DISSERTATIONES ARCHAEOLOGICAE

ex Instituto Archaeologico Universitatis de Rolando Eötvös nominatae

„Hadak útján”

A népvándorláskor fiatal kutatóinak XXVI. konferenciája

GAZDASÁG – KERESKEDELEM – KÉZMŰVESSÉG

26th Conference of Young Scholars on the Migration Period

ECONOMY – TRADE – CRAFTSMANSHIP

Supplementum 2. | 2018

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Budapest, 2016. november 3–4.

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A *„Hadak útján" – A népvándorláskor fiatal kutatóinak konferenciáját* először 1990-ben, Szentesen rendezték meg nagy érdeklődés közepette. A rendezvény hiánypótlónak számított, korábban ugyanis nem volt lehetősége a pályakezdő népvándorlás koros régészeknek, hogy saját korosztályuk körében megosszák egymással tudományos eredményeiket. Már az első találkozó interdiszciplináris együttműködésre törekedett: régészek mellett történészek, művészettörténészek és nyelvészek is előadást tartottak; az előadások alapján készült tanulmányok külön kötetben jelentek meg. A konferencia elnöki tisztjét az első alkalom óta dr. Tomka Péter, a Kárpát-medencei népvándorlás kor kiemelkedő kutatója tölti be.

A szentesi konferencia egy sikeres sorozat első állomása lett: 2015-ben, Révkomáromban a kezdeményezés már negyedszázados születésnapját ünnepelhette. A „Hadak útján" 26. találkozójának megszervezését – a sorozat történetében először – az ELTE BTK Régészettudományi Intézete vállalta magára. Témájául a népvándorlás kori gazdaság, kereskedelem és kézművesség kérdésköreit választottuk. 2016. november 3–4-én összesen 47 előadótól mintegy 32 előadást hallhattunk, amelyeket témakörök szerint több szekcióba – kapcsolatrendszerek, kereskedelem, gazdálkodás és háztartások, anyag és technológia, valamint kézművesség – soroltunk. Ezek közül most 13 előadás jelenik meg írásos formában is, részben magyarul, részben azonban – a megjelenésnek teret biztosító folyóirat, a *Dissertationes Archaeologicae* irányelvei alapján – angol és német nyelven. Reméljük, hogy az idegen nyelvű kiadás segítségével a konferencián bemutatott sokrétű és gyakran új módszertani megközelítésre támaszkodó eredmények a nemzetközi kutatás számára is hozzáférhetővé válnak.

Budapest, 2018. október 1.

A konferencia eddigi helyszínei

1990 Szentes
1991 Nyíregyháza
1992 Sátoraljaújhely
1993 Visegrád
1994 Szenna
1995 Velem
1996 Pécs
1997 Veszprém
1998 Eger
1999 Szeged – Domaszék
2000 Székesfehérvár
2001 Simontornya
2002 Gyula
2003 Keszthely
2004 Várgesztes
2005 Nagykovácsi
2006 Nagyvárad
2007 Kecskemét
2008 Győr
2010 Budapest – Szigethalom
2011 Szeged
2012 Visegrád
2013 Veszprém
2014 Esztergom
2015 Révkomárom
2016 Budapest
2017 Debrecen
2018 Mosonmagyaróvár

Preliminary micro-XRF study of mosaic face beads found in an Early Sarmatian grave excavated at Dunakeszi – implications for the base glass composition and colourants

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Abstract
Variously coloured (green, red, yellow, white and black) glasses of three mosaic face beads of Selling I type found in an Early Sarmatian grave at Dunakeszi were analysed non-destructively by using micro-XRF (X-ray fluorescence) technique. A tiny green glass fragment detached from one of the beads was investigated by electron microprobe analysis as well.
Chemical composition of some parts of the beads, namely the green and red glasses of two uniform face beads and the black glass of the third face bead, indicates that these glasses were produced, at least partially, from plant-ash alkali flux. Based on the preliminary micro-XRF analysis, it is not yet proved that the two uniform face beads belong to the same glass rod, neither the base glass of their outer green rim is identical to base glass of the inner red parts.
Copper was used to colour both green and red glasses with some antimony-based opacifiers in the green glass. Red glass chemically is of low-lead, low-copper type with some antimony in one of the beads. In white glass the opacifying element is antimony, probably in the form of calcium antimonate. The elevated antimony and lead content of yellow glass indicates the presence of lead antimonate as colourant and opacifier. Black glass is probably coloured by iron.

Introduction

Among the archaeological finds in an Early Sarmatian woman grave excavated at Dunakeszi-Székesdűlő, dated to the end of 1st century – beginning of 2nd century AD, various jewels were found.[1] In addition to round and triangular gold flitters on the clothes and a gold earring decorated with granulation, a necklace of cornelian, amber and chalcedony beads was found. The latter also included a faience lion bead, two metal foil, so-called gold-glass beads, and between them a gold lunula decorated with granulation. Cornelian and amber beads as well as mosaic (millefiori) beads with chessboard and face motifs, so-called checker and face beads, were uncovered in the region of the right wrist.[2]

1 Korom – Reményi 2005.
2 Korom – Reményi 2005; Korom 2018.

 DOI: 10.17204/dissarch.suppl2.33

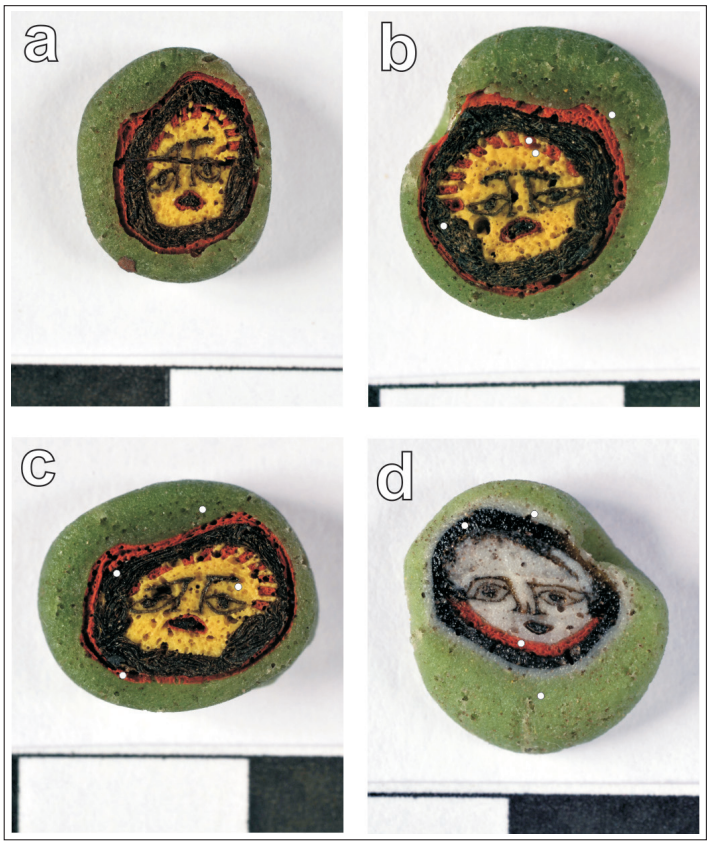

Fig. 1. Face beads found in an Early Sarmatian woman grave excavated at Dunakeszi-Székesdűlő. a – inv. no. 2011.2.118.70, b – inv. no. 2011.2.118.72, c – inv. no. 2011.2.118.79, d – inv. no. 2011.2.118.81. White dots indicate the sites of the micro-XRF measurements with highest Na_2O content for each colour (see *Tab. 1*) (note that for better visibility the size of the white dots is exaggerated by a factor of 3 compared to the diameter of the beam). The face bead 2011.2.118.70 was not analysed in this study

The archaeometric research aims to reveal the material characteristics of both the gold jewels and the glassy (mosaic, metal-foil and faience) beads in order to get data for the material usage and the production technology.[3] This study presents the preliminary analytical results of the face beads. Four, disc-shaped face beads were in the grave, three of them was uniform in terms of the used colours and the portray: the inner face made of yellow, red and black glasses is framed by a black, then a thin red glass band, and finally surrounded by a thick green glass rim (inv. no. 2011.2.118.70, 2011.2.118.72 and 2011.2.118.79, hereafter called beads 70, 72, and 79, *Fig. 1.a-c*). In the fourth glass bead the face is made of white, black and red glasses, surrounded by a black, then a thin white glass band, and the outer glass rim has light green colour (inv. no. 2011.2.118.81, hereafter called bead 81, *Fig. 1.d*).

Archaeological and archaeometric questions about the material of the face beads:

- What are the base glass type and the colourants of the face beads?
- Do the three uniform face beads belong to the same glass rod made by mosaic (millefiori) technique?
- Does the outer green rim have a basic glass composition similar to that of the inner face?

3 Analytical results of the gold jewels are published by Mozgai et al. 2018.

Ancient glass before the medieval period is dominantly sodic glass manufactured by using soda-rich fluxes. Depending on the type of flux used, soda-lime-silica (mineral soda) or plant ash-silica (plant ash) base glasses were produced.[4] The earlier dominated throughout the Roman period, but was in use from the middle of the first millennium BC throughout most of the first millennium AD in the eastern Mediterranean; the latter prevailed in the Bronze Age in Mesopotamia and Egypt, again in the Early Islamic world from the 9th century AD and was typical for Venetian glass from the 13th century AD as well.[5] The chemical composition of glass reflects the flux used, therefore the type of the base glass, in addition can give clues about the colourants and opacifiers. Since sampling from the face beads can hardly be achieved due to their small size, the chemical composition of the face beads was first analysed non-destructively without sampling by using micro-XRF (X-ray fluorescence) technique. In addition, quantitative chemical composition of a tiny green glass sample detached from one of the beads was determined together with the study of the microstructure by using an electron microprobe coupled with energy-dispersive X-ray spectrometer.

Analytical methods

Chemical composition of the variously coloured glasses (red, green, yellow, black and white) in two of the uniform face beads (beads 72 and 79) and the white-faced bead (bead 81) were measured with a laboratory micro-XRF (X-ray fluorescence) equipment. The analysis was performed on a Horiba Jobin Yvon XGT-5000 energy-dispersive micro-XRF instrument operated at 50 keV with Rh target and Peltier cooled Silicon Drift Detector (SDD). Analyses with a 100 μm beam diameter and a count time of 300 sec were performed; therefore, the results represent the chemical composition of the vitreous matrix plus the inclusions if present. The elements are expressed in their oxide form, except for chlorine. Measurement of the low atomic number elements, such as sodium (Na), one of the main components of sodic glasses, and magnesium (Mg) is problematic with the micro-XRF technique;[6] in addition, light elements like alkalis leave glass easily during weathering as well as analysis. Since the instrument normalises all the analytical data to 100 wt% oxide total, in case of decreased Na content (low Na_2O data) due to above-mentioned factors the concentration of other elements (especially Si) becomes artificially elevated. Therefore, several analyses (n = 3–6) were performed on each coloured glass of the beads, and only the measurements with highest amount of Na_2O are discussed in this paper. Among them only measurements showing higher than 10 wt% Na_2O content, based on the typical content of sodic glass,[7] were quantitatively evaluated for base glass composition, whereas the rest of the measurements, in which Na_2O is lower than 10 wt%, were evaluated only qualitatively.

A tiny glass piece was detached from the green rim of one of the face beads (bead 72). The sample was embedded into epoxy resin, ground, polished, and then coated with carbon. The microstructure and inclusions of the glass was studied using the backscattered electron (BSE) mode of a JEOL Superprobe-733 electron microprobe (EMP). The chemical composi-

4 Henderson 1985; 2000; Freestone 2006; Artioli 2010, 285–289.
5 Freestone 2005, OO108.1.1–2; Artioli 2010, 285–289, Tab. 3.2.2.
6 Janssens et al. 2000.
7 Characteristic Na_2O content is 8 to 20 wt% is for plant ash-silica glass (high-Mg glass, HMG) and 13 to 20 wt% for Roman-type soda-lime-silica glass (low-Mg glass, LMG (SLS)) (Artioli 2010, 286, Tab. 3.2.2).

tion of the glass was quantitatively determined using an Oxford Instruments INCA Energy 200 energy dispersive X-ray spectrometer (EDS) attached to the electron microprobe. Analytical conditions were 20 kV acceleration voltage and 6 nA bean current. The 'bulk' chemical composition of the glass (vitreous matrix plus inclusions) was determined by areal analyses with a count time of 100 sec and a typical area of 166×200 μm. The chemical composition of the vitreous matrix and the inclusions was also measured using spot EDS analyses with a count time of 40 sec and an electron beam of 20 μm and 1 μm diameter, respectively. Glass standards (Corning archaeological reference glasses A, B, C and D)[8] provided by the Smithsonian Institution (USA) were used for calibration of the major elements, whereas SnO_2 for Sn and chalcopyrite for Cu were applied. PAP correction was automatically made by the Oxford Instruments software. Several areal and spot measurements were performed and the results were averaged. The elements are expressed in their oxide form, except for chlorine, and the totals were normalised to 100 wt%.

Results

Micro-XRF analysis

Both green and red glasses of the face bead 72 contain more than 10 wt% Na_2O, and both have about 1.5 wt% K_2O, 1.7 wt% MgO and 0.9–1.1 wt% P_2O_5 concentration *(Tab. 1)*. Both glasses show elevated copper content (2.8 and 1.9 wt% CuO) compared to other glasses; in addition, red glass has 4.2 wt% PbO content. In the yellow and black glasses of the same face bead lower Na_2O content was measured, however, K_2O, MgO and P_2O_5 contents are below ~1 wt% and 0.2 wt%, respectively. 1.6 wt% Sb_2O_3 content and 16.1 wt% PbO concentration was measured in the yellow glass, the latter is significantly higher than PbO content of the red glass. Black glass contains slightly higher amount of iron (2.2 wt% Fe_2O_3) than to other glasses (1.3–1.8 wt% Fe_2O_3).

In case of face bead 79 more than 10 wt% Na_2O content was again measured in green and red glasses *(Tab. 1)*. Their K_2O content is 1.3-1.4 wt%, whereas MgO content is 1.5 wt% in green and 2.9 wt% in red glass and P_2O_5 concentration is 0.7 and 1.3 wt%, respectively. The copper content is 2.1 wt% CuO in the green glass and 1.7 wt% CuO in the red glass, the latter also contains 3.8 wt% PbO as well. Up to 1.1 wt% K_2O and MgO and 0.2 wt% P_2O_5 was detected in the yellow and black glasses, although their measured Na_2O concentration is less than 10 wt%. In the yellow glass, elevated amount of antimony and lead (1 wt% Sb_2O_3, 7.5 wt% PbO) was measured, whereas higher iron content is characteristic for black glass (3.5 wt% Fe_2O_3) compared to other glasses (0.8 to 1.5 wt% Fe_2O_3).

16.3 wt% Na_2O accompanied by 1.2 wt% K_2O, 1 wt% MgO and 0.5 wt% P_2O_5 content was detected in the green rim of the white-faced bead (bead 81) *(Tab. 1)*. Significantly lower Na_2O contents were measured in both red and white glasses, and their K_2O, MgO and P_2O_5 contents are different with higher values in the red glass. Red glass contains elevated amount of copper (2.4 wt% CuO) similarly to the green glass (1.7 wt% CuO). More than 3 wt% Sb_2O_3 content was measured in the red glass, and even higher amount of antimony (9.3 wt% Sb_2O_3) in the white glass. The green glass shows 1.6 wt% PbO content. Higher amount of lead (4.8–5.6 wt% PbO)

8 Vicenzi et al. 2002.

occurs in the red and white glasses. The Na_2O content of the black glass exceeds 10 wt% together with 1.4 wt% K_2O, 1.6 wt% MgO and 0.9 wt% P_2O_5 contents, but its iron content seems not to be elevated (1.5 wt% Fe_2O_3) compared to other glasses (0.7–2.1 wt% Fe_2O_3).

Electron microprobe analysis

Backscattered electron images show that the tiny green glass fragment detached from the rim of the face bead 72 has slightly inhomogeneous, striated microstructure with lots of tiny (up to several μm size), bright, angular inclusions *(Fig. 2)*. According to the spot EDS analyses, the inclusions contain elevated amount of lead and antimony or calcium and antimony, respectively, compared to the vitreous matrix indicating that they are probably lead antimonate and calcium antimonate crystals. Higher amount of crystals is present in the light stripes *(Fig. 2)*. Rarely calcium silicate (wollastonite?) crystals also occur in the glass.

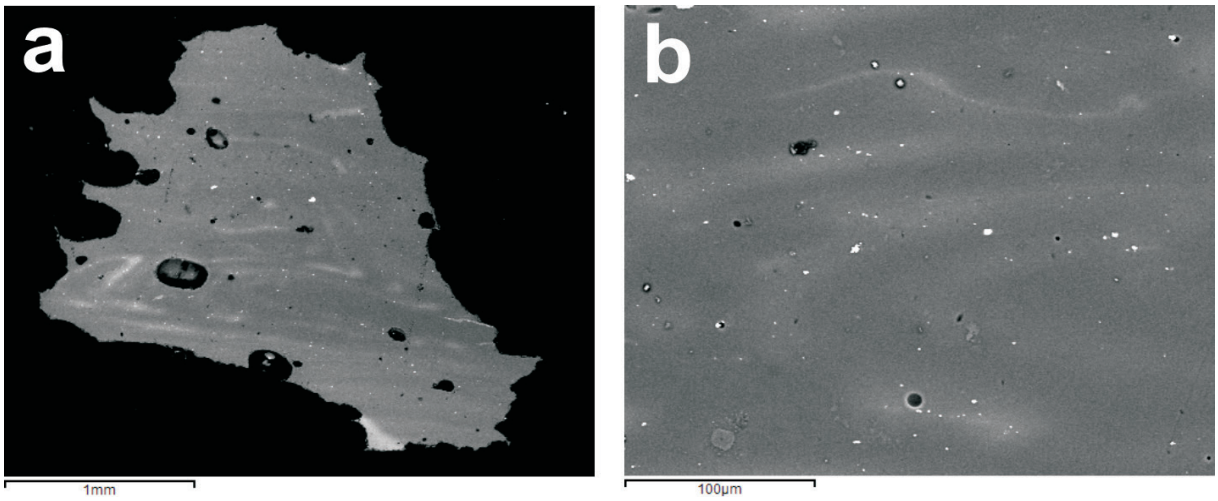

Fig. 2. Backscattered electron images of the green glass fragment detached from the rim of the face bead 72 showing tiny, bright, angular, antimony-based inclusions and lighter stripes in the vitreous matrix

The green glass has 18 wt% Na_2O and 7 wt% CaO *(Tab. 2)*. The main difference between the micro-XRF and the EPM data is the higher concentration of Na_2O measured by EMP, whereas higher concentration of SiO_2 was measured by micro-XRF due the factors discussed above. Both K_2O and MgO contents measured by electron microprobe are 1.9–2 wt%, and P_2O_5 content is 0.7 wt%. The copper content is 2.7–2.8 wt% CuO. Although antimony- and lead-bearing crystals are present, no elevated antimony or lead content was detected in the 'bulk' glass (0.4 wt% Sb_2O_3, 0.7 wt% PbO) compared to the vitreous matrix. Average chemical composition of the vitreous matrix is similar to that of the 'bulk' glass *(Tab. 2)*, however, the matrix probably contains a slightly higher amount of lead (by about 1–2 wt%) in the bright stripes.

Discussion

Base glass

Sodic glass is made from silica, in the form of sand, pebbles, siliceous minerals and rocks, which is fluxed mainly with two types of soda. The source of soda is either (i) evaporites of saline lakes, also called natron salts or mineral soda, mixture of sodium bicarbonates and

carbonates (mainly mineral trona), sulphates and chlorites,[9] or (ii) ashes of salt-tolerant halophytic plants grown in deserts and coastal regions. The types of sodic glass (soda-lime-silica and plant ash-silica) can be distinguished based on the chemical composition of glass, which is related to the use of the raw material, namely the mineral- or plant-derived alkali flux. Natron has low concentration of cations other than Na, i.e. low amount of impurities, and to produce stable glass lime as stabilizer was also added, in the form of limestone or shell fragments, to silica and soda. However, plant ashes are richer in impurities and contain high levels of lime, magnesia, potash and phosphate.[10] Therefore, plant ash-silica glass has higher magnesia and potash, typical more than 4 wt% for MgO and 2 wt% for K_2O[11] or more than 2 wt% for each,[12] and called as high-MgO, high-K_2O (or high-magnesia) glass.[13] Soda-lime-glass has low potash and low magnesia,[14] typically less than 1 wt% for MgO and 1 wt% for K_2O in most samples,[15] or less than 1 wt% for MgO and 1.5 wt% for K_2O,[16] and is called as low-MgO, low-K_2O (or low-magnesia) glass.[17] Glasses containing MgO and K_2O each between 1-1.5 and 2(-3) wt% might have been produced from a mixture of mineral- and plant-derived alkali[18] or from some plant ash different from plant ashes used for the high-magnesia glass.

To determine the base glass type, colouring, decolouring and opacifying components, like Mn, Sn, Pb, Cu and Sb oxides, are subtracted from the bulk chemical composition of glass and the main components like SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, P_2O_5 and Cl are normalized to 100 wt%.[19] Based on the base glass composition calculated from the micro-XRF data, both green and red glasses of face bead 72 fall outside the range typical for soda-lime-silica glass and together with their 0.9-1.1 wt% P_2O_5 content indicate that these glasses contain some plant ash as alkali *(Fig. 3)*. This is supported by the electron microprobe analysis of green glass showing circa 2 wt% K_2O and 2.1 wt% MgO content for the calculated composition of the base glass. Similarly, the composition of the green glass of face bead 79 also suggests, at least partially, the use of plant ash, whereas the red glass of the same bead has higher amount of magnesia (~3 wt% MgO) together with high phosphate (1.3 wt% P_2O_5) content indicating plant ash-silica type base glass *(Fig. 3)*. However, base glass type of yellow and black glasses of beads 72 and 79 cannot be determined due to the ambiguous micro-XRF results with the low Na_2O values.

9 Shortland 2004; Shortland et al. 2006.
10 Freestone 2006, 204; Henderson 2009.
11 Rehren 2000, 1226.
12 Freestone 2005, OO8.1.2; Artioli 2010, 286, Tab. 3.2.2.
13 Sayre – Smith 1961; Freestone 2006, 202–205. This type of glass is called as 'soda ash glass' by Wedepohl et al. 2011, 82.
14 Shortland 2004; Shortland et al. 2006.
15 Rehren 2000, 1225; Artioli 2010, 286, Tab. 3.2.2.
16 Henderson 2000, 58.
17 Sayre – Smith 1961; Freestone 2006, 202–205. This type of glass is called as 'soda lime glass' by Wedepohl et al. 2011, 82.
18 According to Rehren – Freestone (2015, 234) natron (soda-lime-silica) glass with elevated levels of magnesia and potash can indicate (i) the intentional addition of an ash component, (ii) the contamination of glass by the fuel ash during extended periods of firing, or (iii) inherent contribution of magnesia and potash from the sand.
19 Lilyquist – Brill (1993, 36, Tab. 2) suggested to reduce data to seven "base glass" oxides (oxides of Na, Mg, Al, Si, K, Ca and Fe), however, in the reduced compositions we included phosphorous and chlorine, since they are also related to raw material (sodic flux) of the glass. In fact, the reduction only slightly increases the K_2O and MgO contents of glass, by a 0.1 to 0.2 wt%.

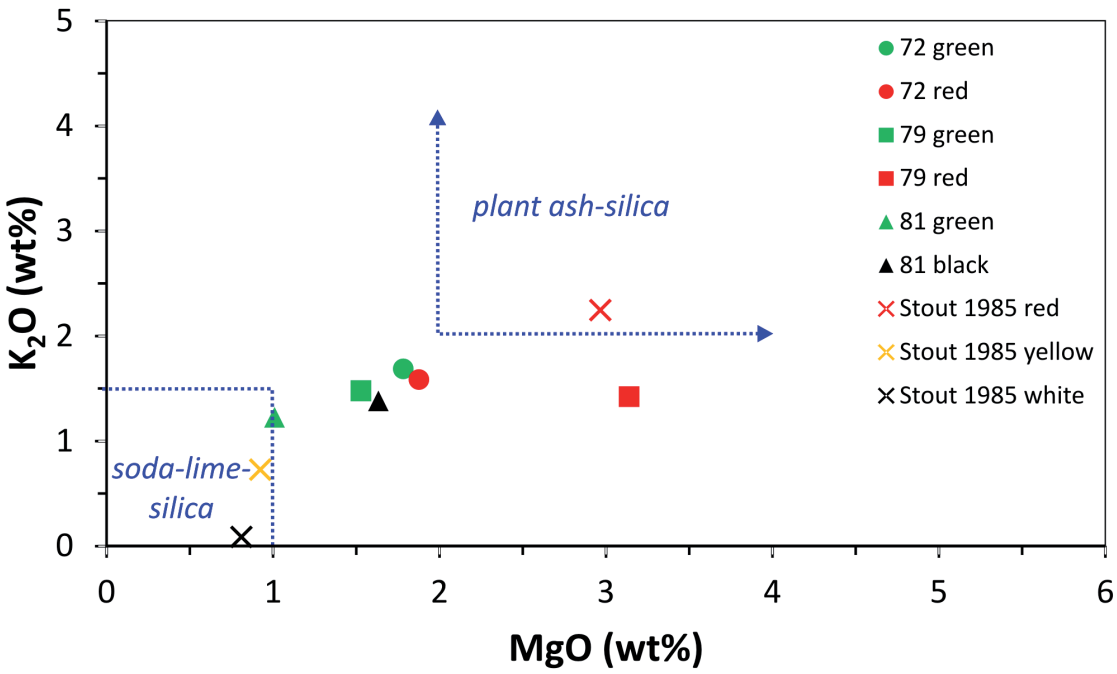

Fig. 3. The base glass composition of coloured (green, red and black) glasses of the face beads (calculated from the micro-XRF data) in the MgO vs. K_2O binary diagram. Typical compositional ranges for soda-lime-silica and plant ash-silica glasses (after Henderson 2000 and Freestone 2005) as well as composition of white, yellow and red glasses of a face bead analysed by Stout (1985) are indicated

Comparing the base glass composition of green glasses with that of red glasses calculated from the micro-XRF values, they are very close to each other for the bead 72 in the MgO-K_2O binary diagram, however, they fall far from each other for the bead 79 *(Fig. 3)*. Therefore, presently we cannot prove that the base glass composition of the outer green rim is identical to that of the red glass in the two uniform face beads.

Although only two of the uniform face beads were measured by micro-XRF technique, their chemical composition is different as glasses coloured with the same colour do not overlap in the binary MgO–K_2O diagram (e.g. green glass of bead 72 vs. green glass of 79 and red glass of bead 72 vs. red glass of 79, *Fig. 3*). Therefore, presently we cannot prove that the two uniform face beads belong to same glass rod.

Regarding the white-faced bead (bead 81) the black glass is out of the range typical for soda-lime-silica glass and together with its 0.9 wt% P_2O_5 content indicates that it contains some plant ash as alkali *(Fig. 3)*. However, the base glass of the green-coloured rim falls at or close to the edge of the chemical range typical for the soda-lime silica glassindicating that this green glass was (mostly) made of mineral soda flux. The base glass type of red and white glasses of bead 81 is not calculated quantitatively due to the ambiguous micro-XRF results with the low Na_2O values. However, compositional data suggest that red glass with high K_2O, MgO and P_2O_5 content, 1.7, 3.6 and 1 wt%, respectively, is most probably of plant ash-silica type, whereas white glass with low MgO, K_2O and P_2O_5 content, less than 0.6 wt% or around 0 wt%, respectively, is most probably of soda-lime-silica type.

There are only a limited number of published compositional data about mosaic face and checker glass beads. Ann M. Stout analysed mosaic glass beads, including one face bead of Selling II

type from 4th to 5th century, and seven checker beads from the 3rd century to the Migration Period by using an electron microprobe and an optical emission spectrophotometer.[20] She stated that the compositions of glasses agree with Roman glasses,[21] i.e. soda-lime-silica base glass, although she noticed that red glasses have relatively high levels of magnesia (2.1 to 2.95 wt% MgO) and potash (2.23 to 2.69 wt% K_2O) compared to other coloured glasses and suggested the use of plant ashes added for some of the alkali.[22] She concluded that different recipes were used for different colours.[23] The compositions of the white, yellow and red glasses of one face bead analysed by her are indicated in *Fig. 3*.[24] White and yellow glasses fall into the typical range of soda-lime-silica glass, whereas red glass is of plant-ash-silica type *(Fig. 3)*. Our study confirms Stout's observation that red glasses of the face beads were in fact produced partly or dominantly from plant ash flux. In addition, we raise the possibility that green and maybe black (?) glasses were also produced from more or less plant ash flux the latter could not have been demonstrated by Stout as the face and checker beads examined by her didn't have these colours.

Colourants

Elevated copper contents (1.7 to 2.8 wt% CuO) detected by micro-XRF in both green and red glasses compared to other coloured glasses indicate that these glasses were coloured with copper. For the green glass, the copper colourant is ionic probably in the form of cupric ion (Cu^{2+}).[25] Presence of lead can turn the copper-bearing glass to green,[26] however, only a low amount of lead (0.5–1.5 wt% PbO) was detected in the green glass by micro-XRF. The opacity of green glass is related to presence of antimony-based colourants and opacifiers, probably lead antimonate and calcium antimonate inclusions (see below), as revealed by the microprobe analysis of bead 72.

Red colour of the glass is caused by the presence of tiny, sub-micron to micron sized cuprous oxide (cuprite, Cu_2O) or metallic copper crystallites or their mixture as colourant and opacifier.[27] The formation of these crystallites in the glass requires reducing atmosphere for which charcoal was used in the furnace.[28] The size and distribution of crystallites also depends on the heat treatment (temperature and period).[29] In addition, presence of lead oxide in the glass, at the 1% level or more, greatly facilitates the precipitation of crystallites.[30] Lead oxide was also deliberately added during preparation of the red glass of the face beads as all of them contain certain amount of lead (3.8 to 5.5 wt% PbO) detected by micro-XRF. However, they fall into the category of low-lead, low-copper opaque red glasses, for which it is generally supposed that internal reducing agent such as iron was added to precipitate

20 Stout 1985, 169–213. She analysed yellow, purplish-brown (wine), red, white, blue, turquoise and clear glasses of the face and checker beads (Stout 1985, 196, Tab. IX).
21 Stout 1985, 187; 1986, 76.
22 Stout 1985, 178.
23 Stout 1985, 186.
24 Only those glasses are indicated in *Fig. 3*, which have colours similar to the face beads investigated in our study.
25 Henderson 1985, 282; Henderson 2000, 32–33.
26 Weyl 1953, 164–165 in Henderson 1985, 282.
27 Henderson 1985, 281; Brill – Cahill 1988; Barber et al. 2009.
28 Henderson 1985, 281.
29 Henderson 1985, 281.
30 Henderson 1985, 281; 2000, 33.

crystallites,[31] although the iron concentration of studied red glasses is not higher compared to other colours. Contrary to the two uniform face beads, the red glass of the bead 81 contains elevated amount of antimony (3.4 wt% Sb_2O_3), which may have been added to enhance the growth of crystallites and/or to act as decolourant.[32]

The elevated antimony and lead contents (1 to 1.6 wt% Sb_2O_3, 7.5 to 16.1 wt% PbO) of the yellow glass in the two uniform face beads (beads 72 and 79) indicate the presence of lead (pyro) antimonate ($Pb_2Sb_2O_7$) as colourant and opacifier.[33]

Similarly, the elevated antimony content (9.3 wt% Sb_2O_3) in the white glass of bead 81 indicates the presence of calcium antimonate ($Ca_2Sb_2O_6$ and/or Ca_2Sb_2O7), a typical opacifier for white glass.[34] The role of lead in the amount of 4.9 wt% PbO was most probably to reduce the melting temperature of white glass.[35]

Similar or higher iron contents (1.5 to 3.5 wt% Fe_2O_3) are detected in black glass compared to other coloured glasses. In addition, manganese content is similar or lower (0.4 to 0.7 wt% MnO_2) compared to other glasses, and no other colouring agents, e.g. copper, can be supposed based on the chemical composition. Therefore, it is assumed that most probably iron causes the colour, which is typical for black glass.[36]

Based on the chemical composition, the face bead and the checker beads analysed earlier by Stout were coloured similarly to the face beads analysed in this study. Stout found that copper (2–2.5 wt% CuO) with very low amount of lead (<1.7 wt% PbO) is responsible for the colour in the red glasses, and detected high levels of lead with some antimony (3.5 to 10.7 wt% PbO and 0.8 to 1.5 wt% Sb_2O_5) in the yellow glasses and antimony (0.9 to 3.8 wt% Sb_2O_5) in the white glasses.[37]

Conclusion

Based on the micro-XRF results it is demonstrated that some parts of three face beads of Selling I type found in an Early Sarmatian grave (green and red glasses of two uniform beads and a black glass of the third bead) were made, at least partially, from plant ash. Since the red glasses of a face bead of Selling II type and some checker beads measured earlier show a similar phenomenon, it seems that a different recipe existed for red glass of mosaic (face and checker) beads already in the 1st century. Our data also suggest that, in addition to red glass, green and maybe black (?) glasses glasses of the beads were also produced from base glasses containing some plant ash. Regarding the colour of the beads the chemical composition indicates the use of colourants and opacifiers typical for ancient glass: copper (as Cu^{2+}) for green

31 Barber et al. 2009. Iron oxide of 1.4 to 2.3 wt% in the glass is suitable for precipitation of copper (Guido et al. 1984 in Henderson 1985, 282; Henderson 2000, 33).
32 Brill – Cahill 1988, 19; Barber et al. 2009, 117.
33 Henderson 1985, 285; Henderson 2000, 35–36; Molina et al. 2014.
34 Henderson 1985, 285; Henderson 2000, 35.
35 Gedzevičite et al. 2009, 28.
36 Henderson 1985, 283; Henderson 2000, 34.
37 Data obtained by optical emission spectrophotometer (Stout 1985, 178–180, 201, 203–204, Tabs. XIII, XV, and XVI). Although Stout also used electron microprobe analysis to investigate variously coloured parts of the beads, she measured only the chemical composition and did not mention the microstructure and inclusions of the glasses.

with some antimony-based opacifiers, copper as cuprous oxide and/or metallic Cu together with lead (and antimony) for red, antimony and lead in the form of lead antimonate for yellow, antimony in the form of calcium antimonate for white and iron for black.

Further analysis is planned on the face beads, namely non-destructive *in situ* electron-microprobe analysis with special sample preparation (selective enwrapment into metal foil) in order to study the microstructure and get quantitative chemical composition about the variously coloured glasses of the beads. Colouring and opacifying particles of coloured glasses (e.g. cuprous oxide and/or metallic copper in red glass, type of calcium antimonate in white glass) will be determined by means of Raman microspectrosocpy and/or micro-X-ray diffraction (micro-XRD) analysis. In addition, other glassy finds of the grave, i.e. checker, metal-foil and faience beads will also be investigated by a detailed electron microprobe study.

References

Artioli, G. 2010: *Scientific methods and cultural heritage. An introduction to the application of materials science to archaeometry and conservation science*. Oxford – New York.

Barber, D. J. – Freestone, I. C. – Moulding, K. M. 2009: Ancient copper red glasses: investigation and analysis by microbeam techniques. In: Shortland, A. J. – Freestone, I. C. – Rehren, T. (eds.): *From mine to microscope. Advances in the study of ancient technology*. Oxford, 116–127.

Brill, R. H. – Cahill, N. D. 1988: A red opaque glass from Sardis and some thoughts on red opaques in general. *The Journal of Glass Studies* 30, 16–27.

Freestone, I. 2005: The provenance of ancient glass through compositional analysis. *Materials Research Society Symposium Proceedings* 852, OO8.1.1–OO8.1.14.

Freestone, I. 2006: Glass production in Late Antiquity and the Early Islamic period: a geochemical perspective. In: Maggetti, M. – Messiga, B. (eds.): *Geomaterials in cultural heritage*. Geological Society Special Publications 257. London, 201–216.

Gedzevičiute, V. – Welter, N. – Schüssler, U. – Weiss, C. 2009: Chemical composition and colouring agents of Roman mosaic and millefiori glass, studied by electron microprobe analysis and Raman microspectroscopy. *Archaeological and Anthropological Sciences* 1, 15–29.

Guido, M. – Henderson, J. – Cable, C. – Bayley, J – Biek, L. 1984: A Bronze Age glass bead from Wilsford, Wiltshire: Barrow G.42 in the Lake group. *Proceedings of the Prehistoric Society* 59, 245–154.

Henderson, J. 1985: The raw materials of early glass production. *Oxford Journal of Archaeology* 5, 267–291.

Henderson, J. 2000: *The science and archaeology of materials. An investigation of inorganic materials*. London – New York.

Henderson, J. 2009: The provenance of archaeological plant ash glasses. In: Shortland, A. J. – Freestone, I. C. – Rehren, T. (eds.): *From mine to microscope. Advances in the study of ancient technology*. Oxford, 129–138.

Janssens, K. – Vittiglio, G. – Deraedt, I. – Aerts, A. – Vekemans, B. – Vincze, L. – Wei, F. – Deryck, I. – Schalm, O. – Adams, F. – Rindby, A. – Knöchel, A. – Simionovici, A. – Snigirev, A. 2000: Use of microscopic XRF for non-destructive analysis in art and archaeometry. *X-ray Spectrometry* 29, 73–91.

Korom, A. 2018: Archaeological study of face beads excavated from an Early Sarmatian grave. In: Rácz, Zs. – Koncz, I. – Gulyás, B. (eds.): "Hadak útján". A népvándorláskor fiatal kutatóinak XXVI. konferenciája (26th Conference of Young Scholars on the Migration Period). *Dissertationes Archaeologicae Supplementum* 2. Budapest, 21–31.

Korom, A. – Reményi, L. 2005: Újabb régészeti kutatások Dunakeszi-Székesdűlőn (Recent archaeological investigations at Dunakeszi-Székesdűlő). *Aquincumi Füzetek* 11, 197–209.

Lilyquist, Chr. – Brill, R. 1993: *Studies in Early Egyptian Glass*. The Metropolitan Museum of Art, New York.

Molina, G. – Odin, G. P. – Pradell, T. – Shortland, A. J. – Tite, M. S. 2014: Production technology and replication of lead antimonate yellow glass from New Kingdom Egypt and the Roman Empire. *Journal of Archaeological Science* 41, 171–184.

Mozgai, V. – Szabó, M. – May, Z. – Bajnóczi, B. 2018: Handheld X-ray fluorescence and electron microprobe analyses of gold artefacts of an early Sarmatian grave, Dunakeszi-Székes-dűlő, Hungary. In: Khrapunov, I. (ed.): *The Crimea in the age of Sarmatians (200 BC – AD 400) III. Collected papers*. „Heritage of Millenia". Simferopol, 42–57.

Rehren, Th. 2000: Rationales in Old World base glass compositions. *Journal of Archaeological Science* 27, 1225–1234.

Rehren, Th. – Freestone, I. C. 2015: Ancient glass: from kaleidoscope to crystal ball. *Journal of Archaeological Science* 56, 233–241.

Sayre, E. V. – Smith, R. W. 1961: Compositional categories of ancient glass. *Science* 133, 1824–1836.

Shortland A. J. 2004: Evaporites of the Wadi Natrun: seasonal and annual variation and its implication for ancient exploitation. *Archaeometry* 46, 497–516.

Shortland, A. – Schachner, L. – Freestone, I. – Tite, M. 2006: Natron as a flux in the early vitreous materials industry: sources, beginnings and reasons for decline. *Journal of Archaeological Science* 33 (4), 521–530.

Stout, A. M. 1985: *Mosaic glass face beads: Their significance in northern Europe during the Later Roman Empire*. I–II. Ph.D. dissertation, University of Minnesota.

Stout, A. M. 1986: The archaeological context of Late Roman period mosaic glass face beads. *Ornament* 9, 58–61, 76–77.

Vicenzi, E. – Eggins, S. – Logan, A. – Wysoczanski, R. 2002: Microbeam characterization of Corning Archeological Reference Glasses: New additions to the Smithsonian Microbeam Standard Collection. *Journal of Research of the National Institute of Standards and Technology* 107, 719–727.

Wedepohl, K. H. – Simon, K. – Kronz, A. 2011: Data on 61 chemical elements for the characterization of three major glass compositions in late Antiquity and the Middle Ages. *Archaeometry* 53 (1) 81–102.

Weyl, W. A. 1953: *Coloured glasses*. New York.

	Colour	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*TiO_2*	*Na_2O*	*K_2O*	*CaO*	*MgO*	*Sb_2O_3*	*MnO_2*	*CuO*	*SnO_2*	*PbO*	*P_2O_5*	*SO_3*	*Cl*	*ZnO*	*SrO*	*ZrO_2*
2011.2.118.72	green	67.00	2.64	1.40	0.25	12.45	1.59	5.92	1.68	0.21	0.72	2.80	0.24	0.82	0.92	0.51	0.75	0.00	0.07	0.03
	red	58.37	2.56	1.75	0.22	16.18	1.46	8.23	1.72	0.52	0.64	1.90	0.23	4.22	1.12	0.05	0.71	0.00	0.09	0.03
	yellow	64.84	1.82	1.26	0.11	6.72	0.53	4.12	0.27	1.62	1.13	0.11	0.10	16.12	0.11	0.05	0.93	0.01	0.08	0.06
	black	75.90	4.38	2.24	0.44	7.58	0.84	5.39	1.06	0.05	0.38	0.09	0.02	0.31	0.17	0.47	0.91	0.01	0.07	0.05
2011.2.118.79	green	62.20	1.89	1.13	0.20	21.21	1.42	5.19	1.47	0.13	0.62	2.10	0.20	0.50	0.67	0.34	0.69	0.01	0.04	0.02
	red	58.44	2.63	1.49	0.19	16.60	1.32	7.67	2.92	0.32	0.54	1.67	0.34	3.76	1.33	0.05	0.61	0.01	0.09	0.03
	yellow	73.81	1.94	0.84	0.09	8.31	0.41	3.38	0.88	1.01	0.81	0.02	0.07	7.49	0.01	0.07	0.83	0.01	0.04	0.02
	black	74.89	3.48	3.46	0.67	6.56	0.73	6.78	1.10	0.06	0.42	0.06	0.03	0.07	0.15	0.50	0.88	0.01	0.10	0.05
2011.2.118.81	green	66.62	2.45	1.14	0.18	16.26	1.16	4.96	0.96	0.65	0.62	1.72	0.12	1.55	0.46	0.21	0.88	0.01	0.05	0.01
	red	61.14	2.38	2.12	0.24	6.04	1.72	8.51	3.59	3.36	0.79	2.36	0.20	5.55	1.22	0.05	0.61	0.01	0.09	0.03
	white	72.57	1.92	0.70	0.01	3.57	0.56	4.28	0.04	9.32	1.11	0.05	0.01	4.88	0.01	0.06	0.70	0.01	0.09	0.03
	black	71.78	2.66	1.49	0.28	11.26	1.36	6.04	1.61	0.18	0.66	0.07	0.01	0.04	0.88	0.49	1.13	0.00	0.06	0.02

Tab. 1. Chemical composition of coloured glasses of the face beads measured by micro-XRF (normalised to 100 wt %). Measurements with ≥10 wt% Na_2O were evaluated quantitatively, others are evaluated only qualitatively. Sites of the measurements are indicated in Fig. 1.

	SiO_2	*Al_2O_3*	*Fe_2O_3*	*TiO_2*	*Na_2O*	*K_2O*	*CaO*	*MgO*	*Sb_2O_3*	*MnO*	*CuO*	*SnO_2*	*PbO*	*P_2O_5*	*SO_3*	*Cl*
areal analysis n = 5	59.09 *± 0.47*	2.66 *± 0.15*	1.22 *± 0.12*	0.27 *± 0.14*	18.59 *± 0.24*	1.88 *± 0.11*	7.15 *± 0.13*	1.98 *± 0.07*	0.37 *± 0.23*	0.48 *± 0.10*	2.86 *± 0.22*	0.53 *± 0.29*	0.71 *± 0.20*	0.75 *± 0.07*	0.43 *± 0.21*	1.02 *± 0.08*
spot analysis n = 12	60.31 *± 0.57*	2.53 *± 0.19*	1.24 *± 0.20*	0.23 *± 0.16*	18.38 *± 0.50*	1.87 *± 0.19*	7.17 *± 0.31*	1.98 *± 0.26*	-0.06 *± 0.31*	0.56 *± 0.14*	2.72 *± 0.33*	0.14 *± 0.29*	0.68 *± 0.40*	0.76 *± 0.22*	0.41 *± 0.28*	1.04 *± 0.12*

Tab. 2. Chemical composition of green glass of the face bead 2011.2.118.72 measured by electron microprobe analysis (energy-dispersive X-ray spectrometer, normalised to 100 wt% oxide total, average ± st. dev., n = number of analyses).