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## CHEMICAL ANALYSIS OF LATE ROMAN GLASS FROM QASR AL RABBAH, JORDAN

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### ABSTRACT

Qasr al rabbah is an exceptional site that lies on the main Trajan road (the royal road) which passing between Debaan and Karak, also provides unique evidence of the characteristics that illustrate its importance in ancient time. X-ray fluorescence (XRF) on Roman glass was chosen as a reliable technique to obtain and identify the raw materials, including the type of modifiers that were used as well as the colorants and opacifiers used in Roman glass objects. Forteen glass samples have been analyzed using XRF technique and statistical analysis both descriptive and multivariate. The study revealed two groups of glass in the same region. The obtained results indicated the use of Natron as fluxing agent with alkali contents as well as using the soda ash too as a second type. Two compositional groups have been identified in this study, potash soda lime silicate  $K_2O (Na_2O)-CaO-SiO_2 (K_2O/Na_2O > 1)$ , soda potash lime silicate  $Na_2O (K_2O)-CaO-SiO_2 (K_2O/Na_2O < 1)$  and potash silicate  $K_2O-SiO_2$  glass systems, respectively. According to the visual inspection of the assemblage different corrosion effects are noted. A few glass fragments show a significantly higher degree of corrosion. It is the only sample in which a silver iridescent and a browning layer have been formed. Biocorrosion also appear as an additional weathering factor. Moreover, the inner surfaces of the walls of some colorless sherds demonstrate high polymerization, which is not noted on the outside surfaces of the same samples. The glass samples slightly tinted in yellow-green by the natural sand impurities, was evidently and heavily corroded and gave indeed Na concentrations well below what was expected from the known historical glassmaking.

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**KEYWORDS:** Glass, Chemical Analysis, XRF, Late roman, Natron, technology, Modifiers, Jordan.

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## 1. INTRODUCTION

People had had natural glass –obsidian– since Stone Age, even before the time he learned how to produce glass. Glass production probably started around 7000 B.C in the Middle East especially in Syria, Palestine and Jordan (Charleston 1960, Folk and Hoops 1982, Weber, Strivay *et al.* 2002, Liritzis and Stevenson 2012). The unlimited uses of glass and plenty of applications give the glass its importance. As a result of that glass production spread out and became one of the valuable and innovative materials in Antiquity and recent time. Studying ancient glass is of that important, where glass analysis could lead us in better understanding other society. Chemical composition of Roman Glass 1st–6th centuries has a low magnesium and a low potassium soda-lime, typically consisting of ca 66–72% SiO<sub>2</sub>, 16–18% Na<sub>2</sub>O and 7–8% CaO. For Roman glass, the major element composition can only be used to verify that a particular fragment or object is genuinely Roman, but usually does not convey other information (Velde and Sennequier 1985), Several primary glass factories were located throughout the Roman Empire No clear distinctions in glass composition and origin between the different origins in the Roman Empire can be made based on the major element composition The components of these glasses are basically sodium and silica. Small amounts of alumina (generally near 2.5 wt.%) and calcium oxide (between 6 and 8%) are characteristically present in these glasses also. Low magnesia and potash contents (-1.5%) distinguish these from other sodic glass types. This Roman glass composition seems to have been in fact discovered during the Hellenistic period (Dussart *et al.* 1990).

The main questions of this project are regard the structure of the glass industry in the Roman, whether or not the glass used throughout time and space was made on the site or whether there was a combination of the ingredients of sand and imported soda on another site. In order to clarify the initial basic question it is essential to provenance the origin of this glass and its raw materials.. Qasr Al-rabah was known by the early travelers as Beit Kerem, a word that has two meanings: the first of which falls under the meaning of generosity and hospitality. The second is attributed to the vineyards that were present there (Tristram 1873). Other travelers called it the palace of Rabba or Khirbat Al Qasr, and according to Glueck. 1939 the site was named by Qasr Al-rabah. The name refers to that in ancient times, were they used to call the monumental buildings by goddess name. Similarity of name Qasr Al bent in Petra to pharos daughter name further supports this hypothesis (Glueck 1937).

The site is located in Al-Qasr town, approximately 5 km to the north of Al-Rabah city, about 5 km to the north of Karak city and 18 km to south of Wadi Al-Mujib. It was built in the center and at the highest point of the old town (Figure 1). This exceptional site lies on the main Trajan road (the royal road) which passing between Debaan and Karak, also provides unique evidence of the characteristics that illustrate its importance in ancient time (Figure 2). The area is surrounded by different settlements remains, mostly dating back to the early Bronze Age. Due to its fertile soil and its strategic location, settlements patterns continued into the Islamic period. In 1993 a team directed by Atef Shiyab surveyed and registered all the archaeological site and monuments located. Structures were mapped and artifacts were collected in order to date this site (Figure 3 and 4). Considerable collections of glass, lead-based scale weights were uncovered, together with plenty of ceramic sherds from different structures (Al Shiyab 1993). The site was ignored and almost there is no publication and very little work was done on materials from the site. Here are some of these studies: architectural study done by Waterhouse (1998), where he studied the construction style of the tombs (Waterhouse, Grauer *et al.* 1998). Abu-Baker *et al.* (2015) studied the composition and corrosion behaviour of five archaeological lead scale weights. In a study conducted by Ahmed Al-shorman and Atef shiyab (2015) several ceramic sherds have been chemically and mineralogically analyzed to investigate the effect of function on selecting raw materials and technology (Abu-Baker, Al Sekhaneh *et al.* 2014, Al-Shorman and Shiyab 2015). The absence of systematic studies involving scientific methods of glass in the area was one of the incentives which lead to conduct such research, The aim of the present study is to characterize most common glass assembly from Qasr Al Rabah and to investigate the origin of raw materials, which can give us better insight into the trade routes and connection of this locality with the rest of other sites in the region. Analyses of glass found at the site, are done by the XRF techniques. Through statistical analyses of obtained results we will discuss the glass groups appearing at qasr al rabbah and possible origin of raw materials for their production, similarities and differences between this and other glasses found in the area, as well as, the relationship of the different glass industries.

Thus present study focuses on the identification of the main glass compositions, identification of provenance of raw glass, and the identification of possible connections between archaeological typology and glass chemical composition. More specifically, the basic aims of the study were the chemical characterization of the glass and the determination of the raw

materials used, as well as, the examination of the corrosion effects on the glass.

X-ray fluorescence (XRF) analysis was chosen as qualitative and quantitative elemental analysis which is based on the ionization of the atoms of the material in question by a beam of primary X-rays with different techniques of (XRF) (Liritzis and Zacharias, 2011; Shackley, 2011; Ferguson, 2012). By analyzing characteristic radiation emitted by the material, it is likely to find out the characteristics and abundance of the elements (Janssens and Van Grieken 2004; Tantrakarn, Kato et al., 2009). Analyti-

cal scientific techniques can help in a much wider sense in that the results that are obtained from individual assemblages can provide information on technology, provenance and trading routes in the past. It aids our understanding of this material and how it was viewed and used by people in the past (Degryse et al. 2014). Scientific XRF analysis which was carried out to determine what type of colourants were used and also allowed the beads, which ranged widely in colour and shape, to be classified according to percentages of trace elements (Warner and Meighan 1994, 53).

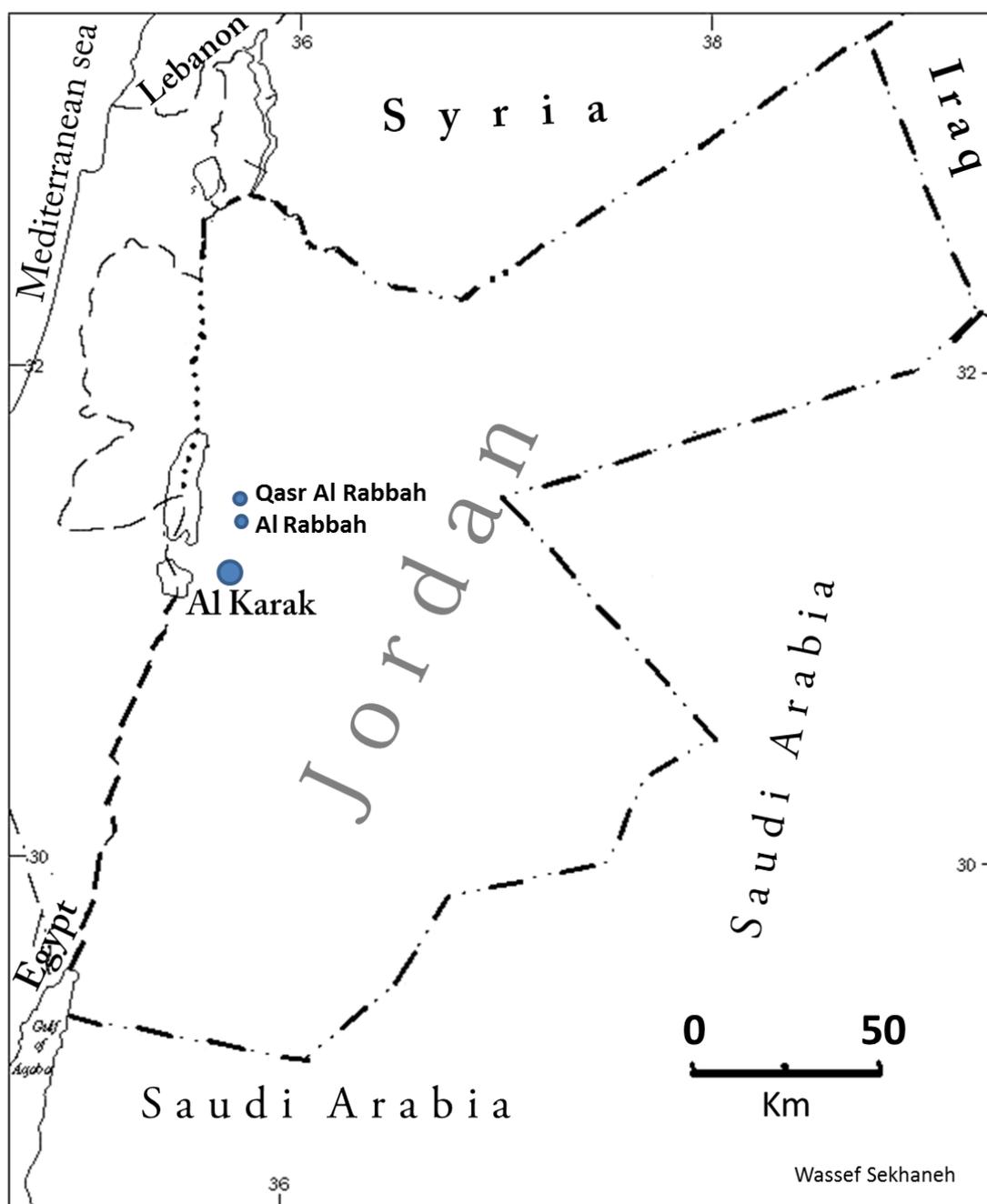


Figure 1. Location map of the studied area (Qasr al Rabbah)

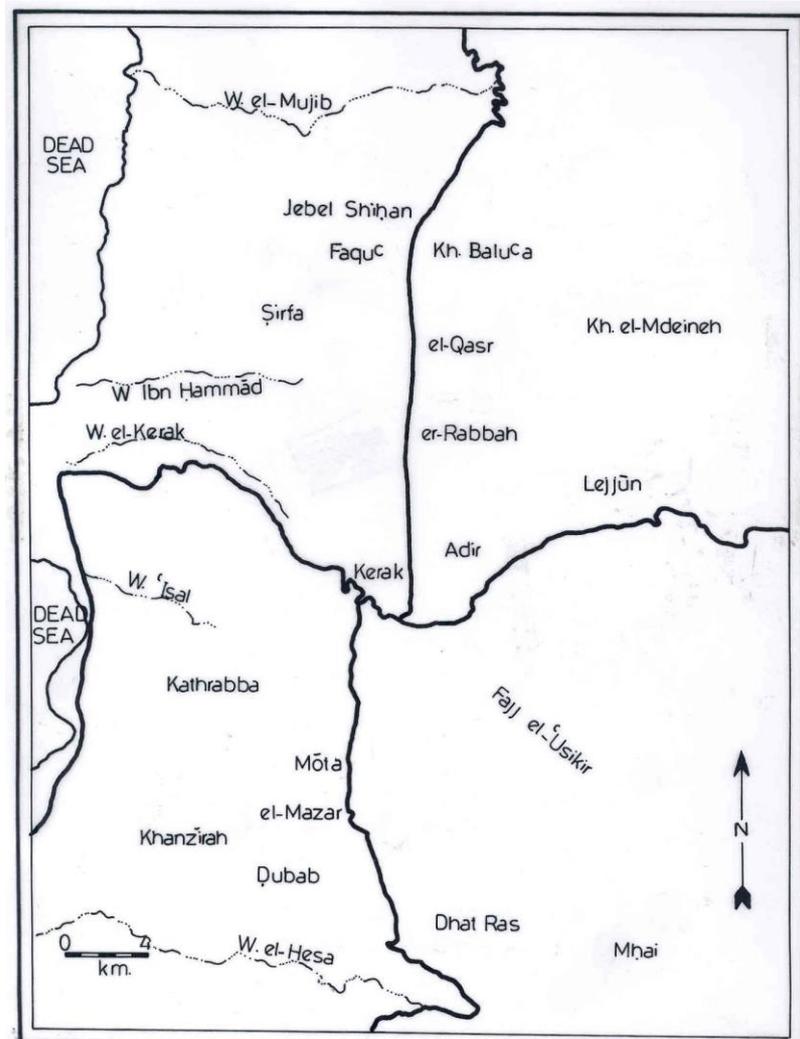


Figure 2. shows the royal road (Trajan) which passes through the studied area



Figure 3. Architectural remains at the excavated site

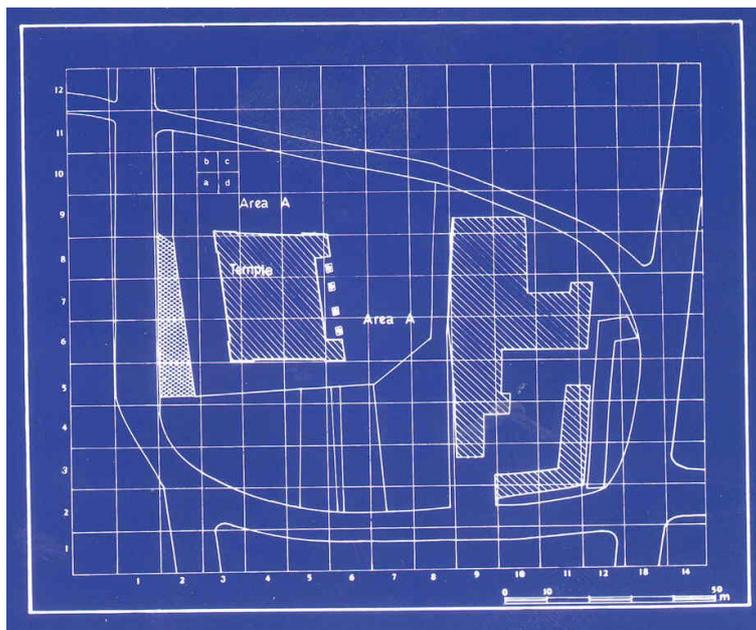


Figure 4. Plan of the architectural remains of the excavated site

2. EXPERIMENTAL PROCEDURES

2.1. Analysed samples

Analytical techniques can help in provide more information on technology, economies and trading routes in the past. All the 14 fragments of glass which were found in house 1, 2, 3 and 4 in trench 1 and in Layer 3 have been classified and visually studied. They represent a range of glass fragments, including indented bodies, a rim bowl, flasks, bottles, beakers, jugs, goblets and knock-off rim vessels. The glass fragments were dated according to their

shapes and by some associated pottery as well as to the architectural remains. Archaeologists suggested that glasses that were found in house 1, 2, and 3 are dated back to the late Roman period (3rd-4th century AD). These glass samples are approximately representative of the entire glass assemblage from qasr al rabbah. Therefore, these glasses were classified according to their location and physical properties into three groups table1, 2 and 3. They represents late Roman glass, each group consists of 5 vessel fragments. Photographs of these glasses are shown in Fig.5.

Table 1. Descriptions of glass fragments from different area

site	Object No	Context- Locus- square	Description	Date	Photograph No
Qasr al- Rabbah	1a	House 1,trench 1Layer 3	Long -necked bottle, circular in shape, Yellowish green to brown ,painted with a layer representing the color of rainbow, cylindrical, soft texture	Late Roman	1a
Qasr al- Rabbah	2a	House 2,trench 1Layer 3	Mouth of glass bottle with part of neck, brownish ,painted on the outside in silver luster , cylindrical, soft texture, well-made	Late Roman	2a
Qasr al- Rabbah	3a	House 3,trench 1Layer 3	Mouth of glass bottle ,rim converted yellowish green , circular in shape , painted on the outside in silver luster , coarse texture, Botched -made	Late Roman	3a
Qasr al- Rabbah	4a	House 4,trench 1Layer 3	Part of Long -necked bottle, colorless with oxidized layer , cylindrical, soft texture	Late Roman	4a
Qasr al- Rabbah	5a	House 4,trench 2Layer 3	Part of glass vessel, colorless with oxidized layer , cylindrical, soft texture, thin and soft texture	Late Roman	5a

**Table 2. Descriptions of glass fragments from different area**

site	Object No	text- Locus- square	Description	date	Photograph No
Qasr al- Rabbah	1B	House 1,trench 1Layer 3	Part of glass vessel , Yellowish green ,painted with a layer representing the color of rainbow, with oxidized layer , thick	Late Roman	1B
Qasr al- Rabbah	2B	House 1,trench 2Layer 3	Part of glass Bracelet , circular in shape, Brownish green , painted on the outside in silver luster, with oxidized layer	Late Roman	2B
Qasr al- Rabbah	3B	House2,trench 1Layer 3	Part of glass Bracelet , circular in shape, color Turquoise , incised decoration or decoration in the form of grooves	Late Roman	3B
Qasr al- Rabbah	4B	House 2,trench 2Layer 3	Part of glass Bracelet , circular in shape, color Turquoise , incised decoration or decoration in the form of grooves	Late Roman	4B

**Table 3. Descriptions of glass fragments from different area**

site	Object No	Context- Locus- square	Description	date	Photograph No
Qasr al- Rabbah	1C	House 3,trench 1Layer 3	Part of glass vessel , circular in shape, light green , painted on the outside in silver luster, with oxidized layer ,coarse textures ,Thick	Late Roman	1C
Qasr al- Rabbah	2C	House 3,trench 2Layer 3	fragment of glass vessel yellowish brown color , ,coarse textures ,Thick	Late Roman	2C
Qasr al- Rabbah	3C	House 4,trench 1Layer 3	Mouth of glass bowl , rim converted to outside , light blue , painted on the outside in silver luster, with oxidized layer ,soft textures ,Thick, well-made	Late Roman	3C
Qasr al- Rabbah	4C	House 4,trench 2Layer 3	Rim of mouth of glass vessel , , color Turquoise , incised decoration from inside and outside or decoration in the form of grooves, coarse textures ,Thick ,Botched mad	Late Roman	4C
Qasr al- Rabbah	5C	House 4,trench 2Layer 3	The upper part of glass bowl , bowl of colorless with a green tinge , soft texture, Thick	Late Roman	5C

**Figure 5. Photographs of glass fragments found at Qasr Alrabbah .**

## 2.2. Method of Analysis

Sample processes and cleaning prior any chemical analysis is a key factor in getting precise results. Analyzing the glass without any preparation methods this could lead in the alteration of the results. To avoid such unwanted results and to remove dirt from the surface of the glass objects, samples were handling with extra precaution, cleaned and washed using an ethanol de-ionized water solution. In some cases dirt and corroded layers were very sticky and this acquired to soak the samples in the solution for a longer time. Furthermore, in order to provide a more homogenous sample a metal scraper was used for the removal of corroded layers of glass or dirt on the surface. All the analysis was carried out after weathering layers were removed and sam-ples were washed with distilled water and dried this step was repeated twice to insure the clearances of the samples. Visual Color measurements were done with washed samples to eliminate the effect of residual and impurities. For the X-Ray Fluorescence (XRF) small fragments were taken from each glass fragments and ground into fine

powder. The elemental composition of glass is highly susceptible to corrosion and leaching of elements and in order to avoid that samples should be treated and prepared as mentioned up (Henderson, 2013). Sample preparation of glass which is much more destructive is sometimes used. Such was the case in the analysis of samples having been highly weathered with flaky surfaces. To obtain more information about the glass, the study involved using XRF (X-ray fluorescence), a non-destructive method capable of multi-elemental analysis, making it ideal for fragile archaeological material. It has additional advantages in that it is relatively cheap to run, requires little or no pre-treatment of samples and produces results quickly compared to other techniques. XRF has been used to great success in the study of not only archaeological glass, but metals, ceramics, pigments, stone and textiles to name just a few. The technique works by exciting part of a sample using X-rays and then analysing the backscattered radiation which is characteristic of the type and quantity of elements in the sample (Healey and Mecholsky 1984, 142; Janssens 2004, 129).

For the purpose of this study, X-ray fluorescence (XRF) was chosen as the analytical method as it is capable of carrying out completely non-destructive multi-elemental analysis, something which is highly desirable for archaeological material. The major advantage of this analytical technique is that it can allow an entirely nondestructive analysis (Polikreti et al. 2011, 2890). Analysis was at the labs of Essen University, Germany, the specimens were examined using an ARL OPTIM'X XRF spectrometer from Thermo Electron Corporation has been used to derive limits of detection and precision for the analysis of glasses. The ARL OPTIM'X is a wavelength dispersive system which provides superior resolution and light elements capability. It is fitted with an Air-cooled Rh End-Window Tube with thin Be win-

dow (0.075 mm) and has a maximum power of 50 Watts.

### 3. RESULT AND DISCUSSION

By examining the results of glass samples which are shown in table 4 and 5, it was possible in some instances to classify the glass into categories. Using elemental analysis, it was possible to identify the raw materials, including the type of modifiers that were used as well as the colorants and pacifiers used. It was also possible to examine levels of corrosion that the surface layers had undergone, based on the amount of elements such as aluminum that they contained. Table 3 highlighted some interesting trends such as increased levels of  $K_2O$  in some glass due to the use of different source of soda. The chemical composition revealed all glass samples have almost the same aluminum content. Liritzis et al (1995) indicate that the ratio  $(Na_2O+K_2O):(CaO+MgO)$  can be used to evaluate the recipe used by the several glassmaking schools (Liritzis, Salter et al. 1995). Therefore, these raw glasses can be classified as soda-lime-silica ( $Na_2O-CaO-SiO_2$ ) glass, the common type of ancient glass for more than three thousand years (Tite, Shortland et al. 2006, Degryse, Scott et al. 2014). The result shows that the glasses are all of the soda-lime-silica type except for samples 3a, 1b, 2b and 2c which have different alkali composition. All samples have MgO and  $K_2O$  compositions of less than 1.5% except 3a, 1b, 2b and 2c. This suggests that natron was the primary alkali flux for these glasses (Liritzis, Salter et al. 1995, Henderson 2013). While the small group of samples 3a, 1b, 2b and 2c used soda ash alkali. All of the glasses in this study were produced using sand as their silica source. Using the major and minor elements two compositional groups have been identified in this study. Their average compositions and compositions are presented in Table 4 and 5 :

Table 4. Chemical composition of glass fragments from Qasr Al rabbah

S	N	Na <sub>2</sub> O	Fe <sub>2</sub> O	MnO	SiO <sub>2</sub>	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
1a		9.50	0.85	0.01	70.10	0.05	7.13	0.75	0.13	0.45	3.15	0.014
2a		7.30	0.77	0.04	70.13	0.07	8.20	1.12	0.20	0.38	3.13	0.033
3a		6.70	1.05	0.03	60.15	0.11	7.15	3.75	0.32	6.11	3.22	0.075
4a		15.10	0.74	0.10	70.41	0.07	7.68	0.68	0.35	0.33	3.08	0.025
5a		14.90	0.66	0.07	70.66	0.01	8.33	0.44	0.11	0.41	3.16	0.041
1b		16.20	1.08	0.03	60.40	0.14	7.44	3.88	0.17	7.01	3.41	0.010
2b		8.30	0.82	0.04	61.22	0.10	7.33	3.96	0.16	7.20	3.33	0.027
3b		14.90	0.58	0.02	72.40	0.06	7.68	0.47	0.17	0.15	2.48	0.019
4b		14.60	0.72	0.01	71.60	0.02	8.33	0.65	0.31	0.16	3.07	0.017
1c		15.10	0.68	0.01	71.70	0.03	7.52	0.72	0.09	1.23	2.77	0.015
2c		6.30	0.84	0.04	60.44	0.10	7.13	3.52	0.23	6.84	3.67	0.010
3c		15.40	0.61	0.09	70.26	0.02	8.19	0.67	0.17	1.17	3.03	0.090
4c		15.10	0.31	0.04	71.10	0.05	7.67	0.64	0.15	1.01	3.55	0.050
5c		15.10	0.43	0.03	71.20	0.09	8.32	0.50	0.11	1.11	2.81	0.070
Avg%		15.23	0.70	0.04	68.12	0.066	7.84	1.56	0.19	2.40	3.20	0.035

**Table 5. Chemical composition of glass fragments from Qasr Al rabbah**

S.N	CuO	BaO	NiO	PbO	ZnO	SrO	Y <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>5</sub>	SnO <sub>2</sub>	Total
1a	0.012	0.010	0.001	0.00	0.012	0.015	0.002	0.012	0.00	0.003	0.009	98.0
2a	0.014	0.013	0.002	0.01	0.025	0.023	0.000	0.009	0.01	0.012	0.010	99.2
3a	0.022	0.027	0.000	0.02	0.033	0.043	0.001	0.005	0.00	0.000	0.012	96.8
4a	0.018	0.00	0.003	0.05	0.000	0.027	0.004	0.002	0.00	0.000	0.014	98.6
5a	0.020	0.010	0.004	0.04	0.071	0.073	0.000	0.010	0.00	0.002	0.087	99.1
1b	0.024	0.032	0.008	0.01	0.084	0.010	0.012	0.007	0.00	0.003	0.010	99.9
2b	0.021	0.017	0.007	0.02	0.060	0.081	0.020	0.003	0.00	0.000	0.023	99.7
3b	0.091	0.072	0.005	0.06	0.023	0.000	0.000	0.021	0.00	0.001	0.018	99.2
4b	0.084	0.035	0.001	0.04	0.021	0.041	0.005	0.019	0.00	0.004	0.013	99.8
1c	0.025	0.021	0.007	0.00	0.015	0.031	0.004	0.003	0.00	0.000	0.008	99.9
2c	0.018	0.014	0.006	0.03	0.011	0.047	0.000	0.001	0.00	0.000	0.011	98.2
3c	0.013	0.022	0.004	0.02	0.040	0.052	0.012	0.000	0.00	0.003	0.012	99.8
4c	0.011	0.041	0.009	0.07	0.090	0.021	0.036	0.004	0.00	0.003	0.010	99.9
5c	0.030	0.028	0.001	0.09	0.00	0.056	0.003	0.002	0.00	0.002	0.009	99.9
Avg%	0.028	0.024	0.004	0.03	0.034	0.037	0.007	0.007	0.001	0.002	0.017	99.1

• **First group:** 10 samples in this group is characterized by low Al<sub>2</sub>O<sub>3</sub> (av. 3.2%) and CaO (av. 7.8%) levels. It is also noted that this glass group has elevated levels of FeO (av. 0.70%), TiO<sub>2</sub> (av. 0.06%) and MnO (0.04%) with negligible amount of CuO, ZnO, SrO, BaO and SnO. The MnO in the glass does not appear to have been present as an impurity. It is likely that manganese was introduced intentionally in the glass to counteract the iron content (Henderson 2013). This group is also characterized by a low level of MgO and a relatively high soda level. The distinctive yellowish green color of most samples is a result of the presence of iron oxide and manganese oxide which appears in the analysis.

• **Second group:** 4 samples in this group have relatively low silica ratio when compare with the first group, and has high concentration of MgO with average of 6.78%. Also it has a high percentage of K<sub>2</sub>O

(3.77%) and high value of Fe<sub>2</sub>O with average of 0.95%. However smaller but significant amount of other ingredients such as TiO<sub>2</sub> (av. 0.06%) and MnO (0.04%), ZnO (0.014%) and other negligible amounts of SrO, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and As<sub>2</sub>O<sub>3</sub>. High levels of impurities, such as titanium, manganese and iron mark the new type of glass that appears in the fourth century AD and whose origin is yet unknown, though Egypt is strongly supposed as its production site (Freestone 2006). The presence of CaO in the samples is distinctive component as impurities in the sand originated in Syria (Stern and Gerber 2004, Stern and Gerber 2009). Figure 5 show the average compositions of the glass fragments presented in Table 5 revealed that the vessels were formed from the same raw glass and are chemically similar except samples 1b, 2b, 2c and 3a.

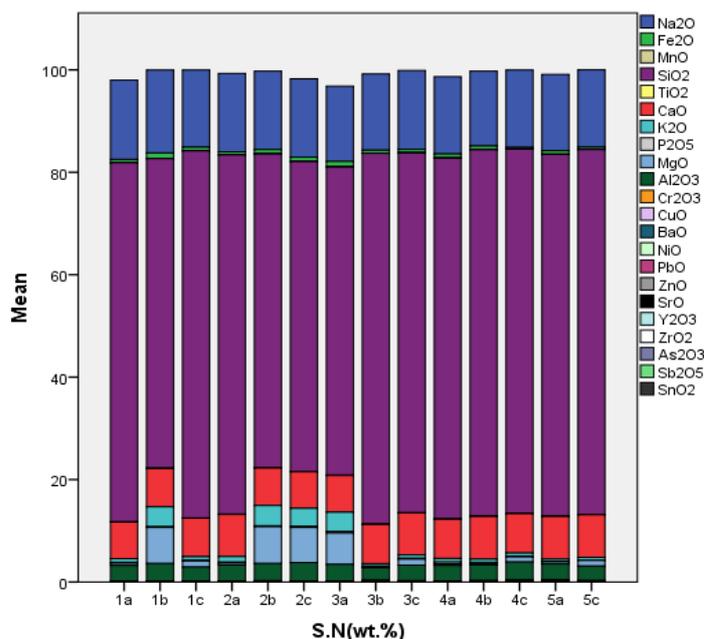


Figure 6. The average composition of glass fragments at Qasr Al rabbah.

Fig. 5 shows a ternary diagram with al-alkaline and alkaline earth ( $\text{Na}_2\text{O}+\text{CaO}$ ,  $\text{K}_2\text{O}+\text{K}_2\text{O}$ ), structural ( $\text{SiO}_2$ ) and other major constituent ( $\text{Al}_2\text{O}_3$ ). All of the glass fragments are located in the right vertex of the triangle. The results indicated that the samples are typical silica-soda-lime glasses with low concentrations of  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{Al}_2\text{O}_3$ , while the other four

sample have high concentration of  $\text{MgO}$  and  $\text{K}_2\text{O}$  the main component of the samples was  $\text{SiO}_2$  with values about 60 % .

As can see in Fig.8 which represent a biplot of  $\text{CaO}$  and  $\text{K}_2\text{O}$  for the glass samples, two groups can be separated based on potassium and lime content.

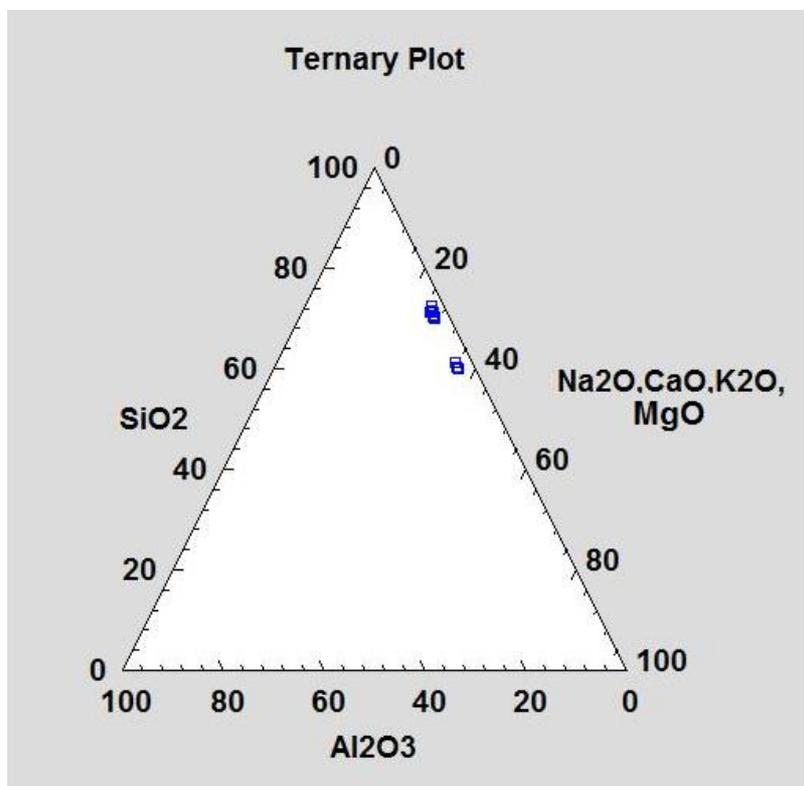


Figure 7. Ternary diagram of  $\text{Al}_2\text{O}_3$  -  $(\text{Na}_2\text{O}+\text{MgO}+\text{CaO}+\text{K}_2\text{O})$  -  $\text{SiO}_2$  for the glass samples.

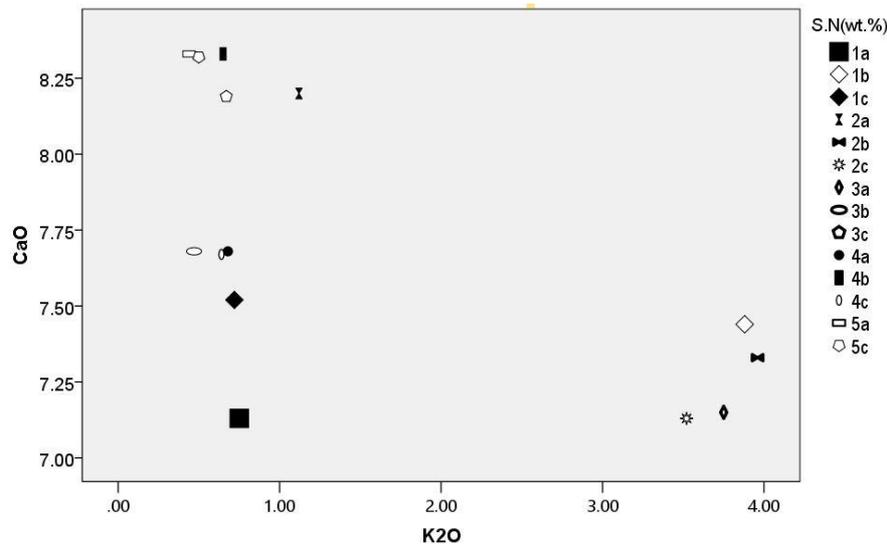


Figure 8. A biplot of  $K_2O$  versus  $CaO$  (wt%) for the glass fragments samples.

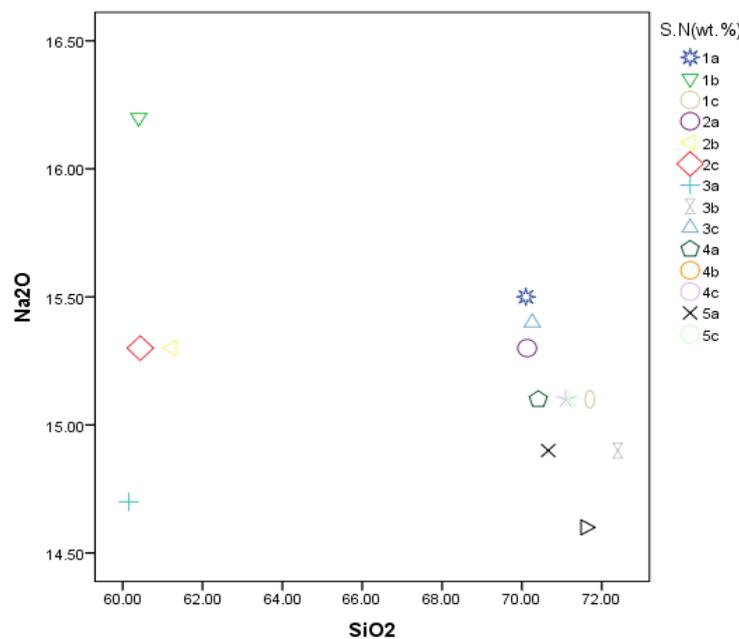


Figure 9. A biplot of  $Na_2O$  versus  $SiO_2$  (wt%) for the glass fragments samples.

The presence of trace elements Mn, Cu, and  $Fe_2O$  which found almost in all samples were used as colorant because of its abundance and continuing use it in glass manufacturing during the roman period. Colorless samples are a result of adding MnO to the mix which in turn eliminates the effect of iron oxide this can seen in sample 4a and 5a. Natron which is available in Egypt was a major source for soda during Roman period Egypt was a major source for soda during Roman period (Newton 1980). The alumina content steady in all samples which may indicate that glass maker calculated the precise amount for glass manufacturing. Alumina increase chemical resistance of glass and help in thermal shock. Also the presence of CaO with high

amount more than 7% which elsewhere show the same high amount (Velde and Gendron 1980, Liritzis *et al.*, 1995).

According to  $Na_2O$ :  $K_2O$  10 samples fall between 20-40, which mean natural soda the natron have been used in the recipe of their manufacture, while the other 5 samples ratio implies using soda ash alkali and have low sodium content. Leaching experiments of alkali-silicate glasses have showed that the exact corrosion process occurring in each case is highly complex and determined by a number of different parameters, more importantly the original composition of the glass and the environment (Tournié *et al.*, 2008). Samples 1a, 2a, 3a, 2b and 2c which excavated in the archaeological site of Qasr Al

Rabah (Jordan), looking at the results given by XRF analysis from the surface (therefore passing through the possible corrosion layer). The glass samples slightly tinted in yellow-green by the natural sand impurities, was evidently and heavily corroded and gave indeed Na concentrations well below what was expected from the known historical glassmaking. The sample had clear blue color, obtained by a small amount of nickel oxide, and showed a Na concentration compatible with ancient Roman recipes. In literature there is wide evidence of an almost constant composition of the natron glasses at Roman times featuring a  $\text{Na}_2\text{O}$  concentration between 15% and 17%.

The two major glass group fall between the natron and plant ash glasses which are investigated in this paper they are consists of Alkali compound  $\text{CaCO}_3$ , mixed lime and soda lime glass and primary source of wood ash mixed with trona as mineral to sodium ash glass as has reported by Kogel et al (Kogel, Society for Mining et al. 2006). Sodium ash glass is made of quartz and the ash of halophytic plants (Chenopodiaceae family). The ash used for the majority of published soda ash glasses contains sodium and calcium in a weight proportion of almost 1.4:1 (Wedepohl, Simon et al. 2011).

Tite et al. (2006) and Barkoudah and Henderson (2006) have demonstrated in their studies plant ash from Syria, that the degree of variation in the chemical composition of halophytic plants with the predominance of either sodium or potassium concentrations, They have sampled a number of different species from different environments according to geography (Barkoudah and Henderson 2006, Tite, Shortland et al. 2006, Henderson 2013). The fact that the published data on halophytic plant ash glasses represent a much smaller chemical variability than the plant ashes provides an explanation for the specialization of the glass production on materials from certain areas. The starting materials for sodium The ash used for the majority of published soda ash glasses contains sodium and calcium in a weight proportion of almost 1.4:1 (Barkoudah and Henderson 2006, Tite, Shortland et al. 2006). These authors have sampled a number of different species from different environments according to geography. The fact that the published data on halophytic plant ash glasses represent a much smaller chemical variability than the plant ashes provides an explanation for the specialization of the glass production on materials from certain areas. Chemical composition of group two is similar to that of Roman glass found in the area, though not completely. This group contains only four samples so it is difficult to give any further conclusions except that it also exhibits lower amount of

$\text{Na}_2\text{O}$  than standard Roman glass. The model of production and distribution of early plant-ash glasses is still unclear. Liritzis et al. (1997) suggest a near eastern influence, based on the  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{CaO} + \text{MgO})$  ratio of the plant-ash glass. The Mesopotamian origin is further corroborated by the reported production of plant-ash glass in the Mesopotamian region under the Sasanian rule (3rd to 7th c. AD) (Mirti et al. 2008). Jackson and Cottam (2015) make a hypothesis for the existence of a set trading framework, resulting in the distribution of emerald green plant-ash glass to a limited number of secondary workshops. The chemical analysis revealed the presence of two principal groups: one soda-lime-silica glass: (1) A low-magnesia, low-potash glass group, with  $\text{K}_2\text{O}$  and  $\text{MgO}$  each below about 1.5 wt%, which is characterized by the use of mineral soda (natron) as the alkali source, and (2) a high-magnesia, highpotash glass group, with  $\text{K}_2\text{O}$  and  $\text{MgO}$  in excess of 1.5 wt%, in which a soda plant-ash is added.

#### 4. CONCLUSION

It's clear that Ancient glassmakers definitely had enormous knowledge regard selecting the suitable raw material and other ingredients, to produce some of the notable specimens according to a specific area and the availability of raw materials. Soda-lime-Silica glass is the common type of ancient glass during Roman period and continues to Byzantine and Islamic period. The two major glass group fall between the natron and plant ash glasses which are investigated in this paper they are consists of alkali compound  $\text{CaCO}_3$ , mixed lime and soda lime glass and primary source of wood ash mixed with trona as mineral to sodium ash glass. The glass chemical composition belonged to alkali lime silicate system and its main characteristics were the content  $\text{K}_2\text{O}$  higher than that of  $\text{Na}_2\text{O}$ , which is different from other glass sample compositions. Two compositional groups have been identified in this study, potash soda lime silicate  $\text{K}_2\text{O}$  ( $\text{Na}_2\text{O}$ )- $\text{CaO}$ - $\text{SiO}_2$  ( $\text{K}_2\text{O}/\text{Na}_2\text{O} > 1$ ), soda potash lime silicate  $\text{Na}_2\text{O}$  ( $\text{K}_2\text{O}$ )- $\text{CaO}$ - $\text{SiO}_2$  ( $\text{K}_2\text{O}/\text{Na}_2\text{O} < 1$ ) and potash silicate  $\text{K}_2\text{O}$ - $\text{SiO}_2$  glass systems, respectively X-ray fluorescence is a useful technique to obtain more information about what processes caused these objects to exist where and how they did. The glass samples slightly tinted in yellow-green by the natural sand impurities, was evidently and heavily corroded and gave indeed Na concentrations well below what was expected from the known historical glassmaking. In order to highlight further indicators of chronology or geographical origin, further analysis of larger groups of samples is needed.

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