

Preliminary Informative Results on Glass Tesserae from Vth-VIth Century AD Mosaics in Albania

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Abstract

This paper discusses some preliminary results regarding raw materials used in ancient glass mosaic tesserae. The studied glass tesserae were recovered during the archeological excavation of the mosaics at the Christian basilicas in Byllis, Lin and Elbasan, which according to the archeologists were built between the end of Vth and beginning of VIth century AD. In the recent years, several studies are performed on opaque coloured glass but in Albania only few studies are performed in this field. These samples are analyzed using optical microscopy and micro X-ray fluorescence. Optical microscopy is used to analyse the microstructure of the glass tesserae. The main elements and trace elements are determined qualitatively from measurements performed with micro X-ray fluorescence. The glass matrix resulted to be very heterogeneous with too many inclusions dispersed on it. Several elements which are responsible for the color and opacity of glass tesserae are determined. Comparisons are made between the same colors of glass tesserae from different archaeological sites.

Keywords

Glass Tesserae, Micro X-Ray Fluorescence, Qualitative Analyses, Optical Microscopy

1. Introduction

Mosaic tesserae are a range of materials of a very varied and complex nature, including pottery, stone and glass. Ancient glasses were generally made up of three main components, silica (SiO₂) for which sand is often used as raw material; an alkali (sodium oxide, Na₂O, or potassium oxide, K₂O), for which either a mineral or a plant ash

can be used as a raw material; and thirdly calcium oxide (CaO) which is often introduced into glass as the fragments in the sand used [1].

Glass was generally colored by adding small amounts of certain salts (mostly copper, iron, and manganese); this addition of colorants was probably the first example of the use of minor ingredients to change glass properties to produce a desired effect. Opaque glasses were obtained by suspension of crystals, quite insoluble within the glass matrix, such as calcium- and lead-antimonate, and tin oxide [2].

The elemental composition of glass reflects the raw materials and the techniques that are employed in its manufacture. The chemical analysis of glass can therefore provide evidence about the origin of the raw materials, coloring and opacifiers used for their production.

One of the reasons for analyzing ancient glass is to establish the relative amounts of these materials and by doing this it is sometimes possible to characterize the glass, since there are some quite clear changes in the proportions of these components over time [3].

Several glass mosaic tesserae were recovered during the archaeological excavation in Byllis, Lin and Elbasan. These three archeological sites are dated between Vth and VIth century AD.

Floors of five basilicas discovered in Byllis are decorated with colorful mosaics with different motives. The mosaic with beautiful figures, such as fish and birds, decorates the floor of the early Christian church in Lin. The mosaics in these two archaeological sites were built mainly with marble tesserae and glass tesserae were partly used in some motifs [4] [5].

The central Nephite mosaic of basilica extra-muros Scampis (Elbasan) has a large quantity of glass tesserae, [6]. They have been extensively used in wall mosaics of the basilica. In mural mosaics of Scampis the glass paste tesserae are used also for geometric motifs [5].

Figure 1 shows the archaeological places in which the samples are taken, and a part of mosaics discovered in each place.

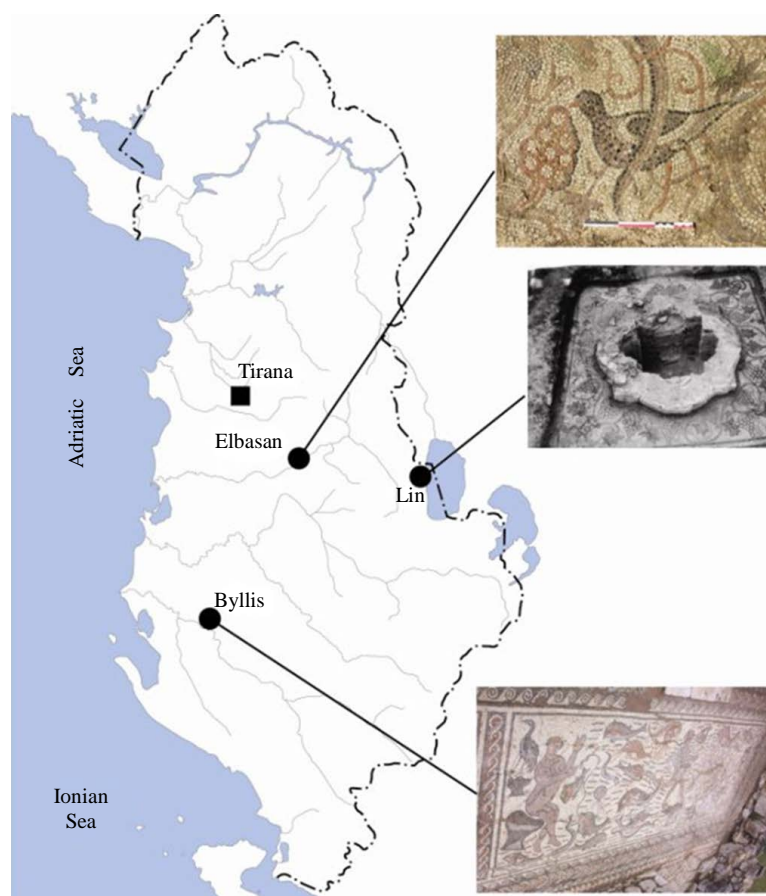


Figure 1. The archaeological places in which the samples are taken.

2. Material and Methods

For this work a total of 71 glass tesserae, coming from excavations in Lin, Byllis and Elbasan and dating between the end of Vth and beginning of VIth century AD, were analyzed. The glass tesserae had different colour and dimensions smaller than 1 cm × 1 cm.

In **Table 1** below are listed the archaeological sites and the number of glass tesserae analysed for each site.

The samples were cleaned with water and brush and the exposed surfaces were polished on successive grades of grinding paper (silicon carbide) 220, 320, 500, 1000, 1200 and 4000. They are cleaned in ultrasound equipment. The final colour determination of each sample was done by visually comparing the samples to a Pantone colour chart. The optical microscope Kozo XJP300 with polarized and reflected light, equipped with a digital camera was used for optical microscopy examination of the samples.

For the determination of elemental composition of the samples micro-XRF was used as a time efficient means of obtaining large quantities of data entirely non-destructively. The polished surfaces of objects were analyzed using Artax (Bruker) micro-XRF spectrometer at the Institute of Applied Nuclear Physics. This system consists of a low power (30 W) rhodium anode X-ray tube equipped with a pollicapillary lens which focuses the radiation to a spot of about 75 µm. The system uses a silicon drift detector which was collecting photons in the energy range of 0 to 50 keV in 4096 channels. The measuring head is mounted on a system that provides automated movement in three directions X, Y, Z. Measurement conditions were: the voltage 45 kV, current 300 µA, time 500 s in helium atmosphere, which enables effective detection of low Z elements down to sodium. For each sample are collected five spectra in different points of the polished surface. As the radiation spot is generally larger than the dimensions of the inclusions we were limited to the measurement of the tesserae matrix.

The quantitative analysis procedure is at an early stage and here we will present and discuss the qualitative information from the XRF spectra.

3. Results and Discussion

Transparent glass tesserae are not found frequently in the studied mosaics. Some pieces of that kind were found in the basilica in Elbasan and they are part of the gold plated tesserae in which a thin gold foil is sealed between the body tesserae and a thinner plate of transparent glass. It is thought that these tesserae should have been part of the mosaics that decorated the side walls of the basilica, of which there is no sign at present [6].

Microscopic examinations of these tesserae show a uniform glass surface with generally a quite small number of air bubbles and/or inclusions (**Figure 2**). Micro-XRF spectra show the presence of Si, Na and Ca as the major constituents of glass, while the presence of smaller amounts of Al, Mg, K, Ti and Fe should be related to the impurities of the raw materials. The presence of Mn indicates the use of Mn compounds as decolorizer, a process that is widely described in the literature [7] [8], according to which, during the Byzantine period, Mn ions were used to remove the green tint of glass due to the presence of Fe ions.

The presence of the gold foil is identified by micro-XRF measurements and published earlier [8] [9].

The yellow colored tesserae are opaque and the microscopic examinations show heterogeneous surfaces with several crystalline inclusions and particles that are not dissolved during the melting process. The micro-XRF spectra of these tesserae indicate the rather strong presence of Pb and Sn compounds which should have been added to the glass matrix composed mainly of Si, Na and Ca (**Figure 3**). The mixture of Pb and Sn compounds was used both as opacifier and colorant. The literature describes the ancient procedures for the preparation of a mixture of Pb and Sn and its use as opacifier and yellow colorant when Lead stannate was formed during the heating with the glass matrix [10]. The literature data also indicate that this type of mixture (Pb + Sn compounds) came in use after the IVth century AD when tin oxide substituted the use of antimony oxide which was extensively used during the previous periods [10]. This find is in support of the archeological dating of the basilicas during the end of Vth and beginning of IVth century AD.

Table 1. Glass tesserae analysed in this paper.

Archaeological sites	Nr. of tesserae/Nr. of colours
Byllis	11 tessera/7 diferent colours
Lin	26 tessera/14 diferent colours
Elbasan	35 tessera/18 diferent colours

The tesserae with colors from green to yellow-green are the most abundant in all the sites. They are opaque and the microscopic examinations show heterogeneous surfaces with a few bubbles and a lot of crystalline inclusions and particles.

The micro XRF spectra of these tesserae show similar general composition with that of the yellow tesserae, meaning the glass is composed of silica-soda-lime and the amount of Pb and Sn compounds used for opacifying the glass looks similar. Main differences are observed in the presence of Mn and Cu. In some tesserae with light green or yellow green color the presence of Mn and Cu is quite low and the green color should be due to the presence of Fe ions from the glass raw materials (Figure 4, red spectrum). The other group with green color has higher amounts of both Mn and Cu (Figure 4, green spectrum). In those cases there exist the possibility that the tesserae are prepared from a transparent glass which already had Mn compensating the green tint of Fe and Cu compounds have been added to give the green tint. The application of both Fe and/or Cu ions for the green color

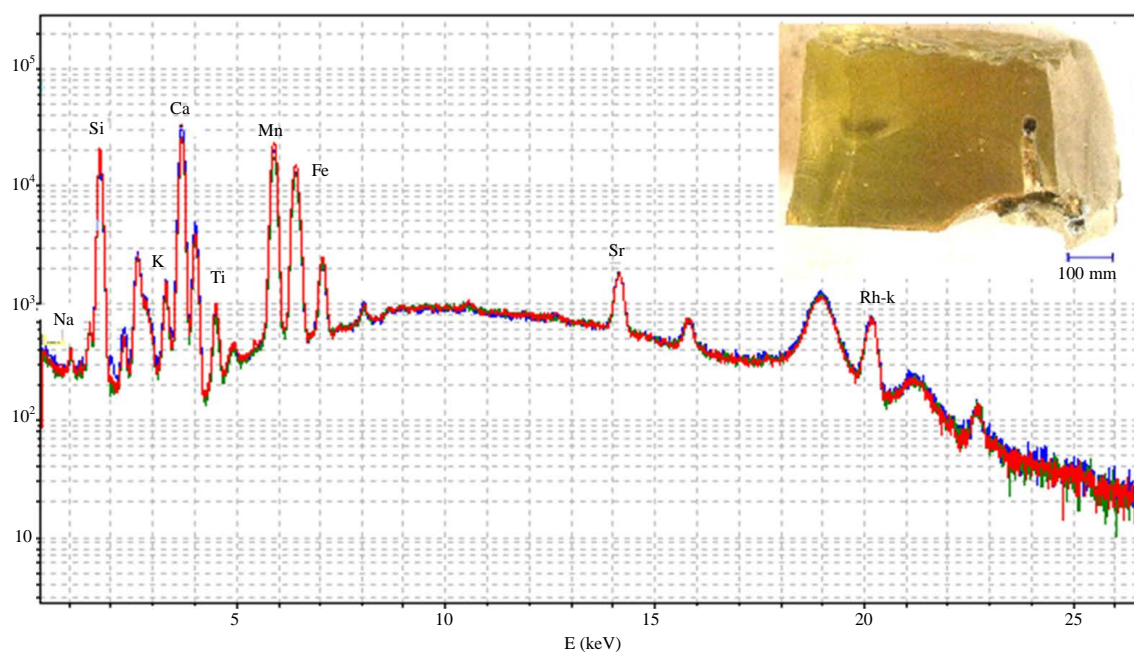


Figure 2. Microscope image and XRF spectrum of glass matrix from transparent tesserae.

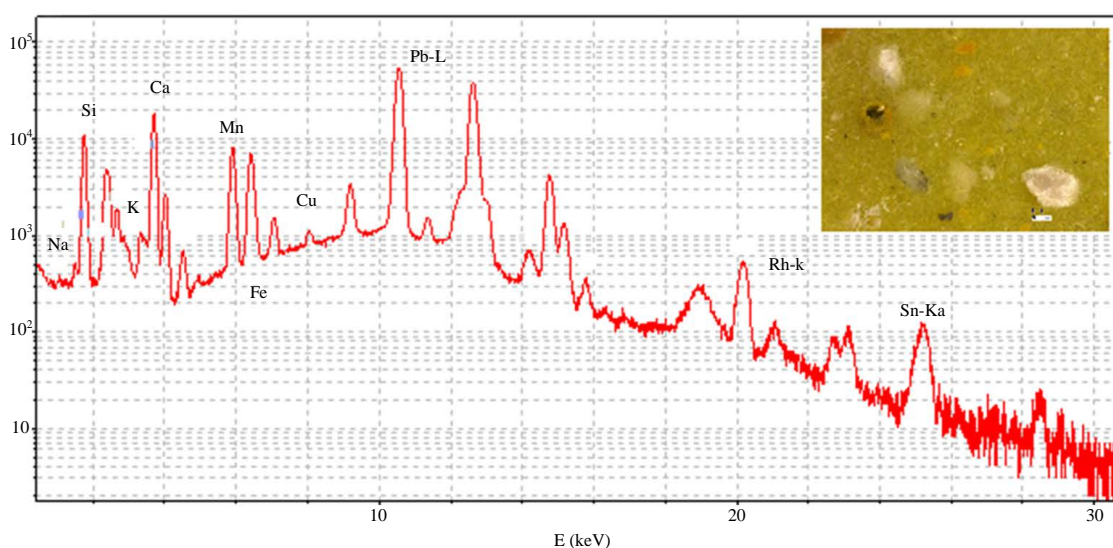


Figure 3. Microscope image and XRF spectrum of glass matrix from yellow tesserae.

of glass and tesserae is widely described in literature [11] [12].

The tesserae with different hues of blue are frequently used in the mosaics of all the sites. Similarly to the previous colored tesserae the blue ones are opaque, with several inclusions and a lot of bubbles. The same type of glass made of Si, Na, Ca is indicated by micro XRF spectra while different colorants and opacifiers are observed in the tesserae with different blue tints. Co compounds with relatively high amounts of Mn and Fe are used for the dark blue color (Figure 5, blue spectrum). It is interesting that the amount of Pb and Sn compounds in these tesserae is quite low. In light blue and turquoise tesserae Co is almost missing and the color should be due to the relatively high presence of Cu compounds (Figure 5, red spectrum). The presence of Pb and Sn compounds in these tesserae is slightly higher than in the dark blue ones but significantly lower than the green ones. It should mean that the opacity of these tesserae should be mainly due to the high presence of bubbles [8] [13].

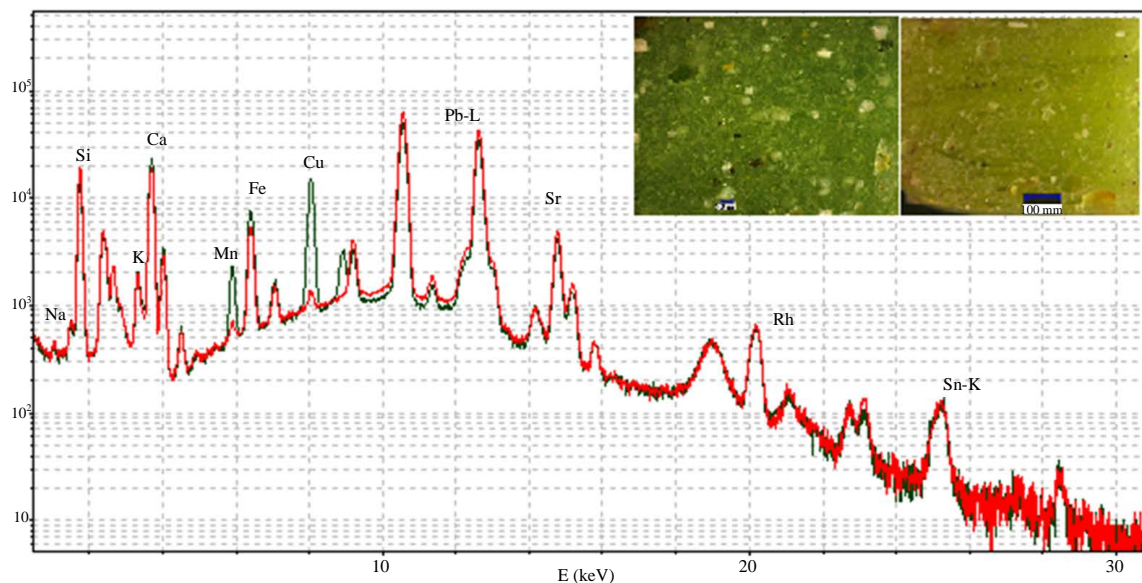


Figure 4. Microscope image and XRF spectrum of glass matrix from yellow-green (red spectrum) and green (green spectrum) tesserae.

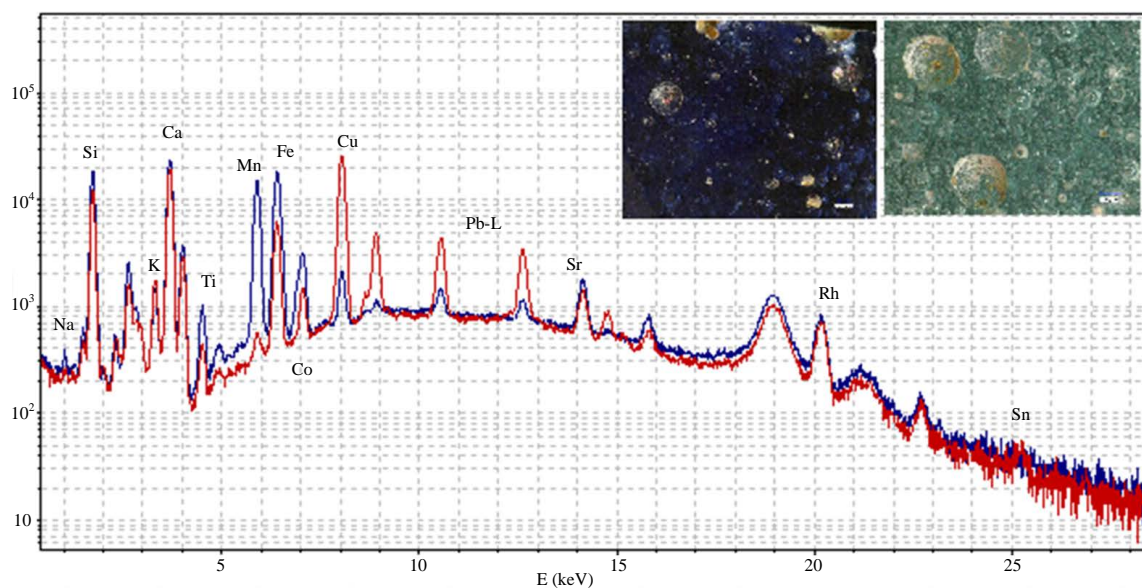


Figure 5. Microscope image and XRF spectrum of glass matrix from dark blue (blue spectrum) and light blue (red spectrum) tesserae.

A similar situation is observed in the case of brown and violet colored tesserae (**Figure 6**). They appear opaque with high presence of bubbles of different dimensions. They are made of the same type of glass (Si, Na, Ca) with relatively low amounts of Pb and Sn compounds and Mn compounds should have been used for the colour [8].

Historically, red glasses were obtained by the combined use of copper and iron in lead-rich matrix. The color was due to precipitated copper compounds, in the form of metal and/or oxide [14] [15]. Iron served the purpose of obtaining increasingly dark shades of red, and also as a flux to promote the formation of coloring particles [3].

The red tesserae were used in the mosaics of all sites. They are quite opaque with striations and strands, several inclusions and a few bubbles. Circular metallic inclusions were identified through microscopic observations with polarized light [9]. The micro-XRF spectra show a glass matrix of Si, Na, Ca type with high amounts of Fe, Cu, Zn, Pb and Sn (**Figure 7**). The red tesserae from all the studied sites show the same basic composition. The presence of metallic inclusions and the relatively high amounts of Cu, Zn and Sn could suggest that the red color is due to the precipitation of metallic Cu introduced as brass [16] [17].

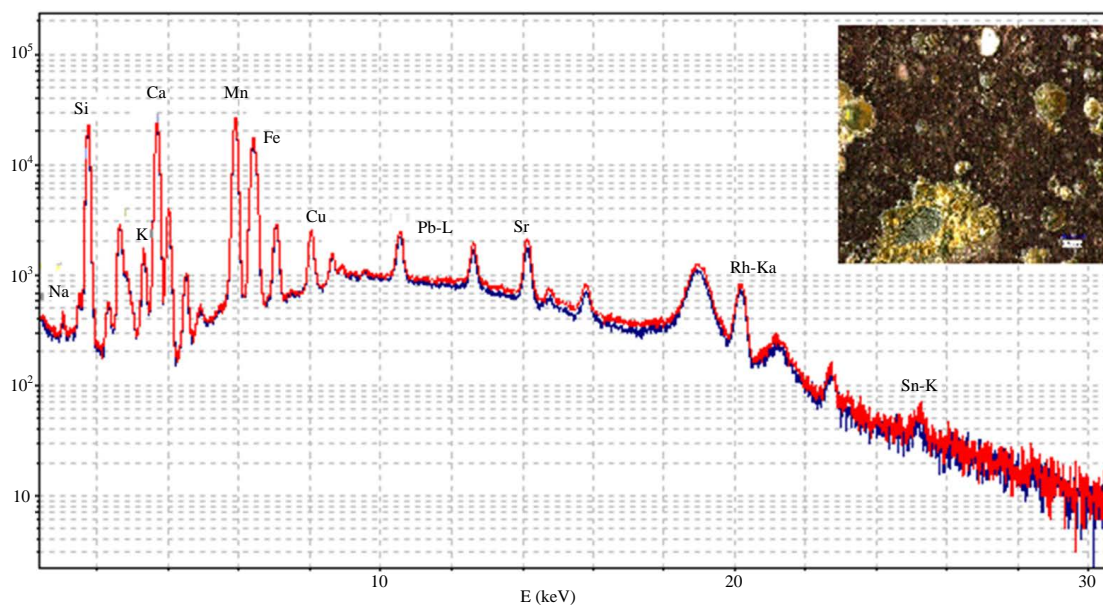


Figure 6. Microscope image and XRF spectrum of glass matrix from brown and violet tesserae.

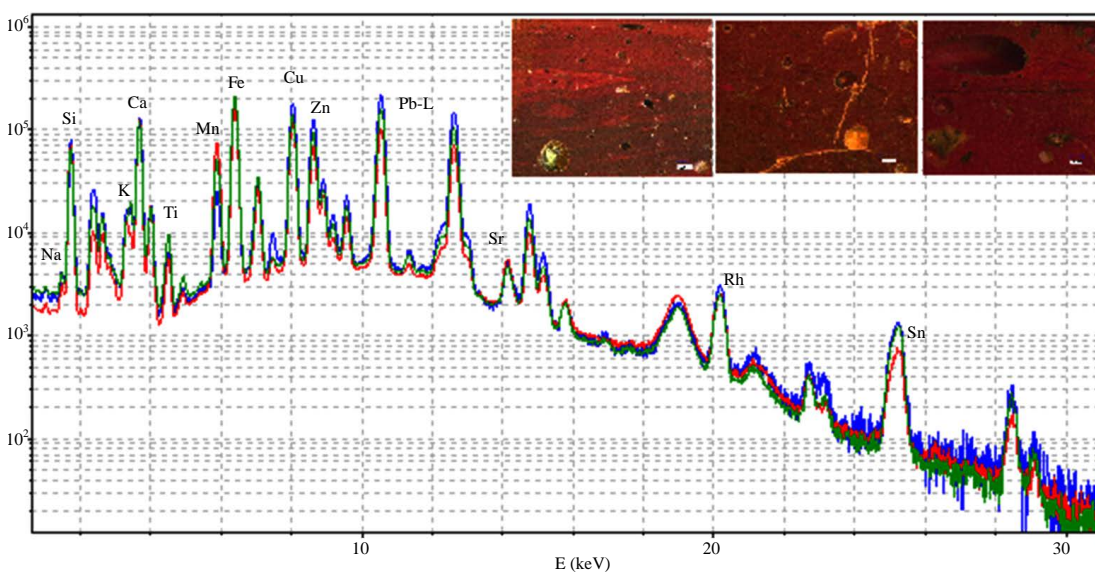


Figure 7. Microscope image and XRF spectrum of red tesserae glass matrix from all the sites.

4. Conclusions

In this paper, some preliminary qualitative results are discussed regarding the microstructure and composition of glass mosaic tesserae excavated in three archaeological sites, dated in the period Vth-VIth century AD, in Albania.

From the optical microscopy examinations results that almost all glass tesserae are heterogeneous, with many inclusions and bubbles dispersed into glass matrix.

The elemental analysis with micro-XRF shows that Si, Na, and Ca should be the main constituents of the glass matrix. The minor elements Mg, Al, P, S, K, Ti, Fe, and Sr should be part of the raw materials used for the glass production while the other elements Mn, Co, Cu, Zn, Sn, and Pb should have been added to the glass for obtaining the desired characteristic, *i.e.* opacity and color. Although our results are at the qualitative stage, they show similarities with the published works on the colored glass and tesserae from the Late Roman and Byzantine period [10]-[12].

Work is underway for the extension of the study of the tesserae that will include the quantification of micro-XRF measurements as well as the analysis using SEM-EDX and micro-Raman spectroscopy for a better characterization of the materials.

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