



## Article

# Glass Finds from the Elite House of Roue, a Sasanian City Building in Western Iran: Composition and Classification Using XRF and Raman Spectroscopy

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**Abstract:** The Silk Road connected the east of Iran to the western world. Roue city is close to the Road. Six glass samples from Roue were classified on the basis of morphology, archaeological context and compositions. The samples were analysed by means of XRF and Raman spectroscopy and two specific groups, namely Roue type 1 and Roue type 2, with close composition to high alumina plant-ash glass in circulation from the 6th to 10th centuries CE in Mesopotamia, Iran and Syria, were identified. The simultaneous occurrence of two types of glass in the excavated layers shows that the house was inhabited in the early Islamic period. Colours (black, amber-green, light and aqua blue) were produced mainly by the amount of iron and sulphur ions required for the amber chromophore and copper ions for the blue colour and the controlling of reducing conditions in the furnace.

**Keywords:** Iran; the early Islamic period; XRF; Raman spectroscopy; glass; composition



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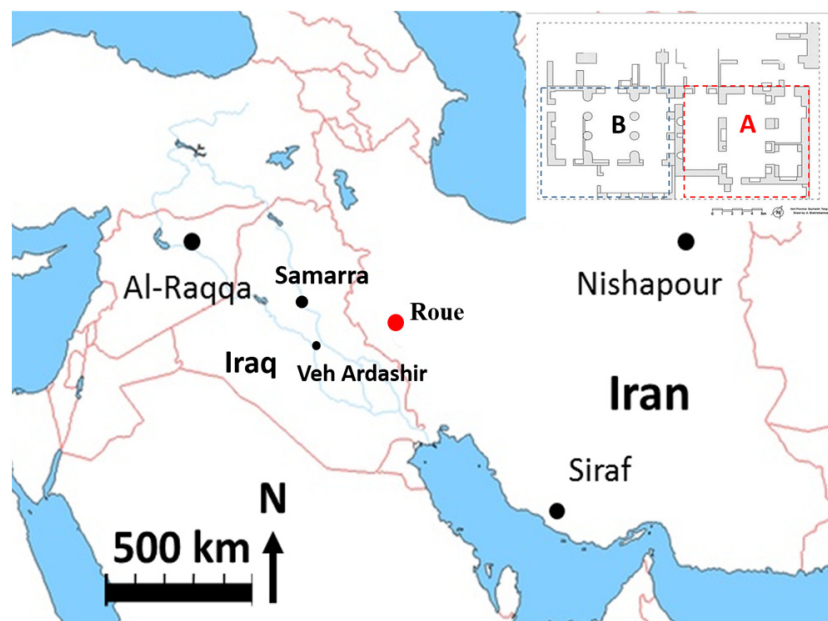
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## 1. Introduction

Glass manufacturing dates back to 1500 BC in the Near East [1], and many objects have been found in the archaeological contexts, including Iran, from that time. However, the glass objects from Iran (within current boundaries), covering a variety of functions from vessels to ornaments, have received less attention for their composition and origin than those of neighbouring geographic areas. Among the finds, ornaments such as glass bracelets are the least studied. Therefore, very little information about the number of finds, manufacturing methods, their decoration and composition is available. The archaeological discoveries in the Near East revealed that bracelets had been common ornaments from the 3rd century CE due to the large number of finds in the eastern Mediterranean region and adjacent countries [2]. These early bracelets are mostly monochrome and have generally an opaque black colour. It was only after the 4th century CE and particularly during the Islamic period (from the 7th century CE) that bracelets were manufactured in a wider variety of styles and colours. Spaer [2] argued that the early pre-Islamic styles had continued to be used in the Islamic period.

In this article, six glass samples excavated from the remains of a house with Sasanian architectural style in the watershed of the Seimare River (Roue city, Figure 1) are studied. The amounts of major and minor oxides of the glasses obtained by XRF measurements are compared with the Sasanian (or Sassanid) (224–651 CE) [3,4] and early Islamic (after 651 CE) samples [5–10] found in the close neighbourhood of the sites in order to find their possible origin and relative date. The selected sites for comparison are Sasanian

and Islamic towns of Veh Ardashir (3rd–7th century CE) [3,4], Samarra (9th century CE) in Iraq [6], the medieval port of Siraf on the northern shore of the Persian Gulf (8th–early 11th century AD) [7] and al-Raqqa in the north of Syria (8th–9th century AD) [8–10]. In addition to the discussion on the glass composition and colouration based on the XRF results, Raman spectroscopy was also used for recognising glass types and pigments. The choice is made to use methods that can be implemented non-invasively on various sites (excavation sites, museum reserves). In addition, we will address comparing the parameters determining the manufacture of glass (network formers and flux, colouring agents).



**Figure 1.** Mesopotamia and Iran geographic area showing location of Sassanid Roue city with detail showing the excavated building plan (Section A and B, after ref. [11]).

## 2. Materials and Methods

### 2.1. Historical Context of the Excavated Samples

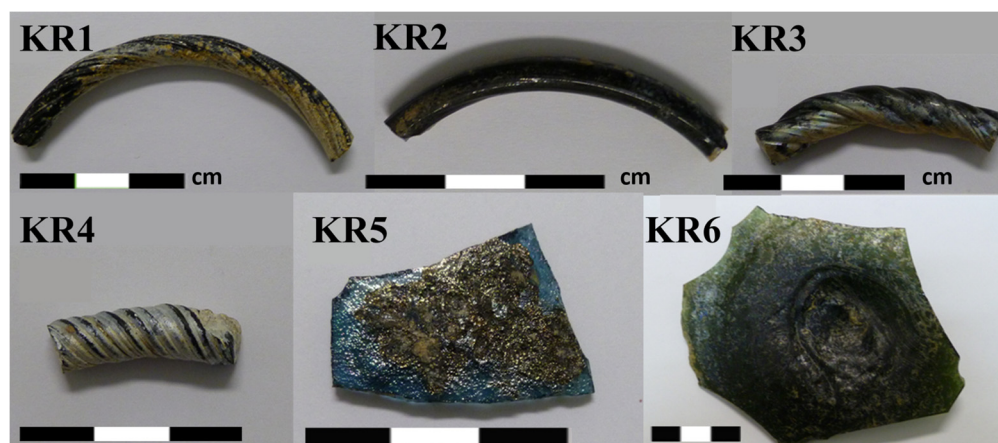
The elite house of Roue is located on the northern slope of the Rouemele Mountain, upstream of the Seimare Dam. The Silk Road connected the east of Iran to the western world, and Roue is close to the Road. The location is adjacent to the Kafari Valley in the Ilam province in the west of Iran (Figure 1). The house shows characteristics of the middle to late Sasanian architecture [11]. The house does not represent the only architectural remains found on the Seimare riverbank. In 1947, Stark [12] referred to the remains of an ancient city in this region where pottery fragments related to the Sasanian-Islamic period have been found. The other Sasanian constructions, such as bridges, buildings, fire temples and castles in the Seimare Valley, demonstrate the historical importance of the area and indicate that the route along the valley was an important connection between Mesopotamia, the Zagros mountains and the southwest plain of Iran (Khuzestan plain) [11,13,14].

The house, as described by Niakan [11], is a one-story building of rubblework masonry with gypsum mortar. The structure consists of two sections (A and B parts), and each section is divided into three non-symmetric chambers. The chambers are connected to each other by arched doorways, which have partially collapsed over time. The surface of the walls and floor were coated with gypsum plaster, and remnants of a stucco relief can still be observed on some parts of the walls. The interior comprises arched and semi-domed niches in the walls. Section B appears to be a later addition to Section A. A small number of glass samples (18 pieces) along with the late Sasanian and early Islamic ceramic shards were found in Section A. The excavation in Kafari Valley was a part of the mission carried out in

a short period of time for rescuing archaeological evidence of the Sassanian and Islamic periods that was later drowned due to the construction of Seimare Dam in 2015. According to Motarjem and Bakhtiari [15], the number of discovered objects in all the excavated sites during this mission was small, probably due to the abandonment of residential structures on the sites before their rehabilitation in the following Islamic period.

## 2.2. Samples Description

Permission was granted to analyse six representative glass samples, 4 monochrome broken bracelets (black, amber, aqua blue) and 2 vessel shards (aqua blue and green) by the chief archaeologist (Lily Niakan) and the Research Institute of Cultural Heritage and Tourism of Iran (Figure 2). The dating of the chosen samples was initially approximated to span from the late Sasanian to the early Islamic period, as inferred from the archaeological context. They are monochrome coloured glass, while completely colourless and colourless glass with a green tint, similar to the Islamic glass of Samarra (Iraq) and Nishapur, was also observed among the samples from layers 1 and 2. The bracelets are of a small size with diameters between 55 and 62 mm, which were appropriate for the use of children. The decoration of the bracelets placed them into two groups of plain (KR2, black colour) and spirally twisted (KR 1 (black), KR3 (amber) and KR4 (light blue)) following Spaer [2].



**Figure 2.** Studied samples: bracelet fragments (KR1, KR2, KR3 and KR4) and pieces of containers (KR5 and KR6); note the pontil mark on KR6 sample.

The cross-sections of the twisted bracelets are circular, and no trace of a fused end is observable on the fragments. The spirally twisted bracelets are generally formed by winding two rods of glass and bending them to form a ring, and the end points are fused together to make a closed ring. The plain bracelet (KR2) is assumed to be seamless due to the cross-section, which is D-shaped. The seamless bracelet is generally formed by pushing a metal rod into a globe of hot glass to form a ring. The above-mentioned manufacturing techniques and the cross-sectional forms (circular and semi-circular) are common in pre-Islamic and Islamic bracelets. Spaer [2] pointed out that both techniques had covered a long period of time from the 3rd or 4th century CE onwards in the Eastern Mediterranean region. Therefore, the manufacturing technique is not a strong clue for dating the bracelets. The attribution to Sasanian production is based first of all on the context of discovery in a building corresponding to this period. There are other evidences that can guide us in connecting the bracelets to the Sasanian and early Islamic periods, such as the small size of the monochrome spiral twisted bracelets, the lack of multi-coloured samples, both of which are more common later in the Islamic period, the type of ceramics found alongside the glass samples, and finally the architectural style of the elite house.

Concerning the morphology of the vessel fragments, one of them (KR6) has a pontil mark that indicates the vessel was manufactured by the free hand-blown technique (Figure 2). In this method, the vessel is shaped by inflating hot molten glass using a blow-

pipe. Then, a glass tip metal rod (extra blowpipe) is used to hold the vessel from the base while the craftsmen manipulate the final form of the vessel mouth. The pipe is finally removed and leaves a scar (pontil mark) at the bottom of the vessel [5]. The scar on the vessel (KR6) consists of two concentric circles that indicate the use of a blowpipe with the diameter of ~3 cm and a wall thickness about 3–4 mm as the pontil (ref. [5] p. 23 mentioned that this kind of pontil mark is commonly observed on vessels belong to the late Sasanian and early Islamic periods). The physical characteristics of the samples are given in Table 1.

### 2.3. Methods

The chemical composition of the samples was examined semi-quantitatively at the laboratory by using a Thermo Scientific ARL PERFORM'X 050 Sequential X-Ray Fluorescence spectrometer (XRF) equipped with Rh anode (up to 60 kV) and LiF200 Ge111 AX03 detector (Thermo Scientific, Waltham, MA, USA). The X-ray path is in vacuum conditions, and the analysed sample area is 25 mm in diameter. The cross-section of the samples was cold-mounted within epoxy resin and polished with diamond paste to obtain an even, un-corroded surface. The samples were washed with distilled water and ethanol to remove traces of polishing material and then dried. The analyses were performed based on the ASTM E1621-13 standard (Available online: <https://www.astm.org/e1621-13.html>, accessed 27 October 2024). UniQuant AS software (Thermo Scientific, Waltham, MA, USA) was used to measure the weight percentage of oxides from fluorine to uranium, and only values were reported that were above the detection limit of the instrument. The statistical uncertainty is less than 0.15% for all the oxides except those with low energy signals, like silica with <0.25%. To compare the composition of Roue samples more accurately with contemporary glass samples from other sites, the relative concentrations of oxides/SiO<sub>2</sub> ratios were used. The comparison of trace elements was not considered because the accuracy of XRF in measuring these elements is not as high as LA-ICP-MS, which has been mostly used for this purpose.

Raman spectroscopy was performed by using a portable HE532 Horiba Jobin Yvon (Longjumeau, France) instrument on polished cross-sections prepared for XRF analyses. A Nd/YAG laser line with a wavelength of 532 nm (Laser Quantum Ventus, Fremont, CA, USA) and with a maximum output power of 80 mW was used for dark samples (about 3 to 5 mW at the sample). The light-coloured samples were analysed using a 300 mW maximum output laser (about 10 to 20 mW at the sample). A Nikon 50× long-working distance microscope objective was used. The surface footprint analysed is about 5 × 5 μm<sup>2</sup>.

**Table 1.** The archaeological context, morphology and estimated date of the samples (TR: excavation trench; L: layer; S: surface according to reference [11]).

Samples	Excavation Context	Object	Shape/Size	Transparency/ Colour	Manufacture/ Decoration	Diameter (mm)	Circulation Technology Period (Century CE)	Chemical Group (Roue)	Date on the Basis of Composition (Century AD)
KR1	Tr: D; L:1	Bracelet	Circular cane/small	Opaque/black	Seamed-loose twisted-monochrome- black	60~	From 4th to 5th onward	Type 2	8th–9th
KR2	Tr: D; L:1	Bracelet	Semi-circular cane/small	Opaque/black	Seamless-plain-monochrome	~55	Early 3rd onward	Type 2	8th–9th
KR3	Tr: D; L:S	Bracelet	Circular cane/small	Opaque-translucent/amber-black	Seamed-loose twist-monochrome	~62	From 4th to 5th onward	Type 2	8th–9th
KR4	Tr: D; L:3	Bracelet	Circular cane/small	Translucent-opaque/light blue	Seamed-dense twisted-monochrome	~60	From 4th to 5th onward	Type 1	9th–10th
KR5	Tr: D; L:1	Vessel fragment	--	Translucent/aqua blue	-	-	?	Type 1	9th–10th
KR6	Tr: D; L:S	Vessel fragment	--	Translucent/amber-green	Free-blown with pontil mark	~30	From 6th to 9th	Type 2	8th–9th



### 3. Results

#### 3.1. Overview of Sassanians and Islamic Mesopotamian Glass

Mirti et al. [3] have published analyses on plant ash glasses from Veh Ardashir and have suggested that the MgO level, MgO/K<sub>2</sub>O ratio and the phosphorus content allow one to recognise two specific groups of glass, namely Sasanian type 1 (S type 1) and type 2 (S type 2). In S type 1, the amount of phosphorus is almost twice as high as in S type 2, and the ratio of MgO/K<sub>2</sub>O (<1.3) is lower than in the latter (>2.3) [3]. Among the Veh Ardashir samples, some of them show different oxide ratios and are situated outside or in an intermediate position compared with the above-mentioned types [3]. The first type was in circulation from the beginning of the Sasanian dynasty, while the S type 2 had been produced from the early 4th century to the early 7th century.

Schibille et al. [6] reported two types of plant-ash glass from Samarra, namely imported glass and Mesopotamian glass. Mesopotamian glass (local productions) contains a high level of magnesia (>4 wt%), and hence a high MgO to CaO ratio, and low phosphorus (<0.15%) and alumina contents (<1.5 wt%). The imported glasses, namely cobalt blue flasks and miscellaneous groups (with some exceptions), show higher alumina content (>1.5 wt%) and lower MgO to CaO ratios compared with Mesopotamian samples. The cobalt blue flasks are assumed to be imported from the eastern Mediterranean, and the miscellaneous samples with high alumina contents (>2.5 wt%) are expected to come from Nishapur (9th–10th century CE), a contemporary central Asian glass-making centre. The latter samples are colourless or green, aqua blue, and amber in colour.

Swan et al. [7] have identified two types of glass in Siraf: the main group and the low zirconium glass. The main group with low magnesia to lime ratios (<0.5) and alumina (<2 wt%) contents is close to Syria-Palestine glass, although no similarity is observed regarding trace elements of zirconium and chromium between these two groups. They concluded that the main group was local production, or the raw glass was imported and worked at the site since its composition is similar to that of the glass-working debris found at the site. The low zirconium glass, regarding the level of major, minor and trace elements, is similar to the 9th–10th century glass of Iran and Iraq, such as Nishapur and Samarra.

Henderson [8] reported three types of plant ash glass that had been produced in al-Raqqa from the 8th to the 9th centuries. Type 1 (R1) contains low alumina and lime derived from pure sand and plant-ash, respectively. Type 2 (R2) glass is a mixture of R1 and natron glass (type 3) imported from the Levantine countries. Type 4 (R4) has a wide range of composition and can therefore be subdivided into two subtypes. The first one is a mixture of sand, plant ash and shell fragments, and the second one comprises quartz, plant ash and probably bone ash.

#### 3.2. Elemental Composition of Roue Samples

The results of the XRF analysis are reported in Table 2. The material is homogeneous and free of weathering regarding the volume analysed (as proven by optically clearness), and the compositions determined by XRF can be considered reliable [16,17]. The results show that all the samples are plant-ash silica-soda-lime glass characterised by MgO and K<sub>2</sub>O levels of 2.4 to 3.8 wt% and 1.4 to 2.4 wt%, respectively. The lead content is low. The Al<sub>2</sub>O<sub>3</sub> level (2.3 to 5 wt%) is high and shows the use of unclean sand as the source of silica in all the samples. The use of unclean sand was common mostly in the production of coloured glass during the Sasanian and later Islamic periods, as it was reported in the case of Sasanian glass type 1 (S type 1) [3], intermediate type (S INT) [3] and some samples of al-Raqqa type 4 (R4) [8,9]: Samarra miscellaneous (Sam misc hAl) [6], Nishapur (Nish hAl) [5] and Siraf low Zr glass (Sir hAl-IZr) [7]. All samples exhibit a certain level (1 to 2.8 wt%) of SO<sub>3</sub> content (Table 2).

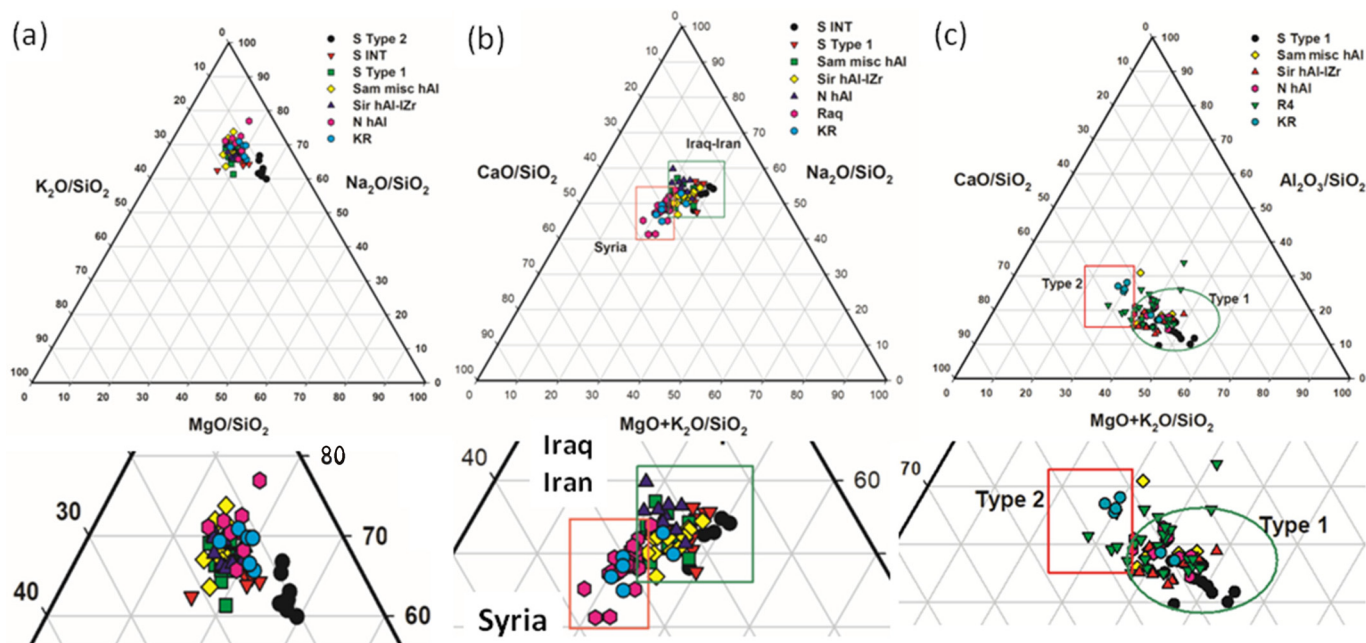
**Table 2.** XRF major and minor oxide composition of the Roue city samples (wt%). The content of the determining colouring element is in bold.

Samples	KR1	KR2	KR3	KR4	KR5	KR6
Colour	<b>Black</b>	<b>Black</b>	<b>Amber-Black</b>	<b>Light Blue</b>	<b>Aqua Blue</b>	<b>Amber-Green</b>
Type	<b>2</b>	<b>2</b>	<b>2</b>	<b>1</b>	<b>1</b>	<b>2</b>
Na <sub>2</sub> O	9.69	9.35	9.11	11.20	11.62	10.49
MgO	2.35	2.53	2.53	2.57	3.84	3.29
Al <sub>2</sub> O <sub>3</sub>	3.38	3.53	3.82	2.31	2.42	5.02
SiO <sub>2</sub>	68.78	66.82	69.04	67.92	67.79	64.64
P <sub>2</sub> O <sub>5</sub>	0.90	0.88	0.76	0.24	0.29	0.55
K <sub>2</sub> O	1.61	1.51	1.40	2.42	2.22	2.00
CaO	5.88	5.95	6.41	5.06	5.59	7.55
TiO <sub>2</sub>	0.18	0.17	0.17	0.10	0.12	0.25
MnO	0.15	0.13	0.12	0.68	0.92	0.09
Fe <sub>2</sub> O <sub>3</sub>	<b>1.19</b>	<b>1.42</b>	<b>1.44</b>	0.74	<b>1.00</b>	<b>2.00</b>
CuO	0.19	0.23	0.16	<b>2.02</b>	0.17	0.08
PbO	0.87	0.82	0.69	1.13	0.57	0.31
SO <sub>3</sub>	<b>1.16</b>	<b>2.78</b>	<b>1.00</b>	0.92	<b>1.04</b>	<b>2.01</b>
Cl	3.67	3.88	3.35	2.68	2.41	1.72
Σ	100	100	100	100	100	100

### 3.3. Comparison with Glass Composition from Near-East Cities

The ternary diagrams in Figure 3 compare the contents of oxide flux (K<sub>2</sub>O, Na<sub>2</sub>O, CaO) with that of elements integrating the polymeric silica network (MgO, Al<sub>2</sub>O<sub>3</sub>). Values are normalised to silica signal. As shown in the diagrams showing the formation temperatures of liquid phases in a system combining network formers (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO) and fluxes (K<sub>2</sub>O, Na<sub>2</sub>O, CaO and PbO [18]), the proportions of these flux components are determining. MgO has a specific behaviour. The relative proportions of these different fluxes also determine synthesis characteristics such as viscosity as a function of temperature. The groups identified in the diagrams are sufficiently different to correspond to different preparation conditions.

Figure 3a shows that Roue house glasses are close to S type 1 [3], S INT [3], Sam misc hAl [6], Nish-hAl [5] and Sir hAl-lZr [7] in their relative concentrations of sodium, potassium and magnesium. However, the relative calcium content of some of the samples (KR1, KR2, KR3 and KR6) is not in the same range as the above-mentioned glass types and is closer to al-Raqqa plant-ash glass (Figure 3b). All Roue samples are separated from Sasanian type 2 glasses due to their magnesium contents, with levels of <4.1 wt% and >6 wt%, respectively.



**Figure 3.** Comparison of the composition ratio (a)  $K_2O$ - $Na_2O$ - $MgO$ ; (b)  $CaO$ - $Na_2O$ - $MgO+K_2O$ ; (c)  $CaO$ - $Al_2O_3$ - $MgO+K_2O$ ) normalised vs.  $SiO_2$  content of studied artefacts (KR) with those identified in the literature for Sasanian glass types and the early Islamic period in the Near to Middle East (Classification types according to Mirti et al. [3]): (a) flux ( $Na_2O$ ,  $K_2O$ ) and  $MgO$  relative content (wt %); (b) flux,  $CaO$  and  $MgO$  relative content (c) Alumina, lime and ( $MgO+K_2O$ ) relative content. S INT: Sasanian intermediate composition; S type 1 and 2: Sassanian type 1 and type 2 glass (after data of Mirti et al. [3]); Sam misc hAl: Samarra miscellaneous glass with high alumina (after data of Schibille et al. [6]); Sir hAl-Izr: Siraf low zirconium glass with high alumina (after data of Swan et al. [7]); N hAl: Nishapour high alumina glass (after data of Kröger [5]); KR: Roue samples; Raq and R4: al-Raqqa type 1 and al-Raqqa type 4 glass (after data of Henderson [8]). Below, a zoom in on the data.

Regarding the major elements, it may be noticed that the relative amounts of alumina and lime develop a distinct differentiation among the samples, leading to the formation of two different groups of glass, namely Roue type 1 and Roue type 2. Roue type 1, with low levels of lime (<6 wt%) and alumina (<2.6 wt%), is close to S type 1 [3], Sam misc hAl [6], Nish-hAl [5], Sir hAl-Izr [7] glasses whereas Roue type 2, with high levels of lime (>6 wt%) and alumina (>3.5 wt%) is similar to some of the al-Raqqa type 4 (R4) with a low magnesium level (Figure 3c). The important point about the alumina and lime contents in all the samples is their direct correlation, so that with the increase in alumina level, the lime content also increases (Figure 4a).

This implies that at least a part of the lime appears in glass composition introduced from the sand as has been reported by Mirti et al. [3] in the case of Sasanian glasses called type 1. The phosphorus content of the samples is between 0.3 and 1 wt%, which is typical of the use of halophytic plant ash [19]. Phosphorus has different amounts in the two specified glass groups. The results in Table 2 show that Roue type 2 has a high phosphorus oxide content (>0.5 wt%) even though in other samples (Roue type 1) with lower levels of alumina and lime, the amount of phosphorus oxide is below 0.28 wt%. The high phosphorus content of Roue type 2 suggests the possible addition of bone ash to the glass although the lime and phosphorus contents have no direct correlation (Figure 4b). The addition of the bone to the batch was also reported in the case of R4 glass [8].



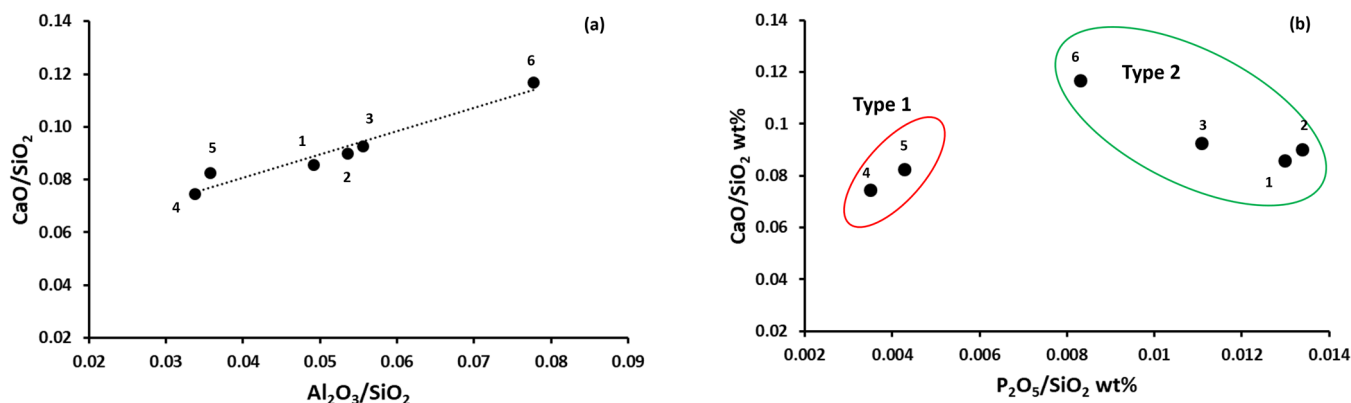


Figure 4. Normalised CaO vs. Al<sub>2</sub>O<sub>3</sub> (a) and vs. P<sub>2</sub>O<sub>5</sub> content (b); (b) (KR Number, see Table 1).

According to the potential colouring elements detected in the samples (Table 2), only one sample (KR4) contains copper ions at a high content (2 wt% CuO) associated with a low amount of iron ions (0.74 wt% Fe<sub>2</sub>O<sub>3</sub>); thus copper determines the colour. In the rest of the samples, iron—sulphur chromophore plays an effective role in creating colour diversity. In all samples, a direct correlation of alumina, iron and titanium oxides shows iron originated from (impure) sand [20–22]. The iron oxide content of all samples except one (KR6) is in the range between 0.7 and 1.5 wt% which fits the common amount for unintentional addition in ancient glass [21–23]. Iron is introduced into the glass naturally along with sand as an impurity and is always found in the glass composition in its two oxidation states of Fe<sup>2+</sup> and Fe<sup>3+</sup>. A decrease in the ratio between Fe<sup>3+</sup> and the total amount of iron usually changes the colour from yellow to green and then to aqua blue, and this might happen due to factors such as glass composition, fabrication technology and oxygen fugacity [24]. KR6 comprises a high amount of iron oxide (1.9 wt%) and likewise has high alumina (>5 wt%). The amount of iron oxide is also reported to be high in al-Raqqa type 4 glass for those with high alumina and low magnesia (<3.5 wt%) contents with green colour [25]. The amber-green colour (KR6) probably developed due to the high amount of iron introduced to the batch along with sand and by the control of the oxygen fugacity in the furnace.

Manganese oxide is present in all samples; however, only the two aqua blue samples, KR4 and KR5, exhibit manganese concentrations exceeding 0.5 wt%, suggesting a deliberate addition [10]. The manganese oxide level in KR4 and KR5 samples is higher than the S type 1 glass (with less than 0.1 wt% MnO content) [3] which indicates that these samples probably belong to the early Islamic period. Manganese oxide affects the proportions of iron ions (Fe<sup>2+</sup> and Fe<sup>3+</sup>) in the melt. However, the aqua blue colour in KR5 shows that the sample still contains a sufficient level of Fe<sup>2+</sup> which should be about 10 to 15% of the total amount of iron ions in the melt [26]. In this case, it is possible that reducing conditions operating in the furnace prevented the oxidation of Fe<sup>2+</sup> in the melt.

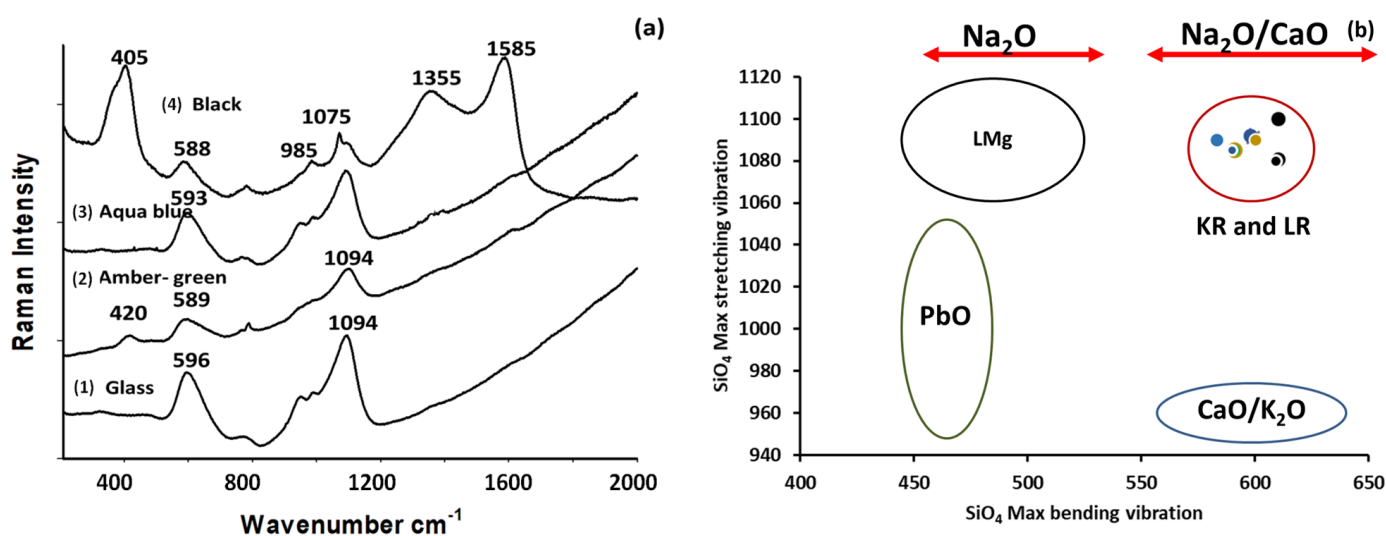
In the black and amber samples (KR1, KR2 and KR3), the amounts of Fe<sub>2</sub>O<sub>3</sub> and S are between 1.2 and 1.4 wt% and 0.39 and 1.11 wt%, respectively. The MnO content is less than 0.2 wt%. Iron is responsible for the black colour in these samples, though the amount of iron oxide is far less than that required to develop the colour in the form of FeO. It is well established that the iron oxide content should be above 6 wt% to obtain a black glass [27,28]. Therefore, the black colour is probably due to the formation of a Fe-S chromophore in the samples, as usually observed for amber and black glasses [29]. Sulphur is usually introduced to the glass in low quantities as impurities in the fluxes [24]. The sulphur content of the black-amber samples (0.4–1.1 wt%) is slightly higher than that measured in other samples (0.4–0.8 wt%), which should be considered an impurity or an accidental addition. Indeed, S<sup>2-</sup> ions are developed in highly reducing conditions of the furnace, and the Fe-S chromophore is formed as a result of the reaction between Fe<sup>3+</sup>

and  $S^{2-}$  in the glass melt during cooling, while the colour intensity (from amber to black) depends on the concentration of  $Fe^{3+}$  and  $S^{2-}$  in the melt [30].

### 3.4. Phases Identification and Raman Classification

The Raman spectrum allows identification of most of the phases built with covalent bonds, amorphous or crystalline. The Raman spectrum of glass shows two broad bands assigned to the bending (at about  $550\text{--}600\text{ cm}^{-1}$ ) and stretching (about  $900\text{--}1100\text{ cm}^{-1}$ ) modes of the  $SiO_4$  vibrational unit whose relative intensity and wavenumber positions depend on the composition, method of fabrication and firing temperature [31,32].

The glass type is determined by plotting the position of the wavenumber maxima of the bending ( $\delta_{\max Si-O}$ ) versus stretching ( $\nu_{\max Si-O}$ ) bands following a procedure that was explained thoroughly in Koleini et al. [33]. The method was previously used to classify Asian and European glasses [34–36]. Stretching components related to poor-connected tetrahedron ( $Q_1$  and  $Q_2$  components in the  $\sim 950$  to  $1000\text{ cm}^{-1}$  spectral range) changes also with the glass network types [31,32]). Three samples (KR2, KR5 and KR6) examined all presented the common spectrum of plant-ash soda-lime-silica glass, as also recorded for glasses from the Middle East [35], as well as the Lalar site, which is located in the vicinity of Roue [37] (Figure 5a spectrum 1). Figure 5b shows peak maxima that have a small shift in the ranges of  $583\text{--}610\text{ cm}^{-1}$  and  $1080\text{--}1100\text{ cm}^{-1}$  regarding the bending and stretching bands, respectively; hence, all the samples are located in the soda-lime area.



**Figure 5.** (a) Representative Raman spectra (1) pale aqua blue KR5 (Roue type 1); (2) amber-green KR6 (Roue type 2); (3) aqua blue KR5 (Roue type 1); (4) black KR2 (Roue type 2); (b)  $SiO_4$  stretching band maximum wavenumber vs.  $SiO_4$  bending band maximum wavenumber abacus of KR and Lalar (LR) sites characteristic flux is given. The regions of the chart characteristic of the different types of glass are indicated according to reference [33] and references herein).

Concerning colours of the samples, the Raman spectrum detects the ( $Fe^{3+}\text{--}S^{2-}$ ) amber chromophore in black and amber-green samples with a characteristic peak around  $405\text{--}420\text{ cm}^{-1}$  under green laser excitation (Figure 5a, spectra 2 and 4) [35]. Indeed, the Raman spectrum of the amber chromophore is clearly recorded under green laser excitation due to the resonance effect: the Raman spectrum corresponds mainly to the signature of the chromophore environment and not of the mean silicate matrix. This explains why the spectrum is a little different from similar glass where the amber chromophore is not present. The doublet peaks at  $1355$  and  $1585\text{ cm}^{-1}$  are characteristic of disordered carbon (D and G bands, respectively). It is mentioned that carbon bearing materials were added to the glass melt as a pigment or as a reducing agent to obtain the amber colour [24] but carbon traces detected by Raman spectroscopy can also be made by degradation of

(bio)organic residues (located at the glass surface) under laser beam, as commonly observed for excavated inorganic samples.

### 3.5. Comparison of the Main Characteristics

The overall results show that the glass samples from the Roue site are plant ash soda-lime glass. The relative concentrations of sodium, potassium (flux ions), and magnesium in Roue building samples are very close to the Sasanian plant-ash glass of Veh Ardashir (S type1) [3], the early Islamic period glass of Samarra (miscellaneous) [6], Siraf (high alumina-low zirconium) [7], Nishapur [5] and al-Raqqa [8,9]. This identical chemistry among low magnesia plant-ash glasses may be related to the use of a similar kind of ash, derived from alkali-rich plants grown in the terrestrial region.

However, a significant differentiation is caused by the relative concentrations of alumina and lime with other flux ions (soda, potash and magnesia) in the samples. Two samples (KR4 blue and KR5 aqua blue) with low alumina and lime levels are similar to S type 1 glass from Veh Ardashir, Samarra (miscellaneous), Siraf (high alumina-low zirconium) and Nishapur (high alumina). Four samples with relatively high alumina and lime contents have no resemblance to those from Mesopotamia and Iran and have a close composition to some of the Syrian glasses (Raqqa type 4) with low magnesium and high alumina contents. The difference in the relative lime contents of Roue types 1 and 2 is partly related to two sources of plant-ash used in their production since lime is one of the main components of plant-ash [9].

The direct correlation of alumina and lime in all samples suggests that part of the lime component originated from sand. However, the difference in the amounts of alumina and lime suggests that the source of the sand was diverse.

The relatively high level of phosphorus in the Roue type 2 glasses might arise from the bone ash incorporated into the melt intentionally to obtain different colours (green, amber and black) by controlling the furnace conditions. Burning green wood provides reducing conditions. The addition of organic materials such as bone or green wood by producing hydrogen makes the reducing conditions stronger, which promotes the formation of ( $\text{Fe}^{3+}$ - $\text{S}^{2-}$ ) chromophore. The colour of Roue glasses was thus mostly obtained by controlling the furnace conditions and the composition of the melt, which were skilfully controlled by the combustion of organic materials as fuel and/or the addition of reducing substances (bone) to the melt. By controlling the oxygen fugacity in the furnace and with the presence of impurities such as iron and sulphur in sand and plant ash, colours such as blue, green and black were obtained with similar raw materials.

It is also noticed that the amount of phosphorus oxide in the samples has gradually increased (from 0.5 to 0.9 wt%) with the change of their colour from green to amber and then black, which indicates the addition of more bone to darken the glass. In these samples, no direct relationship between calcium and phosphorus was observed, which shows that the main source of lime was not the bone alone. However, the relatively high amount of lime in these samples compared to those of Roue type 1 could be due to the addition of bone to the melt. Bone might be the source of carbon detected by Raman because, in addition to the inorganic part (hydroxyapatite), protein compounds make up 35% of its material.

Although manganese oxide was detected in all the samples, it has no effect on the final colour, even in the two samples that had higher levels (KR4 and KR5), in accordance with the firing under reducing conditions. The high manganese oxide level of Roue type 1 is not in the range of S type 1, separating it from Sasanian glass and bringing it closer to early Islamic glass, when glass products contained a higher level of manganese oxide [10].

Based on the amounts of major and minor oxides, Roue type 1 is similar to some of the imported glass to Samarra (miscellaneous) and Siraf (low Zr) with high alumina and has no resemblance to the low alumina local products of these centres. Roue type 1 is probably Iranian glass, such as Nishapur high alumina glass. However, it was not possible to compare the amounts of trace elements with Nishapur glass to prove this claim more

precisely due to the difference in the accuracy of XRF and LA-ICP-MS measurements as the reference.

The results from Raman spectroscopy were in agreement with those of XRF analysis, and it was determined that the glasses belong to the soda-lime-silica group. It was also determined that the black and amber colour of the samples is caused by the Fe-S chromophore, which was created in the reducing conditions of the furnace.

The small number of discovered glass objects that are generally shards of finished objects (bracelets and ordinary utensils) indicates that the residents were consumers and glass-working did not take place there. No complete object was found in the excavation, which indicates that the building was abandoned before the collapse. Roue type 1 and 2 glasses are attributed to the early Islamic period (9th–10th century CE) and (8th–9th century CE), respectively, i.e., after the end of the Sasanian period. The simultaneous presence of Roue type 1 glass, with a composition similar to Nishapur glass, in the first and third layers (Table 1) indicates that the archaeological context is related to the last occupation of the house in the early Islamic period, probably from the 9th to 10th century CE.

#### 4. Conclusions

Two types of glass have been identified from the Roue site with the analysis of six glass samples. The first type (Roue type 1) has the identical composition with the east Iranian glass close to Nishapur high alumina glass. In the other type (Roue type 2) with a composition similar to the Syrian glass, the relative concentration of lime to soda, potash and magnesia is higher than in Roue type 1 glass. The increase in the amount of lime in these samples could be due to the use of a different type of plant-ash and the addition of bone to the melt to control the furnace atmosphere conditions to provide a variety of colours. As a result, the phosphorus content of the samples is higher in Roue type 2 compared to Roue type 1. Raman spectroscopy confirmed the presence of (Fe<sup>3+</sup>-S<sup>2-</sup>) chromophores in green, amber, and black glasses in combination with carbon, indicating that organic compounds were added to the melt. The XRF and Raman analyses are in agreement with the dating resulting from archaeological arguments.

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