

Archaeometric studies on a Pompeian blue glass fragment from *Regio I, Insula 14* for the characterization of glassmaking technology

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Research Article

Keywords: Pompeii, Primary production, Raw materials, Natron-lime glass, Sand, Western Mediterranean, glass compositions

Posted Date: August 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-754282/v1>

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Abstract

A Pompeian glass sample found in *Reg. I, Insula 14*, during the 1950's Pompeii excavation was examined by Raman and Fourier transformed infrared spectroscopy, scanning electron microscopy, and inductively coupled plasma mass spectrometry. The analyzed specimen was selected based on its intense blue color and its well-preserved aspect. The purpose of the work was the chemical characterization of Pompeii's glass in correlation to the actual knowledge of Roman glassmaking technology from the Mediterranean area. The results suggested that the Pompeii's glass was a soda-lime-silica glass, but with a higher calcium content that, given the low content of lead, was used to stabilize the glass. The sample was in origin produced most likely as non-decolorized primary raw materials from eastern Mediterranean sites. Moreover, the intense blue color was related to the use mainly of cobalt, present in a weighty amount, and likely used as important coloring agents in the ancient secondary glass-making workshop.

Introduction

Pliny The Elder, with its *Natural Historia*, represents one of the most relevant written witnesses regarding glass production in Antiquity. Studies made on the glass as archeology material have multiplied in recent years thus contributing to a more accurate description regarding the shapes, the state of conservation, and the production process of the artifact. In the Roman era, the production of glass covered many aspects of daily life. In particular, Pliny described that the achievement of glassmaking was depending on a mixture of soda (*natron*) and the sand, particularly that from a beach near the mouth of the River Belus, on the Syria coast. For several centuries the production of glass was depended exclusively on this area (*Nat. Hist.* book XXXVI. Chapter 65) [1]. However, according to Pliny, this glassmaking description was considered as an old method since also in Italy white sand forming the River of Volturno on about 20 km of the coast between Cuma and Liternum was useful for glassmaking. This kind of sand was softest and grounded in a mortar or mill. The sand was subsequently mixed with soda in a 1:3 ratio and after fusion was then transferred to other furnaces. The molten forms a lump, also known in Greek as sand soda (*hammonitrum*) that was again melted to form a pure colorless glass (*Nat. Hist.* Book XXXVI. Chapter 66) [1, 2].

Besides Pliny's narration, the production of Roman glass, as deduced chemical analyses of Roman specimens (dated from the first century B.C. up to the VII century A.D.) required two major components: sand and natron (probably Egyptian soda) mixed in appropriate proportions [3]. In particular, natron glass was made only in a few numbers of "primary" centers in Egypt and Syro-Palestine [4–6] Several investigations were focused on the identification of the origin of the raw materials and the Roman empire geographical location where the glass was produced [7–9]. The most recognized hypothesis was that the materials for glass production for primary workshops were performed in the Middle East [10]. In particular, Palestine using mainly the sand taken from the river Belus as a primary source to make the raw materials that were then broken into chunks and transported to workshops across the empire for shaping [11]. Generally, the raw material, added with copper and soda (natron), was melted in furnaces where dull black lumps were formed. Subsequently, the reduced lumps were fused in secondary workshops and tinted or shaped by blowing or by lathe machine [5, 12]. Secondary workshops were very productive all over the Roman Empire. The reduction of the melting temperature of the silica (from 1700°C to about 1000°C) was achieved by adding either soda (Na_2O) or potash (K_2O) [13]. However, also other oxides were used such as lead oxide (PbO). Nevertheless, glasses fabricated only from silica and soda resulted unstable and subject to destruction from water. Therefore, glass stabilizers like lime (CaO) or lead (PbO) were required [14],

even though a low amount of these additives contributed to poor chemical durability of the glass while a higher amount rendered the glass prone to devitrification [15]. The presence of alumina (Al_2O_3) or magnesia (MgO) prevents the devitrification of the glass [16].

Regarding Pompeii's glass manufacturers, many studies have been carried following Pompeii's excavations. Vallotto and Verità, 2002 [17], showed no great differences in the content of sodium oxide. In particular, the ratio between silicon and natron did not show great variability. Several Pompeian glasses showed similarity with the sand from the River Belus, thus suggesting the use by Pompeian workshops of primary glass raw coming from the Middle East. Nevertheless, it cannot be excluded primary raw glass production from other sites (perhaps the Volturno river or the provinces of Spain and Gaul) [1]. Also, hundreds of Pompeian glass finds, classified as 'game counters', have been identified. These manufacturers were also described by Pliny the Helder as products of a melting recycling procedure leading to transparent, opaque, or widely colored objects, thus representing an example of glass production activities during the Roman epoch. Several studies on these finds were mainly finalized for the identification of coloring or opacifying compounds [18–21]. Moreover, Pompeii's excavations revealed the presence of glass production workshops probably dated before the Vesuvius eruption in 79 A.D. [12, 22].

Archaeometric methodology applied to cultural heritage is essential to obtain evidence on materials, production techniques, and habits of ancient people [23]. In particular, the multidisciplinary approach allows solving archaeometry problems regarding glass production through Roman times. The present work aims to provide a further contribution to the knowledge of the materials and execution techniques used in Roman glass-making. Therefore, using different analytical approaches, we tried to determine the chemical composition of a Pompeian's blue glass fragment that, as an archaeological find, was quite rare and characterized by excellent durability and a good state of conservation. Besides, we tried to highlight the technology used for its production.

Materials And Methods

Light microscopy and X-ray diffractometry

The specimen was observed using a Nikon Eclipse L 150 reflected light microscope.

X-ray diffractometric analyzes (XRD) were carried out using a Miniflex Rigaku X-ray diffractometer with a Cobaltum tube, operating conditions 30 kV and 15 mA.

Scanning Electron Microscope

Textural and semi-quantitative chemical analyses were performed by using a scanning electron microscope (SEM) JEOL-JSM 5310, coupled with energy dispersive X-Ray spectroscopy (EDS). The setup operated at 15 kV primary beam voltage, 50–100 mA filament current, variable spot size, 20mm WD, and 40 s net acquisition in real-time. The apparatus was equipped with an Oxford Instruments Microanalysis unit and an INCA X-act detector using Energy software with XPP matrix correction scheme and Pulse Pile-up correction. Data were processed with the INCA software, version 4.08 [24].

Back-scattered Electrons (BSE) imaging and semi-quantitative chemical analyses were performed by pressing the glass to a flat surface and then coated with graphite. The sample has been placed at the same height as the

cobalt standard used for routine calibration. Twenty analytical points were collected for each area and natural materials were used as standards.

Raman and FT-IR spectroscopy

Raman spectra were recorded using a confocal Raman microscope (NRS-3100, Jasco Applied Sciences, Halifax, Canada). The 514 nm line of an air-cooled Ar⁺ laser (Melles-Griot) was injected into an integrated Olympus microscope and focused to a spot diameter of approximately 2 μm (100x or 20x objective), with a laser power of 4 mW at the sample. The spectral resolution was 6 cm⁻¹. Raman spectra were recorded at three separate spots on each paint powder to evaluate the heterogeneity. A holographic notch filter was used to reject the excitation laser line. Raman scattering was collected by a Peltier-cooled charge-coupled device photon detector (DU401BVI, Andor Technology, Belfast, Northern Ireland). A complete data set was collected in 100 s.

A small piece of glass (about 2.5 x 2 mm) was deposited on a 3-mm ZnS window and analyzed by Fourier transformed infrared (FT-IR) spectroscopy with a Nicolet 5700 equipped with a microscope Continuum (Thermo, West Palm Beach, FL. USA). Reflection spectra (200 acquisitions) were collected using the microscope focusing windows set at 50x50 mm. Spectra were analyzed by using the Omnic software. Peak assignment was further evaluated based on the data library [25].

Inductively coupled plasma mass spectrometry

A fragment of the sample was grounded in a percussion apparatus used in geology. The sample resulted perfectly pulverized and preserved its blue color. The sample was then analyzed by Inductively coupled plasma mass spectrometry (ICP-MS).

In a first experiment (ICP-MS^a), 100 mg of ground sample was subjected to mineralization in 2.5 ml of a mixture made of 1 part of HF (49% w/w) and three parts of HCl (37% w/w). Sample treatment was carried out inapposite containers in a microwave oven for 24 hours. The solubilized sample was then subjected to the ICP-MS analysis using Argon flux in an Agilent Technology 7506 apparatus (Santa Clara. California. USA).

A subsequent experiment (ICP-MS^b) was carried out on about 50 mg of pulverized glass to detect trace elements (TE) and rare earth elements (REE). The total amount of the sample (46.8 mg) was split into two sub-aliquots (25.7 and 21.1 mg) and completely solubilized by using a reaction mix made of 6 ml HCl. 2 ml HNO₃. and 2 ml of HBF₄ (obtained by adding 30 g of boric acid to 100 ml of HF). Reaction vessels were placed into a microwave apparatus (Milestone Ethos-Easy supplied by FKV S.r.l.. Italy). Acid digestion was carried out according to the following three steps: 1) temperature ramp from 25 to 220 °C for 20 min at 1600 watt. 2) 220 °C for 5 min at 1600 watt. 3) temperature ramp from 220 to 25 °C for 40 min at 0 watts. The samples were then quantitatively recovered, brought to 50.0 mL with ultrapure water in disposable polypropylene falcon, and analyzed using the Nexion 2000 (PerkinElmer, Waltham, USA) inductively coupled plasma mass spectrometer (ICP-MS) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA). A cyclonic spray chamber (Glass Expansion Inc., West Melbourne, Australia) and a quartz torch with a quartz injector tube (2 mm internal diameter) were used. To eliminate isobaric interferences, the kinetic energy discrimination (KED) system was used with helium (99.9999%. high purity) at 4.8 mL/min (high flow) for the determination of Fe. Cr. and V; at 3.7 mL/min (low flow) for the determination of Ni, Ca, As, Se, Co, Zn, Mn, and Cu. Standard mode (without any support gas) was employed for the determination of Li, Be, Mo, Ag, Sr, Sb, Sn, Ba, Cd, Hg, Tl, and Pb and for all the REE. A solution of Bi, Rh, Ga,

and Re (approximately 100 ng/mL) was added on-line as internal standard by using a specific seven-lined mixing valve. To state, the concentration levels of each element were carried out as a preventive semi-quantitative analysis using a multi-element standard. Quantitative determination was carried out using the “internal additions” method in the mineralized solution (previously diluted 1:1 with ultrapure water to avoid the processing of a very acidic solution) through the use of calibration curves at four levels of spiking: for Li, Be, Ag, Cd, Tl, at 0.04 – 0.20 – 1.0 – 4.0 ng/ml; for V, Cr, Ni, Zn, As, Se, Mo, Sn, Sb, and Pb at 0.2 – 1.0 – 5.0 – 20 ng/mL; for Ba, Sr and Co at 1.0 – 5.0 – 25 – 100 ng/mL; for Ca, Al, Mn, Fe, and Cu at 10 – 50 – 250 – 1000 ng/mL. For the 16 REE elements (in detail 14 REE with the addition of U and Th) was used the “internal additions” method at 4 – 20 – 100 – 400 pg/ml. Mg and Zr were determined only by a semi-quantitative method. The correlation coefficients (R^2) of standard calibration curves for all the trace elements were always higher than 0.999, showing a good linear relationship throughout the selected ranges of concentrations. Four mineralization blanks were carried out (the same reaction mix. without ceramic powder) and the mean concentration was subtracted for each element. The TE and REE concentrations were evaluated as the mean of both measurements. Good repeatability (less than 10%) was obtained for all the analytes, except for Cu, probably due to the uneven distribution of Cu salts in the ceramic matrix.

Results And Discussion

Archaeological context and glass sample characterization

The glass sample analyzed, a fragment of intense blue color (Fig. 1), was found in an amphora containing fragmented and intact glass manufactures in Pompeii's excavation, *Reg. I, Insula 14, Casa 14* (Originally numbered as *Reg. II, Insula 14*, and successively, during 1950s excavations, changed to *Reg. I, Insula 14*). *Insula 14* is located in the eastern area of the Regio I of Pompeii, in the median sector of the insulae gravitating on the eastern side on via di Nocera and on the northern side on via di Castricio that determines the prevailing orientation of the housing units. The first information about insula 14 dates back to 1954, the period in which Amedeo Maiuri began an important excavation season to bring to light the entire southeastern sector of the city. In the first phase, the investigations were limited to freeing the southern front between insulae 13 and 14, and only in 1957, the southeast corner was reached, identifying a *thermopolium* pertaining to the current number 15. After the excavation and consolidation of the wall hills that emerged, the research activity was interrupted and resumed in 1984 [26]. The archaeological period of the glass finds was attributable to the earthquake described by Tacitus and Seneca that seriously damaged Pompeii in A.D. 62. However, according to some views, the A.D. 62 earthquake (defined as *terminus post quem*) was not a single event but other seismic activity, occurred over a certain number of years (Neronian and early Flavian periods) [27], generated stratigraphic sequence due to the subsequent demolition and rebuilding thus, suggesting that not all the glass finds have been precisely contemporaneous. All excavated specimens should have been preserved from subsequent potential deterioration caused by the eruption of Vesuvius in 79 A.D. (*terminus ante quem*) [21]. Dr. Piccioli, C., an official of the former Archaeological Superintendence of Naples and Caserta (SANC) selected the distinctive sample that was considered, according to archaeological caution, well preserved and of great significance, because its intense color that appeared identical to that of other intact glass manufactures. The artifact (about 2x3 cm) was carefully handled to avoid additional contamination and softly cleaned with a brush and wet bibula paper to remove dust deposits. The fragment was then stored in a preserved area to avoid further environmental deterioration. The sample did not show any opacity. The glass color, according to the Munsell notation, was

organoleptically corresponding to a saturated and intense color [28]. Reflected light microscopy observation revealed some technical properties such as the absence of bubbles and the refinement in cooking which explained the durability of the material. The glass surface appeared non-homogeneous highlighting forms of yellow, white, and dark blue pitting alterations most likely attributable to the chromophoric elements responsible for the blue color (Fig. 2) whereas, no crystalline phases were observed by XRD (not shown), thus suggesting the absence of devitrification and excellent quality of the glass also in consideration of the elapsed time.

Raman and FT-IR spectroscopy

Raman spectrum of the sample, reported in Fig. 3a, highlighted the presence of two major peaks at 1090 and 584 cm⁻¹ with and two well-defined components at 945 and 995 cm⁻¹. This signature corresponded to common lime-based glass (typically having a composition with about 10 to 15% Na₂O, and about 8 to 15% CaO). In some cases, only one shoulder was observed at 950 or 995 cm⁻¹ [29]. The two major signatures are associated with the Si-O bending (~550 cm⁻¹) components of SiO₄ entities of the more or less polymerized (Si-O)_n framework, and Si-O stretching (~1090 cm⁻¹) [30]. The feature at 773 cm⁻¹ is usually assigned to the vQ₀ mode of isolated not-bridged SiO₄ entities [31]. The position of the maximum of the SiO₄ bending and stretching bands are reported in Table 1. The maximum of the SiO₄ bending and stretching bands in the general database was determined from the Raman characterization of hundreds of different types of glassy silicate whose elemental compositions were determined by classical methods, thus allowing the identification of different types of glass. [32]. Studies made by Colombar et al., 2006, highlighted families of glasses based on the relationship between the Raman peak area ratio (A500/A1000), defined as polymerization index (I_p), of envelopes and wavenumbers of the different Si-O stretching components. The empirical relationship between I_p , glass composition, and the processing temperature was rather well documented [33]. According to this classification, the I_p value calculated from Raman spectra collected in a different area of the sample ($I_p = 0.6 \pm 0.05$) would correspond to a family of silicate-based glasses characterized by an intermediate ratio between flux components (Na₂O + K₂O + CaO) with a very low content of PbO and most likely processed at medium temperature. Regarding the blue color and opacifiers, Raman features did not suggest either the detectable amount of lazurite (Na,Ca)₈(SO₄,S,Cl)₂(AlSiO₄)₆ [34] or Ca₂Sb₂O₇ (no 672 cm⁻¹ bands) [35].

The FT-IR spectra of the sample (Fig. 3b) showed a profile with the presence of bands consistent with the Raman result. Typical spectra showed broadband in the 3590 cm⁻¹ regions arising from stretching of the –OH most likely assigned to the silanol group or in adsorbed water in the sample. The spectrum was characterized by bands at 2926–2844 cm⁻¹ (functional groups region) and 1725–1586 cm⁻¹ (double bond stretching) regions because of C-H bending [36, 37], which could be due to some original organic contamination of organic structures on the silica's surface. Peaks at 1264, 893, and 798 cm⁻¹ could be assigned to Si-O symmetrical stretching vibration, Si-OH bending, and SiO₂ stretching, respectively [38-40]. All the major FT-IR bands observed and the peak assignments are shown in Table 2.

Scanning Electron Microscope

BSE in SEM imaging showed non-homogeneity of the sample (Fig 4a). The semi-quantitative analysis was characterized by a great variability (high S.D. and CV%) because observations were made on different areas of the glass surface. Areas of the sample showed the presence of CoO up to a concentration of about 6.0 wt% (Fig.

4b and 4c, whitish zones) whereas, in other areas, the CoO content ranged from zero to about 1.0 wt%. PbO ranged from zero to about 6.0 wt%. Ti and Fe were also detected as well as minerals attributable to the group of zeolites likely formed by the alteration of glass [41]. Table 3 shows the average composition of the glass. The sample appeared as a soda-lime-silica glass with the average concentration of SiO₂, Na₂O, and CaO of 61.71 wt%, 1.44 wt%, and 5.16 wt% respectively, although the average Na₂O concentration resulted lower compared to that reported in the literature data on glasses of the period [42] whereas, a higher average concentration of MnO, FeO, CoO, and PbO was observed. The latter data suggested that cobalt was most likely the key chromophoric element responsible for the sample blue color. [43-48].

Inductively coupled plasma mass spectrometry

Because ICP-MS measurements of silicon at m/z 28 suffer from numerous spectral interferences that could include C, O, and N (the latter most likely coming from nitric acid), we first analyzed the presence of trace elements (TE) in the Pompeian glass powder after its digestion in HF and HCl in a 1:3 ratio (ICP-MS^a). We expected a Si concentration above detection limits thus, it was not necessary to pre-concentrating the sample. Silicon does not require significant amounts of strong acid and low levels (< ~10 ppm) are soluble and stable in water. Moreover, the ICP-MS used allowed Si measurements in the range of a few ppm. The ICP mass analytical results are summarized in Table 4. In particular, the sample showed a relatively high content of Si, Na, and Ca and a lower content of Fe, Al, Co, Mn, Cu, Sb, Pb, and K. The amount of these elements, converted in the corresponding oxides, highlighted a composition similar to that observed in several Roman glasses [20]. In fact, the percentage (w%) of SiO₂, Na₂O, CaO, Al₂O₃, K₂O, MgO, FeO, MnO, PbO, and CuO were 43.8, 5.6, 5.4, 1.0, 0.66, 0.28, 0.7, 0.24, 0.09, and 0.08, respectively. The MgO and K₂O compositions were less than 1.5%. This data suggested that natron was the primary alkali flux for this glass [49-51]. It is also worth noting that the amount of Sb observed (0.99 w%) was not sufficient as an antimony-based opacifier as instead observed for other Roman and Pompeian glasses [42, 52].

ICP-MS was also performed after-treatment of the sample with HCl, HNO₃, and HBF₄ at a 2:1:1 ratio (v/v) in a temperature ramp (ICP-MS^b). The results are reported in Table 4. Although with this procedure it was not possible to detect Si, K, and Na, also here was observed a moderate-high content of Fe, Al, Ca, Co, Mn, Cu, and Mg. The weight percentage (w%) of the corresponding oxides FeO, Al₂O₃, CaO, CoO, MnO, CuO, and MgO were 0.79, 2.74, 8.06, 0.20, 0.52, 0.68, and 0.65, respectively [53]. The CaO content evaluated by ICP-MS^a and ICP-MS^b (5.4 w% and 8.05 w%, respectively) was slightly higher compared to that reported for Pompeian glasses by [42] (average 7.215%) and according to the literature data on a glass of the period [43-48]. This value could be related to the percentage of sodium present in the natron to flux the silica [6, 54] and the higher quantity of lime was used to stabilize the glass thus, suggesting that the sample represented a specialized production, perhaps using a plant-ash component, during the 1st century A.D.

The relationship between the composition of Al₂O₃ (1.0 w% by ICP-MS^a and 2.74 w% by ICP-MS^b) and that of CaO showed to be very close to that reported for Pompeii glasses within the area of Roman Western European sites and in the Mediterranean area in the 1st - 3rd century A.D. [55]. As suggested, these values could be due to the employment for the glass productions of similar raw materials along with the Empire and most likely from the Middle-East region [39, 44, 56-58].

The relatively high content of FeO (0.7 w% by ICP-MS^a and 0.79 wt% by ICP-MS^b) as already reported by [42] can be found in blue-colored Roman glasses. However, its amount might be depending upon the MnO concentration. In this case, the manganese oxide concentration (0.24 w% by ICP-MS^a and 0.52 wt% by ICP-MS^b) was within natural limits, thus suggesting the use of iron-containing raw material that was most likely not subjected to the decoloring procedure. Decolorized glasses generally show MnO concentration > of 0.5 wt% probably due to the addition of manganese as pyrolusite (MnO₂). The latter was particularly widespread in the Roman period to neutralize the color due to the iron oxides naturally present in the primary raw materials [44, 59, 60, 61]. These findings support the hypothesis that the Pompeian glass could have been produced from the sands from the Middle-East region [62].

Also, copper and cobalt, contained in the sample at a concentration of 5467 ppm and 1615 ppm, respectively (0.20 w% and 0.68 w% by ICP-MS) were important coloring agents in the ancient glass-making workshop [18]. For instance, copper might produce blue color depending on its interaction with iron and on some level with manganese and lead. However, deep blue glass showed significant amounts of copper and cobalt in the order of 1930 ppm and 1453 ppm [63]. Therefore, the deep blue color of the sample, besides the iron present in the raw material, might be due to the presence of copper and cobalt probably added as 2Co₂O • CuO • 6H₂O (trianite). This compound was often used for the production of Roman blue glass [63]. Therefore, as also clearly shown by BSE imaging (Fig. 4b and 4c), the blue color of the glass sample was essentially due to cobalt probably used in Pompeian secondary furnaces for glasses manufacture production [42].

ICP-MS^b was also used to determine the content of rare earth elements (REE). The results, reported in Table 4, showed that neodymium (Nd) was the most preponderant rare earth element present in the sample with a concentration of 13.629 ppm. This element belongs to the light rare earth elements (LREE) of the lanthanide series and its concentration is in the range of the concentration of Nd in silica-based, non-carbonaceous sediments and sedimentary rocks that generally is in the order of 5–50 ppm [64]. Neodymium content in glass components such as shell and limestone as well as natron is much lower (around 0.5–10 ppm, and 20–40 ppb, respectively [64–66]. These findings suggest that Roman glasses were originated from heavy minerals or a fraction of non-quartz minerals of the silica-based raw material [46]. Under this aspect, sands from the Campanian beaches by the Garigliano and Volturno Rivers were likely not used in this case [67] since this area all contained more Nd, even up to 296 ppm [68]. Moreover, these sands contained high percentages of heavy minerals, resulting in high Fe₂O₃ and Al₂O₃ levels, making them unsuitable for glass production [46, 69].

Conclusions

In this study, by applying a combination of Raman and FTIR spectroscopy, SEM, and ICP-MS, the chemical composition of a Pompeian's glass blue fragment has been determined, thus representing a possible contribution to the archaeological knowledge on Pompeian's glass manufactory. The sample appeared as a refined glass and was most likely obtained from secondary raw materials. By evaluating the composition of the sample, we tried to define possible areas where suitable sand raw materials would have been available.

The glass sample analyzed was a soda-lime-silica glass containing a slightly higher CaO content most likely used to stabilize the glass. Moreover, as suggested by the *Ip* value, the sample was a lower lead-based silicate most likely processed at medium temperature. Furthermore, the amount of Al₂O₃ and CaO suggested the employment of similar raw materials along with the Empire and most likely that from the Middle-East region. The

Nd content (ppm) of the blue sample, excluded the use of the sand of Campanian beaches for primary raw material.

The FeO content was within natural limits and closer for other Roman glasses thus indicating the use of iron-containing raw material that was not subjected to the decoloring procedure.

The deep blue color was most likely due to the cobalt, present in a substantial amount, and possibly used as an important coloring agent in the secondary glass-making workshop.

These results suggested the presence of the primary glass production industry and a possible Pompeian secondary workshop for the production of glass manufactures during the first century AD.

Declarations

Availability of data and materials

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing Interests

The authors declare that they have no competing interests.

Funding

This work was supported by funds from Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale (2012CK5RPF_004), PON Ricerca e Competitività 2007–2013 (PON01_02782) and POR Campania FSE 2007–2013, Project CRÈME. AV acknowledges for financial support the MISE (Ministero per lo Sviluppo economico) for a grant entitled "Sistema Informativo Social per Stabiae Intelligente".

Authors' Contribution

MG, GC, OM, and AEC were involved in ICP-MS sample analyses. CP and OA were involved in the archaeological classification of the sample. AV performed Raman spectroscopy and analysis of the data. MR was involved in SEM analysis and data interpretation. GC and PA made contributions to the interpretation of data, drafting, and revision of the manuscript. All authors have read and approved the final manuscript.

Acknowledgment

We wish to thank prof. Massimo Osanna, Director of the Archaeological Park of Pompeii for the permission to access to Pompeii's excavation, and to the Anthropologist Dr. Valeria Amoretti and the Archaeologist Dr. Alessandro Russo, for their valuable help for *in situ* research work.

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Tables

Table 1. Frequencies (cm^{-1}) of Raman bands observed in Pompeii's blu glass sample

Sample	SiO_4 Bending Band/ cm^{-1}	νQ_0 mode Band/ cm^{-1}	SiO_4 Stretching Band/ cm^{-1}
Blue (soda-lime glass)	~585	~777	~1096 ~945 sh; ~987 sh

Table 2. Frequencies (cm^{-1}) of major infrared bands observed in Pompeii's blu glass sample and peak assignment

Frequency (cm^{-1})	Predicted Peak
3590	Symmetric stretching of O-H groups ($\nu \text{O-H}$). Silanol group (Si-OH).
2926	C-H stretching ($\nu_{\text{as}} \text{CH}_3$)
	CH_3 asymmetric stretching organic structure ($\nu_{\text{as}} \text{CH}_2$)
2844	CH_2 symmetric stretching organic structure ($\nu_s \text{CH}_2$)
1725	Carbonyl stretch ($\nu \text{C=O}$)
1634	Molecular water
1566	C=C stretching Carbonate group stretch OH bending
1264	Si-O-Si stretching vibration
893	Si-OH bending
798	SiO_2 stretching CH bending

Table 3. Major elements. Results of SEM semi-quantitative analysis performed on Pompeii's blue glass sample. Elements are expressed in wt%.

Oxides	Average	SD	CV
	%		
	w%		
SiO ₂	61.71	16.41	26.59
Na ₂ O	1.44	1.71	118.75
MgO	1.71	3.01	176.02
P ₂ O ₅	0.62	2.10	338.71
SO ₃	1.07	0.63	58.88
CaO	5.16	6.85	132.75
TiO ₂	0.61	0.61	100.00
MnO	5.54	6.18	111.55
FeO	3.37	3.30	97.92
CoO	1.16	1.53	131.90
PbO	1.24	1.85	149.19
F	1.25	3.28	262.40
Cl	1.89	5.76	304.76

SD, Standard Deviation; CV, Coefficient of Variability

Table 4. Elemental composition of Pompeii's blu glass sample evaluated by ICP-MS

TE	Average µg/g (ppm)	SD (CV 17%)	Average mg/100mg	Average µg/g (ppm)	SD (CV 15%)	Average mg/100mg	REE	Average µg/g (ppm)	S.D. (CV 15%)
ICP-MS^a					ICP-MS^b				
V	n.d.	-	n.d.	11.98	1.80	0.0012	Y	7.595	1139.2
Cr	30.0	5.1	0.003	14.43	2.16	0.0014	La	9.725	1458.7
Fe	2550.0	433.5	0.255	6166.24	924.94	0.6166	Pr	1.715	257.3
Al	3160.0	537.2	0.316	14510.16	2176.52	1.4510	Nd	13.629	2044.4
Ni	110.0	18.7	0.011	67.33	10.10	0.0067	Sm	1.466	220.0
Ca	39100.0	6647	3.91	57580.72	8637.11	5.7581	Eu	0.435	65.3
As	10.0	1.7	0.001	18.31	2.75	0.0018	Gd	1.588	238.3
Se	n.d.	-	n.d.	1.82	0.27	0.0002	Tb	0.220	22.1
Co	340.0	57.8	0.034	1615.30	242.29	0.1615	Dy	1.277	191.7
Zn	n.d.	-	n.d.	53.62	8.04	0.0054	Ho	0.249	37.5
Mn	1100.0	187	0.110	4084.11	612.62	0.4084	Er	0.752	112,8
Cu	660.0	112.2	0.066	5467.89	820.18	0.5468	Tm	0.099	15.0
Li	n.d.	-	n.d.	<1	-	< 10 ⁻⁵	Yb	0.642	96.3
Be	n.d.	-	n.d.	<1	-	< 10 ⁻⁵	Lu	95.07	14.3
Mo	n.d.	-	n.d.	5.33	0.80	0.0005	Th	0.865	129-9
Ag	n.d.	-	n.d.	<1	-	< 10 ⁻⁵	U	0.924	138.7
Sr	320.0	54.4	0.032	504.72	75.71	0.0505			
Sb	9940.0	1689.8	0.994	23.33	3.50	0.0023			
Sn	n.d.	-	n.d.	<3	-	< 10 ⁻⁵			
Ba	1500.0	255	0.150	261.12	39.17	0.0261			
Cd	n.d.	-	n.d.	<0.5	-	< 10 ⁻⁵			
Hg	n.d.	-	n.d.	<0.1	-	< 10 ⁻⁵			
Tl	n.d.	-	n.d.	0.054	0.008	0.0000			
Pb	870.0	147.9	0.087	10.89	1.63	0.0011			
Mg	1740.0	295.8	0.174	3960.45	594.07	0.3960			
Zr	n.d.	-	n.d.	35.11	5.30	0.0035			

K	2740.0	465.8	0.274	n.d.	-	n.d.
Si	205000.0	34850	20.5	n.d.	-	n.d.
Na	42000.0	7140	4.20	n.d.	-	n.d.
Ti	220.0	37.4	0.022	n.d.	-	n.d.

TE, Trace Elements; REE, Rare Earth Elements; SD, Standard Deviation; CV, Coefficient of Variability

Figures

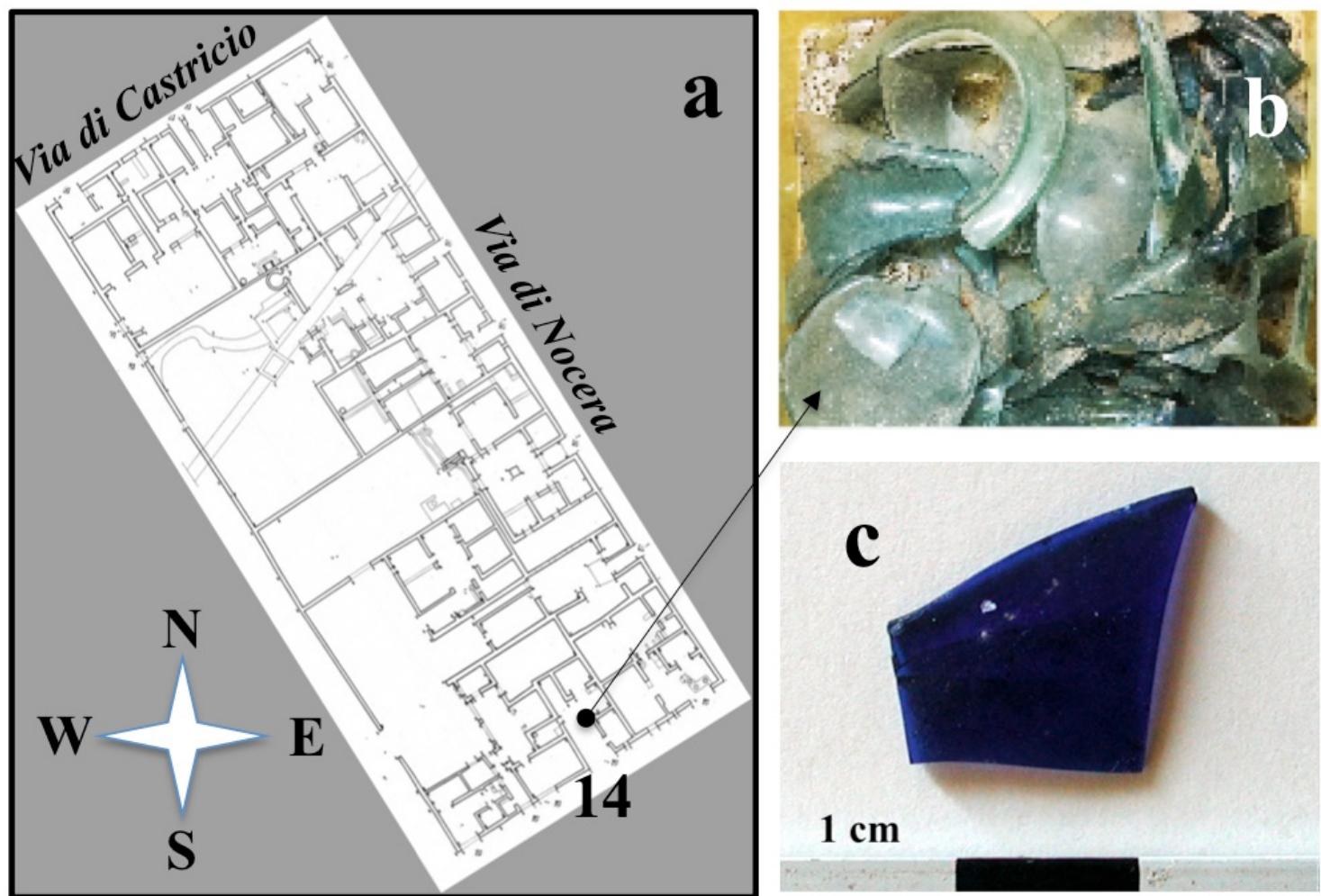


Figure 1

(a) Recent planimetry of the Regio I, Insula 14, Casa 14 (archive of Archaeological Park of Pompeii) where the amphora containing intact and glass fragments (b) were found. (c) Blue glass sample analyzed

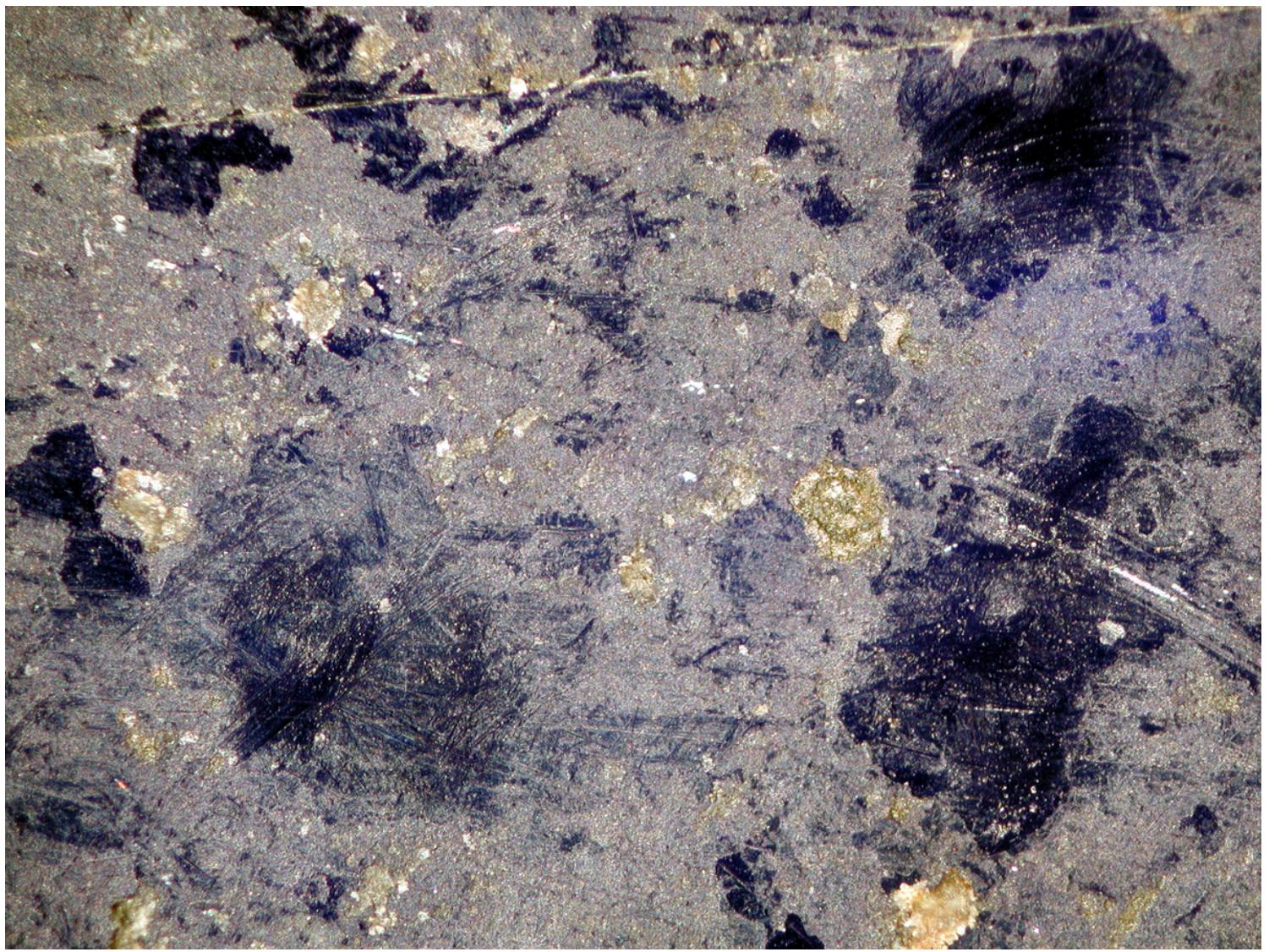


Figure 2

Light microscopic image of the Pompeian's blu fragment (50X)

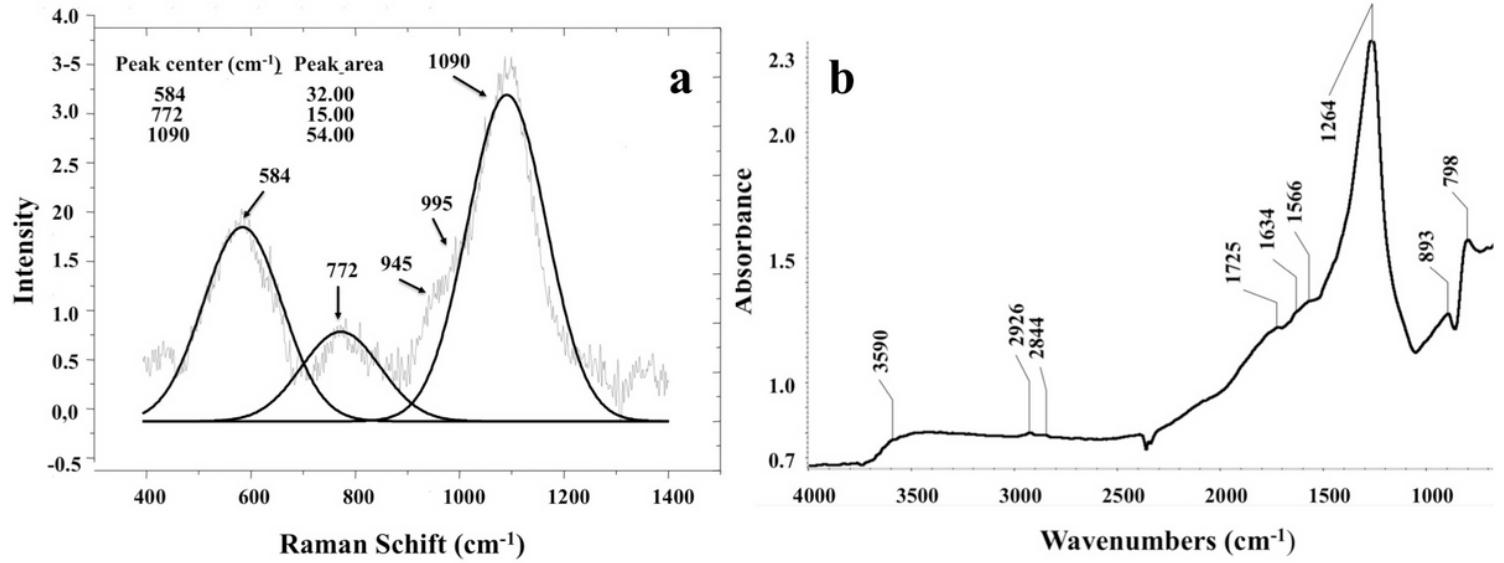


Figure 3

(a) Raman spectra of Pompeian's blue glass; (b) Representative FT-IR spectra of Pompeian's blue glass

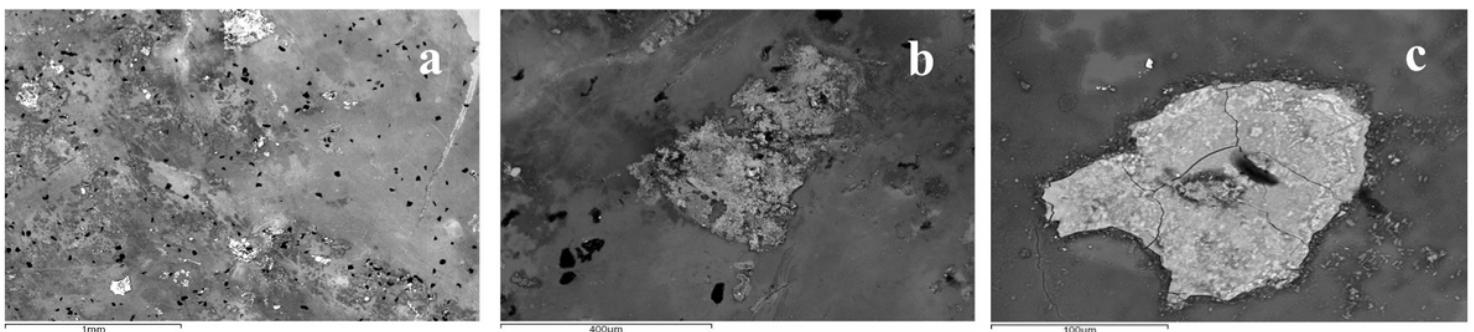


Figure 4

BSE images of Pompeii's blue fragment. (a) Image showing the variable composition of the sample. (b) Sample area containing about 2 w% of Co. (c) Sample area containing about 6 w% of Co.