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ORIGINAL PAPER

New insights into Byzantine glass technology from loose mosaic tesserae from Hierapolis (Turkey): PIXE/PIGE and EPMA analyses

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Abstract This study focuses on the Byzantine glass tesserae from Hierapolis (Phrygia, central Turkey). Fifty-seven samples of loose tesserae from two sites in the town (the theatre and the church of St. Philip) are analysed by particule-induced X-ray emission and particule-induced gamma ray emission and electron probe X-ray microanalysis to obtain the chemical composition and identify the colourants and opacifiers. The aims are to add new information to the scant knowledge of the Byzantine glassmaking technology, to constrain the chronology of the mosaics and to trace the supply routes of the tesserae. In the destruction layers of the theatre, tesserae produced following the Roman glassmaking technology (natron glass opacified by calcium and lead antimonate) were found. They were made using a Levantine 1 raw glass, generally attributed to the early Byzantine period (fifth to sixth c.). In the church, the samples attest a technological change from Roman tradition, and a complex pattern according to building history (two phases are attested, probably in the sixth and eighth to ninth c.), and a multiplicity of supply. Three glass types and some recipes not attested before in this chronological range for the production of tesserae are documented, such as the use of a local low-chlorine natron glass for the production of black and red tesserae, the blue colouring by a source of cobalt with zinc in a natron glass tessera and the opacification with tin oxide (both in a lead-free and in a high-lead natron glass), as well as with quartz.

Keywords Mosaics · Byzantine glass tesserae · Asia Minor · Colourants · Opacifiers

Highlights
-Fifth-to-ninth c. loose tesserae from Hierapolis (central Turkey) are analysed by PIXE/PIGE and EPMA.
-The first occurrence of local low-chlorine raw natron glass is attested in the production of tesserae.
-The first occurrence of blue colouring by cobalt with zinc in a natron glass tessera is shown.
-The first occurrence of opacification with quartz in natron glass is observed.
-The chronology of mosaics is refined by the primary raw glass chronology and the technical changes.

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Introduction

The study of loose glass tesserae and mosaic fragments from archaeological excavations can substantially contribute to our understanding of mosaics as an artistic medium and its geographical and chronological distribution (James et al. 2013). However, the fragments rarely allow recomposing meaningful pictures and therefore cannot be dated by stylistic or iconographic comparison. Moreover, the archaeological context can often provide a chronological framework typically spanning several centuries between the construction and the collapse of the building. In this frame, the physicochemical analyses of glass tesserae can constrain the archaeological chronology and provide indications on their provenance.

This paper presents the analyses of loose glass tesserae from two Byzantine contexts of the important holy city of

Hierapolis in Phrygia (central Turkey), relevant from before the Hellenistic period to Late Antiquity and into the early Byzantine period (fifth to sixth CE), when it is the place of the martyrdom and burial of Philip the Apostle (D'Andria 2013). The aim is to define the chronology and supply of mosaics by combining the chemical analyses with information from the archaeological context. Moreover, the analytical data will increase the scant published analyses of mosaic tesserae of the Byzantine period in Asia Minor (Lachin et al. 2009; Schibille et al. 2012; Schibille and McKenzie 2014) and in nearby sites (Bonnerot et al. 2016), contributing to trace the supply routes, the technological changes and the organization of their production.

Glass tesserae technology in the Mediterranean area

For a correct interpretation of the analytical data, an overview of the current knowledge on making glass tesserae during the Late Roman and Byzantine period is first reported.

The glass melting was performed in primary workshops identified up today in Palestine and Egypt, where the batch of silica-lime sand and natron (a natural mineral soda) was melt in large tank furnaces. Subsequently, the raw glass in form of slabs (primary glass) was transported to secondary workshops to be remelted (glass cullet could be added at this step), coloured, opacified and manufactured in form of glass cakes from which the tesserae were subsequently cut (Freestone and Stapleton 2015; Neri 2016a, b).

The chemical identification of raw materials and their provenance was recently improved by the compositional classification of raw glass (Foy et al. 2003; Freestone 2005; Henderson 2013; Degryse 2014; Gliozzo et al. 2013; Gliozzo 2016), offering markers of chronology, provenance and organization of the production.

The transition from a centralized to a local glass melting system and the melting of new batches made of a silica source and plant ash (potash-lime in Northern Europe, soda-lime in the Mediterranean area) occurred around the eighth to ninth c.

In this technological and productive background, the chemical composition of the raw glass of the *tesserae* is not specific to the workshop producing the glass cakes, but rather to the primary melting furnace. In the case of mosaic glass tesserae, the identification of opacifiers and colourants through the chemical analysis allows further information to be obtained. In this case, the diffused practice of reuse of glass tesserae from the dismantling of ancient mosaics must also be taken into account. The studies on glass mosaic tesserae production are debating about the localization of workshops: either at the building site, according to late medieval sources (Harding 1989), or in few centralized workshops (Neri 2016a, b). The high skill required for the production of some colours allowed some scholars to suggest the existence of centres specialized in a specific production, as hypothesized for red (Freestone et al. 2003), for flesh tones (Verità and Santopadre 2010), for yellow (Verità et al. 2013), for blue (Gratuze et al. 1992) and for gold leaf tesserae (Neri and Verità 2013). Gold tesserae were made by sandwiching a beaten gold (or silver) leaf between a layer of poured glass (support) and a thin blown glass (*cartellina*). Their complex production and chronology were recently investigated, indicating the use of monetary alloys for the leaves (Neri and Verità 2013; Neri et al. 2016).

Archaeological context

Byzantine Hierapolis was an important pilgrimage and curative city: since the fourth century CE, a cultural complex began developing on the Western hill, monumentalized from the fifth to sixth c. onwards. A central-plan *martyrion* on the site of the Apostle's martyrdom and a church around his tomb were built (D'Andria 2013). Two other churches are located in the district of the city closer to the theatre and to the ancient sanctuaries (Arthur 2012) (Fig. 1).

Two Byzantine archaeological contexts are considered in this paper: the demolition layers of the theatre and the church of St. Philip (Fig. 1). Built in the second c. CE, the theatre partially lost its function in the fifth to sixth c., when houses were built near the northern *analemma* (D'Andria 2014). A Christian inscription, reused in the theatre's *logeion*, and a cross-shaped reliquary, both dated to the sixth c., are the only remains of a Christian occupation of the site (Arthur 2006). During the extensive excavations in the 1970s, 800 mosaic fragments were found in the destruction layers of the building near the southwestern corner of the stage. Although the fragments cannot be associated with an architectural context, some can be linked to a Byzantine mosaic: clothing elements, angel wings and monumental figures are recognized (Fig. 2) (Neri 2016a). The background was probably yellow, being the most represented colour (47%). The tesserae (0.3–0.5 cm wide) are prevailingly made of glass; stone tesserae were used for white (few are made of glass) and flesh tones. They are laid on detailed and realistic painting. The setting bed plaster has three layers: the two superficial ones are made of lime with scarce aggregate (quartz sand millimetre-sized clasts, vegetal fibres and terracotta), and the third layer in contact with the wall is made of *cocciopesto*.[1]

The original mosaics may have belonged to a chapel within the theatre no longer preserved. Alternatively, they might have come from another church, for instance the one located above the theatre (fifth to sixth c.). Finally, it is also possible that the theatre merely served as a storage space for materials to be recycled: a phenomenon which has been observed in the

[1] Nine samples of mortar (two from the theatre and seven from the church) from mosaic fragments were analysed. The thin-section, SEM/EDS and XRD analyses were conducted in collaboration with R. Bugini at Università degli Studi di Milano Bicocca. The analytical results will be presented in another dedicated paper.

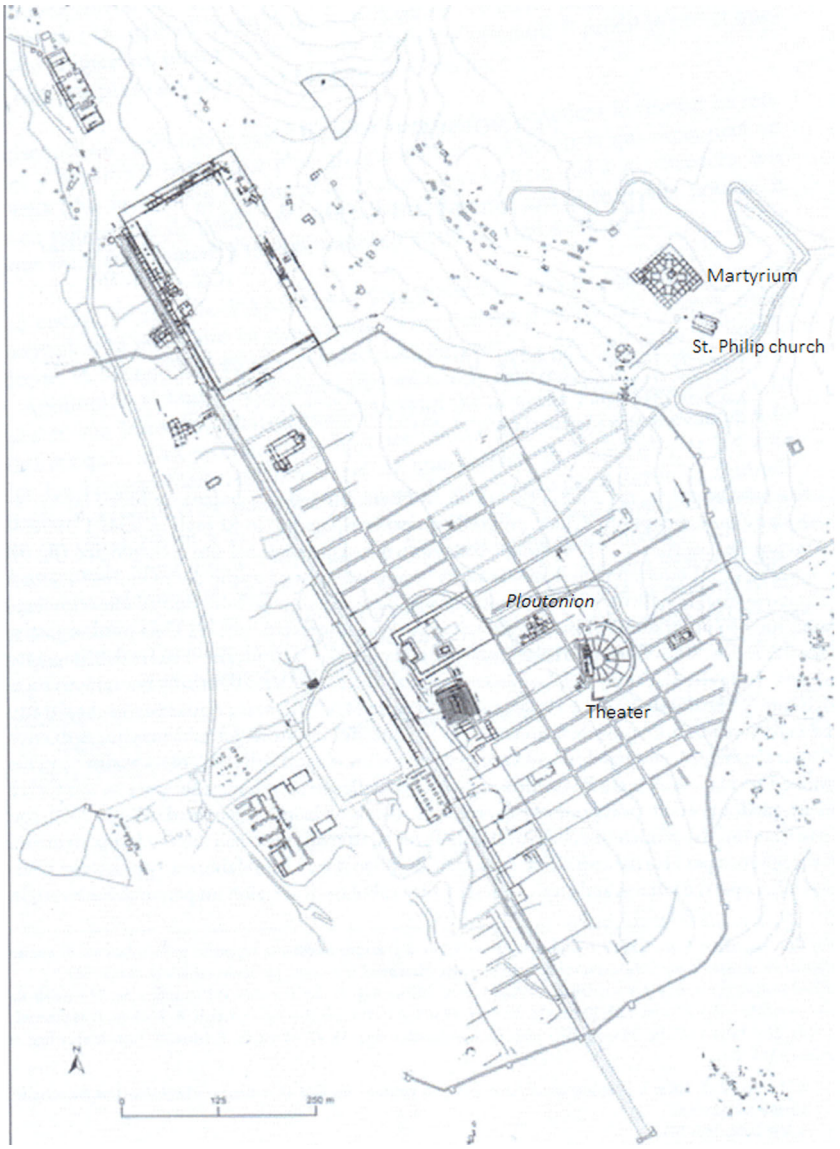

Fig. 1 Plan of Hierapolis with indication of the sites quoted in the text

Laodikeia church (Simsek 2015), in the Sardis synagogue and in several other cases (Neri 2016a, b). This hypothesis is supported by the finding of a seventh c. recycling workshop for tesserae and other glass materials in the burial layers of the *Ploutonion* (Neri and Catacchio 2016), not far from the theatre. In this case, the archaeological context suggests a date for the tesserae of the theatre between the fifth and the seventh centuries.

The church of St. Philip, built in the sixth c., incorporated a smaller fourth c. chapel. It underwent significant renovation after an earthquake in the eighth to ninth c. 6000 tesserae, and 450 fragments of wall mosaics were found in layers of landfill, levelling and filling (Seljuq phases of the church, eleventh c.) in a chapel beside the tomb, in the narthex and in the apse areas, probably decorated with mosaics (Fig. 3). The group of fragments found in the narthex belonged to a mosaic from the higher part of the facade, partly rebuilt in the ninth c. (Neri and Caggia 2016). The morphology of the fragments and of the tesserae was similar in the chapel and in the apse (group 1), but different in the narthex (group 2). The fragments of group 1 probably belong to a mosaic with natural-size faces (Fig. 3a), with small tesserae (0.3 cm) laying narrowly in the painting layer. The prevalence of gold (66%) and blue (14%) tesserae suggests a background in these colours. The tesserae are mostly made of glass; flesh-tone and grey tesserae and most of the white ones are of limestone or local marble.

The fragments of group 2 have geometric, vegetal motifs and vases: a repertoire typical of an aniconic mosaic (Fig. 3b, c). The tesserae have irregular sizes (0.3–1.1 cm) and shape. The tesserae of this mosaic are mostly made of glass, but also

Fig. 2 Some fragments from the theatre mosaic. **a** Fragment of carnation. **b** Fragments of background (water and landscape?). **c**, **d** Macrograph of the fragments

stone, terracotta, painted stone and mother of pearl. Blue (45%) and black (25%) are the prevalent colours that probably characterized the background.

For the mosaics of the St. Philip's church, the archaeological context suggests a date between the sixth and the eleventh c.

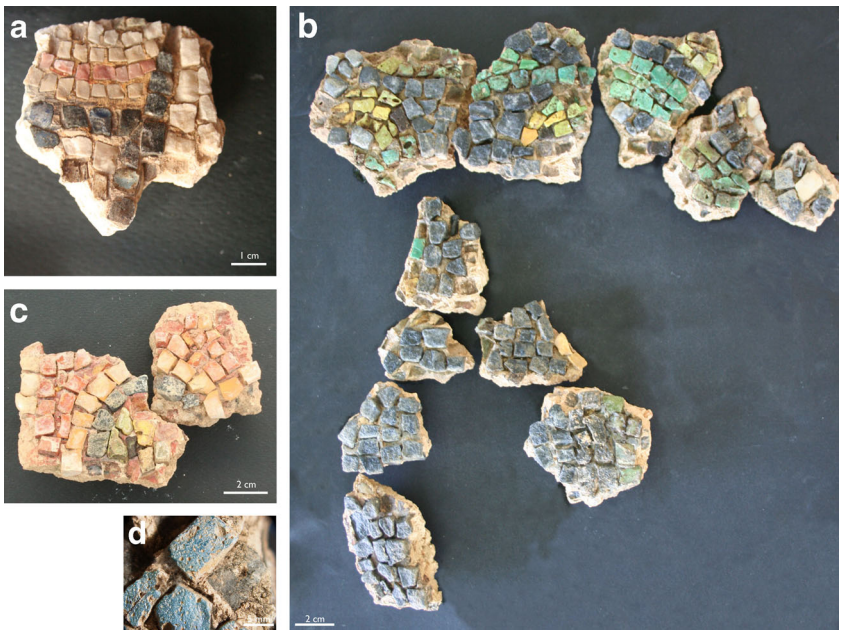

Fig. 3 Some fragments from St. Philip. **a** Fragments of carnation. **b** Fragments of a vase with vegetal racemes. **c** A fragment of decorative frame. **d** Macrograph of the tesserae

Materials and methods

Glass tesserae representing all colours and shapes were sampled from the theatre (indicated as HT in the follow) and from the St. Philip church (indicated as H in the follow). The tesserae were preliminary examined under a stereomicroscope equipped with a digital camera. Because of the severe deterioration (most of the tesserae are covered of a yellowish-white crust), the tesserae were grinded and polished using abrasive papers on one surface before observation under the optical microscope. The quantitative chemical analysis was carried out by particule-induced X-ray emission and particule-induced gamma ray emission (PIXE/PIGE) or electron probe X-ray microanalysis (EPMA).

Particule-induced X-ray emission and particule-induced gamma ray emission

The surface of the polished tesserae was analysed using a proton beam of 2.95 MeV extracted in air of the accelerator AGLAE in the C2RMF. The beam size is about 30–50 μm square; the current of 1–2 nA and an acquisition time of a few minutes were used. To get a complete and precise chemical composition for the glass, several silicon drift detectors (SDD) cooled by Peltier effect were used (Pichon et al. 2014) and one high-purity germanium (HPGe) detector.

In the PIXE analysis, two SDD detectors allow the detection of high X-ray energies (3–40 keV)—both are covered by an aluminium filter with a thickness of 50 μm, while another SDD detector under an helium flux allows the detection of low X-ray energies (1–10 keV). Thus, the quantification of sodium to uranium can be obtained. In the PIGE analysis, an HpGe detector helped the detection and accurate quantification of the sodium levels coming from the pristine glass as well as the detection of boron and lithium using, respectively, the following nuclear reactions (^{23}Na(p, p$_1\gamma$)^{23}Na-Eγ 440 keV/^{10}B(p, $\alpha_1\gamma$)^{7}Be-Eγ 429 keV/^{7}Li(p, p$_1\gamma$)^{7}Li-Eγ 478 keV). To obtain a composition as representative as possible of the glass, two or three analysis were made in different points and the analysed area was as large as possible using the beam scan.

The treatment of the spectra to obtain quantitative analysis was carried out with the GUPIX software (Campbell et al. 2010), which was coupled to the in-house TRAUPIXE software developed at the AGLAE facility (Pichon et al. 2014). For the quantification of sodium and for the calibration of the Gupix software for the PIXE analysis, a set of reference glasses (Corning B, C and D and BGIRA) was analysed under the same experimental conditions as for the tesserae.

The accuracy for SiO_2, Na_2O and CaO is below 1 wt% and for the minor oxides and traces is below 5 wt%. Limits of detection in the range of 0.02–0.05 wt% for most of the oxides were calculated.

Electron probe X-ray microanalysis and SEM-EDS

For microprobe and scanning electron microscope investigation, small fragments were cut from the tesserae, embedded in acrylic resin prepared in polished cross section down to 1-μm diamond paste and vacuum coated with carbon. A microprobe (Cameca SX-50) equipped with three wavelength-dispersive X-ray spectrometers (PET, LiF and TAP crystals) was used. Twenty elements were quantified: X-ray Kα-lines were used except for Pb (Mα-line), Sb, As and Sn (Lα-lines). Operating conditions were accelerating potential 15 kV, beam current 20 nA (major and minor components) or 100 nA (trace elements). A 40 μm × 50 μm scanning electron beam and limited counting time (10 s for major and minor elements, 20 to 30 s for trace elements) were employed to minimize alkali drift during the irradiation. The net X-ray intensities were quantified by means of a PAP correction program supplied by Cameca. Reference glasses of certified composition (Corning B, C and D and NBS 620) were analysed under the same experimental conditions. The EPMA setting used in this work allows most of the oxides to be analysed in concentrations as low as 0.02–0.05%.

A thorough discussion of the precision, accuracy and detection limits of PIXE-PIGE and EPMA, applied to the study of ancient glass, can be found in the study by Kuisma-Kursula (2000) and for EPMA and SEM-EDS in the study by Verità et al. (1994). Semi-quantitative identification of the opacifiers and pigments was performed at the SEM (Philips XL30) by energy-dispersive X-ray microanalysis (EDAX Ametek).

Results and discussion

The quantitative chemical composition of the tesserae is reported in Table 1 for the theatre and in Table 2 for the church of St. Philip. The analytical techniques are indicated for each sample. Average values of oxides are reported for the coloured tesserae, which include the glassy phase and the opacifier and/or colouring particles. Only the composition of the glass phase is reported for tesserae opacified by ground quartz. However, in the latter, the silica content can be overestimated (and other oxides underestimated), due to the partial dissolution of quartz grains in the melt. Hereafter, the base glass composition is discussed separately from colourants, pigments and opacifiers for both contexts (Brill 1999).

Base glass

The composition of the base glass was calculated by subtracting from the composition of the tesserae the content of the contents of colourants (Cu, Co, Fe, Mn), decolourants (Mn, Sb), opacifiers (Sb, Sn) and related elements (Pb) and then normalizing to 100 wt%. The differences in the contents of some oxides in

Table 1 Chemical composition of glass tesserae from the theatre (expressed in wt% of oxides)

Sample	Analytical technique	Colour	Glass type	Opacifier	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	P_2O_5	SO_3
HT1	PIXE/PIGE	blue	LI-lowNa	CaSb	67.0	2.45	16.1	0.54	7.74	0.42	0.15	0.48
HT2	PIXE/PIGE	blue	LI-lowNa	CaSb	66.8	2.42	15.6	0.57	7.84	0.44	0.14	0.54
HT3	PIXE/PIGE	blue	LI-lowNa	CaSb	68.3	2.59	14.9	0.59	7.58	0.46	0.14	0.42
HT4	PIXE/PIGE	blue	LI-lowNa	CaSb	67.5	2.45	15.8	0.54	7.54	0.42	0.15	0.40
HT5	PIXE/PIGE	blue	LI-lowNa	CaSb	67.3	2.81	15.4	0.62	7.89	0.43	0.15	0.38
HT6	PIXE/PIGE+SEM/EDS	blue	LI-lowNa	CaSb	66.1	2.41	16.4	0.59	7.79	0.49	0.13	0.47
HT7	PIXE/PIGE	blue dark	LI	Bubbles	66.7	2.36	18.7	0.74	6.04	0.52	0.17	0.35
HT31	PIXE/PIGE	black (blue purple)	LI	CaSb	63.5	2.30	18.0	0.65	6.58	0.47	0.06	0.35
HT12	PIXE/PIGE	turquoise light	LI	CaSb	65.4	2.70	18.6	0.71	6.67	0.52	0.08	0.46
HT11	PIXE/PIGE	turquoise	LI	CaSb	63.9	3.09	18.8	0.89	6.79	0.60	0.12	0.43
HT10	PIXE/PIGE+SEM/EDS	turquoise	LI	CaSb	63.8	2.53	19.9	0.73	6.91	0.48	0.15	0.45
HT26	PIXE/PIGE	turquoise green	LI-P	CaSb + PbSb	60.2	2.06	18.0	0.83	5.74	0.79	0.22	0.00
HT8	PIXE/PIGE	turquoise dark	LI	Bubbles	64.3	2.82	18.8	0.78	7.11	0.60	0.12	0.27
HT22	PIXE/PIGE	yellow	LI	PbSb	56.7	2.08	16.3	0.64	6.69	0.37	0.07	0.52
HT21	PIXE/PIGE+SEM/EDS	yellow green	LI	PbSb	58.8	2.64	16.7	0.75	5.72	0.52	0.11	
HT27	PIXE/PIGE	green yellow	LI	PbSb	61.8	2.13	18.6	0.56	5.49	0.45	0.07	0.03
HT23	PIXE/PIGE+SEM/EDS	green	LI	CaSb + PbSb	64.6	3.00	17.5	0.93	7.19	0.61	0.15	0.43
HT24	PIXE/PIGE	green	LI	CaSb + PbSb	65.9	2.25	18.3	0.65	6.02	0.46	0.06	0.33
HT14	PIXE/PIGE	green dark	LI	CaSb	62.1	2.37	18.2	0.73	6.36	0.56	0.15	0.30
HT9	PIXE/PIGE	green dark	LI-P	Bubbles	63.2	2.20	20.5	0.82	6.16	0.85	0.20	0.28
HT34	PIXE/PIGE	white	LI	CaSb	67.5	2.77	16.7	0.81	6.53	0.53	0.10	
HT16	PIXE/PIGE+SEM/EDS	gray	LI	CaSb	65.0	2.39	19.0	0.79	6.46	0.51	0.09	0.58
HT30	PIXE/PIGE	gray	LI	CaSb	66.1	2.50	17.6	0.66	6.78	0.46	0.08	0.70
HT13	PIXE/PIGE	gray	LI-P	CaSb	63.6	3.39	17.1	0.98	5.46	0.75	0.21	0.20
HT17	PIXE/PIGE	gray purple	LI	CaSb	64.9	2.81	17.3	0.99	7.05	0.60	0.12	
HT15	PIXE/PIGE	brown purple	LI	CaSb	64.8	2.79	17.0	0.89	7.16	0.55	0.07	0.58
HT18	PIXE/PIGE	brown	LI	CaSb	65.0	2.41	18.1	0.67	6.01	0.50	0.05	
HT19	PIXE/PIGE	brown green	LI	CaSb + PbSb	58.6	2.31	16.7	0.64	5.65	0.40	0.08	
HT29	PIXE/PIGE	brown green	LI	CaSb + PbSb	61.4	2.41	17.1	0.70	6.42	0.46	0.09	0.25
HT20	PIXE/PIGE	brown dark	LI	CaSb + PbSb	59.0	2.37	17.2	0.77	6.64	0.54	0.09	0.26

Sample	Cl	TiO_2	MnO	Fe_2O_3	Sb_2O_3	CuO	SrO	SnO_2	ZnO	BaO	PbO	CoO	As2O3
HT1	0.84	0.10	0.42	0.78	2.31	0.08	0.05	0.01	n.d.	n.d.	0.43	0.07	n.d.
HT2	0.86	0.13	0.44	0.83	2.58	0.09	0.05	0.01	n.d.	0.022	0.47	0.08	n.d.
HT3	0.81	0.09	0.41	0.77	2.27	0.08	0.05	0.01	n.d.	0.021	0.41	0.07	n.d.
HT4	0.80	0.07	0.43	0.80	2.43	0.08	0.05	0.01	n.d.	0.049	0.44	0.07	n.d.
HT5	0.83	0.07	0.41	0.78	2.30	0.08	0.05	0.02	n.d.	0.010	0.43	0.07	n.d.
HT6	0.75	0.08	0.90	0.91	2.67	0.14	0.06	n.d.	0.006	0.026	0.01	0.08	0.008
HT7	1.11	0.09	1.19	0.63	0.51	0.66	0.05	0.16	0.019	0.033	0.03	0.00	0.005
HT31	1.02	0.07	0.40	0.49	0.69	2.32	0.04	0.07	0.142	0.021	2.80	0.00	0.017
HT12	0.79	0.09	0.86	0.52	1.40	0.93	0.05	0.07	0.029	0.044	0.05	n.d.	0.009

Table 1 (continued)

Sample	Cl	TiO_2	MnO	Fe_2O_3	Sb_2O_3	CuO	SrO	SnO_2	ZnO	BaO	PbO	CoO	As2O3
HT11	0.74	0.10	0.77	0.69	1.37	1.43	0.05	0.07	0.013	0.019	0.04	n.d.	0.010
HT10	0.78	0.11	0.49	0.60	1.42	1.49	0.04	0.05	0.023	0.020	0.03	n.d.	0.012
HT26	0.93	0.09	0.23	0.81	0.74	1.96	0.05	0.17	0.091	0.072	6.97	0.01	0.010
HT8	0.91	0.10	1.04	0.66	0.25	1.87	0.06	0.09	0.044	0.037	0.06	n.d.	0.006
HT22	0.76	0.08	0.42	0.69	2.03	0.02	0.04	0.04	0.010	0.064	12.5	n.d.	0.011
HT21	0.88	0.06	0.51	0.72	1.22	0.94	0.05	0.18	0.087	0.019	10.1	0.01	0.006
HT27	1.01	0.06	0.25	0.61	0.80	1.31	0.04	0.12	0.061	0.016	6.60	n.d.	0.011
HT23	0.77	0.11	0.78	0.74	1.61	1.27	0.06	0.07	0.018	0.043	0.13	0.01	0.009
HT24	0.98	0.07	0.46	0.53	0.62	1.25	0.05	0.06	0.011	0.020	1.94	0.01	0.009
HT14	0.94	0.09	0.41	0.72	0.66	3.49	0.05	0.15	0.054	0.011	2.56	n.d.	0.016
HT9	0.87	0.10	0.27	0.71	0.46	2.77	0.05	0.17	0.107	0.010	0.26	0.02	0.006
HT34	0.82	0.08	0.85	0.55	2.48	0.01	0.05	0.01	0.007	0.049	0.02	n.d.	0.016
HT16	0.81	0.12	1.13	0.56	2.38	0.02	0.05	0.01	0.007	n.d.	0.07	n.d.	0.004
HT30	0.86	0.06	1.77	0.54	1.70	0.02	0.07	0.02	0.007	0.026	0.02	n.d.	0.008
HT13	0.85	0.09	0.30	0.91	0.68	1.98	0.04	0.08	0.007	n.d.	3.34	n.d.	0.010
HT17	0.65	0.11	0.93	0.64	3.64	0.02	0.07	0.02	0.011	0.054	0.02	n.d.	0.020
HT15	0.76	0.09	2.73	0.69	1.79	0.01	0.07	0.01	0.011	0.016	0.03	n.d.	0.008
HT18	1.10	0.06	2.26	0.64	1.58	1.31	0.09	0.08	0.014	0.073	0.04	0.01	0.013
HT19	0.81	0.10	0.33	3.03	1.38	0.71	0.04	0.13	0.010	0.027	9.00	0.01	0.007
HT29	0.93	0.06	1.81	0.77	0.74	0.02	0.06	0.05	0.005	0.085	6.60	n.d.	0.004
HT20	0.82	0.07	1.06	5.11	1.30	0.43	0.06	0.05	0.016	0.032	4.10	0.01	0.016

The method of analysis (PIXE/PIGE sometime associated to SEM-EDS, EPMA), the type of natron glass (*L1* Levantine 1, *L1-lowNa* Levantine 1, low in natron, *L1-P* Levantine 1, high phosphorous) and the opacifiers (*CaSb* calcium antimonite, *PbSb* lead antimonite, *CaSb* + *PbSb* calcium antimonate and lead antimonate) are also reported

Table 2 Chemical composition of glass tesserae from the church of St. Philip (expressed in wt% of oxides)

Sample	Analytical technique	Colour	Glass type	Opacifier	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	P_2O_5	SO_3
HA7(sc)	PIXE/PIGE	Gold, (brown glass)	HIMT		64.2	2.70	17.1	1.00	7.76	1.39	n.d.	0.35
HA11(sc)	EPMA	Gold (yellow glass)	HIMT		65.9	2.60	16.2	1.00	8.40	1.30	n.d.	0.40
HA15(sc)	PIXE/PIGE	Gold (green-brown glass)	HIMT		64.4	2.69	17.0	0.74	9.19	1.12	0.15	0.48
HA1(sc)	PIXE/PIGE	Gold (colourless glass)	C		69.3	1.55	12.3	2.37	9.28	2.91	0.23	0.25
HA2(sc)	EPMA	Gold (brown glass)	C		65.2	1.70	12.8	2.80	11.0	3.00	0.25	0.30
HA10(sc)	PIXE/PIGE	Gold (brown glass)	C		69.9	1.81	11.8	2.68	8.05	1.67	0.38	0.15
H9.3	EPMA	Black (green-brown glass)	lowCl		64.0	3.20	15.4	1.70	9.20	2.42	0.09	0.33
H13.1	EPMA	Black (green-brown glass)	lowCl		64.0	3.25	15.0	1.60	9.00	2.48	0.06	0.28
H13.4	EPMA	Black (green-brown glass)	lowCl		63.4	3.80	14.8	1.55	9.30	2.85	n.d.	0.40
H9.5	EPMA	Black (green-brown glass)	lowCl		63.2	3.90	15.2	1.55	9.50	2.75	n.d.	0.35
H13.6	EPMA	Black (green-brown glass)	lowCl		63.2	3.80	15.0	1.52	9.40	2.85	n.d.	0.22
H9.6	EPMA	Colourless (natural colour)	lowCl		69.0	2.85	12.8	1.68	8.80	2.60	0.05	0.32
H13.3	EPMA	Red-brown	lowCl	Cu	64.0	3.20	13.2	1.67	10.0	2.73	0.11	0.42
HA13.5	EPMA	Red-brown	lowCl	Cu	63.5	3.25	14.2	1.65	10.0	2.73	0.08	0.42
HAB	PIXE/PIGE + SEM/EDS	Red-brown	lowCl	Cu	63.6	3.35	13.7	1.59	9.48	2.47	0.04	0.55
H9.4	EPMA	Red-brown	lowCl	Cu	62.0	3.50	13.6	1.75	10.9	2.75	0.12	0.37
HAC	PIXE/PIGE	Blue	LI	SnO_2	65.0	2.35	15.3	0.48	8.09	0.38	0.10	0.36
HAD1	PIXE/PIGE	Blue dark	LI	Qu	68.6	2.47	15.0	0.56	7.77	0.41	0.10	0.16
H9.2	EPMA	Blue		Qu	73.5	1.75	15.0	0.57	4.95	0.58	0.16	0.05
H9.1	EPMA	Turquoise		Qu	68.7	1.60	19.8	0.45	5.55	0.51	0.05	0.30
HAE	PIXE/PIGE + SEM/EDS	Turquoise green	LI	SnO_2-Pb	61.4	2.46	16.4	0.76	6.58	0.52	0.13	0.07
HAL1	PIXE/PIGE	Turquoise green	LI	SnO_2-Pb	64.5	2.32	15.7	0.71	6.91	0.49	0.15	0.06
H13.2	EPMA	Turquoise green light	LI	SnO_2-Pb	67.0	2.40	12.8	1.22	7.15	0.53	0.14	0.06
HAG	PIXE/PIGE	Yellow	LI	PbSn	60.0	1.93	17.3	0.50	5.45	0.34	0.05	0.10
HAF1	PIXE/PIGE	Green yellow	HIMT	PbSn	57.7	4.04	15.0	0.76	5.42	1.03	0.14	0.14
HAA1	PIXE/PIGE + SEM/EDS	White	LI	SnO_2	68.0	2.47	14.6	0.46	6.74	0.44	0.14	0.47

Sample	Cl	TiO_2	MnO	Fe_2O_3	Sb_2O_3	CuO	SrO	SnO_2	ZnO	PbO	CoO	As_2O_3
HA7(sc)	0.76	0.24	2.92	1.38	0.04	0.01	0.11	n.d.	n.d.	0.01	n.d.	n.d.
HA11(sc)	0.80	0.20	2.10	1.10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HA15(sc)	0.84	0.20	1.95	1.10	0.04	0.01	0.01	n.d.	n.d.	0.01	n.d.	n.d.
HA1(sc)	0.84	0.10	0.34	0.40	0.01	n.d.	0.09	0.01	n.d.	n.d.	n.d.	n.d.
HA2(sc)	0.60	0.10	1.60	0.60	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HA10(sc)	0.82	0.13	1.56	0.93	0.01	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.
H9.3	0.15	0.11	n.d.	3.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H13.1	0.18	0.10	0.02	4.00	n.d.	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H13.4	0.22	0.10	n.d.	3.55	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H9.5	0.20	0.12	n.d.	3.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H13.6	0.15	0.13	n.d.	3.70	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
H9.6	0.35	0.09	n.d.	1.40	n.d.	n.d.	n.d.	n.d.	n.d.	0.10	n.d.	n.d.
H13.3	0.22	0.08	0.03	2.40	n.d.	1.30	n.d.	0.36	n.d.	0.25	n.d.	n.d.
HA13.5	0.25	0.12	0.03	2.20	n.d.	1.20	n.d.	0.20	n.d.	0.20	n.d.	n.d.
HAB	0.17	0.20	0.03	2.81	0.01	1.51	0.01	0.04	0.09	0.28	0.01	0.032
H9.4	0.17	0.11	0.05	3.53	n.d.	0.82	n.d.	0.25	n.d.	0.10	n.d.	n.d.
HAC	0.79	0.11	0.56	1.09	0.03	0.12	0.01	4.22	n.d.	0.73	0.10	n.d.
HAD1	1.00	0.10	2.32	1.04	0.05	0.13	0.01	0.02	0.01	0.01	0.08	n.d.

Table 2 (continued)

Sample	Cl	TiO_2	MnO	Fe_2O_3	Sb_2O_3	CuO	SrO	SnO_2	ZnO	PbO	CoO	As_2O_3
H9.2	0.95	0.06	0.25	1.15	n.d.	0.23	n.d.	n.d.	0.35	0.25	0.20	n.d.
H9.1	1.34	0.06	0.02	0.48	n.d.	0.90	n.d.	0.10	n.d.	0.14	n.d.	n.d.
HAE	0.98	0.12	0.58	0.89	0.04	1.99	n.d.	0.89	0.04	6.13	n.d.	0.012
HAL1	0.88	0.10	0.39	0.67	0.03	1.29	n.d.	0.60	0.01	5.15	n.d.	0.011
H13.2	0.85	0.08	0.02	0.43	n.d.	0.52	n.d.	0.47	n.d.	6.30	n.d.	n.d.
HAG	1.01	0.10	0.42	0.76	0.02	0.40	n.d.	1.64	0.01	9.89	n.d.	0.007
HAF1	0.60	0.18	1.08	1.30	0.05	2.30	0.01	0.99	0.02	9.21	0.01	0.013
HAA1	0.59	0.09	0.11	0.35	0.02	n.d.	n.d.	5.48	n.d.	0.02	n.d.	

The method of analysis (PIXE/PIGE, EPMA) and the type of glass (*C* soda plant ash, *L1* Levantine 1, *HIMT* high iron, magnesium and titanium natron glass, *HLiB-lowCl* high lithium, boron and low chlorine) and the opacifiers (*Cu* copper, SnO_2 cassiterite, *Qu* ground quartz, SnO_2-*Pb* cassiterite in a high lead glass, *PbSn* lead stannate) are also reported. In samples indicated with (sc), the *cartellina* and the support were analysed separately

the base glass allow a few compositional groups to be established.

The tesserae are made of soda-lime-silica glass to which colourants and/or opacifiers were added. By reporting in diagrams the contents of potassium, magnesium (Fig. 4) and phosphorus, three compositional groups can be identified:

1. The first is a natron glass group, having potassium and magnesium oxide contents below 1.5% and phosphorus content below 0.2%. It can be identified as natron glass in agreement with the glass type prevailing in the Roman time.
2. The second is an intermediate group, having potassium content between 1.5 and 2.0% and magnesium between 1.5 and 2.0%
3. The last has high potassium content (2.53.0%).

In the first group, the contents of calcium oxide and alumina as well as of other oxides allow separating the natron-type tesserae into two groups dominating the archaeological record during the Late Antique and Early Byzantine periods: one group produced on the Levantine coast (Roman, Levantine 1) and the other in Egypt (high iron, manganese and titanium glass (HIMT) (Foy et al. 2003; Freestone et al. 2000).

All the tesserae of the theatre and some tesserae of St. Philip church can be identified as Levantine 1 (indicated as L1 in Tables 1 and 2), based on the high alumina (Al_2O_3 2.5–3%) and lime content (CaO 6–9%). As far as we know, this type of natron glass was produced in Palestine between the fourth and seventh c. (Freestone et al. 2008).

The blue tesserae from the theatre and some from the church (HT1–6, HAC, HAD1) form a sub-group characterized by a batch prepared with higher silica-lime sand content (SiO_2 68.2–70.4%) and lower natron content (Na_2O 15.3–16.9%). These samples have also a lower potassium content (K_2O 0.55–0.64%) (indicated as L1-lowNa in Table 1).

Three tesserae from the theatre (HT9, 13, 26) are similar to Levantine 1 group according to calcium and alumina contents but show an unusually high content of phosphorus for a natron glass (P_2O_5 0.21–0.24%; in general P_2O_5 <0.2%) (indicated as L1-P in Table 1). It cannot be excluded that a certain amount of phosphorous entered the melt with the ashes of wood used as a fuel, but these elements could also indicate a different source of sand. Natron glass tesserae with a similar phosphorus concentration were identified in St. Theodore basilica in Rome (second half of the sixth c.) (Verità, in press).

Four tesserae from the church (three gold tesserae: HA7, HA11, HA15 and one green yellow HAF1) were produced with a natron glass with high iron (Fe_2O_3 1.1–1.5%), magnesium (MgO 1.1–1.4%) and titanium contents (TiO_2 0.2–0.24%). These tesserae show a good positive correlation between MgO and K_2O oxides, not

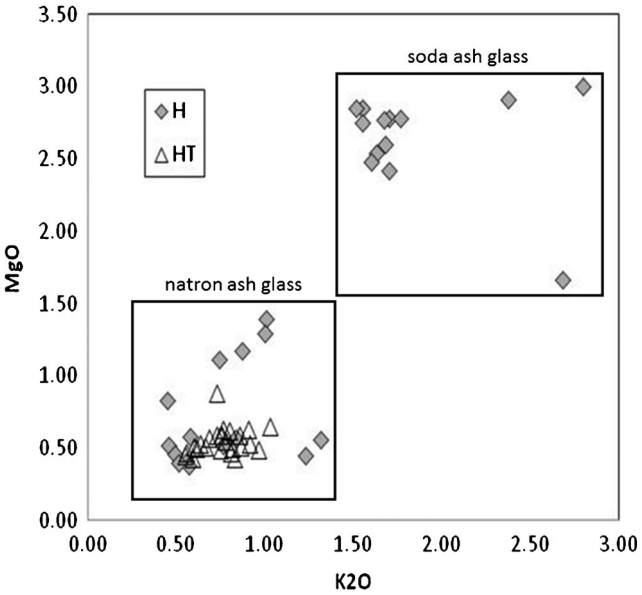

Fig. 4 Potassium oxide versus magnesium oxide (wt%) in the base glass for the investigated tesserae (*triangles*: theatre; *diamonds*: St. Philip church)

observed in other natron glass tesserae (Fig. 4). This group is identified as HIMT.

Finally, two samples from the church (H9.1 and H9.2) both opacified with quartz have low contents of calcium (CaO 5–5.8%) and alumina (Al_2O_3 1.6–1.8%) and cannot be included in the natron-type compositional groups known in the literature.

A second group of tesserae is made of red and black tesserae, showing higher potassium (K_2O 1.5–1.8%) and magnesium contents (MgO 2.4–2.9%) (labelled lowCl in Table 2). The glass of this group is relatively rich in alumina (Al_2O_3 2.9–3.9%), and the sodium (Na_2O 12.8–15.5%) and calcium (CaO 8.8–11.0%) contents could correspond to natron type as well as to soda ash-type glass. However the low phosphorous content (P_2O_5 <0.12%) of this group excludes the possibility of a soda plant ash glass, as well as the unusual low concentration of chlorine (Cl 0.22–0.35%). The high iron (Fe_2O_3 2–4%) and low titanium (TiO_2 0.08–0.13% for most of the samples) contents suggest the use of a relatively low-contaminated silica-lime sand and the voluntary addition of iron as a colourant.

A similar low chlorine composition is attested in Middle-Byzantine beakers and bracelets from Pergamon (Schibille 2011; Rehren et al. 2015), but with a higher alumina content (Al_2O_3 5.0–11.0%), linked to silica sources, and a high boron (500–1000 ppm) and lithium (300–1000 ppm) content, correlated to the natron sources (Schibille 2011). Schibille (2011) and Rehren et al. (2015) suggest the use of a local natron source with a low chlorine content, recognized in the evaporitic lakes of the western part of Asia Minor, near Hierapolis. Also, early Byzantine glass from Aphrodisias shows a similar composition, closer to Hierapolis samples (Brill 1968). Brill linked this composition to a local source of raw materials, either salts from the colemanite and ulexite deposits (Ca and Na–Ca borate formations) or the ashes from plants growing there and highly contaminated by boron, lithium and strontium (Brill 1999). The natron flux used for the tesserae of the second group shows clear similarities with the flux identified for Pergamon glasses, even if boron and lithium were not detected in our series. In fact, all tesserae of this group except one were analysed by EPMA for which lithium cannot be detected and boron has a limit of detection of about B_2O_3 2%. This later is higher than the amounts of boron found in glasses studied by the previous authors. But in this study, the presence of boron and lithium has been detected by PIGE analysis in only one tessera, the HAB, which belongs to this group. The quantification of these elements has not been realized, but the level of boron seems to be higher than the detection limit (a few 0.1%), as well as the one of lithium which detection limit is not yet clearly defined but a quite intense peak is observed at 478 keV (see "Materials and methods" section). These results allow to identify hereafter a group of composition close to HLiBAl for flux source (low chlorine and high boron and lithium content), but different for the silica sources, defined by the alumina content, to which belongs the tessera HAB and possibly the other tesserae of this second group, but the detection of boron and lithium has to be confirmed. Then, the samples of Hierapolis attest the earliest use of this local natron sources for the production of black and red mosaic tesserae.

Finally, three gold tesserae from St. Philip church (HA1, HA2 and HA10) show higher magnesium, potassium and phosphorus contents, indicating that they were melted from a batch made of soda plant ash and a silica source (Lilyquist and Brill 1993). This type of glass replaced progressively natron glass in the Levant since the eighth to ninth c. (Henderson 2002).

In synthesis, raw natron glass-type Levantine 1 was used to produce most of the tesserae (tesserae HT9, 13 and 26 could have been made with another silica source) found in the destruction layer of the theatre. Also, the blue tesserae produced with a different recipe, with a lower soda higher silica-lime content, belong to this group. The Levantine 1 base glass suggests a production period of the tesserae between fourth and sixth c.

A complex picture is evidenced by the tesserae of St. Philip church. The majority of coloured tesserae (white, yellow, turquoise, blue and green) were produced with a natron raw glass-type Levantine 1 and four tesserae with raw HIMT glass probably from Egypt. A raw glass melted locally (indicated as lowCl) with low-chlorine natron was used to produce red and black tesserae. Furthermore, two tesserae were made with a low-alumina natron glass that cannot be classified. Finally, three gold tesserae were produced with soda plant ash glass, whose use is attested since the eighth to ninth c.

Colour

A particular attention has been paid for the description of the colours on the polished tesserae and the correspondence between these visual colours and the chemical compositions to identify the colouring agents.

Gold Gold tesserae were found only in the church area of St. Philip and were recently studied (Neri et al. 2016). Their analyses are reported in Table 2. The glass of tessera HA1 was perfectly decolourized by the addition of manganese oxide. The glass of the other tesserae was intensely coloured in brown or green, a feature never observed in before in gold tesserae of the same period from occidental mosaics. Their colour is due to iron (Fe_2O_3 1.1–1.4%) with significant additions of manganese (MnO 1.4–2.9%) and the melting conditions and the final redox state of the glass (Verità and Santopadre, in press). The natron glass of three tesserae corresponds to the HIMT group, and the composition of their gold leaves (Au 98.6%, Ag 1.3% and Cu 0.1%), discussed in (Neri et al. 2016), matches the sixth c. circulating coins. Other three tesserae show a plant-ash glass composition (HA10, HA1, HA2), indicating that some of the tesserae were made not before the eighth to ninth c., as suggested also by the gold leaf composition of tessera HA10 (Au 98.9%, Ag 0.9% and Cu 0.2%), that is, similar to the composition of coins from the first quarter of the ninth c.

Blue The blue tesserae were coloured with cobalt oxide, added to a low-natron high-silica glass. These tesserae contain copper, lead and iron, in higher concentrations compared with other samples. They were probably introduced unintentionally through a cobalt ore attested in the Roman period (Gratuze et al. 1992). The high concentration of manganese (MnO 0.9% and 2.3%, respectively) of HT6 and HAD1 tesserae seems to indicate a voluntary addition to modify the blue colour giving an amethyst shade. Despite the use of the same cobalt ore, the blue tesserae from the theatre and the church differ by the nature of the opacifiers, marking a technological change; the tesserae from theatre were opacified with calcium antimonate, following the Roman technology, while those from the church with cassiterite (HA-C) and quartz (HAD1) (see in the following).

Tessera H9.2 produced with a low alumina (Al_2O_3 1.75%) raw natron glass and opacified with ground quartz was coloured with a cobalt ore containing also zinc (ZnO 0.35%) beside iron and copper. The use of this cobalt ore to colour glass and glazes is attested in medieval glassmaking, rarely before the eighth c. (Gratuze et al. 1992; Henderson 2003; Wood et al. 2007).

Black Different recipes were used to colour black tesserae of the two archaeological contexts. Those from the theatre are strongly coloured in purple-blue, by adding copper and manganese. Those from the church are made of a transparent green-brown glass showing dark brown streaks alternated with transparent green ones (Fig. 5). The chemical compositions of the dark and transparent green streaks are similar, indicating that colour was obtained keeping the melt in reducing conditions (with low oxygen) so as to favour the formation of the iron-sulphur amber chromophore.

Turquoise Turquoise tesserae of the theatre were coloured by adding copper oxide to a base glass decolourized by antimony and manganese and decolourized by manganese in the church (H9.1, not decolourized glass). Copper oxide produces a light blue colour, and the presence of oxidized iron tends to shift the colour towards turquoise or green, according to the composition and the oxidizing conditions of the melt. Apparently, copper was added as a pure oxide in the turquoise tesserae of the theatre, while traces of lead and tin suggest the use of a lead tin bronze alloy in tessera H9.1 of the church.

The peculiar hue of the turquoise green tessera HT26 was obtained by adding small amounts of cobalt (80 ppm) and yellow pigments to a turquoise glass; the high content of lead (PbO 7%) of this tessera can be explained by the addition of a lead antimonate yellow pigment, a half-product synthesized in a high-lead glass. The turquoise green hue of the HAE and HAL1 tesserae from the church is instead the result of a turquoise glass coloured by copper and iron, white tin oxide crystals and few lead stannate yellow particles; these tesserae will be discussed in the following in relation to opacifiers.

Yellow and green The glass of the green tesserae is coloured by copper and iron. Dark streaks of the non-dissolved colourant indicate the addition of copper to the glass melt. The same pigments colour the yellow tesserae. Yellow lead

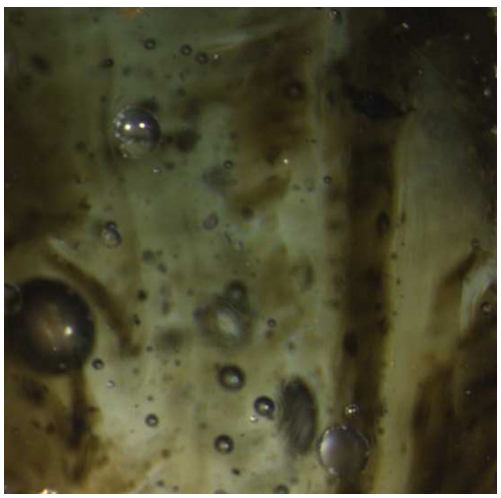

Fig. 5 Optical micrograph of the black tessera H9.3 (long size of the micrograph 2.5 mm)

antimonate pigments were identified in the theatre tesserae and lead stannate pigments in the church tesserae. SEM micrographs of the yellow green tesserae from the theatre evidence particles of lead antimonate both as aggregates (up to 25 μm) and as micrometric dispersed crystals (Fig. 6, tessera HT21). The morphology of the crystals indicating their reaction with the glass matrix and the heterogeneous structure of these tesserae (steaks of high-lead glass) suggest an addition to the base glass of a yellow intermediate product.

Similar patterns are observed in the green and yellow tesserae from the church coloured by yellow lead stannate particles. Lead stannate is considered by many scholars to be typical of Byzantine glassmaking technology (Tite et al. 2008), in contrast to Roman tradition with lead antimonate. Nevertheless, recent studies showed the simultaneous use of both lead antimonate and lead stannate yellow pigments already in the Roman period to produce different yellow hues (Verità et al. 2013).

According to Renaissance Muranese glassmaker recipes, the yellow pigments, called *anime*, were first prepared by firing mixtures of minium, lead-tin calx, antimony and silica, sometimes with the addition of iron or zinc. The intermediate yellow colourant was then added to the molten soda-lime-silica glass (colourless or green), quickly stirred and poured into slabs to avoid the dissolution of the pigment (Moretti and Hreglich 1984).

Red Red-brown tesserae are attested only in the church. They are coloured and opacified by micrometric spheres of metallic copper, observed by SEM (CuO 0.8–1.5%). Under strong reducing conditions (no manganese was detected in these tesserae), copper ions dissolved in the melt are converted to reduced metallic copper (Freestone et al. 2003). Iron present in large amounts (Fe_2O_3 2.4–3.5%) was probably added directly to the melt as a FeO compound to reduce the cuprous ions to metallic copper. The iron content also modifies the colour, shifting it progressively to a brown hue. The majority of the tesserae show opaque red streaks alternated with transparent green ones. The chemical compositions of the opaque and of the transparent streaks are similar, demonstrating that in the latter, the pigment has dissolved due to oxidation of the glass.

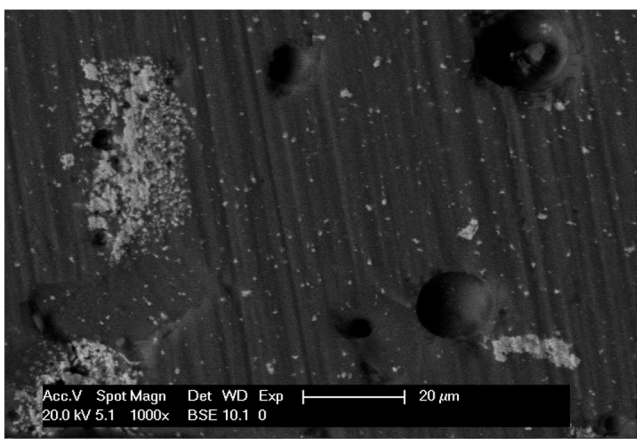

Fig. 6 SEM micrograph of the yellow-green tessera HT21 opacified and coloured by lead antimonate particles

Brown A complex range of brown colours, not attested in Western mosaic glass tesserae, is documented with a large variety of hues in the tesserae from the theatre (shades from grey to brown, green-brown, grey purple and brown dark). The combination of different methods was employed to obtain these heterogeneous and streaky colours. Transparent glasses coloured by combinations of ions were used, as for instance copper and iron in the HT19 brown-green tessera or manganese and copper in the HT18 brown tessera. Black (manganese oxide), yellow (lead antimonate) and red (*terracotta*) pigments were also added. The final colours are in general the result of roughly mixing different coloured melts, as for instance in the brown-green tessera HT29 obtained by mixing transparent green glass, opaque purple-brown glass and opaque grey glass.

White and grey In East Byzantine mosaics, white glass tesserae are generally replaced by stone tesserae. Nevertheless, white glass tesserae were found both in the theatre and in the church areas. They were obtained following different recipes: calcium antimonate small crystals (0.5–1.2 μm) were used in the theatre, according to the Roman technology, and tin oxide (cassiterite) crystals were employed in the church tesserae. The earliest examples of white tesserae opacified with cassiterite are until now attested in fifth to sixth c. mosaics in Milan (Neri et al. 2013; Neri et al. 2016).

Opacifiers

Through the chemical composition of the glass, two kinds of opacifiers were identified in the theatre tesserae and three in the church tesserae. Those for the theatre tesserae are different from those used for the church tesserae.

Theatre White, blue, brown and grey tesserae are opacified with calcium antimonate (Fig. 7) typical of the Roman period (Lahlil et al. 2008) but used also in some cases in Late Antique and Byzantine period. In particular, the opacification of white and blue tesserae with calcium antimonate is observed in Turkey during the Byzantine period: at Antioch in the fourth to fifth c. (Wypyski and Becker 2005), at Sagalassos in the fifth c. (Schibille et al. 2012) and at Hagios Polyeuktos in Constantinople in the sixth c. (Schibille and McKenzie 2014). One dark turquoise (HT8) and one green dark tessera (HT9) are opacified by bubbles according to a technique attested in the Roman and late Roman period (Verità 2000; Maltoni and Silvestri 2016).

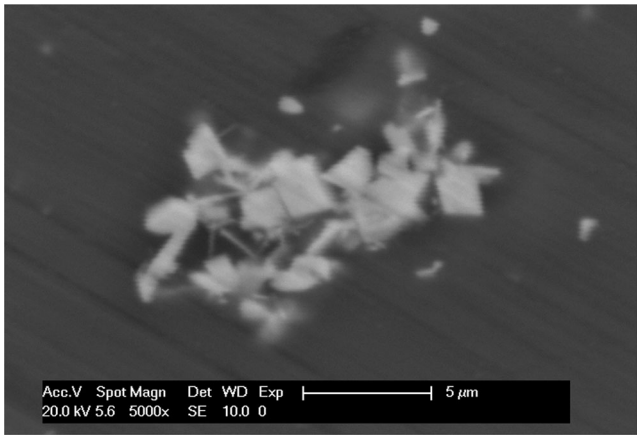

Fig. 7 SEM micrograph of calcium antimonate crystals in the tessera HT6

St. Philip church One white (HAA1) and one blue tessera (HAC) were opacified with cassiterite crystals (SnO_2 4.2–5.5 wt%) in a lead-free glass. SEM imaging shows microcrystals dispersed or aggregated in clusters, both made of tin oxide (Fig. 8). Unlike later opaque glass, in which tin was introduced as a lead-tin calx, no lead was detected in these tesserae. Until now, this technique has been attested in fifth to sixth c. tesserae from Cyprus (Bonnerot et al. 2016), Tyana (Cappadocia) (Lachin et al. 2009) and Milan (Italy) (Neri et al. 2013). No tesserae opacified by calcium antimonate or bone ash (a Byzantine opacifier in use between the fifth and the eighth c.: Marii 2013; Verità and Santopadre, in press) were identified.

Three tesserae classified as "turquoise green" (H13.2, HAE and HAL1) were opacified by tin oxide (SnO_2 0.5–0.9%) in a glass containing significant amounts of lead (PbO 5.1–6.3%) (Fig. 9a). SEM micrographs show needle-like tin oxide crystals forming aggregates or surrounding round crystals of lead stannate (Fig. 10). This pattern is explained by the fact that lead stannate begins to decompose in the glass melt at high temperature to form secondary cassiterite crystals (Tite et al. 2008). The PbO/SnO_2 ratio in these tesserae close to 10/1 is similar to the ratio found for these elements in tesserae opacified and coloured by lead stannate yellow particles. SEM micrographs at low magnification of these tesserae evidence a quite heterogeneous pattern for lead-rich white strikes (SEM micrograph of Fig. 9b), quite similar to the pattern observed by SEM in yellow tesserae.

Finally, two blue tesserae (H9.2 and HAD1) and one turquoise (H9.1) are made of natron glass opacified by ground quartz (Fig. 11). Until now, ground quartz opacification was attested only in soda ash glass tesserae of eleventh c. Byzantine mosaics of Hosios Loukas and Daphni (Arletti et al. 2010), Sicily (Verità and Rapisarda 2008; Arletti et al. 2010) and Torcello (Venice) (Verità and Zecchin 2012).

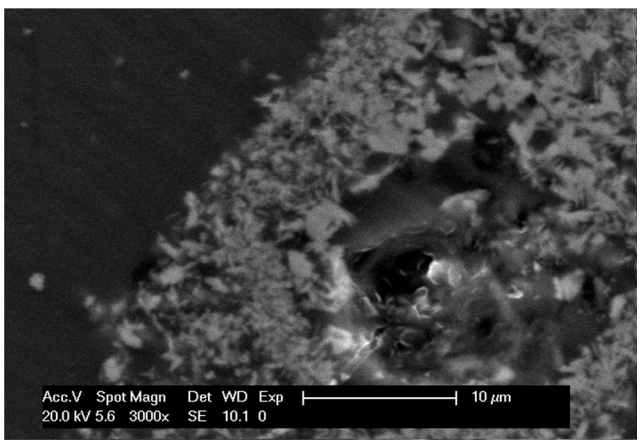

Fig. 8 SEM micrograph of an aggregate of cassiterite crystals in the lead-free glass of the white tessera HAA1

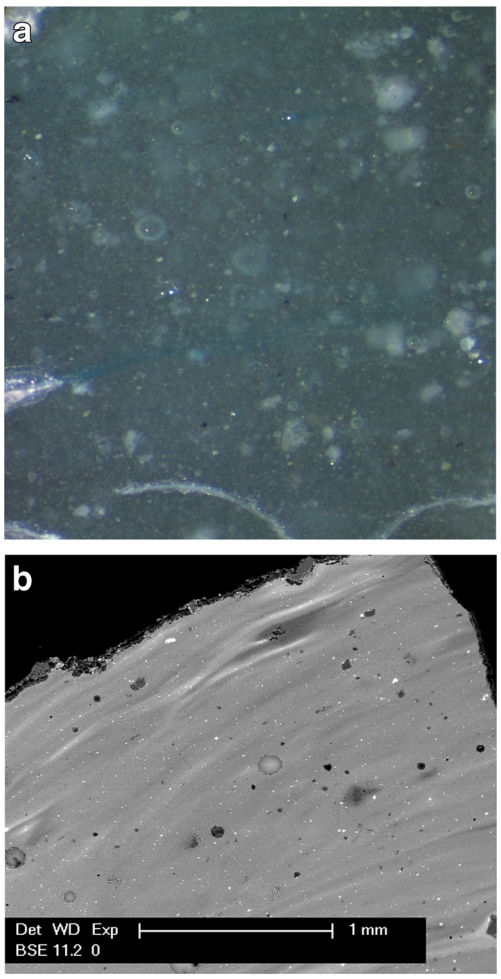

Fig. 9 Micrographs of the turquoise green tessera HA13.2 observed in polished section at the OM microscope **a** and at SEM **b**. Tin oxide crystals (*white spots*) and high-lead glass (*white areas*) are randomly dispersed in the glass matrix

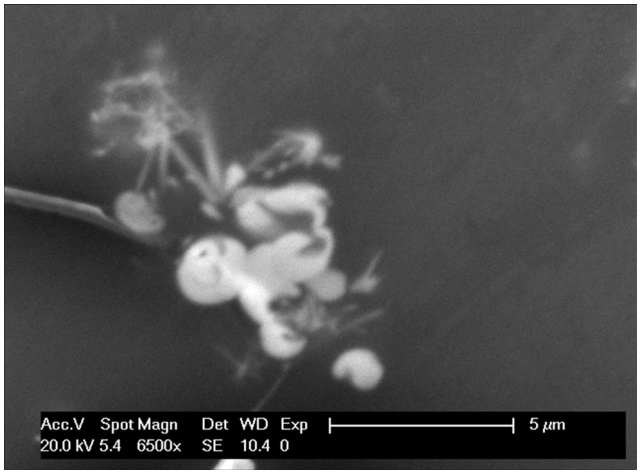

Fig. 10 SEM micrograph of lead stannate (*rounded white*) and cassiterite needle-like crystals in the turquoise-green tessera HAE

Discussion

The analyses of the glass tesserae from Hierapolis reveal a complex picture. The technological continuity (theatre) or discontinuity (church) with respect to the Roman tradition allows a chronological range to be proposed and some distinctive features to be observed as compared to the glass tesserae used in other Levantine sites.

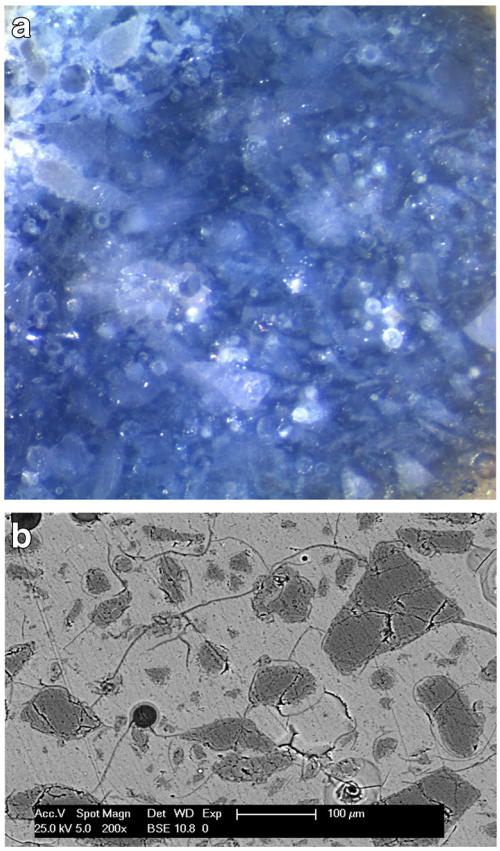

Fig. 11 Micrographs of the polished section of a fragment of the blue tessera H9.2 opacified by ground quartz observed at the OM (**a**; long side of the micrograph 3 mm) and at the SEM **b**

Chronology and technology

The analyses confirm and refine the dating ranges suggested by the archaeological context, i.e. a range between the fifth and seventh c. for the theatre and sixth and ninth c. for the church.

The tesserae used for the decoration of the theatre are made with a homogeneous recipe, according to the Roman tradition (*natron* glass opacified by calcium antimonate and yellow or yellow-green tesserae coloured and opacified with lead antimonate particles). The Levantine 1 natron glass was typically identified in glass artworks of the fifth to sixth c. This feature, beside the subject of the mosaic, can suggest a proto-Byzantine chronology for the tesserae of the theatre and some tesserae from the church. Furthermore, Levantine 1 tesserae were opacified with calcium antimonate, which confirms that antimony was still in use in the fifth to sixth c., in contrast to what is generally stated in the literature (Turner and Rooksby 1959). In this regard, Hierapolis is not an isolated case: the use of antimony is attested until the sixth c. in Constantinople and Sagalassos (Schibille et al. 2012; Schibille and McKenzie 2014) and in mosaics in Rome at least until the eighth century (Verità, in press).

The tesserae from the church of St. Philip seem to identify two phases, also attested by the two groups of fragments, according to the architectonical history of the church: the first corresponding to the sixth c. building and the second belonging to a restoration phase around the ninth c.

The raw natron glasses HIMT and Levantine 1 of the church tesserae were in use in the fourth to sixth c., while the opacification by cassiterite is attested from the fifth c.

The use of gold tesserae made with plant ash glass and the opacification with quartz, and the use of a cobalt ore containing zinc for the blue tesserae attests that interventions on the mosaics (restoration or new mosaics) did not occur before the eighth to ninth c. Moreover, since the church of St. Philip underwent a last building phase in the ninth c., before being defunctionalized in the eleventh c., some technical innovations and supply routes usually considered to be more recent can be dated back to the ninth to eleventh c.

The analyses allow to identify the earliest occurrence of some type of raw glass and recipes to make mosaic tesserae.

– In particular, soda ash glass is attested after the tenth c. in mosaic tesserae production: the most ancient well-dated cases are Hosios Loukas and Daphni (eleventh c.) (Arletti et al. 2010). Other examples are attested at Hagios Polyeuktos in Constantinople (Schibille and McKenzie 2014), St. Vitale in Ravenna (Neri and Verità 2013), St. Ambrose in Milan (Fiori et al. 1999) and St. Prosdocimus

in Padua (Silvestri et al. 2012), but in all these cases, soda ash glass tesserae are attributed to medieval restoration.
- The use of lowCl raw glass to make glass tesserae (HAB and possibly the others) is attested in the church of Hierapolis for the first time, confirming the existence in central Anatolia of a Byzantine glass melting site using local natron source.
- The opacification with quartz of natron glass tesserae is also attested here for the first time.

The opacification of mosaic glass tesserae by tin oxide is known in Milan in the fifth c. and in twelfth to thirteenth c. mosaics in Rome (added as lead-tin calx to a soda plant ash glass) (Verità, in press).

- The colouring of blue glass with a cobalt ore containing zinc is attested so far from the eleventh c. (Henderson 2003). It is also possible that a similar cobalt ore was used in the blue tesserae of Hosios Loukas and Daphni, but unfortunately, the authors have not investigated the presence of zinc (Arletti et al. 2010). The presence of such tesserae in Hierapolis suggests the use of this cobalt ore before the eleventh c.

A group of anise-coloured tesserae (varying between turquoise, light blue and green-blue) indicated as *turquoise green* in this text deserves specific attention. Similar tesserae were found in Byzantine mosaics in Cyprus (Bonnerot et al. 2016) but are extremely rare or absent in Western mosaics. The tesserae from Cyprus were classified by the authors as *green* or *blue* (coloured by copper). Nevertheless, the description of the crystalline pattern and their chemical composition correspond quite well to the turquoise green tesserae of the St. Philip church.

This group includes a tessera of the theatre (HT26) in which the anise colour was obtained by adding small amounts of cobalt and of yellow lead antimonate particles to a turquoise glass opacified with calcium antimonate. Instead, in tesserae HAE, HAL1 and H13.1 from the church, the same colour is the result of a mixture of turquoise transparent glass, needle-like tin oxide crystals and very rare lead stannate yellow particles. This pattern is typical of the addition of lead stannate particles to a soda-lime-silica glass melt and of the subsequent thermal decomposition of the yellow pigment at high temperature. It is unclear what procedure was followed to obtain this colour, for which a high lead content seems to play an important role. For the Cypriot tesserae, Bonnerot et al. (2016) suggested the addition of lead oxide to the glass melt to decrease the decomposition temperature of yellow lead stannate particles. This proposal can hardly be agreed upon, because it presupposes a technical knowledge (addition of lead oxide to modify the viscosity of a soda-lime-silica glass) probably not available at that time. An alternative technique could be the addition to a turquoise melt of orthorhombic lead stannate (Pb_2SnO_4), a slightly yellow intermediate product that forms during the synthesis process of cubic yellow lead stannate ($PbSnO_3$) (Tite et al. 2008). However, the glass-workers followed an empiric practice, observing their successes and mistakes, without knowing the scientific explanation of their practices. So, it is also possible that in a crucible where yellow green glass was produced by adding lead stannate particles, after a certain time, glass could have formed in which most of the lead stannate particles had decomposed to form cassiterite crystals. The casual addition of this glass to a transparent turquoise glass could have yielded the turquoise green colour of the tesserae from the church. Finally, it cannot be excluded that the colouring procedure was to add lead stannate yellow particles to the melt of a turquoise transparent glass to opacify the glass. In contrast to the usual practice (a rapid mixing and working of the glass cakes to avoid decomposition of lead stannate and loss of the yellow colour), the melt could have been held at a high temperature to allow a large amount of yellow lead stannate particles time to transform into white tin oxide crystals. Once the turquoise green colour was obtained, the melt could have been worked into cakes. This issue deserves further research to be explained exhaustively.

Supply routes

By considering the opacification and colouring recipes and the type of raw glass employed, specific recipes could begin to be localized, and supply routes from the secondary workshops to the buildings could be proposed.

The tesserae from the theatre produced following the Roman glassmaking technology (natron glass opacified by calcium antimonate) are similar to those of Sagalassos (fourth to sixth c.) (Schibille et al. 2012) and Antioch (second to fourth c.) (Wypyski and Becker 2005) in Asia Minor and show a uniform supply.

The tesserae from the church, on the other hand, were made with a variety of recipes. This may follow from the fact that they were made in different periods but could also indicate different supply routes from different workshops.

The white and blue tesserae opacified by cassiterite, also recognized in Cyprus and in Tyana (Lachin et al. 2009), could display a specific workshop from Asia Minor. No tesserae opacified with bone ash, a peculiar Byzantine technique widespread in the Levantine area (Syria, Jordan, Cyprus, south and central Turkey: Marii 2013; Lachin et al. 2009; Wypyski 2005; Bonnerot et al. 2016) and in few sites in northern Italy (Ravenna, Milan, Padua: Verità 2010; Neri 2016a, b; Silvestri et al. 2016), have been found in Hierapolis.

The samples attributed to the medieval phase for the recipes (plant ash glass, the use of a cobalt ore with zinc and the

opacification with ground quartz) show a variety of glass and underline probably, the supply from different workshops.

The use of stone tesserae for flesh tones and the majority of white, grey and orange tesserae can be attributed to an easy supply of stone and marble from the many quarries near Hierapolis that had been exploited since ancient times (Scardozzi 2012), suggesting a local provenance of these tesserae. However, aesthetic and economic reasons influence the realization of a mosaic and the choice of its materials. The use of stone and glass, materials with different light reflection properties, is observed in most Byzantine mosaics and is interpreted by some scholars as an artistic solution to give relief and movement to the mosaic and to suggest a means of reflection of divine light, according to the Byzantine aesthetics, cannot be excluded (James 1996). Moreover, the manufacture of glass flesh tone tesserae required a complex and sophisticated technology attested in Roman mosaics (Verità and Santopadre 2010), but unknown to the Byzantine glassmakers; the use of stone was not a choice but a necessity. Moreover, studies on Byzantine mosaics have emphasized the effort of reducing the extremely high costs of the glass tesserae (Neri 2016a). This is demonstrated for instance by the use of ground quartz as an opacifier for coloured tesserae to replace expensive tin oxide. But quartz is a week opacifier, and it is impossible to obtain white glass: when added to a colourless glass, it yields a grey translucent material. This explains the need of Byzantine mosaicists to utilize white stone instead of glass (Verità and Zecchin 2012).

Chronology of mosaics

The homogeneity of the laying technique of the fragments and the opacification by antimony-based recipes of the tesserae from the theatre suggest that they come indeed from one mosaic and from one or more workshops, following the Roman technology.

The different laying techniques of the fragments, different types of opacifiers and base glass types in the tesserae from St. Philip's church suggest chronological developments and repairs and/or a differentiation of supply. Whilst the opacification with cassiterite is practiced from the sixth c. and could be pertinent to the early Byzantine phase, the use of quartz is typical of the Middle Byzantine period. This could correspond to two architectonical phases of the basilica. However, since quartz was used for natron glass in Hierapolis, we can suppose a multiplicity of supply from different workshops following different technologies, in the early Byzantine phase.

No antimony was detected in the glass tesserae from St. Philip's church, excluding reuse of tesserae from dismantled Roman mosaics. This is surprising, as the reuse of glass tesserae was common practice, and we can suppose that the tesserae found in the theatre were still on place in a mosaic when the St. Philip's mosaics were made (sixth c.) and restored (ninth c.).

The glass tesserae from the church were made following manufacturing recipes never attested before the sixth c., which confirms that the church mosaics were made with newly made glass tesserae.

Conclusions

The transition from the sophisticated Roman glassmaking tradition towards the use of new, less expensive technological solutions (colourants, opacifiers, use of stone tesserae) is documented by the analyses of Hierapolis glass mosaic tesserae shading new light on today scant knowledge of Byzantine glassmaking technology.

The analytical investigation of loose glass tesserae also improves the present knowledge of the history of the mosaics in Hierapolis, refining the archaeological chronology and suggesting different supplies for the theatre and church mosaics, showing a change in the organization of the manufacturing process.

The theatre tesserae (and the mosaic they belonged to) could be attributed to the fifth to sixth c., and the tesserae were maybe produced in one workshop, following the Roman technology. No traces of remake or restoration were detected.

The St. Philip's church mosaics display an early Byzantine phase (sixth c.) and a later restoration (eighth to ninth c.), as attested by the use of plant-ash glass in gold tesserae, the widespread use of ground quartz as an opacifier and the use of a source of cobalt with zinc, all attesting a medieval phase. This confirms the importance of the church and its decoration during or after the final period of the iconoclastic crisis. Surprisingly, no reuse of ancient tesserae is attested in the church mosaics.

The analyses underlined a technological change and a diversification of the supply as compared to the theatre mosaic. In particular, we can observe the use of blue and white tesserae (opacified by cassiterite), similar to those employed in the mosaics of Cyprus and Tyana. The use of yellow, green and turquoise green tesserae coloured and opacified with lead stannate, recognized in many sites of Asia Minor, is also underlined, beside a production of black and red-brown tesserae, made with a peculiar raw natron glass produced with a local soda source.

Comparing the two sites, a shift from a uniform to a diversified supply is shown for St. Philip's church mosaics, attesting also a more localized and small-scale production.

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