Supplementary information

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

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Fig. S1 Map showing the location of the sites described in the paper

Table S1 Morphological classification for the imported beads to southern Africa before the 18th century AD (Wood 2011, 2012)

Bead series	Period traded in southern Africa	Method of manufacture	Size	Colour	Shape	Type
Chibuene	AD 7-10th c.	Drawn	Small-medium 2.5-4.5 mm diameter	Greyish Blue, blue-green, green, yellow	Vary- most are tube and cylinder	Plant-ash lAl-lCa
Zhizo	AD 8-mid-10th	Drawn	Small-medium 2.5-4.5 mm diameter 0.7-25mm long	Dark blue, blue-green, yellow, green	Tubes	Plant-ash lAl-hCa
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	Soda-alumina
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	Soda-alumina
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	Plant-ash hAl-lCa
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	Plant-ash hAl-lCa
Khami-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	Soda-alumina

Table S2 Summary of European soda rich plant ash glass composition and distribution in Europe from the10th to the 17th centuries

	Ash/purity	Glass type	Date/AD	Locations
Southern Europe high alumina	LV/unrefined	-	10th-17th c.	**Italy**: Savona (10-16 c.)[6], Tuscan (13-16 c.)[7]/ **Spain**: Vascos (10-12 c.)[8]/ **Portugal**: Silves (11-13 c.), Coimbra (17 c.)[3], Tarouca Monastery (17c.)[3]
	LV/pure	-	16th-17th c.	**Portugal**: Beja (16-17)[3] Coimbra (16-17)[3]
	WM/unrefined		13th-17th c.	**Italy**: Savona (13-16 c.)[8], Tuscan (mid-16 c.)[7]/**Portugal**: Coimbra (16-17 c.)[3]
	WM/pure		17thc.	**Portugal**: Tarouca Monastry (17c.)[3]
Southern Europe low alumina	LV/unrefined	Vitrum Blanchum/ Spanish II[1]	14th-18th	**Venice** (14-18 c.) [2]; **Spain** (16-17 c.)/**Portugal**: Coimbra (17 c.)[3], Tarouca Monastery (17c.)[3]
	LV/pure	Cristallo	15th-18th c.[2]	**Venice** (15-18 c.)[2]
	WM/unrefined	Spanish I[1]	16th-17th c.	**Italy**: Tuscan (16 c.)[7]/ **Spain** (16-17 c.)[1]
	WM/pure		17th c.	**Portugal**: Coimbra (17 c.)[3]
Northern Europe low alumina	LV/unrefined	Vitrum Blanchum/ Amsterdam (unknown?)/	17th c.	**Belgium**: Antwerp (17c.)/ Amsterdam[5] /London (17c.)[5]/
	LV/pure	Antwerp Cristallo;	17th c.	**Belgium**: Antwerp[4] (17thc.), London[5] (17th c.)
	WM/unrefined	Façon de Venise/;	17th c.	**Belgium**: Antwerp (17), Amsterdam[4] (17 c.), London and Aldgate[4] (17c.),
	WM/pure	Amsterdam Group3/ Antwerp Cristallo	17th c.	Amsterdam[5] (17th c.); **Belgium**: Antwerp (17th c.)

Note: LV=Levantine (K_2O<4%); WM=West Mediterranean ash (K_2O>4.5%); High alumina=(alumina>3.5%); Low alumina= (alumina<2.5%); Pure=pure ash (CaO<4%); Unrefined=unrefined ash (CaO>6%).

References: [1]Ulitzka 1994; [2] De Raedt et al. 1999; Verità & Zecchin, 2009; [3] Coutinho 2016; [4]De Raedt et al. 2002; [5]Dussubieux and Karklins 2016; [6] Cagno et al. 2012; [7]Cagno et al. 2010; [8]de Juan Ares and Schibille 2017

Table S4 Comparison of 19 major, minor and trace element wt% in glass references B, C and D obtained by pXRF and LA-ICP-MS (193nm laser ablation)*

Samples	B (mean±Std)	Certified value B*	NF	C(mean±Std)	Certified value C*	NF	D (mean±std)	Certified value D*	Normalisation factor
Na_2O	N/D	16.5±0.5	-	N/D	0.97±0.6	-	N/D	1.30±1.4	-
MgO	1.47±0.24	0.99± 0.7	0.67	12.50±1.67	2.50±0.7	0.2	3.08±1.53	3.87±1.3	1.26
Al_2O_3	5.35±0.04	4.63±1.3	0.87	4.49±0.58	0.739±1.2	0.16	5.82±0.20	5.19±3.0	0.89
SiO_2	79.71±0.19	62.02±0.3	0.78	36.18±0.50	31.41±0.5	0.868	63.66±1.95	54.15±1.2	0.85
P_2O_5	1.00±0.05	0.61±0.8	0.61	1.48±0.10	0.07±1.8	0.047	3.98±0.10	3.05±0.9	0.77
K_2O	1.06±0.03	1.30±1.4	1.22	2.28±0.02	3.21±0.3	1.41	10.42±0.21	14.2±0.7	1.36
CaO	7.05±0.13	8.75±1.4	1.24	3.25±0.20	4.75±0.8	1.46	10.19±0.23	14.7±2.4	1.44
TiO_2	0.05±0.04	0.1±1.9	2	0.19±0.17	0.71±0.6	3.74	0.24±0.01	0.36±2.7	1.5
MnO	0.17±0.03	0.24±1.2	1.4	0.12±0.10	0.001±3.1	-	0.42±0.05	0.60±1.1	1.5
Fe_2O_3	0.33±0.01	0.3±1.5	0.91	0.13±0.12	0.262±0.8	2.02	0.47±0.06	0.46±2.1	0.99
CoO	0.04±0.00	0.04±0.8	1	0.15±0.02	0.164±0.4	1.09	0.01±0.00	0.018±1.3	1.8
CuO	2.61±0.07	2.82±1.7	1.1	0.91±0.12	1.10±0.5	1.2	0.34±0.05	0.37±1.6	1.1
ZnO	0.18±0.01	0.21±1.7	1.17	0.06±0.01	0.042±1.1	0.7	0.08±0.01	0.1±1.6	1.25
SrO	0.01±0.00	0.02±1.9	2	0.14±0.01	0.333±0.439	2.38	0.04±0.00	0.06±2.6	1.5
Ag_2O	0.02±0.00	-	-	0.05±0.02	-	-	0.01±0.00	-	
SnO_2	0.05±0.00	0.02±0.9	0.4	0.22±0.01	0.163±0.8	0.74	0.13±0.01	0.08±1.9	0.62
Sb_2O_5	0.35±0.01	0.42±1.8	1.2	N/D	N/D	-	0.64±0.05	0.96±1.9	1.5
BaO	0.08±0.00	0.08±2.5	1	9.08±0.58	13.3±0.6	1.47	0.24±0.02	0.29±1.8	1.21
PbO	0.48±0.01	0.53±2.5	1.1	28.78±1.77	39.8±0.5	1.38	0.23±0.02	0.24±1.4	1

Note: *The values available in (Wagner *et al*. 2012), Nf: Normalization Factor

Table S6 Pigments, opacifiers and colorants detected in glass beads by Raman spectroscopy and pXRF

Pigments/Opacifiers	Date[1]	Sample colour	Other colorants/phase	Glass type/Beads
Ca-antimonate ($CaSb_2O_7$)	From antiquity/ The Mid of 17th c.	white	-	**LV**/Map116, Bd14,Bd35, Bd37, Mag8,D11,Ba6; **WM**/ K2-112, K2-113, K2-117, Map130, Map132, NHA1, Pr56, Pr81, Pr82, Pr93, Mag5, Mag10,
		Brownish red	Fe, Cu	**LV**/ Map125, Map140, D4, Pr58, Pr89, Pr96, Pr97; **WM**/ Map124, D6, D7, D9, Ml63
		Dark blue	Co	**LV**/Pr52, Mag2; **WM**/ Map118, Map119, Map142, Bd25, Bd26, Bd27, D12, Mag21; **Mineral soda**/ Pr57, Pr99, Bd13, Bd17, Bd18
		Light blue	Cu	**LV**/Bd152, Pr51; **WM**/ Ml64
		Powdery blue	Cu, Co	**WM**/Bd163
Manganese oxide/spinel	16th c.	Black	-	**LV**/Mag1
			Sb	**LV**/Ml62, Ml73; **WM**/Ml65
Lazurite	Roman period/ Mid of 17th c.	Light blue	Cu/ $CaSb_2O_7$	**LV**/ Mag25, Map122; **WM**/ Bd120,
Naples Yellow (Pb-Sn-Sb triple oxides)	From 16thc.	Green	Cu	**Lead soda**/ K2-111, Map148, Map149, Pr98
Arsenate	The early 19th c.	Various	Cu, Co	**Lead soda**/Map114, Map133, Map147, Map150, Map159, Bd16, Bd38, Bd104, Bd105, Bd106, Bd160, Bd166, Bd168, Bd169, Bd197, K2-39, K2-40, K2-41, Ml79, Pr83, Pr85, Pr86, Pr91, Pr92,
-	The Mid of 17th c.	Dark blue	Co, Sb	**WM**/Pr90
-	Early 19th c.	Dark blue	Co	**Potash rich**/ K2-1, k2-2, K2-3, K2-4, K2-30, k2-31, K2-32, K2-33, K2-42, K2-43, K2-107, K2-108, K2-153, K2-155, Map45, Bd157, Pr49, Mag-30
	Late 19th c.			**Synthetic soda**/ K2-9, K2-11, K2-12, k2-28, K2-29, Bd5, Bd6, Bd7, Bd8, Bd158
	From early to late 19th c.			**Mixed alkali**/ Mag31, Mag32, Bd156
-	Late 16th c.	Brownish red on black	Fe, Cu	**LV**/Map123,
-	From antiquity	Light blue	Cu	**LV**/Mag4, Bd44 **Mixed alkali**/Mag3
-		Plum	Fe	**WM**/Pr94

Note: 1 references for dating of the pigments and beads were presented in the text. LV=Levantine ash, WM=West Mediterranean ash, c.=Century