Post-15th century European glass beads in southern Africa: composition and classification using pXRF and Raman spectroscopy

Farahnaz Koleini[1*], Philippe Colomban[2], Innocent Pikirayi[1]

[1]*Department of Anthropology and Archaeology, Faculty of Humanities, University of Pretoria, Pretoria, Gauteng, South Africa.*
[2] *Sorbonne Université, CNRS, MONARIS UMR8233, 4 Place Jussieu, 75005 Paris, France, ORCID:0000-0001-6099-5423*

**corresponding author: farakoleini@gmail.con, cell number:+27628009368, ORCID: orcid.org/0000-0002-3981-4285*

Abstract

A hundred and twenty-seven glass beads found at archaeological sites in southern Africa were analysed using pXRF and Raman spectroscopy. The beads are identified as European production on the base of their particular composition and morphology in order to classify beads traded to the region after the 15th century AD. Six major groups of glass, namely, soda base plant ashes (61%), potash rich wood ash (14%), synthetic soda (8%), mixed alkali (4%), lead soda (22%) and natron (4%) were identified. Except for soda base plant ashes and natron (outliers), all the groups date back to the 19th century. Calcium antimonate in the majority of soda based plant ash glasses (87%) indicated some of the beads were imported from Europe since the 17th century.

Keywords: Trade glass beads, provenance, Europe, pigments, southern Africa

1. Introduction

Glass beads have been produced and traded since the 7th century to southern Africa for use as everyday items of adornment, ceremonial costumes or objects of barter. The preservation of glass beads is good and large hoards have been found in archaeological sites. However, European producers copied the shapes and colours of ancient beads, highly prized by the African communities, that makes difficult their identification using morphological criteria [1]. For the preservation of artefacts non-invasive analyse is needed. The first European glass beads were brought to southern Africa by Portuguese traders in the 15th century AD [1]. Wood [2] mentioned that these beads were rejected by native Africans due to their unfamiliar appearance when compared to the beads (Asian beads) used by their ancestors. It forced the traders to continue bringing South and South-East Asian beads to southern Africa instead. These glass beads are known as Khami Indo Pacific series and imported from the 15th to the 17th centuries [1]. However, beads assigned to European origins are generally found alongside with Khami bead series at very top layers of archaeological sites [3]. These European beads were presumably imported through Dutch and British trading posts in southern Africa inland after the 17th century while some pre-European beads found along European ones could be heirlooms.

Some annular and hexagonal as well as opaque white European beads can be easily discriminated by visual examination from the pre-European series found in southern Africa sites. However, some of the monochrome drawn beads look very similar in morphology to the former Asian series [4]. Accordingly, it is possible that some beads such as the simple brownish-red, and, black, were imported earlier from Europe and distributed along with the beads of the Khami series in southern Africa. These beads might be differentiated on the basis of their composition, pigments and opacifiers.

Morphology, composition and pigments can be used for dating European glass beads [1]. In the present paper, the composition of European glass beads found at Mapungubwe, Bambandyanalo, Parma and Maryland farms in northern South Africa (Figure 1) were examined using portable XRF. The results will be compared with similar European beads that were found at Magoro Hill in South Africa [4], Danamombe [5] and Baranda in Zimbabwe [3] (Fig. S1). Then, the results were associated with recorded Raman data of beads available in Tournié et al. [6] and Koleini et al. [4] obtained on beads from K2, Mapungubwe and Magoro Hill sites. PXRF is widely used for material detection in different domains, namely geology, environment, pollution, agriculture and specifically cultural heritage due to its non-destructive character [7-10]. Mobile Raman micro-spectroscopy is also non-destructive and an immediate technique that can be used as a complementary technique with pXRF

for the classification of glass beads at archaeological sites [11]. Finally, the beads were classified and dated by considering the glass production sequence in Europe.

The history of glass making in the Mediterranean region shows that mineral flux (natron) was in use from Roman times until about the 10th century AD [12,13]. After the 8th century, and due to some political problems in the importing of natron from Egypt, glassmakers of eastern and southern Europe gradually started to use plant ashes from Syria and Lebanon in the Middle-East (Levantine ash) and from the west Mediterranean (Barilla ash) (see summary in Table S1). Natron was completely replaced with Levantine ash in Venice during the 14th century [14]. Indeed, Levantine ash was produced by burring of *Salsola soda* plant species and was in use in Venice and Italy (Tuscan, Savona) in the production of glass from the 10th century [15-17]. Later on, in the 17th century, Levantine ash was gradually replaced by other west Mediterranean coastal ashes because it was no longer exported to Europe from the Levant [18]. Barilla ash was produced by burning costal plants (*Salsola kali*) growing in various places in the west Mediterranean [15]. Barilla, along with Levantine ash, was employed in glass production from the 13th century [16] and was in use until the 17th century [18]. Barilla ash can be differentiated from Levantine ash by its higher K_2O content (>5 wt%) than Levantine ash (<4 wt%) [16, 19].

From the 16th century and with the movements of Italian glass makers, very close glass compositions to Venetian productions, known as *Façon-de-Venise* were produced in other parts of Europe [20]. From the late 17th century onwards, two different kinds of glass - pure potassium ash glass found in Central Europe and lead-based glass in Britain - were produced [21]. Pure potassium-lime silica glass was produced by mixing purified wood ash with other very pure raw minerals [22]. Finally, in the 19th century, plant ash was replaced by synthetic soda and potash in Central Europe [23-25].
We present here the first classification of southern Africa traded European beads based on morphology and composition that hardly discussed thoroughly by previous researchers who focused mainly on pre-colonial period. With clarifying the composition of beads, the earlier Asian monochrome drawn beads can be separated from European replicas. Furthermore, it would be a start for gathering information on extent and distribution model of different exotic beads in southern Africa after arrival of European.

2. Materials and methods

2.1 Samples and archaeological context

One hundred and twenty-seven European glass beads lounge at University of Pretoria Museum and found in southern Africa archaeological sites (Fig. 1) were classified according to morphology (Table S2) and material composition. From that 105 beads were excavated at Parma (Pr), Maryland (Ml), Mapungubwe (Map), Bambandyanlo (Bd) and K2 sites in the Limpopo valley, South Africa (Fig. S1). Thirty-five beads from Mapungubwe and Bambandyanalo were previously examined by Raman spectroscopy and the results published [6,26]. The XRF and Raman results of European beads from Magoro Hill (Mag) (13 beads) in South Africa [4], Baranda (Ba) (1 bead) and Danamombe (D) (8 beads) in Zimbabwe [3,5] were also added to the data for comparative purposes. The samples are labelled with the acronym of site followed by XRF test number of the beads as reported in Figure 1.

Bambandyanalo and adjacent test excavation location (K2) (10th-11th century), Mapungubwe (13th century), Parma and Maryland sites are located along the middle Limpopo River and close to the current boarders of Zimbabwe, Botswana and South Africa. All the sites were homesteads of Iron-Age farmers during the early second millennium AD. In the case of Bambandyanalo and Mapungubwe, there is no further evidence of occupancy of the sites following their abandonment after the 11th and the 13th century respectively [27]. Therefore, European beads found at these two sites probably belong to later human activity that continued up to the mid-19th century [26]. Ceramics and glass finds from the elementary excavation in Parma shows that the occupation started from Bambandyanalo phase and continued with a later one with an interval between two phases [28]. Three packets of glass bead are attributed to Parma site in University of Pretoria Museum. The information on the packets refer to three locations namely Parma midden, Parma X1 and Parma. Fouché [28] reported that Maryland was occupied for a short period and consisted of a shallow deposit. Beads were collected from two locations, close to the stonewall, and a cattle pen next to the main site. Two packets of beads, labelled as Maryland 1 and 2 in University of Pretoria Museum are attributed to this site. The occupation date of the site is not clear.

2.2 Analytical methods

X-ray fluorescence was performed by using a handheld Niton Thermo Scientific XL3t GOLDD. The details of the instrument and analysis procedure are reported in [29]. The elemental concentrations measured by XRF were converted to oxide forms and then normalized to 100%. Due to the limitation in measuring of low Z-elements using pXRF instrument, standard glass samples B, C and D of Corning Museum of Glass were used as reference to obtain (semi-) quantitative data. Each reference was analysed three times and normalisation factor was calculated by comparing the average result with the certified values (Table S3). The sample results were corrected by the normalisation factor to bring them in line with the results from reference samples. In the case of plant ash glasses the average

of normalization factors of standards B (Mineral soda glass) and D (potash glass) was used for correcting the results. The XRF results of beads that contain less than 15 wt% PbO were corrected by averaging the calculated normalization factors for standard samples B (Mineral soda glass) and C (lead glass). The lead oxide content of these beads lie between the measured amounts for standard samples B (0.48 wt%) and C (28.78 wt%).

Raman spectra of the samples were recorded by three instruments namely, a portable HE532 (Horiba JobinYvon, France) with a 532 nm Nd/YAG Ventus laser, a HR Raman instrument (Horiba JobinYvon, France) with a 458 nm laser line of Ar-ion Coherent laser and T64000 micro-Raman spectrometer (HORIBA JobinYvon, France) with a 514.6 nm laser line with krypton-argon Coherent laser line. The details of the instruments, the procedure of recording and enhancing of Raman spectra by correcting the baseline, are described in [29].

3. XRF and Raman results

3.1 The composition of glass

The beads are classified based on flux composition and silica source following Cagno et al. [30] to 6 groups. In this classification, the amount of K_2O and CaO reflects the kind of flux used in the production of glass while the Al_2O_3 content gives information on the purity level of the silica source. The average concentrations of 7 major oxides (Table 1) measured by XRF show that the majority of the beads are plant-ash silica glass with average K_2O content above 1.5 wt%. Five beads are outliers, with less than 1 wt% K_2O (c-739a, c-739e, c-739f, c-1835i, c-1843j). Figure 2 plotted K_2O against CaO contents for tested glass beads that clearly shows different groups: 1 (Soda-lime plant-ash), 2 (potash rich), 4 (mixed alkali) and 5 (mineral soda: outliers). The relative concentrations of Al_2O_3, CaO, K_2O and MgO are plotted in Figure 3 that shows the same clusters of composition with some dispersion due to the binary effects of Al_2O_3 and CaO on the composition. Concentrations of chlorine and lead oxide were other criteria that added two extra groups 3 (synthetic soda) and 6 (lead soda) to the abovementioned list.

The position and intensity of peaks in Raman spectrum of an aluminosilicate glass are under effect of the composition (Al/Si ratio, flux cations) and method of fabrication (melting temperature determining the nanostructure) [31], thus, the difference in any of these criteria might modify the spectrum of the glass. The low covalence of Al-O bonds makes possible to consider SiO_4 tetrahedron as the effective vibrational unit and to establish relationships between spectral and structural characteristics [31-33]. Recorded spectra of the beads belonging to groups 1 to 5, all show very close

positions of maximum peak intensity of SiO_4 in bending and stretching counterparts (Fig.4a). The maximum peak intensity for these beads ranged from 537 to 570 cm^{-1} in the SiO_4 bending band and from 1092 to 1100 cm^{-1} in the SiO_4 stretching band, which is characteristic of soda-lime glass. Table 2 shows a representative selection of the analysed beads in each group. The composition of each group is discussed as follows:

3.1.1 Group 1 (Soda-lime plant-ash glass)

The beads have K_2O concentration between 1.8 and 6.4 wt% typical of ashes were used in the production of glass in the Mediterranean region, e.g. Levantine and Barilla ashes [16,30]. CaO content stretched over a wide range from 2.1 to 13.8 wt% (Fig. 2 and Fig. 3) that might have several reasons. CaO content less than 4 wt% in glass might be due to the purification of the soda ash or using plant ash with low lime content [34]. The CaO content between 6 and 9 wt% shows the use of un-purified plant ash and the excess amount might be due to the addition of a calcium-rich raw material [34]. A part of lime content of glass may also originate from the silica source [35]. Except for the twelve beads (Map122, 123, pr51, Ml62, 64, 65,73, Mag4, 14, 21, 25, and Bd120) with less than 4.6 wt% CaO content, beads have CaO concentrations above 5.5 wt%, which indicate use of un-purified soda-ash in the production of majority of the beads.

The majority of the beads (64%) in this group contain Al_2O_3 of more than 3 wt%, which is compatible with the produced high alumina soda-rich glass in southern part of Europe except Venice during the Medieval and post-Medieval periods [15,16]. Soda-rich glass from central and northern parts of Europe (*Façon-de-Venise*) usually contains low Al_2O_3 ($\leq$2 wt%) [20,21] (see Table S1). These high alumina beads were made of purified or unrefined ash (CaO>6 wt%) (see Figs. 3). Those beads (Ml62, 73, Mag4, 14, 25) made of a mixture of impure silica and refined ash (hAl-lCa) show dispersion towards the points with high alumina and low CaO wt% in figure 3. This composition is very close to beads of Mapungubwe series. Close compositions to above mentioned subgroups were reported for glass objects (*Façon-de-Venise*) that were found in Portugal (14th-17th century) and Italy (13th-16th century) [15,21]. The use of such purified ash in the production of glass only started during the second half of the 15th century in Venice [21].

Twenty-three samples (36%) with less than 2.5 wt% Al_2O_3 content are consistent with glass made from pure silica (likely quartz or flint pebbles). Low alumina glass was produced in a wider region, from southern to northern parts of Europe. Fifteen of these were made of unrefined ash (Fig. 1). Of these, some with K_2O less than 3.5 wt% caused dispersion of the beads towards lK-hCa composition which is similar to use of unrefined Levantine ash (Fig.3). The zirconium and strontium contents of all low alumina beads in this group except Pr52, 58 and 94 are in accordance with the Venetian and

Amsterdam glasses, with concentrations lower than 20 ppm and 400 ppm respectively [17]. A mixture of pure silica and unrefined Levantine ash (CaO>6 wt%) was in use in the production of glass (*Vitrum Blanchum*) in Venice since the 11th century and later in Tuscan Italy (13th century) [15,18]. A close composition was also reported for glass samples (*Façon-de-Venise*) found in Portugal, Spain, Antwerp, Amsterdam and London dated to the 16th and 17th century AD [17,21,36,37]. Only eight samples of this subgroup (see Table 2) were made of pure ash (CaO<6 wt%) and siliceous pebble (Fig. 2). These beads contain higher alumina than the usual Venetian *Cristallo* (0.68±0.14 wt%) as reported by Verità and Zecchin [18]. Close compositions to these subgroups has been reported from the 17th century productions of Antwerp [20], London, Amsterdam [36] and Coimbra [21].

Raman shows two different glass structures for beads classified in group 1. The beads with low K_2O content (<4 wt%), show the typical spectrum 1 (Fig. 4a). Spectrum 2 represents Raman signature of those beads with K_2O content of more than 5 wt%. The spectrum shows a broad peak at 948 cm^{-1} which makes it different from the spectrum of beads with lower K_2O content. Fukumi et al. [38] mention that the kind and concentration of alkali have a direct effect on the intensity of the peaks at 950 cm^{-1} in the silicate glass. They showed that the alkalis with higher atomic number as seen in the case of potassium here, will increase the peak intensity at 950 cm^{-1} more than the lower atomic number alkalis such as soda. These beads are produced with western Mediterranean ash that contains high K_2O content as compared to Levantine ash.

3.1.2 Group 2 (potash-rich glass)

All the 18 beads in this group are hexagonal cobalt blue except one annular cobalt blue bead (K2-153). Two hexagonal beads (K2-107, 108) are simple while the rest of beads are compound in structure. The K_2O content of the beads is between 10.9 and 18.6 wt%. The CaO content varies between 5.9 and 10.5 wt% (Figs. 2 and 3). Simple and compound hexagonal beads show differences in phosphate concentration, which places them in two subgroups with high and low phosphate content.

The majority of the beads except the simple hexagonal beads and one annular bead (K2-107, 108, 153), contain high P_2O_5 (1.2-2.5 wt%) which is characteristic of wood-ash alkali (Table S4). The K_2O/CaO ratio of the samples is between 1.3 and 2.7 that make them close to potash-rich glass, introduced as K-Ca-3 glass by Stern and Gerber [39]. According to the authors [39], K-Ca-3 glass was manufactured by the addition of a potash rich material (extracted potash) to the leached vegetable ash and silica source. Extracted potash is produced by leaching of the fresh wood ash, and as such is poor in insoluble oxides like lime, magnesia, phosphate, iron and manganese [39]. Leached ash, however,

contains insoluble minerals of wood ash that could be the most probable source of phosphate and lime in this type of glass [39,40].

In the case of samples with phosphate content lower than 0.5 wt% (K2-107, 108, 153) the leached ash has been probably replaced by a mineral source of calcium such as limestone (potash-lime glass) [39]. The latter beads also contain MnO_2 (0.4-3.3 wt%) which is reported as a substance added in production of ordinary colourless glass, a mixture of sand, lime and potash ash, in central Europe in the beginning of the 18th century [21,22].

It is impossible to determine the Na_2O content of the samples using pXRF for comparing the results with K-Ca-3 glass with soda content lower than 1wt%. However, the correction of the oxides concentration with the impact of normalisation factor (NF), gained from measuring the Corning glass sample C (potash glass), gives possibilities to estimate the soda content in glass beads. The results show that the samples may have soda content of between 3.4 and 8.1wt% (Table 1). The amount of soda higher than 1wt% indicates the probable addition of soda-glass culet to the composition [39]. It seems, therefore, that the potash-rich samples were probably made of a mixture of extracted potash, pebbles and soda-glass culet. However, the source of calcium (leached ash or a natural mineral) divides them further into two subgroups as also demonstrated by Raman spectra 3 and 4. The spectra show that the peak with maximum intensity in the bending band appeared in a lower wavenumber (535-540 cm^{-1}) compared to the beads in group 1. Spectrum 3 is related to potash rich glass with high phosphate content. The strong peak at 960 cm^{-1} is the signature of calcium phosphate crystalline precipitates [41]. The same spectra were reported for some hexagonal and one annular beads from Congo [42] and one Mapungubwe hexagonal bead [6]. Accordingly, the peak at 960 cm^{-1} is not observed in potash rich beads with low phosphate content (spectrum 4).

3.1.3 Group 3 (Synthetic Soda glass)

All the beads in this group are annular dark blue. The beads contain K_2O in the range 2- 3.6 wt% and CaO, in the range 5 -7.4 wt%. These beads have lower concentrations of MgO (mean value= 0.5 wt%) and chlorine (mean value = 0.3wt%) compared to the low K_2O content beads in group 1 (see Tables 1 and S4). Low chlorine indicates the alkali has a mineral synthetic source although the potassium content of the samples is higher than usual synthetic soda glass with <0.5 wt% K_2O in the composition [25]. These samples have a close composition with the annular beads found at Fichtelgebirge and Mehlmeisel, Germany, dated to the late 19th and the early 20th century [43]. It was indicated that the high concentration of K_2O (2.2-5.7 wt%) in the annular beads of Fichtelgebirge is probably due to the feldspar in the sand. This might be also due to the addition of saltpetre (potassium nitrate) which was in use as a refining agent from 1870s onwards [25].

The Raman spectrum of these beads is the same as low potassium content (K_2O<4 wt%) beads in group 1 (Fig.4, spectrum 1).

3.1.4 Group 4 (Mixed alkali glass)

Only five beads belong to this group, all of them except one being hexagonal and annular, and, on morphology, similar to the beads in groups 2 and 3 (potash-rich and synthetic soda). The samples in this group contain K_2O between of 7.8 and 9.5 wt%, which is high for usual soda-rich glasses with K_2O content typically less than 5 wt% [44]. In the same way, the K_2O content is lower than usual potash-rich glass with K_2O content more than 10 wt% in composition [21]. The amount of CaO fluctuated between 6 and 8.5 wt% which is too low to be a high lime low alkali glass. Figures 2 and 3 show that these samples have a composition of between potash-rich glass (forest and wood ash glass) and plant ash soda-lime glasses as mentioned by Dungworth and Mortimer [45] and Coutinho [21]. It was reported that low quality or purification of the consumed plant ash might be the reason behind the formation of these mixed alkali glass [19,44].

All the beads in this group except the annular bead (Mag32) contain less than of 0.6 wt% phosphate (Table S4). Therefore, it is possible that the hexagonal beads were produced by adding a higher amount of soda (soda culet) to the composition of low phosphate content potash-rich glass in group 2. The annular bead (Mag32) contains 1 wt% phosphate that indicates the use of wood ash as a part of alkalis used in its production. Raman spectrum 5 was recorded on mixed alkali glass (group 4).

3.1.5 Group 5 (Outliers)

This group consists of five beads with less than 1.1 wt% K_2O and high chlorine content (mean value = 1.2 wt%) (Tables 1 and S4). The low alumina content (<2.5 wt%), indicates the use of pebble as the source of silica. CaO content is high with the mean value of 8.45 wt%. Four white beads contain lead oxide (mean value = 8.5 wt%) which discriminates them from the only cobalt blue bead (Pr99) in this cluster. The composition of these beads is compatible with mineral soda glass (natron) produced since Roman times until the early medieval period in Europe [46]. However, the presence of natron glass does not coincide chronologically with the archaeological context where the beads were found. On the other hand, the high chlorine content shows that the beads could not be made with synthetic soda. The Raman spectrum of these beads is the same as the low K_2O content beads in group 1 and synthetic soda glass of group 3 (Fig.4, spectrum 1).

3.1.6 Group 6 (lead-soda glass)

Among the analysed beads, 28 samples contain high level of lead (Table 1). The majority of these beads (24 samples) contain also elevated amounts of arsenate (>9 wt%). The composition indicates that these beads opacified with lead arsenate. Lead arsenate beads consist of some simple beads in white, pink, powdery light and powdery dark blue colours. White hearth and striped beads that are compound in the structure (the beads are made of two different coloured layers) are found in this group as well (Fig. 1). Due to the lack of a standard sample with close composition to these beads, their compositions were reported as measured by XRF in Table S4.

Four green beads (K2-111, Pr98, Map148-149) contain lead oxide above 40 wt% and a low arsenate content (<6 wt%) that discriminates these beads from the above mentioned composition (Table 1). These beads are opacified with calcium antimonate. Previous Raman spectroscopy placed both categories of lead glasses in lead-soda glass [4,6].

Raman spectrum 6 is related to the beads with high lead content. After baseline subtraction eliminating the strong Boson peak below 300 cm^{-1} the peak maxima of Si-O have a lower position in the bending (450-500cm^{-1}) and stretching bands (949-1060 cm^{-1}) in the recorded spectra [6]. No lead arsenate phase is observed in beads with low arsenate content.

3.2 Pigments and opacifiers

Figure 4b shows spectra with the significant contribution of pigments and opacifiers in the beads. Pigments identified are listed in Table S5. Calcium antimonate with two strong peaks at 480 cm^{-1} and 630 cm^{-1} was detected as opacifier in some of the beads in groups 1, 5 and 6 (spectrum 1). Calcium antimonate was in use since antiquity. However, it was the predominant opacifier from the middle of the 17th to 19th centuries in Europe [47]. The presence of antimonates in soda rich plant ash glass (group 1) shows that the samples are contemporary with the decline of Venetian glass during the mid-17th century and the spread of *Façon de Venise* in Europe [21,46].

Arsenate-based phases are characterized with a strong peak at around 815-830 cm^{-1}, as detected in lead-soda glass of group 6 (spectrum 2) [48-50]. Lead Arsenate was in use since the 16th century in the production of *lattimo* glass in Venice [41] although due to its toxicity, predominant use only started in the 19th century and continued into the 20th [51,52]. Therefore, all the beads with lead arsenate are attributed from the early 19th to the 20th centuries.

Ultramarine (synthetic) or lapis lazuli (natural rock with blue mineral lazurite), with the characteristic sharp peak at 533 cm^{-1} of S-S bond chromophore which is hosted in zeolithe (synthetic) or feldspar

(natural) framework, was detected in three light blue beads (Bd120, Map122 and Mag25) (spectrum 3) [4,6]. The beads also contain antimony and copper ions as the opacifier and a blue colorant respectively (Table S4). Swirls of different shades of blue are visible on the surface of these three oblate shaped beads that indicates chromophore did not distribute evenly in the glass matrix, according to a dispersion of pigments. The beads have different glass compositions due to their alumina (Map122 and Mag25) or K_2O content (Bd120) (Table S4).

The natural mineral (Lazurite) was in use since antiquity [53] and artificial ultramarine was produced during the early 19th century, but its use as glass or glaze pigment not reported at our knowledge. The natural lazurite is found in the Islamic glaze and enamel from Iran (13th-14th century), the Mamluk Sultanate (13th-15th century) and Italy (13th c. AD) [54,55]. Natural lazurite is probably used for colouring of the beads since the beads fall in soda-rich alkali group (group 1) which its production came into decline in the 18th century [21]. Tournié et al. [6] attributed these beads to production in Fustat and Iran, although it is possible that the beads were produced in southern Europe where their glass industry was influenced by traditional Islamic glass recipes until the 15th century [46].

Modified Naples Yellow (Pb-Sn-Sb triple oxides) with peaks at 125 cm^{-1} (Pb ion mode), 458 cm^{-1} (Sn-O mode) and 507 cm^{-1} (Sb-O mode) [56] was detected in three green beads in group 6 (spectrum 4). The pigment was in use since antiquity. However, the antimony in the composition of southern Africa yellow and green beads was only detected in European beads [4,6]. Manganese/iron oxide spinel with typical strong peaks around 470 cm^{-1} and 600-640 cm^{-1} (Spectrum 5) was detected in four black beads (Mag1, Ml62, 65 and 73) in group 1 [4,6]. The beads have a high manganese oxide content (mean value =16.87 wt%). Black beads with manganese oxide were also reported from Kindoki in Congo [42]. Manganese oxide as a black pigment was in use since Antiquity in eastern Anatolia and later spread out towards the southern Balkans and northern Italy [57,58]. Mn-rich spinel reported as black pigment in the glazed pottery fragments and glass from the 13th to 16th centuries in Italy [59]. Three of the black beads contain a low amount of lead oxide (7-10 wt%) that makes them different from Mag1.

A low amount of lead oxide (2.5-13 wt%) was also detected in some of the white, light blue and brownish-red beads in groups 1 and 5 (Table S4). These beads are coloured or opacified with calcium antimonate or contain cuprous oxide in the case of brownish-red beads. This low amount of lead shows a slight downward shift of stretching maximum in some of these beads. Sayre and Smith [60] reported that the addition of lead in glass increases the solubility of copper, antimony and tin oxides at high temperatures that may direct to glass opacification by precipitation of oxide particles at lower temperatures. The method was in practice for production of brownish-red glass coloured with copper

nanoparticle since Antiquity [61,62] and continued in Islamic glass production [63] and later, in post-medieval Europe [36]. The opacification of glass with antimony in the presence of lead was practiced in Roman times [64]. In the case of antimony, lead concentrations of between 4 wt% and 25 wt% facilitate the formation of $Ca_2Sb_2O_7$ instead of $CaSb_2O_6$ in the glass [64]. As the result, the brownish-red, black and antimonate opacified beads were manufactured using two different methods, with or without the addition of lead oxide in the composition. This indicates the possible different origins of the beads.

4. Discussion

We identified six different glass compositions among imported European beads to southern Africa (Table 1). The glass beads in group 1 are soda-lime plant ash which were produced using Levantine or West Mediterranean ashes. These could be the earliest European beads to have been imported into southern Africa from the late 15th century onwards. However, the majority of the beads in this group contain calcium antimonate that shows the beads predominantly belong to the second half of the 17th century. This date coincides with the arrival of Dutch and English traders in southern Africa [65,66]. There are only 8 beads with no antimony content in black, brownish red on black, plum, light and dark blue. Large differences in CaO and Al_2O_3 content of the beads in group 1 are consistent with different workshops/factories. Both high and low alumina glass beads are found in group 1. While soda-glass with high alumina content is confined to southern Europe, the low alumina glass has been produced in a wider region from southern into central Europe (see Table S1). The concentration of Sr and Zr in low alumina beads shows that some of the beads are close with the glass productions in Amsterdam and Venice. Although, the amount of alumina in these beads is not in the range of Venetian beads. Therefore, it would need a more detailed study to indicate where in Europe the low alumina beads may have been produced. The composition of European high alumina glass produced by purified plant ash is close to Mapungubwe series imported to southern Africa between 1240 and 1300 AD. Morphology and the kind of opacifier which is calcium antimonate in European beads are the differences of these two series.

The beads analysed here are black, dark and light blue, plum as well as a series of compound beads such as brownish-red on black and green or blue on light grey. Francis [67] and Karklins [68] reported that compound brownish-red beads were produced in Venice and Amsterdam respectively during the late 16th century. All of the compound beads of this assemblage, except Map123, contain calcium antimonate that attribute them to the second half of the 17th century. The date is in accordance with Beck who mentioned these beads were brought into southern Africa from the 18th to the 19th century [69].

Hexagonal beads were common in southern Africa since the early 19th century [70-72]. The beads have compound or simple structure and find in different sizes. Venice was mentioned as a production centre [72,73]. Francis [74] reported that these beads were also produced at Bohemia (now Czech Republic). The compound beads (dark blue on white) are known as *Ambassador* beads and were produced in both Venice and Bohemia [74]. The morphology of compound beads of this assemblage are similar to Bohemian beads reported in Francis and dated to the late 19th century [74]. All the compound hexagonal beads are potassium rich glass with high phosphate content (group 2). Although similar glass composition with as high potash-high phosphate beads has been reported for cobalt blue annular beads from Fichtelgebirge in Bavaria [43] no compound hexagonal beads were among this collection.

Simple hexagonal beads (small and large) are among low phosphate beads in group 2 or mixed alkali glass in group 4. A small imported hexagonal bead with the same composition as the low phosphate beads in group 2 was reported from North America dated to the early 19th century [43]. This composition is attributed to the glass production of central Europe from the 18th century [21,22] to the 19th century [43]. The differences in the phosphate concentration of beads in group 2 is due to different sources of the lime in the beads. The mixed alkali beads seem to have been produced by the addition of soda culet to the potash-low phosphate glass. Therefore, the hexagonal beads were produced with three recipes and may be of three separate origins.

Annular beads have three different compositions although the majority of them are made of synthetic soda (group 3). Two annular beads, K2-153 and Mag32, have been placed in the rich potash glass with low phosphate content (group 2) and the mixed alkali glass (group 4) respectively. Different compositions indicate that the beads were manufactured in three different places. K2-153 has the same composition as that of the small hexagonal beads (K2-107 and 108) with low phosphate content, and as such, are probably of the same origin. The same composition was reported for amber annular beads found at Fichtelgebirge [43]. The cobalt blue beads were probably imported together with amber annular beads to southern Africa during the early 19th century [75]. It should be mentioned that potash glass was in production until the mid-19th century in England. The annular beads made of synthetic soda might be later in date because the synthetic soda was used in the production of glass (first Leblanc, and then, Solvay soda glass) from 1830 onwards in Europe [25]. This later composition is probably related to annular cobalt blue beads that Francis [75] referred to in terms of their importation to southern Africa during the late 19th century.

The mixed alkali beads with the same morphology as the simple hexagonal and annular beads in groups 2 and 3 respectively are also similar in P_2O_5 and chlorine content. Low phosphate content of simple hexagonal shows the beads were probably made by the addition of excess amount of other

alkali such as soda or limestone to the potash rich glass. Mixed alkali hexagonal and annular beads were also reported from archaeological sites in the Congo, in central Africa [42].

Although it is clear that the mineral soda beads in group 5 were made by natron as alkali, dating of the beads remains problematic. Here, calcium antimonate in the white beads cannot be used as a chronological marker since the pigment was in use during Roman times as well. On the other hand, the beads were found along with later European beads in the same context in Parma Farm and Bambandyanalo in southern Africa. It is possible these beads were made from recycling earlier glass probably dating to the Medieval Period in Europe.

The lead soda glass (group 6) shows two different compositions. Some of these beads are opacified with arsenate. These beads were being produced from the 19th to the 20th centuries. The second part of beads is opacified with calcium antimonate, which attributes them to a period from the late 17th to the late 19th century. The latter are close in terms of morphology and composition to drawn green beads found in Garumele, in West African Niger [76].

5. Conclusion

Raman and pXRF as two non-destructive methods are significantly effective in detecting different types of glass represented in this paper. We identified six different glass compositions among imported European beads to southern Africa and proposed some provenances. The results show that Raman can detect soda-lime, potash and lead-soda glass by recording a single spectrum. Although Raman put a difference between low and high K_2O content soda-lime glass it cannot discriminate synthetic soda, natron and mixed alkali types from them. XRF could fill this gap by semi-quantitative measuring elemental concentrations. Raman with detecting pigments and opacifiers in glass shed a new light for dating the beads.

Acknowledgments

The authors would like to thanks University of Pretoria Museum for the glass beads used in the analyses and Stephen P. Koob and Corning Museum of glass for supplying the standard glass samples. Farahnaz Koleini and Innocent Pikirayi acknowledge the financial contribution from the South African National Research Foundation (NRF) Competitive Program for Rated Researchers (CPRR) project titled Great Zimbabwe's Complexity (2017-2019) grant no. 105866.

References

[1] F. Koleini, Ph. Colomban, I. Pikirayi, L.C. Prinsloo, Glass beads, markers of ancient trade in sub-Saharan Africa: methodology, state of the art and perspectives, *Heritage* 2 (2019) 2343–2369

[2] M. Wood, A glass bead sequence for Southern Africa from the 8th to the 16th century AD, *J. Afr. Archaeol*. 9 (2011) 67-84.

[3] F. Koleini, I. Pikirayi, Ph. Colomban, Revisiting Baranda: a multi-analytical approach in classifying sixteenth/seventeenth-century glass beads from northern Zimbabwe, *Antiq.* 91(2017) 751–764.

[4] F. Koleini, L.C. Prinsloo, W.M. Biemond, Ph. Colomban, A.T. Ngo, J. Boeyens, M. van der Ryst, K. van Brakel, Unravelling the glass trade bead sequence from Magoro Hill, South Africa: separating pre-17th-century Asian imports from later European counterparts, *Heritage Sci*. 4:43 (2016).

[5] F. Koleini, L.H. Machiridza, I. Pikirayi, Ph. Colomban, The chronology of Insiza cluster Khami-phase sites in south-western Zimbabwe: compositional insights from pXRF and Raman analysis of excavated exotic glass finds, *Archaeom.* 61 (2019) 874-890. DOI :10.1111/arcm.12463.

[6] A. Tournié, L.C. Prinsloo, Ph. Colomban, Raman classification of the glass beads excavated on Mapungubwe hill and K2, two archaeological sites in South Africa, *J. Raman Spectrosc.* 43 (2012) 532-42.

[7] P. D. Rostron, M. H. Ramsey, Quantifying Heterogeneity of Small Test Portion Masses of Geological Reference Materials by Portable XRF Spectrometry: Implications for Uncertainty of Reference Values, Geo Stand. Geo Anal. Res. 41 (2017) 459-473. DOI: 10.1111/ggr.12162.

[8] F. Martín Peinado, S. Morales Ruano, M.G. Bagur González, C. Estepa Molina, A rapid field procedure for screening trace elements in polluted soil using portable X-ray fluorescence (PXRF), Geoderma 159 (2010) 76-82. https://doi.org/10.1016/j.geoderma.2010.06.019.

[9] N. Craig, R. J. Speakman, R. S.Popelka-Filcoff, M. D. Glascock, J. D. Robertson, M. S. Shackley, M.S. Aldenderfer, Comparison of XRF and PXRF for analysis of archaeological obsidian from southern Perú, *J. Archaeol. Sci*. 34 (2007) 2012-2024.

[10] H. X. Zhao, Q.H. Li, Combined spectroscopic analysis of stratified glass eye beads from China dated to the Warring States Period, *J. Raman spectrosc*. 48 (2017) 1103-1110. DOI: 10.1002/jrs.5177.

[11] G. Simsek, Ph.Colomban, S. Wong, B. Zhao, A. Rougeulle, N.Q. Liem, Toward a fast non-destructive identification of pottery: the sourcing of 14th-16th century Vietnamese and Chinese ceramic shards, *J. Cult. Heritage* 16 (2015) 159-172.

[12] I.C. Freestone, Y. Gorin-Rosen, M.J. Hughes, Composition of primary glass from Israel, In: M.D. Nenna (Ed.), Ateliers primaires et secondaires de verriers du second millénaire av. J.-C. au Moyen-Age, Travaux de la Maison de l'Orient Méditerranéen no. 33, Lyon, 2000, pp. 65-84.

[13] B. Gratuze, Provenance analysis of glass artefacts, In: K. Janssens (Ed.), *Modern methods for analysing archaeological and historical glass*, John Wiley and Sons, Chichester, UK, 2013, pp. 311-340. Available at: http://onlinelibrary.wiley.com/book/10.1002/9781118314234.

[14] A. Shortland, L. Schachner, I. Freestone, M. Tite, Natron as a Flux in the Early Vitreous Materials Industry: Sources, Beginnings and Reasons for Decline, *J. Archaeol. Sci*. 33 (2006) 521-530.

[15] S. Cagno, M. Mendera, T. Jeffries, K. Janssens, Raw materials for medieval to post-medieval Tuscan glassmaking: new insight from LA-ICP-MS analyses, *J. Archaeol. Sci*. 37 (2010) 3030-3036.

[16] S. Cagno, M. Brondi Badano, F. Mathis, D. Strivay, K. Janssen, Study of medieval glass from Savona (Italy) and their relation with the glass produced in Altare, *J. Archaeol. Sci*. 39 (2012) 2191-2197.

[17] I. De Raedt, K. Janssens, J. Veeckman, L. Vincze, B. Vekemans, T.E. Jeffries, Trace analysis for distinguishing between Venetian and Façon-de-Venise glass vessels of the 16th and 17th century, *J. Anal. At. Spectrom*. 16 (2001)1012–1017.

[18] M. Verità, S. Zecchin, Thousand years of Venetian glass: the evolution of chemical composition from the origins to the 18th century. In: K. Janssens, P. Degryse, P. Cosyns, J. Caen, L. Van't dack (Eds.), Annales du 17e Congrès de l'Association Internationale pour l'Histoire du Verre (AIHV), Belgium, 4th to 8th September 2006. Aspeditions, Antwerp, 2009, pp. 602-613.

[19] M.S. Tite, A. Shortland, Y. Maniatis, D. Kavoussanaki, S.A. Harris, The Composition of the soda-rich and mixed alkali plant ashes used in the production of glass, *J. Archaeol. Sci.* 33 (2006) 1284-1292.

[20] I. De Raedt, K. Janssens, J. Veeckman, On the distinction between 16th and 17th century Venetian and Façon-de-Venise glass. In: J. Veeckman (Ed.), Majolica and Glass: from Italy to Antwerp and Beyond. The Transfer of Technology in the 16th - early 17th Century, Stad Antwerpen, Antwerp, 2002, pp. 95-121.

[21] I. Coutinho, New insights into 17th and 18th century glass from Portugal: Study and Preservation. Dissertation, Universidade Nova de Lisboa, 2016.

[22] J.J. Kunicki-Goldfinger, J. Kierzek, P. Dzierzanowski, A. Kasprzak, Central European crystal glass of the girst half of the 18th century. In: Annales du 16th Congrès de l'Association Internationale pour l'Histoire du Verre (AIHV), 7th to 13th September 2003. Nottingham, London, 2005, pp. 258-262.

[23] W. Coope, *The Crown Glass Cutter and Glazier's Manual*, Oliver and Boyd, Edinburgh, 1835.

[24] L. Milner, A. Butterworth, *The Manufacture of Glass*, Pitman, London, 1948.

[25] D. Dungworth, The value of historic window glass, Hist. Environ. Policy & Pract. 2 (2011) 21-48. https://doi.org/10.1179/175675011X12943261434567.

[26] L.C. Prinsloo, A. Tournié, Ph. Colomban, A Raman spectroscopic study of glass trade beads excavated at Mapungubwe hill and K2, two archaeological sites in southern Africa, raises questions about the last occupation date of the hill, *J. Archaeol. Sci.* 38 (2011) 3264-3277.

[27] T. Huffman, Mapungubwe and the origins of the Zimbabwe culture, *S. Afr. Archaeol. Soc*. Goodwin Ser. 8 (2000) 14-29.

[28] L. Fouché, *Mapungubwe*. University Press, Cambridge, 1937.

[29] F. Koleini, L.C. Prinsloo, W.M. Biemond, Ph. Colomban, A. Nego, J. Boeyens, M. van der Ryst, Towards refining the classification of glass trade beads imported into southern Africa from the 8th to the 16th century AD, *J. Cult. Heritage* 19 (2016) 435-444.

[30] S. Cagno, K. Janssens, M. Mendera, Compositional analysis of Tuscan glass samples: in search of raw material fingerprints, *Anal. BioAnal. Chem*. 391 (2008) 1389-1395.

[31] Ph. Colomban, Polymerization degree and Raman identification of ancient glasses used for jewelry, ceramic enamels and mosaics, *J. Non-Cryst. Solids* 323 (2003) 180-187.

[32] Ph. Colomban, O. Paulsen, Raman Determination of the Structure and Composition of Glazes, *J. Amer. Ceram. Soc*. 88 (2005) 390-395.

[33] V. Labet, Ph. Colomban, Vibrational properties of silicates: A cluster model able to reproduce the effect of "SiO_4" polymerization on Raman intensities, *J. Non-Cryst. Solids* 370 (2013) 10-17.

[34] Y. Barkoudah, J. Henderson, Plant ashes from Syria and the manufacture of ancient glass: ethnographic and scientific aspects, *J. Glass Stud*. 48 (2006) 297-321.

[35] J. de Juan Ares, N. Schibille, 2017. Glass import and production in Hispania during the early medieval period: The glass from Ciudad de Vascos (Toledo). *PLOS ONE*. 12, e0182129. https://doi.org/10.1371/journal.pone.0182129.

[36] L.Dussubieux, K. Karklins, Glass bead production in Europe during the 17th century: elemental analysis of glass material found in London and Amsterdam, *J. Archaeol. Sci.* Reports 5 (2016) 574-589.

[37] S. Ulitzka, Analysen von historischen Gläsern – Licht im Dunkel der Geschichte? In: A. Theuerkauff-Liederwald (Ed.), Venezianisches Glas der Kunstsammlungen der Veste Coburg. Die Sammlung Herzog Alfreds von Sachsen-Coburg und Gotha (1844-1900): Venedig, á la façon-de-Venise, Spanien, Mitteleuropa, Luca verlag, Lingen, 1994, pp. 40-53.

[38] K. Fukumi, J. Hayakawa, T. Komiyama, Intensity of Raman band in silicate glasses, *J. Non-Cryst. solids* 119 (1990) 297-302.

[39] W.B. Stern, Y. Gerber, Potassium-Calcium glass: new data and experiments, *Archaeom.* 46 (2004)137-156.

[40] Z. Cílová, J. Woitsch, Potash e a key raw material of glass batch for Bohemian glasses from 14the17th centuries? *J. Archaeol. Sci.* 39 (2012) 371-380.

[41] P. Ricciardi, Ph. Colomban, A. Tournie, V. Milande, Non-destructive on-site identification of ancient glasses: genuine artefacts, embellished pieces or forgeries? *J. Raman Spectrosc*. 40 (2009) 604-17.

[42] A. Rousaki, A. Coccato, C. Verhaeghe, B.O. Clist, K. Bostoen, P. Vandenabeele, L. Moens, Combined spectroscopic analysis of beads from the tombs of Kindoki, Lower Congo Province (Democratic Republic of the Congo), *Appl. Spectrosc*. 70 (2016) 76-93.

[43] K. Karklins, S. Jargstorf, G. Zeh, L. Dussubieux, The Fichtelgebirge bead and button industry of Bavaria, *J. Soc. Bead Res*. 28 (2016) 16-37.

[44] D. Dungworth, T. Cromwell, D. Ashurst, C. Cumberpatch, D. Higgins, H. Willmott, Glass and pottery manufacture at Silkstone, Yorkshire, *Post-Medieval Archaeol.* 40 (2006) 160-190.

[45] D. Dungworth, C. Mortimer, *Examination of Glassworking Materials from Cheese Lane, Bristol,* Centre for Archaeology Report Series, English Heritage, no. 6/2005. ISSN 1473-9224, 2005.

[46] M. Verità, Venetian soda glass, In: K. Janssens (Ed.), *Modern Methods for Analysing Archaeological and Historical Glass,* Vol. I. Wiley, Chichester, 2013, pp. 515-536.

[47] R.G.V. Hancock, S. Aufreiter, I. Kenyon, European white glass trade beads as chronological and trade markers, In: P. Vandiver, J.R. Druzik, J.F. Merkel, J. Stewart (Eds.), Materials Issues in Art and Archaeology V, Materials Research Society Symposium Proceedings, vol. 462. Materials Research Society, Pittsburgh, PA, 1997, pp. 181-191.

[48] B. Manoun, M. Azdouz, M. Azrour, R. Essehli, S. Benmokhtar, L. El Ammari, A. Ezzahi, A. Ider, P. Lazor, Synthesis, Rietveld refinements and Raman spectroscopic studies of tricationic lacunar apatites $Na_{1-x}K_xPb_4(AsO_4)_3$ ($0 < x < 1$), J. Mol. Struct. 986 (2011) 1-9.

[49] J. Van Pevenage, D. Lauwers, D. Herremans, E. Verhaeven, B. Vekemans, W. De Clercq, L. Vincze, L. Moens, P. Vandenabeele, Anal. Meth. *6* (2014) 387-394.

[50] Ph. Colomban, M. Maggetti, A. d'Albis, Raman Identification of the arsenic apatite opacifier and associated phases in the blue and green décor of a 1781 Sèvres soft paste porcelain, *J. Eur. Ceram. Soc. 38* (2018) 5228-5233.

[51] B. Kirmizi, Ph. Colomban, M. Blanc, On-site analysis of Limoges enamels from sixteenth to nineteenth centuries: an attempt to differentiate between genuine artefacts and copies, *J. Raman Spectrosc.* 41(2010) 1240-47.

[52] A. Bonneau, J. Moreau, R. Auger, R.G.V. Hancock, B. Émard, Analyses physico-chimiques des perles de traite en verre de facture européenne: quelles instrumentations pour quels résultats? *Archéologiques* 26 (2013) 109-132.

[53] H.G.M. Edwards, E.S.J. Villar, K.A. Eremin, Raman spectroscopic analysis of pigments from dynastic Egyptian funerary artefacts, *J. Raman spectrosc.* 35 (2004) 786-795.

[54] Ph. Colomban, Lapis lazuli as unexpected blue pigment in Iranian Lâjvardina ceramics, *J. Raman Spectrosc*. 34 (2003) 420-423.

[55] M.C. Caggiani, Ph. Colomban, C. Valotteau, A. Mangone, P. Cambon, Mobile Raman spectroscopy analysis of ancient enamelled glass masterpieces. *Anal. Methods* 5 (2013) 4345-4354.

[56] F. Rosi, V. Manuali, C. Miliani, B.G. Brunetti, A. Sgamelloti, T. Grygar, D. Hradil, Raman scattering features of lead pyroantimonate compounds. Pat I: XRD and Raman characterization of $Pb_2Sb_2O_7$ doped with tin and zinc, *J. Raman Spectrosc*. 40 (2009) 107-111.

[57] W. Noll, Anorganische Pigmente in der Vorgeschichte und Antike, Fortschr Miner 57 (1979) 203-263.

[58] F. Schweizer, A. Rinuy, Manganese black as an Etruscan pigment. *Stud. Conservation* 27 (1982) 118-123.

[59] R.J.H. Clark, L. Curri, G.S. Henshaw, Characterization of brown-black and blue pigments in glazed pottery fragments from Castel Fiorentino (Foggia, Italy) by Raman microscopy, X-ray photoelectron spectroscopy, *J. Raman Spectrosc*. 28 (1997) 105-109.

[60] E.V. Sayre, R.W. Smith, Some materials of glass manufacturing in antiquity, In: M. Levey (Ed.), *Archaeological Chemistry: A Symposium, 3rd Symposium on Archaeological Chemistr*y, University of Pennsylvania Press, Philadelphia, 1967, pp. 279-312.

[61] J. Henderson, The raw material of early glass production, *Oxford J. Archaeol.* 4 (1985) 267-291.

[62] I.C. Freestone, Composition and Microstructure of Early Opaque Red Glass, In: M. Bimson, I. Freestone (Eds), *Early Vitreous Materials*, British Museum occasional paper 56, 1987, pp. 173-191.

[63] O. Mecking, Medieval lead glass in central Europe, *Archaeom*. 55 (2013) 640-662.

[64] S. Lahlil, I. Biron, M. Cotte, J. Susini, New insight on the in situ crystallization of calcium antimonite opacified glass during the Roman period, *Appl. Phys. A* 100 (2010) 683-692.

[65] G.M. Theal, *The beginning of South African history*, T. Fisher Unwin, London,1902.

[66] A.K. Smith, The struggle for the control of Southern Mozambique, Ph.D. Thesis, University of California, 1970.
[67] P. Francis Jr., The Venetian Bead Story, part 1: history, *The Margaretologist,* 11 (1998), 3-12.

[68] K. Karklins, Early Amsterdam trade beads, *Ornament* 9 (1985) 36-41.

[69] G. Caton-Thompson, *The Zimbabwe Culture,* Clarendon Press, Oxford, 1931.

[70] P. Francis Jr., *Beads of the World,* Atglen. Schiffer Publishing Ltd, PA, 1994.

[71] W. G. N. Van der Sleen, *A Handbook on Beads*, George Shumway, York, Pennsylvania, 1967.

[72] M. Wood, Post-European contact glass beads from the southern African interior: a tentative look at trade, consumption and identities, In: N. Swanepoel, A. Esterhuysen, P. Bonner (Eds.), *Five hundred years rediscovered*, Witwatersrand University Press, Johannesburg, 2008, pp. 183-196.

[73] C.R. DeCorse, F.G. Thiaw, I. Thiaw, Toward a systematic bead description system: a view from the Lower Falemme, Senegal, *J. Afr. Archaeol.* 1 (2003)77-110.

[74] P. Francis Jr., *The Czech Bead Story*, World of Beads Monograph Series 2, Lapis route book, New York, 1979.

[75] P. Francis Jr., *Advanced bead identification*, The Center for Bead Research Lake Placid, NY, 1993.

[76] P. Robertshaw, M. Wood, A. Haour, K. Karklins, H. Neff, Chemical analysis, Chronology, and context of a European glass bead assemblage from Garumele, Niger. *J. Archaeol. Sci*. 4 (2014) 591-604.

Figure captions and tables titles

Fig. 1 Representative analysed beads classified in 6 different compositional groups. ↓= Low lime (pure ash), *=Calcium antimoniate, ■=Lead <13%, ●=Manganese, ▲=Arsenate, ┼=Pb-Sn-Sb triple oxides, ♦=Lazurite

Fig. 2 Plot of CaO versus to K_2O concentration of European glass beads

Fig. 3 Ternary diagram of CaO, Al_2O_3 and K_2O + MgO concentrations

Fig. 4 Recorded Raman spectra of European glass beads a) glass matrix b) pigments and opacifiers

Table 1. As measured and corrected major and minor element oxides concentration of glass beads presented in wt%

Table 2. Dispersion of analysed beads in selected sites by type, date and possible origins of them. (The beads are kept in University of Pretoria Museum)

Fig S1. Representative analysed beads in 7 different compositional groups

Table S1. Summary of European soda rich plant ash glass composition and distribution in Europe from the10^{th} to the 17^{th} centuries

Table S2. Archaeological context, morphology and series of 188 analysed glass beads with pXRF after Wood (2011)

Table S3. Comparison of 19 major, minor and trace element wt% in glass references B and D obtained by pXRF and LA-ICP-MS (193nm laser ablation)*

Table S4 Corrected major and minor element oxides concentration (wt%) of glass beads with the impact of normalization factors (NF) of Corning samples A, C and D. The results for glass beads with arsenate content are reported as measured after normalisation.

Table S5 Pigments, opacifiers and colorants detected in glass beads by Raman spectroscopy and XRF analysing in addition to the estimated date

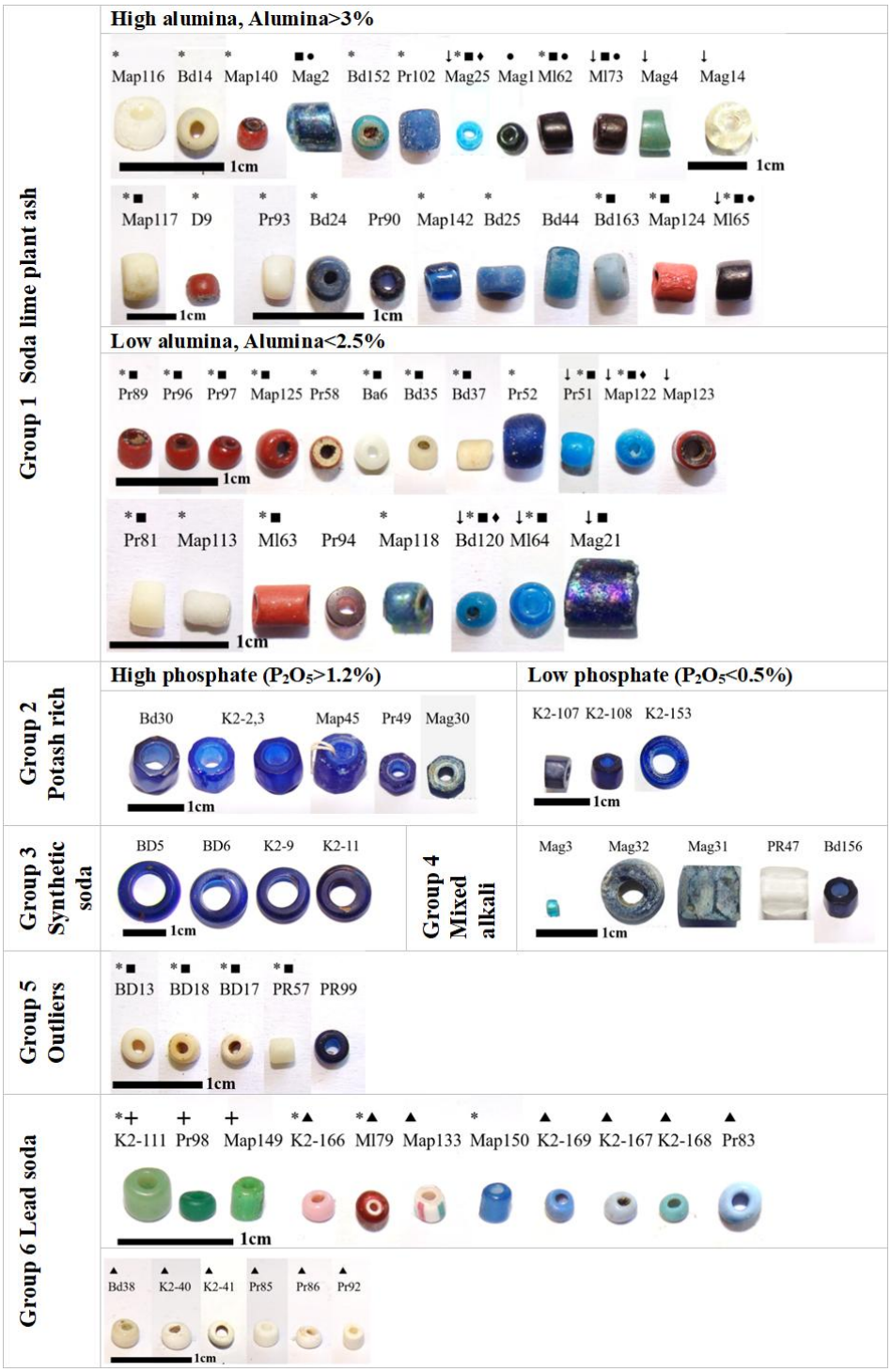


Fig. 1 Representative analysed beads classified in 6 different compositional groups. ↓= Low lime (pure ash), *=Calcium antimoniate, ■=Lead <13%, ●=Manganese, ▲=Arsenate, ┼=Pb-Sn-Sb triple oxides, ♦=Lazurite

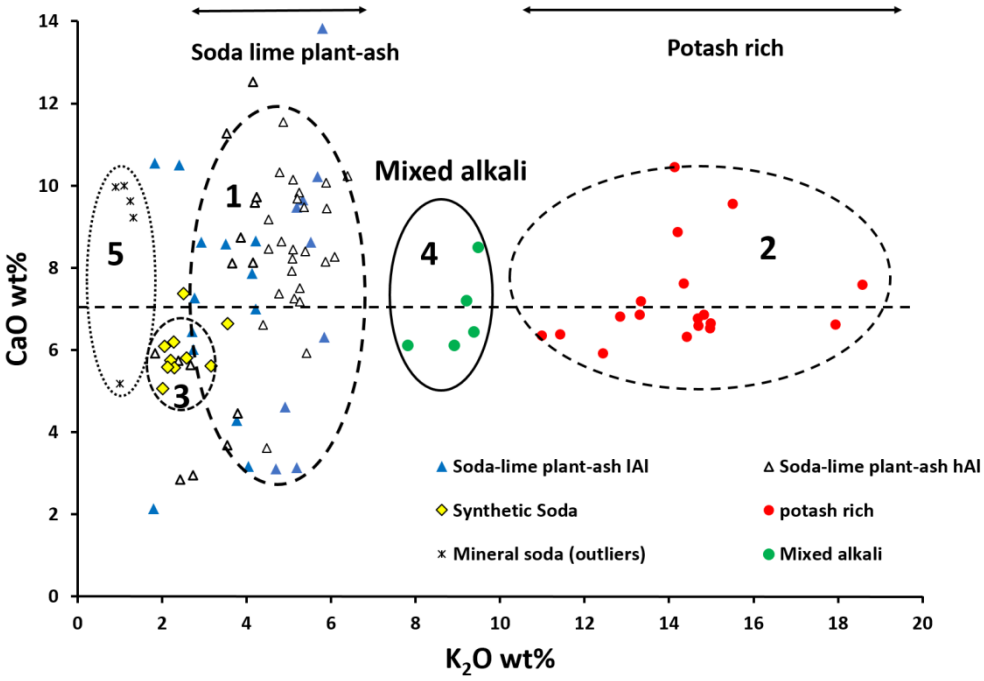


Fig. 2 Plot of CaO versus to K_2O concentration of European glass beads

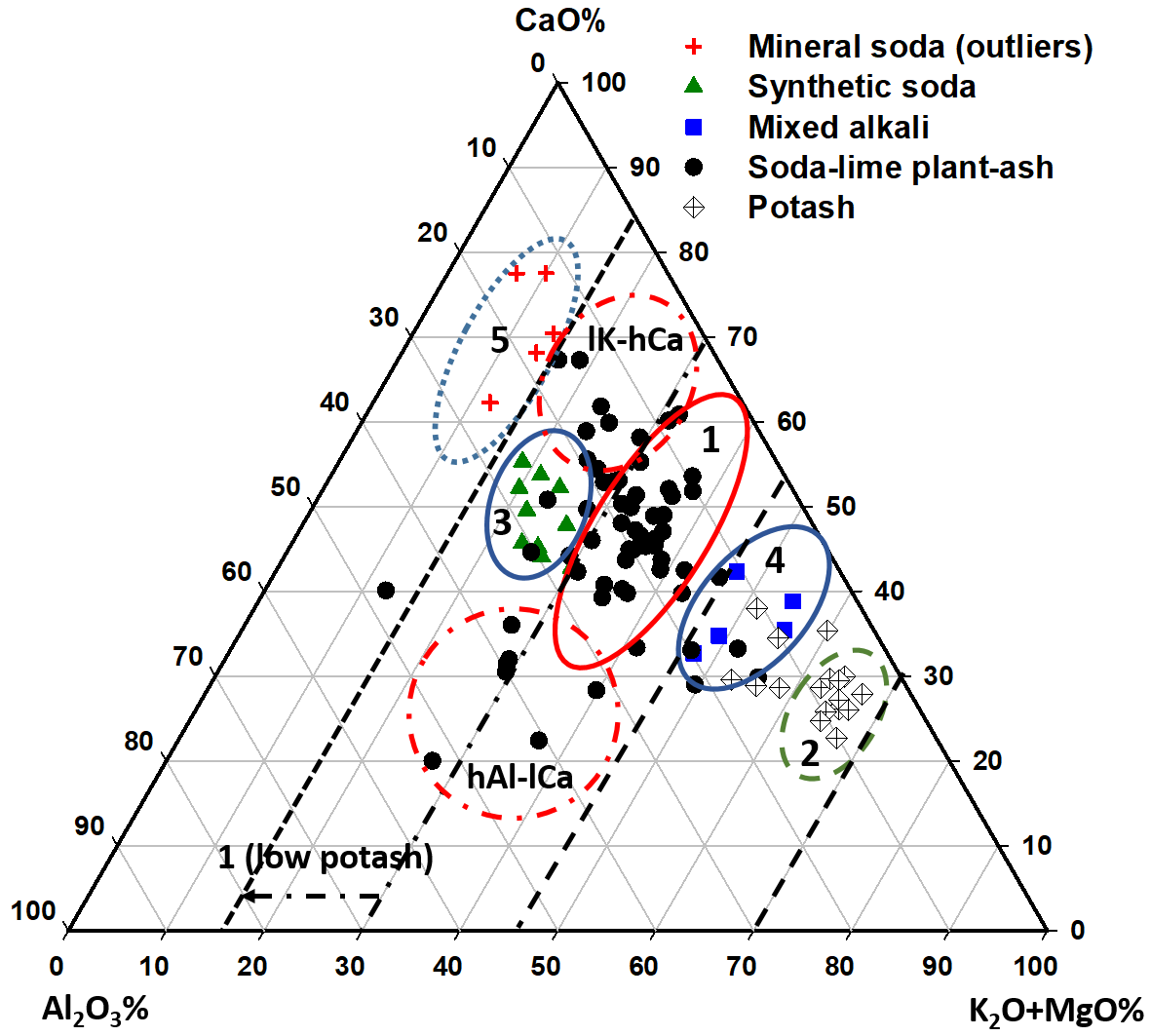


Fig. 3 Ternary diagram of CaO, Al_2O_3 and K_2O + MgO concentrations

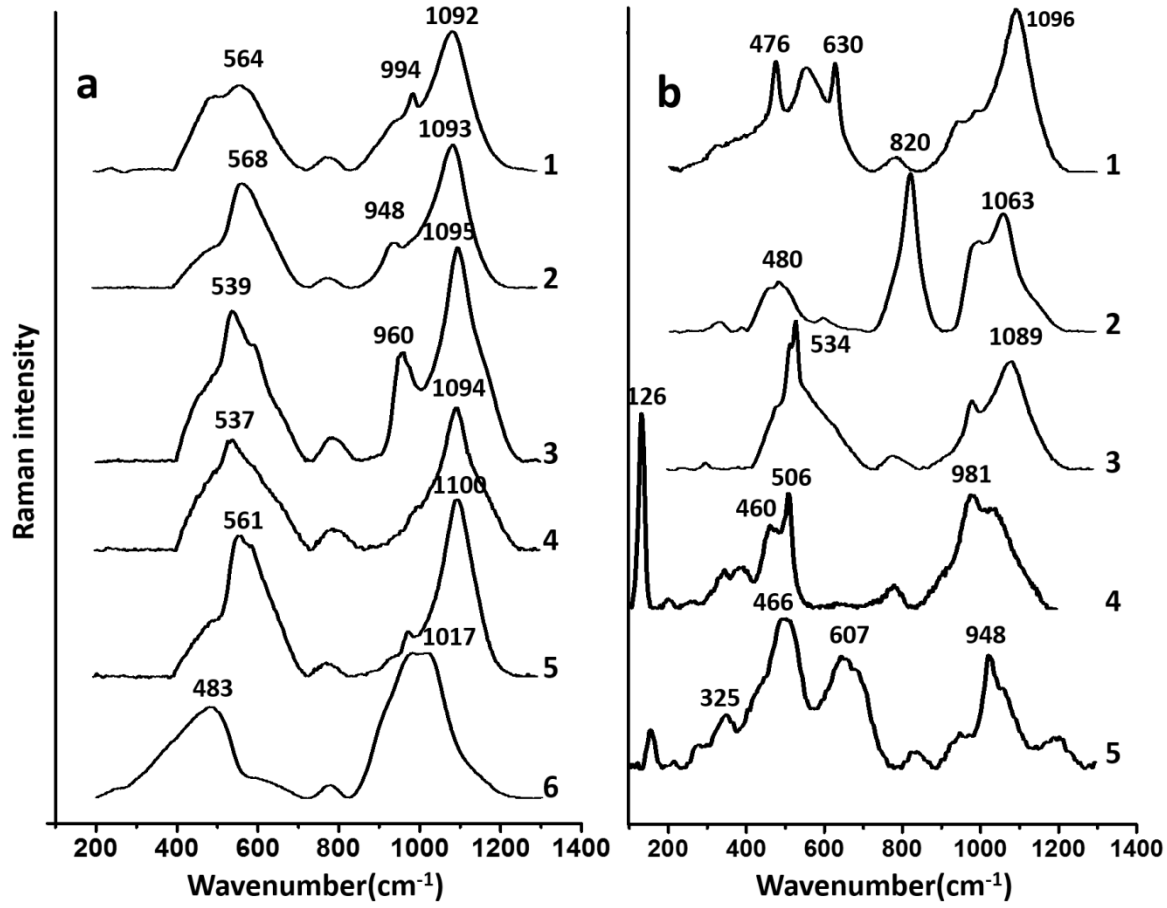


Fig. 4 Recorded Raman spectra of European glass beads a) glass matrix b) pigments and opacifiers

Table 1 As measured and corrected major and minor element oxides concentration of glass beads presented in wt%

Groups		SiO_2	Al_2O_3	MgO	CaO	K_2O	Fe_2O_3	PbO	Balance
Group1 soda lime plant ash	Min	63.67	0.93	-	2.14	1.80	0.19	-	9.23
	Max	76.61	9.73	3.00	13.83	6.39	5.78	-	16.18
	Average	69.61	3.49	1.13	7.73	4.36	1.33	-	12.35
	STD	3.12	1.71	0.70	2.59	1.18	1.24	-	1.43
Group 2 Potash rich	Min	65.72	1.18	-	5.92	10.98	0.09	-	3.37
	Max	70.13	3.77	2.27	10.45	18.57	0.90	-	8.13
	Average	68.35	2.31	1.20	7.22	14.30	0.18	-	6.43
	STD	1.29	0.81	0.86	1.21	1.90	0.18	-	1.21
Group 3 Synthetic soda	Min	70.01	2.34	-	5.06	2.02	0.36	-	13.97
	Max	74.75	4.23	1.19	7.37	3.55	0.57	-	15.46
	Average	72.47	3.36	0.50	5.97	2.48	0.44	-	14.78
	STD	1.38	0.58	0.54	0.65	0.50	0.06	-	0.44
Group 4 Mixed alkali	Min	66.97	1.04	-	6.11	7.81	0.04	-	11.47
	Max	71.14	3.90	0.97	8.51	9.48	0.94	-	13.06
	Average	68.71	2.40	0.48	6.88	8.95	0.37	-	12.21
	STD	1.79	1.20	0.45	1.01	0.67	0.37	-	0.67
Group 5 Mineral soda	Min	71.43	1.54	-	5.18	0.90	0.39	-	11.50
	Max	75.67	2.45	0.93	9.99	1.33	0.93	-	19.31
	Average	73.69	2.04	0.34	8.45	1.11	0.57	-	14.01
	STD	1.72	0.33	0.42	2.04	0.17	0.23	-	3.31
Group 6 Lead soda	Min	35.48	0.71	1.31	1.09	0.85	0.29	41.91	6.91
	Max	39.85	1.05	1.90	3.34	2.85	0.91	47.46	10.60
	Average	37.48	0.82	1.56	2.37	2.00	0.68	43.96	8.95
	STD	1.95	0.16	0.26	0.94	0.90	0.27	2.46	1.71

Table 2 Dispersion of analysed beads by type, date and possible origins in selected sites. (The beads are kept in University of Pretoria museum.

Glass groups/ types	Subgroups/bead%/Origin/date	Sites	XRF test No.	N.
Group1	High alumina + pure ash/ (8%)	Ml	62-73	2
Soda-lime plant-ash	Southern Europe	Mag	**4**-**14**-25	3
	15th-late 17th c.			
	High alumina + unrefined ash / (56%)	Bd	14-24-25-26-27-**44**-152-163	8
	Southern Europe	Ml		1
	15th-late 17th c.	Pr	56-**90**-93-102-82	5
		Map	112-116-117-124-130-132-140-142	8
		Mag	**1**-2-5-10	4
		D	1-4-6-7-9-11-12-**13**	8
	Low Al + pure ash/ (11.5%)	Bd	120	1
	South and central Europe	Ml	64-65	2
		Pr	51	1
		Map	122-**123**	2
		Mag	21-8	2
	Low Al + unrefined ash/ (24.5%)	Bd	35-37	2
	South and central Europe	Ml	63	1
		Pr	52-58-81-89-**94**-96-97	7
		Map	113-118-125-119	4
		Ba	6	1
Group 2	High P_2O_5 (1.2-2.5 wt%)/ (83%)	Bd	30-31	1
Potash rich	Bohemian	Pr	49	1
	Late 19th c.	Map	45	1
		Mag	30	1
		K2	1-2-3-4-32-33-42-43	8
	Low P_2O_5 (<0.5 wt%)/ (17%)	K2	107-108-153	3
	Early 19th c.			
Groupe3	K_2O< 4wt% , mean Cl=0.5	Bd	5-6-7-8-158	5
Synthetic soda	Mean MgO=0.5wt%	K2	9-11-12-28-29	5
	Late 19th-20th c.			
Group 4	19^{th} c.	Bd	156	1
Mixed alkali		Pr	47	1
		Mag	3-31-32	3
Group 5	Natron/?	Bd	13-17-18	3
Mineral soda/		PR	99-57	2
Group 6	High lead oxide and low arsenate	Pr	98	1
Lead soda	PbO>40% and As_2O_3<6% wt%	Map	148-149	2
	Late 17th c.	K2	111	1
	Low lead oxide and high arsenate	Bd	16-38-104-105-106-160-166-167-168-169	10
	PbO<37% and As_2O_3>9 wt%			
	Early 19^{th} c.	Pr	83-85-86-91-92	5
		Ml	79	1
		Map	133-147-159	3
		K2	39-40-41-114	4
		Total		127

Note. Labels with underline show the beads with K2O<3.5wt%. Bd: Bambandyanalo, Ml: Maryland, Pr: Parma, Map: Mapungubwe, Mag:,Magoro Hill, D: Danamombe