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Characterisation of archaeological glass mosaics by electron microscopy and X-ray microanalysis

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Abstract. The combined techniques of scanning electron microscopy, energy dispersive X-ray analysis, transmission electron microscopy (TEM) and selected area electron diffraction are used to characterise the microstructures of opaque coloured glass mosaics from a mediaeval church in Torcello, Italy. Comparison of MgO/K2O ratios allows distinction between mediaeval and modern glass artefacts to be made. TEM investigation of inclusions indicates that relict silica is responsible for the speckled appearance of an impure mediaeval glass artefact, whilst a fine scale dispersion of elemental Cu nanoparticles is considered responsible for the orange-red colouration of a modern glass artefact.

1. Introduction
Modern day techniques for materials characterisation are gaining increasing usage in the area of archaeological materials science. There is a well established literature on the application of scanning electron microscopy (SEM) and X-ray diffraction (XRD) for the characterisation of ancient pottery [1]. Similarly, the application of electron probe microanalysis (EPMA) for the study of the materials used in early glass production is well covered [2]. However, transmission electron microscopy (TEM) still represents a relatively novel approach for the study of archaeological artefacts. For example, the distinctive red/green dichroism of the Lycergus cup, a 4th century AD Roman artefact, when viewed in transmitted or reflected light, is attributed to the fine scale dispersion of gold and silver nanoparticles within the glass matrix [3]. A high concentration of silver nanoparticles has similarly been identified as being responsible for the lustre decoration of 13th century Islamic ware [4]. In this paper, the application of the combined techniques of SEM, energy dispersive X-ray (EDX) analysis, TEM and selected area electron diffraction (SAED) to characterise the microstructures of opaque coloured glass mosaics from a mediaeval church in Torcello, Italy, is demonstrated. Quantitative EDX analysis of the glass matrices allows distinction to be made between mediaeval and modern artefacts. Characterisation of the fine scale inclusions using TEM provides explanation for the glass colouration.

2. Experimental
Two representative mosaic tesserae are compared here to illustrate how these electron beam assessment techniques may be used in support of sample provenance studies. Artefact A, considered to be mediaeval (11th to 14th century) in origin, was opaque and turquoise in colour with white speckles.

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Figure 1 (a) BSE image of a turquoise mediaeval glass artefact A showing a dispersion of silica grains (dark contrast), and CaSiO₃ and Ca₂SiO₄ crystals (light contrast) and (b) an associated EDX spectrum acquired from the glass matrix.

Figure 2 (a) BSE image of an orange-red modern glass artefact B showing a dispersion of Cu inclusions and (b) an associated EDX spectrum acquired from the glass matrix.

Table 1 Quantitative EDX analysis of the glass matrices of artefacts A and B (all values in wt%)

|          | Na₂O | MgO | Al₂O₃ | SiO₂ | SO₃ | Cl | K₂O | CaO | TiO₂ | Fe₂O₃ | SrO | BaO | P₂O₅ | Total alkali (K₂O+Na₂O) |
|----------|------|-----|-------|------|-----|----|-----|-----|------|-------|-----|-----|------|--------------------------|
| Mediaeval| 11.94| 1.12| 2.13  | 57.92| 0.21| 0.33| 1.19| 5.85| 0.09 | 0.93  | 1.31 | 5.55| -   | -   | 12.94                    |
| Modern   | 13.58| 0.71| 0.60  | 59.50| 0.47| 0.46| 2.12| 5.27| -    | 0.08  | 3.84 | 2.25| 0.50| 0.61| 0.11 | 4.75 | 10.9                      |

Table 2 Comparison of K₂O and MgO compositional values allowing the distinction between mediaeval and modern glass tesserae, and the assignment of alkali source.

|          | Mediaeval | K₂O  | Modern | MgO |
|----------|-----------|------|--------|-----|
| 1.5 wt% to 1.0 wt% | 2.3 wt% K₂O | 3 to 7% K₂O | 0.5 wt% MgO |
| (lower wt%) Mineral Na source | (higher wt%) Plant ash Na source | Pure compound K₂CO₃ or Na₂CO₃ | No silicates |

Artefact B, considered to be post-mediaeval or modern (17th to 19th century) in origin, was opaque exhibiting a uniform orange-red colouration.

Samples for SEM investigation were mounted in cold setting epoxy resin, sequentially ground and polished to produce a smooth surface, and coated under high vacuum with a ~20nm thick layer of carbon. Backscattered electron (BSE) images were acquired using an FEI XL30 SEM operated at 20kV. Quantitative elemental analysis was performed using an Oxford Instruments ISIS EDX system with an ultra-thin window facilitating light element analysis. The sample/detector geometry, with a working distance of 10mm and take off angle of 35°, was maintained identical to that used for reference sample analysis, whilst gain calibration of the beam current was performed at regular intervals using a cobalt standard. Compositional analysis of the sample matrices in terms of weight...
percent oxide was performed, in the first instance, assuming oxygen to be bound with predefined stoichiometry to all the detectable elements within the samples. Iteration of this process for known metal oxide compounds and silicate phases followed with recalculation of the oxide concentrations based on ionic formulae, based on knowledge of the predominant valencies. Samples for TEM investigation were crushed and dispersed on to holey carbon on Ni support grids. TEM investigations were performed using a Jeol 2000fx TEM operated at 200kV. Fine scale inclusions were characterised using the combined techniques of SAED and qualitative EDX analysis (with a beryllium window detector elements lighter than Na are not detected).

Figure 3 TEM image (SAED pattern inset) of a relict silica grain within Sample A (Mediaeval glass)

Figure 4a TEM image of a fine scale dispersion of precipitates within Sample B (Modern glass)

Figure 4b higher magnification dark field image of an inclusion within sample B with inset SAED (the strong systematic row of diffraction spots are indexed as \{111\}Cu and (c) associated EDX spectrum consistent with the presence of elemental Cu. (Note: however, the TEM EDX detector window is made of beryllium and thus oxygen is not detected).

3. Results and Discussion

The fine scale microstructures of artefacts A and B are compared in Figures 1 and 2, respectively. Both samples exhibited a basic soda-lime-silica matrix composition with notable differences in the inclusion content. The BSE image of Figure 1a shows a dispersion of angular fragments of silica grains (dark contrast) surrounded by a mixture of CaSiO$_3$ and Ca$_2$SiO$_4$ crystals (light contrast), as confirmed by EDX analysis, consistent with low purity mediaeval glass. Conversely, the BSE image of Figure 2a shows a fine scale distribution of Cu inclusions, in the absence of relict silica grains,
consistent with higher purity glass associated with the modern era. The associated EDX spectra acquired from the matrices of both samples are shown in Figures 1b and 2b, respectively. The spectra look visibly very similar, although there are significant differences in the calculated oxide concentrations, as summarised in Table 1.

The matrix compositional values of artefacts A and B are representative of the two principal soda-lime-silica groupings of glass samples that have been studied. The bulk matrix compositions show significant differences in the major oxide components and comparison of the K₂O/MgO ratios in particular allows distinction between mediaeval and modern glass artefacts to be made. The oxide content and ratios also reflect differences in the origin of the raw materials used in their manufacture, as summarised in Table 2. The mediaeval glasses show positively correlated MgO/K₂O ratios (e.g. 1.12/1.10wt% for the case of artefact A) are indicative of the use of a Na-rich mineral alkali source such as natron, a hydrated carbonate of sodium found on some lake borders. Conversely, the higher correlated MgO/K₂O ratio of ~2.3/2.2wt% for a glass artefact would be associated with the use of a Na-rich plant ash alkali source during glass manufacture. EDX assessment of the matrix composition of artefact B revealed a distinctly different MgO/K₂O ratio of 0.71/4.12wt%. Such low values of MgO (more typically <0.5wt%) combined with higher values of K₂O (3 to 7wt%) are strongly associated with the use of purer sources of alkali (Na₂CO₃ and K₂CO₃) in modern glass production.

Appraisal of the fine scale microstructure of such glass artefacts may be achieved by TEM investigation. Figure 3 presents a conventional bright field image, with associated SAED pattern inset, of a crushed fragment of artefact A, being a relict crystalline silica grain. Indeed, dispersions of free silica (probably remnant partially fused quartz sand grains) are common in mediaeval glass but absent in the modern tesserae. Mediaeval tesserae also tend to contain calcium silicate crystals (also not found in the modern tesserae) with CaSiO₃ being dominant and Ca₂SiO₄ being less common. The presence of calcium silicate crystals, probably due to the lack of controlled cooling, together with partially fused silica sand grains reflects the more primitive technologies employed in the production of the mediaeval glasses. These inclusions are either symptomatic of a relatively low processing temperature, associated with mediaeval glass production in this instance, or are an intentional addition to the melt during cool down to provide the contrast revealed by such artefacts.

By way of comparison, Figure 4a presents a bright field image of the dispersed fine scale particles within artefact B. Figure 4b presents a dark field image of one such particle, with the inset SAED pattern, combined with the associated EDX spectrum of Figure 4c, confirming the presence of elemental Cu, as distinct from Cu₂O. Indeed, opacity within glass is caused by the dispersion of minute crystals and it is well known that Cu or Cu₂O metal particles are responsible for red colouration in glass. Conversely, the turquoise colouration associated with artefact A, in this instance, was attributed to the presence of high levels of CuO within the matrix.

4. Summary
The assessment of the matrix composition of archaeological glass mosaics allows distinction to be made between mediaeval and modern artefacts, whilst analysis of the nature and dispersion of inclusions provides supporting evidence for sample opacity and colouration. The sophistication of glass making technology in antiquity, e.g. in terms of the purity of source materials and the temperatures associated with sample processing, can be inferred from such studies of the remnant fine scale microstructure.

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