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Analysis of glass from the post-Roman settlement Tonovcov grad (Slovenia) by PIXE–PIGE and LA-ICP-MS

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Abstract

The combined PIXE–PIGE method was used for the analysis of 43 glass fragments from the archaeological site Tonovcov grad in western Slovenia, with 10 of these additionally being analysed by LA-ICP-MS. The glass objects were attributed to the Late Antique production of the 4th–7th c. AD, with two examples of early Roman glass and three glass beads, one of them presumably of oriental origin. The analysis showed typical natron-type glass, produced in the Levantine region around the river Belus, and a few examples of HIMT glass, which could be recognized also in several other recycled objects. Only one glass bead, found in Early Medieval context, was made of the ash of halophytic plants.

1. Introduction

The fortified settlement of Tonovcov grad is located on a steep isolated hill above the Socˇa River near the modern city of Kobarid in western Slovenia; its position is strategic and controls the traffic towards the upper Socˇa valley. In spite of this and sporadic remarks in older historic literature it was recognized as a site rather late, in 1991 [1]. In subsequent years, systematic excavations were performed, revealing several buildings, a water cistern and a complex of Early Christian churches. Though several finds indicate that the site was populated from prehistory and Early Roman period until the Carolingian and Medieval period, its main settlement phase is Late Antiquity and involves two sub-phases: the first in the second half of the 4th and beginning of the 5th century, and the second between the end of the 5th and beginning of the 7th century [2]. Among the finds, which are predominantly from these two periods, there are also numerous fragments of glass. The majority of them (118) were discovered in the so-called building 1, situated on the slope below the church complex and dated to the second Late Antique phase. Typologically, they include stemmed goblets, footed beakers, beakers, bottles, lamps, plates, bowls and window glass. Elongated bubbles in the window glass indicate that it was produced by the cylinder technique. According to the dating based on the archaeological evidence, the glass of Tonovcov grad belongs to the period between the 4th and early 7th centuries; only two glass fragments can be typologically dated to an earlier period of 1st–3rd centuries [2].

Glass of the Late Antique period had already attracted several research interests of the analysts [3–22], though Tonovcov grad is the first Slovenian site to be analysed. The site where the closest analogies with Tonovcov grad are anticipated are San Martino di Ovaro, which is only 58 km away as the crow flies; however, several mountain ranges and passes make the ground communication between the two sites difficult. Numerous glass finds from San Martino di Ovaro were analyzed by PIXE [14]; the glass composition of Late Antique samples agreed well with the Levantine I glass samples according to Freestone [23], indicating intense commercial relations between Northern Italy and the raw glass production area in the Palestinian coast. A similar scheme of the glass from Tonovcov grad is expected.

2. Experimental

The glass objects were analyzed in air by a proton beam of 3 MeV nominal energy, provided by the Tandetron accelerator of the Jozˇef Stefan Institute in Ljubljana. Due to stopping in the exit window and about 1 cm wide air gap between the window and target, the projectile impact energy at the target was about 2.7 MeV. The intensity profile of the beam was Gaussian, with 0.8 mm full width at half maximum. A combined PIXE–PIGE method was applied. For PIXE, the exit window of 8 μm aluminium foil was used, in order to avoid the presence of scattered high energy X-ray lines in the spectra. The path-length of induced X-rays in the air was about 5.7 cm. Precise values of both air gaps (with an accuracy of 0.1 mm) was determined by a series of measurements on known metal and simple chemical compound targets, using the argon signal induced in air as an internal standard [24]. Spacers made of nylon rods were used to keep the experimental geometry fixed. Two X-ray spectra were measured in each measuring spot. Using air as the only absorber, the lightest element detected was silicon. Running the measurement at a current of a few tenths of nA for about 500 s, the counting statistics limited detection of elements heavier than iron. For detection of heavier elements, the detector was equipped with an additional absorber of 0.1 mm aluminium foil, while the proton current was increased to a few nA at a measuring time of 400–500 s. The two spectra were combined into one using the Ka line of iron for normalization.

The concentrations of Na, Mg and Al, essential elements for glass characterization, were determined according to their induced gamma ray emissions (PIGE). The exit window for PIGE measurements was a 2 lm tantalum foil, which emits proton-induced gamma rays below 300 keV. The proton current was about 3 nA and the measurements lasted about 30 min. The proton current was measured by a thin wire mesh intersecting the beam; transmission of the mesh was 58% [25]. The gamma rays employed for the analysis were 440 keV for Na, 585 for Mg and 1014 keV for Al. The latter line is also induced in Mg, but with negligible intensity at proton energies above 2.4 MeV [26]. Its production becomes important at lower energies, for example at 1.77 MeV its production in Mg is 8% of that in Al [27], but the production in Al at 1.7 MeV is only 0.3% of that at 2.4 MeV [26]. We therefore estimate the Mg contribution of 1014 keV line in our spectra was minute.

The concentrations of Na, Mg and Al were determined according to the known values in the standard glass NIST 620, using the surface approximation [28]. As this approach requires the proton stopping power in the sample and standard, the unknown concentrations were determined by an iterative procedure, considering both X-ray and gamma-ray intensities simultaneously. The matrix effects for X-ray and gamma ray production were calculated individually for each iteration step. The sum of all metal oxides was normalized to unity. For monitoring the accuracy of the procedure, the sum of metal oxides was also calculated according to the X-ray yield of argon from the air. These values typically departed from unity within ±10%, though a few samples with irregular or corroded surfaces exhibited larger differences, up to 30%. For control purposes, the standard glasses NIST 620 and 621 were analyzed periodically as unknown samples.

The concentration uncertainties for major elements were ±5%, but increased to 10–20% for trace elements close to their detection limits. A peculiar example was Mg, whose detection limit was about 0.2% due to interference of its 585 keV line with the line of 583 keV from the natural background, and due to strong Compton background of sodium lines at 1634 and 1636 keV. The two effects imply that magnesium concentrations were uncertain by 10%. The limit of detection for aluminium was about 20 μg/g. For the heavier elements obtained from the X-ray spectra, the limits of detection between Co and Zr (and Pb with its L lines) were about 10 μg/g, and for Sn and Sb they were about 50 μg/g.

Ten samples were also selected accidentally from the set and analyzed by LA-ICP-MS at the CNRS/IRAMAT laboratory in Orléans. These values were used as a test of our procedures, but they also provided concentrations of several elements present in concentrations below 1 μg/g level.

3. Results

The analytical results obtained by the PIXE–PIGE method are shown in Table 1. Single zeros denote non-detected elements. Elemental concentrations are shown in the form of oxides, whose sum was normalized to unity. For iron we formally adopted the oxide form Fe2O3, which, however, does not exclude the presence of FeO; the ratio of the two oxides determines the blue-green or yellow tint of glass [4,16,29]. The oxidation number of iron could not be detected by our methods.

The LA-ICP-MS values were first used for comparison with the PIXE–PIGE data. Table 2 shows the concentration ratios of representative elements obtained by both methods. The agreement is generally good, though some systematic differences are evident. Sodium values are generally 13% higher for PIGE, which is contrary to expectations, as the surface concentrations (probed by PIGE) should be somewhat smaller than the bulk values on account of surface leaching. The magnesium concentrations are also higher, though the magnesium data show prominent scattering, which is result of poor counting statistics and high background contribution close to the detection limit. Aluminium concentrations are also scattered by 10%, though their mean is closer to unity, which excludes systematic normalization error in PIGE measurements. Among the X-ray determined concentrations, potassium values are overestimated between 20% and 95%. The reasons for these differences cannot be explained by X-ray techniques only, as potassium neighbours, chlorine and calcium show very good agreement with the LA-ICP-MS data. The only possible reason could be improper subtraction of the X-ray background or interference of potassium Ka and argon Kb lines, but these effects would be detected at the analysis of NIST 620 glass standard. Systematic underestimation of PIXE values by 20% is observed for manganese and iron, however, small scattering of the iron data indicates the error was introduced by the calibration procedure.

The concentrations of trace elements that were detected by LA-ICP-MS only are listed in Table 3; it is split into two parts, the first showing the contents of rare earths, and the second the remaining light and heavy elements.

4. Discussion

The data of Table 1 were first studied for characteristic grouping using the principal component analysis (Fig. 1) of the oxides Na2O, MgO, Al2O3, SiO2, K2O, CaO, TiO2 and Fe2O3. The selection of oxides reflects basic properties of the glassmaking process of the raw glass, but excludes its discoloration and pigmentation. Fig. 1 shows that the glasses of Tonovcov grad form quite a compact group. Only three data depart considerably from the main group: two glass beads and one vessel (23592 goblet foot). Fig. 1 also reveals that the three lamps are quite similar to each other, but distant from the two fragments of early Roman glass. A noticeable feature is three samples marked by an oval, whose raw material is identified further in Figs. 3 and 4.

The type of the flux is typically identified in the bivariate MgO– K2O plot [14], as shown in Fig. 2. As expected, all investigated glass objects (except one) belong to natron-type glass, identified by MgO concentrations below 1.6% and K2O concentrations below 1% [30]. The same three samples as identified in Fig. 1 largely depart from the main group: two glass beads and a goblet foot. One of the two beads (22304) shows an MgO content of 5.7%, which qualifies it as glass made of the ash of halophytic plants. This type of glass appears in Europe regularly only after 800 AD and its early examples represent import from the Byzantine and Islamic world [23]. The glass bead 22304 is indeed of the oriental type and may be related to the short Carolingian period phase of the site. The other two items (bead 23653 and goblet foot 23592) show a higher content of K2O (1.72 and 3.59%, respectively). Such high K2O concentrations are not uncommon among the Late Roman glass [15,22,31] and may result, for example, from the presence of alkali feldspars in the glass batch.

The main group of Fig. 2 also shows an interesting time structure. The two Early Roman glass samples (23060/1, 23007) are characterized by low MgO values around 0.5%, while the 4th–7th century samples (lamps) contain MgO concentrations around 1.5%. Similar high MgO values were observed in the 7th century glass from Crypta Balbi in Rome [4]; lower MgO concentrations were found for the 8th c. glass from the same site, which may be explained by a higher content of recycled earlier glass in the objects [5].

Production places of primary raw glass are identified according to the calcareous component of the siliceous sand and the admixture of aluminium oxides [23]. In Fig. 3, we plotted results of our measurements together with the elemental ranges found in the literature; for the sake of clarity we have limited ourselves to the compositional groups that coincide with our measurements only. Group 3 of Foy [11] designates glass production in the Levantine area around the Belus River in a rather broad time period between the 3rd c. BC and 9th c AD. The subgroup of group 3 involves early Roman glass of the Imperial period (we denote it as 3/3.1–3.3 as it was derived from the group 3 subtracting the post-Roman groups 3.1–3.3 [11]); this group nicely coincides with the two groups of coloured glass from the shipwreck of Iulia Felix [32]. Group 4 of Foy [11,33] designates glass of the 2nd and 3rd c. AD that was decolorized by antimony. The origin of group 4 remained unknown until recently; isotopic studies of glass from the Ouest Embiez and Iulia Felix shipwrecks suggest this glass was also made in Palestine, but likely in a different workshop [34]. All these groups are shown as ellipses with the axes that measure four standard deviations. Beside this, Fig. 3 also shows the Late Roman glass groups as defined by Freestone [23]: HIMT and Levantine I and II. These groups are plotted as rectangles, following the method of Zucchiatti [14]. We can see that nearly all our samples coincide with Foy's group 3 and Freestone's Levantine I glass, so they originate from the Palestinian glassmaking area. A slight shift between the group 3 and Levantine I denotes a minor variation of the glass composition with time, as the Levantine I glass is dated to the 5th–7th c. AD [23]. The reason for this variation may be geological or anthropogenic, i.e., gradual moving of the production site. As the analyzed glass selection involves only two examples of early Roman glass, it is not surprising that the region of group 4 in Fig. 3 remained empty.

The only example of window glass (23060/4) is located at the low Al_2O_3 border of Levantine I glass; this type of glass was widely used for glass manufacture in different geographic regions [14,35,36]. The three glass samples isolated in Fig. 1 contain the lowest CaO concentrations and are located in the cross-section of the group 3 and HIMT in Fig. 3. These samples (23054, 23674 and 23424) contain more than 0.46 TiO_2, 1.76% Fe_2O_3 and 1.38% MnO, which characterizes them as HIMT glass. This glass was first observed by Freestone among the glasses of Carthage, but it appeared also among the glasses of Aoste [29] and in south France [10]. In Britain, HIMT glass appeared as early as 330 AD and represents the most wide-spread glass type in Late Antiquity [37]. For the window glass, it was recognized among the glass fragments from the Theoderic's villa in Galeata [17]. Glass belonging to the Levantine I and HIMT types was also discovered among the Early Byzantine glass in Ganzirri, Sicily [16]. The sand source of HIMT glass is different from the Palestinian sources, but has not been identified yet; Egypt is one of the possible locations.

The distinction of the HIMT glass from the Levantine I is evident in Fig. 4, which shows the contents of siliceous sand impurities Ti, Sr and Zr. In Fig. 4a we observe linear correlation between TiO_2 and Fe_2O_3, which indicates mineral origin of both elements. Exceptions are two glass beads (23653, 23654) and HIMT glass that are evidently of different origins. SrO concentrations are above 440 lg/g, which is consistent with the composition of the maritime siliceous sand that contains shell fragments as a source of CaO [23].

HIMT glass is characterized by a high content of zirconium [9], which is also observed in our case (Fig. 4c). Two correlation lines are further observed in Fig. 4c, which clearly indicate two sand sources. The glasses arranged around the HIMT line contain lower ZrO_2 values and were very likely recycled using HIMT glass.

The rare earth pattern is shown in Fig. 5, normalizing the elemental concentrations to the mean values encountered in the upper continental crust [38]. It seems there is no significant time structure, except the values for the 4th–5th c. being higher than those in the later glass. However, this is on account of the sample 23054, which is the only example of HIMT glass in Table 3. In comparison with the glasses from Ganzirri, Sicily [16], glass of the 5th– 7th c. from Tonovcov grad corresponds to group 1 of Ganzirri; this is understandable, as the glass in both cases is of Levantine I type. Group 2 of Ganzirri represents HIMT glass; in our case it is sample 23054 that fits into this group. The rare earth pattern from both sites is therefore matching and confirms distinction between Levantine I and HIMT glass according to the rare earth elements.

Summarizing, there are 26 samples identified as Levantine I, while another 11 show significant similarities to Roman blue/green glass. Of these, the two early Roman samples stand out with a lower strontium content relative to the lime content; the remaining nine samples fall into two nearly equally strong groups of low and elevated titania, respectively. It is possible that the four samples with higher titania include a proportion of recycled HIMT glass in them; most other oxide concentrations are also consistent with this, except for magnesia, which is slightly too high in the mixed group compared to HIMT. Thus, it is also possible that the four samples with elevated titania content were produced from a less pure sand, due to the before-mentioned geological or anthropogenic changes in sand source.

For decoloration, MnO was used for all investigated glasses. MnO concentrations are spanning an interval between 0.23% and 2.14%, which agrees with the decoloration method in group 3. The concentrations of Sb_2O_3 are typically below 0.06%, which may indicate values not added on purpose, but the presence of antimony as the result of recycling; the source of antimony may be opaque tesserae added to the glass batch [4]. Only one sample of early Roman glass (23060/1) contains a higher content of Sb2O3 of 0.13%: however, even this value is not high enough to denote intentional decoloration by antimony. For antimony oxide, the concentrations added on purpose should be higher than 0.2% [30] and for manganese higher than 0.5% [39]. The antimony content in the fragment 23060/1 is then result of recycling during an early Roman period.

Among the other elements used for pigmentation, three blue samples (two beads and an early Roman cup) were pigmented by a combination of cobalt and copper oxides on 0.1% level. The red colour of the bead 23653 was attained by addition of 2.5% CuO; this bead also contains 1.8% SnO2, which may indicate bronze as a copper source.

The recycling history may also be followed according to the content of heavy elements that increase with the number of recycling steps. The contents of Cu and Zn suggest similarity between the three lamps, which may indicate production in the same secondary workshop (see Fig. 6).

5. Conclusion

The glasses of Tonovcov grad show two characteristic glass sources: glass from the Levantine area near the River Belus, which represents the majority of the investigated samples, and a small group of three samples that are characterized as HIMT glass according to their high titanium, iron and manganese contents. Further, the contents of zirconium and strontium reveal that certain glasses were recycled with the HIMT glass. The presence of HIMT glass makes distinction between the glass inventories of Tonovcov grad and San Martino di Ovaro, which is archaeologically and geographically its closest (analyzed) parallel. The joint occurrence of Levantine I and HIMT glass makes the glass inventory of Tonovcov grad more similar to that of Ganzirri in Sicily. This shows that the settlement of Tonovcov grad retained strong economic and political contacts with the Mediterranean world. However, the large fractions of Levantine I glass make the three sites specifically different from the Western Europe, which was main consumer of HIMT glass. This indicates specific trade routes in Late Antiquity. The production of Levantine I glass probably boomed after that of HIMT glass, in a period when the economic connections between the Mediterranean and Atlantic Europe were already in decline.

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No.		Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	Br	Rb_2O	SrO	ZrO_2	SnO_2	Sb_2O_3	PbO
23654	Quadruple glass bead	18.5	1.11	2.66	65.3	0.77	1.04	0.90	6.62	0.16	0.81	1.56	0.100	0.0087	0.1137	0.0069	0.0012	0.0013	0.056	0.023	0	0.016	0.124
23653	Small glass bead (red)	15.0	0.98	2.59	54.6	0.29	1.26	1.72	9.00	0.23	0.42	2.29	0	0.0140	2.5160	0.8526	0.0104	0	0.103	0.009	1.32	0	6.679
22304	Glass bead (blue)	14.3	5.70	1.80	65.3	0.53	0.69	3.19	6.52	0.08	0.51	0.77	0.067	0.0035	0.0806	0.3622	0.0010	0	0.053	0.012	0.011	0	0.049
23060/1	Bluish glass	17.5	0.48	2.27	69.3	0.53	0.96	0.84	6.91	0.08	0.40	0.37	0	0.0013	0.0228	0.0029	0.0004	0.0009	0.045	0.006	0	0.129	0.054
23007	Cup (early; blue)	18.1	0.63	2.31	68.5	0.51	1.05	0.69	7.12	0.05	0.23	0.60	0.057	0.0027	0.1277	0.0072	0.0006	0.0014	0.044	0.004	0.008	0.024	0.018
23014	Lamp	17.7	1.42	2.53	63.8	0.64	0.84	0.87	9.21	0.14	1.55	1.04	0	0.0027	0.0068	0.0037	0.0017	0	0.094	0.012	0	0.028	0.015
23426	Lamp (church)	17.8	1.30	2.65	65.3	0.60	0.77	0.95	7.54	0.14	1.78	1.12	0	0.0030	0.0075	0.0037	0.0017	0.0008	0.085	0.011	0	0	0.013
23427	Lamp (church)	19.7	1.30	3.17	62.3	0.72	0.80	0.80	8.54	0.15	1.41	0.93	0	0.0032	0.0129	0.0037	0.0016	0.0010	0.094	0.013	0	0.015	0.028
23060/2	Goblet foot	17.7	1.13	3.14	65.7	0.64	0.74	0.80	7.82	0.13	1.33	0.76	0	0.0016	0.0066	0.0020	0.0015	0.0009	0.079	0.011	0	0.020	0.012
23060/3	Fire-rounded rim	17.4	1.41	2.48	64.8	0.54	0.69	1.11	8.94	0.14	1.51	0.81	0	0.0020	0.0079	0.0027	0.0010	0.0008	0.082	0.008	0	0.013	0.010
23017	Glass handle	18.6	1.03	2.61	66.3	0.49	0.85	0.86	6.51	0.23	0.99	1.27	0	0.0021	0.0064	0.0029	0.0014	0.0011	0.056	0.016	0	0	0.009
23034	Fire-rounded rim	20.5	1.29	2.34	65.9	0.74	0.78	0.54	6.24	0.10	0.93	0.57	0	0.0013	0.0038	0.0018	0.0011	0.0006	0.055	0.009	0	0.004	0.005
23055	Bottle	19.4	1.49	2.65	63.8	0.64	0.84	0.68	8.10	0.14	1.32	0.76	0	0.0015	0.0042	0.0021	0.0011	0.0007	0.074	0.010	0	0.016	0.005
23074	Beaker base	18.9	0.94	2.27	67.4	0.46	0.97	0.54	6.17	0.19	0.85	1.08	0	0.0016	0.0038	0.0021	0.0012	0.0011	0.050	0.013	0	0.004	0.005
23069	Balsamarium (base)	20.2	0.70	2.19	65.5	0.70	0.77	0.63	7.36	0.11	1.10	0.64	0	0.0018	0.0046	0.0031	0.0010	0.0005	0.073	0.008	0	0.016	0.004
23026	Fire-rounded rim	17.5	1.33	2.51	64.0	0.65	0.79	0.94	9.46	0.14	1.50	0.85	0	0.0013	0.0096	0.0024	0.0014	0.0006	0.092	0.010	0.005	0.014	0.016
23071	Goblet foot	20.8	0.72	2.38	66.3	0.67	0.99	0.55	5.95	0.11	0.77	0.65	0	0.0013	0.0093	0.0020	0.0010	0.0009	0.048	0.008	0	0	0.011
23078	Plate	15.8	1.07	3.14	67.8	0.59	0.80	0.86	8.75	0.06	0.75	0.34	0	0.0009	0.0010	0.0016	0.0006	0.0011	0.057	0.005	0	0	0.002
23082	Goblet foot	20.6	1.19	2.57	64.0	0.67	0.93	0.65	7.33	0.12	1.17	0.61	0	0.0007	0.0047	0.0018	0.0014	0.0010	0.065	0.009	0	0.023	0.007
23009	Fire-rounded rim	17.4	1.42	2.40	64.4	0.62	0.91	0.90	9.08	0.14	1.49	1.03	0	0.0023	0.0053	0.0033	0.0016	0.0009	0.087	0.010	0	0.028	0.013
23068	Beaker base	20.4	1.00	2.17	65.5	0.77	0.85	0.62	7.26	0.09	0.73	0.51	0	0.0009	0.0016	0.0016	0.0015	0.0011	0.072	0.008	0	0	0.001
23033	Bottle rim	20.0	1.45	2.34	66.1	0.51	0.92	0.52	6.49	0.25	0.46	0.78	0	0.0010	0.0028	0.0020	0.0009	0.0008	0.058	0.018	0	0	0.004
23400	Goblet foot	19.0	0.98	2.21	64.8	0.67	0.90	0.84	8.59	0.13	1.01	0.71	0	0.0009	0.0038	0.0028	0.0011	0.0009	0.077	0.009	0	0.026	0.005
23083	Goblet foot	20.5	0.54	2.12	67.4	0.59	0.94	0.43	6.42	0.07	0.61	0.32	0	0.0009	0.0019	0.0013	0.0009	0.0005	0.052	0.005	0	0	0.002
23607	Goblet foot	20.6	0.39	2.31	67.0	0.73	0.94	0.77	5.96	0.08	0.68	0.38	0	0.0011	0.0030	0.0042	0.0013	0.0009	0.049	0.006	0	0	0.001
23030	Cup Foy 21a	19.7	0.83	1.89	67.2	0.72	1.10	0.51	6.83	0.07	0.70	0.36	0	0.0009	0.0022	0.0016	0.0009	0.0005	0.054	0.005	0	0	0.001
22994	Rim	17.9	1.52	2.95	63.1	0.57	0.66	1.04	9.88	0.15	1.14	0.85	0	0.0012	0.0027	0.0025	0.0007	0.0009	0.090	0.011	0	0	0.002
23029	Goblet wall	17.8	1.45	2.76	63.3	0.67	0.66	0.85	9.70	0.15	1.42	0.91	0	0.0013	0.0037	0.0026	0.0009	0.0011	0.092	0.012	0	0	0.004
23054	Base (olive color)	17.7	1.23	2.42	66.8	0.41	0.87	0.67	5.75	0.52	2.12	1.38	0	0.0016	0.0056	0.0036	0.0011	0	0.054	0.036	0	0	0.003
23576	Goblet rim	19.8	1.37	2.87	63.1	0.57	0.82	0.91	7.98	0.14	1.45	0.80	0	0.0022	0.0072	0.0031	0.0016	0.0010	0.083	0.009	0	0	0.010
23594	Goblet rim	18.3	1.41	2.74	65.7	0.59	0.86	0.75	7.12	0.18	1.13	0.87	0	0.0011	0.0125	0.0037	0.0009	0.0009	0.058	0.012	0	0.056	0.018
23674	Cut rim	18.7	0.92	2.70	65.5	0.51	0.94	0.48	6.27	0.50	1.76	1.49	0	0.0011	0.0057	0.0030	0.0011	0	0.060	0.037	0	0	0.002
23424	Cut rim	17.0	1.09	2.91	66.5	0.42	0.97	0.59	6.25	0.46	2.05	1.58	0	0.0011	0.0063	0.0034	0.0009	0	0.053	0.030	0	0	0.001
23501	Goblet rim	19.8	1.31	2.78	62.5	0.64	0.90	0.81	8.87	0.15	1.21	0.84	0	0.0014	0.0080	0.0034	0.0011	0	0.083	0.010	0	0.020	0.035
23502	Goblet rim	18.3	1.30	2.65	64.6	0.67	0.81	1.01	7.64	0.15	1.42	1.16	0	0.0025	0.0429	0.0043	0.0014	0.0012	0.083	0.010	0	0.039	0.047
23425	Goblet foot	17.8	1.29	2.23	65.5	0.60	0.81	0.70	8.93	0.12	1.24	0.65	0	0.0011	0.0034	0.0016	0.0008	0	0.086	0.010	0	0.023	0.004
23498	Goblet foot	17.9	1.68	2.48	65.3	0.58	0.82	1.01	7.63	0.15	1.58	0.71	0	0.0016	0.0046	0.0048	0.0010	0.0010	0.077	0.011	0	0.013	0.008
23433	Beaker base	17.5	1.41	2.68	65.0	0.68	0.77	0.97	7.36	0.14	2.14	1.13	0	0.0027	0.0082	0.0037	0.0015	0	0.094	0.011	0	0	0.013
23497	Beaker base	20.1	1.10	2.49	64.4	0.58	0.79	0.82	7.42	0.11	1.26	0.70	0	0.0025	0.0054	0.0033	0.0013	0.0008	0.073	0.007	0	0	0.011
23829	Goblet rim	19.8	1.42	2.38	63.8	0.59	0.85	0.87	7.84	0.13	1.36	0.74	0	0.0019	0.0060	0.0029	0.0014	0	0.081	0.008	0	0	0.012
23828	Goblet foot	18.3	1.44	2.61	62.7	0.68	0.60	0.93	9.89	0.14	1.26	1.27	0	0.0019	0.0054	0.0032	0.0009	0	0.110	0.010	0	0	0.013
23592	Goblet foot	17.1	1.04	2.91	64.6	0.43	0.74	3.59	7.35	0.11	1.24	0.71	0	0.0013	0.0065	0.0019	0.0013	0	0.074	0.010	0	0.024	0.011
23060/4	Window glass	17.3	0.99	2.48	66.1	0.49	0.69	0.66	8.79	0.13	1.46	0.77	0	0.0020	0.0054	0.0019	0.0009	0.0008	0.081	0.011	0	0.029	0.009

Table 1

Composition of the glass from Tonovcov grad – concentrations of oxides in mass%. Single zeros denote the elements below detection limits.

			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
23426	Lamp	5–7c.	8	13.5	1.9	7.9	1.6	0.4	1.3	0.2	1.4	0.3	0.8	0.1	0.8	0.1
23069	Bals.	5–7c.	6.4	11.2	1.5	6.5	1.3	0.3	1.2	0.2	1.2	0.2	0.7	0.1	0.7	0.1
23078	Plate	5–7.c	5	10.7	1.3	5.1	1	0.3	0.9	0.1	0.9	0.2	0.5	0.1	0.5	0.1
23082	Goblet	5–7.c	6.6	12.4	1.6	6.3	1.3	0.3	1.1	0.2	1.1	0.2	0.7	0.1	0.7	0.1
23033	Bottle	4–7c.	7.3	13.6	1.8	7.5	1.5	0.4	1.4	0.2	1.4	0.3	0.8	0.1	0.9	0.1
23607	Goblet	5.c	5.1	9.1	1.2	5	1	0.3	0.9	0.2	1	0.2	0.5	0.1	0.5	0.1
23030	Cup	5–6.c.	4.7	8.5	1.1	4.6	0.9	0.3	0.8	0.1	0.8	0.2	0.5	0.1	0.5	0.1
23054	Base	4–5c.	10.8	19.3	2.5	10.9	2.2	0.5	1.9	0.3	2.3	0.4	1.3	0.2	1.4	0.2
23497	Beaker	4–5c.	7.5	13.3	1.7	7.3	1.5	0.4	1.4	0.2	1.2	0.2	0.7	0.1	0.7	0.1
23068	Beaker	4–5c.	6.3	11.9	1.5	5.8	1.1	0.3	1	0.2	1	0.2	0.6	0.1	0.6	0.1
			Li	B	P_2O_5	V	Cr	As	Y	Nb	In	Ba	Hf	Ta	Th	U
23426	Lamp	5–7c.	6.44	172	2101	33	16	6	7	2.5	0.2	296	2.1	0.2	1.4	1.2
23069	Bals.	5–7c.	3.12	206	770	26	12	4.2	7	1.9	0	333	1.6	0.1	1.1	1.3
23078	Plate	5–7.c	2.52	94	1062	11	9	2.5	5	1.2	0	271	0.7	0.1	0.6	0.6
23082	Goblet	5–7.c	3.23	169	728	21	13	4	6	2.2	0	256	1.7	0.1	1.2	1.1
23033	Bottle	4–7c.	1.28	94	738	25	11	2.9	6	1.7	0	310	1.5	0.1	1	1.2
23607	Goblet	5.c	4.6	195	1262	21	37	2.5	7	3.2	0.1	180	3.6	0.2	1.5	1.4
23030	Cup	5–6.c.	2.51	116	465	17	9	2.7	5	1.2	0	197	1.1	0.2	0.8	0.8
23054	Base	4–5c.	2.37	160	373	18	10	3.5	5	1.1	0	183	0.9	0.1	0.6	0.9
23497	Beaker	4–5c.	2.35	158	542	52	63	5	11	5.4	0.1	976	7.7	0.4	2.6	1.6
23068	Beaker	4–5c.	3.52	142	1248	26	13	6	7	2.4	0.1	275	1.9	0.2	1.3	1

Table 3

Elemental or oxide concentrations (in μg/g) that were only detected by LA-ICP-MS; rare earths (top) and several others (below).