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COMPOSITIONAL ANALYSES OF ISACCEA MOSAIC GLASS TESSERAE (11th CENTURY AD)

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Abstract. A set of colored glass tesserae (yellow, blue turquoise and green turquoise) discovered at Isaccea and dated to the 11th century AD was investigated using Ion Beam Analysis (IBA) techniques to determine their chemical composition. Particular attention was paid to identify the glass chromophores and opacifiers. Based on the analytical results, several conclusions about the way these archaeological finds were manufactured, particularly on the raw materials and employed techniques were deduced.

Key words: historical glass, glass tesserae, chemical composition, PIXE, PIGE, Isaccea.

1. INTRODUCTION

1.1. CHEMICAL COMPOSITION OF ANCIENT GLASS ARTEFACTS

The scientific study of archaeological glass artefacts can provide insights on how these utilitarian or decorative objects were produced. In particular, glass chemical composition can suggest which were the raw materials and manufacturing techniques. Based on hard science arguments, indications about the way the ancient societies functioned – access to resources and level of craftsmanship – can be obtained [1].

This paper focuses on five glass mosaic tesserae discovered in archaeological context at Isaccea and dated to the 11th century AD. They have been the analyzed for their chemical composition using a combination of two non-destructive external IBA methods, namely Particle Induced X-ray Emission (PIXE) and Particle Induced Gamma-ray Emission (PIGE).

The measurements were carried out using the external micro-beam facility of the AGLAE accelerator from Centre de Recherche et de Restauration des Musées de France (C2RMF) in Paris, in the frame of CHARISMA EU FP7 project (http://www.charismaproject.eu/). The glass samples were bombarded with a 3

MeV proton beam and the characteristic X-rays and the prompt gamma rays were measured with a complex detection system. Bulk glass composition was obtained by combining the PIXE and the PIGE data.

The aim of this archaeometric study was to identify the glass recipes, raw materials and manufacturing procedures.

1.2. GLASS MOSAIC TESSERAE

First of all, one should answer a very basic question: “What is a tessera?” Tessera (plural tesserae) comes from the Latin words “cube” or “die” that, in turn, come from the Greek term “four-sided”. A tessera is a small piece of stone, glass, ceramic or any other hard material cut in a cubical (or other polyhedral) shape that is employed as a constitutive element for a mosaic work. Any mosaic decoration consists in the juxtaposition on a large scale of numerous tesserae combined in an artistic manner [2].

During the Roman period, mosaics were made out of stone or ceramic, being mostly used for floor decorations. During the Early Christian and Byzantine time, glass mosaics were frequently utilized to adorn the walls and vaults of the religious sites, such as churches and baptisteries. Glass tesserae were employed for parietal decoration, since, contrary to floor tiling, they are less affected by wear and mechanical stress.

The aesthetic value of glass mosaics is strongly influenced by the variety of colors and shades of the individual elements, which sometimes were enriched by the use of gold – or silver – leaf. Glass – be it transparent, translucent or opaque – is a material that interacts with light in a complex manner, producing spectacular visual effects.

Color is a very important characteristic of glass mosaic tesserae. Visual analysis of the surviving old mosaics suggests that the ancient masters were skilled enough to obtain a huge range of hues. They knew what chromophores to add to the basic glass recipe and in which amounts. Moreover, they also controlled the melting atmosphere and temperature in the furnace. Transparency is another important feature of glass mosaic tesserae and to obtain certain artistic effects, opaque glass was sometimes employed.

In some cases, thin precious metal foils (gold, silver) were used to create special regions of the mosaic decorations – *e.g*. saint haloes or gold stars [2]. These tesserae were prepared by hot fixing a thin sheet of precious metal between two colorless glass sheets. The glass sheets had the function of protecting the metal leaf from detachment and deterioration and to increase its shining.

A quick survey of the archaeometric literature led to the identification of a relatively reduced number of publications reporting chemical analyses of ancient glass mosaic tesserae, compared to studies of other kind of ancient vitreous artefacts (*e.g*. Roman glass) [3–10].

This paper will bring fresh information about these rarely studied ancient finds, enlarging the corpus of analyses of archaeological glass objects excavated on Romanian territory [11–14].

2. MATERIAL AND METHODS

2.1. ARCHAEOLOGICAL SAMPLES

The artefacts analyzed in this archaeometric study were five glass mosaic tesserae discovered in 2005 in the fortified urban settlement from Isaccea [15]. They were excavated from depths between 0.2 m and 1.0 m from Curtina A area, in layers disturbed by the 13th–14th centuries habitation. The tesserae feature different colors (yellow, green turquoise and blue turquoise) and they present traces of mortar on their surfaces (Fig. 1). Based on the discovery of particular ceramic shards at the same location, the tesserae were dated to the 11th century AD. The archaeologists suspected that the tesserae belonged to the mosaic decoration of a church located in Isaccea. The existence of this church was suggested by other archaeological finds, such as fresco fragments. These five glass mosaic tesserae are singular discoveries among the 11th century AD archaeological artefacts from Isaccea, as well as from other Byzantine sites from Dobrogea.

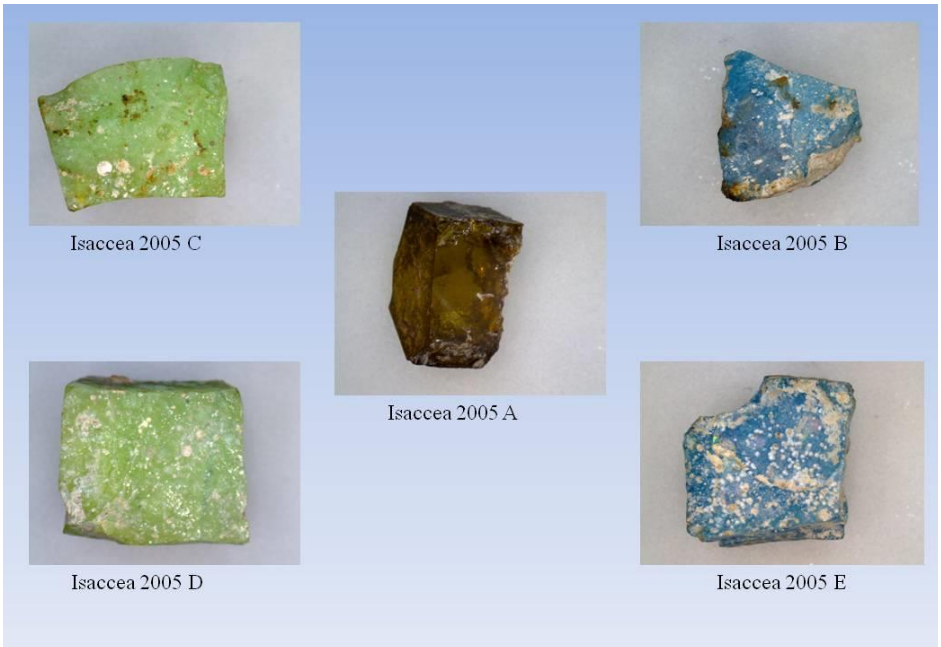

Fig. 1 – Photos of the Isaccea mosaic tesserae.

Their uniqueness reinforces the special status of Isaccea in the Lower Danube region during the Byzantine period, supporting its identification as Vicina, settlement mentioned in the writings of Anna Comnena [16].

2.2. SAMPLE PREPARATION

During their burial, the glass tesserae were exposed to a humid environment for a very long period of time (almost a millennium). Weathering phenomena affected the chemical composition of the glass and thick (up to hundreds of micrometers) layers of alteration products are present on the surface of archaeological glass objects [17]. To determine the composition of pristine glass, small regions on the tesserae surfaces were wet polished using silicon carbide paper (1200 grit), producing millimeter-size cleaned flat areas suitable for IBA analyses. This preparation procedure implied just a minimal damage of the archaeological artefact, just a tiny area from the glass surface being polished.

2.3. EXPERIMENTAL

The tesserae were measured using the external beam set-up of the AGLAE accelerator [18] using a 3 MeV external proton beam focused to 50 μm diameter, with current intensities of 0.5…1 nA, acquisition times of 4 to 8 minutes, leading to a total accumulated charge of 0.15 μC. The beam was scanned over a 200 × 200 μm^2 area in order to obtain average values of the elemental concentrations.

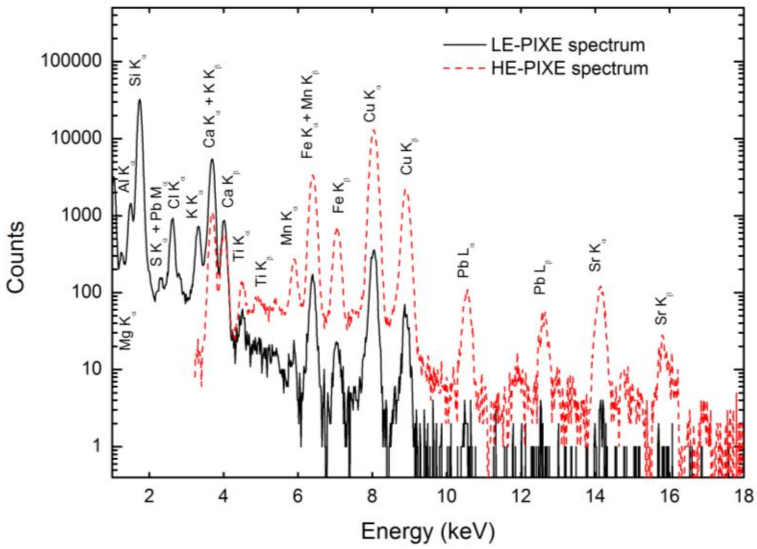

Fig. 2 – PIXE spectra for Isaccea 2005 E blue turquoise tessera.

For the acquisition of the PIXE spectra, two Si(Li) detectors were used: one for major and minor elements, and another, filtered by a 50 μm Al foil, for trace-elements. The entire volume between the sample surface and the detection system was flushed with a 2 litre/min stream of gaseous helium, to improve the detection limits for light elements. An example of two PIXE spectra simultaneously acquired on the same sample using these Si(Li) detectors is given in Fig. 2.

A 30% efficiency HPGe detector was used to measure the 440 keV gamma rays emitted by the ^{23}Na nuclei – see, for example, the PIGE spectrum shown in Fig. 3.

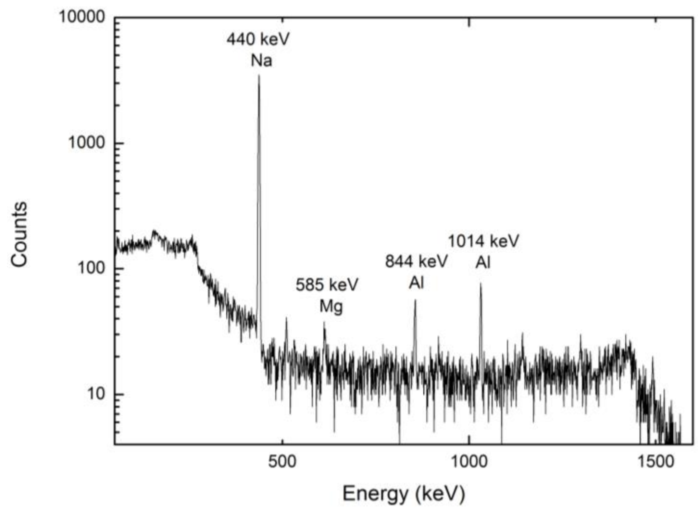

Fig. 3 – PIGE spectrum for sample Isaccea 2005 D green turquoise tessera.

The limits of detection under these experimental conditions range from 10 ppm up to 1000 ppm, depending on the element [19].

PIXE concentrations were obtained using TRAUPIXE software [20] based upon GUPIXWIN engine [21] with the assumption that targets were thick and homogeneous and all elements present in oxide form – except for Cl. The Na_2O concentrations were derived from the intensity of the 440 keV gamma line with reference to the intensity of the same gamma line in artificially synthesized glasses with known composition – Brill from Corning Museum of Glass and BGIRA (British Glass Industry Research Association). Other glass standards from the same providers were used to check the accuracy of the determined concentrations.

The compositional results of the analyzed tesserae expressed in parts per million (ppm) and normalized to 1,000,000, together with a brief description of the samples, are given in Table 1. The overall uncertainties (relative values) of the reported concentrations were estimated to be 5–10 % for the major and minor elements, increasing up to 20% for trace elements.

Table 1

Chemical composition of the five Isaccea mosaic tesserae expressed in ppm – N.D. means Not Detected

Sample	**Color**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**
Isaccea 2005 A	YELLOW	133820	7781	16888	479624	145705	4924	11416	5986	129373	4581	22060
Isaccea 2005 B	TURQUOISE BLUE	115309	5526	61517	704006	1646	1550	5323	15182	72667	1804	259
Isaccea 2005 C	TURQUOISE GREEN	141062	4589	25728	633249	N.D.	N.D.	10114	7387	80441	779	167
Isaccea 2005 D	TURQUOISE GREEN	145525	5090	26402	626131	807	N.D.	8493	7600	78734	670	158
Isaccea 2005 E	TURQUOISE BLUE	144644	6001	26681	692339	N.D.	2278	11157	8339	86281	817	320

Sample	**Color**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**SrO**	**ZrO_2**	**SnO_2**	**PbO**
Isaccea 2005 A	YELLOW	36753	75	47	90	56	767	N.D.	N.D.	54
Isaccea 2005 B	TURQUOISE BLUE	5168	N.D.	N.D.	8064	46	601	98	576	657
Isaccea 2005 C	TURQUOISE GREEN	3396	N.D.	10	13429	29	629	69	8258	70663
Isaccea 2005 D	TURQUOISE GREEN	3455	N.D.	N.D.	6434	N.D.	561	N.D.	10916	79023
Isaccea 2005 E	TURQUOISE BLUE	4739	N.D.	N.D.	15216	N.D.	752	N.D.	N.D.	437

3. RESULTS AND DISCUSSIONS

Three of the analyzed tesserae, namely the yellow and blue turquoise samples are soda-lime glasses, with the following mean values for the main oxides: 13.1 wt% Na_2O, 9.6 wt % CaO, 62.5 wt% SiO_2.

With 14.3 wt% Na_2O, 8.0 wt % CaO, 63.0 wt% SiO_2 and 7.5 wt% PbO (mean values) – see Table 1 and Fig. 4, the green turquoise samples can be classified as soda-lime-leaded glasses [10].

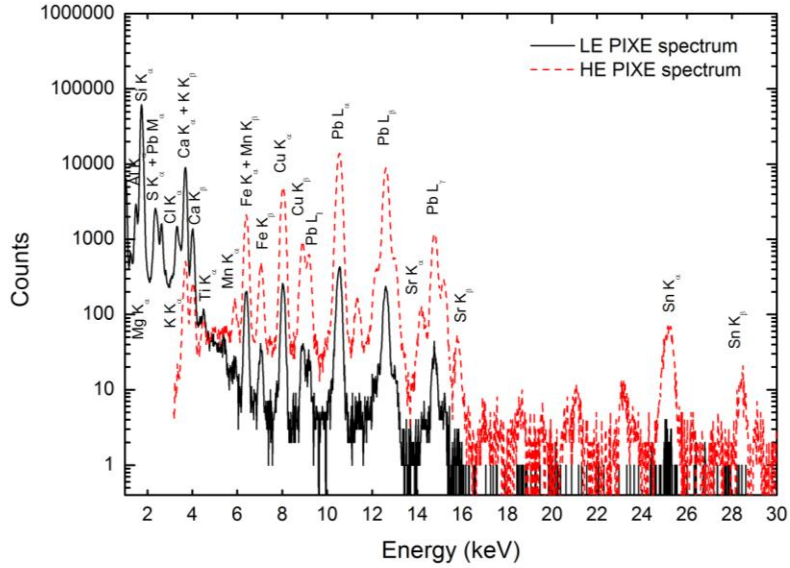

Fig. 4 – Superposed PIXE spectra for Isaccea 2005 D green turquoise tessera.

The low content of K_2O (~ 0.9 wt% mean value) and MgO (~ 0.6 wt% mean value) of all samples testify for the use of mineral *natron* (also known as *trona*) as a flux. Plant ashes were clearly not used for their production, since in that case, higher amounts of K, Mg and P oxides ($\geq$ 2.5 wt%) would have been determined [22]. *Natron* is a mineral mixture of salts (sodium carbonates, sulphates and chlorides) that during the Roman period was mainly extracted from the evaporitic deposits of Wadi El Natrun, Egypt. *Natron* was the most widely used fluxing agent for glassmaking in the Mediterranean area until the 9th century AD, when it started to be replaced by plant/wood ashes [1]. Reduced levels of minor and trace elements were detected in all samples, indicating that the raw glass was manufactured from relatively pure raw materials.

One of the tesserae, namely Isaccea 2005 A shows somehow unusual values of the Na_2O, Al_2O_3, CaO and SiO_2 concentrations compared to the rest of the samples. A possible interpretation for these discrepancies might be the fact that that despite all the precautions, the proton beam actually hit an altered glass surface and the concentrations of all these chemical elements were affected by the weathering phenomena.

Antimony compounds/minerals were employed either as opacifiers or as decolorizers, especially in glass artefacts produced before the 4th century AD [1]. However, no antimony was detected in any of the Isaccea tesserae (estimated limits of detection ~ 200 ppm).

It is worth mentioning here the comparison with the contemporary Byzantine glass bracelets from Nufăru and Isaccea [12–14]. The majority of those vitreous items turned out to have intermediate compositions ("mixed natron-plant ashes"), indicating extensive recycling, while Isaccea tesserae are exclusively *natron* glasses.

The concentrations reported in Table 1 show that the main differences in chemical composition of these five samples stem from the chromophoric elements.

The color of ancient glass is determined by the amount and the oxidation state of one of the following chemical elements: Mn, Fe, Cu and Co [1]. Even if PIXE is not the ideal technique for the identification of the glass chromophores (it does not specify the oxidation state of the metallic ion), such measurements might provide enough information to deduce the most likely candidate for the minerals/compounds employed to induce the coloration.

Relatively high amounts of copper (~ 1.0 wt% on average) were found in the turquoise blue and turquoise green tesserae.

The essential difference between the turquoise green and the turquoise blue tesserae consists in the fact that the turquoise green samples contain high amounts of SnO_2 (~ 0.9 wt%) and PbO (~ 7.5 wt%). These samples were already identified as soda-lime-leaded glasses.

One can speculate that lead-tin yellow – a variety of lead stannate, with one of the following chemical formulations: $PbSnO_3$ or $Pb(Sn,Si)O_3$, an opacifier traditionally used to render glass opaque yellow, might have been added to the batch [23–25]. The combination between the yellow opacifier and a copper alloy – possibly bronze or lead tin bronze – might have induced the particular hues and opacity of the green turquoise tesserae.

To clarify the precise nature of the opacifiers, additional UV-VIS spectroscopy, X-ray Diffraction and Scanning Electron Microscopy measurements could be performed on these particular samples.

The amber yellow tessera Isaccea 2005 A contains a high amount of Fe_2O_3 (~ 3.7 wt%). Most likely, an oxidizing atmosphere was prevalent in the kiln during the melting of this glass; iron in the upper oxidation state being the chromophore responsible for this particular hue.

Sample Isaccea 2005 A has a gilded side, as demonstrated by the presence of the gold peaks in the PIXE spectrum from Fig. 5. Most likely, initially this tessera had another glass sheet that protected the metallic foil, but unfortunately, that component – the so-called *cartellina* – was lost. The presence of gold foil on the surface of one the Isaccea tesserae demonstrates the fact that the glassmakers could access precious resources and they were skilled enough to induce special visual effects in certain constructive elements, such as metallic yellow shine.

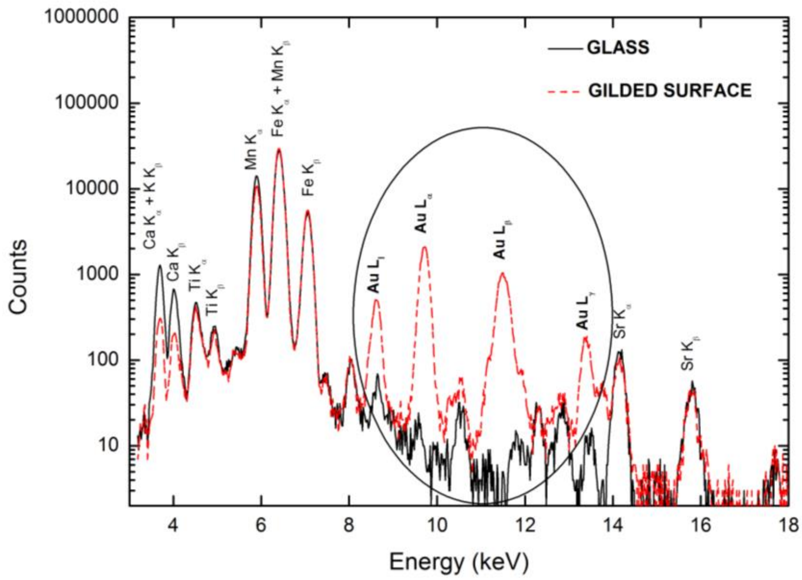

Fig. 5 – Superposition of the PIXE spectra taken on the golden side and on the pristine glass – tessera Isaccea 2005 A.

The chemical analyses of Isaccea mosaic tesserae demonstrate that they were made out of glass produced in pure Roman tradition processed through the addition of particular chromophores and opacifiers that induced special coloring and transparency effects needed to produce a skilled mosaic work.

1. CONCLUSIONS

PIXE-PIGE measurements of five glass mosaic tesserae discovered at Isaccea and dated to the Byzantine period were used to determine the bulk glass composition and to subsequently extract information about the raw materials and manufacturing practices.

The external IBA measurements showed that the Byzantine glass tesserae from Isaccea can be divided into two main compositional groups: soda-lime glasses and soda-lime-leaded glass, with a moderate PbO content (~ 7.5 wt%).

The low content of MgO and K_2O (both oxides in concentrations below 1.5 wt%) indicated that all these vitreous fragments are *natron*-based glasses, pointing to their manufacture in Roman tradition.

As color is an essential attribute of mosaic glass tesserae, the compositional data were used to get hints about the glass chromophores – iron in the upper oxidation state for the amber yellow tessera and copper for the green and blue turquoise samples. The high lead and tin concentrations in the turquoise green tesserae indicate the intentional addition of lead tin yellow, opacifier that in combination with a copper alloy produced the particular green turquoise hues.

PIXE spectra showed that one side of a tessera – sample Isaccea 2005 A – was gilded.

The slightly different chemical compositions identified in Isaccea glass mosaic tesserae testify for the intentional choice of additives – colorants and opacifiers – that helped obtaining tesserae with different appearances.

The analytical results demonstrate the skills of the Isaccea glassmakers, craftsmen that were able to obtain tesserae with distinct features, guaranteeing spectacular aesthetic effects in the resulting mosaic.

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