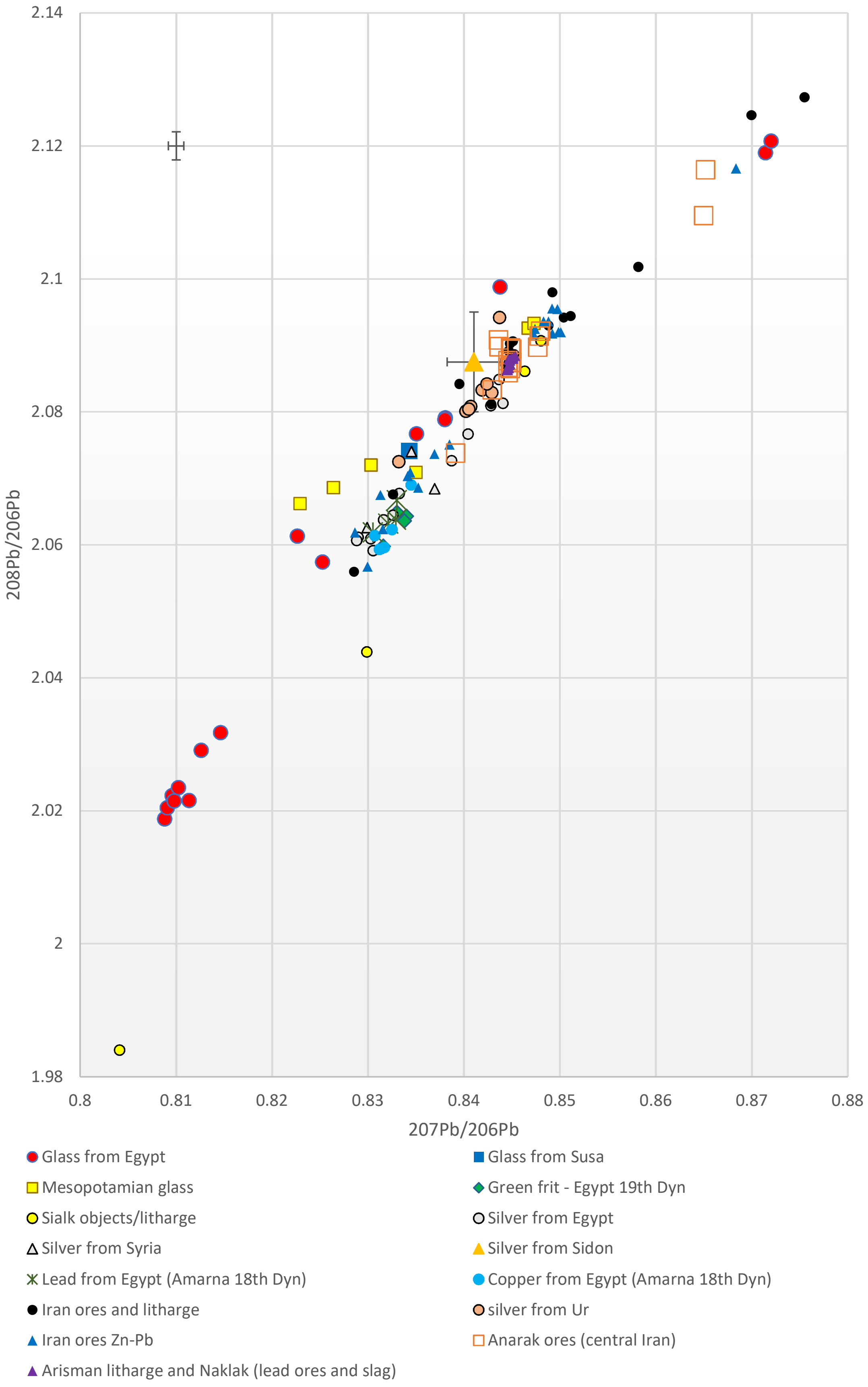

2.14
2.12
2.1
2.08
2.06
2.04
2.02
2
1.98
208Pb/206Pb
0.8
0.81
0.82
0.83
0.84
0.85
0.86
0.87
0.88
207Pb/206Pb
Glass from Egypt
Glass from Susa
Mesopotamian glass
Green frit - Egypt 19th Dyn
Sialk objects/litharge
Silver from Egypt
Silver from Syria
Silver from Sidon
Lead from Egypt (Amarna 18th Dyn)
Copper from Egypt (Amarna 18th Dyn)
Iran ores and litharge
silver from Ur
Iran ores Zn-Pb
Anarak ores (central Iran)
Arisman litharge and Naklak (lead ores and slag)

Figure 28 Lead isotope mirror plots. Glass from Mesopotamia (i.e. Tell Brak and Tell Rimah) (Shortland, 2006), Egypt and Susa (data from Lilyquist and Brill, 1993: 66); green glass frit from El Rakham, Egypt (19th Dynasty) (Shortland, 2006); Tappeh Sialk objects and litharge (data from Nezafati et al. 2008); silver from Egypt and Syria (data from Oxalid, 2018); silver from Sidon (data from Veron and Roux, 2004); silver from Ur (data from Klein et al., 2016); Iran ores and litharge (Stos-Gale, 2001: 56); Anarak ores (data from Pernicka et al., 2011; Nezafati et al. 2008: Fig 4c); Arisman litharge and Naklak lead ores and slag (Pernicka et al., 2011); Iran ores from UDZ and SSZ zones in Iran (Mirnejad et al., 2011); copper and lead objects found in Egypt (data from Shortland, 2006). Glass from Egypt and Susa and silver from Egypt, Syria, Ur and Sidon are consistent with ores in Iran, particularly the Anarak district of central Iran. Silver from Sidon shows a tight range of values which covers all the silver artefacts tested from Burial 27. Copper and lead objects found at Amarna also fall near Iranian ores. Note colours depicted on plot do not represent the colours of the glasses.

About half of the Egyptian glass samples are not only consistent with Iranian ores (i.e. Pb207/Pb206>0.82), with three being close to the ore values of the Anarak region, but some are also consistent with glass from Susa and silver from Syria, Sidon, Ur and Egypt. The eight samples closest to the Iranian ore 'field', in order of ascending Pb207/Pb206 are samples 2168 (Wadt Qirud – Tomb of foreign wives of Thutmosis III – red part – c. 1425 BC), 2169 (Assasif Tomb 37 – from a tin bead – c. 1460 BC), 2166 (Susa, c. 15th century BC), 1119 (Lisht excavations – Later New Kingdom), 2184 (Thutmosis III's tomb c. 1425 BC), 2178 (Lisht excavations – Later New Kingdom), 1118 (Lisht excavations – Later New Kingdom) and 2177 (Lisht excavations – Later New Kingdom) (Lilyquist and Brill, 1993).

The issue with ore 'fields' is that they often overlap with other geographically separated areas. However, the fact that the some of the glass from Egypt is also consistent with glass from Susa, silver from Syria, Sidon, Ur and Egypt as well as ores and slag from Iran, suggests that some of the Egyptian yellow and red glass derived its isotopic signature from lead from Iran, lead found in areas with similar isotopic signatures to silver. Although the default position would suggest silver derived from an argentiferous lead ore, it needs to be considered that the lead used for lead antimonate (i.e. yellow glass) was not necessarily argentiferous. In other words, lead associated with the five-element ore mineralisation would provide a similar LIA signature to the silver. These LIA data clearly support that there was movement of silver and yellow and red glass to Egypt as well as silver to Sidon. Green glass frit recovered in Egypt also appears to be consistent with glass from Egypt, silver from Egypt, Syria and Ur, and Iranian ores, which could suggest that copper-based frit was also produced in the Near East, especially when it considered that the Anarak mining district has two unusually large deposits of native copper at Talmessi and Meskani (Piggot, 2004: 28-43). Copper and lead objects recovered from 18th Dynasty Amarna also appear to fall close to Iranian ores, litharge and objects. It is therefore conceivable that cobalt blue frit made a similar journey to Egypt.

5. Experimental

Experiments and analyses were carried out on a five-element ore system in order to:

a) to determine whether it was feasible to flux a five-element ore system in order to extract silver and produce a concentrated cobalt-blue glass.
b) to determine how elements from the ore partition into the glass slag and the silver metal.

Ore from the Silverfields deposit in Cobalt, Ontario in Canada was obtained for the experiments, as this system is well-characterised and was available. The ore occurs as nearly vertical veins in Huronian sedimentary rocks below a sill-like body of Nipissing diabase. The ore veins are composed of carbonates, arsenides, native silver and sulfides, and are zoned with respect to type of arsenides and grade of silver ore. The predominant arsenides in the upper parts of the ore veins are those of nickel, in the mid-portions, cobalt, and in the lower parts, iron. High-grade silver ore is generally associated with mixtures of nickel and cobalt arsenides, medium-grade with cobalt arsenides, and low- to very low-grade with either iron or nickel arsenides. Textural relations suggest that the arsenides and native silver have a common origin, while the sulphides were in the rocks prior to ore deposition but re-mobilised and redeposited in and around the ore veins as grains during the mineralization period (Petruk, 1968).

Figure 29 shows photographs of the ore slab and the ore surface using a Dino-Lite digital microscope. In terms of silver, it can be classified as a high-grade ore, exhibiting dendritic growth of silver into a cobalt-arsenide matrix with some silver growing at the core of large arsenide ‘rosettes’. Figure 29 shows that the ore was heterogenous at a macroscopic scale. A section of the ore was removed which contained all the phases that could be observed macroscopically. No attempt was made to examine representative sections in terms of the amount of each phase, i.e. the analyses were not conducted as a quantitative measure of the grade of the silver ore.

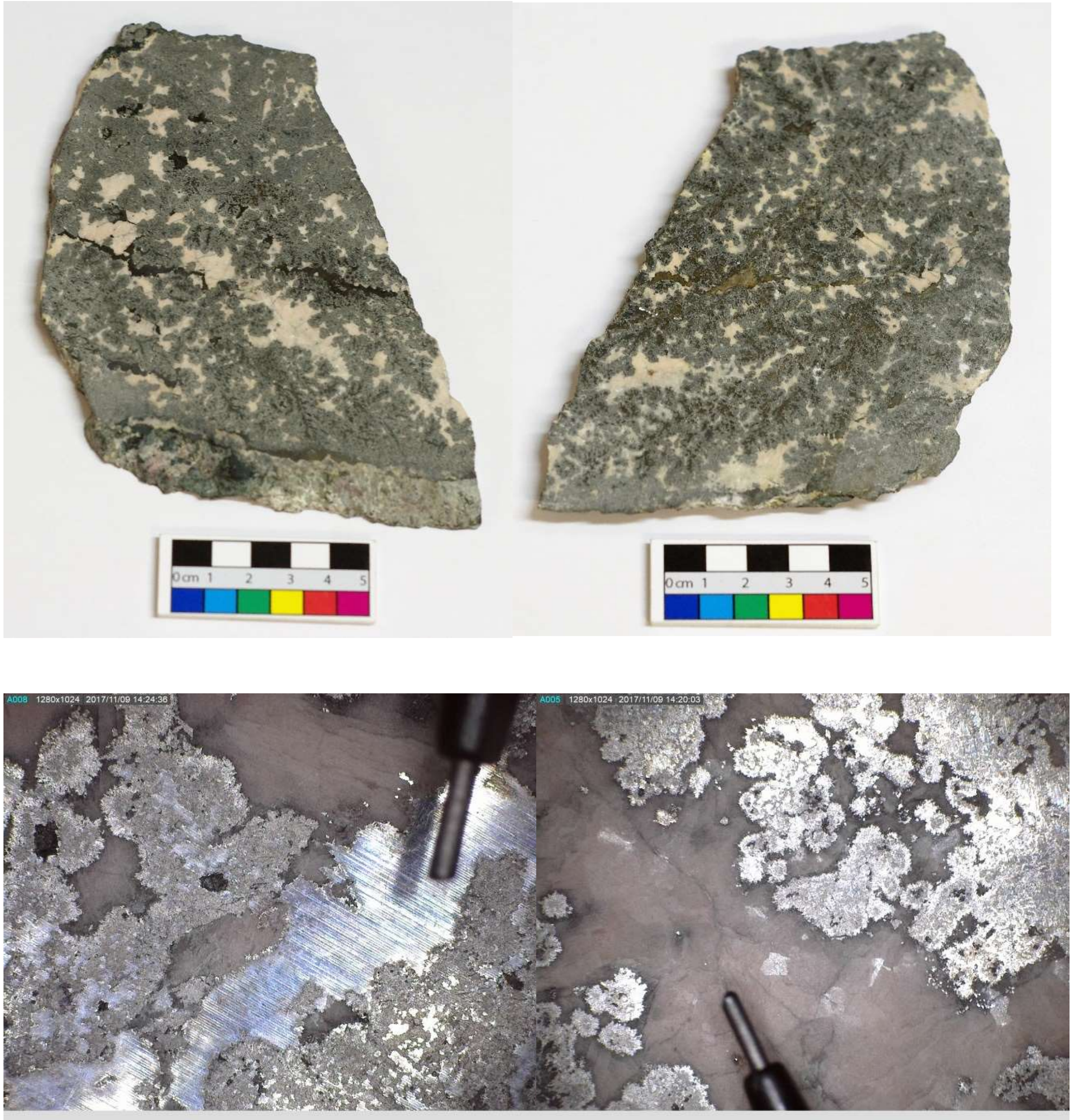


Figure 29 The faces of the ore slab from the Silverfields mine, Cobalt, Canada (upper). Images captured using a Dino-Lite digital microscope showing the native silver and cobalt arsenide phases (lower).

A small section of ore was cut from the slab and crushed to flakes. Some of these flakes were ground up using a mortar and pestle to determine which mineral phases were present using XRD. A sample (about 0.1g) was placed in a Rigaku Miniflex 600, with a scan range of 5°-90°, a scan step of 0.1° and scan speed of 1.5° per minute. The resulting diffraction pattern (Figure 30) was matched to databases to aid identification. The results show that apart from silver, the main component of the ore were cobalt arsenides, with skutterudite having the highest confidence in terms of identified minerals.

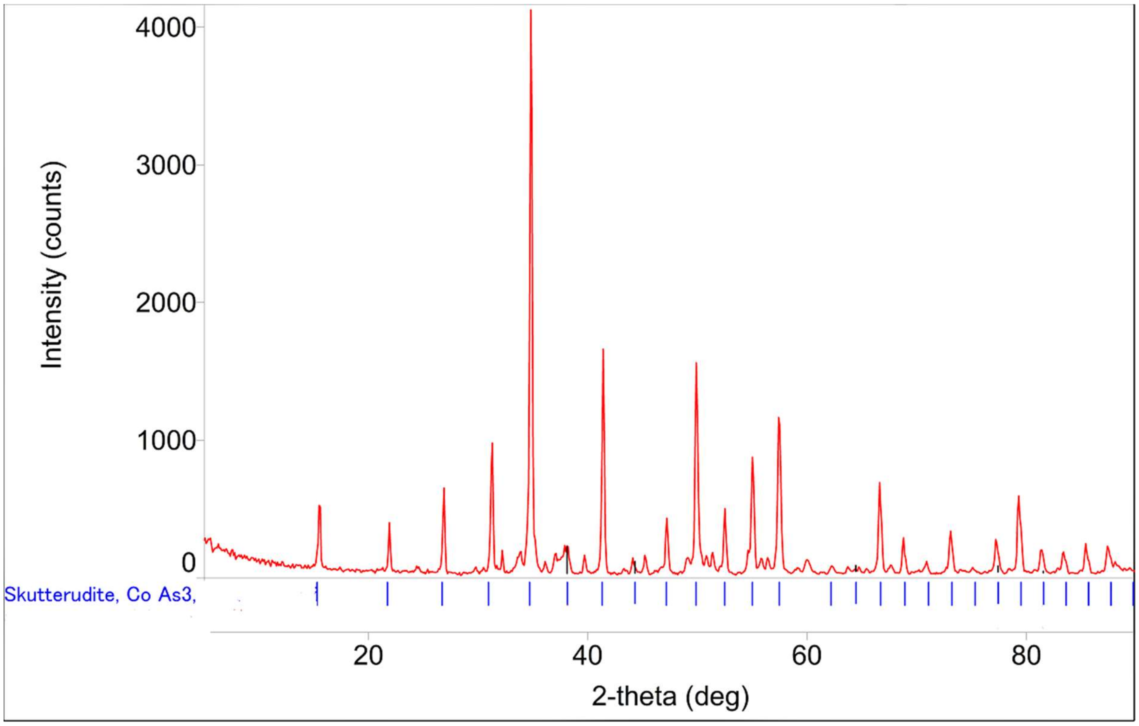


Figure 30 XRD diffractogram for a representative section of the ore, showing skutterudite as the main mineral phase.

The remainder of the crushed ore was placed in a conical carbon crucible with laboratory grade silica, sodium carbonate and calcium carbonate. As it was unknown *a priori* which components of the ore would enter the glass slag, the amounts of silica, sodium carbonate and calcium carbonate were selected based on percentages to form a glass (i.e. 65%SiO_2; 20%Na_2CO_3; 15%$CaCO_3$). The percentage of each component were as follows: ore (31.3%), silica (44.6%), Na_2CO_3(13.8%) and $CaCO_3$(10.3%). The crucible charge was heated in a closed furnace at a rate of about 10°C/hour. The temperature was held at 750°C for 1 hour in order to allow partial vitrification and removal of entrapped air before being heated to 1100°C where it was held for 1 hour before cooling down to room temperature. The sample was removed from the partially oxidised carbon crucible, before being sectioned for SEM analysis (Figure 31). The metallic and glassy parts were analysed. The remaining glassy part of the sectioned sample was re-heated to determine any compositional changes in this glassy material on subsequent re-heating cycles. The glass was re-heated in a carbon crucible at a rate of about 10°C/hour to 1300°C and cooled without any dwell time to simulate reprocessing of glass. Part of this glass was removed, mounted and polished for SEM-EDS analysis. The other parts were reheated two further times under the same processing conditions. In effect, the reheating experiments produced three glass samples (in addition to the originally produced sample) which had been re-heated to 1300°C from one to three times.

SEM-EDS was conducted on the ore from Silverfields, Cobalt, Ontario and the sample produced. The ore, the produced sample and the re-heated glasses were mounted in resin and polished down to 1μm using alumina paste. In the case of the produced sample, the section of the sample with the silvery phase still attached (Figure 31) was mounted and polished for SEM-EDS analysis. Figure 31 shows the sectioned sample, demonstrating clear separation of the cobalt-blue glass and a large shiny silvery bead, which collected at the base of the crucible (i.e. the sample has been inverted for the photograph).

A Hitachi S-3400N SEM attached to an INCA EDS (Oxford Instruments, UK) was used. A conductive carbon-coating was applied to the sample, which was examined at working distance of 10mm using a voltage of 20keV. Carbon was removed subsequently from all elemental analyses. Backscattered electron imaging (BSE) was used to help identify differences in phase and particle composition. EDS was used to generate elemental composition of certain areas of the samples to understand the chemical structure and the distribution of elements. An acquisition time of 100 seconds was used with a dead time between 35-40%. The SEM-EDS was optimised using cobalt prior to any analytical work, and approximately every 90 minutes during scanning. The count rate on the cobalt was 3500 counts/second. Corning A was used as a certified reference material, primarily because it was a soda-lime-silica glass with measurable cobalt levels for SEM-EDS, i.e. 0.17%CoO. Errors were high on the cobalt (20%) standard, mainly because levels are close to the detection limits of the EDS. Two additional soda-lime-silica glass reference materials were used to determine measurement errors, specifically for arsenic. These standards (LOP07-C006 and LOP07-C057) were selected as they have much higher arsenic concentrations than any other soda-lime-silica glass standard reference materials. The errors for As_2O_3 were 14% and 5.5% for the two standards, respectively. All standard measurements were conducted at the same magnification as the bulk sample measurements (x200).

Figure 31 The sectioned sample showing the cobalt-blue glass and the metallic bead. Unreacted silica can be seen in the glass part. Note that the sample has been inverted from its position in the conical carbon crucible, i.e. the metallic phase was at the bottom.

5.1 Results

As mentioned above, the ore was macroscopically heterogenous and glass formers had been added. The SEM-EDS analyses were therefore not conducted as a quantitative assessment of the grade of the silver ore, nor to determine the composition of the sample produced *per se*, but as an exploratory investigation to determine how elements present in the ore partitioned between the glassy and metallic phases of the sample (see Table 6).

Back scattered images showed that the ore had a variable composition (Figure 32a). Table 4 presents the normalised results in weight percent based on three analyses from low magnification scans. At least four separate phases were discernible. The silver rich phase in the ore (Figure 32b) had a normalised composition of: Ag (91.9%), Hg (4.9%), Sb (3.2%). Cobalt and nickel were found in association with arsenic in two discrete phases with sulphur and iron (Figure 32c and 32d). A phase composed primarily of Mg and Ca was also present in the ore (Figure 32e), which by stoichiometry of oxides was composed of mainly of 36.7%MgO and 57.9%CaO, the remainder being 3.6%Fe_2O_3, 1.1%MnO and 0.5%As_2O_3.

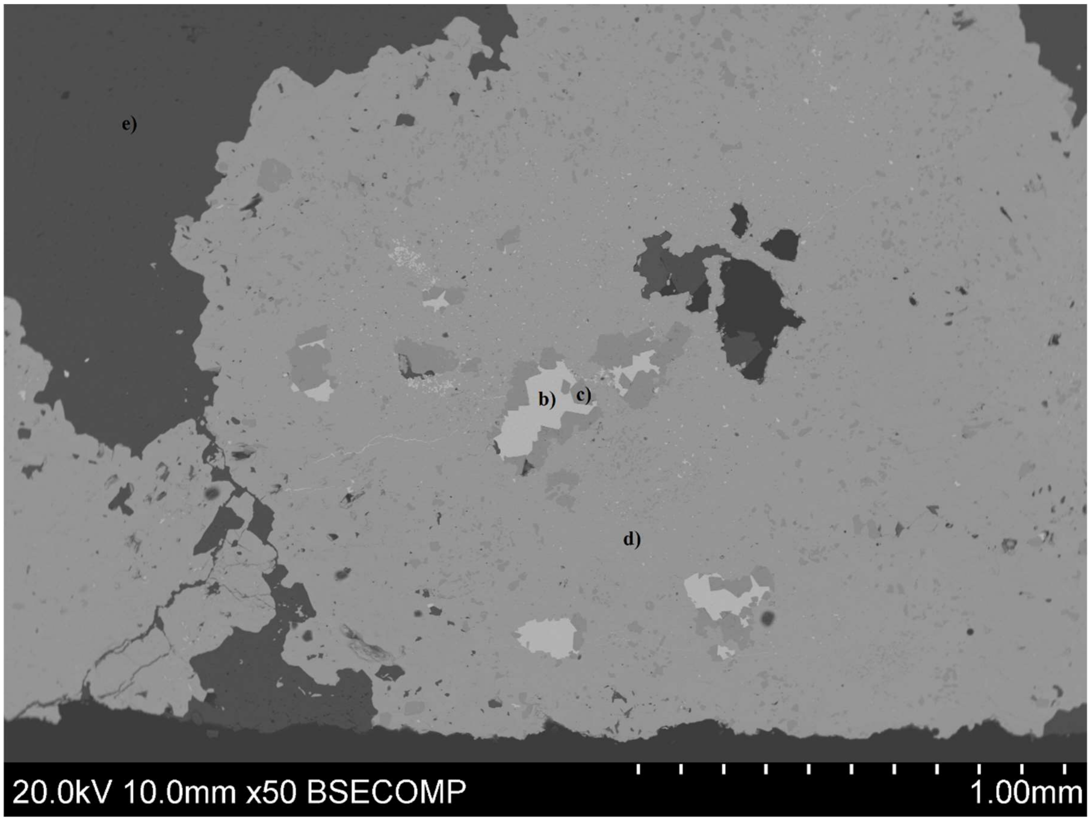


Figure 32 Backscattered images of the ore showing the phases described in the text: a) the variable composition of the ore (field of view); b) the silver rich phase; c) and d) Cobalt and nickel were found in association with arsenic in two discrete phases with sulphur and iron; e) Mg and Ca was also present in the ore. All compositions are in normalised wt%.

Table 4. The bulk chemical composition of silver ore by SEM-EDS in normalized wt%.

% (n=3)	O	Mg	Si	S	Ca	Mn	Fe	Co	Ni	As	Ag
Area a)	18.3	3.7	0.5	1.4	4.4	0.2	3.6	10.6	1.2	51.5	8.0
st. dev.	15.1	-	-	0.6	3.9	-	1.0	1.7	0.1	12.0	5.8

% (n=5)	O	Mg	S	Ca	Mn	Fe	Co	Ni	As	Ag	Sb	Hg
Area b)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	91.9	3.2	4.9
Area c)	bdl	bdl	17.6	bdl	bdl	30.2	3.1	0.5*	49.0	bdl	bdl	bdl
Area d)	bdl	bdl	0.3	bdl	bdl	2.5	15.5	2.0	79.8	bdl	bdl	bdl
Area e)	68.0	11.0	bdl	19.1	0.4	1.28	bdl	bdl	0.19	bdl	bdl	bdl

* Ni detected in one of the 5 area scans.

Table 5 shows the composition of the glass slag. Small silver-rich prills were also found in the glass. Figure 33 shows a prill of about 6μm in diameter surrounded by the glass matrix. Silica-rich needles were observed in the glass (Figure 36). These needles were avoided for bulk compositional measurements.

Table 5 The bulk chemical composition of glass part by SEM-EDS in normalised wt% oxides by stoichiometry.

%	Na_2O	MgO	SiO_2	CaO	Fe_2O_3	CoO	As_2O_3
mean (n=5)	11.1	1.4	60.0	11.3	2.9	5.2	8.1
st.dev.	0.2	0.2	0.3	0.4	0.4	1.0	2.0

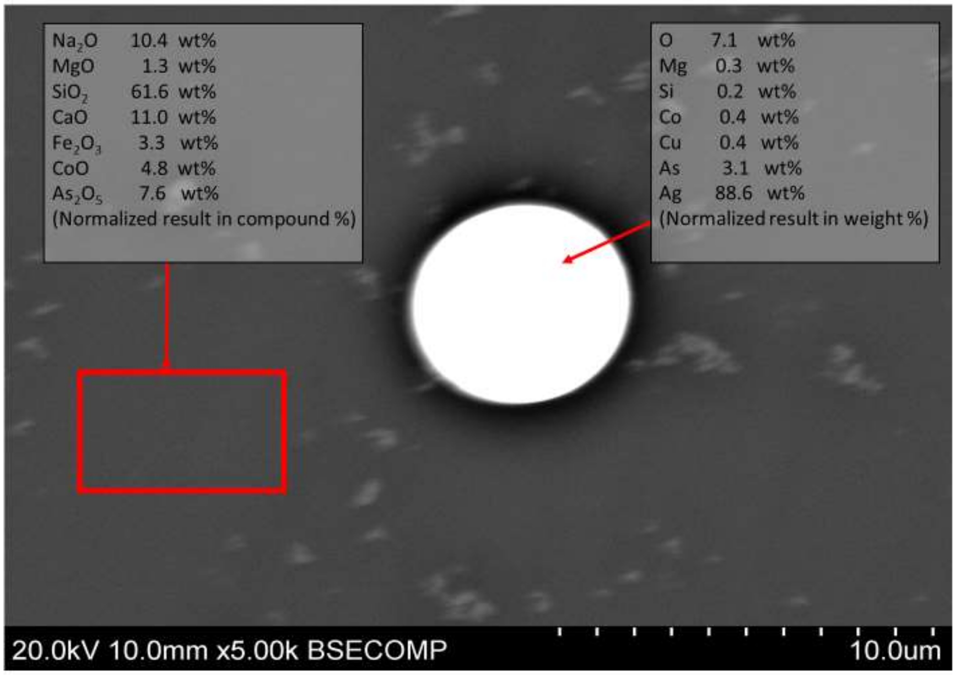


Figure 33 Silver prill entrapped in the glass part of the sample. Copper is also present in the silver. Note that the lower amounts of silver in this prill are potentially a consequence of penetration depth and area of the EDS, which at this magnification has scanned part of the area around the prill.

The metallic bead had a variable composition comprising two main phases: one silver-rich, the other cobalt-rich. The cobalt-rich phase was mainly composed of cobalt-nickel arsenides. The presence of a cobalt-rich phase suggests that the glass slag could not dissolve any more cobalt (i.e. around 5% CoO may have saturated the glassy matrix). The silver-rich phase contained arsenic, copper and some sulphur. Antimony and some cobalt-nickel arsenides were present only in small discrete phases within the silver-rich phase. In essence, the metallic bead was a composite of silver and Co-Ni-As.

Figure 34 shows the bulk of the metallic bead with brighter silver-rich areas (e.g. Area A) and the darker Co-Ni-As phase (e.g. Area B). Many spherical voids were found (Figure 35), possibly suggesting that metallic silver prills were lost during the polishing (very dark areas), indicating a weak interface between the Co-Ni-As phase and the silver-rich phases.

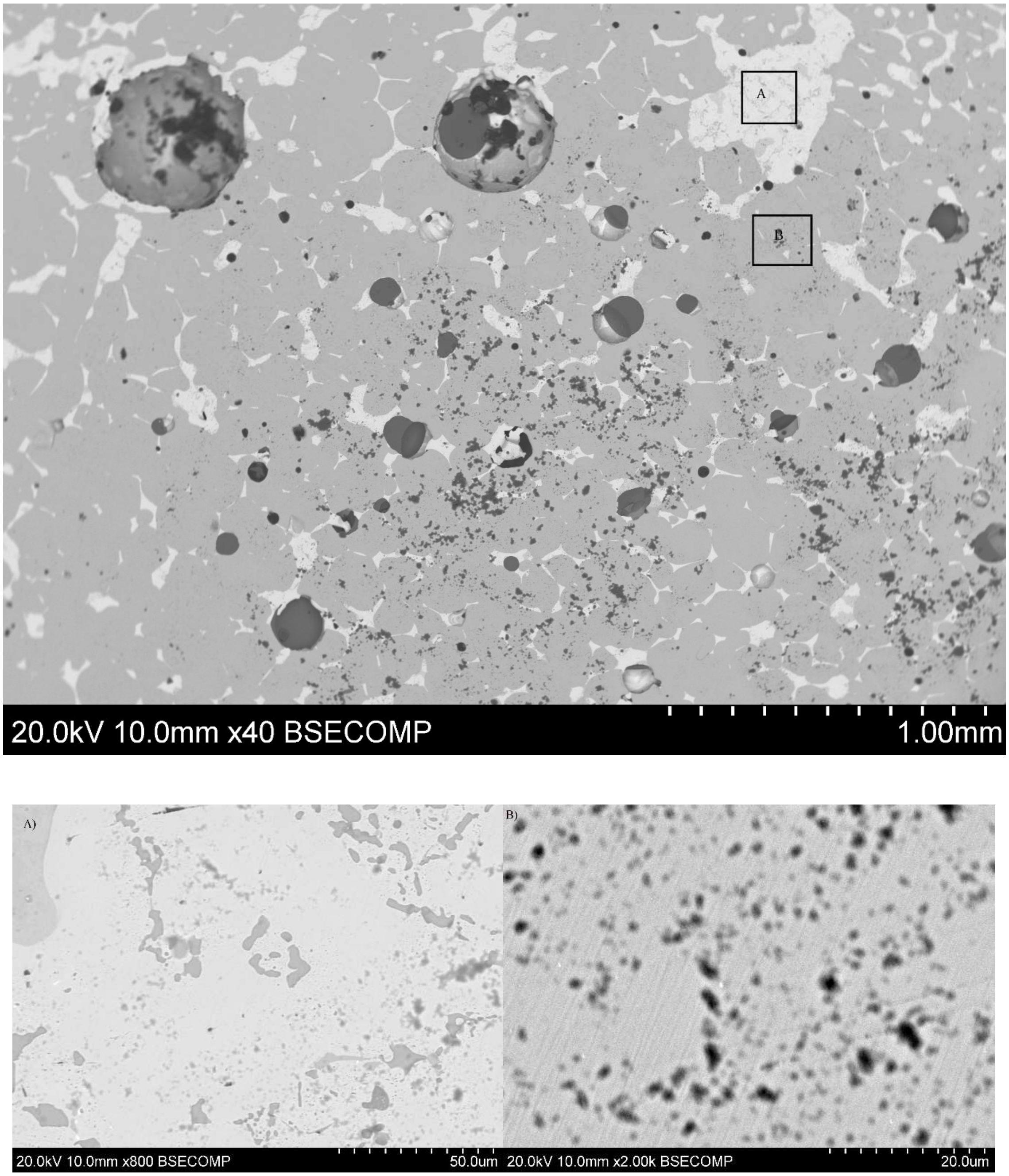


Figure 34 (top) Backscattered image of the metallic bead showing silver-rich (brighter) and cobalt-nickel-arsenic rich (darker) areas. The round, dark areas are voids possibly indicating the presence of silver prills which were lost during polishing (see Figure 35). Silver-rich Area A (lower left) had a composition of 70%Ag, 13.6%As, 3.2%Cu, 0.6%S and 11%O (normalised by element); the cobalt-nickel-arsenic rich Area B (lower right) had a composition of 33.5%Co, 51.7%As, 6.7%Ni, 0.2%S and 5.7%O (normalised by element).

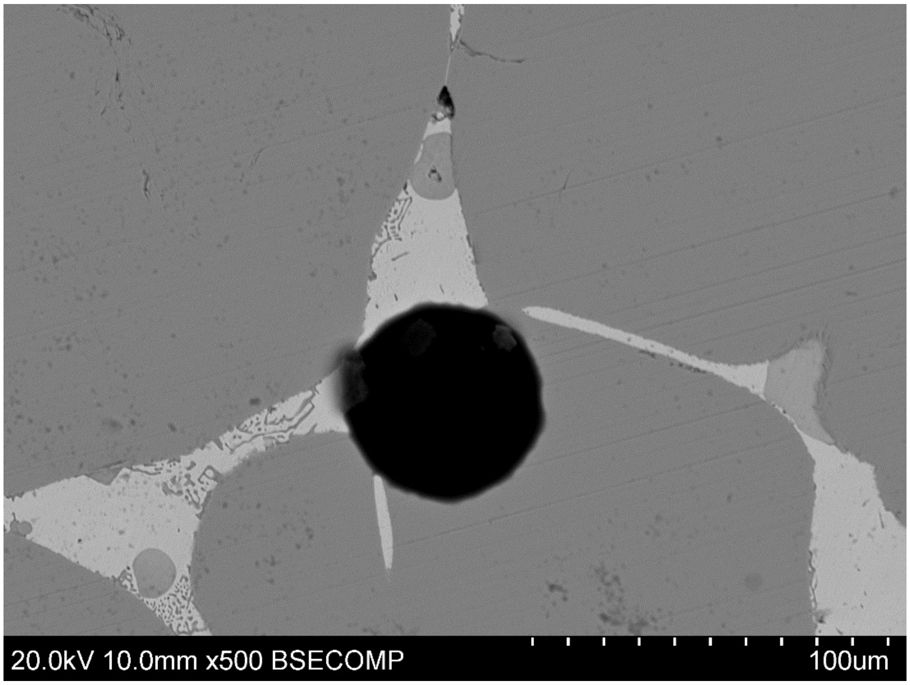


Figure 35 A spherical void possibly indicating a lost silver prill in the metallic part of the sample. Surrounding the spherical void, the dark grey area is predominantly Co-Ni-As (normalised by element: 56.6%As, 37.0%Co, 5.6%Ni, 0.58%O, 0.25%S) and a light grey silver-rich phase (normalised by element: 91.9%Ag, 5.5%As, 0.26%Co, 2.3%O). The loss of the prill could indicate that the interface between metallic silver and the surrounding phases was weak.

The following table (Table 6) shows how the components from the ore partitioned into the glass and the metallic parts of the sample. Ticks denote whether an element was detected, even if it was only a minor component. More details are presented in the following text:

Table 6 Ticks represent the components detected in each phase or the ore, the glass and the bead. The components added are also presented.

	Raw materials			Products			
				slag/glass		metal	
Element	**bulk ore**	**silver phase in ore**	**added to ore**	**glass**	**metallic prills in glass**	**silver phase**	**non-silver phase**
Silicon	✓	X	✓	✓	✓*	X	X
Sodium	X	X	✓	✓	X	X	X
Calcium	✓	X	✓	✓	✓*	X	X
Silver	✓	✓	X	X	✓	✓	X
Copper	X	X	X	X	X	✓	X
Nickel	✓	X	X	X	✓	✓	✓
Manganese	✓	X	X	X	X	X	X
Iron	✓	X	X	✓	X	X	X
Mercury	✓	✓	X	X	X	X	X
Antimony	✓	✓	X	X	X	✓	X
Magnesium	✓	✓	X	✓	X	✓	X
Sulphur	✓	X	X	X	✓	✓	✓
Cobalt	✓	X	X	✓	✓	✓	✓
Arsenic	✓	X	X	✓	✓	✓	✓
Tin	✓**	X	X	X	X	X	X
Aluminium	X	X	✓	X	✓	✓	✓

* probably from glass surrounding the prill
**only found in one analysis at 0.57%Sn

The added glass forming materials (silica-soda-lime) were found predominantly in the glass part of the sample, with only very low amounts in the metallic bead. Alumina was not added or found in the ore but was used as an abrasive to polish the sample. Its presence in the metallic bead can therefore be attributed to contamination.

Silver was only detected in the metallic bead, apart from some small isolated prills found in the glass (Figure 33). Copper, which had not been detected in the ore, was only found in the metallic bead

(Figure 34), suggesting that the low amounts in the ore concentrated in the metallic bead with the silver. Nickel also appears to concentrate in the metallic part as it was not detected in the glass. However, apart from some discrete particles found at high magnification, it was not found in the silver-rich phases. Manganese, which was detected at low percentages (0.4%) in one phase of the ore was not found either in the glass or the metallic part of the sample, suggesting that it must form an unfound discrete phase, or that it was diluted beyond the limits of detection of the instrument. Iron was only detected in the glass. Mercury was detected in the silver phase of the ore, but not in the sample. This is probably because it is volatile and boiled off during processing. Antimony was found in the metallic bead as one of the phases within the silver-rich phase. Magnesium was found predominantly in the glass, with only low concentrations found in the non-silver phases of the metallic bead. Sulphur was only detected in the metallic bead, where it appeared to be associated with copper. Arsenic was detected in the glass and metallic bead. Cobalt was detected in the glass at quite high percentages (average 5.2%CoO). It was not found in the silver-rich phase of the metallic bead, apart from a few isolated particles of cobalt arsenide found at high magnifications (x5000). CoO was present at high concentrations (up to 30%CoO) in the cobalt-rich phase of the metallic part in association with nickel (4.4%NiO) and arsenic (42.9%As_2O_3) (Figure 35).

The main conclusion from these experiments is that a five-element ore can be fluxed to produce a cobalt-rich glassy material, and to separate the silver from components found in the ore. Although the metallic bead still contained cobalt in association with arsenic and nickel, it was malleable as the silver formed a discrete phase from the Ni-Co arsenides, i.e. working the bead or re-heating it would easily remove the silver. The spherical voids possibly indicate that silver prills would separate easily from the surrounding phases (Figure 35).

In terms of partitioning, the experiments and the analytical method used suggest that any object made from the silver from such an ore system would have only copper, arsenic and sulphur distributed with the bulk, with antimony, nickel and cobalt being in discrete phases. The glass would have the usual base glass components, with arsenic in association with the cobalt. No silver was found in the glass, apart from isolated prills, suggesting that it would also not generally be detected in archaeological cobalt glass or frit. Iron would be elevated in the glass, although this may be difficult to ascertain because the silica source probably has variable levels of iron. However, it provides a possible explanation for the semblance of linearity between CoO and FeO in the frit (Figure 25), in that iron from skutterudite maintains some association with the cobalt in the glass phase. Furthermore, the fact that copper partitions with the silver provides an explanation for its low co-dependence with cobalt and with the other components in the glasses and frit. However, the experiments also show that when cobalt and nickel arsenides are abundant in the ore, they separate out into a discrete phase with the silver (probably because they have reached their solubility limit within the glass). This will not affect the relationship between cobalt and nickel found in cobalt-blue glass from both Egypt and Mesopotamia, as both separate out together. In other words, nickel only appears to partition in association with cobalt, which potentially explains why the linear relationship between nickel and cobalt prevails in the glasses (Figure 2, 6 and 24). However, it will clearly affect the absolute amounts of cobalt, nickel and arsenic present in the glassy slag (and therefore any glass subsequently coloured with this frit), potentially depending not only on the initial concentrations of these components but also on the processing conditions.

Re-heating experiments conducted on the glassy part of the sample showed that arsenic and cobalt levels decreased, and silica levels increased with respect to the sample produced (Table 7). The increase in silica concentration is probably a consequence of silica-rich phases dissolving into the glassy matrix, as evidenced by a noted decrease in the number of silica needles on each successive re-heating cycle. Arsenic levels decreased from 8% in the produced sample to just over 1% after the first re-heating cycle, to 0.6% after the second re-heating and below the detection limit after the third cycle (highlighted in Table 7). These decreases in arsenic concentration were associated with decreases in the size and number of the bright phase (Figure 36). This was particularly evident after the third re-heating cycle. Closer examination of this bright phase showed that it was predominantly cobalt and arsenic with a low percentage of nickel (58%Co, 28%As and 2%Ni, by element in normalised weight percent).

Figure 36 (top) shows a Co-As rich particle on a silica-rich needle, indicating that the silica provided a substrate for a reaction between cobalt and silica, potentially forming cobalt silicate, the compound responsible for the dark blue colour. The darker area surrounding the bright particle in Figure 36 (middle and bottom) was predominantly cobalt and silica, without any detectable arsenic. This suggests that arsenic within the Co-As phase oxidised (probably forming As_2O_3, which has a boiling point of 465^{o}C) as cobalt reacted with silica. Table 7 shows the composition of the original sample (from Table 4) and after three successive re-heating cycles.

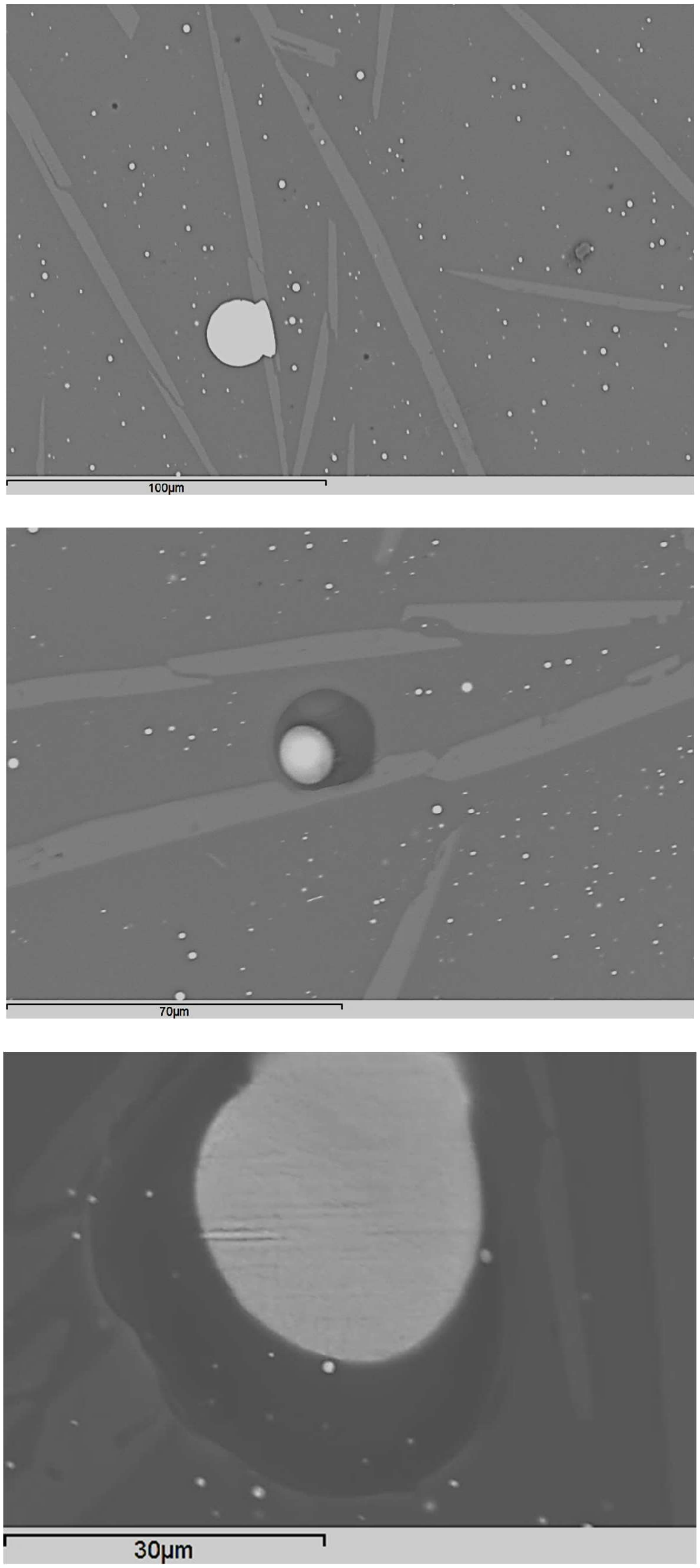


Figure 36 Cobalt-blue glass part of sample (Figure 9.32) after re-heating to 1300°C. Silica-rich needles are present in the glass. Bright areas are Co-As phases which appear to have reacted with the silica (top) producing a cobalt silicate phase without detectable levels of arsenic surrounding the particle (middle and bottom).

Table 7 The bulk chemical composition of glass part by SEM-EDS in normalised wt% oxides by stoichiometry of the produced sample, and after three successive re-heating cycles.

%	Na_2O	MgO	SiO_2	CaO	Fe_2O_3	CoO	As_2O_3
sample (n=5)	11.1	1.4	60.0	11.3	2.9	5.2	**8.1**
st. dev.	0.2	0.2	0.3	0.4	0.4	1.0	2.0
reheat 1 (n=5)	11.3	1.7	68.6	11.5	2.7	3.1	**1.1**
st. dev.	0.2	0.0	0.1	0.1	0.1	0.1	0.1
reheat 2 (n=5)	10.9	1.7	69.2	12.0	2.8	2.7	**0.6**
st. dev.	0.0	0.0	0.4	0.2	0.0	0.3	0.1
reheat 3 (n=5)	10.6	1.8	70.8	11.9	2.5	2.4	**bdl**
st. dev.	0.1	0.1	0.3	0.1	0.1	0.2	-

These experiments suggest that arsenic deriving from the Co-Ni-As ore is volatile. CoO levels also decreased on re-heating (Table 7). Although cobalt oxides may convert to different forms at higher temperatures, they are unlikely to form volatile compounds. It is more likely that cobalt in the bulk glass reacted with the silica with successive heating as observed in Figure 36 (i.e. areas which were avoided for bulk measurements), thereby reducing the amount of cobalt in the bulk. This is supported by the decrease in variation in cobalt concentrations after re-heating (Table 7). In effect, successive re-heating of the glass resulted in further dissolution of silica, reactions between silica and cobalt, and the release of arsenic, probably in the form of a gaseous product. It should also be noted that these re-heating experiments were conducted without stirring or working the glass, which would presumably remove arsenic even more readily.

In effect, these re-heating experiments suggest that arsenic is not a reliable indicator to provenance glass, and that glass with low arsenic levels could have derived from an arsenic-rich ore as suggested in Section 4.5 with regard to archaeological cobalt-blue glasses and frit.

6. Discussion

Cobalt introduced in New Kingdom times almost disappears as a constituent of faience in the Third Intermediate period (Kaczmarczyk and Hedges, 1983: 259), at the same time when there is little evidence of glass production. Several possibilities have been proposed for cobalt's short time-span of use. Blom-Boer (1994:62 in Lee and Quirke, 2000) suggested that it may be linked to a connection between cobalt blue and the sun-cult as interpreted in the reign of Akhenaten. Lee and Quirke (2000: 111) noted that, apart from the Predynastic period, pottery was commonly painted only in the late 18th to early 19th Dynasties, and therefore the absence of cobalt as a pigment in other periods might relate more to the choice of surface than to the availability of the mineral within Egypt. To some extent, this is something substantiated by its presence on pottery of the Amarna period but not on the so-called talalat blocks in temples or the temple chapel wall reliefs of the same period (Lee and Quirke, 2000: 111). Limits on accessibility have also been considered by questioning the cobalt source itself. However, this suggests that the cobalt source is known. Although generally accepted to derive from the Kharga Oasis (e.g. Rehren, 2001), a central European provenance has also been proposed as there seems to have been more intensive Aegean-Egyptian contacts – either direct or via Syria – during the reigns of Amenhotep III and Akhenaten in the late 18th Dynasty, thereby providing the trading network for a short-lived cobalt supply from the far side of the Balkans (Lee and Quirke, 2000:111). However, there are also other locations where cobalt could have been derived. One of these locations could be the Anarak district of central Iran, which not only has deposits with the same suite of elements found in cobalt blue glasses, but has Ni and Co in close association due to its mineralisation (i.e. skutterudite) but also has variability in its associated minerals thereby explaining why the relationship between NiO and CoO prevails for both Egyptian and Mesopotamian cobalt blue glasses but only Egyptian glass exhibits linearity between CoO and MnO and ZnO. Despite these differing speculations, what is clear is that the appearance and disappearance of glass and cobalt seem chronologically linked, at least in Egypt.

The reanalyses of the glass data from the 18th and 19-20th Dynasties show quite convincingly that a lot of glass was recycled. This is particularly noticeable in the Ramesside period, suggesting that glass was no longer being produced. This recycling was probably specialised. For example, despite some contamination, glass appears to have been separated by colour before re-melting. Recycling also appears to be accompanied with dilutions using a base glass, but only to the point where the deep blue colour was unaffected. This may have been common practice, although by the 19-20th Dynasties most glass seems to have been mixed, which suggests that dilutions may have been through necessity in the later Ramesside period. This necessity appears to coincide with the disappearance of cobalt, not only for glass but for other materials, suggesting that the full suite of colours was prerequisite for the glass-making to flourish. In other words, without the basic colour palette, glass was no longer considered a valuable commodity. This is supported when it is considered that blue was the colour of supplication and 'lapis-like' was a metaphor for great riches in both Egypt and Mesopotamia (Wengrow, 2018: 32-40), with lapis lazuli itself having been part of ancient trade routes between Afghanistan and the Mediterranean from the 3rd millennium BC.

The reasons behind the decrease in the appearance of cobalt glass after 1250 BC are still debated. However, from the reanalyses presented above, it appears that it is unrelated to the alum sources of Egypt's Western Desert. The elevated alumina levels cobalt blue glass, which for so long has been used to identify the Dakhla and Kharga oases as the source of Egyptian cobalt, can be better explained by the presence of compounds in the glass associated with igneous rocks. Igneous rocks are not unique to Egypt, nor is the titania, which is found in association with the alumina. However, titania has not been detected in the alum sources. Furthermore, the low levels of K_2O, which have also been used as a discriminator for cobalt blue glass can be explained through the addition of a vitreous cobalt-rich frit with low soda, high silica and low K_2O being added to local plant-ash fluxed base glasses.

This opens up the debate about where the cobalt used in Egyptian and Mesopotamian glass derived, or more precisely where and how the cobalt frit was produced which was subsequently used as a concentrated vitreous colourant to produce cobalt blue glass.

The compositional reanalyses of both cobalt blue glass and cobalt blue frit provide some indication of potential cobalt sources. Nickel, zinc, and manganese are potentially found with the cobalt along with compounds associated with aluminium, titanium, magnesium, potassium and silicon. Concentrations of sulphur and arsenic found in the glasses and frit suggest that some of these elements were in the form of arsenides and sulphides. This suggests Co-Ni-As mineralisation within a siliceous igneous rock which contains alumina, titania, magnesia and potassium oxide. Such mineralisation is often associated with metallic bismuth, native silver and sometimes uranium in what are known as five-element ores with cobalt arsenide minerals often being associated with sphalerite (ZnS).

It is likely that interest in the five-ore system was for its visible but dispersed silver concentration rather than directly for cobalt. It should be noted that connections between silver and cobalt have been made before. Although criticised (Kaczmarczyk and Hedges, 1983), the work of Dayton (1981; 1993) attempted to link the silver-bearing cobalt ores of Erzgebirge on the Czech-Germany border (i.e. the far side of the Balkans) with Egyptian and Mycenaean glass. The criticism, however, was perhaps directed at how the connection was presented based on the limited analyses conducted rather than the fact that silver and cobalt are intimately associated in these ore deposits. Nevertheless, to quote Nikita and Henderson (2006: 76) “The information on the provenance of cobalt in Mycenaean blue provided by Dayton is confusing at best and inaccurate at worst”. This criticism, of course, does not provide any validation for Egypt’s Western desert as the source for cobalt.

To retrieve the silver from five element ores a flux, such as soda, would need to be added to the ore charge in order to melt the siliceous rock in a similar way to how glass was used to extract metals from associated minerals, in 7th century AD Islamic contexts in West Africa (Rehren and Nixon, 2014). Silica was probably added when it was noticed that the glassy phase produced was coloured blue. This scenario would explain the close compositional variation between Na_2O and SiO_2 found in the frit found at Amarna. The experimental work presented in Section 5 shows that a five-element ore can be fluxed in order to retrieve the silver and produce a concentrated cobalt blue glass slag. It was also shown that copper partitioned preferentially into the metallic phase, potentially the reason for the low association that copper has with the other components in cobalt blue frit and glass. It is proposed that this slag, the by-product of the system, was in effect a valuable and traded commodity. However, this also suggests that its availability to the glass-makers was determined directly by the accessibility to and availability of the silver-bearing ores.

This leads to the question as to why such silver-cobalt sources would suddenly become unavailable. It is here that we need to consider how, where and when silver was exploited in antiquity. Native silver or minerals concentrated enough to be smelted directly only occur in very limited quantities (Patterson, 1972) and were probably rare even in antiquity (Forbes, 1950: 169-230). This has led many researchers to assume that silver derived from argentiferous lead, such as cerussite or galena, from very early on. Meyers (2003), however, developed a model, which attempted to describe the trajectory of use of silver-based ores. This was based primarily on the empirical observation that gold levels are generally much lower in galena than in cerussite due to the gold content concentrating in the oxidised ores, i.e. cerussite. The model suggested that objects analysed with gold contents greater than 0.1% gold derive potentially from cerussite rather than galena, allowing transitions in the technologies to exploit silver-bearing ores to be identified. The transitions proposed were that silver ores (e.g. cerargyrite) were exploited first followed by oxidised lead ores (e.g. cerussite) and finally, the primary sulphide ores (e.g. galena), in line with the view that near-surface deposits would be expected to be the first exploited.

According to the Meyers' model (Figure 37), the first transition (native silver and dry silver ores to oxidised argentiferous lead ores such as cerussite) took place in the 3rd Millennium BC for the regions of Laurion/Aegean, Anatolia and Iran/Afghanistan while the second transition (oxidised argentiferous lead ores to primary ores such as galena) took place in about 1000 BC for Laurion/Aegean but not until the Arab conquest (circa 700 AD) for Anatolia and Iran/Afghanistan. Regardless of whether this tentative timeline is accurate, what it demonstrates is that already by the 1st millennium BC virtually all silver must have come from ores containing only a few thousand parts per million at most (Craddock, 2014).

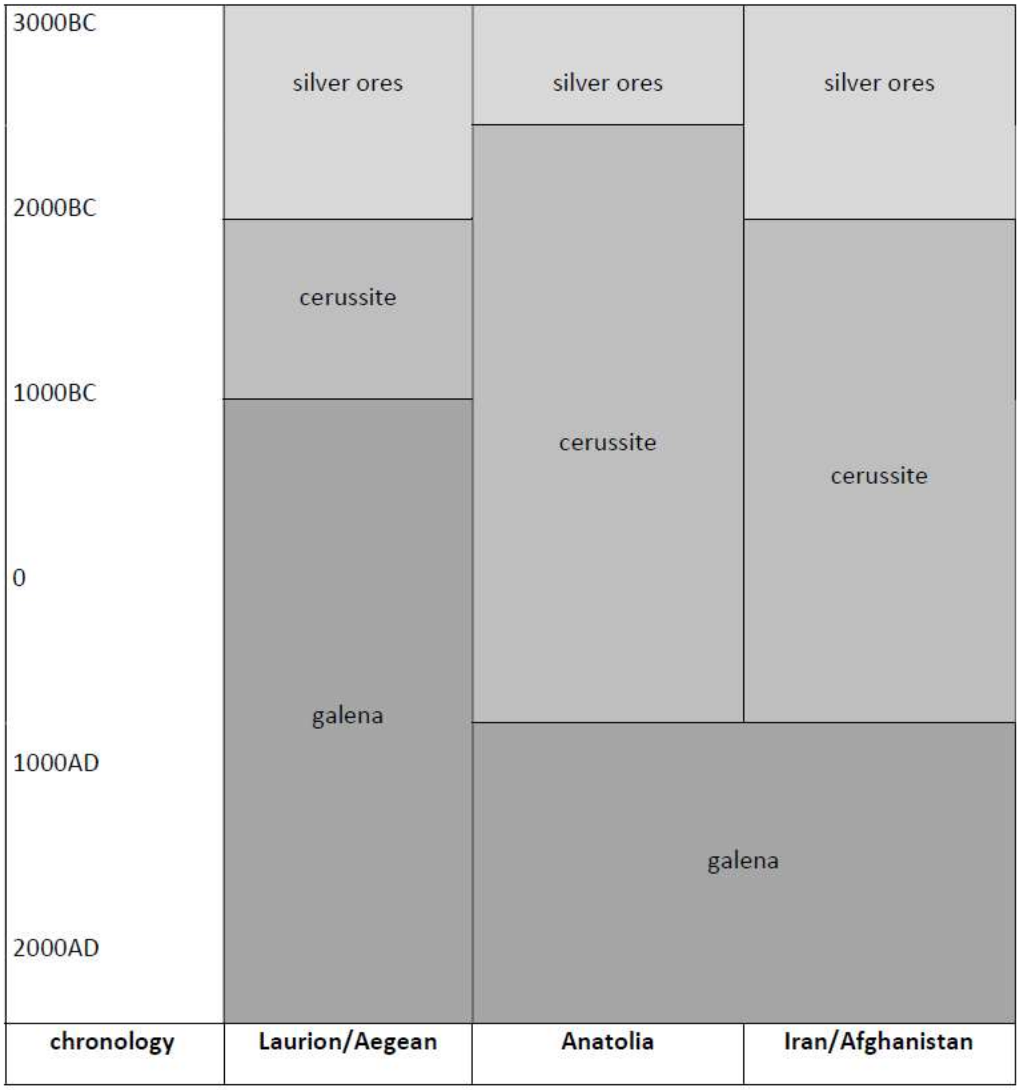


Figure 37 Visual representation of Meyers' model (2003) for the exploitation of silver ores.

As well as suggesting that surface deposits were more likely to be exploited earlier, the model also implies that extracting silver from native silver and siliceous silver ores is relatively straight forward compared to the extraction of silver from argentiferous lead, which was in effect the first time that trace amounts of one metal were separated from another. On first inspection, this would seem to be true, with the process of cupellation, by which the argentiferous lead was subjected to an oxidising blast at around 1000°C, oxidising the lead to litharge (PbO) but leaving small quantities of silver as a separate metal phase, being a more complex operation that direct melting or smelting. Although evidence of this operation has been found from 3300 BC (Pernicka et al., 1998), the issue here is not when argentiferous lead ores were first exploited, but that certain ores were exhausted, thereby reducing the number of feasible methods to acquire silver.

As mentioned earlier, Smith (1967) argued that the earliest silver objects were made of native metal or of cerargyrite, both of which form silver on melting under a cover of charcoal. Such a method is true for relatively pure silver ores containing large crystals of the silver mineral. However, native silver and siliceous ores are not only present as wires and large crystals but also as plates over quartz, as dendrites inside quartz fissures, and as grains, scales and as tiny groups of crystals within volcanic basalt minerals such as plagioclase ($NaAlSi_3O_8$ – $CaAl_2Si_2O_8$), i.e. minerals with appreciable alumina concentrations. Native silver, for example, is well known to often be mixed with quartz (Bastin, 1922). This suggests that even though the silver may be visible to the naked eye, unless it is possible to separate out by mechanical means (e.g. concentrating by selecting the purest ores and/or by crushing and milling to extract silver or silver minerals), extraction requires the removal of the surrounding siliceous matrix. This requires smelting the ores at high temperatures in a furnace with a flux to reduce the melting point of the silica matrix, i.e. silver is unlikely to be extracted completely from the host mineral over a simple charcoal fire.

In effect, this suggests another early transition is required in Meyers's model: once the relatively pure and mechanically refineable silver minerals had been exhausted, there would have been a need to extract potentially visible silver/silver minerals that were embedded and dispersed within a siliceous matrix. To place this transition onto the timeline mentioned above, it would have been most prodigiously applied after the exhaustion of native silver and easily accessible dry silver ores, and before the purposeful exploitation of argentiferous lead-bearing ores such as cerussite and galena. In other words, it probably occurred around the same time as when cerussite began to be exploited, reflecting the need to employ more complicated processes to maintain the demand for silver, i.e. around the middle of the 2nd millennium. Moreover, considering that it later became more judicious to exploit cerussite and galena, suggests that the exploitation of these increasingly difficult to exploit native and dry silver sources had a limited time-frame.

Evidence for the use of native silver or siliceous silver ores is generally indirect. As described above, Meyers uses gold levels as a proxy to assign silver to silver ore types. However, it should be noted that despite the limited amounts of Egyptian silver (and the even fewer analyses that record elements other than silver, gold and copper), early Egyptian silver is often effectively lead-free (Mishara and Meyers, 1974: 29-45). This could suggest that some silver, deriving from the five-element ore deposits, travelled with the cobalt. Despite low lead levels (i.e. most Egyptian objects on the Oxalid database (2018) have <0.1%Pb; Mishara and Meyers, 1974:29-45), the low gold levels have led to the suggestion that Egyptian silver which was not from an electrum source, must have derived from argentiferous galena (e.g. Gale and Stos-Gale, 1981[1]; Gale and Stos-Gale, 1981[2]). However, if the data is taken at face value, the absence of lead is more indicative of native silver or silver-bearing ores which do not contain lead, unless the cupellation process was so sophisticated to remove all the lead (as it may have been in later periods). As mentioned earlier, the silver from Early Bronze Age silver objects recovered at Ur were interpreted to have originated from a fahlore (Salzmann et al., 2016), similar to the mineralisation found at five element deposits in central Iran, objects which suggested a silver, copper, lead and zinc mineralisation, as well as traces of cobalt. However, this silver is still viewed as product of cupellation despite lead levels being as low as 0.1% for some samples (Salzmann et al., 2016). Furthermore, in Egypt there is very little evidence of any metal being added deliberately to silver at this time. The copper concentration of ancient Egyptian silver has levels below that required to improve the mechanical properties (<5%) until the Late period. This suggests that silver was not intentionally alloyed at all, which along with the absence of lead could be interpreted as deliberate avoidance of contaminating silver (Ransom Williams, 1924: 28-30), in a similar fashion to how tin-bronze was resisted in Egypt until the 2nd millennium BC and, even at that time, was accorded a lower value to pure (unalloyed) copper (Wengrow, 2018: 94). There is also no evidence that Egypt went through the stage of using coarse alloys of silver and lead as found on Cyprus (about 2000-1500 BC) (Ransom Williams, 1924), which could suggest that silver used in Egypt derived from native silver or siliceous silver ores throughout the New Kingdom period. Moreover, lead isotope analyses show that some Egyptian yellow and red glass is consistent with Mesopotamian glass from Tell Brak and Tell Rimah, glass from Susa and ores, litharge and slag from Iran, as well as silver recovered in Egypt, Sidon, Ur and Syria, copper and lead objects recovered at Amarna and green frit from El Rakham in Egypt (Figure 28). Thus, silver could have travelled from Iran to Egypt along with yellow glass, cobalt-blue glass and frit perhaps using similar trade routes to those for lapis lazuli from Afghanistan.

In essence, the arguments presented above suggest that the exhaustion of easily accessible silver provoked a need to exploit native silver and silver minerals in visible but less accessible sources. This resulted in the production of cobalt blue frit as a by-product of this extraction process. This vitreous concentrated colourant was used to colour base glasses across the ancient world, until even these less accessible silver sources became depleted. The demand for silver was maintained by exploiting argentiferous lead ores and eventually jarosite from south west Iberia. New sources of cobalt, however, were not utilised for glass for another five hundred years.

7. Concluding Remarks

It should be noted that there are very few convincing explanations for the unusual composition of cobalt-blue glass, with respect to other colours. Furthermore, there are very few attempts to explain the disappearance of glass from the archaeological record at the end of the LBA. What has been shown here is that the cobalt blue colourant connects these two issues. Furthermore, the exhaustion of easily accessible silver-bearing ores, thereby requiring the expeditious exploitation of less accessible silver sources, potentially resulted in the development of a system where the by-product was also a valuable commodity. Cobalt frit as a transportable and valued commodity is verified to some degree in the illustration in the *Annals of Thutmosis III* at Karnak (Figure 1). Here, the king lists glass after gold and silver, suggesting its importance (Nolte, 1968: 12-13). Some of the glass is seen as circular pieces of fairly consistent size, perhaps ingots, while other pieces are shown as irregular lumps. 60 kilograms of the dark blue glass is represented as ingots, with an additional 55 kilograms appearing as lumps, for a total of 115 kilograms (Bianchi, 2002: 20). This could suggest that two forms of dark blue glass were travelling: coloured ingots and concentrated vitreous colourants (i.e. frit). Furthermore, the fact that the Hurrian and Akkadian words *ehlipakku* and *mekku*, recorded in the Amarna letters regarding the 'stones-of-casting', were both used to denote glass (Oppenheim, 1973), not only suggest that New Kingdom glass was a foreign import, but may also hint at the two distinct forms which were imported to Egypt (possibly as tribute), along with other raw materials including lapis lazuli, malachite and silver, from an unknown land after Thutmosis III's campaigns into the Near East from the middle of the 15th century BC. This unknown land may have been in modern-day Iran, where native silver ores in association with cobalt were exploited, exported and exhausted within time frame of the New Kingdom.

The repercussions of the cobalt colourant for ancient glass deriving from the Near East will clearly have ramifications on how ancient trade networks worked. The glass found at Mycenae and on the Uluburun, for example, may have been made with base glasses from Egypt, but the cobalt required to provide value to this glass required interactions with those regions exploiting five-element ores for both silver and cobalt. As the five-element ores in Iran appear to have a compositional signature consistent with the elements found in ancient glass of both Egypt and Mesopotamia, this region must therefore re-emerge as a potential source for the concentrated cobalt frit.

The transition from native silver to argentiferous lead sources reflects the exhaustion of easily extracted silver, which in turn affected the production of cobalt blue frit in the form of slag. The exploitation and exhaustion of these cobaltiferous silver-bearing ores would have been sandwiched between the exploitation of easily extracted silver from native silver and dry silver sources and those requiring the smelting and refining of silver from argentiferous lead. This suggests a short flowering of these sources before they were exhausted, in a similar fashion to cobalt glass' sudden arrival and departure in the New Kingdom period in Egypt, and its limited presence in the archaeological record from Mesopotamia. In essence, the depletion of cobalt resulted in a decrease in glass production and an increase in recycling after the 18th Dynasty until both cobalt and glass almost completely disappear around 1250 BC.

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