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Towards refining the classification of glass trade beads imported into Southern Africa from the 8th to the 16th century AD

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Abstract

Tracing the origin of glass trade beads excavated at archaeological sites can contribute significantly to dating a site and reconstructing prehistoric trade routes. Wood developed a temporally sensitive bead sequence dating from the 8th to the 16th century AD for beads excavated at southern African sites that is commonly used by archaeologists to classify beads according to their morphology. In this study, we develop a multidisciplinary methodology to refine the classification of glass beads based on morphology alone. Glass trade beads excavated at 11 sites along the upper reaches of the Limpopo River in east-central Botswana are used as case study. The beads were visually classified according to their morphological properties (colour, size, etc.) and analysed with Raman spectroscopy and portable X-ray fluorescence (XRF). Energy Dispersive Spectroscopy (EDS) of one bead showed that two types of glass were sintered together to form a recycled product, explaining the divergence of Raman spectra recorded on different zones. The study confirms the value of a morphological classification based on existing data sets as a first approach, but demonstrates that both Raman and XRF measurements can contribute to a more exact classification of glass beads imported into southern Africa from the East before the 17th century AD.

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TOWARDS REFINING THE CLASSIFICATION OF GLASS TRADE BEADS IMPORTED INTO SOUTHERN AFRICA FROM THE 8th TO THE 16th CENTURY AD

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ABSTRACT

Tracing the origin of glass trade beads excavated at archaeological sites can contribute significantly to dating a site and reconstructing prehistoric trade routes. Wood developed a temporally sensitive bead sequence dating from the 8th to the 16th century AD for beads excavated at southern African sites that is commonly used by archaeologists to classify beads according to their morphology. In this study we develop a multidisciplinary methodology to refine the classification of glass beads based on morphology alone. Glass trade beads excavated at 11 sites along the upper reaches of the Limpopo River in east-central Botswana are used as case study. The beads were visually classified according to their morphological properties (colour, size, etc.) and analysed with Raman spectroscopy and portable X-ray fluorescence (XRF). Energy Dispersive Spectroscopy (EDS) of one bead showed that two types of glass were sintered together to form a recycled product, explaining the divergence of Raman spectra recorded on different zones. The study confirms the value of a morphological classification based on existing data sets as a first approach, but demonstrates that both Raman and XRF measurements can contribute to a more exact classification of glass beads imported into southern Africa from the East before the 17th century AD.

Keywords: Glass trade beads/Iron Age/Botswana/Raman spectroscopy/X-ray fluorescence spectroscopy (XRF)/ Energy dispersive spectroscopy (EDS)

Research aims

Glass beads have been part of indigenous southern African culture and tradition since they were first imported into the region during the 7th century AD [1, 2]. In order to date sites and accurately reconstruct trade routes or connections, appropriate analytical techniques are essential to correctly classify bead assemblages. Although a substantial amount of scientific research has been conducted on the classification of glass trade beads, the field archaeologist still largely depends on classification by means of morphological parameters, which may lead to wrongful attributions. In this study we aim to assess the viability of using two unbiased techniques, namely Raman spectroscopy and X-ray fluorescence spectroscopy (XRF), to refine a bead classification system that relies on morphological parameters.

Introduction

The most commonly used system to classify beads recovered at archaeological sites dating from the 8th to the 16th century AD in southern Africa is the temporally sensitive bead sequence (Table S1) developed by Wood [1, 2]. The sequence was developed by classifying beads from securely dated sites according to morphological parameters, after which the attributions were chemically tested by Robertshaw et al. [3] using Laser ablation - Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS).

Bead series	Period traded in southern Africa	Method of manufacture	Size	Colour	Shape
K2-IP	ca. AD 980-1200	Drawn	Minute-small 2-3.5 mm diameter 1.2-4 mm long	Transparent to translucent blue-green to light green	Tubes
EC-IP	ca. AD 1000-1250	Drawn	Minute- large 2-5 mm diameter	Opaque black and brownish-red; yellow, soft orange, green and blue-green are translucent	Vary - most are cylindrical
Map Oblate	ca. AD 1240-1300	Drawn, Heat rounded	Minute-small 2-3.5 mm diameter	Translucent blue-green, dark blue, yellow, orange and plum. Opaque black the most common	Uniform oblates
Zimbabwe	ca AD 1300-1430	Drawn	Minute-small 2-3.5 mm diameter	Translucent blue-green, blue, yellow; transparent dark green, opaque black	Cylinders and oblates
K-IP	ca.AD 1430-1650	Drawn	Medium-large 3.5-5.5 mm diameter	Opaque black, brownish red; translucent blue-green, green, yellow, orange, blue and white	Vary - most are irregular cylinders

In most instances the beads retrieved from southern African archaeological sites are small monochrome drawn beads and, as a result, they are difficult to classify unambiguously in the field. The means to chemically analyse beads using LA-ICP-MS as applied by Robertshaw et al. [3] are also not always readily available and, due to very large variations in the chemical composition of each

bead series, assignments are not always clear-cut (Table S2). Raman spectroscopy has been successfully used to classify glass trade beads [4-7] and has the advantage that information about the composition of the glass, as well as pigments colouring the glass, can be obtained from the same spectrum or by more than one spectrum, focusing either on the glass or the pigment. However, Raman spectroscopy also has its limitations as the intensity of a Raman signature greatly depends on the number of electrons involved in the bond and some phases are hardly detected. Furthermore, ions that are in many instances the origin of glass colour do not give special Raman signals, and if classifications depend on the presence of trace elements (eg. uranium), Raman spectroscopy is not useful.

Table S2: Average composition of some glass bead series from southern Africa (oxides wt%) (Robertshaw et al. 2010)

Bead series	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃
K2-IP	10.91-22.37	0.16-0.83	6.40-17.66	57.89-73.58	1.98-5.11	1.53-3.37	0.55-3.46
EC-IP	11.26-20.23	0.24-1.78	4.21-21.09	55.26-71.96	1.90-5.5	1.73-4.84	0.64-5.84
Map Oblate	10.38-19.51	2.68-10.16	5.01-11.93	51.34-70.06	2.02-5.31	3.35-12.41	0.52-2.54
Zimbabwe	10.31-20.89	2.97-6.02	2.98-9.77	51.21-67.26	2.21-5.13	4.27-11.30	0.64-3.26
K-IP	10.42-31.76	0.47-2.73	5.39-16.22	48.65-74.95	1.45-9.2	1.71-6.61	0.76-7.30

Recently the progress in developing portable instruments (Raman and XRF) has made these techniques more accessible to archaeologists. In this study we endeavour to develop a multidisciplinary methodology to classify glass trade beads, using as case study glass trade beads excavated at 11 sites in the Upper Limpopo River region in east-central Botswana (Fig. 1). An experienced field archaeologist classified the beads based on morphological parameters [8], according to the bead sequence developed by Wood [1, 2]. Using this classification as a guideline, representative beads were selected for Raman measurements and the spectra compared to the spectral database of the beads excavated at Mapungubwe [4, 5]. Based on the classification of bead types according to their Raman spectra, beads were selected for XRF analyses in order to form a link between the chemical composition and Raman spectrum of a bead.

Materials and methods

3.1 Archaeological context and samples

A substantial number of glass trade beads (1014) were recovered from Iron Age sites in the Mahalapye area of east-central Botswana (Fig.1). The sites are in the proximity of the upper reaches of the Limpopo River on Basinghall Farm, at Kudumatse Village and at the Mmamabula Energy Project [8]. These locations are about 280 km south-west of Mapungubwe and 120 km south of Toutswemogala, two prominent Middle Iron Age capitals in southern Africa. The

excavations were carried out as part of a formal research project on Basinghall Farm [8], as well as Cultural Resource Management (CRM) impact assessments in the adjacent area [unpublished reports].

Figure 1: Map of the region indicating the sites where the beads were excavated. (K - Kudumatse Village; MEP - Mmamabula Energy Project) in relation to the important archaeological sites of K2 and Mapungubwe.

The excavated sites on Basinghall and adjacent areas, as well as their allocated site numbers, are shown in Fig. 1. Middle Iron Age (c. AD 900–1300) African farmer sites in the research area can be assigned either to the dominant Toutswe chiefdom in the region or to the minority or subject Eiland people on its fringes [9]. All the Toutswe and Eiland sites from which beads were retrieved for this analysis can be classified as small commoner settlements or outposts. Extensive trade networks were established between the Toutswe chiefdom in eastern Botswana and K2 (c. AD 1020–1220) and its successor, Mapungubwe (c. AD 1220–1300), two major political centres situated near the confluence of the Shashe and Limpopo Rivers. K2 and Mapungubwe served as key nodes for the import and distribution of glass beads that reached the southern African interior through the Indian Ocean trading network [1].

Late Iron Age sites (c. AD 1300–1850) in the study area can be attributed to Tswana-speaking African farmers who were the producers of distinctive red- and black-coloured Letsibogo facies pottery. They settled in small villages in which residential units were arranged around central cattle byres [10]. Letsibogo communities traded with Shona (Kalanga-speaking) groups to the north which were located within the sphere of influence of the Khami state (15th century to mid-17th century AD) with its headquarters in south-western Zimbabwe. Khami was one of the successor states that emerged after the decline of Great Zimbabwe (c. AD 1300–1450) [8].

Table 1: The archaeological sites investigated during the project.

Site	Location	Ceramic facies	C-14 date	Bead series	Total beads
37-A3-1	Basinghall	Toutswe	BP 1010±40 (Pta 9392)	K2-IP, EC-IP, K-IP, EU	53
37-C1-4	Basinghall	Toutswe	BP 760±50 (Pta-9169)	K2-IP, EC-IP, Map, K-IP	77
37-C1-7	Basinghall	Eiland	BP 670±50 (Pta-9442)	EC-IP	170
37-C1-8	Basinghall	Toutswe	BP 870±45 (Pta-9167)	K2-IP, EC-IP, Map, K-IP	104
37-C1-19	Basinghall	Letsibogo	BP 300±15 (Pta-9303)	K-IP	4
37-C1-25	Basinghall	Letsibogo	BP 315±25 (UGAMS 03982)	K-IP	33
37-A3-16	Kudumatse	Toutswe	BP 970±40 (Beta 296842)	K2-IP, EC-IP	542
36-D2-35	Mmamabula	Toutswe	BP 910±30 (UGAMS 03595)	K2-IP, EC-IP	17
36-D2-14	Mmamabula	Letsibogo	BP 390±30 (UGAMS 02961)	Zimbabwe/K-IP	7
36-D1-3	Mmamabula	Letsibogo	BP 295±30 (UGAMS 03593)	Zimbabwe/K-IP	3
35-D3-1	Lephepe	Letsibogo	BP 320±25 (UGAMS 09973)	K-IP	4
				Total	1014

K2-IP – K2 Indo-Pacific; EC-IP – East Coast Indo-Pacific; Map – Mapungubwe Oblate; K-IP – Khami Indo-Pacific; EU - European (after Wood, 2011)

A list of the excavated sites, including their location, associated radiocarbon dates and the number of beads retrieved from each site, is given in Table 1 [8]. The beads were labelled according to the site of origin, followed by the colour of the bead (in abbreviation), as well as its number. Sites 37-A3-1, 37-A3-16, 37-C1-4, 37-C1-8 and 36-D2-35 are associated with the Toutswe ceramic facies, while

Figure 2: Colour distribution of the beads excavated at Toutswe and Letsibogo sites and their morphological assignment to the East Coast-Indo Pacific (EC-IP), K2-Indo-Pacific (K2-IP), Mapungubwe (Map), Zimbabwe (Zim), Khami (K-IP) and European (EU) series. Beads marked with an X were reclassified after Raman and XRF analyses.

37-C1-19, 37-C1-25, 36-D2-14, 35-D3-1 and 36-D1-3 represent the Letsibogo ceramic facies. Only one site yielded ceramics from the Eiland ceramic facies, namely 37-C1-7. The retrieved beads were tentatively classified (Table 1) according to Wood's morphological classification system (given in Table S1) based on colour, size, shape, glass translucency and method of manufacture.

The 72 beads selected for Raman analyses, constituting a representative sample of the types that were excavated, are shown in Fig. 2. A few Zimbabwe series beads from the Van Riet Lowe (VRL) bead collection housed at the University of the Witwatersrand were also used as reference material. These beads were visually classified by Marilee Wood.

3.2 Raman measurements

Raman spectra of the beads were recorded with three different Raman instruments. The majority of the beads were analysed with an HR Raman instrument (Horiba JobinYvon, France). A 458 nm line of an Ar⁺ ion Coherent laser was used as excitation source and a microscope attachment (Olympus) made it possible to focus on a selected area on the bead using a 50x objective.

Some beads were analysed with a portable HE532 (Horiba JobinYvon, France) spectrometer equipped with a Peltier effect-cooled CCD detector. A 532 nm Nd/YAG Ventus laser (Quantum, UK) excitation source with a maximum power output of 80 mW (for dark coloured beads) or 300 mW (for clear lighter coloured beads) was used for the analysis. The laser power at the sample was about 4 mW and 20 mW respectively. The laser source was connected by means of optic fibres to a remote SuperHead® (Horiba JobinYvon), equipped with Nikon 50x or Mitutoyo 50x and 200x long working distance objectives. It was previously observed that, due to the optical fibre connection between the remote optical head and an edge filter to eliminate the Rayleigh scattering, the background of the spectra recorded with the portable instrument is artificially increased [11]. This problem was solved by changing the first point for baseline correction from 200 cm⁻¹ to 400 cm⁻¹, which results in spectra similar to those recorded by high-resolution laboratory Raman instruments [11].

A few beads were also analysed using a T64000 Raman spectrometer (Horiba JobinYvon, France). A 514.6 nm laser line from a mixed gas Krypton-Argon laser (Coherent) was used as excitation source. A long working distance 50x objective fixed to an Olympus microscope was used to obtain spectra with a spectral resolution of ~2 cm⁻¹. Laser power at the sample was 10 mW.

3.3 XRF measurements

A portable Thermo Scientific Niton XL3t GOLDD spectrometer was used for the semi-quantitative X-ray fluorescence (XRF) measurements of the selected glass beads. The spectrometer consists of a 4 Watt Ag anode X-ray tube, capable of a maximum voltage output of 50 kV at a current of 200 µA as well as a Geometrically Optimized Large area Drift Detector (GOLDD). Due to the small sizes of the beads a Niton XL3 portable test stand was used to measure the beads. The instrument was calibrated by using the fundamental parameters as employed

by Mining Cu/Zn modes. Four range methods, namely main, low, high and light with measurement duration of 100 seconds each, were applied to detect amounts/traces of 36 elements. The limit of detection of the elements (LOD) was calculated using a 2-sigma range. The concentration of an element in each sample is given in parts per million (ppm) and then manually converted to wt%. The concentration of the elements lighter than Mg, such as sodium and oxygen, which could not be directly detected with the portable instrument used, was calculated by subtracting the sum of the weight percent of the measured elements from the total weight.

3.4 Energy dispersive spectroscopy (EDS)

A green opaque bead (C1-19-g1) (Fig. 6), which produced different Raman signatures depending on the zone of the bead that was sampled, was sliced using a Struers Minatom Diamond disk. A JEOL JSM 55 10LV SEM microscope coupled with a 500 Digital Processing XRF system was used for local analysis and to obtain an elemental distribution map of a bead cross section.

Results and discussion

Colour and morphological parameters

The beads were rinsed in sterile water to clear away the surface dirt but some corrosion products may still be present. The beads were then classified according to morphological parameters using Wood's southern African bead sequence (Table S1, Fig. 2). They were grouped into the K2-Indo-Pacific (K2-IP), East Coast Indo-Pacific (EC-IP), Mapungubwe Oblate (Map), Zimbabwe (Zim) and Khami-Indo-Pacific (K-IP) series. It should be noted that all the IP series are related in terms of origin — they come from South Asia and could therefore have a similar base chemical composition. Such beads were made for over 2000 years, so through time (and even at any one time) they would have been made at different places in the region, accounting for differences in chemistry. Thus the differences between the K2-IP/EC-IP and the Khami (K-IP) series have temporal significance. Based on the Raman results 26 beads were selected for analyses with XRF measurements.

4.2 Raman and XRF results for the glass matrix

The Raman spectrum of glass consists of two broad bands, one around 500 cm^{-1} (SiO_4 bending vibrations), and one around 1000 cm^{-1} (SiO_4 stretching vibrations). Previous studies on glass and glass beads [4, 11-16] developed a useful method for the classification of glass spectra based on the plot of

Figure 3. Classification of bead spectra by plotting maximum intensity peak positions of the bending and stretching bands against each other. (■ Toutswe; ▲ Letsibogo and ▣ Eiland. Colour fill represents the colour of the beads).

wavenumber positions of the peak maxima of the bending against stretching envelopes. Based on the results from this study (Fig. 3), four groups can be distinguished, with one group containing only one bead. A representative Raman spectrum of each group is presented in Fig. 4A and the XRF results of 26 beads selected are given in Table 2 and Fig. 5A. The four groups based on Raman spectra can be defined as follows:

4.2.1 Group 1 (Fig. 3)

All the black beads in this study fall into this group displaying spectra with strong peaks around 400-410 cm^{-1} and 1073-1110 cm^{-1} (Fig. 4A, a & b), similar to spectra reported for black EC-IP beads excavated at Mapungubwe and for black glass samples from India [4, 5]. The strong peak between 408-415 cm^{-1} (Fig. 4A, a & b) is attributed to the Fe-S chromophore, with the shoulder at ca. 350 cm^{-1} (Fig. 4A, b) appearing when a higher concentration of chromophore is present [4, 5]. Black beads from the Mapungubwe Oblate [4] and Zimbabwe series were also coloured by the Fe-S chromophore, but have different Raman spectra as can be

A)

B)

C)

Figure 4 A) Baseline-subtracted Raman spectra representative of the groups identified in Figure 3: a and b = Group 1; c and d = Group 2; e = Group 3a; f = Group 3b and g = Group 4. B) a) Fe-S chromophore in a black Zimbabwe series bead b) Glass matrix of the same black Zimbabwe series bead c) Fe-S chromophore in a black Mapungubwe oblate d) Tin oxide opacifier in a light blue Zimbabwe series bead. C): Raman spectra of a) Yellow pigment - lead tin yellow (type II) b) Light yellow-orange pigment c) White bead d) Tin oxide recorded as opacifier in the Mapungubwe bead series.

seen in Fig. 4B (a), a spectrum recorded on a black Zimbabwe bead (classified by Wood) from the VRL collection. Raman spectroscopy can thus effectively distinguish between black beads from the Indo-Pacific (EC-IP and K-IP) and Mapungubwe Oblate/Zimbabwe series. Bead D2-14-b1 was classified as a Zimbabwe series bead based on its apparent morphology, but the Raman spectrum places it in Group 1. It therefore rather belongs to the EC-IP or K-IP bead series.

Raman spectroscopy cannot determine the glass type (soda/soda-lime) for black beads where the band of the FeS chromophore dominates the spectra, but according to XRF measurements (Group 1, Table 2) all the black beads are made of soda-based glass with high aluminium content (7%) and low amounts of calcium (<1.5%) and magnesium (<0.3%). This is compatible with an Indo-Pacific origin. Bead C1-19-b1 with higher aluminium (10%) and calcium (5.8%) content is also consistent with an Indo-Pacific origin, but contains no uranium (Fig. 5C) and therefore does not fit into the EC-IP and K-IP series which have a high uranium content [3]. This bead might originate from a production site where different raw materials were used.

Group 2 (Fig.3)

Typical for soda (Na_2O) glass spectra have strong peaks around 490-500 cm^{-1} and 1073-1110 cm^{-1} [17] and two categories of spectra were identified (Fig. 4A, c, d) that differ in the shape of the stretching band. The first group (blue to blue-green K2-IP) has a weak peak around 990 cm^{-1} and a strong peak around 1090 cm^{-1} (Fig.4A, c), which was previously reported for the K2-IP bead series [5]. A few K-IP beads have similar spectra, indicating that the glass structure is similar to K2-IP beads, as also noted by Robertshaw et al. [3]. The second spectrum type (Fig. 4A, d), has two strong and broad peaks in the stretching envelope (947 cm^{-1} and 1070-1090 cm^{-1}) and was recorded for blue-green to green K2-IP beads, one yellow and one red K-IP bead. The increase of iron ions in a glass matrix causes an increase in the intensity of the peak at ca. 940 cm^{-1} [18]. It is suspected Fe was added to shift the blue colour (due to Cu) to green for the K2-IP series and also to change the shade of the yellow and red colours of the K-IP beads, thus increasing the intensity of this peak.

4.2.3 Group 3 (Fig. 3)

Spectra with strong peaks around ca. 540-600 cm^{-1} and 1060-1090 cm^{-1} are typical of soda-lime ($\text{Na}_2\text{O}/\text{CaO}$) glass. Two categories of spectra were recorded for this group. The first type, with bending and stretching envelopes at ca. 570-600 and 1070-1090 cm^{-1} respectively (Fig. 4A, e), is typical of Mapungubwe Oblates [4, 5] and Zimbabwe series beads (see spectra of Zimbabwe series beads from the VRL Collection in Fig. 4B, a, b). According to the Raman spectra,

Figure 5: a) XRF measurement results of the principal glass matrix elements b) colouring agents and c) uranium content for individual beads. K2-IP, Mapungubwe Oblate and EC-IP beads blue, green and black respectively. Red arrows indicate beads reclassified due to a too high Uranium content (Mapungubwe oblate) or the absence of Uranium (Khami bead).

Zimbabwe and Mapungubwe Oblate beads have the same basic glass structure, as also highlighted in the study of Robertshaw et al. [3]. The same type of spectrum was recorded for a number of beads classified morphologically as K-IP (C1-4-db4-5; C1-25-lb12, 16, 17; C1-25-g7), as well as for one K2-IP bead (C1-8-lb8) and one large dark green-blue European (A3-1-db4) bead. Bead C1-8-lb8 was reclassified as a K-IP bead, as K2-IP beads are made of soda glass and do not

belong in this soda-lime glass group. With the exception of one green bead, the colours of the beads in this group range from light blue to dark (cobalt) blue. It should be noted that K-IP beads excavated in South Africa and Zimbabwe were made of soda glass. The K-IP beads from elsewhere in Botswana (Bosutswe, Tora Nju, Toutswemogala) contain high levels of magnesium and calcium, indicating that they were made of plant-ash glass [3]. Most of the Khami beads in this study were made of soda-lime glasses with low concentrations of magnesium, pointing to the existence of another category of K-IP beads.

The second type of spectra, with bending and stretching maxima around ca. 540-560 and 1060-1080 cm^{-1} respectively (Fig. 4A, f), is associated with blue-green, green and yellow beads, which are represented by Zimbabwe (D1-3-g2, D2-14-y1) and K-IP (D3-1-g2, A3-1-g1, C1-19-y1) beads in this study. The increase in intensity of the peak around ca. 920-940 cm^{-1} can be attributed to higher levels of iron in the glass matrix. The Raman spectra of the two above-mentioned Zimbabwe series beads, which were found at Letsibogo sites, indicate that they belong to the K-IP series due to their higher iron content. Zimbabwe and Mapungubwe Oblate series beads contain iron in the ordinary range [3].

The glass composition of the K-IP beads in Group 3a and b is the same except for higher concentrations of iron which is acting as colouring agent in Group 3b (Table 2). In the soda/lime-based glasses the difference between the Mapungubwe Oblate/Zimbabwe and K-IP beads is related to a higher aluminium and iron content in the latter (see Table 2). The low uranium content of Mapungubwe Oblates (see green circled beads in Fig. 5C) and the Zimbabwe series beads (<5ppm) in comparison to the other bead series (see Fig. 5C) can be used to distinguish between them [3]. The uranium content of the cobalt blue Mapungubwe Oblate classified bead C1-8-db4 is much higher uranium than the other Mapungubwe Oblates (see Fig. 5C) and is probably an intrusion of a K-IP series bead into the 13th-century Toutswe site.

4.2.4 Group 4 (Fig.3)

A 17th-century Letsibogo site yielded a pale green opaque K-IP bead (C1-19-g1) with a unique spectrum indicating a considerable amount of calcite (characteristic peaks at 1080 cm^{-1} and 274 cm^{-1}) and a strong peak at 983 cm^{-1} usually attributed to lead-containing glass (Fig.4A, g). The strong peak at ca. 980 cm^{-1} shows that the glass has a depolymerised structure (similar to lead-rich glass) [12,13] with only two oxygen bridges connecting the SiO_4 tetrahedra. In this case the high calcium content (25%) of the glass might be responsible for depolymerising the glass structure (Table 2, Group 4 and Fig. 5A). Additional Raman measurements on the bead showed that the bead is heterogeneous in composition as different types of Raman spectra were recorded on different zones

(Fig. 6 bottom). Spectra of zones 1 and 2 are typical of soda-lime glass, while for zone 3 a spectrum similar to Fig. 4A, g, with the stretching envelope at 988 cm^{-1} and the peaks of calcite very prominent. Additional EDS analyses confirmed the heterogeneous composition of this glass bead.

4.3 EDS measurements of the green K-IP glass bead C1-19-g1

EDS measurements on the green bead C1-19-g1 at three separate localities (Fig. 6) show diverse ratios for some principal glass elements (K/Na/Ca/Si), namely:

Spot 1: (15% K; 6.6% Na; 5.8% Ca; 72.6% Si) points to a potassium glass (Raman spectra of zones 1&2 in Fig. 6).

Spot 2: (4% K; 32.9% Na; 6.1% Ca; 57% Si) indicates a sodium-based glass.

Spot 3 (50x): (17.7% K; 30% Na; 31% Ca; 20.6% Si) indicates a substantial concentration of the three fluxing agents (Na, K and Ca) and forms a third phase or it may be relics of the raw material used.

Spot 4 (100x): (17.7% K; 30% Na; 31% Ca; 21.3% Si) has the same composition as Spot 3. Spots 3 and 4 correlate with the Raman spectrum of zone 3 in Fig. 6.

In general a high level of chlorine is also present. (This is likely a characteristic of the raw material used.)

The SEM image (Fig.6, top right) and the corresponding soda and potassium elemental distribution maps (Fig.6, blue and green image) show that two distinctive glass grains were cemented by a calcium-rich interphase. This bead therefore consists of different glass types (recycling), which were processed again with incomplete melting as previously reported for Roman/Punic glass beads [16]. A similar process was documented by Wood [1] for garden roller glass beads that were locally made from recycled K2-IP series glass beads. The origin of this bead is unknown. Glass containing a high amount of potassium is quite rare, but typical of glass used for stained glass windows in Europe [13, 19]. In the southern African context, the only other example of a glass bead containing such high potassium content is a large round black bead found among black beads recovered from the grave area on Mapungubwe Hill [4]. Raman and EDS measurements suggest that C1-19-g1 is a new variety of bead produced from recycled glass rather than a K-IP series bead. The study also demonstrates that analyses in which mean composition measurements are used to classify beads, or where only one small spot is probed, are not very appropriate to characterise glass beads containing a mixture of different types of glass.

Figure 6. Glass bead C1-19-g1; Top - the SEM image and corresponding Na and K maps. Bottom - Raman spectra recorded at different localities (zones).

4.4 Pigments and opacifiers

Two yellow pigments were detected in yellow and green beads through their Raman spectra, namely lead tin yellow (type II) as seen in Fig. 4C (a) [20] and a yellow/orange pigment (Fig. 4C, b). Both these pigments were also used to colour the yellow and orange Mapungubwe Oblates [4 - 6]. It appears that between the 8th and 16th centuries yellow beads were coloured using the same pyrochlore pigments and therefore cannot be diagnostic of a specific kind of bead. No antimony was detected by the XRF measurements on the yellow beads.

Calcium carbonate (characteristic peak at 1085 cm^{-1} , Fig. 4C, c), detected in the spectrum of an off-white K-IP bead (C1-25-w1), acted as pigment in the

absence of other pigments/colouring agents. XRF measurements confirm the higher calcium content (5.3%) in comparison to other beads in the soda group (Fig.5A).

Tin oxide (cassiterite), with a sharp strong peak at 633 cm^{-1} and a medium peak at 775 cm^{-1} (Fig. 4C, d), was reported as opacifier in turquoise, bright green, bright yellow and orange-coloured Mapungubwe Oblates [4] and also in Zimbabwe series beads (Fig. 4B, d).

The presence of metallic ions cannot be detected using Raman spectroscopy but XRF measurements showed that copper (0.5-1%) was used to colour blue-green K2-IP and some K-IP series beads, as well as the European bead (A3-1-db4) (Fig. 5B). The cobalt (dark blue) beads were coloured by cobalt (0.1-0.2 wt%) in association with arsenic (As) ($\sim 450\text{-}750\text{ ppm}$). Indications are that the ancient source of cobalt was an arsenate-bearing mineral such as erythrite ($\text{Co}_3(\text{AsO}_4)_2$) that was imported from Iran (Quansar, Kashan) [21,22], Oman and Northern Hijaz [23].

XRF measurements show that iron in the glass was deliberately added to alter the shade of blue towards green as blue-green beads have higher concentrations of iron ($>4\%$) than light blue beads (1-1.6%) (Fig. 5B).

A combination of Cu, Fe and lead tin yellow was used to colour beads from the K-IP series (A3-1-g1 and D3-1-g2) green, while for the remaining yellow and green beads the same mixture of Cu and lead tin yellow type (II) was used as previously detected in the Mapungubwe Oblates (Fig. 5B).

The XRF measurements on the red K-IP bead (C1-25-r8) reveal a higher concentration of iron (3.1 wt%), which was used as a reducing agent to form atomic copper or cuprite (Cu_2O) in the glass melt as also reported in red EC-IP beads by Robertshaw et al. [3].

4.5 Proposed methodology to classify glass trade beads

A **first approach** is to classify beads according to morphological parameters as described by Wood [2] and then select representative beads for Raman analyses.

Raman spectra should enable the separation of the beads into four groups (Fig. 3):

Group 1: Fe-S chromophore: EC-IP and K-IP series black beads only.

Group 2: Soda glass: K2-IP, EC-IP and K-IP series beads.

Group 3: Soda-lime glass: Mapungubwe Oblate, Zimbabwe and K-IP series beads.

Group 4: Glass with a higher lead/calcium content

XRF measurements

Group 1: In general black K-IP beads reveal a higher Al (10%) and Ca content (5%) than black K2-IP beads.

Group 2: In general K-IP beads have higher Al (10%), Ca (5%) and Fe (3%) contents than K2-IP beads.

Group 3: Iron content of Map/Zim beads is less than in K-IP beads. SnO₂ present in opaque Map and Zim beads.

Group 4: Beads with a high calcium/potassium content.

Further checkpoints

Groups 1 and 2: Uranium content of K2-IP < EC-IP/K-IP.

Group 3: Uranium content of Mapungubwe Oblate/Zimbabwe series beads <5ppm.

Group 4: Detection of CaCO₃ on nearly all spots using Raman spectroscopy.

Recycled glass

Group 4: Confirm the use of recycled glass by Raman and EDS measurements at multiple spots on the bead.

Figure 7. Schematic diagram of proposed classification methodology of glass trade beads excavated at archaeological sites in southern Africa (8th -16th centuries).

Conclusions

Raman and XRF measurements confirmed that the morphological classification of the selected beads was 92% correct. Only a few beads were reclassified based on

the basic chemical composition of the glass or uranium content (Fig. 2). In these cases the morphology of the beads is similar, although they are chemically different. A combination of visual classification, Raman spectroscopy and an elemental study (XRF) of the beads is a satisfactory non-destructive method to classify beads into specific series.

The advantages of Raman spectroscopy are that by recording one spectrum on a glass bead it is possible to distinguish between soda and soda-lime glass, black beads from an Indo-Pacific origin can be recognised immediately and the identification of some pigments and opacifiers can help to classify beads unambiguously. We have also demonstrated that the results obtained using LA-ICP-MS can be correlated to the results of XRF analyses using a portable instrument eg. and that the determination of uranium content in glass is a very useful parameter to assist in the correct classification of beads. Where the classification of beads is dependent on the concentration of trace elements LA-ICP-MS is a better technique to use.

An EDS study of an opaque green bead showed that it was made by recycling different glasses with the addition of compound(s) to generate a liquid phase to promote the sintering of the glass grains. Different Raman signatures as a function of the sampling spot are an indication of recycled glasses, which was confirmed by elemental mapping. This bead does not belong in any of the existing bead series and its provenance is unknown.

The sites that we studied mostly date to one period of time and occupation, a fact which facilitated the correct morphological identification of the beads. Our next step will be to analyse bead assemblages from sites that are not so securely dated and where beads imported from Europe are mixed with earlier beads. Hopefully the guidelines established in this study will assist in differentiating between beads imported into southern Africa before the 17th century AD from the East and those beads imported subsequently from Europe that in many cases were copies of the older beads.

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REFERENCES

- [1] M. Wood, Making connections: relationships between international trade and glass beads from the Shashe-Limpopo Area, South African Archaeological Society, Goodwin Series 8 (2000) 78-90.
- [2] M. Wood, A glass bead sequence for Southern Africa from the 8th to the 16th century AD, J AfriArchaeo 9(1) (2011) 67-84.
- [3] P. Robertshaw, M. Wood, E. Melchiorre, R.S. Popelka-Filcoff, M.D. Glascock, Southern African glass beads: chemistry, glass sources and patterns of trade, J ArchaeolSci37(8) (2010) 1898-1912.
- [4] L.C. Prinsloo, Ph. Colomban, A Raman spectroscopic study of the Mapungubwe Oblates: glass trade beads excavated at an Iron Age archaeological site in South Africa, J Raman Spectrosc39(1) (2008) 79-90.
- [5] 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 ArchaeolSci38(12) (2011) 3264-3277.
- [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 Spectrosc43(4) (2012) 532-542.
- [7] L.C. Prinsloo, J.C.A. Boeyens, M.M. Van der Ryst, G. Webb., Raman signatures of the modern pigment $(\text{Zn,Cd})\text{S}_{1-x}\text{Se}_x$ and glass matrix of a red bead from Magoro Hill, an archaeological site in Limpopo Province, South Africa, recalibrate the settlement chronology, J MolStruct1023 (2012) 123-127.
- [8] W.M. Biemond, The Iron Age sequence around a Limpopo river floodplain on Basinghall Farm, Tuli Block, Botswana, during the second millennium AD, MA dissertation in Archaeology, University of South Africa, 2014.
- [9] J.R. Denbow, Iron Age economics: herding, wealth and politics along the fringes of the Kalahari Desert during the Early Iron Age. Ph.D. thesis, Indiana University, Bloomington, U.S.A, 1983.

- [10] T.N. Huffman, Handbook to the Iron Age: the archaeology of pre-colonial farming societies in southern Africa, Pietermaritzburg, University of KwaZulu-Natal Press, 2007.
- [11] 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.
- [12] Ph. Colomban, Polymerisation degree and Raman identification of ancient glasses used for jewellery, ceramics enamels and mosaics, *J Non-Cryst Solids* 323 (2003) 180-187.
- [13] Ph. Colomban, A. Tournié, L. Bellot-Gurlet, Raman identification of glassy silicates used in ceramics, glass and jewellery: a tentative differentiation guide, *J Raman Spectrosc* 37(8) (2006) 841-852.
- [14] P. Ricciardi, P. Colomban, A. Tournié, M. Macchiarola, N. Ayed, A non-invasive study of Roman Age mosaic glass tesserae by means of Raman spectroscopy, *J Archaeol Sci* 36 (2009) 2551-2559.
- [15] A. Ceglia, G. Nuyts, S. Cagno, W. Meulebroeck, K. Baert, P. Cosyns, K. Nys, H. Thienpont, K. Janssens, H. Terryn, A XANES study of chromophores: the case of black glass, *Anal Methods* 6 (2014) 2662-2671.
- [16] Ph. Colomban, G. March, L. Mazerolles, T. Karmous, N. Ayed, A. Ennabli, H. Slim, Raman identification of materials used for jewellery and mosaics in Ifriqiya, *J Raman Spectrosc* 34(3) (2003) 205-213.
- [17] P. Colomban, A. Tournié, M.C. Caggiani, C. Paris, Pigments and enamelling/gilding technology of Mamluk mosque lamps and bottle, *J Raman Spectrosc* 43 (2012) 1975-1984.
- [18] K. Baert, W. Meulebroeck, H. Wouters, P. Cosyns, K. Nys, H. Thienpont, H. Terryn, Using Raman spectroscopy as a tool for the detection of iron in glass, *J Raman Spectrosc* 42(9) (2011) 1789-1795.
- [19] A. Tournié, P. Ricciardi, Ph. Colomban, Glass corrosion mechanisms: A multiscale analysis, *Solid State Ionics* 179(38) (2008) 2142-2154.

[20] I.M. Bell, R.J.H. Clark, P.J. Gibbs, Raman spectroscopic library of natural and synthetic pigments pre- ~1850 AD, *Spectrochim Acta A-M* 53(12) (1997) 2159-2179.

[21] Y. Porter, Shargarf et Lâzhvarddans le monde iranien, in “Circulation des monnaies, des marchandises et des biens”, *Res. Orientales*, V, Groupe pour l’Etude de la Civilisation du Moyen-Orient (1993) 147-157.

[22] Y. Porter, Le cobalt dans le monde iranien (IXe-XVIe siècles). Notes sur son utilisation en céramique et son commerce, *TAOCI* 1 (2000) 5-14.

[23] Ph. Colomban, Rocks as blue, green and black pigments/dyes of glazed pottery and enameled glass artefacts - A review, *Eur J Mineral* 25 (2013) 863–879.