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Glass mosaic tesserae from Pompeii: an archeometrical investigation

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ABSTRACT. — This work reports the results of an archaeometrical investigation performed, through a multi-technique approach, on a series of Roman glass mosaic tesserae found in Pompeii excavations. Chemical and mineralogical analyses of mosaic tesserae of different colours were performed in order to single out the colouring and opacifying agents employed during the Roman Imperial Age. Moreover, due to the paucity of information on the production technology of mosaic tesserae, the chemical data are compared with that of common transparent glass found at the same site, in order to evaluate whether vessels and mosaic tesserae could have been prepared with the same recipes and starting from the same glass batch. The chemical analyses were performed by electron microprobe, whereas the mineralogical investigation on the opaque samples were carried out by coupling scanning electron microscopy and X-ray powder diffraction. The results obtained show that all the samples analysed have the typical composition of natron-based glass. The similarities with the chemical composition - at least in terms of major elements - of common transparent glass could suggest the use of the same raw materials for the preparation of the batch. All opaque blue and green tesserae contain crystalline aggregates respectively of calcium and lead antimonates, except one blue tessera, which contains traces of cuprorivaite and quartz (Egyptian blue pigment). The red sample

shows the presence of cuprite aggregates dispersed in a lead-rich matrix.

This paper is dedicated to the memory of the friend and colleague Filippo Olmi, who prematurely passed away few months ago.

RIASSUNTO. — In questo lavoro vengono presentati i risultati di uno studio archeometrico condotto su tessere di mosaico provenienti dagli scavi di Pompei. Su numerosi campioni di diverse colorazioni sono state condotte analisi chimiche e mineralogiche al fine di caratterizzare gli elementi cromofori e opacizzanti impiegati in epoca imperiale. A causa della scarsità di informazioni disponibili riguardo la metodologia di produzione delle tessere musive di questo periodo storico, i dati chimici di tali reperti sono stati confrontati con quelli relativi a vetri trasparenti di uso comune rinvenuti negli stessi scavi, allo scopo di valutare l'eventuale uso delle stesse ricette e/o dello stesso vetro grezzo per la produzione di mosaici e di vasellame trasparente. I dati chimici sono stati ottenuti utilizzando la microsonda elettronica, mentre le fasi cristalline, presenti come opacizzanti, sono state caratterizzate con diffrazione X da polveri e osservazioni al microscopio elettronico a scansione. I risultati ottenuti mostrano che tutti i campioni analizzati hanno la composizione tipica del vetro romano al natron. Le strette somiglianze tra la composizione in elementi maggiori delle tessere e dei manufatti trasparenti vitrei provenienti dallo stesso sito, suggeriscono l'impiego delle stesse materie prime per la loro produzione. Tutte le tessere opache analizzate hanno mostrato la presenza di fasi

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cristalline, in particolare antimoniati di calcio nei campioni blu, antimoniati di piombo nei campioni verdi. Solo una tessera blu è risultata essere costituita da blu egizio (cuprorivaite + quarzo). Infine la tessera rossa mostra la presenza di aggregati dendritici di cuprite dispersi in una matrice al piombo.

Key Words: Glass, Pompeii, opacifiers, colorants, EMPA, XRPD, SEM-EDS.

INTRODUCTION

Mosaics are often considered to be one of the most outstanding and elaborate form of wall decoration in antiquity. Yet, little is known about their manufacturing technique and where the raw materials came from. Archeometrical investigations, aimed at understanding the composition and production techniques of these materials, have been performed in recent years, however some issues are still unresolved (see e.g. Brun *et al.*, 1991; Fiori and Vandini, 1996; Mass *et al.*, 2002; Mirti *et al.*, 2002; Shortland, 2002a).

In the Roman age, beginning in the first half of the first century B.C., mosaics became an autonomous form of artistic expression. Stone mosaics - in general built with coloured rock fragments - were at first used exclusively for the decoration of floors, meeting the need to create works of art that would persist over time. This form of artistic expression aimed at creating visual decorations that, contrary to paintings, could be walked on and could easily be washed. The first most outstanding examples of these mosaics were situated in the dining rooms of the houses where simple terracotta was not sufficiently decorative. Paintings adorned the walls, but the mosaic flooring was ideal from the point of view of both its beauty and its practical aspects. At Pompei mosaics were widely used also to decorate the walls of fountains, swimming pools, columns and vaulted ceilings, particularly in the fountains set in the gardens. These wall mosaic, that become well diffused in the Imperial Age, were made with glass paste, shells, and enamels to accentuate their brilliance.

The knowledge of Roman glass comes mainly from Plinius's writings (Naturalis Historia XXXVI), from archaeological excavations and from chemical analysis of the finds. The most reliable hypothesis regarding the production and distribution of glass in the Roman Age is that most of the glass produced in the Western provinces of the Empire came from large primary furnace sites in Middle Eastern regions (e.g. Turner, 1956; Picon and Vichy, 2003; Nenna, 1998), where sand and flux were melted together to produce large glass chunks. Following the Plinius description, the melting process took place in several steps and in different ovens in order to obtain a workable melt, homogeneous and without bubbles. Then the raw chunks were exported to be worked in widely distributed secondary production sites in the West, where the ingots were re-melted, coloured (or decolorized) and shaped (Freestone, 1994; Freestone et al., 2000; Vallotto and Verità, 2000). It thus seems logical that the basic recipe for the production of opaque glass in Roman times, would have been the same employed for the manufacture of vessels, and that only colouring and opacifying agents were added to the batch during the re-melting and shaping. The colouring of glass was probably the main issue, since it represents a difficult process for a variety of reasons. The first was knowing which ingredients to add: some colours were easy to produce, others, particularly the opaque colours, were far more complex. For example, opaque yellow and green required much skill in preparing the intermediate compound, dark blue required the addition of cobalt, a relatively rare component; red opaque tesserae require careful control of the oxidation condition of the furnaces. The heat of the furnace, the base composition of the glass, the temperature reached in the furnace, and the duration of heating were additional factors affecting the colour of the finished product (Newton, 1980). Hence, after James (2006), it is unlikely that raw or recycled glass was imported for tesserae manufacture, since it would be much easier to use coloured glass, in cake or sheets.

In this work several tesserae of different colours – coming from Pompeii excavations – were selected in order to obtain information about the production cycles and the raw materials employed. Unfortunately, the precise provenance of these finds is not clear, since they were stored in Pompeii excavation deposits and precise data about the archaeological context were not available. However, their archaeometrical investigation represents a

very useful mean to add important information to the poor knowledge of mosaic glass manufacture of Imperial Age. In fact, it is still unclear whether opaque glass (in particular mosaic tesserae) and common trasparent glass were produced at the same sites and with the same recipes through the centuries. The aim of this work is twofold: i) to characterize, from the chemical and mineralogical point of view, the colouring and opacifying agents used, ii) to compare the results obtained here with literature data referred to transparent Pompeian glass (Arletti et al., 2006a, Vallotto and Verità, 2000) to find similarities or discrepancies, at least as regards the major elements, and to evaluate the hypothesis of a common origin for these two kinds of material.

ANALYSED SAMPLES

Eight mosaic tesserae (about 5×5 mm) of different colours, were analysed:

• Blue and light blue samples (PM 003, PM 005, PM 007, PM 002).

Two of the three blue samples (PM 003 and PM 005) are opaque with a very dark blue colour; their surface is quite smooth and numerous bubbles are present. Sample PM 007 has a different appearance and an irregular surface, it seems to be an aggregate of small spherules of different blue nuances, suggesting it is a fragment of a pigment rather than a mosaic tessera. Sample PM 002 has a very light turquoise tint, few bubbles are present but its surface is visibly streaked.

• Green and yellow tesserae (PM 004, PM 006, PM 008).

The dark green tessera (PM 004) is slightly transparent with a very uniform appearance; only few circular bubbles are present. By contrast yellow samples PM 006 and PM 008 - which differ only for a green nuance of the latter - have heterogeneous surfaces, with several bubbles and crystalline inclusions.

• Red tessera (PM 012).

In the sample set only one tessera is red and its appearance is only slightly vitreous. A strongly opaque light green rim on all the sides of the tessera is observed, probably the result of surface weathering.

EXPERIMENTAL

EPMA analysis

Wavelength dispersive Electron Microprobe Analysis (EPMA) was used to determine the chemical composition of major and minor elements. Small glass fragments of almost 1 mm³ were removed from the glass artefacts and mounted in a epoxy resin. After preparation the samples were polished using a series of diamond pastes from 6 to 1µm. A carbon coating was applied to the polished sections to prevent charging under the electron beam. The analyses were carried out by an ARL - SEMO electron microprobe equipped with four scanning wavelength spectrometers at the Department of Earth Science of Modena and Reggio Emilia University. The elements analysed were: Si, Ti, Al, Mn, Mg, Fe, Ca, K, Na, P, Co, Sb, Cu. Pb. A series of certified natural standards were employed. The analyses were performed operating at 15 kV, 20 nA, using counting times of 5,10,5 sec. on background-peak-background respectively (Arletti, 2005). To prevent the known migration phenomenon of alkalis under the electron beam (Rinaldi, 1981), a 30 µm defocused beam was used. Several points were analysed on each sample and the mean value of all the measurements was calculated. The results were processed for matrix effects using the PHI(pZ) absorption correction of the Probe program (Donovan and Rivers, 1990). The results for major and minor elements are reported in Table 1.

Scanning Electron Microscopy

Backscattered electron images (BSE) and energy-dispersive (EDS) spectra were collected on polished samples, using a Philips XL40 electron scanning microscope equipped with an energy dispersive spectrometer OXFORD - SATW at the *Centro Interdipartimentale Grandi Strumenti* of the University of Modena and Reggio Emilia. The analyses were performed using an acceleration voltage of 25 kV and a working distance of 12 mm. BSE images were mainly collected on opaque glasses to highlight the presence of crystalline opacifying agents in the glass matrix, and EDS analyses were run to obtain qualitative chemical analysis of the inclusions.

Samples	PM 002 Light-blue	PM 003 Dark-blue	PM 004 Dark-green	PM 005 Dark-blue	PM 006 Yellow	PM 007a Blue	PM 007b Blue	PM 008 Yellow-green	PM 012 Red
Al_2O_3	2.39	2.48	2.57	2.70	2.48	0.25	0.01	2.81	1.57
TiO ₂	0.09	0.09	0.11	0.07	0.08	0.02	0.04	0.17	0.26
MnO	0.43	0.50	0.63	0.66	0.41	0.00	0.02	0.45	0.01
MgO	0.67	0.56	0.98	0.59	0.58	0.09	0.01	1.01	0.47
FeO	0.52	0.91	0.84	0.87	0.70	0.09	0.00	0.92	0.64
CaO	7.52	7.25	6.72	7.81	6.79	14.30	0.02	6.51	3.03
Na ₂ O	16.57	17.29	16.43	17.83	16.33	0.45	0.08	18.23	14.33
K ₂ O	0.66	0.60	0.90	0.61	0.63	0.09	0.00	0.79	0.22
P_2O_5	0.24	0.08	0.26	0.11	0.12	0.00	0.00	0.28	0.02
Sb ₂ O ₅	3.20	1.48	0.14	3.59	0.44	0.00	0.00	0.21	1.45
Cu ₂ O	0.43	0.23	3.46	0.11	0.41	19.27	0.21	0.97	8.40
PbO	0.77	0.04	2.24	0.02	4.55	0.00	0.00	3.08	23.88
СоО	0.01	0.12	0.00	0.10	0.01	0.01	0.02	0.00	0.39
Totals	99.04	99.58	98.85	98.71	98.72	97.29	99.07	99.08	101.03

TABLE 1 – Electron microprobe analyses (wt% in oxides)*.

* average of 8 analyses on different spots.

X-Ray Powder Diffraction

X-ray powder diffraction spectra were collected from all the samples, with the aim of identifying the crystalline phases dispersed in the glass matrix. The analyses were carried out on few mgs of glass powder using a Philips PW1729 diffractometer with Bragg-Brentano geometry θ - 2θ and CuK α radiation using a zero background quartz holder. The spectra were collected from 5 to 80° 2 θ by using a 0.02° θ step and counting time of 4 sec for each step.

RESULTS

Chemical analyses

From the chemical results of the major elements in the mosaic tesserae (Table 1) it is clear that sample PM 007 is not a glassy tessera, but a heterogeneous mixture of at least two different phases – reported in two different columns of Table 1: a) a phase rich in Cu, Ca and Si, and b) quartz.

The chemical data of the other tesserae show that almost all the samples have the characteristic composition of silica-soda-lime Roman glass typical of the Imperial Age, showing high levels of SiO₂ (ranging from 62.73 to 67.95%), Na₂O (16.33 - 17.83%) and CaO (6.72 - 7.81%) (e.g. Turner, 1956; Sayre and Smith, 1961; Henderson. 1985; Verità, 1995). The Al₂O₃ content is quite low and constant over the whole sample set, probably reflecting the constant presence of feldspar in the sands used for production (Freestone, 1994). In fact, the levels of CaO and Al_2O_3 of these tesserae roughly match the ratio found in typical Roman glass, suggesting the use of calcareous sands containing feldspar as impurities. The only exception is sample PM 012, with lower levels of these elements as a consequence of high levels of lead (PbO exceeding 20 %) present in this tessera. The low concentrations of K_2O , MgO and P_2O_5 suggest that almost all samples were produced using natron as flux. Natron is a natural sodium sesquicarbonate (Na₂CO₃·NaHCO₃·2H₂O) that, especially during Roman Age, was mined in Egypt

(Wadi Natrun, North-West of Cairo) and used in glass-making activities throughout the Empire. The glass produced using this mineral source of alkalis is well discriminated from that produced using flux from organic sources (i.e. plant ash), which, along with Na₂O, generally presents higher levels of K₂O and MgO (Lilyquist and Brill, 1995).

The amount of TiO_2 , FeO and MnO are very low, never exceeding 1%, and hence these elements were probably present as impurities in the sands. In general, intentional addition of iron, to confer a green nuance to the glass, or of manganese, as decolouring agent, is shown by higher percentages of these oxides in the glass composition (Henderson, 1985).

The elements responsible of the colour and the opacity of these tesserae are Sb, Pb, Cu and Co. These elements are present in a wide range of concentrations (Table 1), in relation to the colour gradation and opaque effects of the tesserae. These issues will be dealt with in detail in the next sections.

The chemical results reported here were compared with literature data for transparent glass found at Pompeii excavations (Arletti *et al.*, 2006a, Vallotto and Verità, 2000) to evaluate a possible common origin for opaque and transparent glass coming from the same site. In Figures 1 and 2 the levels of CaO vs Al₂O₃, and of K₂O vs MgO for the samples analysed in this work are compared with literature data for Roman glass from Pompeii. In Figure 1, where the compositional field of European Roman glass is drawn with dashes, almost all the samples (transparent and opaque) fall inside this area. Only PM 012 tessera shows lower levels of CaO and Al₂O₃, as a consequence of its high content of lead (which induces a dilution in the other oxides). The chemical data for transparent samples from literature have a spreader distribution, however the compositional field of the 2 sample sets are almost overlaid. In Figure 2 the compositional range of natron-based glass and plant ash-based glass are delimited. All the samples studied in this work fall inside the first field and for only two Pompeian transparent samples the levels of MgO are slightly higher.

Figures 3 and 4 report the data for TiO_2 , MnO and FeO contents. The levels of the minor elements MnO and TiO_2 , non intentionally added to the glass, are comparable for transparent common glass and mosaic tesserae. Only the sample PM 012 has a different composition, since it does not

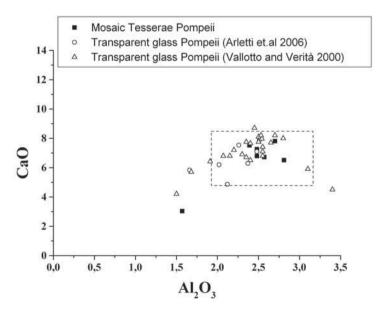


Fig. 1 – CaO vs Al_2O_3 for analysed samples and for the finds reported by Arletti *et al.* (2006a) and Vallotto and Verità (2000). The compositional field of European Roman glass is drawn with dashes.

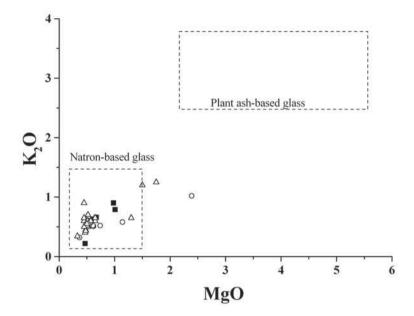


Fig. $2 - K_2O$ vs MgO for analysed samples and for the finds reported by Arletti *et al.* (2006a) and Vallotto and Verità (2000). Rectangles represent compositional classes for natron and Na-plant ash based glass (Lilyquist and Brill, 1995). Symbols are the same of Figure 1.

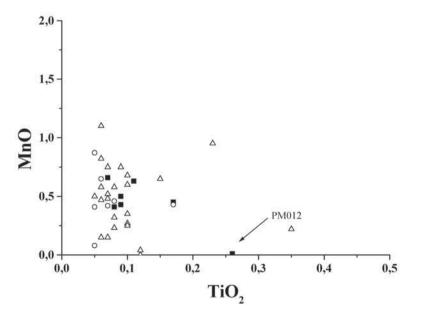


Fig. 3 – MnO vs TiO₂ for the analysed samples and for the finds reported by Arletti *et al.* (2006a) and Vallotto and Verità (2000). Symbols are the same of Figure 1.

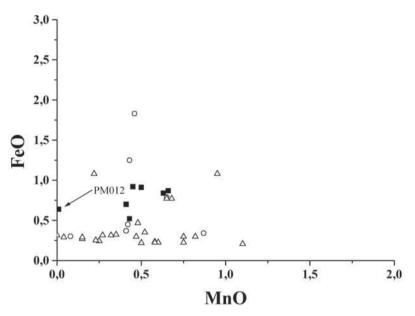


Fig. 4 – FeO vs MnO for the analysed samples and for the finds reported by Arletti *et al.* (2006a) and Vallotto and Verità (2000). Symbols are the same of Figure 1.

contain manganese at all, but it is rich in titanium. This, along with the high level of lead and copper, makes this sample an exception from a chemical point of view. The situation is slightly different when FeO content is taken into account; in fact the plot of Figure 4, shows that, on average, the mosaic tesserae have higher iron contents than the transparent samples. Only four samples taken from literature have higher contents, but it is worth noting that these are deeply coloured transparent glass. It is hence reasonable to conclude that the higher levels of iron in coloured samples (though never exceeding 1%) could be the consequence of successive addition to the batch of colouring compounds, containing iron as impurity.

Colouring and opacifying elements

As reported in the previous paragraph, one of the blue samples (PM 007) is not a homogeneous vitreous material but it is composed by two phases: quartz and a phase rich in Si, Ca, and Cu. XRD analysis of this last phase corresponds to cuprorivaite CaCuSi₄O₁₀. In addition to the crystalline phases, the spectral background

suggests the presence of an amorphous one (Noll et al., 1975). BSE image (Figure 5) confirmed the presence of two different phases. Cuprorivaite, also known as Egyptian Blue, was the first synthetic pigment even produced. It appeared for the first time in Egypt in the 3rd millennium B.C. (Fouqué, 1889; Ullrich, 1987); later Vitruvius (VII, 11) reports that its formula was brought from Egypt to Pozzuoli, hence Egyptian blue became very common in Pompeii and Herculeneum (Chase, 1971). This pigment has been widely analysed and characterized in recent years (Pabs, 1959; Mirti et al., 1995; Bianchetti et al., 2000). It was prepared by melting silica, calcium carbonate, and sodium flux at about 900°C, while, as Cu source, either malachite or scrap metals were used. Small amounts of tin could prove the use of scrap metals (Damiani et al., 2003); in this study, however, tin analysis was not performed, so it is impossible to define the copper source used. Cuprorivaite also occurs in nature near Naples (Mount Vesuvius area) but it is in general a very rare mineral phase (Minguzzi, 1938).

Samples PM 003 and PM 005 show a very dark blue colour, consistent with the presence of

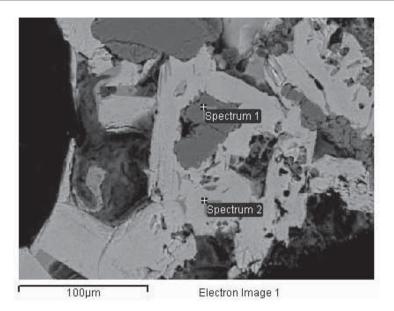


Fig. 5 – BSE image of sample PM 007 showing the presence of quartz (dark grey) and of a silicatic phase rich in Ca and Cu (light grey). The labels indicate the points where the EDS analyses were performed.

relatively high amounts of cobalt (CoO around 0.10%, see Table 1). The SEM-EDS analyses performed on these tesserae show the presence of crystals of 1-2 µm containing calcium and antimony (Figure 6). Sample PM 002 has a lighter colour when compared with the previous ones, consistent with the chemical analysis that indicates a non detectable Co level. The light blue colour is probably due to the presence of low amounts of copper (see Table 1). Among the blue samples, PM 002 has the highest antimony oxide content (3.2%), in agreement with the backscattered image (Figure 7), which shows the presence of an high amount of calcium antimonate crystals of few microns across. Although the presence of dispersed opacifying particles was verified by BSE image for all the blue tesserae (even if in different amounts) none of XRPD spectra presented diffraction peaks.

Two green tesserae were analysed, a transparent dark green (PM 004) and an opaque yellow-green (PM 008). As expected, no particles were identified in the first sample by SEM observations. The BSE image (Figure 8) shows a stripy surface, with two different grey tonalities. However, the qualitative chemical analysis of the two portions does not show significant compositional differences. The intense green colour of tessera PM 004 is probably mainly due to copper, which is present in a very high percentage (Cu₂O = 3.46%, Table 1).

SEM-EDS investigation carried out on the yellow–green sample (PM 008) revealed large particle aggregates, containing lead and antimony, dispersed in a lead-rich matrix (Figure 9). The same aggregates were also found in the yellow tessera (PM 006), in agreement with the EPMA results. XRPD analyses performed on these two samples allowed to identify the presence of $Pb_2Sb_2O_7$. The red tessera PM 012 has a green rim probably due to marked weathering. XRPD pattern of the whole tessera indicated the presence of malachite and cuprite in the rim and bulk, respectively. Large dendritic crystals of cuprite are responsible for the red opaque effect of the inner part of this tessera as demonstrated by SEM analysis (Figure 10).

DISCUSSION AND CONCLUSIONS

The parameters that affect the colour and the opacity of glass are complex. The most common

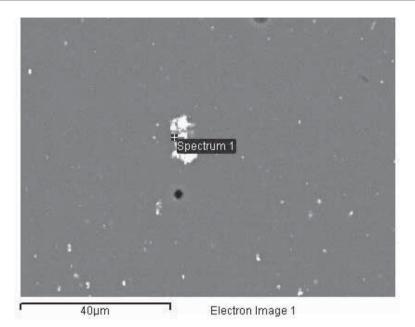


Fig. 6 - BSE image of sample PM 003. The label indicates the point where the EDS analysis was performed.

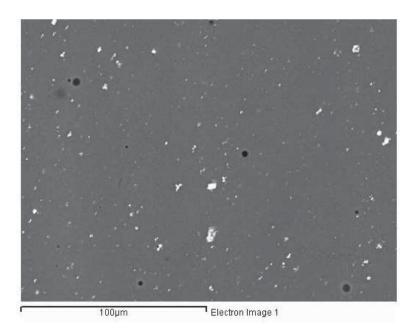


Fig. 7 – BSE image of sample PM 002.

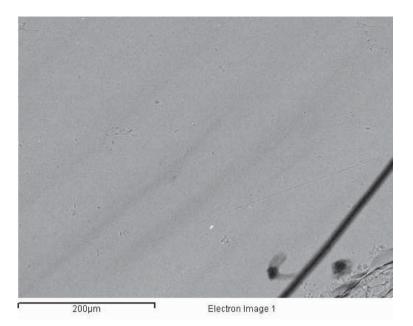


Fig. 8 – BSE image of sample PM 004.

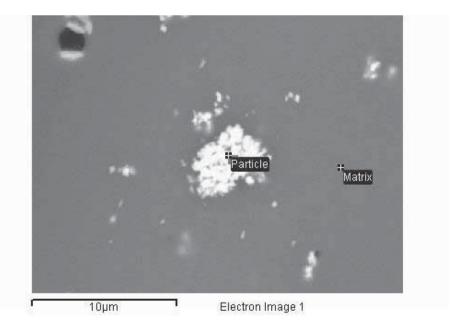


Fig. 9 - BSE image of yellow sample PM 008. The labels indicate the points where the EDS analyses were performed.

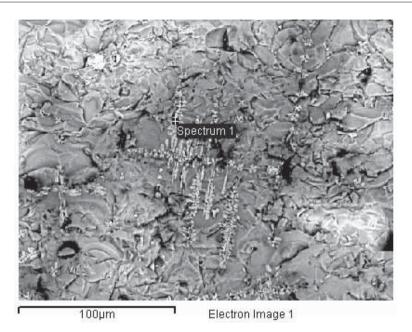


Fig. 10 - BSE image of sample PM 012 showing the presence of dendrites of cuprite.

colorants used in the production of coloured glass are transition metals; the colour of glass depends on the characteristic frequencies of the visible light absorbed by the colorant in the glass as the result of a d-d electronic transition. The opaque effect in glass is obtained by the scattering of crystals of appropriate size (less than the incident light wavelength) dispersed in the glass matrix. The scattering of crystals dispersed in a glassy matrix has been studied in detail by Mie (1908), demonstrating that the intensity of the opacifying effect depends on the number and dimension of the particles, and on the difference between the refraction index of the opacifier and that of the matrix.

The opaque effect of the blue vitreous samples studied is certainly due to the presence of calcium antimoniate crystals, although XRPD experiments did not reveal the presence of the corresponding peaks, due to the strong background of the glass matrix. Our results are in agreement with several studies on white, turquoise, and some deep blue opaque glass, which revealed that the opacity is caused by small particles of calcium antimonate $(Ca_2Sb_2O_7 \text{ or } CaSb_2O_6)$ within the matrix (Calvi

et al., 1963; Mirti et al., 2002; Shortland, 2002a, Arletti et al., 2006a). These particles are mostly small and well dispersed in the glass and are new formed phases obtained by adding an antimony source, probably roasted stibnite, to a Ca-bearing batch. The deep blue colour is induced by the presence of very low amounts of cobalt, the most powerful blue colorant used in ancient times. Thanks to its linear absorption coefficient, the colouring power is five time greater than that of other transition metals: to produce a deep blue colour only a few hundred ppm are needed. All the blue samples have rather high amounts of copper associated to cobalt, suggesting that these two elements were associated in the Co-bearing raw materials. Cobalt, in fact, is often present in rock mineralisations associated to copper, like in trianite (2Co₂O·CuO·6H₂O) or to arsenic in the sulfide cobaltite (CoAsS) or to other transition metals, like iron, nickel, and arsenic (Co, Fe, Ni)As₃. Gratuze and co-workers (1992) analysed several blue glass coming from France, from the Bronze age to the 18th century and found three main groups of samples on the basis of the elements associated to cobalt. One set containing Co associated to Zn-InPb, one set containing sample high in Co, Ni and As and one including glass containing high cobalt amount, sometimes related to high nickel contents, sometimes not related to any particular element. However, these elements were not determined in this study, so it is impossible to classify the finds in one of the three compositional groups.

The yellow nuance and the opaque effect in samples PM 006 and PM 008 (yellow and yellowgreen tesserae) are due to Pb₂Sb₂O₇ particles (Caley, 1962; Lilyquist and Brill, 1995; Shortland, 2002a). If we consider the PbO/Sb₂O₅ ratio in a yellow opaque glass, we notice that, in general, it is much higher than that required by the stochiometry of the lead antimonate. This means that lead antimonate was added to the glass along with other additional lead compounds. The origin of this lead antimonate in the glass is still uncertain and several hypotheses have been proposed concerning the production of yellow opaque glass. The most likely is that the minerals used are galena (PbS), as a source for lead, and stibnite (Sb_2S_2) for antimony. The ragged edges of the crystals suggest that they were added to the glass as lead antimonate in the presence of a lead excess, rather than as two different compounds (Shortland, 2002 a,b). The resulting green colour of sample PM 008 is produced by the co-presence of copper (which in its oxidised form confers a green colour) and of yellow lead antimonate.

In recent years, several studies on red opaque glass have been performed to single out the agents responsible of both colour and opacity. Following Weyl (1951), the colour in red glass is produced by crystals of metallic copper dispersed in the glass matrix, the differences in the resulting nuances being mainly related to the dimensions of the particles. Mirti et al. (2002), studying glass fragments of the 7th-8th century from Cripta Balbi in Rome, found some red opaque samples containing small spherules of metallic copper, smaller than 1µm across, dispersed in a homogeneous matrix. Padovani and co-workers (2003, 2004) in a study of red lustre decorations of Italian Renaissance pottery, found that the majority of copper was present as monovalent species, along with a minor level of metallic nano-particles. They concluded that the chromatic effect was determined only by the fraction of metal ions reduced to nano-particles. Also an EXAFS study performed on opaque red glass of the Roman Age from Italy (Arletti et *al.*, 2006b) demonstrates that copper is present as monovalent cations coordinated to the oxygen atoms of the glass framework, accompanied by metallic clusters. A study on Celtic opaque red glass containing lead (Brun *et al.*, 1991), revealed the presence of a large number of dendritic crystals of cuprous oxide (Cu₂O), together with a few metallic copper nodules. Thus, red opaque glass can contain metallic copper clusters along with cuprous oxide particles, and copper cations dispersed in the glass matrix.

In the red tessera studied in this paper (PM 012), a large number of dendritic crystal of cuprite were found dispersed in the lead-rich matrix in agreement with the results of Brun et al., (1991). The glass composition and the melting conditions are the parameters that control the copper oxidation state. The presence of lead in the glass batch greatly facilitates the achievement of reducing conditions (Ahmed and Ashour, 1981), since this element displaces the redox equilibrium of copper to the cuprous state (Cu $^{2+} \rightarrow$ Cu⁺) whereas to obtain metallic copper (Cu⁰) a stronger reducing condition - obtained usually with the addition of Fe-is needed. The presence of cuprite as opacifier, and the related high level of lead, is very unusual in Roman times, when for red tesserae the opaque effect was generally achieved by means of metallic copper particles (Arletti et al., 2006b). This could suggest that the sample PM 012 is either a failed production of glass with metallic Cu or a tessera of successive restoration, even though no literature data on Pompeii mosaic restorations is known. As seen in the previous section, a strong weathered malachite rim is present on our red tessera. None of the metallic Cu-bearing opaque red glass previously analysed and reported in literature show a similar weathering rim. Probably, the presence of cuprite crystals favours glass weathering, since monovalent copper is less stable and more alterable and subject to oxidation processes than metallic particles.

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REFERENCES

- AHMED A.A. and ASHOUR G.M. (1981) Effect of heat treatment on the crystallisation of cuprous oxide in glass. Glass Tech., 22, 24-34.
- ARLETTI R. (2005) *The ancient Roman glass:* an Archaeometrical investigation. PhD thesis, University of Modena and Reggio Emilia.
- ARLETTI R., CIARALLO A., QUARTIERI S., SABATINO G. and VEZZALINI G. (2006a) – Archaeometrical Analyses of Game Counters from Pompeii. In: "Geomaterial in cultural heritage", ed. M. Maggetti and B. Messiga, Special Publication Geological Society of London, 257, 175-186.
- ARLETTI R., DALCONI M.C., QUARTIERI S., TRISCARI M. and VEZZALINI G. (2006b) – *The Ancient Glass Production: XAFS study on Roman opaque glass*. Appl. Phys. A, **83**, 239-245.
- BIANCHETTI P., TALARICO F., VIGLIANO M.G. and ALI M.F. (2000) – Production and characterization of Egyptian Blue and Egyptian green frit. J. Cultural Heritage, 1, 179-188.
- BRUN N., MAZEROLLES L. and PERNOT M. (1991) – *Microstructure of opaque red glass containing copper.* J. Mat. Sci. Lett., **10**, 1418-1420.
- CALEY E.R. (1962) Analyses of ancient glasses 1790-1957: a comprehensive and critical survey. Corning Museum of Glass, Corning, New York.
- CALVI M.C., TORNATI M. and SCANDELLARI. M.L. (1963) – Ricerche tecnologiche. In: "I Vetri Romani del museo di Aquileia". Calvi M.C ed., Aquileia, 195-208.
- CHASE W. T. (1971) Egyptian Blue as a Pigment and Ceramic Material. In: "Science and Archaeology", MIT Press, Cambridge.
- DAMIANI D., GLIOZZO E., MEMMI TURBANTI I. and SPANGENBERG E. (2003) – Pigments and plasters discovered in the house of Diana (Cosa, Grosseto, Italy): an integrated study between art history, archaeology and scientific analyses. Archaeometry, 45, 341-354.
- DONOVAN J.J. and RIVERS M.L.(1990) PRSUPR - a PC- based automation and analysis software package for Wavelength-Dispersive Electron-

Beam microanalysis.In: *MicrobeamAnalysis*", J.R. Micheal and P. Ingram eds., San Francisco Press, San Francisco, 66-68.

- FIORI C. and VANDINI M. (1996) Chemical composition of glass and its raw materials: chronological and geographical development in the first millennium A.D. Firenze, Leo S. Olschki Editore.
- FOUQUÉ F. (1889) Sur le bleu Egyptien ou vestorien. Bull, Soc. Fr. Minéral., **12**, 36–38.
- FREESTONE I.C. (1994) Chemical analysis of "raw" glass fragments. In: "Excavation of Chartage, Vol II". Hurst H.R ed, The Circular Harbour, North Side, Oxford University Press.
- FREESTONE I.C., GORIN ROSEN Y. and HUGHES M.J. (2000) – Primary glass from Israel and the production of glass in late antiquity and in the early Islamic period. In: "La route du Verre. Ateliers primaires et secondaires de verriers du second milliaire av J.C. au moyen –Age", Travaux de la maison de l'Orient Méditerranéen, 33, (ed M.D. Nenna) Jean Poilloux, Lyon, 65-84.
- GRATUZE B., SOULIER I., BARRANDON J.N. and FOY D. (1992) *De l'origine du cobalt dans les verre*. Revue d'Archeometrie, **16**, 97-108.
- HENDERSON J. (1985) The raw materials of early glass production. Oxford J. Arch., 4, 267-291.
- JAMES L. (2006) *Bizantine glass mosaic tesserae: some materials considerations*, Byzantine and modern Greek studies, **30**, 29-47.
- LILYQUIST C. and BRILL R.H. (1995) *Studies in ancient Egyptian glass.* Metropolitan Museum of Art, New York.
- MASS J.L., WYPYSKY M.T. and STONE R.E. (2002) – Malkata and Lisht glassmaking technologies: toward a specific link between second millennium BC metallurgist and glassmaker. Archaeometry, 44, 67-82.
- MIE G. (1908) Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. Ann. der Phys., 25, 377-445.
- MINGUZZI C. (1938) Cuprorivaite un nuovo minerale. Per. Mineral., 8, 333-345.
- MIRTI P., DAVIT P. and GULMINI M. (2002) Colourants and opacifiers in seventh and eight century glass investigated by spectroscopic techniques. An. Bioanal. Chem., **372**, 221-229.
- MIRTI P., APPOLONIA L., CASOLI A., FERRERI R.P. and LAURENTI E. (1995) – *Spectrochemical and structural studies on a Roman sample of Egyptian Blue*. Spectrochim. Acta, **51**, 437-446.
- NENNA M.D. (1998) Atéliers de production et sites de consummation en Egypte (V siècle av. J.c.

VIII s.ap. I.C.). In: "Annales 14^e Congrès AIHV, Venezia", Milano, 20-24.

- NEWTON E.G. (1980) Recent views on ancient glass. Glass Tech., 21, 173-183.
- NOLL W. and HANGST K. (1975) Ancient green and blue pigments. N. Jahr. Min. Monat., **1975**, 529-540.
- PADOVANI S., SADA C., MAZZOLDI P., BRUNETTI B., BORGIA I., GIULIVIA., SGAMELLOTTI S., D'ACAPITO F. and BATTAGLIN. G. (2003) – Copper in glazes of Renaissance luster pottery: Nanoparticles, ions, and local environment. J. Appl Phys., 93, 158.
- PADOVANI S., BORGIA I., BRUNETTI B., SGAMELLOTTI S., GIULIVI A., D'ACAPITO F., SADA. C. and BATTAGLIN G. (2004) – Silver and copper nanocluster in the lustre decoration of Italian reinassance pottery: an EXAFS study. Appl. Phys. A., 79, 229-233.
- PABS A. (1959) Structure of some tetragonal sheet silicates. Acta Cryst., 12, 733.
- PICON M. and VICHY M. (2003) D'Orient et Occident: l'origine de verre à l'époque romaine et durant le haut Moyen Âge. In: 'Échanges et commerce du verre dans le monde antique', Foy D. and Nenna M.D. eds, Éditions Monique Mergoil, Montagnac, 17–31.
- PLINIO, Naturalis Historia XXXVI, 199.
- RINALDI R. (1981) La microsonda elettronica. In: "Microscopia elettronica a scansione e microanalisi, parte II" Armigliato A., Valdrè U. eds., Lo Scarabeo, Bologna.

- SAYRE E.V. and SMITH R.V. (1961) Compositional Categories of Ancient Glass. Science, **133**, 1827-1826.
- SHORTLAND A.J. (2002a) The use of antimonate colorants in Early Egyptian Glass. Archaeometry, 44, 517-530.
- SHORTLAND A.J. (2002b) Comment II Mass J.L., Wypysky M.T., Stone R.E. (2002) - Malkata and Lisht glassmaking technologies: toward a specific link between second millennium BC metallurgist and glassmaker. Archaeometry, 44, 67-82, and Reply, Archaeometry, 45, 185-198.
- TURNER W.E.S (1956) Studies in ancient Glasses and Glassmaking Processes. Part IV: The chemical composition of ancient glasses. J. Soc. Glass Technol., 40, 162-86.
- ULLRICH D. (1987) Egyptian Blue and green frits characterisation, history and occurrence, synthesis. PACT, **17**, 323-332.
- VALLOTTO M. and VERITÀ M. (2000) Glasses from Pompeii and Herculaneum and the sands of the River Belus and Volturno. In: "Homo Faber: Studies on Nature, Technology, and Science at the time of Pompeii", Munich.
- VERITÀ M. (1995) Le analisi dei vetri. In: 'Le Verre de l'Antiquite Tardive et du Haut Moyen Age', Foy D. (ed) Musee Archeologique Departemental du Val d'Oise, 291-300.
- WEYL W.A. (1951) Coloured Glass, Corning Museum of Glass, New York.