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The use of *vitrum obsianum* in the Roman Empire: some new insights and future prospects

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Abstract

The research on the use of obsidian in the Mediterranean is extensive but concerns almost exclusively volcanic glass from prehistoric and Bronze Age contexts. The consumption of obsidian during the Roman imperial period, however, has only occasionally received attention. Never a comprehensive account on what the Romans made in *vitrum obsianum* has been set up, nor have the sources exploited by them been examined. This paper provides a concise overview of the current knowledge on obsidian during the Roman imperial period and offers an introductory outline on potential research.

The ancient writers inform us about the use of volcanic glass to create exclusive vessels, gemstones, mirrors and sculpture, but also about the creation of black appearing man-made glass initiated as a cheap and easier workable substitute of obsidian. The archaeological data on the other hand propose a more complex story with the occurrence of obsidian chunks in early Roman secondary glass workshops, and the bulky use of obsidian in late Antiquity to produce *tesserae* for the creation of wall and vault mosaics. Because it is extremely difficult to visually distinguish natural obsidian from man-made glass imitations we present in this paper data collected by means of non-destructive chemico-physical analyses SEM-EDX, portable X-ray fluorescence (p-XRF) and Raman spectroscopy to easily distinguish man-made glass from natural obsidian. In particular the use of portable instruments makes possible in situ analysis of objects in archaeological depots or museum collections to help defining distribution networks to better understand the shifting consumption patterns in Antiquity.

Key words: Roman glass; obsidian; XRF; Raman; SEM-EDX; non-destructive.

Introduction

The study of obsidian within archaeological research is perhaps numerous, but to this point the debate basically remains focused on the provenance of the raw material from the Palaeolithic to Bronze Age sites in the Mediterranean Basin (Shelford et al., 1982; Tykot, 1997; 2002; Gratuze, 1999; Bigazzi et al., 2005; Carter, 2008; 2014). The interest in studying obsidian from pre- and protohistoric sites is to ascertain the movement of hunter-gatherer communities or some form of exchange relationships with neighbouring groups by assessing distribution patterns as well as contributing to the discussion concerning the exploration, colonization and full occupation of the Aegean Sea and the Central Mediterranean Basin (Carter, 2014).

The knowledge on Roman objects in *vitrum obsianum* on the other hand remains up to now very partial (Froehner, 1903; Edgar, 1905; Haevernick, 1963; Goldstein, 1979; Grose 1989; Cagno et al., 2010). Assessing the well-known fragmented obsidian artefacts, carefully fostered in museum collections worldwide, have great potential in view of distribution patterning and trade networks within a more complex and multifaceted society.

The use of obsidian in Roman times is well stated by Pliny the Elder who considered the use of obsidian for the production of vessels and statuary (Historia Naturalis*,* book 36, 196-197). The exceptionality of obsidian statuary can be deduced from Pliny's reference, whereas the use of vessels in *vitrum obsianum* appeared to be more common. Undoubtedly *vitrum obsianum* presents some uncertainties on its production, and this since Pliny describes that obsidian, a volcanic glass, is imitated by man-made glass. This creativity of Roman glassworkers to bypass the supply of raw obsidian as well as the limited dimensions of the obsidian blocks confuses scholars. Even today, careful observation is needed in order to visually distinguish real obsidian from black appearing glass. A difference in colour perception, however, has caused misunderstandings in literature because the black objects have been catalogued as obsidian, but when the colour is faintly observable they were described as man-made glass (Haevernick, 1963). Recent research on Roman black glass has demonstrated that black glass, natural or man-made, does not occur and that the black appearance of glass is only due to a strong colouring and/or opacifying agent (Cosyns, 2011; 2015). Furthermore, when observing obsidian in detail, the hue can vary due to its composition from opaque black to greyish, blue-greyish or even brownish, whereas Roman man-made black-appearing glass is made from nearly opaque olive green, emerald green, brown, blue or purple coloured glass. It is nonetheless important to realize that Romans produced glass according to the final appearance they desired, in this case by adding colouring agents to achieve a macroscopically black and incidentally deeply coloured glass. For instance the right foreleg of a free-standing statue of a horse within the British Museum collections since 1814 has been originally described as being made in obsidian, but afterwards it has been determined as cast in black appearing deep purple glass (Harden et al., 1987, 28, no. 6). Later chemical analysis by means of scanning electron microscope clearly defined the artefact as obsidian (internal report by British Museum). It needs to be verified whether the high alumina and iron oxide composition in combination with the brownish hue corresponds with the East African obsidian (personal communication by Ian Freestone, January 2015)

This renewed study on *vitrum obsianum* aims to prove that by using modern analytical techniques (both in situ and laboratory-based) it is easy to attribute museum objects in *vitrum obsianum* to obsidian or to man-made glass. To demonstrate the feasibility of these objectives we present the analysis results of some vessels characteristic to the first part of the 1st century AD and late antique mosaic *tesserae*. Since a visual discrimination of both black-appearing glassy materials is not straightforward and can lead to confusion in the classification of the objects, a methodical separation of the natural volcanic glass and man-made black glass is needed to assess the so far overlooked obsidian consumption in Roman imperial times up to the mid-7th century AD. This discrimination is important in order to estimate the impact of both materials on the consumption market since natural and man-made black glasses were simultaneously used to produce identical consumers' goods. Noteworthy is that the value of obsidian shifts from an exclusive and exotic material during the early Roman imperial period towards a randomly available cheap raw material in late Antiquity. The exquisite obsidian statuary, jewellery and vessels got imitated in commoner and cheaper black man-made glass during the 1st century AD, while in late Antiquity obsidian got reintroduced, for instance for mosaic *tesserae*, to bypass the production costs to fabricate black man-made glass, thus economizing on time, fuel, infrastructure, ingredients and skilled people.

Furthermore, some non-destructive, or micro-destructive analysis techniques like the here applied portable X-ray fluorescence (p-XRF) and Raman spectroscopy, or laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), not only can clearly separate obsidian from man-made glass, but can also discern specific obsidian sources (Acquafredda et al., 1999; Barca et al., 2007; De Francesco et al., 2008). Within the Mediterranean three source areas have been recognized that were responsible for the supply of obsidian in Antiquity: various Italian and Greek islands (such as Pantelleria, Lipari, Sardinia, Melos, Giali) and eastern Turkey (Cappadocia, Lake Van district). The characterization of known Roman obsidian material offers many opportunities to establish the specific obsidian sources used by the Romans and define their distribution networks. By defining what source(s) the Romans used, it can be evaluated, for instance, whether obsidian from nearby sources was obtained for processing or whether long-distance distribution also occurred. An advance in this research can evaluate whether Pliny the Elder was right by mentioning an Ethiopian provenance for obsidian in the 1st century AD while there are various Italian sources attested, e.g. Pantelleria, Lipari, Sardinia, Phlegraean islands.

Vessels in vitrum obsianum

Research on Roman artefacts in obsidian remains scarce and vessels in *vitrum obsianum* are to this point reported as very exclusive objects, merely representing an insignificant portion of what Romans have been consuming on the other hand. Most exceptional pieces are the three complete cylindrical cups with two elaborate handles (*skyphoi*) and a broken shallow bowl (*patera*) from the villa San Marco at Castellammare di Stabia (Italy) with inlaid Egyptianized figural scenes (Elia, 1957). However, the largest part of the obsidian vessels is decorated with a floral scene or with a wreathed pattern. The meaning, value and appreciation Romans gave to artefacts in *vitrum obsianum* is solely based on literary sources and the very limited information of not more than 14 known pieces up till now (Table 1). We are aware however of the necessity of thorough heuristics seeing that for instance numerous other black appearing glass artefacts from sites in the Gulf of Naples and the Gorga collection (Rome) most likely can higher significantly the occurrence of vessel fragments in obsidian.

Some pieces have Nilotic scenery or Egyptianized figural scenes supporting the belief that these vessels were produced in Alexandria (Egypt) (De Vos, 1980), especially in connection with Pliny who mentions an Ethiopian origin of the obsidian. This hypothesis is somewhat

Table 1. List of early Roman objects in vitrum obsianum.

Museum	Provenance	Vessel shape	Reference
Royal Museums of Art & History, Brussels (cat. no. R1610)	unknown (possibly Rome, Italy)	undefined	De Meester De Ravestein, 1884, 463, no. 1610; Haevernick, 1963, 123, Taf. 2:1; Cagno et al., 2010, fig. 1
Toledo Museum of Art, Toledo (Ohio)	unknown (possibly Rome, Italy)	shallow plate	Grose, 1989, 342, no. 618
Toledo Museum of Art, Toledo (Ohio)	unknown (possibly Rome, Italy)	shallow plate	Grose, 1989, 342, no. 619
Unkown	Stanwick (UK)	undefined	Personal communication by Jennifer Price, 2010
Discarded	Xanten (Germany)	undefined	Haevernick, 1963, 122
Akademischen Museum, Bonn	unknown (possibly Rome, Italy)	undefined	Haevernick, 1963, 123, Taf. 2:2-7
Pogliaghi-Varesse collection	unknown (possibly Rome, Italy)	undefined	Personal communication by Maria Grazia Diani, 2010
Corning Museum of Glass, Corning (cat.no. 66.1.144)	unknown (possibly Rome, Italy)	plate	Goldstein, 1979, 285, no.858
Archaeological Museum, Naples			
(cat.no. 294471)	Villa San Marco, room 37, Castellammare di Stabia (Italy)	skyphos	Elia, 1957, 97-103; Haevernick, 1963, 122-123, pl.21
Archaeological Museum, Naples			
(cat.no. 294472)	Villa San Marco, room 37, Castellammare di Stabia (Italy)	skyphos	Elia, 1957, 97-103; Haevernick, 1963, 122-123, pl.21
Archaeological Museum, Naples			
(cat.no. 294473)	Villa San Marco, room 37, Castellammare di Stabia (Italy)	skyphos	Elia, 1957, 97-103; Haevernick, 1963, 122-123, pl.21
Archaeological Museum, Naples			
(cat.no. 294474)	Villa San Marco, room 37, Castellammare di Stabia (Italy)	patera/phialè	Barbet, Miniero (eds.) 1999
British Museum, London			
(cat.no. 1976.1103.1)	unknown	dish	unpublished
Metropolitan Museum of Art, New York (cat.no. 17.194.2359)	unknown	revetment plaque	Froehner, 1903. 80, no. 555, pl. 57.1-6; Caron, 1997, 19, fig.1
Metropolitan Museum of Art, New York (cat.no. 17.194.2360)	unknown	revetment plaque	Froehner, 1903. 80, no. 556, pl. 57.1-7
Metropolitan Museum of Art, New York (cat.no. 74.51.5871)	unknown	revetment plaque	unpublished

puzzling because several obsidian sources are located within the Central Mediterranean. It is thus intriguing to analyse the vessels from Rome and the Gulf of Naples, in order to establish what particular obsidian source has been used, if not black appearing man-made glass, at least in certain circumstances.

Late Antique tesserae

In the early Christian basilicas from the 4th to 7th century AD glass *tesserae* appear to have been used in large quantities to embellish the interior with colourful wall and vault mosaics (James, 2006; 2010; Foy, 2007). From this point of view we may presume the possibility of *tesserae* production in large glass workshops like the one at Sainte Menehould (France) of 3th-5th century AD date, where large amounts of various brightly coloured opaque glass *tesserae* and crucibles with the same coloured glass were found including those with a black appearance (Cosyns, 2011). These *fabrica*-like workshops processed glass on a large scale by pouring the glass of a crucible on a stone worktable to form large plano-convex glass cakes. Not only these glass cakes were distributed to supply the mosaicists, but a part of them got chopped up into small *tesserae* in the glass workshop and transported in (large) quantities. It is not excluded that the strongly coloured glass *tesserae* were also used in secondary glass workshops to colour the batch, in particular to produce opaque coloured glasses for decorating vessels and jewellery.

Yet, the black glass *tesserae* seem to have been equally made from obsidian especially the black *tesserae* from 6th-7th century dated contexts as for instance observed in the early Byzantine mosaics from the basilicas of Carthage and Sidi Jdidi (Tunisia) (Foy, 2004; Cosyns, 2011). In particular the six large black glass chunks from the early Christian basilica of Bir Messaouda in Carthage (Tunisia) are significant, because these lumps were found in the *diakonikon,* an adjacent sacristy room south of the central apse, together with the remains of a mosaicist's work material (unpublished). This specific Tunisian material with its context makes us understand that in late Antiquity obsidian chunks were used to generate *tesserae* for mosaics in large public buildings where millions of glass *tesserae* were used for wall and vault mosaics. Additionally, unexpected results have been mentioned in various recent researches, though never defined as obsidian, like the 6th-7th century "cross church" in Jerash (Jordan) (Arinat et al., 2014) and from 6th century stratigraphic loose finds in Sagalassos (Turkey) (Schibille et al., 2012).

Integrating 6th-7th century AD glass in the present research is perhaps colouring beyond the lines, but it is imperative to tackle the economical cause-effect relation on glass supply for mosaicists in late Antiquity as the situation dramatically changed compared to the 3rd-5th century. Combining the chemical composition of this specific Tunisian material with its context makes us understand that in the early Byzantine period lumps of obsidian were used to make *tesserae* for mosaics in large public buildings demonstrating a clearly different composition of the 3rd-4th century AD man-made glass cakes. We assume that early Byzantine mosaic workers recycled large lumps of glass to produce *tesserae*. From this point of view we may presume the possibility of *tesserae* production in large glass workshops like the one at Sainte Menehould where *tesserae* in various opaque colours were produced including those with a black appearance. A large-scale assessment on the chemical composition of the vast amount of diverse glass *tesserae* and crucibles from Les Houis nearby Sainte Menehould and the glass cakes reported by Foy (2007) would be very useful to get an overview on the recipes and technologies applied in late Antiquity. The use of *tesserae* in the early medieval period to recycle the glass for the manufacturing of beads (Lundström, 1976; Sablerolles et al., 1997; Foy, 2007).

Materials of this study

For what concerns the vessels, we carried out a comparative study on glass, obsidian as well as undecided glass/obsidian pieces, and added new data to the published results (see Table 2). The purpose is to display a spectrum of techniques that can clearly help discriminating glass from obsidian in museum collections and archaeological contexts, and to provide a preliminary overview on the use of obsidian in the Roman times as well as present some future prospects within this field of research.

First of all, the body fragment R1610 of the Royal Museums of Art and History (MRAH) in Brussels (Figure 1) was analysed by p-XRF. This decorated piece has a superficially engraved floral motif of circular garlands and ivy leaves that seems encrusted by white material. The fragment measures 40 x 29 mm, with a thickness of 3-3.5 mm. Its provenance is somewhat unclear, but it can be related to a first century Roman context (Cagno et al., 2010).

To have comparative material, we have carried out p-XRF analysis on Melos obsidian, and an object in deep green black-appearing man-made glass (PC1_3).

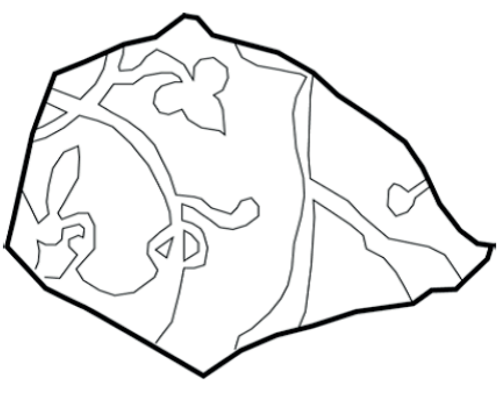

Figure 1. Fragment R1610 of MRAH - Brussels

Additionally, semi-quantitative XRF analyses were performed on the above-mentioned R1610 fragment, together with other objects of the collections of the MRAH in Brussels. These are the two counters B934, found in a rich tomb context in Herstal dated to the 2nd century AD, the two counters B13, found in a rich tumulus tomb in Cortil-Noirmont, dated to the second half of the 2nd century AD, the bracelet type C2 originating from the Basse-Wavre area (Belgium) and dated to the period 200-350 AD, and the bracelet type A3 from Tongeren, of the same period.

More analyses included samples from two black glassy chunks (PC50_1 and PC50_2 in Table 2) from the 1st century AD secondary glass workshop of 'La Montée de la Butte' in Lyon (Motte and Martin, 2003; Robin, 2008; 2012; Cosyns, 2011). This early Roman secondary workshop could be connected to glass vessel production: not only this raised questions on the obsidian market in the Roman time (composition shown in Table 2), but also generates new questions as it is not sure whether the glassworkers drilled, tooled and polished the rough blocks into unique pieces or whether they melted crushed obsidian to cast vessels. An experiment with obsidian from Monte Arci, Sardinia at the Archaeological Museum of Velzeke demonstrated that (1) grinded obsidian was successfully melted in the reconstructed Roman furnace by adding soda and (2) that the batch could be used for blowing vessels (Cagno et al., 2010).

Finally samples of early Byzantine *tesserae* are also part of this study. These have been analysed by means of SEM-EDX and Raman spectroscopy. First, a *tessera* in black glass from the early Christian south basilica of Sidi Jdidi (Tunisia) was the start of some unexpected glass consumption in the 5th-6th century AD. Secondly, after analysis of the six lumps of black glass found with material pointing to a mosaic workshop in the contemporaneous

Table 2. Summary of the samples analysed in this study.

Sample	Provenance	Type	SEM-EDX	p-XRF	Raman
PC1_3	Rumst (BE)	vessel (LMg glass, high Fe)	Van der Linden et al., 2009	This study	This study
PC1_8	Magdalensberg (AT)	vessel (HMg glass)	Van der Linden et al., 2009	-	Ceglia et al., 2014
PC11_14	Sidi Jdidi (TN)	tessera	Cosyns, 2011	-	This study
PC13_5	Trier (DE)	bracelet (HIMT high Fe)	Cagno et al., 2013	-	Ceglia et al., 2014
PC22_4	Avenches (CH)	vessel (LMg glass, high Fe)	Cagno et al., 2013	-	Ceglia et al., 2014
PC28_4	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC28_5	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC28_6	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC28_7	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC28_8	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC28_9	Carthage (TN)	obsidian chunk	Cosyns, 2011	-	This study
PC29_6	East Turkey (TR)	obsidian	Cosyns, 2011	-	This study
PC44_9	Monte Arci (IT)	obsidian	Cosyns, 2011	-	This study
PC50_1	Lyon (FR)	obsidian chunk	Cosyns, 2011	-	-
PC50_2	Lyon (FR)	obsidian chunk	Cosyns, 2011	-	-
R1610	Rome?	vitrum obsianum	-	Cagno et al., 2010	-
B934_1	Herstal (BE)	Counter (black glass), 2nd century AD	-	This study	-
B934_2	Herstal (BE)	Counter (black glass), 2nd century AD	-	This study	-
B13_1	Cortil-Noirmont (BE)	Counter (black glass), 2nd century AD	-	This study	-
B13_2	Cortil-Noirmont (BE)	Counter (black glass), 2nd century AD	-	This study	-
NO_INV_C2	Basse-Wavre (BE)	Bracelet C2 (black glass) 200-350 AD	-	This study	-
2836E	Tongeren (BE)	Bracelet A3 (black glass) 200-350 AD	-	This study	-

Table 3. Composition of obsidian material analysed with SEM-EDX (Cosyns, 2011). Values in wt%.

sample	provenance	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
PC11_14	Sidi Jdidi (TN)	7.5	<0.1	6.4	72.0	<0.1.	<0.1	0.3	4.4	0.3	0.2	0.3	8.8
PC28_4	Carthage (TN)	7.9	0.1	6.2	71.0	<0.1	<0.1	0.4	4.3	0.3	0.3	0.3	8.6
PC28_5	Carthage (TN)	7.9	0.1	5.9	72.0	<0.1	0.1	0.5	4.4	0.3	0.3	0.3	8.7
PC28_6	Carthage (TN)	8.0	0.1	6.2	71.0	<0.1	<0.1	0.5	4.4	0.3	0.3	0.3	8.6
PC28_7	Carthage (TN)	8.0	0.1	6.0	71.0	<0.1	<0.1	0.5	4.4	0.3	0.3	0.3	8.8
PC28_8	Carthage (TN)	5.3	0.1	10.0	75.0	<0.1	<0.1	0.3	4.9	0.8	0.2	0.1	2.9
PC28_9	Carthage (TN)	8.1	<0.1	6.3	71.0	<0.1	<0.1	0.4	4.4	0.3	0.3	0.3	8.6
PC44_9	Monte Arci (IT)	3.6	0.2	11.9	74.9	<0.1	<0.1	<0.1	6.1	0.9	0.4	0.1	1.8
PC29_6	East Turkey (TR)	4.6	0.2	10.2	78.3	<0.1	0.1	<0.1	5.0	0.4	0.2	0.1	0.9
PC37_7	East Turkey (TR)	4.3	<0.1	10.7	78.4	0.1	0.1	0.1	4.8	0.5	0.1	0.1	0.7
PC37_8	East Turkey (TR)	4.3	<0.1	10.7	78.6	<0.1	0.1	0.1	4.7	0.5	0.1	0.1	0.8
PC50_1	Lyon (FR)	4.8	0.3	12.0	74.0	<0.1	<0.1	0.2	4.7	0.8	0.3	<0.1	3.1
PC50_2	Lyon (FR)	4.8	0.3	12.0	74.0	<0.1	<0.1	0.2	4.6	0.7	0.3	<0.1	3.0

church of Bir Messaouda in Carthage (Tunisia), we understood its importance (composition shown in Table 3).

In order to highlight the capabilities of Raman spectroscopy in distinguishing man-made glass and obsidian, known obsidian (PC44_9 from Sardinia and PC29_6 from Eastern Turkey) and man-made black glass were analysed with this technique. Selected pieces were chosen, representing typical Roman compositions, namely Low Magnesium Glass (LMG) with high iron content (up to 10%) or high manganese content (up to 8%); High Magnesium Glass (HMG) with 1-2% iron oxide, and High Iron Manganese Titanium glass (HIMT) with high iron content (up to 10%). While their chemical composition was published elsewhere (Table 2), their Raman spectra have been acquired specifically in the present study. Samples PC1_3 from Rumst (Belgium) and PC22_4 from Avenches (Switzerland) represent the LMG composition with high Fe, sample PC10_3 from Meteren (the Netherlands) the LMG with high Fe group, sample PC1_8 from Magdalensberg (Austria) stands for the HMG composition, while sample PC13_5 from Trier (Germany) represents the HIMT glass group.

Methods

Due to the impossibility of sampling the unique museum artefacts, a quick, portable and non-destructive method of analysis is the only viable choice. Therefore a portable X-ray fluorescence analyser was chosen as it can be brought in situ at the very location where the objects are preserved. Such technique does not allow a full quantitative analysis of the composition, because not all elements can be detected as the air between the sample and the detector attenuates X-rays. Thus, elements lighter than Si cannot be measured. If the spectra are collected in identical circumstances, they can be compared allowing us to distinguish between man-made glass and obsidian. Further, semi-quantitative information can be obtained on the ratio between couples of adjacent elements (Van der Linden et al., 2011). For the distinction glass/obsidian the following couples of elements have been used: K/Ca and Mn/Fe.

Two different XRF instruments were employed in this study: the first instrument used was a Tracer; III-V, a p-XRF with a Rh anode and a Si PIN diode as a detector. The conditions of analysis were: 40 keV voltage, 2 mA and 100s spectrum collection. A complementary analysis was performed by using a micro-XRF with a X-ray tube with Mo-cathode, a polycapillary lens and a Si(Li) detector. The polycapillary lens allows focusing the X-rays to a spot of 50-100 micron at a distance of approximately 1.5 cm from the X-ray tube. The conditions were: 35 keV, 0.2 mA, 300s spectra collection.

Such measures are non-destructive and can be performed on the object as such, excluding the necessity of sampling. With a portable instrument the analyses can be done in-situ at the museum. However, for this study we focused on highlighting the possibility of application of non-destructive techniques. Therefore, the laboratory-based Raman measurements were considered sufficient within the scope of this paper. This non-destructive method of analysis has been applied on known man-made glass and obsidian, in order to highlight the spectral differences that can be used in order to unambiguously identify either type of objects (Figure 2).

The Raman spectra have been recorded between 150 cm^{-1} and 1500 cm^{-1} using a LabRam Raman spectrometer (Horiba Jobin Yvon S.A.S, France) equipped with a 600 line/mm grating, an integrated Olympus BX40 microscope and a solid state green laser emitting at 532 nm. On each sample three spectra were recorded with 20 seconds of acquisition time.

For the objects that could be sampled, SEM-EDX has been applied; this technique allows, in optimal conditions, quantitative analysis of all elements down to levels of 0.1% w/w (expressed in oxides) (Schalm and Janssens 2003). In this study, SEM-EDX data constitute the base of information with which the unknown objects are to be compared.

SEM-EDX measurements were performed with a JEOL 6300 SEM equipped with an energy-dispersive X-ray detector. The spectra were collected for 100 seconds by using a 2 nA electron beam current, an accelerating voltage of 20 kV and a microscope magnification of 500. The net intensities were calculated with the program AXIL and quantified by means of a standardless ZAF program (Schalm and Janssens 2003).

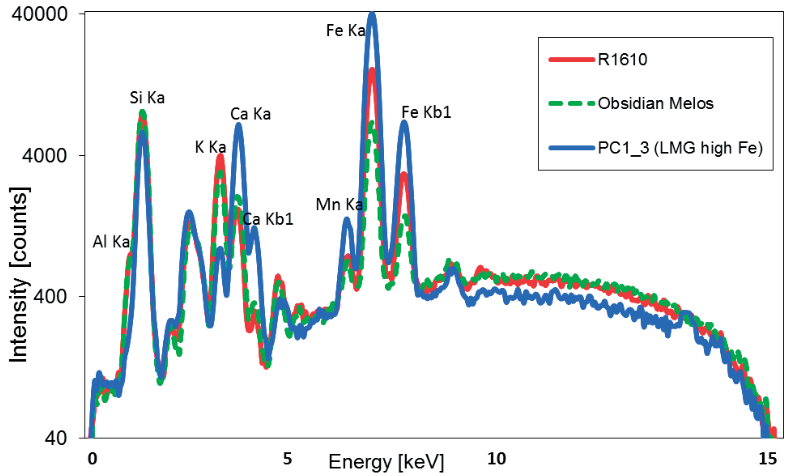

Figure 2. The X-ray fluorescence spectra of fragment R1610, an obsidian fragment from Melos (GR) and a late late 2nd-early 3rd c. AD deep green (black appearing) glass from Rumst, Belgium (Cosyns, 2011).

Results and discussion

In this study we applied the procedure usually adopted in archaeometry, i.e. attempting to univocally distinguish obsidian from man-made glass on the basis of their chemical composition. This can be performed with a large spectrum of elemental or molecular techniques.

SEM-EDX

The composition of black glass and obsidian from different locations has recently been frequently published (Van der Linden et al., 2009; Cagno et al., 2013; Cagno et al., 2014; Tykot, 1996; 1997; 2002; 2010; De Francesco et al., 2012). When deriving general criteria from the large set of published data, these are the main differences: man-made Roman glass has a high soda content, always above 10%, potash and magnesia are generally below 1% and lime is around 5% (values expressed in % w/w of oxides). The colouring agent of black glass is either iron or manganese, with contents as high as 10%. The composition of obsidian is rather variable, depending on the composition of the volcanic melt that created a new obsidian outcrop. Generally obsidian is characterized by amounts of alumina at least double than Roman man-made glass (5-6%), and high silica content, over 70%. As opposite to black glass, the content of potash is much higher (5-10 times) than lime. The natural content of Fe in obsidian is generally situated between 1 and 3%. Of all Mediterranean obsidian, only the obsidian from Pantelleria has high Fe (9%), thus in the same range as man-made deep green glass (Tykot et al., 2013; De Francesco et al., 2007; 2008; 2012). In Table 2 the composition of the analysed obsidian pieces described in the introduction is presented. These pieces were first identified as outliers from known Roman compositions in a large collection of deeply coloured and black-appearing glass (Cosyns, 2011).

Of these, the Tunisian *tessera* and the chunks have a similar composition deviating only in one case (PC28_9) from the average composition of this group. All six samples from Bir Messaouda (Carthage) and the Sidi Jdidi-*tessera* show a mixed-alkali glass composition with high alumina and iron content while lime is lacking, differently from man-made glass and compatible with volcanic glass (Table 3). Compared with the fragments found in a vessel workshop (Lyon), we see in the Tunisian fragments generally a higher content of soda and iron, as well as lower alumina and silica, indicative of a different composition of the volcanic melt. In particular, the high amount of iron oxide (about 9%) of this group of samples matches with that of Pantellerian obsidian (Tykot et al., 2013; De Francesco et al., 2007; 2008; 2012). Thus, also considering the geographical location, we appear to have gathered evidence on the provenance of (part) of the obsidian used for architectural decoration in the Late Antique period. When comparing the Tunisian glass cakes and *tesserae* with those from Petra, Jordan (Schibille et al., 2008) we notice a marked difference in the P_2O_5 and CaO-content. The Petra material has higher concentrations of calcium, between 5% and 15%, compatible with man-made glass, and P_2O_5 between 0.1% and 1%, while this is below the limit of detection for the Tunisian material.

p-XRF

The p-XRF analyses provide qualitative results. In order to prove/disprove the material is obsidian, the X-ray spectra have to be compared with those of known material. Portable XRF instruments have been largely used to measure Roman glasses (e.g. Tantrakarn et al., 2009) or obsidian (Tykot et al., 2013; Frahm, 2013; Frahm et al., 2014), helping to prove/disprove hypotheses on their provenance. In this case, fragment R1610 was compared with man-made black glass dated to the 1st century AD and with obsidian from Melos (from the collection of the MRAH - Brussels).

The spectrum of fragment R1610 (Figure 2) is very similar to that of the obsidian. In particular, the intensity of the Si, K and Ca peaks is very similar to that of the piece of Melos obsidian; moreover the left shoulder (1.5 keV) of the Si K-emission line indicates a very high Al-content of R1610, similarly as in obsidian. The high K-peak indicates a high potash content, incompatible with Roman glass produced with natron as a flux. These data exclude the possibility that the object is made in man-made glass in the Roman age and positively confirm R1610 is made of obsidian. Additionally, the height of the Fe peak of R1610 is somewhere in between the measured black glass and obsidian, indicating that this particular type of obsidian features a very high iron content. Of the known obsidians in use in the Roman age, only the one from Pantelleria has a compatibly high Fe_2O_3 content (around 9%) (Tykot et al., 2010).

The semi-quantitative analysis is made possible by comparing ratios of neighbouring elements, as explained by Van der Linden et al. (2011). This approach, applied to the museum pieces described in the introduction, provides us with similar results as the previous analyses: R1610 is clearly in the opposite part of the field in Figure 3 with a Mn/Fe ratio lower than 1, thus compatible with deep green black-appearing glass, but with a K/Ca ratio over 7, incompatible with Roman glass, characterized by typical values of e.g. 0.5% K and 5% Ca (see potash and lime contents Table 2 and previous section).

The other Belgian finds (Figure 3) show typical values for deep green man-made glass, colored by means by a high amount of iron compatible with either LMG or HIMT base glass (as identified in Cosyns, 2011; Cagno et al., 2014). A further distinction between HIMT and LMG could be done on the basis of the Mn/Fe ratio, but more measurements would be needed to further prove/disprove this point. For the counter B13_1, instead, Mn has been used as colouring agent, and it belongs to the LMG high Mn group already identified in Van

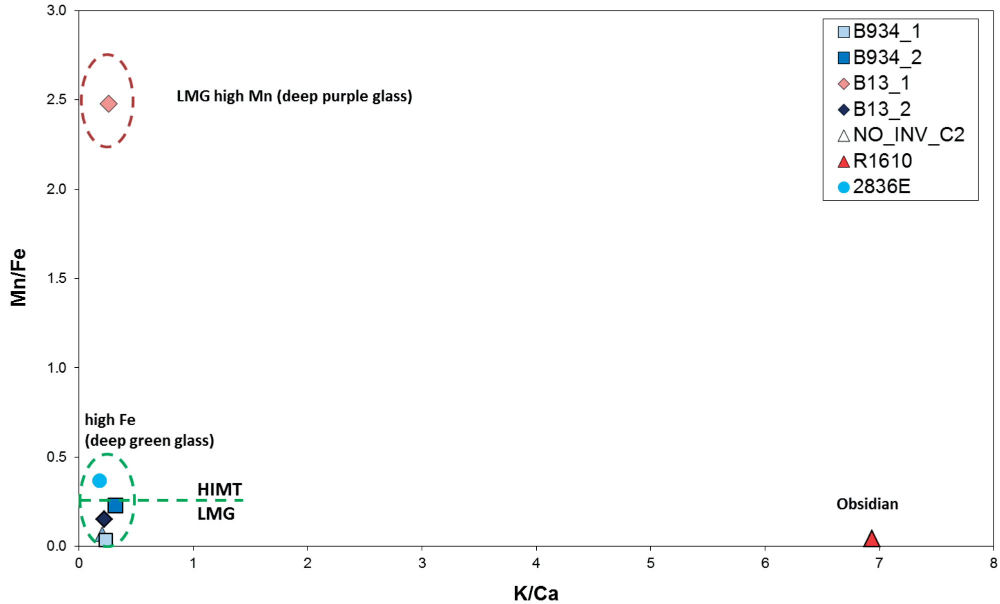

Figure 3. Plot of the Mn/Fe versus K/Ca ratios (results based on semi-quantitative micro-XRF) of R1610 and other Roman man-made glass. The Mn/Fe ratio identifies the Mn purple-coloured glasses from the Fe-green coloured. A K/Ca ratio lower than 0.3 is typical for Roman man-made glass, while a K/Ca ratio of 7 is characteristic to obsidian.

der Linden et al. (2009). The semi-quantitative p-XRF analyses further confirm that the R1610 is obsidian, and not of man-made glass of the Roman age. A further comparison with different types of obsidian could possibly provide more information on the geographical origin of fragment R1610.

Summarizing, the two possible options on the production of the *vitrum obsianum* fragment R1610 are that:

a) the object is made from Fe-rich obsidian, such as the Pantelleria one, by cold-working using drilling, cutting, grinding and polishing techniques in order to obtain the desired shape and decoration;
b) the object is made by re-melting pulverized obsidian mixed with an iron source. An experiment to verify if the first option could even be possible was conducted at the Provincial Archaeological Museum (PAM) of Velzeke, Belgium, where a replica of a Roman furnace was built. Obsidian from Monte Arci, Sardinia, was ground to a particle size of 150-500 micron. This was mixed in crucibles with industrial sodium carbonate 1:1, substituting natron. A glassblowing attempt of this melt resulted positive. More details on this particular experiment are presented in Cagno et al. (2010).

Raman spectroscopy

Some of the aforementioned samples have been measured by Raman spectroscopy. In particular the obsidian from Tunisian sites described earlier was measured, together with obsidian from Monte Arci (Sardinia) and Turkey.

The Raman signal of glass is mainly characterized by two broad bands: the first occurs at low wavenumber (~ 500 cm^{-1}) and is assigned to the vibrations due to the bending motions of Si–O–Si and to the breathing modes of the silica network (McMillan, 1984; Colomban, 2008). The second broad band occurs at high wavenumber (~1000 cm^{-1}) and it is ascribed to the stretching vibration modes of Si–O bond in the SiO_4 tetrahedra. The bands are very large due to the actual superimposition of the different silica units, so-called Q_n species, where n represents the number of bridging oxygen by silicon (McMillan, 1984).

The degree of polymerization of glass is strongly linked to the presence of disruptive elements of the network, i.e. alkalis and at lower extent alkaline earths. On the other hand, increasing amounts of glass forming oxides, such as Al_2O_3, intensifies the polymerization of the network. The bending modes are more important in polymerized glasses, while the stretching band is related to depolymerized network. Consequently it is relatively simple to distinguish the Raman signature of natural obsidian and Roman black appearing glass. The differences in the respective spectra are highlighted in Figure 4 and in the following paragraphs.

Obsidians are glasses rich in silica and aluminum, whilst the alkali content is quite low. The silica network is highly polymerized and the bending mode is strongly pronounced. The main peak of the bending band is at about 460 cm^{-1} as reported in literature for high silica soda-lime-silicate glasses (Matson, 1983). The study of the shape of the stretching envelope can be related, in some cases, to the provenance of the obsidian (Bellot-Gurlet, 2006).

In man-made black glass the content of alkalis, particularly Na_2O, is relatively high. The band at 460 cm^{-1} decreases in intensity, while a band at 560 cm^{-1} becomes evident. The exact position of this band is linked to the content of alkalis (Matson, 1983). Furthermore the stretching band is much more intense than for the natural obsidian. The band at about 415 cm^{-1} that is visible in black appearing ancient glass is due to the strongly reducing conditions, which promoted the formation of Fe-S complex. This

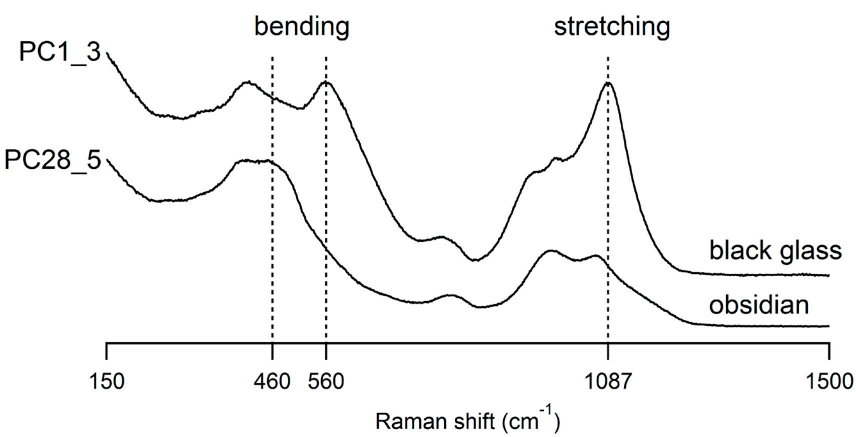

Figure 4. The Raman signal of a Roman black glass (Low magnesium glass, high iron) and a natural obsidian glass (Carthage). The bending modes are more relevant in obsidian than in man-made glass (peak at 460 cm^{-1}). On the contrary, the stretching band at 1087 cm^{-1}, due to Q_3 species is more prominent in Roman glass. The band at 560 cm^{-1} is due to bending motions of depolymerized network.

is a strong chromophore that contributes to the formation of the black hue (Baert et al., 2011; Ceglia et al., 2014).

In Figure 5 we present the Raman spectra of different samples of Roman age obsidian and three compositional types of man-made black glass (Ceglia et al., 2014). The composition of the Carthage and Sidi-Jdidi fragments can be observed in Table 3. The Raman spectra of all Tunisian material corroborates the SEM-EDX measurements showing all Carthaginian material has identical spectra except one (Table 2 - PC28-8 green) and the Sidi Jdidi *tessera* is similar to the Carthaginian set. We can therefore assume that the Sidi Jdidi *tessera* and the Bir Messaouda chunks most likely are coming from the same obsidian source.

These spectra are an addition to the data already available on Roman black appearing glass (Baert et al., 2011; Cosyns, 2011, Ceglia et al., 2014), and representing the three main groups of black-appearing glass: Low Magnesium Glass (LMG), High Magnesium Glass (HMG), and High Iron Manganese Titanium (HIMT). These glasses, in the upper part of Figure 5, can be clearly distinguished from obsidian (in the lower part of Figure 5), from the bands highlighted in Figure 4. Consequently, Raman spectroscopy proves to be a suitable method to help distinguishing objectively man-made glass from obsidian. If a portable Raman spectrometer is available, such analyses can be performed in situ, e.g. in museums or archaeological excavations.

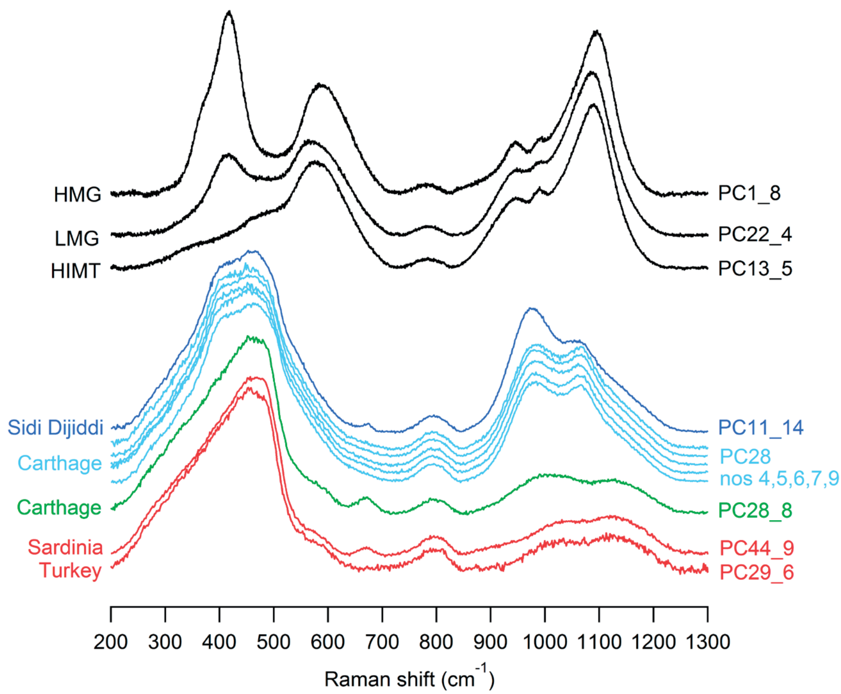

Figure 5. Raman spectra of Roman obsidian and man-made glass from different locations. When compared with Fig. 2 it is clear how the bending modes peak at 460 cm^{-1} are evident and the stretching band at 1087 cm^{-1} is lower than in man-made glass. Examples of Raman spectra of black Roman glass can be found in Baert et al. (2011).

Conclusion

Firstly this paper emphasizes the lack of good indications on the use of obsidian material in Roman imperial times and late Antiquity. Only through a large-scale inventory and a targeted research including material sciences it is possible to develop a detailed overview on the consumption of obsidian from the 1st to mid-7th centuries AD. To this point no attention is paid to the occurrence of obsidian *tesserae* in many sample sets of glass *tesserae*. However, the supply of obsidian to produce mosaic stones is evidence to assume that from the 5th-6th century onwards mosaic workers rather recycled large amounts of glass *tesserae* from abandoned or destroyed buildings than to produce glass cakes as in the prior 3rd-5th century AD.

The analysis results show clearly that all material can be easily defined by means of non-destructive methods. In a first step the use of p-XRF can clearly differentiate obsidian artefacts from man-made glass. More advanced analytical studies with this device on pre- and protohistoric obsidian has also shown the possibility to define the different sources and subsources and can thus be useful to define in a semi-quantitative way the Roman and late Antique obsidian sources. The same outcome can be obtained from Raman spectroscopy, though solely in a qualitative way. For the origin of fragment R1610 two options remain open on the basis of the high iron content: either 1) the glassworkers added iron (oxide) when remelting the obsidian or 2) for this particular object iron-rich obsidian such as the one from Pantelleria was used. Only a quantitative measurement by means of (nearly) non-destructive laboratory techniques such as SEM-EDX and LA-ICP-MS will define whether the piece has been cold-processed from a block of obsidian or by re-melting obsidian.

Furthermore, from the 1st century AD glass workshop of 'La Montée de la Butte' in Lyon it is clear from the chemical composition that these chunks are obsidian of unknown Mediterranean origin, while for most of the Late Antique material from the early Christian basilica of Bir Messaouda in Carthage and the early Christian southern basilica in Sidi Jdidi a Pantellerian origin can be put forward, due to their high iron content. Further confirmation comes from the non-destructive Raman measurements, that clearly show, among the measured material, two different obsidian groups, one comprising Sardinian, Turkish and one Tunisian obsidian, while the other made of the remaining Carthage samples and Sidi Jdidi one. Only additional research on Roman and late antique obsidian artefacts will provide information on the possible role of Pantellerian obsidian in the production of *tesserae* for applying wall and vault mosaics, and whether the Romans had a preference for this very opaque black obsidian from Pantelleria, or also made use of other obsidian sources.

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