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Mediterranean Archaeology and Archaeometry
Vol. 20, No 1, (2020), pp. 45-57
Open Access. Online & Print.

DOI: 10.5281/zenodo.3605660

IDENTIFICATION OF COBALT-COLOURED EGYPTIAN GLASS OBJECTS BY LA-ICP-MS: A CASE STUDY FROM THE 18TH DYNASTY WORKSHOPS AT AMARNA, EGYPT

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Received: 23/10/2019
Accepted: 14/01/2020

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ABSTRACT

This paper presents the elemental composition of a representative group of glass-working and -production samples from Amarna in the collection of the Ägyptisches Museum und Papyrussammlung Berlin, obtained by quantitative laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). These analyses were carried out to verify the results from a set of on site analyses of glass objects at Amarna, carried out by pXRF. The main research question of this study was whether the various sources of Co-ore can be identified using transition metal data from pXRF analysis only. The 40 samples from the Berlin collection were confirmed as belonging to the group of Type A, Co- and Co-Cu coloured glass objects, produced in the Egyptian 18th dynasty, coloured with cobalt-containing ores originating from the western desert in Egypt (close to the Dakhla and Kharga Oases). The element composition revealed correlations between Co and Al, Mn, Fe, Ni and the REEs. However, the major, minor and trace element composition revealed no further distinction between the various workshops in the collection, indicating that similar recipes and raw materials were used in the workshops at Amarna. Thus, quantitative pXRF using Co, Ni, Mn and Zn concentrations alone, such as by pXRF, can be used as an indicative instrument for provenancing cobalt in glass objects, directly on site of objects that cannot be removed from a site or a museum collection.

KEYWORDS: Glass, cobalt, Egypt, Amarna, Late Bronze Age, LA-ICP-MS, pXRF

1. 1. INTRODUCTION

1.1. Cobalt-coloured glass

This paper presents and discusses the results of a set of 40 Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) analyses carried out on a group of glass-working and -production samples from Amarna from the collection of the Ägyptisches Museum und Papyrussammlung Berlin, without a finer archaeological context, and two samples of cobalt ore. The analyses were carried out at the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) at GFZ Potsdam. These analyses were carried out in order to verify the results from a set of analyses carried out by portable X-Ray fluorescence (pXRF) on c. 370 well-provenanced glass objects at Amarna (Hodgkinson *et al.* 2019a and 2019b). The main research question of each set of analyses was the provenance of the cobalt colourant, which can be established based on a transition element pattern comprising Ni, Mn, Zn, and Al.

During the Egyptian 18th dynasty, blue Co-coloured glass was very popular and was worked into jewellery and core-formed vessels. Even though two production sites, Malqata and Amarna, are well known, the sources and trade routes for the cobalt ores remain unconfirmed. This study aims to investigate possible geographical variations in the Co-ores used for glass production in Amarna.

Cobalt ore was mined and processed to be used as a colourant in the manufacture of glass, faience and blue-painted pottery during the Egyptian 18th dynasty (c. 1550–1292 BC). Co-coloured glasses have a mid- to dark blue colour, which was very popular during this period. During this time, glass was manufactured and worked predominantly at two sites, Malqata and Amarna (Fig. 1), the latter being the focus of the present investigation. Dark blue glass in particular, was produced to imitate the semi-precious stone lapis lazuli, and it was worked into core-formed vessels and jewellery. In addition, much raw glass was found at Amarna, indicating that it was being produced in local workshops. In fact, evidence of primary glass production at Amarna has been identified by two independent studies: Jackson and Nicholson (2007), on archaeological material excavated at Amarna site O45.1, and Smirniou and Rehren (2011), on material housed in the Petrie Museum of Egyptian Archaeology, London.

LA-ICP-MS is not available when samples cannot be transported to a laboratory, necessitating on site analyses of LBA coloured glasses from Egypt. For this reason, the quantitative LA-ICP-MS results were compared with data obtained by semi-quantitative, portable X-ray fluorescence. For the transition metals (Mn, Co, Ni and Zn) the results from both methods are in agreement, and based on those elements alone, a differentiation between the LBA sources is possible.

The Egyptian Museum and Papyrus Collection in Berlin (ÄMP) houses an extensive collection of glass objects, both finished and indicative of glass-processing, from Amarna, which had been brought to Berlin subsequent to the 1911–1914 excavations at Amarna carried out under the direction of Ludwig Borchardt on behalf of the Deutsche Orient-Gesellschaft (Borchardt and Ricke 1980). Unfortunately, most of these have lost their specific find locations. However, these objects are still very useful for comparative analytical purposes such as the one outlined below.

1.2. Allocations of artefacts with archaeological sites

By means of chemical analysis focussing on transition metals such as Ni, Mn, Zn, which correlate with Co and other elements that entered the batch mixture through the addition of processed cobalt ore, it has been possible to distinguish between types of cobalt mines exploited in various geographical regions used in antiquity (Kaczmarczyk 1986, Shortland *et al.* 2006, Abe *et al.* 2012, Smirniou and Rehren 2013). While it is not certain whether the processing of the cobalt ore took place at the mine or at the workshop, Shortland and colleagues have established by means of experimental archaeology that the ore was most likely mixed with water and an alkali. The resulting precipitate of this process subsequently provided the blue colourant which was added to the glass (Shortland *et al.* 2006, pp. 159–162). It has been suggested that copper (Cu) was also present in the cobalt alum as a transition metal, although quantities vary in samples analysed by Smirniou and Rehren; therefore it may also have entered the glass mixture in a secondary process (Smirniou and Rehren 2013, pp. 4738–4739). Glass objects analysed by a number of scholars date to various chronological periods within the Late Bronze Age (LBA) and come from a variety of sites. The following types of cobalt have been identified, although not all of these areas have been located, the only known Egyptian geographical source being that located in the area of the oases Kharga and Dakhla in the western desert of Egypt.

- Type A: used in the 18th dynasty, from the western desert (Dakhla and Kharga Oases, Fig. 1).
- Type R: used in the Ramesside period (c. 1292–1069 BC), from an unknown - possibly Iranian - source; low in Zn (Abe *et al.* 2012).

- Type N: used in the Ptolemaic / Roman Period (post 332 BC) – source unknown. Two variants exist, both of which are low in Ni, and high or low in Co, and high or low in Mn (Abe *et al.* 2012).

Two groups (2a and 2b) defined by Walton and colleagues, as having been used in cobalt-coloured axes and other dark blue glass objects from the Mesopotamian site of Nippur (Walton *et al.* 2012; Fig. 1). Both of these groups are low in Ni, Mn and Zn, while one of them (group 2b1) is high in As and group 2 overall is high in Pb. The source of the cobalt ore used in these glass objects has not been located; it differs, however, from the Egyptian cobalt.

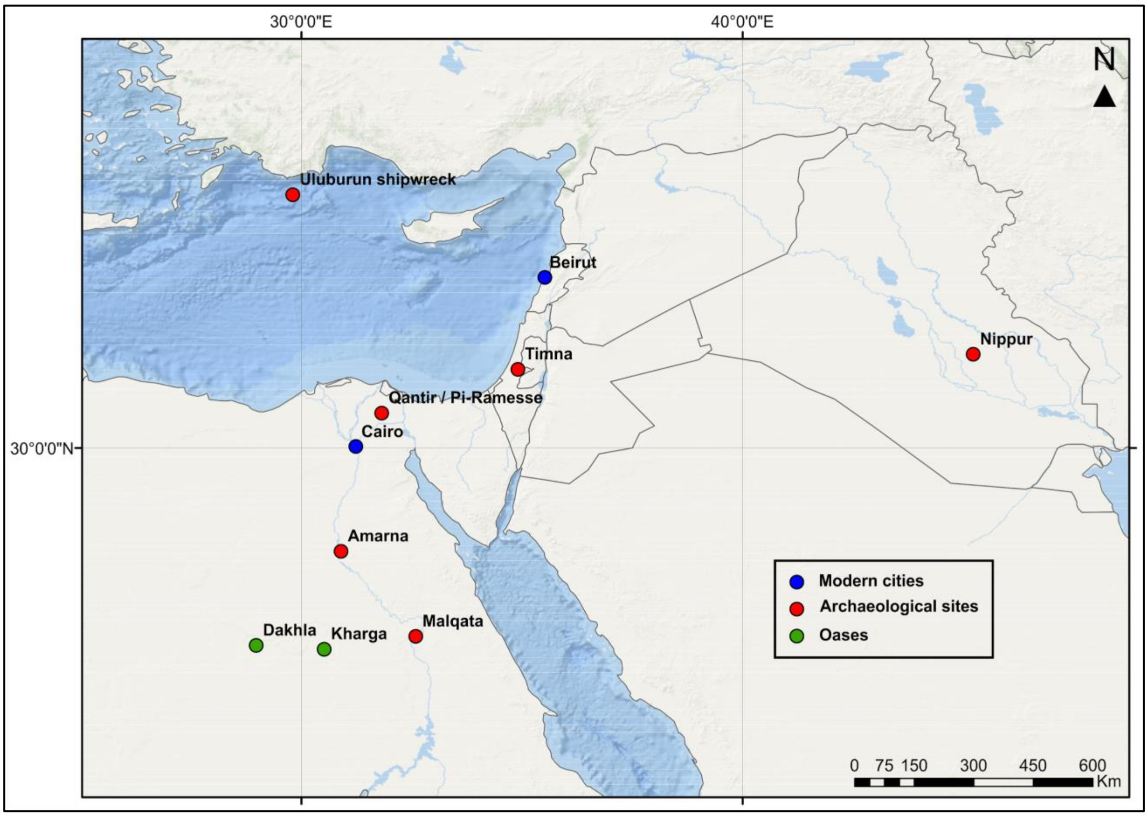

Figure 1: Map showing archaeological sites mentioned in this paper. Map source: ARCGIS with 'World Countries' by Esri, DeLorme Publishing Company, Inc. and World Ocean Base' by Esri, GEBCO, NOAA, Garmin, HERE, and other contributors. GPS locations from archaeological sites are from 'ANE Placemarks for Google Earth' by Pedersén 2015.

This distinction has been possible by means of both laboratory-based analytical techniques, but also by portable X-Ray fluorescence (pXRF). Abe and colleagues achieved the quantification of some light elements using a custom-designed pXRF device (Abe *et al.* 2012; see also an archaeometry overview including glass in Liritzis *et al.* 2020).

Another recent study carried out by pXRF on well-provenanced material from various workshops at the Middle Egyptian site of Tell el-Amarna has identified the use of cobalt ore from the western desert (Type A), albeit with variations in the clustering of transition metals in the material found at different workshop sites within the ancient city (see Hodgkinson *et al.* 2019a and 2019b). A loose clustering of data points with regard to the transition metals may therefore indicate the use of cobalt ore from a greater variety of geographical sub-sources or from an ore source with greater chemical compositional variations. This was found to have been the case in the workshops located in the Main City South at Amarna. The material from the workshops located in the Main City North formed tighter clusters, which may possibly demonstrate that they used less cobalt and came from fewer geographical sub-sources (see Fig. 2).

pXRF, however, does not usually deliver any quantitative information regarding light and trace elements, which may add valuable information for the identification of the various types of cobalt, including a possible sub-division of types. The Egyptian antiquities law prohibits the export of any archaeological samples from Egypt, thus the analysis of the artefacts needs to be done on site. There are two strategies for quasi non-destructive element composition analysis, either using a handheld XRF spectrometer on site or using an LA-ICP-MS laboratory in Egypt.

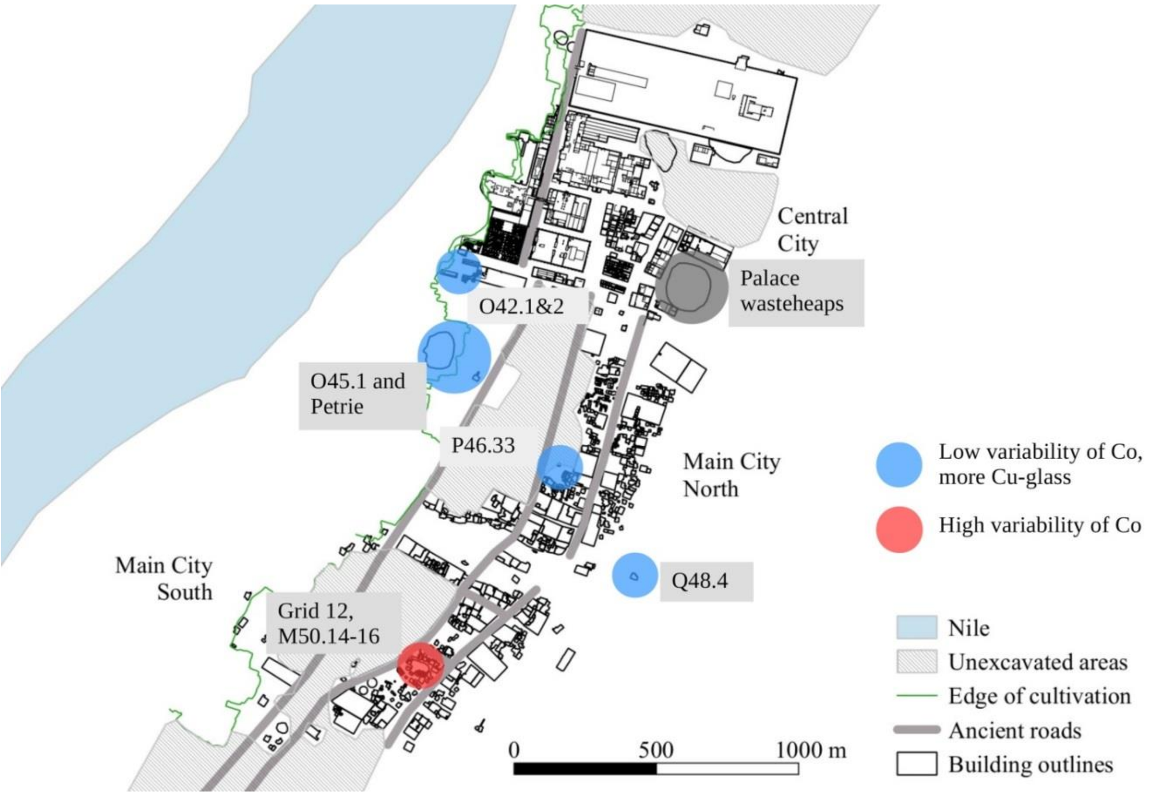

Figure 2: Map of Amarna showing the workshop sites, the material of which was analysed on site by pXRF, and the resulting information regarding variety (see Hodgkinson et al. 2019a and 2019b).

1.3. Allocations of artefacts with archaeological sites

The main purpose of the present study is to establish the reliability of the results obtained from the pXRF study mentioned above (Hodgkinson *et al.* 2019a and 2019b), thus providing proof of concept for further analyses of archaeological material that cannot be removed from the site by pXRF. Therefore, the data presented here does not include the analysis of well-contextualised objects from Amarna.

This study furthermore fulfils the purpose of identifying the usefulness of light elements and rare earth elements in the identification of the various types of cobalt. For this reason, the focal analyses of this study will be the correlation between Co and the transition elements (Ni, Mn and Zn) and elements lighter than Si. In addition, principal component analysis (PCA) will be conducted in order to detect groups of objects of specific compositions.

A set of 40 objects was selected for LA-ICP-MS analysis at the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) at GFZ Potsdam. The results of these analyses, which include light, trace elements, and transition metals, are presented in this study, and compared with published data from other Ancient Near Eastern and Egyptian sites from the LBA in order to enhance our understanding of the chemical properties and characteristics of cobalt in LBA glass in Egypt (Shortland *et al.* 2006; Shortland *et al.* 2007; Smirniou *et al.* 2012; Rehren unpublished; Jackson and Nicholson 2010; Anastassiades and Ellis 2008/Brill 1999b); Walton *et al.* 2009; Walton *et al.* 2012).

2. MATERIALS AND METHODS

2.1. *Samples*

A total of 40 mid- to dark blue glass objects were obtained from the collection at the ÄMP including two colourless raw glass objects for comparison as a base glass mixture (Fig. 3, see Hodgkinson and Frick 2020, Table S1 for individual results). These objects are almost colourless, showing only a tinge of light blue (ÄM 39979) or light green (ÄM 39978) (see Shortland 2012, pp. 25–26 and 104–105 on the topic of colourless glass from LBA Egypt). In addition, two samples of cobalt ore from the region of Ain Asil, near Dakhla oasis, were also included in the analysis. These samples, which had initially been collected by A. Kaczmarczyk and supplied to the authors by A. Shortland (samples K-3 and K-6 as published in Shortland *et al.* 2006), consist mainly of pickerinite, an aluminium sulphate. The 40 analysed objects form a representative sample of glass-working and -production related objects from Amarna in the collection of the ÄMP. Both translucent and opaque glass objects were selected for analysis, the opaque objects being opacified with antimony (Sb).

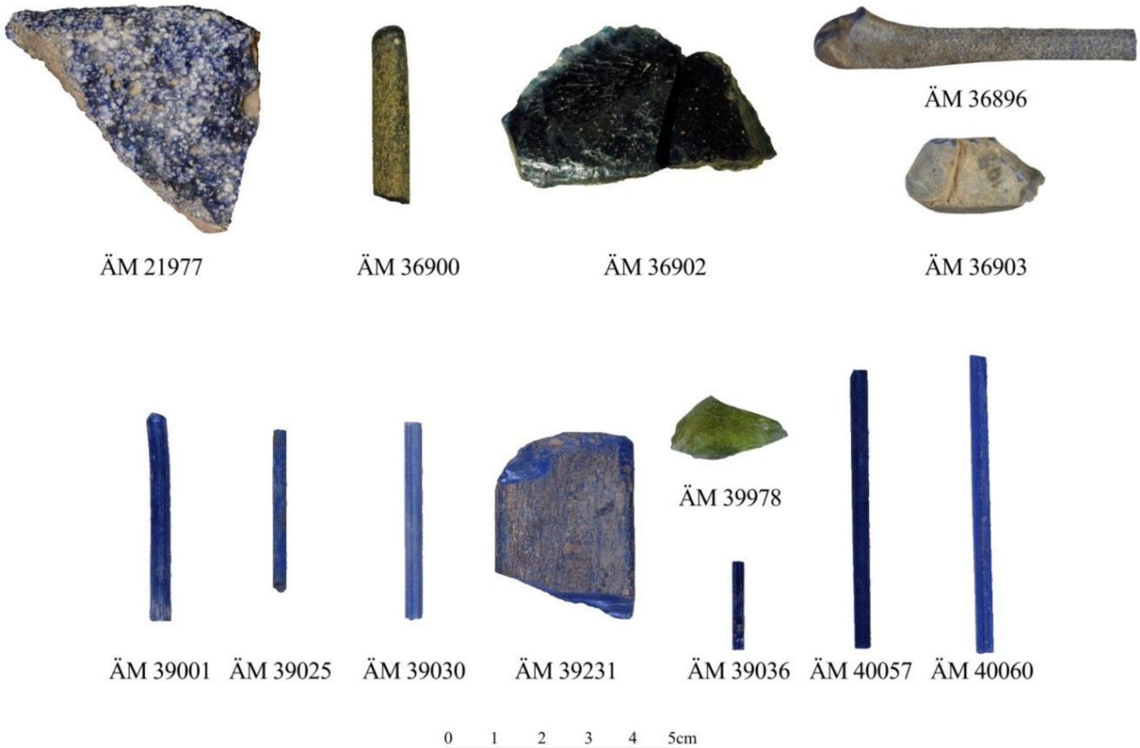

Figure 3: Glass- and glass-working related objects from Amarna in the Egyptian Museum and Papyrus Collection, National Museum in Berlin. © Ägyptisches Museum und Papyrussammlung, Staatliche Museen zu Berlin. Photographers: Anna Hodgkinson und Sandra Steiß (see Table 1).

2.2. *Trace element analysis by LA-ICP-MS*

Major, minor and trace elements were analysed using an Analyte Excite (Teledyne Cetac Technologies, Bozeman, USA) coupled to an iCAP rq (ThermoFisher Scientific, Bremen, Germany). LA and ICP-MS were tuned daily for highest sensitivity, while maintaining a $^{238}U^+/^{232}Th^+$ ratio on NIST SRM610 close to 1 and $^{232}Th^{16}O^+/^{232}Th^+$ below 0.7%. Instrument settings for LA and ICP-MS are reported in the supplement in Table S1.

The surfaces of the samples were cleaned with *i*-PrOH and lintless wipes to remove possible contamination. The glass rods were analysed along the length of each rod, avoiding possible cross sections where contaminations from manufacturing tools (e.g. tweezers for cutting and pulling the rods) may have been deposited. Glass rods, ceramic with glass and ore samples were analysed as provided, without the weathered surface being removed. From samples ÄM 21977, ÄM 36902/001 and ÄM 39231 small parts were chipped off and fixed on a PMMA microscope slide using double sided tape. Each sample was analysed at least twice on opposite ends. Data evaluation for chemical composition analysis was carried out in StalQuant, a Python-based program, to quantify large numbers of LA-ICP-MS data (Fricker 2012). Modifications to the original StalQuant code were made in order to allow direct import of iCAP-Qc data. NIST SRM610 was used as an external standard, while differences in the ablation yield were corrected by means of a 100% weight oxide approach (Liu *et al*. 2008). For the two ore samples consisting of two phases, granular kieserite and/or pentahydrite, and pickeringite, Al was used as an internal standard, with the concentration reported by Shortland *et al*. (2006). Reference values for standard reference materials were taken from Jochum *et al*. (2011) and the GeoReM database from Jochum *et al*. (2005). Precision and accuracy within each analytical sequence were estimated from the repeated determination of Corning-A, Corning-B, NIST SRM612, and NIST SRM614, each being treated as an unknown sample. Typically, the accuracy and precision were better than 10% for most reported elements (see Table S2 for element specific remarks). Results not reported were those below the limit of quantification (LOQ), see (Longerich et al. 1996) for the LOQ estimation for LA-ICP-MS.

2.3. *Classifications and statistical analysis*

The samples investigated in this study were classified according to the dominant blue colourant used in the glass mixture based on Smirniou and Rehren (2013, p. 4632, see Fig. 4).

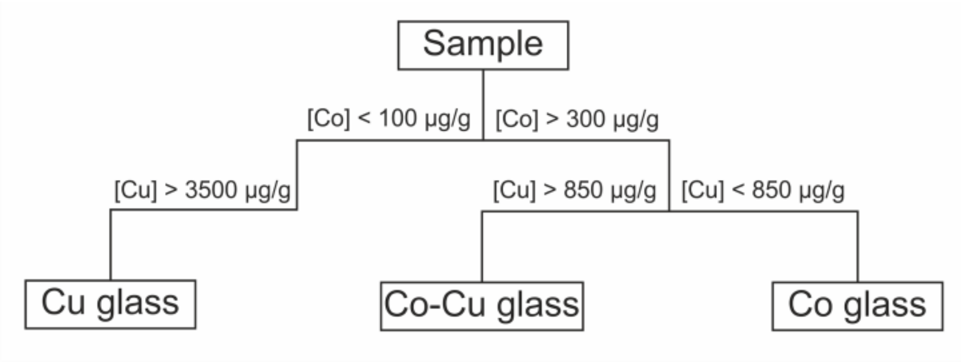

Figure 4: Classification of Co and Cu coloured glasses according to Smirniou and Rehren (2013).

The investigated samples were additionally classified according to their period of manufacture. For this, a combination of three element concentration (Co, Ni, Mn and Zn) was normalised, plotted in ternary diagrams and compared with characterised sample groups from the literature (Type A, Type R, Type N and Types 2a and 2b from Nippur, the latter having been included in order to highlight the differences between the various types of Co-ore). Concentration data from other ancient Near Eastern and Egyptian sites from the LBA were obtained from the literature, mainly, from Walton *et al.* 2012, Anastassiades and Ellis 2008, Shortland *et al.* 2007, Smirniou and Rehren 2013, and Brill 1999b. The characterised sample groups from the literature and the obtained concentration data from the ÄMP samples were statistically processed in R using principal component analysis.

3. RESULTS

An overview of the analysed samples including photographs and additional information from the collection as well as the measured chemical composition are available in Hodgkinson and Frick 2020: Table S1.

On sample ÄM 36896 two different parts of the object were analysed: Along the weathered rod and on the cross section, where a tool was probably used during the glass processing to pull or cut the hot glass. ÄM 36896-1 (cross section) shows 9-times increased concentration of Cu and Sn compared to the side of the glass rod (ÄM 36896-2).

Table 1: Objects included in the present study and colourants detected.

Object ID	Object type	Colourants	Object ID	Object type	Colourants
ÄM 21977	potsherd with frit	Co	ÄM 39035	rod	Co
ÄM 36902/001	ingot fragment	Co	ÄM 39036	rod	Co-Cu
ÄM 36900	rod	Co-Cu	ÄM 39037	rod	Co
ÄM 36896	rod	Co-Cu	ÄM 39038	rod	Co
ÄM 36903	ingot fragment	Co	ÄM 39039	strip	Co-Cu
ÄM 39000	rod	Co-Cu	ÄM 39040	strip	Co-Cu
ÄM 39001	rod	Co	ÄM 39231	bar	Co-Cu
ÄM 39021	rod	Co-Cu	ÄM 39240	slag	Co-Cu
ÄM 39022	rod	Co-Cu	ÄM 39834	lump	Co
ÄM 39023	rod	Co-Cu	ÄM 39978	fragment	colourless
ÄM 39024	rod	Co-Cu	ÄM 39979	fragment	colourless
ÄM 39025	rod	Co-Cu	ÄM 40043	rod	Co-Cu
ÄM 39026	rod	Co-Cu	ÄM 40052	rod	Co-Cu
ÄM 39027	rod	Co-Cu	ÄM 40055	rod	Co-Cu
ÄM 39028	rod	Co-Cu	ÄM 40057	rod	Co-Cu
ÄM 39029	rod	Co-Cu	ÄM 40060	rod	Co
ÄM 39030	rod	Co-Cu	ÄM 40067	rod	Co
ÄM 39031	rod	Co-Cu	ÄM 40073	rod	Co-Cu
ÄM 39032	rod	Co-Cu	ÄM 40088	rod	Co-Cu
ÄM 39033	rod	Co-Cu	K-3	cobalt ore	-
ÄM 39034	rod	Co	K-6	cobalt ore	-

3.1. *Colour classification*

Based on the classification carried out by Smirniou and Rehren (2013, p. 4632) and our refinement (see Fig. 4), the samples were classified according to the colourants used in the glass mixture (Table 1). All analysed blue samples are either Co- or Co-Cu coloured glass objects.

3.2. *Period classification*

All objects analysed in this study fall, in ternary diagrams (Co-Ni-, Co-Ni-Mn and Ni-Mn-Zn) into the same cluster belonging to Type A cobalt (Fig. 5). This cluster lies in the range of relatively low Ni, medium Co, Zn and medium to high Mn. The group of objects from Amarna can be distinguished from, and overlap with other, contemporary LBA Co-coloured glass objects analysed by other scholars. As a comparison, these have been included in fig. 5: Co-coloured glass from the slightly earlier Malqata (Shortland *et al.* 2007), from Mycenaen Greek sites (Walton *et al.* 2009, Smirniou *et al.* 2012), the glass ingots found onboard the Uluburun shipwreck (Anastassiades and Ellis 2008, data taken from Brill 1999b), and the one object found at the ramesside site of Qantir / Pi-Ramesse (Rehren, unpublished, reported in Smirniou and Rehren 2013) fall into the same correlation cluster as those from Amarna, indicating the use of Co ore from the same general geographical source, namely the western desert of Egypt. This is also reflected in the fact that the average values measured by LA-ICP-MS as part of the present study for the two Co ore samples, K-3 and K-6, also fall within this range. This is in agreement with what has been reported by Shortland *et al.* (2006) and Abe *et al.* (2012). Even the Co-Cu coloured glass objects can be found to adhere to this pattern, although more loosely. By contrast, Co-coloured glass found at the Mesopotamian site of Nippur (Walton groups 2a and 2b) is generally lower in Mn, Ni and Zn than Type A. No cobalt belonging to Type N appears to have been used.

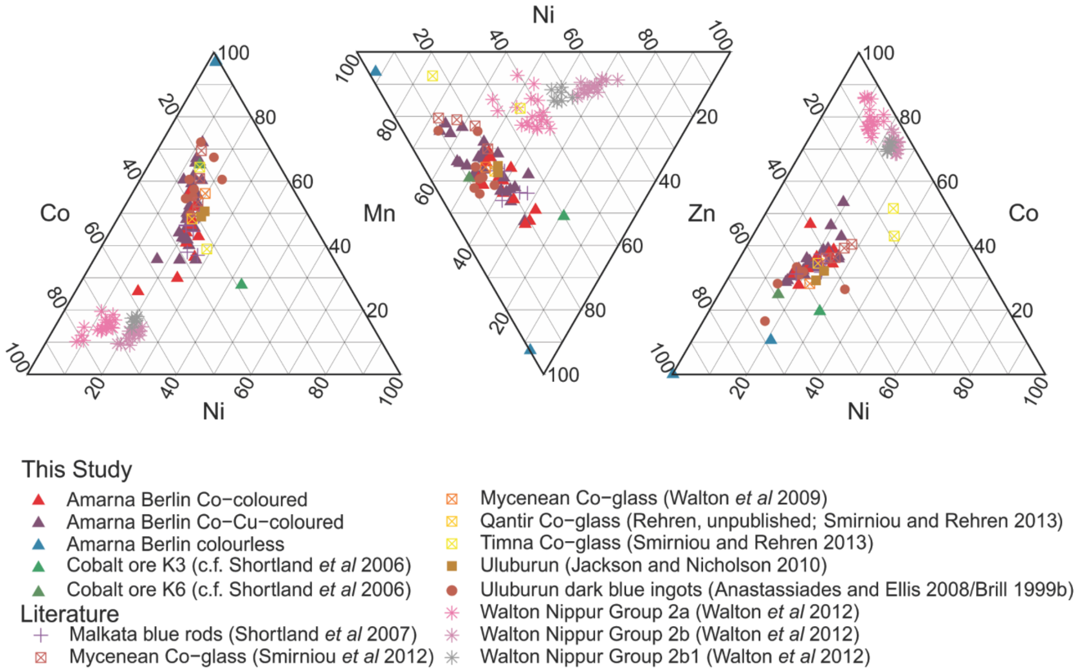

Figure 5: Ternary diagrams showing the correlation between Co and the transition metals, Ni, Mn and Zn for the analysed glass objects from Amarna in the ÄMP and other LBA sites (literature).

The comparison of the ternary diagrams based on the correlation of the transition metals Co, Mn and Zn, with Ni, for both Co- and Co-Cu coloured glass objects, and for the results from both the pXRF and the LA-ICP-MS analyses (Fig. 8) shows that the distribution pattern is similar. This demonstrates that the pXRF data obtained for Co, Ni, Zn and Mn for the well-provenanced objects on site is reliable in terms of their correlation.

By using a purpose-built pXRF device with vacuum conditions, Abe and colleagues were able to detect and semi-quantify Mg, Al and K. This has not been possible to achieve with the ELIO device used for the previous study. By plotting the correlation of CoO to Al_2O_3 (both in wt%), it was possible to differentiate between the Type A (18th dynasty) and the Type R (ramesside) cobalt used in glass objects (Abe *et al.* 2012, p. 1804).

We found that CoO does not correlate with MgO, NaO or K_2O. K_2O is overall higher in the Nippur group 2 glass objects, which is generally the case with LBA glass objects coloured with cobalt rather than Type A from the Egyptian western desert. This is possibly caused by the use of a different plant ash from the one used in Egypt and/or different geological source materials (Shortland 2012, p. 135).

However, as has already been found to be the case with the transition metals, a strong correlation between CoO and Al_2O_3, as well as with Fe_2O_3, can be observed in the objects from Amarna (Figs. 6A and 6B). As has been shown by Abe and colleagues, the proportion of Al_2O_3 observed in the composition of objects using Type A cobalt ore from the western oases of Egypt is greater than in objects coloured with Type R cobalt ore, which was an aluminium-depleted ore from a from a different, unknown source, used during the Ramesside Period in the Memphite region (Abe *et al.* 2012, p. 1805). The objects from Mycenaean Greece, Timna and the Uluburun shipwreck, which do fall into the Type A range with regard to only transition metals, are lower in terms of Al_2O_3, indicating a slightly different, less Co-rich sub-source of Type A cobalt ore. The Nippur objects are generally higher in CoO, and their Al_2O_3 content is not very variable, indicating a more homogenous, albeit unknown, source of cobalt ore. However, Rehren discusses the issue of adding (unprocessed) Co-ore to the glass mixture and the different melting temperatures of the contained salts, which results in different ratios of MgO to Al_2O_3 in both the ore and the finished glass, and this has to be borne in mind when discussing this data (Rehren 2001, pp. 484–485).

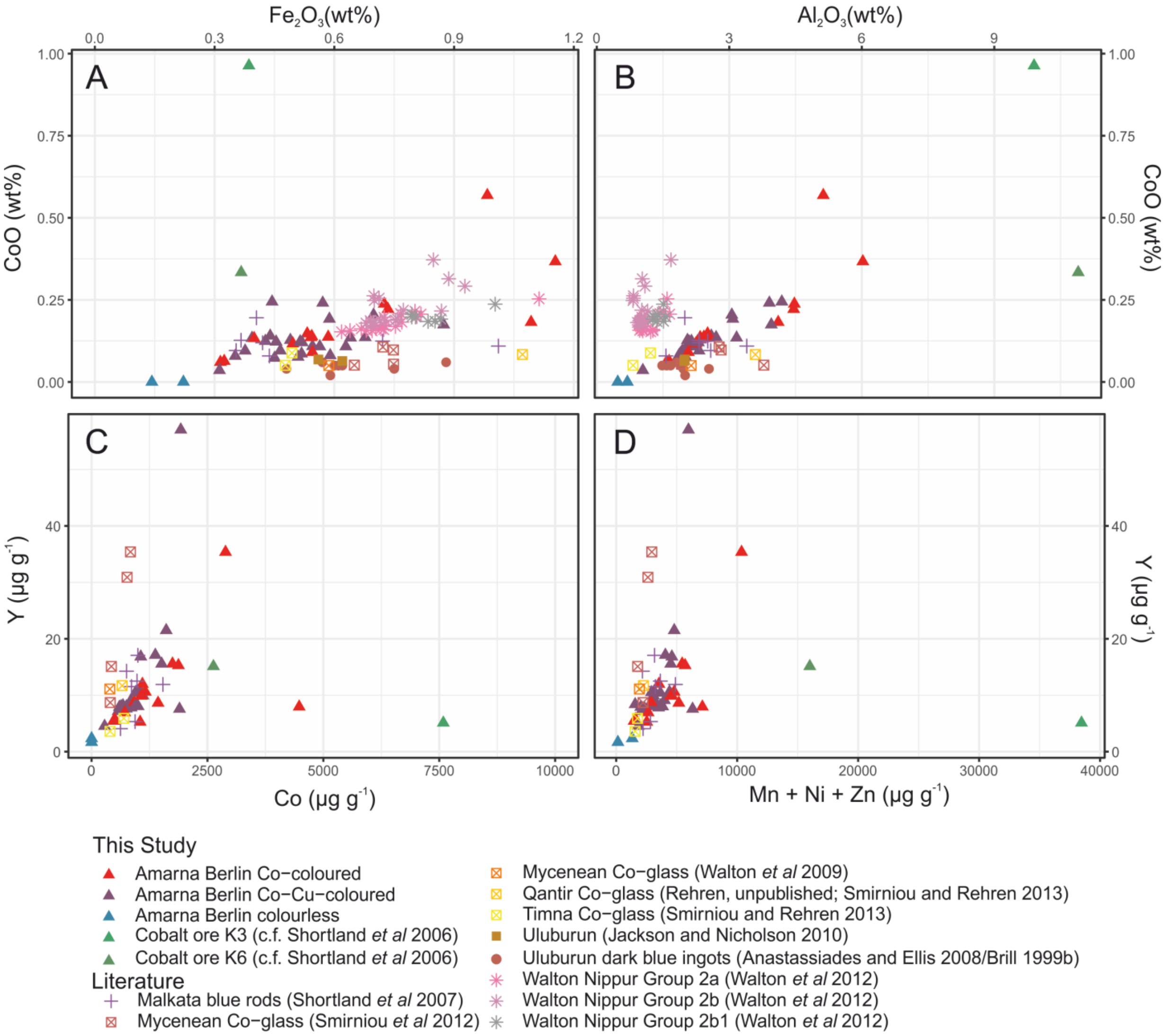

Figure 6: Correlation between CoO and Al_2O_3 (A) and Fe_2O_3 (B) and plot showing the positive correlation of Y with Co (C) and the sum of the transition metals Mn, Ni and Zn (D).

The correlation between CoO and Fe_2O_3 (Fig. 6B) demonstrates that the objects from Nippur form a semi-tight cluster, and that they contain more CoO and Fe_2O_3 compared to the Egyptian and Greek objects. The correlation of the CoO and Fe_2O_3 contained in these is somewhat loose in contrast to the correlation of CoO and Al_2O_3. While the Nippur glass is low in transition metals, these also do not correlate with Al_2O_3 and Fe_2O_3 in these objects. Type A cobalt covers a wide correlation range, which may indicate that Type A cobalt was found over a wider geographical area. This is again reflected in the objects from Mycenaean Greece, Timna and the Uluburun shipwreck, which are also lower in Fe_2O_3.

3.2.1. Rare Earth Elements (REEs)

The sum of the REE concentrations, including the concentration for Y alone, were found to correlate with both Co and the sum of the transition metals (Ni, Mn, Zn). This suggests that the pattern of REE is indicative of the geological origin of the cobalt ore, together with the transition metals. The analysed objects from Amarna in the collection of the ÄMP all group in the same point cloud, indicating one broad geographical region as their origin (see figs. 6C and 6D).

Unfortunately, the data for the REEs, including Y, has frequently not been published, resulting in incomplete and inaccessible datasets. In order to gain a better understanding of the role of the REEs in the determination of the Co source, it would be advisable to publish the full dataset, in particular where glass objects that have been coloured with a cobalt ore from an unknown source are concerned.

3.2.2. Principal Component Analysis (PCA)

A PCA was performed using a subset of the elements identified as relevant for the colouring of the glass (Al, Mn, Fe, Co, Ni, Zn, Y: Fig. 7). The published literature data was used as a practice set, and the Amarna objects were treated as unknowns. The PCA revealed three main clusters. Co- and Co-Cu coloured glass objects from Amarna analysed by LA-ICP-MS cluster with the contemporary glass rods from Malqata. The ore samples K6 and K3 were close to this group. The objects from Nippur formed a tight cluster, and the third, broader cluster was made up of the Uluburun and Mycenaean objects, together with those from Timna and Qantir. The colourless objects (ÄM39978 and ÄM39979) are not part of the Amarna/Malqata cluster, since the objects revealed only a tinge of colouring and no cobalt.

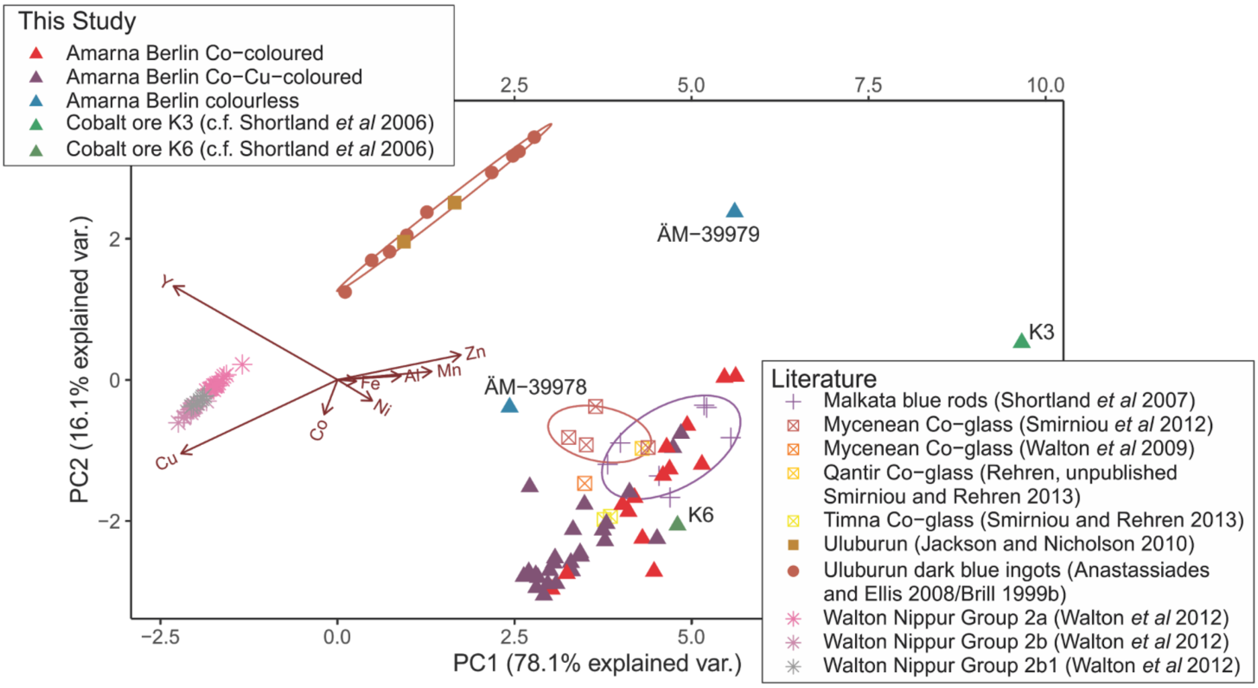

Figure 7: PCA based on Al, Mn, Fe, Co, Ni, Cu, Zn, and Y, showing groups of objects possibly coloured with Co ore from various geographical sources.

4. DISCUSSION

4.1. *Classification*

The 40 analysed objects are a representative sample of glass-working and -production related objects from Amarna in the collection of the ÄMP. Both the translucent and opaque glass objects were classified as Type A cobalt coloured objects by LA-ICP-MS. Although the objects have lost their exact provenancing since being collected at Amarna at the beginning of the 20th century, the glass objects are similar in composition to well-provenanced objects produced in the 18th dynasty. It is likely that the blue colour of those 40 analysed objects originates from Co containing ores from the western desert (near the Dakhla and Kharga Oases).

4.2. *Element correlations*

The elements Al, Mn, Fe, Ni, Zn, Y and REEs are associated with the cobalt containing ore, and are positively correlated with Co. No other element correlations were visible in the investigated samples. It was noted that the Co-coloured, blue glass objects from some workshops at Amarna formed looser clusters than others, albeit including the tighter clusters; thus it is impossible to reassign a particular workshop context to the objects from the Berlin collection (Hodgkinson *et al*. 2019a and 2019b).

4.3. Comparison of on site with laboratory analysis

Well-provenanced samples excavated at archaeological sites may not be exported from Egypt and thus have to be analysed on site. To accurately classify the samples from museum collections with those found at archaeological sites it is important to be able to compare semi-quantitative results obtained in the field by pXRF with quantitative data obtained in the laboratory by LA-ICP-MS. Almost all of the 40 samples from the ÄMP collection were also analysed by pXRF (Hodgkinson *et al.* 2019a and 2019b). The semi-quantitative pXRF data, when converted to µg/g, results in similar transition element values as LA-ICP-MS, suggesting that the data obtained in the field at Amarna is reliable in terms of the correlation cobalt sources (Fig. 8).

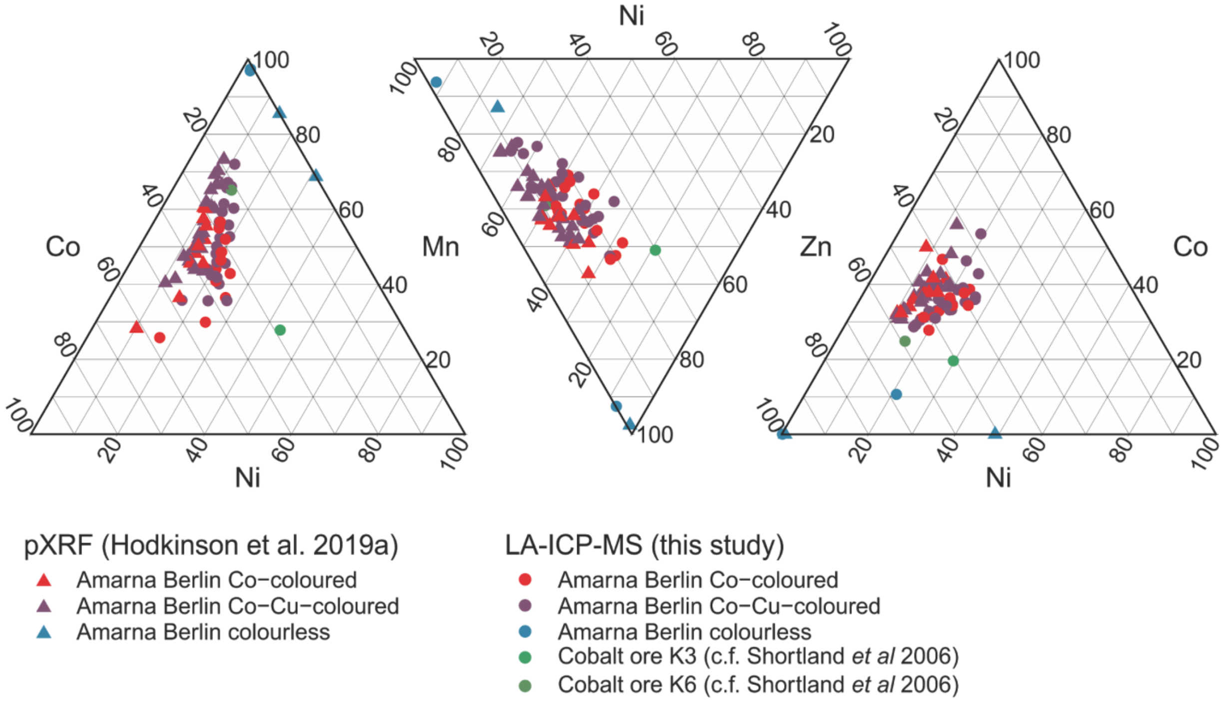

Figure 8: Ternary diagrams showing the correlation of Co with the transition metals, Ni, Mn and Zn, based on both pXRF and LA-ICP-MS data obtained from the same set of objects.

With regard to the evaluation and distinction of the different types of cobalt ore used in the Ancient Near East and Egypt during the Late Bronze Age, it was possible to identify Type A cobalt based on transition metals only. Elements such as Al, Fe and the REEs, which are not accessible, or difficult to quantify, by pXRF, might help in the identification of sub-sources of Co ore used in the glass workshops. However, from the samples analysed in this study, no further sub-sources were identified.

5. CONCLUSION

A representative group of glass-working and -production samples from Amarna in the collection of the Ägyptisches Museum und Papyrussammlung Berlin (ÄMP) were analysed for their elemental composition by LA-ICP-MS. The 40 samples were confirmed as belonging to the group of Type A, Co- and Co-Cu coloured glass objects, produced in the Egyptian 18th dynasty, coloured with Co-containing ores originating from the western desert in Egypt (close to the Dakhla and Kharga Oases). The element composition revealed correlations between Co and Al, Mn, Fe, Ni and the REEs. However, the major, minor and trace element composition revealed no further distinction between the various workshops in the collection, indicating that similar recipes and raw materials were used in the workshops at Amarna. In future work, the use of stable metal isotope ratios may hold the key to distinguish sub-sources and variations in the recipes used in the glass workshops in Amarna.

The comparison of pXRF with LA-ICP-MS on the same set of objects confirmed that the data were comparable with regard to the transition metals Co, Ni, Mn and Zn. The additional elements accessible by LA-ICP-MS add no further distinction into sub-sources. Thus, pXRF can be used as a portable, cost-effective and indicative instrument for the provenancing of cobalt ores in glass objects, using Co, Ni, Mn and Zn concentrations. It will therefore be possible in the future to carry out analyses on site on objects that cannot be removed from a site or a museum collection.

ACKNOWLEDGEMENTS

The authors are also grateful to the National Museums in Berlin (Staatliche Museen zu Berlin, Stiftung Preußischer Kulturbesitz), in particular the staff at the Egyptian Museum and Papyrus Collection (Ägyptisches Museum und Papyrussammlung), and the Rathgen Research-Laboratory for providing access to the samples and the pXRF device, in addition to giving invaluable advice. The authors furthermore thank the GFZ German Research Centre for Geosciences and the Helmholtz Laboratory for the Geochemistry of the Earth Surface (HELGES) for providing access to the laboratory infrastructure.

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SUPPLEMENTARY INFORMATION

Supplementary Table 1: Laser and ICP-MS settings used for the quantitative major, minor and trace element composition analysis by LA-ICP-MS.

Analyte Excite		
Spot size	40	[µm]
Repetition Rate	10	[Hz]
Output Energy	4.97	[J·cm^{-2}]
Wavelength	193	[nm]
Laser shots	600	
Cup gas flow	0.200	[L·min^{-1}]
Cell gas flow	0.400	[L·min^{-1}]
iCAP rq		
Cone Inset	High Sensitivity	
Cool Gas Flow	14.00	[L min^{-1}]
Auxiliary Gas Flow	0.8	[L min^{-1}]
Nebuliser Gas Flow	0.7983	[L min^{-1}]
RF Power	1550	[W]
X	0.48	[mm]
Y	1.28	[mm]
Z	4.0	[mm]
Extraction Lens	-166.10	[V]
CCT Focus Lens	-4.20	[V]

Supplementary Table 2: Average concentration and standard deviation from the repeated determination of Corning-A, Corning-B, NIST SRM612, and NIST SRM614 using NIST SRM610 as external standard and a 100wt% oxide normalisation approach. Concentrations below 40 µg/g (for K) or 100 µg/g (for Mg and Fe) are not reported (NA) due to interferences affecting the accuracy of the concentration determination. Concentration below the limits of quantification (< LOQ) based on 10 standard deviation of the background.

Standard	Corning A			Corning B			NIST612			NIST614		
	Average	s	n	Average	s	n	Average	s	n	Average	s	n
Element	µg/g	µg/g		µg/g	µg/g		µg/g	µg/g		µg/g	µg/g	
Li7	49.8	0.8	15	10.8	0.3	14	40	0.7	18	1.7	0.1	13
B11	633	11	15	98	2	14	36	2	18	< LOQ		
Na23	106578	936	15	127058	1069	14	101610	860	18	100849	1504	14
Mg24	13231	151	15	5344	68	14	NA			NA		
Al27	5109	51	15	22158	227	14	10768	79	18	10712	167	14
Si29	317740	1404	15	295567	1261	14	337597	817	18	339157	2252	14
K39	23562	566	15	8246	140	14	57	9	18	NA		
Ca43	36833	467	15	62812	985	14	84684	737	18	84368	1907	14
Ti49	4753	54	15	625	13	14	39.9	1.2	18	< LOQ		
V51	37.6	0.4	15	194	2	14	38.5	0.6	18	1	0.11	14
Cr52	20.1	0.4	15	61.4	0.8	14	35.8	0.4	18	< LOQ		
Mn55	7406	95	15	1817	14	14	38.5	0.5	18	1.39	0.1	14
Fe57	6213	247	15	2000	75	14	NA			NA		
Co59	1350	16	15	348	3	14	35	0.5	18	0.72	0.05	14
Ni60	187	2	15	766	8	14	39.4	0.8	18	1.4	0.2	6
Cu63	9880	272	15	21939	594	14	40.6	1.2	18	2.34	0.29	14
Zn66	424	12	15	1764	35	14	37	1.4	18	< LOQ		
As75	26.3	1.1	15	19.4	0.9	14	33.8	1.1	18	< LOQ		
Rb85	88.3	1.1	15	11.5	0.2	14	31.4	0.4	18	0.87	0.05	14
Sr88	937	13	15	155	1.4	14	78.5	0.7	18	45.6	0.9	14
Y89	0.3	0.02	15	0.44	0.02	14	38.6	0.3	18	0.78	0.03	14
Zr90	40.1	0.5	15	176.6	2.3	14	38.2	0.4	18	0.86	0.03	14
Sn118	1460	17	15	204	2	14	38.3	0.9	18	2.01	0.56	14
Sb121	11975	223	15	3264	48	14	33.9	0.7	18	< LOQ		
Ba137	4542	66	15	743	8	14	39.5	0.6	18	3.3	0.2	14
La139	0.56	0.05	15	0.26	0.02	14	35.8	0.3	18	0.71	0.03	14
Ce140	0.26	0.01	15	0.17	0.01	14	38.4	0.6	18	0.77	0.03	14
Pr141	0.03	0.01	15	0.018	0.004	8	37.8	0.5	18	0.76	0.03	14
Nd146	0.12	0.03	14	0.07	0.01	9	35.5	0.7	18	0.71	0.09	14
Sm147	< LOQ			< LOQ			37.7	0.7	18	0.76	0.09	14
Eu153	0.19	0.06	15	0.04	0.01	14	35.5	0.5	18	0.75	0.05	14
Gd157	0.06	0.02	8	< LOQ			38	0.6	18	0.77	0.07	14
Tb159	< LOQ			< LOQ			37	0.5	18	0.74	0.03	14
Dy163	0.03	0.01	10	0.05	0.01	14	35.9	0.6	18	0.76	0.05	14
Ho165	< LOQ			0.016	0.003	12	38.1	0.5	18	0.75	0.03	14
Er166	0.03	0.01	9	0.06	0.01	14	38.1	0.7	18	0.75	0.07	14
Tm169	< LOQ			0.012	0.003	14	36.9	0.5	18	0.73	0.04	14
Yb172	< LOQ			0.08	0.02	14	38.6	0.8	18	0.76	0.08	14
Lu175	< LOQ			0.02	0.005	14	36.7	0.5	18	0.72	0.02	14
Pb208	674	16	15	4491	89	14	38.4	0.9	18	2.35	0.34	14