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Evidences of glass-ceramic white opaque *tesserae* from Roman age: a thermo-analytical approach

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Abstract

Mosaic white *tesserae* of the Roman Age were analyzed from compositional and structural viewpoints. Interestingly, the *tesserae* exhibited an internal silicate glass core surrounded by a glass-ceramic layer constituted by $CaSiO_3$ and $Na_2Ca(Si_6O_{12})$ crystals embedded in the glass matrix. Opaque white colour of the *tesserae* was due to the presence of these crystalline phases developed during a thermal treatment above ∼850 °C, as assessed from thermal analysis of the reproduced starting parent glass of the *tesserae*. Devitrification through an appropriate thermal treatment was used as a deliberate technique by Roman glassmakers to impart an opaque (white) colour and superior mechanical properties to the *tesserae*.

1. Introduction

Our knowledge about the use of glass during the Roman Age mainly comes from Plinius's writings (book XXXVI of the treatise *Naturalis Historia*, 1st century AD) and from recent analysis of archaeological finds. The acknowledged view of glass manufacture during the Roman Age proposes that there was a wide number of glass factories across the Empire especially in the Middle Eastern regions such as Levant, Egypt and Italy, where raw materials were melted together to produce large glass disks or sheets of various thickness [1,2]. Homogeneous glass chunks were then exported to be worked in widely distributed secondary production sites, where the raw glass pieces could be re-melted, coloured/decoloured and shaped. The major issue in making opaque glasses, such as mosaic glass *tesserae*, was in their colouring. Raw glasses of Roman times essentially belonged to the SiO_2-Na_2O-CaO system and were colourless and transparent; addition of metals or metal oxides to the basic glass composition was the most commonly adopted method to obtain a specific colour [5,6,7]. Only later, during the Medieval Age, devitrification by thermal treatment will be commonly performed as an alternative technique to impart colours to glass products [8].

The present works reports the results of compositional, structural and mechanical analyses carried out on Roman mosaic *tesserae*. Furthermore, by using an interesting approach based on thermal analysis, new knowledge about the raw materials employed, production cycles and technological "know-how" of Roman glass craftsmen was acquired.

2. Materials and methods

Fourteen intact mosaic *tesserae*, all characterized by an opaque white colour, and ten fragments were found in the course of excavations in the "St. John's site" near the Cathedral of Asti [9].

The *tesserae* underwent wide-angle X-ray diffraction (WAXRD; 2θ range within 10-70°) in order to identify the possible presence of crystalline phases by using a X'Pert Philips diffractometer (Bragg-Brentano camera geometry; Cu $K\alpha$ incident radiation with wavelength λ = 1.5405 Å; working conditions: voltage 40 kV, current 30 mA, step size 0.02°, counting time 1 s per step).

Two *tesserae* were embedded in epoxy resin (Struers Epofix), cut and polished by using #600 to #4000 grit SiC papers; the polished cross-sections were investigated by scanning electron microscopy (SEM; Philips 525M) in back-scattering electron (BSE) mode (accelerating voltage: 15 kV) to highlight the presence of crystalline phases. Energy dispersive X-ray spectroscopy (EDXS; Philips EDAX 9100) was performed on the polished samples to obtain quantitative data about material composition.

Hardness was evaluated by indenting the surface of two *tesserae* through a Vickers tester (Leitz Microsystem; applied load L = 5 N); Vickers hardness, H_V (GPa), was calculated as $H_V = \dfrac{2L\sin(\beta/2)}{d^2}$, where β = 136° is the angle of the indenting tip and d (μm) is the mean length of the imprint diagonals).

On the basis of WAXRD and EDXS data, *tesserae* glass was reproduced and investigated by differential thermal analysis (DTA). DTA of glass powders (50 mg) was carried out by using a DTA7 Perkin-Elmer instrument (temperature range: 25-1,300 °C; heating rate: 20 °C min^{-1}); pure alumina powder (Sigma-Aldrich) was used as a reference material and for baseline determination.

3. Results and discussion

The *tesserae*, characterized by an approximately rectangular shape with a thickness of ~2 mm (Fig. 1a) and found in an excellent state of conservation, came from the deepest stratification of the archaeological site (3rd century AD). By simple visual inspection of *tesserae* fragments, it was noticed that the opaque white colour characterizing the surface appearance was not homogeneously distributed in the whole material volume. Interestingly, the *tesserae* exhibited a semi-transparent core (aesthetic appearance like a "whitish scum") surrounded by a opaque, white region similar to a thin "skin".

Fig. 1b shows SEM investigations (BSE mode) along the cross-section of a *tessera*: interestingly, the material was not in a glass state, but the presence of crystalline phases was well distinguishable. Specifically, two types of needle-shaped crystalline phases were identified (Fig. 1c): (i) white crystals (length within 10-50 μm, thickness around few microns), located at the *tessera* surface and underneath up to ~200 μm of depth and (ii) grey, slightly smaller crystals below the above-mentioned external layer towards the sample core and in the space among the white crystals. Compositional analysis of different regions of the *tessera* cross-section are reported in Table 1; analogous results were obtained for both the analyzed *tesserae*.

Fig. 2 collects WAXRD spectra acquired at different "levels of depth" of the *tessera*, as clarified in the scheme attached to the diffraction patterns. First, the *tessera* surface as-such was investigated; then, after removing by polishing a 200 μm-thick layer of material – i.e. approximately the thickness of the external layer containing white crystals (Fig. 1a) – WAXRD analysis on this new polished surface was performed; finally, a 500 μm-thick layer of material was removed to reach the core region of the original *tessera*, that was also investigated by WAXRD. Crystalline phases assignment can be resumed as follows: the outer layer of the *tesserae* was mainly constituted by $CaSiO_3$ (wollastonite) together with the secondary phase $Na_2Ca(Si_6O_{12})$, the intermediate layer contained only $Na_2Ca(Si_6O_{12})$ and the *tessera* core was

completely amorphous. Crystalline phase identification obtained by WAXRD is consistent with the EDXS data reported in Table 1: the previously designed "white" and "grey" crystals (see Fig. 1) corresponded to $CaSiO_3$ and $Na_2Ca(Si_6O_{12})$, respectively.

From these data, it is evident that the opaque white colour of the *tesserae* surface was not attributable to the presence of specific metal oxides, such as tin, arsenic or antimony oxides [10], that were usually introduced in glass composition by the glassmakers, but was due to the presence of crystalline phases nucleated and grown in the glass matrix as a consequence of a thermal treatment. This is a significant finding that integrates the current knowledge about glass manufacturing in the Roman Age [5,8,10]: as far as the analyzed *tesserae* is concerned, it is reasonable to hypothesize that Roman craftsmen bought chunk, sheets or even *tesserae* of a relatively cheap, colourless and transparent glass and, in a second manufacturing step, deliberately heat-treated the raw glass to transform it in a glass-ceramic material to be used in the final form of opaque white *tesserae*. This hypothesis can be also supported by the observations of other authors, who found partially crystallized opaque glass *tesserae* [11,12].

The presence of the starting, original glass in the *tesserae* core was demonstrated by the corresponding WAXRD spectrum reported in Fig. 2; furthermore, from the EDXS data reported in Table 1, we can derive the precise molar composition of the original raw glass: 61.28% SiO_2, 11.12% Na_2O, 24.58% CaO, 1.34% MgO, 0.99% K_2O, 0.69% Al_2O_3.

Tesserae raw glass has the typical composition of silica-soda-lime Roman glass used during the Imperial Age, showing a relevant amount of SiO_2 (above 60 %mol.) and high levels of Na_2O and CaO [2]. Quartz sand was reasonably used as SiO_2 source; the low content of Al_2O_3 seems to suggest the use of calcareous sands (CaO source) containing feldspar as impurities. Furthermore, the low concentrations of K_2O and MgO suggest that the glass was produced by using natron, a naturally occurring mixture of sodium carbonate decahydrate ($Na_2CO_3 \cdot 10H_2O$) and sodium bicarbonate ($NaHCO_3$) along with small quantities of salts as impurities. During Roman Age, natron was mined in Egypt (Wadi El-Natrun, North-West of Cairo) and commonly used in glass-making activities throughout the Empire. Roman glasses produced using natron as Na_2O source are well distinguishable from those synthesized using other raw materials, as they generally exhibit very low levels of K_2O and MgO [2], like the glass investigated in the present work.

In order to acquire more details about the technical manufacturing of the *tesserae*, we first reproduced the *tesserae* glass, as also proposed elsewhere [13], and then investigated it to assess the temperature of the thermal treatment inducing devitrification of the starting raw glass. We synthesized *ex novo* the *tesserae* basic glass, hereafter designed as reconstructed parent glass (RPG), by melting high-purity reactants (SiO_2, Na_2CO_3, $CaCO_3$, $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, K_2CO_3, Al_2O_3, all purchased from Sigma-Aldrich) in a platinum crucible at 1,500 °C for 1 h in air (heating rate: 10 °C min^{-1}); the melt was quenched in water to obtain a "frit", that was ground in a mortar to obtain a fine powder. The DTA

plot resulting from RPG thermal analysis is reported in Fig. 3; the characteristic temperatures of the RPG, assessed directly from DTA curve, were the following (values reported as mean ± SD of three different DTA measurements): glass transition temperature, $T_g = 658 \pm 7$ °C; onset crystallization temperature, $T_x = 848 \pm 8$ °C; peak crystallization temperature, $T_c = 923 \pm 10$ °C. In conclusion, it is possible to hypothesize that Roman craftsmen thermally treated raw glass pieces at a temperature above T_x in order to obtain the glass-ceramic white *tesserae* analyzed in this work.

To the best of our knowledge, no data about hardness and mechanical properties of ancient glass *tesserae* are available in the literature. In this work, for the first time Vickers indentations were performed on Roman *tesserae* (original surface), as well as on slices of the RPG for purpose of comparison. Hardness values for the *tesserae* and the RPG, expressed as mean ± SD of ten measurements, were 10.5 ± 2.1 GPa and 7.9 ± 1.8 GPa, respectively; as expected, glass-ceramic *tesserae* exhibited a higher hardness in comparison to the RPG. It is likely that Roman glassmakers had adequate experience about glass manufacturing to know that glass-ceramics generally exhibited superior durability and resistance to weathering in comparison to their parent glass; therefore, the thermal treatment inducing glass devitrification might have been deliberately carried out not only for aesthetic purpose with the aim to obtain an opaque white colour of the final *tesserae*, but also to impart better properties to the material, such as higher hardness and wear resistance.

4. Conclusions

The opaque white colour of the Roman *tesserae* analyzed in this work can be imputed to the presence of crystalline phases developed during a thermal treatment above ~850 °C. Reproduction and DTA analysis of *tesserae* glass represent an interesting approach to study glass-derived archaeological finds and allow to acquire valuable information about glass processing conditions. It is reasonable to suppose that Roman craftsmen deliberately induced devitrification of raw, transparent glass both to easily produce opaque white glass-derived *tesserae* avoiding the need for adding colouring agents in the glass composition (aesthetic reason) and to impart superior surface properties, such as high hardness, to the material (functional reason).

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Figure

Fig. 1. Morphological investigation of the *tesserae*: (a) photograph of two samples; (b,c) SEM micrographs of the polished cross-section of a *tessera* (BSE mode). Specifically, (b) shows the region close to the surface (magnification 1000×), (c) is a high magnification of crystalline phases (magnification 5000×). The symbol '*' indicates a white crystal, whereas the symbol '▲' labels grey crystals.
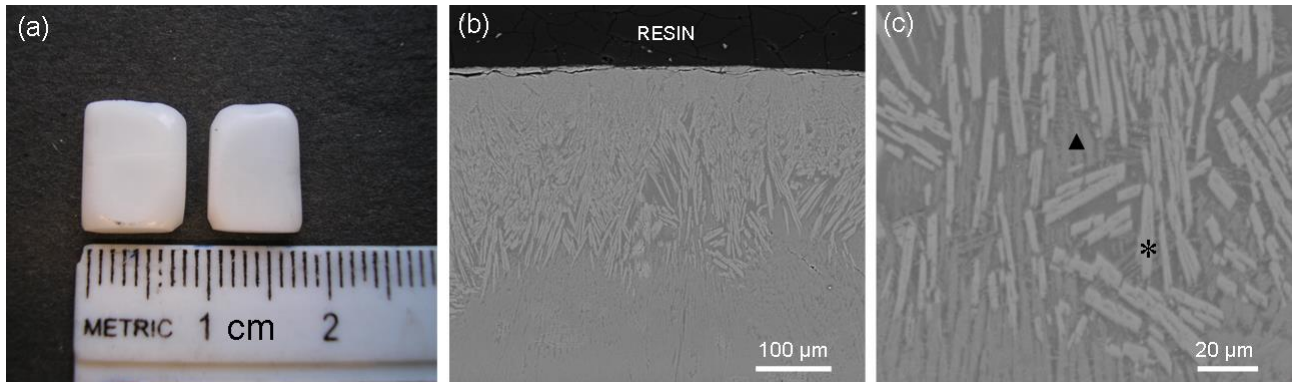
Fig. 2. WAXRD on different regions of the Roman *tessera*.
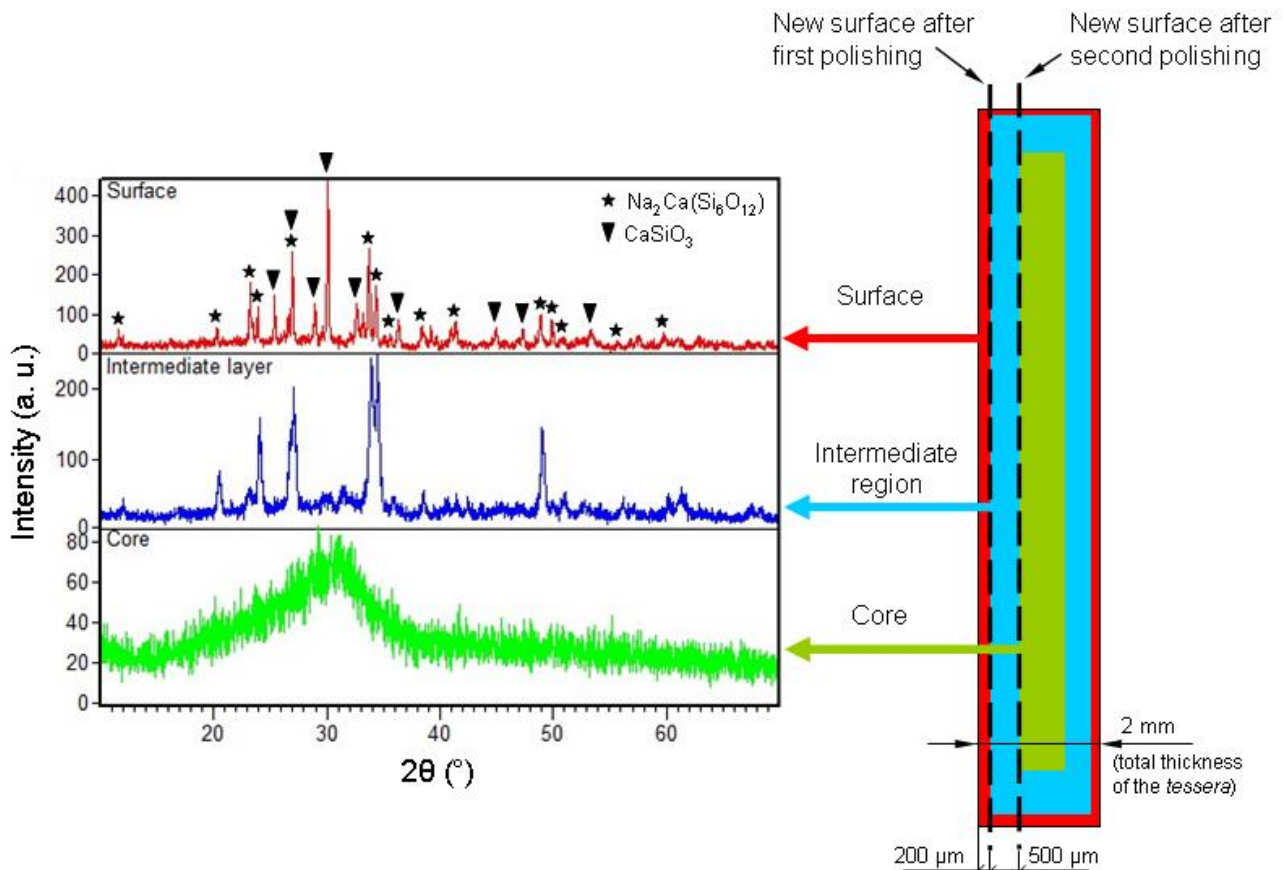
Fig. 3. DTA plot of the reproduced parent (raw) glass (RPG) of the Roman *tesserae*.
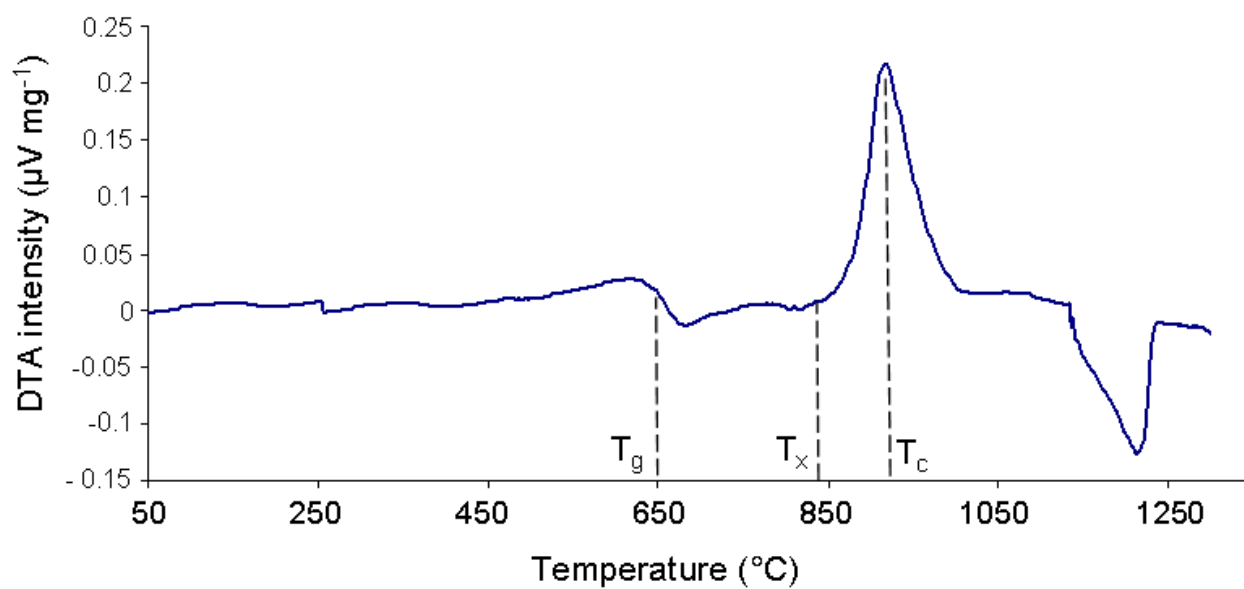
Tables

Table 1. Compositional analysis from EDXS investigations performed along the polished cross-sections of a *tessera*; the data are reported as mean ± SD calculated on five different spots for each region.

Element	Composition (%mol.)		
	White crystals[a]	Fine grey crystals[a]	*Tessera* core[b]
Si	58.22 ± 0.04	55.19 ± 0.03	55.18 ± 0.05
Na	< 0.01[c]	19.47 ± 0.02	20.04 ± 0.03
Ca	41.77 ± 0.03	25.33 ± 0.02	22.14 ± 0.03
Mg	-	-	1.21 ± 0.01
K	-	-	0.18 ± 0.01
Al	-	< 0.01[c]	1.25 ± 0.02

[a] The analysis can be easily interpreted in the light of Fig. 1c, where the "white crystals" are marked with the symbol '*'and the "fine grey crystals" are identified by the symbol '▲'.

[b] Analysis performed exactly at half thickness of the *tessera* cross-section.

[c] Negligible traces, probably due to a "boundary effect" of the surrounding material.