

EARLY OPACIFIERS IN THE GLAZE INDUSTRY OF FIRST MILLENNIUM BC PERSIA: PERSEPOLIS AND TEPE RABAT*

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This study characterizes the opacifiers and colouring agents used in the glazed bricks of Persepolis (mid-first millennium BC) and the Mannean site of Tepe Rabat in north-western Iran (eighth to seventh centuries BC). Various analytical studies show that lead antimonate and brizziite (NaSbO_3) were used as the yellow and white opacifiers in the glazes of Persepolis and Tepe Rabat. Brizziite is shown to be incorporated in the white, green and turquoise glazes, and is also associated with lead antimonate and CaSb_2O_6 in some yellow and white opacifiers. The simultaneous formation of these opacifiers in one glaze might have been accidental. A possible connection between the Achaemenid glaze industry and the Mannean glaze production at Tepe Rabat is discussed.

KEYWORDS: BRIZZIITE, EARLY OPACIFIERS, PERSEPOLIS, TEPE RABAT, LEAD ANTIMONITE, CALCIUM ANTIMONITE, MICRO-RAMAN SPECTROSCOPY, XRD

INTRODUCTION

Evidence of early glazed objects is reported from various archaeological sites in Mesopotamia and Iran (Fig. 1). The early glaze industry is mostly known to begin in the 14th century BC, with the glazed objects of Nuzi (Vandiver 1983) and Tell Brak (Henderson 1997) in Mesopotamia. Soon after, different colouring agents and opacifiers were introduced to the glaze industry at Tchogha Zanbil in south-western Iran (Ghirshman 1966). The tradition of glaze-making was then pursued at Hasanlu, north-western Iran (Stapleton 2012), at the very beginning of the first millennium BC and reached to a turning point with the neo-Assyrians in the ninth century BC (Freestone 1991). The glaze industry was then continuously evolved in north-western Iran during the eighth to seventh centuries BC at Qalaichi (Hassanzadeh and Mollasalehi 2011), Tepe Rabat (Kargar and Binandeh 2009) and Ziwiye (Barnett 1956), and was followed by the neo-Elamites at Susa, south-western Iran (Amiet 1967). The summit of early glaze technology may, however, be found

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Figure 1 Archaeological sites in Mesopotamia and Iran with evidence of early glazed objects.

in the neo-Babylonian glazed bricks (Fitz 1983; Matson 1986). The last links in this chain may be found in the Achaemenid period, after which the glaze industry attracted less attention in terms of colours and opacifiers.

The Achaemenid glazed objects have been reported to be found at Tol-e Ajori (Askari Chaverdi *et al.* 2013), Susa (Caubet 1992), Babylon (Haerincx 1973) and Persepolis (Schmidt 1953), among which analytical studies have only been directed on the glazed bricks of Susa. Bigot (1913) was the first to analyse the glazed bricks of Susa, not long after their excavation. Caubet and Kaczmarczyk (1998) then qualitatively analysed these glazed bricks and provided an insight into their colouring agents and opacifiers. Using scanning electron microscopy (SEM) and scanning electron microscopy – energy-dispersive X-ray spectroscopy (SEM–EDS) and X-ray diffraction (XRD), the studies of Tite and Shortland (2004) and Jung and Hauptmann (2004) gave a more detailed picture of the glaze industry in the Achaemenid period. Accordingly, Caubet (2007) suggested elements responsible for opacifying and colouring the Achaemenid glazed bricks at Susa. These studies were followed by Holakooei (2013), who used micro-Raman spectroscopy (μ -Raman) and micro X-ray fluorescence spectrometry (μ -XRF) to determine both the colouring agents and the opacifiers of an Achaemenid glazed brick excavated at Susa. As far as the Tepe Rabat glazed bricks are concerned, using SEM–EDS and XRD, Ahmadi (2010) has analysed both bodies and their covering glazes, and has discussed the opacifiers and colouring agents of the glazes.

Studies conducted on early opacifiers used in ancient Mesopotamia and Iran are rare. Most of these studies are based on the elemental composition of the glazes and determination of the opacifiers based on the elements of which they are composed. There are also some other attempts based on using methods such as XRD (Tite and Shortland 2004; Holakooei 2014) and μ -Raman (Holakooei 2013, 2014), which are able to determine the mineralogical composition of the opacifiers. Most of the previous literature is based on the fact that these glazes are opacified with only one type of opacifier. These opacifiers have been usually reported to be lead antimonate

($\text{Pb}_2\text{Sb}_2\text{O}_7$), calcium antimonate (CaSb_2O_6) or sodium antimonate (NaSbO_3), which create yellow and white colours in the glazes. However, as discussed by Holakooei (2013, 2014), rather than a unique opacifier being used in an individual glaze, a mixture of opacifiers might have been used. This research is mainly focused on the opacifiers of the less technologically known glazes excavated at Persepolis and Tepe Rabat, using SEM-EDS, μ -Raman, μ -XRF and XRD to identify the possible opacifiers used in the glazes, and to provide a note on the colouring agents and the chemical composition of the glazes. This study was also directed at the Achaemenid glazes of Persepolis and their precedents in Tepe Rabat to shed light on any possible connection between the glaze industries of the two sites in the first millennium BC.

EXPERIMENTAL

Samples

The studied glazed bricks of Persepolis contained only one or two coloured glazes on top of a siliceous body. These glazed bricks were from those materials recently excavated from the water canals of Persepolis. The glazes encompassed turquoise, green, yellow and white colours separated by a relief glaze, which had a dark blue colour (hereafter, 'the dark blue separating glaze'). Although most of these glazes were severely deteriorated, remains of the glazes were tightly fused to the siliceous bodies of the Persepolis glazed bricks. No glazed brick had an accession number and the coloured glazes were sampled from four glazed brick shards shown in Figures 2 (a) – 2 (d); that is, the yellow, white, turquoise, green and dark blue separating glazes were sampled from the glazed bricks represented in Figures 2 (a), 2 (b), 2 (c) (both turquoise and green) and Figure 2 (d), respectively.

Several types of glazed materials, including ordinary, serrated and stair-shaped glazed bricks, together with glazed doornails, have recently been excavated at Tepe Rabat in Sardasht, north-western Iran. These glazed objects are dated back to the eighth to seventh centuries BC (Kargar and Binandeh 2009). Unlike the Persepolis glazed bricks, the Tepe Rabat coloured glazes were applied on red clay-based bodies. The palette of the glazes was comprised of green, white, turquoise and yellow colours, sometimes separated by either black or dark green glazes (Figs 2 (e) – 2 (i)). In the Tepe Rabat glazed bricks, however, the separating glaze was not the same as that of Persepolis; that is, it was mostly either greater in width (Figs 2 (f) and 2 (h)) or it did not exist at all (Fig. 2 (i)). In comparison with the Persepolis glazes, the Tepe Rabat glazes were more severely deteriorated, so that they could be easily removed by a slight touch of hand. In some cases, however, the glazes were entirely removed from the bodies, so that only a trace of a previous glaze could be observed on the bodies (Fig. 2 (h)). Five glazed brick shards from Tepe Rabat that had reference numbers were selected to be investigated; that is, RAB.2006.C5III6.33, RAB.2006.C5III6.14, RAB.2006.C3III7.27, RAB.2006.C3III7.120 and RAB.2006.C5III5.34. These shards were labelled as RAB14, RAB27, RAB33, RAB34 and RAB120 to simplify further analytical descriptions.

Analytical procedure

The μ -XRF spectrometer was a portable ARTAXTM 200 from Bruker AXS Microanalysis GmbH. The instrument consisted of an X-ray tube equipped with a Mo target placed at 6° and a Be window. The measurements were performed at 50 kV and 700 μ A for 120 s through a collimator with a diameter of 0.65 mm. An SSD Peltier-cooled detector (10 mm² active area

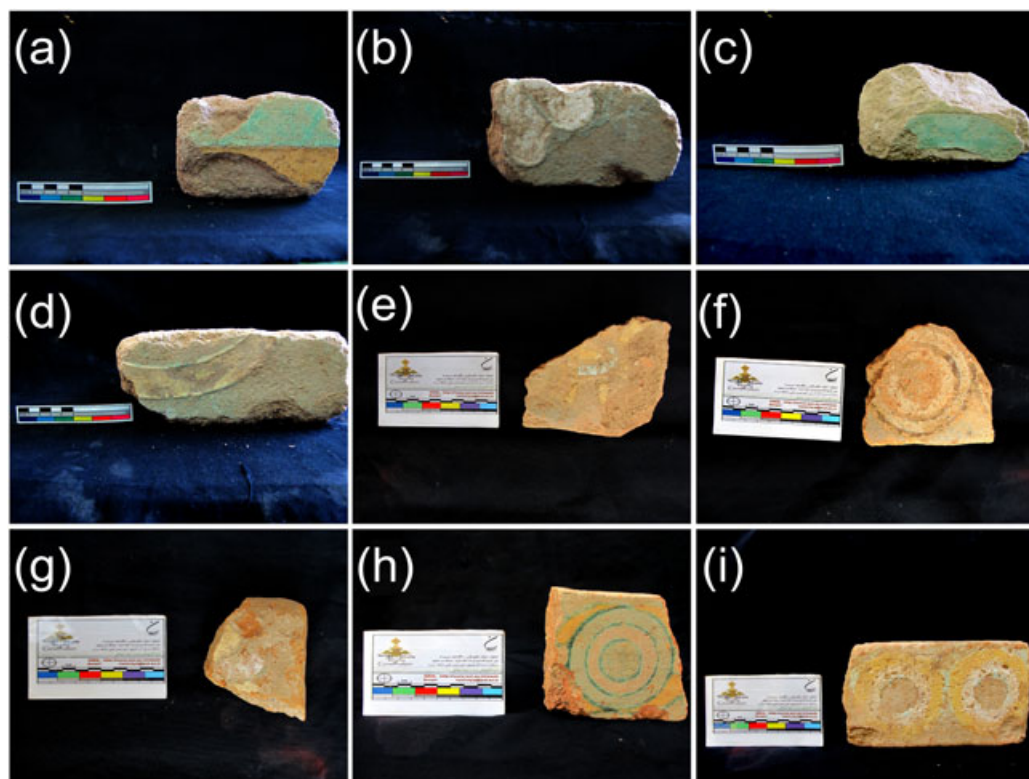


Figure 2 Four glazed brick shards from Persepolis (a–d) and glazed bricks (e) RAB14, (f) RAB27, (g) RAB33, (h) RAB34 and (i) RAB120 from Tepe Rabat.

and resolution of < 155 eV at 10 kcps) was used for the detection of the secondary fluorescent X-rays. As the thickness of glazes was very small and they were very friable and powdery, EDS microanalyses were performed on small chips of the glazes rather than on their cross-sections. Due to severe weathering, the EDS results on the glassy matrix of the glazes were misleading, as their alkali content was markedly leached out. Thus, EDS microanalysis was limited to the opacifiers observed under backscattered electron micrographs. SEM observations and EDS microanalyses were carried out under variable pressure using a Zeiss EVO MA 15-HR SEM, equipped with an INCA Energy 250 x-act Oxford EDS microanalysis system and working at 20 kV.

As the glazes were severely deteriorated, it was not practically feasible to acquire adequate amounts of sample to perform XRD analyses on all of the glazes. XRD patterns of samples were acquired using an Ultima IV Rigaku X-ray diffractometer, working with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA, and with a step size of 0.02° in the $5\text{--}90^\circ 2\theta$ range. Crystalline phases were identified based on the International Centre for Diffraction Data Powder Diffraction Files (ICDD PDF2). Since it was not possible to carry out XRD analyses on all glazes, μ -Raman, as a non-invasive method, was also used to characterize the opacifiers of the glazes. A LabRam HR800 spectrometer (Horiba Jobin Yvon, France), equipped with an air-cooled CCD detector (1024×256 pixels) at -70°C , an Olympus BXFM microscope and a 600 grooves per millimetre

grating were used to acquire Raman spectra of the opacifiers. The focal length of the spectrometer was 80 mm and the Raman spectra were recorded using a He–Ne laser, with a wavelength of 632.8 nm as excitation source: the laser power ranged between 0.2 and 20 mW and the exposure time was 10–20 s, with 10 accumulations. The spectrometer was calibrated using silicon at 520 cm^{-1} and the measurements were achieved with 50 \times and 100 \times objectives.

RESULTS

The chemistry of the opacifiers

According to the μ -XRF analysis, all opacified glazes had Sb in their composition, conveying the fact that Sb-based opacifiers were used for opacifying the glazes (Table 1). However, EDS micro-analysis on various spots of the opacifiers from different-coloured glazes showed more interesting details (Table 2 and Fig. 3 (a)). As shown in Figure 3 (a), except for the opacifiers used in the yellow glazes of Tepe Rabat, no Pb-incorporated opacifier was used in the Tepe Rabat glazes. In other words, the opacifiers used in the green, white and turquoise glazes of Tepe Rabat had various proportions of the Ca/Sb and Na/Sb atomic ratios. On the contrary, except for the opacifiers used in the Achaemenid white glazes of Persepolis, which appeared to have only Na and Sb in their composition, the coloured glazes of Persepolis were opacified using various quantities of Pb, Ca and Na. It was interesting to see that no unique chemical composition could be considered for a certain type of opacifier; for example, the white opacifiers of Tepe Rabat.

On the other hand, the opacifiers used in the Persepolis glazes showed, on average, 7.4 at% of Si ($\sigma = 4.4$ for 132 spots analysed by EDS). Similarly, the Si content was 8.1 at% on average ($\sigma = 4.6$ for 78 spots analysed by EDS) for the Tepe Rabat opacifiers. Moreover, the correlation coefficient for the Si–Na, Si–Ca, Si–Sb, Si–Pb and Si–O pairs of atomic percentages for the Achaemenid opacifiers were recorded as -0.14 , -0.41 , -0.64 , -0.38 and -0.34 , respectively. The correlation coefficients of these pairs for the Tepe Rabat opacifiers were calculated at -0.54 , -0.43 , -0.40 , 0.00 and -0.25 , respectively. The negative and small correlation coefficient of Si and other elements showed that the chemical composition of the opacifiers does not significantly depend on the Si content. Thus, one may suggest that the Si content in the composition of the opacifiers is related to the weathered glazes surrounding the opacifiers rather than the opacifiers themselves.

As far as the EDS results on the opacifiers of the white glazes of Tepe Rabat are concerned, it seems that three groups of white opacifiers were used in these glazes, the first of which was composed of fairly equal atomic proportions of Sb and Na; that is, a Na/Sb atomic ratio of about 1 (Figs 3 (a) and 3 (b)). Supporting this idea, μ -Raman registered Raman bands at 157, 230, 303, 314, 616 and 660 cm^{-1} consistent with the mineral brizziite; that is, sodium antimonate (NaSbO_3) (Frost and Bahfenne 2010) (Fig. 4 (a)), the Na/Sb atomic ratio of which is 1. The second group of the white opacifiers seemed to be composed of Ca, Na and Sb, with Na/Sb and Ca/Sb atomic ratios of 0.6 and 0.4 on average, respectively. Interestingly, μ -Raman registered calcium antimonate, CaSb_2O_6 , associated with brizziite, with the Raman bands at 238, 326, 338 and 670 cm^{-1} (Ricciardi *et al.* 2009) in the white glaze of RAB34 (Fig. 4 (c)). A Na/Sb atomic ratio of less than 1 in some white glazes of Tepe Rabat showed that the excess amount of antimony could be incorporated in the composition of other opacifiers; that is, CaSb_2O_6 . The third group of opacifiers used in the Tepe Rabat glazes was only sparsely observed with a low Na/Sb and a high Ca/Sb atomic ratio. This opacifier was apparently composed of a form of calcium antimonate. Accordingly, a μ -Raman study confirmed the sporadic presence of CaSb_2O_6 in the white glaze of RAB34, with Raman bands at 236, 325, 335, 518 and 670 cm^{-1}

Table 1 A summary of the μ -XRF, XRD and μ -Raman results on the Persepolis and Tepe Rabat glazes and opacifiers

Coloured glazes	Samples	μ -XRF results	XRD results	μ -Raman results	
				Raman bands (cm^{-1})	Compound
Green	Persepolis	Si, K, Ca, <u>Cu</u> ,* Sb , [†] Pb (Ti, Mn, Fe, Zn, Rb, Sr) [‡]	Pb ₂ Sb ₂ O ₇ NaSbO ₃ (Na,Sb)Sb ₂ O ₇ SiO ₂ CaCO ₃	107, 514	Lead antimonate
				159, 229, 304, 314, 615, 660	Brizziite
				1086	Calcite
				157, [§] 230, 659 157, 280, 714, 1087	Brizziite Calcite
RAB27	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	156, 229, 658	Brizziite
				156, 279, 714, 1086	Calcite
				239, 324, 338, 670	Calcium antimonate
				278, 1087	Calcite
RAB33	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	Si, K, Ca, <u>Cu</u> , Sb , Fe (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)	156, 228, 305, 613, 659	Brizziite
				128, 205, 465	Quartz
				154, 279, 712, 1084	Calcite
				155, 228, 302, 312, 614, 659	Brizziite
RAB120	Si, K, Ca, Sb , Fe, <u>Cu</u> (Ti, Cr, Mn, Ni, Zn, Sr, Pb)	Si, K, Ca, Sb , Fe, <u>Cu</u> (Ti, Cr, Mn, Ni, Zn, Sr, Pb)	Si, K, Ca, Sb , Fe, <u>Cu</u> (Ti, Cr, Mn, Ni, Zn, Sr, Pb)	154, 280, 712, 1086	Calcite
				155, 229, 303, 313, 615, 660	Brizziite
				155, 280, 711, 1086	Calcite
				155, 280, 712, 1087	Calcite
White	Persepolis	Si, K, Ca, Sb , Fe (Ti, Cr, Mn, Ni, Cu, Zn, Sr, Pb)	NaSbO ₃ CaCO ₃ SiO ₂	155, 280, 712, 1087	Calcite
				155, 659	Brizziite
				154, 229, 612, 658	Brizziite
				154, 278, 711, 1085	Calcite
RAB33	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Pb)	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Pb)	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Rb, Sr, Pb)	238, 326, 338, 670	Calcium antimonate
				157, 230, 303, 314, 616, 660	Brizziite
				154, 281, 711, 1086	Calcite
				157, 231, 304, 314, 615, 660	Brizziite
RAB120	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Sr, Pb)	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Sr, Pb)	Si, K, Ca, Fe, Sb (Ti, Cr, Mn, Ni, Cu, Zn, Sr, Pb)	281, 711, 1087	Calcite
				72, 200, 140, 300, 334, 455, 511, 752	Lead antimonate
				70, 90, 142, 201, 300, 336, 382, 453, 512, 745	Lead antimonate
				154, 280, 712, 1087	Calcite
Yellow	Persepolis	Si, K, Ca, Fe, Sb , Pb (Ti, Cr, Mn, Ni, Cu, Zn, Rb, Sr)	Pb ₂ Sb ₂ O ₇ Pb ₃ Sb ₂ -z(O,OH,H ₂ O) ₆ SiO ₂	72, 200, 140, 300, 334, 455, 511, 752	Lead antimonate
				70, 90, 142, 201, 300, 336, 382, 453, 512, 745	Lead antimonate
				154, 280, 712, 1087	Calcite
				154, 280, 712, 1087	Calcite

(Continues)

Table 1 (Continued)

Coloured glazes	Samples	μ -XRF results	XRD results	μ -Raman results	
				Raman bands (cm^{-1})	Compound
	RAB33	Si, K, Ca, Fe, Sb, Pb (Ti, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr)	$\text{Pb}_2\text{Sb}_2\text{O}_7$ PbCO_3 SiO_2	70, 87, 140, 200, 299, 333, 450, 511, 744 151, 279, 709, 1086	Lead antimonate Cerussite
	RAB34	Si, K, Ca, Fe, Sb, Pb (Ti, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr)		67, 86, 140, 199, 297, 332, 448, 510, 745	Lead antimonate
	RAB120	Si, K, Ca, Fe, Sb, Pb (Ti, Cr, Mn, Ni, Cu, Zn, As, Rb, Sr)	$\text{Pb}_2\text{Sb}_2\text{O}_7$ SiO_2	72, 91, 143, 201, 299, 337, 452, 513, 745	Lead antimonate
Separating glaze (Fig. 2 (d))	Persepolis (Fig. 2 (d))	Si, K, Ca, Fe, <u>Co</u> , <u>Cu</u> , Sb (Ti, Mn, Zn, As, Rb, Sr, Pb)		223, 241, 289, 407, 493, 608, 657 305, 550, 680 465	Haematite Magnetite Quartz
				154, 280, 711, 1086	Calcite
				221, 243, 289, 407, 608, 660 68, 88, 140, 199, 293, 332, 451, 510, 746	Haematite Lead antimonate
	RAB27 (black)	Si, K, Ca, <u>Fe</u> , <u>Cu</u> , Sb, Pb (Ti, Cr, Mn, Ni, Zn, Rb, Sr)		155, 228, 303, 312, 614, 660	Brizziite
	RAB34 (green)	Si, K, Ca, Fe, <u>Cu</u> , Sb (Ti, Cr, Mn, Ni, Zn, Rb, Sr, Pb)			

*Colouring agents are underlined.

†Elements participating in opacifiers are shown in bold type.

‡Minor and trace elements are in parentheses.

§The underlined values are common Raman bands between two constituents.

(Fig. 4 (b) and Table 1). According to EDS microanalysis, the Achaemenid white glazes of Persepolis, however, seemed to have minor quantities of Ca in their composition, showing that a form of sodium antimonate was predominantly used in their composition (Fig. 3 (a) and Table 2). XRD and μ -Raman also supported the EDS results, showing NaSbO_3 as the main opacifier of the Persepolis white glaze (Table 1).

The opacifiers used in the green glazes of Tepe Rabat and Persepolis were entirely different. As μ -XRF suggested, while the green glazes of Persepolis showed Pb in their composition, the green glaze of Tepe Rabat proved to be lead free, suggesting sodium and calcium antimonate as possible opacifiers of the glazes (Table 1). As the EDS microanalysis suggested, various opacifier particles in the Persepolis green glazes showed a fairly broad range of Na, Ca and Pb antimony-based opacifiers, with various proportions of sodium antimonate, calcium antimonate and lead antimonate (Figs 3 (a) and 3 (d), and Table 2). As XRD suggested, the green glazes of Persepolis were not only opacified with brizziite, but also with lead antimonate yellow (Table 1). A μ -Raman study, however, revealed more details about the lead antimonate used in

Table 2 The semi-quantitative EDS elemental data of the opacifiers (results in at%)

Coloured glaze	Site	Figure	Group	Spots	O	Na	Si	Ca	Sb	Pb	Na/Sb	Ca/Sb	Pb/Sb	
White	Persepolis	2 (b)	1	14	70.1	5.4	16.9	1.0	6.7	n.d.*	0.8	0.2	0.0	
				σ^\dagger	(1.4)	(0.7)	(1.5)	(0.2)	(0.7)	(0.0)	(0.1)	(0.0)		
	Tepe Rabat	2 (g)	1	6	74.5	7.3	9.1	1.7	7.4	n.d.	1.0	0.2	0.0	
				σ	(2.3)	(2.7)	(4.7)	(1.3)	(2.2)	(0.0)	(0.1)	(0.2)		
	Turquoise	Persepolis	2 (c)	3	7	73.1	5.0	11.6	2.4	7.9	n.d.	0.6	0.4	0.0
					σ	(3.7)	(2.3)	(4.6)	(1.1)	(3.9)	(0.0)	(0.1)	(0.2)	
1					84.6	0.1	9.4	3.5	2.5	n.d.	0.0	1.4	0.0	
Tepe Rabat		2 (i)	1	12	72.0	6.7	2.8	4.0	12.6	2.0	0.5	0.3	0.2	0.0
				σ	(1.4)	(0.6)	(1.6)	(0.4)	(2.0)	(0.2)	(0.1)	(0.1)	(0.0)	
				2	69.4	6.0	7.4	2.6	11.2	3.5	0.6	0.2	0.3	0.3
Green	Persepolis	2 (c)	1	21	(3.1)	(0.9)	(2.6)	(0.4)	(2.5)	(0.7)	(0.1)	(0.0)	(0.1)	
				σ	71.0	8.2	5.5	1.8	10.5	3.0	0.8	0.2	0.3	0.3
				29	(1.4)	(0.7)	(2.8)	(0.2)	(1.8)	(0.4)	(0.2)	(0.1)	(0.0)	(0.0)
	Tepe Rabat	2 (i)	2	24	71.9	8.0	8.6	1.7	9.6	0.1	0.8	0.2	0.0	0.0
				σ	(2.8)	(2.8)	(5.2)	(0.8)	(2.4)	(0.1)	(0.2)	(0.1)	(0.0)	
				29	77.1	6.7	5.8	4.5	5.8	0.1	1.2	0.9	0.0	0.0
Yellow	Tepe Rabat	2 (g)	1	22	(2.3)	(2.3)	(3.2)	(2.1)	(1.7)	(0.1)	(0.2)	(0.5)	(0.0)	
				σ	74.2	2.1	7.5	2.9	9.0	4.3	0.2	0.3	0.5	0.5
				2	(2.1)	(0.7)	(2.1)	(0.6)	(1.5)	(1.0)	(0.1)	(0.1)	(0.1)	
Yellow	Persepolis	2 (a)	1	2	76.0	2.1	19.1	1.1	1.8	n.d.	1.3	1.0	0.0	
				σ	(2.0)	(2.0)	(2.5)	(0.6)	(1.9)	(0.0)	(0.2)	(0.8)	(0.0)	
				34	75.6	0.5	7.3	1.3	7.7	7.7	0.1	0.2	1.0	1.0
Yellow	Tepe Rabat	2 (i)	1	9	(3.9)	(0.3)	(3.1)	(0.7)	(1.6)	(1.6)	(0.0)	(0.1)	(0.1)	
				σ	76.7	0.6	8.7	1.5	5.8	6.8	0.1	0.3	1.2	1.2
				9	(2.3)	(0.3)	(3.1)	(0.6)	(1.6)	(1.7)	(0.1)	(0.3)	(0.3)	(0.3)

*Not detected.

†Standard deviations in parentheses.

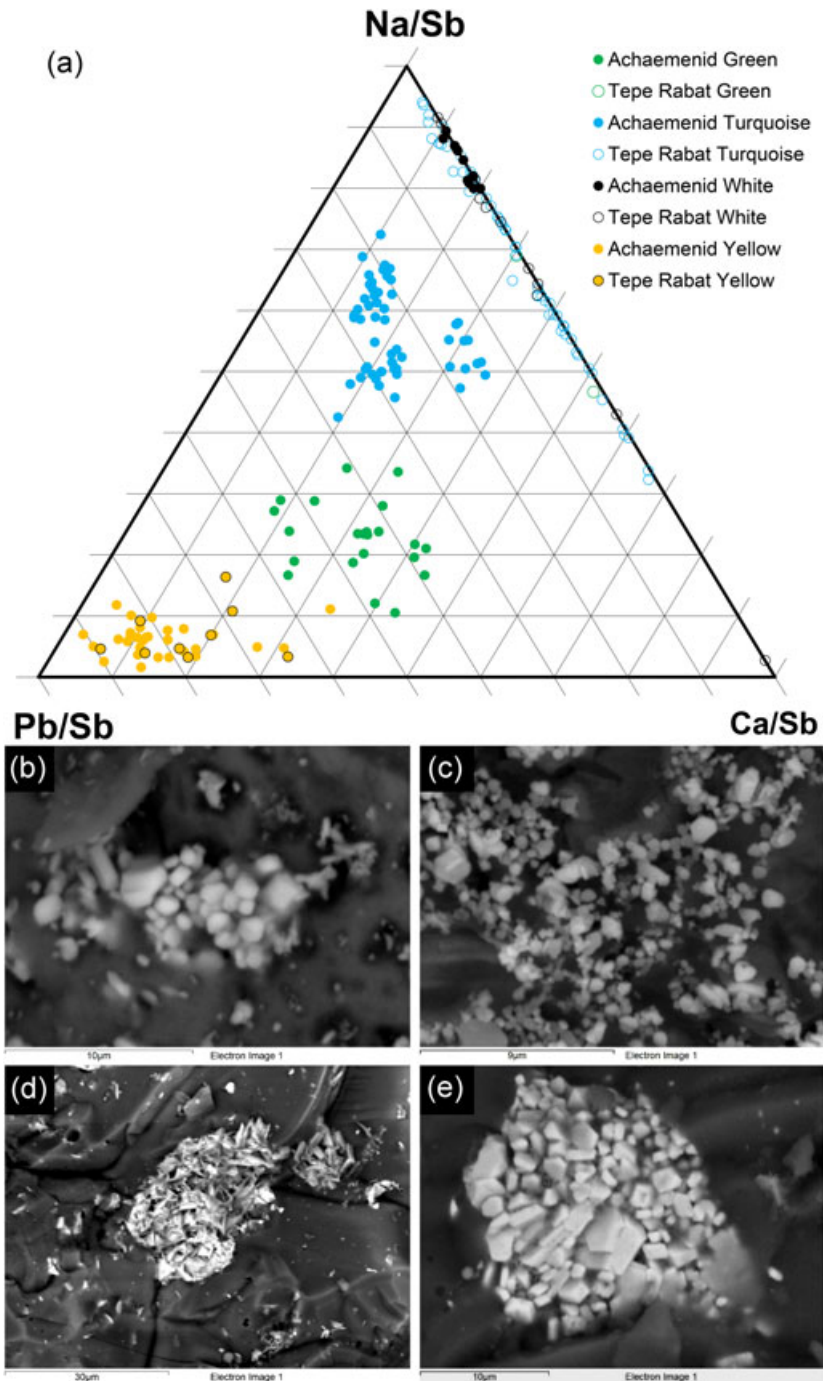


Figure 3 A ternary diagram (a) of the EDS semi-quantitative microanalyses of various opacifiers of Persepolis and Tepe Rabat, together with SEM backscattered images of (b) NaSbO_3 crystals in the white glaze of RAB33, (c) NaSbO_3 crystals in the turquoise glaze of RAB120, (d) a mixture of lead antimonate and NaSbO_3 in the green glaze of Persepolis and (e) $\text{Pb}_2\text{Sb}_2\text{O}_7$ crystals in the yellow glaze of Persepolis.

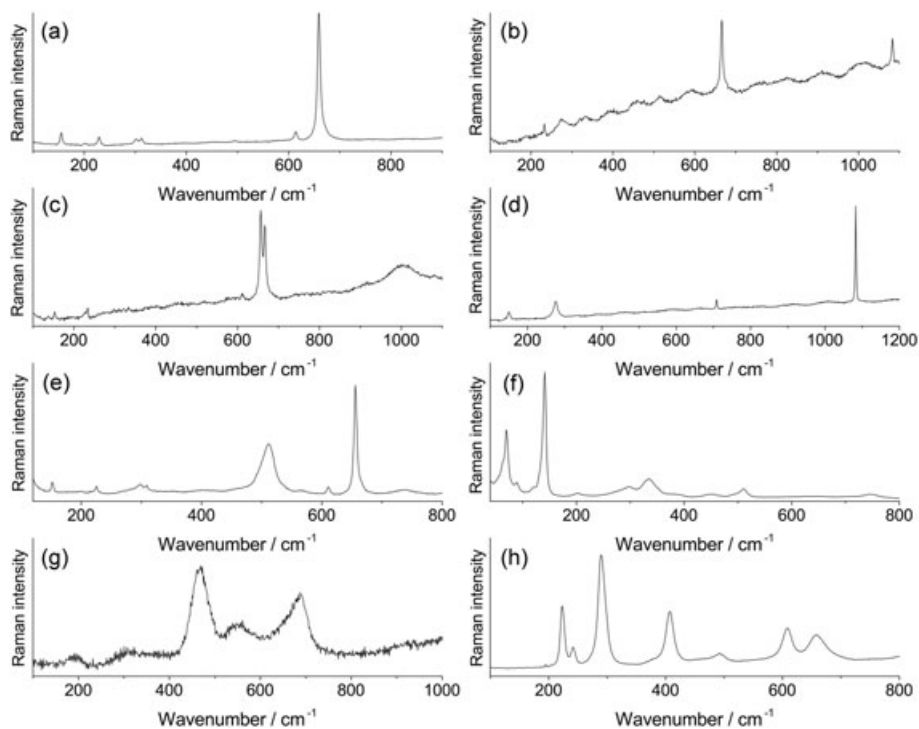


Figure 4 Raman spectra of (a) NaSbO_3 in the white glaze of Persepolis, (b) CaCO_3 and CaSb_2O_6 in the white glaze of RAB34, (c) a mixture of NaSbO_3 and CaSb_2O_6 in the white glaze of RAB34, (d) CaCO_3 in the white glaze of RAB14, (e) a mixture of NaSbO_3 and lead antimonate in the green glaze of Persepolis, (f) $\text{Pb}_2\text{Sb}_2\text{O}_7$ in the yellow glaze of Persepolis, (g) a mixture of quartz and magnetite, and (h) haematite in the dark blue separating glaze of Persepolis.

the Persepolis green glaze, with the Raman band centred at 514 cm^{-1} (Fig. 4 (e)). Rosi *et al.* (2009) have discussed how a Sb/Pb ratio greater than 1 in the composition of lead antimonate gives a higher intensity of the Raman band at 513 cm^{-1} . Apart from lead antimonate, μ -Raman showed brizziite mixed with lead antimonate in the composition of the opacifiers of the Persepolis green glaze (Fig. 4 (e)). Moreover, XRD showed a minor occurrence of another form of sodium antimonate—that is, $(\text{Na,Sb})\text{Sb}_2\text{O}_7$ —in the Persepolis green glaze, which contains higher proportions of Sb in its composition (Table 1). As far as the Tepe Rabat green glazes are concerned, μ -Raman showed brizziite associated with CaSb_2O_6 as opacifiers used in these glazes. It was very interesting that μ -Raman did not show brizziite as opacifier of RAB34, but CaSb_2O_6 . Unfortunately, the very thin layer of deteriorated Tepe Rabat green glazes did not permit further analytical studies on the opacifiers of those glazes (Table 1).

The yellow glazes of both Tepe Rabat and Persepolis glazed bricks were shown to be mainly composed of Pb and Sb, as suggested by μ -XRF (Table 1). According to the EDS microanalyses, a Pb/Sb atomic ratio close to 1 suggested that a form of lead antimonate with equal atomic percentages of Pb and Sb, such as bindheimite ($\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$), was used in these glazes as opacifier (Table 2 and Fig. 3 (e)). The XRD analysis on the yellow glazes showed that the main component opacifying the yellow glazes was $\text{Pb}_2\text{Sb}_2\text{O}_7$ (Table 1). Supporting the XRD and EDS results, Raman bands centred at 70, 90, 142, 201, 300, 336, 382, 453, 512 and 745 cm^{-1} showed

that $\text{Pb}_2\text{Sb}_2\text{O}_7$ was the yellow opacifier (Clark *et al.* 1995) (Fig. 4 (f)) with which the yellow glazes of both Persepolis and Tepe Rabat were associated. The lower intensity of the Raman band at 512 cm^{-1} and the higher intensity of the Raman band at 142 cm^{-1} showed that the Pb/Sb atomic ratio should be close to 1 (Rosi *et al.* 2009). XRD also showed $\text{Pb}_x\text{Sb}_{2-x}(\text{O},\text{OH},\text{H}_2\text{O})_6$ associated with $\text{Pb}_2\text{Sb}_2\text{O}_7$ in the Persepolis yellow glazes (Table 1).

As the μ -XRF studies showed, while the opacifiers of the Achaemenid turquoise glazes were shown to be composed of Sb, Ca and Pb, the Tepe Rabat turquoise glazes showed no Pb in their composition (Table 1). EDS microanalysis confirmed this observation, showing that Na was also taking part in the composition of the opacifiers of the turquoise glazes. EDS, moreover, showed three variations of composition in the opacifiers of the Persepolis turquoise glaze (Fig. 3 (a) and Table 2). Apart from Sb, the main composing element of most of these opacifiers was Na, with which lower quantities of Ca and Pb were associated. In other words, the EDS results showed that the opacifiers of the Persepolis turquoise glazes could be sodium antimonate, calcium antimonate or lead antimonate. Although μ -Raman confirmed the occurrence of brizziite in the composition of the Persepolis turquoise glazes, it showed no evidence of Ca- and Pb-incorporated opacifiers in these glazes. This conflicts with the EDS results on these opacifiers, which showed fairly high Ca/Sb and Pb/Sb atomic ratios in two groups of opacifiers of the Persepolis turquoise glazes (Table 2). On the other hand, the opacifiers of the Tepe Rabat turquoise glazes were shown to be mainly composed of Na and Ca, the atomic percentages of which showed sodium antimonate and calcium antimonate as possible opacifiers of the glazes. XRD and μ -Raman on the opacifiers of the turquoise glazes of Tepe Rabat supported the EDS results, showing brizziite as the main opacifier of these glazes (Fig. 3 (c)). Although Ca was shown to be incorporated in a set of Tepe Rabat turquoise glazes, no evidence of any form of calcium antimonate was proved by μ -Raman or XRD (Table 1). One should take into account the fact that the opacifiers used in the glazes of Tepe Rabat showed a relatively high concentration of Ca (2.81 at% on average, with $\sigma = 1.97$ for 78 EDS measurements). This may be explained by the burial environment from which the Tepe Rabat glazed bricks were excavated (see the following paragraph).

Apart from the above-mentioned opacifiers, calcite (CaCO_3) was abundantly detected in white, green and turquoise glazes either by μ -Raman, with Raman bands at 154, 278, 711 and 1085 cm^{-1} (Krishnamurti 1957) (Fig. 4 (d)), or by XRD analysis (Table 1). Calcite most probably has a secondary origin, as its chance of surviving during firing is very low. The abundant occurrence of the secondary calcite, especially in the Tepe Rabat opacifiers, may explain the high concentration of Ca in the composition of these opacifiers. Another interesting issue was the presence of cerussite, PbCO_3 , in the composition of the yellow glaze of RAB33 (Table 1). Cerussite can be considered as a weathering product of the highly Pb containing yellow glaze of Tepe Rabat, or it may be formed as a weathering product of Pb-bearing minerals such as galena (Lara *et al.* 2011), which may have been used in the glazes of Tepe Rabat. As the XRD analysis suggested (Table 1), quartz was also found to be in all of the glazes, probably because of the burial deposits.

A note on the colouring agents and the chemical composition of the glazes

Apart from the opacifiers observed in the glazes of Persepolis and Tepe Rabat, other issues were revealed during the analytical studies, amongst which the question of the colouring agent of the glazes was interesting. The most important colouring agent used in the glazes of both Persepolis and Tepe Rabat was Cu, which had contributed to colouring the turquoise and green glazes of

both sites and to the dark blue separating glaze of Persepolis. Moreover, Co was only found to be incorporated in the turquoise glaze and the dark blue separating glaze of Persepolis. There might be different proportions of Co and Cu incorporated in the glazes to create the two shades of blue; that is, turquoise and dark blue separating glazes (Table 1).

On the other hand, Fe played an important part in the glaze composition at both sites. Although the presence of Fe can be mostly attributed to impurities and burial contaminations, evidence of the deliberate use of iron oxides in the composition of the dark blue separating glaze of Persepolis was provided by μ -Raman. The Raman bands centred at 223, 241, 289, 407, 493, 608 and 657 cm^{-1} and those at 305, 550 and 680 cm^{-1} are associated with haematite (Fe_2O_3) and magnetite (Fe_3O_4), respectively (Hanesch 2009) (Figs 4 (g) and 4 (h)). Apart from the iron oxides, the dark blue separating glaze showed a fairly broad Raman band at 465 cm^{-1} , which can be attributed to quartz (Kingma and Hemley 1994) (Fig. 4 (g)). The association of iron oxides, Co, Cu and quartz could be a good way to create a very dark shade in a glaze with a fairly high maturing temperature. This was due to the need of the glaze-makers to avoid the juxtaposed glazes running together prior to and during firing. However, as indicated in Table 1, the green and black separating glazes in the Tepe Rabat glazed bricks did not seem to play the same role as the dark blue separating glaze of Persepolis, as they did not have a high concentration of quartz in their composition and, conversely, they were opacified with either lead antimonate or brizziite.

Another important issue concerning the chemical composition of the glazes was their particular associations with As, Ni, Zn, Rb and Cr. As can be seen in Table 1, As was only associated with the yellow glazes of Tepe Rabat and the dark blue separating glaze of Persepolis. Since As was not observed in other glazes of Tepe Rabat with a low Pb content, it may be associated with the Pb-bearing material used in the yellow glazes of Tepe Rabat. However, the association of the dark blue separating glaze of Persepolis with As may not have the same explanation (see the Discussion section). Attributing other elements such as Ni, Rb and Cr to a certain substance or glaze may, however, be confusing. For instance, as can be seen in Table 1, Ni and Cr were associated with the white and yellow glazes of Persepolis. This may suggest that these elements are linked with the Sb used in these glazes. Nonetheless, these elements were not detected in other Sb-bearing glazes of Persepolis; that is, the green and turquoise glazes. Moreover, it is not clear what Rb may be linked with. However, looking at Table 1, some issues can be perceived from these elements. For example, Ni and Cr were shown to be highly correlated; that is, Ni was associated with those glazes that contained Cr. One cannot exclude the possibility that all these may be due to burial condition and the places from which these glazed bricks were excavated.

DISCUSSION

The presence of brizziite as the main opacifier of the glazes was an interesting issue. Considering stibnite (Sb_2S_3) and natron as possible raw materials for producing brizziite, the formation of NaSbO_3 from these materials needs a long firing process (about 7 days) (Ramírez-Meneses *et al.* 2007). As it does not seem likely that the ancient glaze-makers would have been able to employ a long soaking time for firing glazes on bodies, it can be suggested that NaSbO_3 may have been precipitated instead of calcium antimonate in the glazes incorporating a low level of Ca, as discussed by Tite and Shortland (2004).

The occurrence of brizziite as white opacifier was also of major interest from another standpoint. Although most of previous studies report CaSb_2O_6 as white opacifier of early vitreous materials (Shortland 2002; Holakoei 2013, 2014), Stapleton (2012) reported NaSbO_3 associated with lead antimonate and calcium antimonate as the white opacifier of Iron Age glasses from Hasanlu, north-

western Iran, which chronologically and geographically has close ties with Tepe Rabat (Fig. 1). It is interesting that while Tite and Shortland (2004) document the use of NaSbO_3 as the white opacifier of an Achaemenid glazed brick from Susa, Holakooei (2013) records CaSb_2O_6 as the opacifier of another Achaemenid glazed brick from Susa. This may be due to the fact that these two studies have investigated the Achaemenid glazed bricks from two production centres or two glaze technologies or two different periods of time during the long period of Achaemenid rule (550–330 BC). Moreover, the formation of CaSb_2O_6 instead of another form of calcium antimonite— that is, $\text{Ca}_2\text{Sb}_2\text{O}_7$ —was totally to be expected, because of the higher temperatures that $\text{Ca}_2\text{Sb}_2\text{O}_7$ needs to form, which are usually achievable in ancient glasses (Lahlil *et al.* 2010).

The differences between the glaze production in Susa and Persepolis are not only limited to the use of white opacifiers, but also to other aspects, amongst which the composition of the dark glaze used as a barrier between the coloured glazes is interesting. As Holakooei (2013) showed, the dark separating glaze of the Achaemenid glazed brick was achieved by mixing quartz, haematite and magnetite, to which Cu was added to produce a darker colour. The composition suggested in this study for the separating glazes of Persepolis also had Co as a colouring agent, although the remaining ingredients were the same as those for the dark glazes of Susa. The role of the separating dark glaze was to keep glazes separated prior to and during firing, because of the high maturing temperature caused by the high quartz content.

It should be mentioned that the separating glazes of Tepe Rabat glazed bricks seem to be different with respect to the Achaemenid glazed bricks. While the separating glazes of Tepe Rabat recall the neo-Assyrian low-relief separating glazes, the Achaemenid separating glazes seem to be narrower and with higher relief, better suited to act as a barrier between two coloured glazes. One should note, however, that the Tepe Rabat separating glazes may have been abraded off the surface of the bricks as a result of their severe weathering and their burial environment. Taken together, it does not seem that the separating glazes in the Tepe Rabat glazed bricks have the same functionality as those of the Achaemenid glazed bricks in Susa and Persepolis, as the separating glazes are sometimes entirely absent in the Tepe Rabat glazed bricks (Fig. 2 (i)).

The use of lead antimonate has always been the sole means of achieving yellow colours in glassy materials in the ancient Near East (Hedges and Moorey 1975; Pollard and Moorey 1982; Fitz 1983; Freestone 1991; Caubet and Kaczmarczyk 1998; Caubet 2007; Holakooei 2013, 2014). Two key points may, however, be highlighted in this regard. First, as this study has shown, lead antimonate yellow may be formed in the composition of glazes with various Pb/Sb atomic ratios. Second, lead antimonate may be associated with other opacifiers such as calcium antimonate (Holakooei 2013) or sodium antimonate for opacifying glazes, as proved in this study.

As far as the colouring agents of the studied glazes are concerned, Cu has been the most usual element historically used to achieve green and turquoise glazes. The use of iron oxides in early glazes to achieve a range of colours from orange to dark black colour in early glazes has already been documented (Holakooei 2013, 2014). The interesting point, however, relates to the use of Co in the composition of the turquoise and dark blue separating glazes of Persepolis. Unlike the blue glaze of the Achaemenid glazed brick of Susa (Holakooei 2013), the dark blue separating glaze of Persepolis was associated with As. Dark blue shades have already been reported to be achieved by Cu in association with Fe and Co in the neo-Babylonian glazes (Fitz 1983; Matson 1986) and the Achaemenid dark blue glazes of Susa (Holakooei 2013). The particular association of As with Co observed in the dark blue separating glaze of Persepolis may be attributed to As-bearing minerals of Co; that is, erythrite ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) and cobaltite (CoAsS). These minerals have been reported to be quarried in Qamsar, near Kashan in central Iran (Stöllner 2004), for use in Islamic glazes (Matin and Pollard 2015). Since As was not detected in other

glazes of Persepolis, it is most probably linked to Co. However, due to the complex composition of the glazes under study, this assumption may need to be investigated with more appropriate analytical tools. One reason for this claim is that if As was associated with Co, it should also have been detected in the other Co-incorporated glaze of Persepolis; that is, the turquoise glaze.

CONCLUSION

This paper has suggested that a mixture of opacifiers may be detected in an archaeological glaze. Although the formation of these opacifiers has mostly been intentional, some opacifiers might also have been formed arbitrarily in the glazes. In other words, a minor occurrence of randomly formed opacifiers may be seen in the early opacified glazes in addition to the principal opacifier initially intended to be incorporated in the glazes.

The production of glazed bricks in Persepolis and Tepe Rabat shows a puzzling technological association. While the use of the same opacifiers— that is, Na and Pb antimonate—may be the most important common point between the two technologies, the incorporation of Co as a colouring agent in the glazes of Persepolis may be an important difference. Moreover, it seems that Pb was basically an important element in the composition of Persepolis opacifiers, whereas Pb only plays a part in the yellow opacifiers used in the Tepe Rabat glazes, which highlights another difference between these two technologies.

According to the inscription of Darius I (Kent 1950, 144), he moved Babylonians to Susa to make glazed bricks for his palace. This may explain why the Achaemenid glazed bricks show similarities to their Babylonian antecedents. However, it should be mentioned that the Achaemenid glazed technology may not have remained identical during the long rule of the Achaemenids in Persia (550–330 BC). A more systematic analytical study on the Achaemenid glazed bricks excavated at Susa, Babylon and Tol-e Ajori (an early Achaemenid archaeological site located 3 km west of Persepolis) may play a key role in characterizing the Achaemenid glaze industry. Moreover, a more in-depth study of the neo-Assyrian, neo-Elamite and neo-Babylonian glazes may shed light on the dark angles of glaze production in the first millennium BC in Mesopotamia and, moreover, open a new window towards the characterization of the Achaemenid glaze technology. Future research may study how much the glaze industry in north-western Iran influenced the Achaemenid glaze production and, moreover, the extent to which the Achaemenid glaze industry owes its advances to the preceding Babylonian glaze technology.

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REFERENCES

- Ahmadi, M., 2010, *Technical studies and conservation of glazed bricks of Tepe Rabat (Sardasht)*, Art University of Isfahan, Isfahan, Master of Arts thesis (in Farsi).
- Amiet, P., 1967, *Éléments émaillés du décor architectural néo-Élamite*, *Syria*, **44**, 27–46.

- Askari Chaverdi, A., Callieri, P. F., and Gondet, S., 2013, Tol-e Ajori, a new monumental building in Parsa: preliminary cross interpretations from recent surveys and excavations works around Persepolis (2005–2012), *ARTA*, **2013-006**, 1–40.
- Barnett, R. D., 1956, The treasure of Ziwiye, *Iraq*, **18**, 111–6.
- Bigot, A., 1913, Les frises du palais de Darius et leur fabrication (V^e siècle av. J.-C.), *Comptes-rendus des séances de l'Académie des Inscriptions et Belles-Lettres*, **4**, 247–80.
- Caubet, A., 1992, Achaemenid brick decoration, in *The royal city of Susa: ancient Near Eastern treasures in the Louvre* (eds. P. O. Harper, J. Aruz, and F. Tallon), 223–36, The Metropolitan Museum of Art, New York.
- Caubet, A., 2007, in *Faïences et matières vitreuses de l'Orient ancien: étude physico-chimique et catalogue des oeuvres du département des Antiquités orientales* (eds. A. Caubet, A. Bouquillon, A. Kaczmarczyk, and V. Matoian), 101–37, Musée du Louvre, Paris.
- Caubet, A., and Kaczmarczyk, A., 1998, Les briques glaçurées du palais de Darius, *Techné*, **7**, 23–6.
- Clark, R. J. H., Cridland, L., Kariuki, B. M., Harris, K. D. M., and Withnall, R., 1995, Synthesis, structural characterisation and Raman spectroscopy of the inorganic pigments lead tin yellow types I and II and lead antimonate yellow: their identification on medieval paintings and manuscripts, *Journal of the Chemical Society, Dalton Transactions*, **16**, 2577–82.
- Fitz, S. C., 1983, The coloured glazes of neo-Babylonian wall facings, *Ceramic Forum International: Berichte der Deutsch Keramischen Gesellschaft*, **59**, 179–85.
- Freestone, I. C., 1991, Technical examination of neo-Assyrian glazed wall plaques, *Iraq*, **53**, 55–8.
- Frost, R. L., and Bahfenne, S., 2010, Raman spectroscopic study of the antimonate mineral brizziite NaSbO₃, *Radiation Effects and Defects in Solids: Incorporating Plasma Science and Plasma Technology*, **165**, 206–10.
- Ghirshman, R., 1966, *Tchogha Zanbil (Dur-Untash): la ziggurat*, Mémoires de la Mission Archéologique en Iran, XXIX, Paris.
- Haerincq, E., 1973, Le palais achéménide de Babylone, *Iranica Antiqua*, **10**, 108–32.
- Hanesch, M., 2009, Raman spectroscopy of iron oxides and (oxy)hydroxides at low laser power and possible applications in environmental magnetic studies, *Geophysical Journal International*, **177**, 941–8.
- Hassanzadeh, Y., and Mollasalehi, H., 2011, New evidence for Mannean art: an assessment of three glazed tiles from Qalaichi (Izirtu), in *Elam and Persia* (eds. J. Álvarez-Mon and M. B. Garrison), 407–17, Eisenbrauns, Winona Lake, IN.
- Hedges, R. E. M., and Moorey, P. R. S., 1975, Pre-Islamic ceramic glazes at Kish and Nineveh in Iraq, *Archaeometry*, **17**, 25–43.
- Henderson, J., 1997, Scientific analysis of glass and glaze from Tell Brak and its archaeological implications, in *Excavations at Tell Brak*, vol. 1: *Mitanni and Old Babylonian periods* (eds. D. Oates, J. Oates, and H. McDonald), 94–100, Macdonald Institute, Cambridge.
- Holakooei, P., 2013, A multi-spectroscopic approach to the characterization of early glaze opacifiers: studies on an Achaemenid glazed brick found at Susa, south-western Iran (mid-first millennium BC), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **116**, 49–56.
- Holakooei, P., 2014, A technological study of the Elamite polychrome glazed bricks at Susa, south-western Iran, *Archaeometry*, **56**, 764–83.
- Jung, M., and Hauptmann, A., 2004, Report on the scientific examination of a glazed brick from Susa: colours, in *Persiens antike pracht—Band 2* (eds. T. Stöller, R. Slotta, and A. Vatandoust), 390–2, Deutschen Bergbau-Museums Bochum, Bochum.
- Kargar, B., and Binandeh, A., 2009, A preliminary report of excavations at Rabat Tepe, northwestern Iran, *Iranica Antiqua*, **44**, 113–29.
- Kent, R. G., 1950, *Old Persian: grammar, texts, lexicon*, American Oriental Society, New Haven, CT.
- Kingma, K. J., and Hemley, R. J., 1994, Raman spectroscopics study of microcrystalline silica, *American Mineralogist*, **79**, 269–73.
- Krishnamurti, D., 1957, The Raman spectrum of calcite and its interpretation, *Proceedings of the Indian Academy of Sciences—Section A, Mathematical Sciences*, **46**, 183–202.
- Lahlil, S., Biron, I., Cotte, M., and Susini, J., 2010, New insight on the *in situ* crystallization of calcium antimonate opacified glass during the Roman period, *Applied Physics A*, **100**, 683–92.
- Lara, R. H., Briones, R., Monroy, M. G., Mullet, M., Humbert, B., Dossot, M., Naja, G. M., and Cruz, R., 2011, Galena weathering under simulated calcareous soil conditions, *Science of the Total Environment*, **409**, 3971–9.
- Matin, M., and Pollard, M., 2015, Historical accounts of cobalt ore processing from the Kashan mine, Iran, *IRAN*, **53**, 171–83.
- Matson, F. R., 1986, Glazed bricks from Babylon: historical setting and microprobe analyses, in *Ceramics and civilization*, vol. 2: *Technology and style* (ed. W. D. Kingery), 133–56, American Ceramic Society, Columbus, OH.
- Pollard, A. M., and Moorey, P. R. S., 1982, Some analyses of middle Assyrian faïence and related materials from Tell al-Rimah in Iraq, *Archaeometry*, **24**, 45–50.
- Ramírez-Meneses, E., Chavira, E., Domínguez-Crespo, M. A., Escamilla, R., Flores-Flores, J. O., and Soto-Guzmán, A. B., 2007, Synthesis and characterization of NaSbO₃ compound, *Superficies y Vacío*, **20**, 14–8.

- Ricciardi, P., Colomban, P., Tournié, A., Macchiarola, M., and Ayed, N., 2009, A non-invasive study of Roman age mosaic glass tesserae by means of Raman spectroscopy, *Journal of Archaeological Science*, **36**, 2551–9.
- Rosi, F., Manuali, V., Miliani, C., Brunetti, B. G., Sgamellotti, A., Grygar, T., and Hradil, D., 2009, Raman scattering features of lead pyroantimonate compounds, part I: XRD and Raman characterization of $\text{Pb}_2\text{Sb}_2\text{O}_7$ doped with tin and zinc, *Journal of Raman Spectroscopy*, **40**, 107–11.
- Schmidt, E. F., 1953, *Persepolis I: structures, reliefs, inscriptions*, The University of Chicago Press, Chicago.
- Shortland, A. J., 2002, The use and origin of antimonate colorants in early Egyptian glass, *Archaeometry*, **44**, 517–31.
- Stapleton, C. P., 2012, Glass and glaze analysis and technology from Hasanlu, period IVB, in *Peoples and crafts in Period IVB at Hasanlu, Iran* (ed. M. de Schauensee), 87–102, University of Pennsylvania Press, Philadelphia, PA.
- Stöllner, T., 2004, Notes on mining archaeological structures at the cobalt mine of Qamsar, in *Persiens antike Pracht: Bergbau, Handwerk, Archäologie: Katalog der Ausstellung des Deutschen Bergbau-Museums Bochum vom 28. November 2004 bis 29. Mai 2005* (eds. T. Stöllner, R. Slotta, and A. Vatandoust), 515, Deutschen Bergbau-Museums Bochum, Bochum.
- Tite, M. S., and Shortland, A. J., 2004, Report on the scientific examination of a glazed brick from Susa: glazes, in *Persiens antike Pracht: Bergbau, Handwerk, Archäologie: Katalog der Ausstellung des Deutschen Bergbau-Museums Bochum vom 28. November 2004 bis 29. Mai 2005—Band 2* (eds. T. Stöllner, R. Slotta, and A. Vatandoust), 388–90, Deutschen Bergbau-Museums Bochum, Bochum.
- Vandiver, P. B., 1983, Glass technology at the mid-second millennium BC Hurrian site of Nuzi, *Journal of Glass Studies*, **25**, 239–47.