

Tradition and Experiment in First Millennium A.D. Glass Production—The Emergence of Early Islamic Glass Technology in Late Antiquity

JULIAN HENDERSON

Department of Archaeology, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

Received August 14, 2001

ABSTRACT

Following a brief history of analytical research into ancient glasses, the emergence of early Islamic glasses in the Middle East in late antiquity is discussed. Data sets for Roman and Byzantine glasses are compared to those of the early Islamic period. This is a rare period of technological transition when responses to the “drying up” of the traditional mineral alkali source resulted in experimentation, which can be demonstrated analytically.

Introduction

The chemical analyses of ancient materials can be interpreted purely scientifically, or in a more integrated way to include archaeological and historical parameters. From their chemical compositions, it is possible to infer the raw materials used to make glass¹ and to calculate its transition, melting, and working temperatures.² Since the chemical composition of the glass, determined by the raw materials use to make it, will determine its fusion and working properties, it is clear that any change in raw materials used will impact directly on production processes, including molding and blowing.

With a more integrated approach, the archaeological and historical contexts as well as the social/economic value of glasses can be included in the overall interpretation of their production and use. This approach, based on the chemical analysis of a carefully selected and representative range of glass objects from a range of archaeological contexts, such as occupation, ritual, burial, and industrial, can provide a basis for creating links between these contexts and both the technology used to make the objects and the occurrence of the artifact types. Although rare, if a glass compositional type is found to

be diagnostic to a period or an area of production, then a range of potentially interesting inferences can be made relating to production, trade and exchange of that glass. As is the case for obsidian found on archaeological sites,³ this could, eventually, provide the essential data for building up “glass interaction zones”.

The assemblage of data sets of ancient glass compositions has a relatively short history. In the 1950s and 1960s,⁴ Turner's papers, based mainly on the results of wet chemical analyses, contributed especially to the inferred kinds of raw materials used to make ancient glasses. In 1961, Sayre and Smith published a seminal paper based on neutron activation analysis of ancient glasses, in which they identified clear compositional types⁵ that were used at different times and in different parts of the world. Sayre's later papers,⁶ and those published with R. W. Smith,⁷ focused on discrete archaeological groupings of glasses that reflected the use of specific raw materials to make them. For example, they identified a group of Egyptian glasses that contained characteristically low calcium oxide levels.⁸ These have now been placed in a broader context and found to be characteristic to a region in Egypt near Wadi Natrun. Sayre⁹ noted the important distinction between soda–lime–silica glasses containing high and low magnesia levels (HMGs and LMGs, respectively), which account for a high proportion of ancient glasses dating to before 1000 A.D. This apparently conservative use of glass raw materials over long time periods implies either that there was a small number of glass production centers or that a larger number of centers used the same or very similar raw materials to make glass. Brill's volume of ancient glass compositions¹⁰ bears this implication out.

To increase the number of samples and the speed with which they can be analyzed, glass studies have benefited increasingly from the introduction of more automated analytical techniques,¹¹ generating larger databases, which are often archaeologically coherent. The range includes energy- and wavelength-dispersive X-ray fluorescence spectroscopy, electron-probe microanalysis, scanning-electron microscopy, proton-induced X-ray emission, atomic absorption spectrometry, inductively coupled plasma emission spectroscopy, laser-ablated inductively coupled plasma mass spectrometry, neutron-activation analysis, X-ray diffraction, mass spectrometry, and X-ray fluorescence using a synchrotron radiation source.¹² All of these techniques have their strengths and weaknesses in terms of accuracy and precision, the sample size accommodated and their levels of detection. While for major and minor components the size of databases is steadily increasing in ancient glasses, trace levels of impurities are still to be investigated properly on the same scale.

One result of using increasingly more automated techniques of analysis had been to identify new ancient glass compositional types. The compositional groups Sayre and Smith identified⁵ were plant ash HMGs between *ca.*

Julian Henderson (born 1953) obtained his B.A. (archaeology) from Queen's University of Belfast and his Ph.D. (physics, archaeological science) from the University of Bradford. He held postdoctoral positions at the Smithsonian Institution's Conversion-Analytical Laboratory, at the Oxford University Research Laboratory for Archaeology and the History of Art, and at St Cross College, University of Oxford. He was then appointed to a lectureship at Sheffield University and is now Professor of Archaeological Science and Chair of the Department of Archaeology at the University of Nottingham, UK. His main research interests are (1) the relationships between science and archaeology and (2) the scientific analysis of the remains of ancient industries, especially the production and use of ancient vitreous materials from their origins until the 17th century A.D.

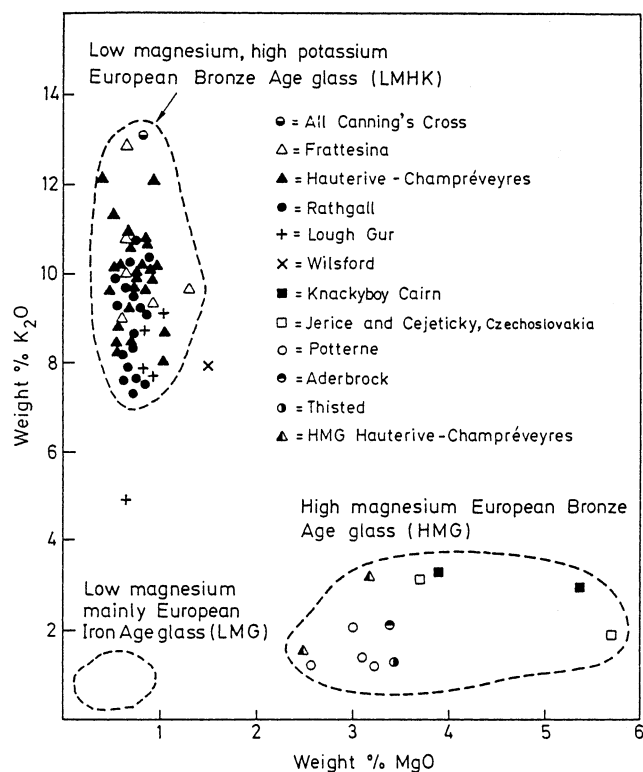


FIGURE 1. Bivariate plot of weight % MgO vs weight % K₂O in glass dating to between ca. 1400 and 800 B.C. ("Bronze Age") of plant ash (HMG) and mixed-alkali (LMHK) compositions. There was a radical change to a natron alkali source (LMG) after ca. 800 B.C. and this alkali continued in use through the European Iron Age and the Hellenistic, Roman and Byzantine periods, to be largely replaced (in the Orient) by the reintroduction of plant ash glass ca. 800 A.D.

1500 and 800 B.C., natron LMGs between ca. 800 B.C. and 800 A.D. (see Figure 1), high antimony LMGs between ca. 600 and 200 B.C., Islamic high lead glasses between ca. 1000 and 1400 A.D., and Islamic HMGs between ca. 800 and 1400 A.D. Subsequent analytical studies have revealed a range of other ancient glass compositional types. The first is a low magnesia, high potassium oxide glass (LMHK) that occurs between ca. 1200 and 700 B.C. in Europe¹³ (relative levels of MgO and K₂O in the LMHK, LMG, and HMG are given in Figure 1). Since then, the earliest potassium oxide glass in the world has been discovered dating as far back as 1100 B.C.¹⁴ A second high potassium oxide glass comes from Han Dynasty China (206 B.C.–221 A.D.) which also contains diagnostically high barium oxide levels.¹⁵ A third potassium-rich glass which dates to the western high medieval period—so-called "forest" glass—was frequently used for the production of medieval window glass,¹⁶ and for vessels as late as the 17th century. A further new kind of glass, a high alumina type dating to the first millennium A.D. has been found in India.¹⁷ Lead oxide–silica glasses from ca. 10th–14th century A.D. are the earliest examples of the use of a high level of lead oxide as a glass-former in the West; some contain lead oxide levels as high as 65% and may be linked to the appearance of this glass type in the Islamic world.¹⁸ Last, a variety of post-medieval glass compositions of mixed alkali, low alkali–high calcium, and soda–lime–silica compositions

has been identified.¹⁹ To modify the appearance of ancient glasses, opacifying crystals were added, or they were developed out of solution by heat-treating the glass. Opacifiers used include yellow lead antimonite (Pb₂Sb₂O₇), yellow lead–tin oxide (PbSnO₃), white calcium antimonite (Ca₂Sb₂O₇), white tin oxide (SnO₂), and red cuprous oxide (Cu₂O). Transition metal ions, such as those of manganese (Mn²⁺), iron (Fe²⁺/Fe³⁺), cobalt (Co²⁺), and copper (Cu²⁺/Cu⁺), acted as colorants in ancient glasses. In addition, a variety of complex parameters such as preparation of the glass batch, the heating cycle of the furnace, the fuels used, the gaseous atmosphere of the furnace and the chemical environment of the colorants will have had important roles to play in determining the final glass color produced.²⁰

Currently, chemical investigations of ancient glasses tend to focus on early, especially Egyptian, glasses and their relationship to faience,²¹ Roman and Islamic glasses (see below), and medieval and post-medieval glass.^{16,19} Some current researchers focus purely on the technology of glass²²—others focus on the relationship between glass compositions and the society in which the glass was made and used.

Soda–Lime Glasses in the Middle East: The Origins of Islamic Glass Technologies

During the Islamic period (after 640 A.D.), the Muslims conquered a maximum area extending, during the Abbasid caliphate, from southern Spain to northern India. During the height of centralized control, the caliph was located in one place, such as Baghdad, and was able to summon artisans from all over the Middle East for large construction works. By the 9th century, the capitals of the caliphate were complex settlements with cities, palaces, and industrial complexes. Examples of such capitals are al-Raqqa (Syria) from 796 to 808 A.D. and Samarra (Iraq) from 836 to ca. 882 A.D. Glass was therefore produced in an urban environment, often on a large scale, the caliph being able to control both the supply of labor and (probably) raw materials.

In an earlier urban environment, the Romans introduced glass-blowing in the 1st century B.C., which ultimately led to the mass production of glass vessels. The Romans produced soda–lime glasses (LMGs) using a mineral source of alkali, natron, an evaporite found in upper Egypt. The silica source was sand and the calcium oxide was provided by shell fragments in the sand. It was this combination of raw materials, used for the manufacture of low magnesia soda–lime–silica glasses (LMGs), that had originated ca. 800 B.C. and which continued for about 1600 years, up to the early part of the Islamic period ca. 800 A.D. Over this period, complex molding techniques were introduced and, in the 1st century B.C., glass-blowing.

Sometime shortly after ca. 800 A.D., a "revolution" in raw material use is apparent in the glass compositions, both in the Islamic world and in the West.²³ For some reason, whether political or not, the source of the alkali,

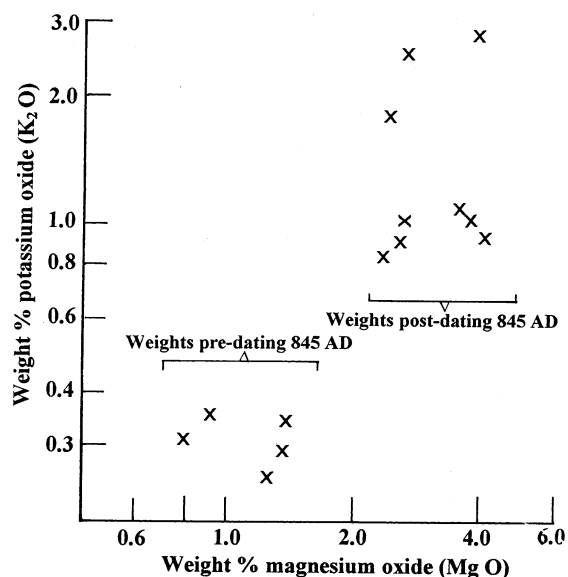


FIGURE 2. Bi-plot of weight % MgO vs weight % K₂O in dated Islamic glass weights from Egypt, showing the distinct change after 845 A.D. from a low MgO natron glass to the high MgO plant ash glass.

natron, started to “dry up”. In both areas, a search for new alkali sources is reflected in glass compositions. The result was that plant ashes were used as alkalis instead of the mineral. In the West, following a period of transition of about 200 years between *ca.* 800 and 1000 A.D., tree ash was set become the principal alkali source for the manufacture of the massive quantity of glass needed for glazing cathedrals outside the circum-Mediterranean area. In the Middle East, halophytic plants of the Chenopodiaceae family, such as of the genus *Salsola*, *Salicornia*, or *Hamada*, were used. This new pattern of alkali use was set for hundreds of years to come, with plant ashes being imported from the Middle East first to Italy as early as the 14th century²⁴ and later to produce the famous Venetian vessel glass and northern European glass vessels *à la Façon de Venise*.²⁵ It is the responses to the impact of such an important change in raw material supply, as may be discerned among the chemical compositions of Middle Eastern glasses dated to both before and after the event, that will be considered here.

The chemical analysis of Egyptian glass weights (which have the year in which they were made stamped on them) show a clear change from the use of a mineral alkali to a plant ash alkali *ca.* 840²⁶ A.D. (Figure 2) and a contemporary change from a sand to a purer silica source—either quartz or chert pebbles (i.e., a change from natron LMGs to plant ash HMGs). This might suggest that there was a tight (political) control over the production of Islamic soda–lime–silica glass in the 9th century. However, since an increasing number of chemical analyses of Roman, Byzantine, and Islamic glasses have now become available, a far more complex picture is starting to emerge.

First, although a tacit assumption has been made that it is impossible to link Roman glass compositions to production zones, there is now evidence that this may be wrong. For example, glass fused using silica with slightly

elevated alumina impurities seems to be characteristic of a Levantine silica source which occurs close to the mouth of the River Belus of antiquity.²⁷ Another high alumina Roman natron LMG compositional group, but with much lower calcium oxide levels, is thought to be characteristic of glasses made at Zakik and Beni Salama and one other new site at Wadi Natrun, Egypt, which probably date to between early Roman and the 8th century (Nenna, personal communication).²⁸ Both of these natron glass compositions appear to differ from the vast majority of Roman glasses found in the West which, in general, have lower calcium and aluminum oxide levels. So, although it may not be possible in many cases to source Roman glass to a production zone easily, it has now become possible to suggest where the glass was *not* manufactured with more confidence.

Glass of Byzantine date (5th century and later) from the Levant also seems to be characterized by a high alumina level.²⁹ As Von Saldern³⁰ notes, “By the second quarter of the seventh century, the Byzantine empire had lost its territories (and glass workshops) in North Africa and Palestine to the Muslims.” Although there are some differences in the vessel forms moving from the late Roman period into the Byzantine period, there was also a degree of continuity. One question, then, is the extent to which the original groups or families of glass artisans continued to use the same raw materials despite the appearance of their new political masters. One way of investigating this is by comparing the soda–lime LMG technologies used between the 1st and the 9th centuries A.D. What has become clear is that soda–lime glasses, *some* with elevated calcium and aluminum oxide levels, were in use at Jalame in Palestine in the late 4th century³¹ (Table 1). It is, however, notable that glasses with elevated calcium oxide levels, similar to those found in late Roman and Byzantine glasses, were in use at 1st century Qumrân, though they contained alumina levels comparable to those of western Roman glasses of $\sim 2.5\%$ or less (see Table 1). In addition, alumina levels detected in Jalame glasses, though elevated, do not reach the levels detected in later Levantine natron LMGs (see Table 1). This suggests first that the tradition of producing calcareous natron glasses started at least as early as the 1st century and second that exploitation of sand deposits with slight mineralogical variations may be a reflection of the time of production. As can be seen in Table 1, there is a gradual increase in alumina levels from *ca.* 2.5% in 1st century A.D. glass (a level comparable to that found in “Western” glasses), to *ca.* 2.7% in 4th century A.D. glass, increasing to *ca.* 3% in 6th–7th century A.D. glass and *ca.* 3.2% by the 8th–9th century A.D. in “Islamic” glass. There are exceptions to this trend, but in general, it holds. Freestone et al.³² have labeled the late Roman and Byzantine natron glasses “Levantine type I”. A glance at Figure 3 and Table 1 reinforces the similarity between late Roman and Byzantine glasses from 4th century Jalame and 6th–7th century Apollonia. However, some of 6th–7th century glasses from Dor contain higher soda (and the highest calcium oxide) of all the glasses plotted, and Bet Eli’ezer, a 6th–8th

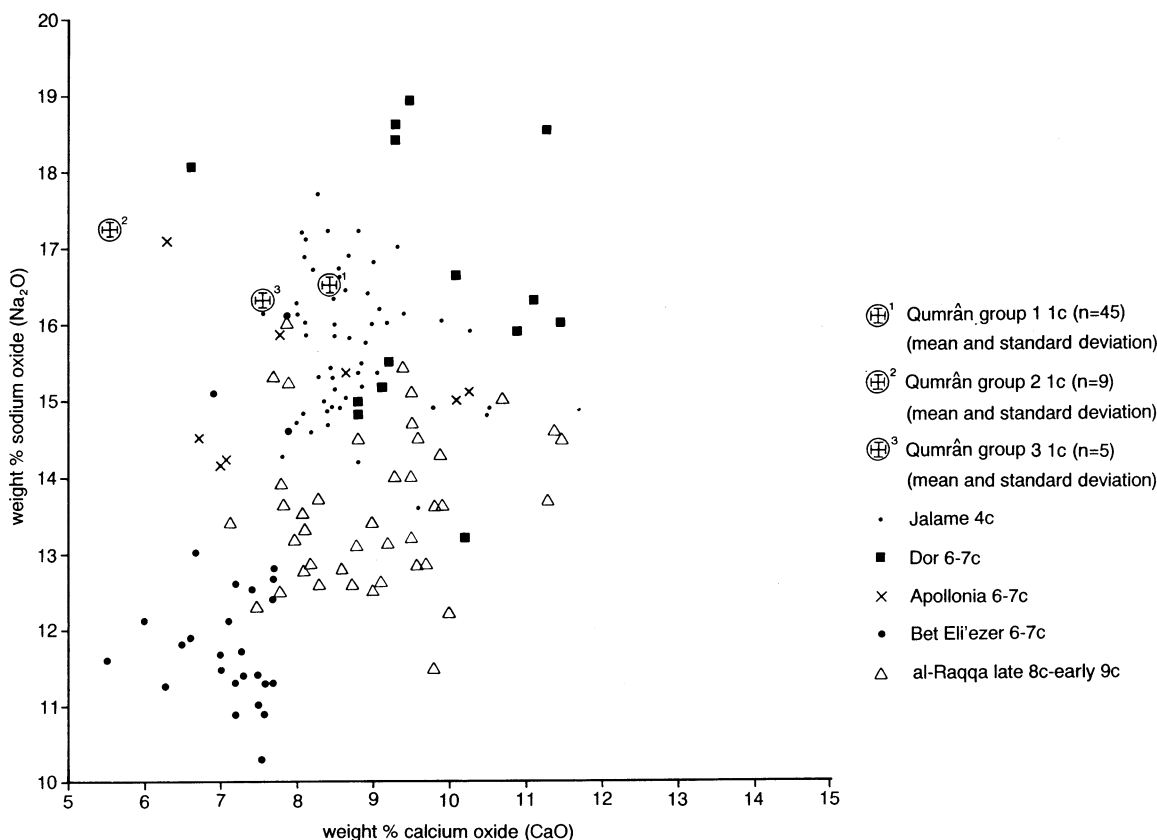


FIGURE 3. Ai-plot of weight % Na₂O vs weight % CaO in Middle Eastern natron glasses dating to sites between the 1st century A.D. and the 9th century A.D.

Table 1. Means and Standard Deviations for Middle Eastern 1st Millennium A.D. Natron Glasses (LMGs)

	Early Roman			Late Roman	Byzantine		Byzantine/ Early Islamic	Early Islamic
	Qumrân I, 1st cent., <i>n</i> = 45	Qumrân II, 1st cent., <i>n</i> = 9	Qumrân III, 1st cent., <i>n</i> = 5	Jalame, 4th cent., <i>n</i> = 40	Apollonia, 6th–7th cent., <i>n</i> = 9	Dor, 6th–7th cent., <i>n</i> = 14	Bet Eli'ezer 6th–8th cent., <i>n</i> = 27	al-Raqqa (type 3) 8th–9th cent., <i>n</i> = 61
Na ₂ O	16.48 ± 0.4	17.2 ± 0.35	16.28 ± 0.6	15.78 ± 0.81	15.17 ± 0.86	16.49 ± 1.67	12.12 ± 1.29	13.82 ± 0.88
CaO	8.41 ± 0.55	5.52 ± 0.61	7.54 ± 0.42	8.77 ± 0.63	8.07 ± 1.39	9.7 ± 1.23	7.16 ± 0.59	9.07 ± 1.09
SiO ₂	69.46 ± 0.62	71.69 ± 0.42	70.92 ± 1.62	69.9 ± 1.55	70.64 ± 1.87	68.97 ± 2.0	74.89 ± 1.4	71.17 ± 1.67
MgO	0.23 ± 0.13	0.01 ± 0.01	0.07 ± 0.13	0.59 ± 0.13	0.63 ± 0.83	0.63 ± 0.1	0.63 ± 0.09	0.73 ± 0.35
Al ₂ O ₃	2.51 ± 0.07	2.35 ± 0.34	2.42 ± 0.10	2.7 ± 0.13	3.05 ± 0.15	2.96 ± 0.24	3.32 ± 0.27	3.19 ± 0.28
K ₂ O	0.84 ± 0.06	0.58 ± 0.12	0.61 ± 0.11	0.8 ± 0.10	0.71 ± 0.31	0.91 ± 0.2	0.46 ± 0.08	0.61 ± 0.21
total mean alkali	17.32	17.78	16.89	16.58	15.88	17.4	12.58	14.43

century site, some of the lowest. There is, therefore, a possibility that with more chemical analyses of Levantine Roman and Byzantine glasses, clearer chronological/spacial correlations with composition will become apparent. Brill, for example, has noted a compositional distinction between 4th century Jalame glass and glass from a contemporary glass-making site at Kafr Yasif 25 km away based on soda to calcium oxide ratios.³³ Later Byzantine glasses of 11th–12th century date from Constantinople contain elevated alumina levels, providing evidence for the continuing use of glasses made in the “Christian” tradition.³⁴

Three compositional groups of 1st century Qumrân, Levant glasses were identified by Aerts et al.,³⁵ their means and standard deviations are plotted in Figure 3 (see also Table 1). Standard deviations of the oxides of these earlier Roman Qumrân glasses have lower values, forming very

tight compositional groupings (especially for soda), compared with the later Roman, 4th century, glasses from Jalame and other glasses in Table 1. This appears to reflect the difference between the products of more centralized production centers of the 1st century A.D. and products of multiple smaller production centers of the 4th century. However, although the analyzed glass from Jalame came from the same production site, there is no way of being absolutely sure that it was all made there.

How do these compositional patterns for Roman and Byzantine glasses from the Levant help us to explain the emergence of a “new” Islamic glass technology in the 8th–9th centuries? There is now evidence that, in the late 8th to early 9th century at al-Raqqa, Syria, a similar high calcium oxide/high alumina natron LMG was in use.³⁶ Again, the alumina levels are above 3%, which is higher than those found in Jalame glasses but comparable to

Table 2. Chemical Compositions of Mixed Natron and Plant Ash Glasses (8th–9th Century) from Islamic al-Raqqa (Type 2)

	<i>n</i> = 11
Na ₂ O	15.08 ± 1.89
CaO	5.35 ± 0.64
SiO ₂	67.86 ± 1.67
MgO	2.79 ± 0.26
Al ₂ O ₃	1.89 ± 0.21
K ₂ O	2.16 ± 0.49
total mean alkali	17.28

levels found in Byzantine glasses from the Levant (Table 1). The inference here is that the same or similar primary raw materials were used in the production of some Byzantine glass as in early Islamic LMG (sand, natron and shell fragments). We are faced, therefore, with the possibility that the same families of glass workers were involved in the Levant, using the same raw materials from the late 4th to the 7th centuries. What is more intriguing is that, while al-Raqqa natron glasses contain alumina and calcium oxide levels similar to those found in some Byzantine glasses from the Levant, the al-Raqqa glasses can nevertheless be distinguished from them by their lower mean soda levels and mean total alkali (Na₂O and K₂O) contents (see Table 1). Dor (Levant) natron glasses have a mean total alkali level of 17.4%, Apollonia (Levant) 15.88%, and al-Raqqa (Syria) 14.43% (see Table 1). With reference to Table 1, if the Dor values are ignored initially, a clear trend in mean soda levels in natron LMGs is discernible, from the highest in 1st century type II Qumrān glasses of 17.2% through 15.47% in 4th century Jalame glasses to 12.1% in 6th–8th century Bet Eli'ezer glass and 13.82% in 8th–9th century al-Raqqa glass; this trend is found in other data.³⁷ So, although the Islamic natron glasses from al-Raqqa contain slightly elevated calcium and aluminum oxide levels when compared with some earlier, Roman, natron glasses, it is possible to demonstrate that, by the late 8th to early 9th centuries, soda levels were markedly lower—and that soda contents generally remained at these levels for another 600 years. However, consideration of the glass analyses from 17 6th–8th century tank furnaces at Bet Eli'ezer³⁸ (see Table 1) and from 8th century Ramla³⁹ suggests something else. They contain low mean soda levels which are as low as the levels detected in later 8th to 9th century (Islamic) glasses. Moreover they contain higher levels of silica and lower levels of both calcium oxide and soda than detected in al-Raqqa natron glasses, showing that a regional distinction can be made (see Figure 3 and Table 1). In any case the analyses suggest that the trend in producing

glass with lower soda levels, and increasingly higher melting points, started in the 6th–7th centuries. Indeed, these low soda levels in Byzantine glasses may reflect a first phase of “shock” in the region during which the glass-makers attempted to adjust to the decreasing availability of their flux, soda. However, although it is clear that the supply of natron was running out, it is not entirely clear why higher proportions could not have been used in the melt. If a change in the mineralogical nature of the natron had, for some reason, led to the overall reduction of the soda retrievable for making glass, the glassmakers would have become aware of this because of the resulting elevated melting and working temperatures of the glass. Perhaps the *scale* of production dictated that a larger volume of glass needed to be produced, rather than a smaller volume with a higher soda level and a lower melting temperature. The net effect of reducing the level of the principal flux, soda, while retaining calcium oxide levels of up to 11.5%, alumina levels of up to 3.5%, and silica levels of up to 73%, was to increase markedly the melting point of the glass, making it more viscous and “shorter” (i.e., with a shorter working period). This would undoubtedly have made it more difficult to blow glass. It is evident that it took around 100–150 years before a solution to the consequent ever-increasing glass melting temperatures was found: to replace natron with plant ash (ca. 800 B.C. natron glass largely replaced plant ash glass, see Figure 1).

The “revolution” in glass technology therefore seems to have been stimulated by a shortage of mineral-based soda and once the change had occurred the Wadi Natrun, Egypt, natron source was never to be exploited again to make ancient glasses, suggesting that for some (geological?) reason it was no longer usable. The change to plant ash from a mineral alkali source brought about three things in glass technology simultaneously. First, the new alkali would have been far easier to obtain because suitable halophytic plants grew, and continue to grow, commonly in the Middle East on desert margins. Second, glass melting temperatures would have fallen: although the soda levels fell, the total alkali levels increased (Table 3) from ~12–14% to ~16–17.5% because both soda and higher potassium oxide levels were introduced in the plant ash used. At the same time, levels of silica and alumina fell—and in some glasses the calcium oxide levels also fell, all of which would reduce melting temperatures. Third, because the glass melting temperatures fell, the amount of fuel that was needed to melt the glass would have been lower. Given that the fuel was the most expensive raw

Table 3. Chemical Compositions of Plant Ash Glasses from Islamic al-Raqqa (8th–11th Century) (HMGs)

	8th–9th cent. al-Raqqa (type 1) (<i>n</i> = 34)	11th cent. al-Raqqa (subtype 1) (<i>n</i> = 49)	8th–9th cent., al-Raqqa (type 4)		
			hi Al (<i>n</i> = 12)	mid Al (<i>n</i> = 40)	lo Al (<i>n</i> = 13)
Na ₂ O	13.7 ± 1.11	12.18 ± 0.95	14.6 ± 0.88	13.89 ± 0.79	14.38 ± 1.2
CaO	8.51 ± 1.02	10.18 ± 1.00	7.61 ± 0.72	6.12 ± 1.26	4.99 ± 0.8
SiO ₂	67.55 ± 1.46	67.66 ± 1.49	63.5 ± 2.19	66.94 ± 2.5	67.9 ± 2.4
MgO	3.55 ± 0.33	3.38 ± 0.28	3.79 ± 0.71	4.48 ± 0.64	6.31 ± 0.76
Al ₂ O ₃	1.17 ± 0.17	1.24 ± 0.17	3.8 ± 0.55	2.28 ± 0.52	1.33 ± 0.2
K ₂ O	2.47 ± 0.19	2.48 ± 0.33	2.88 ± 0.37	2.87 ± 0.72	2.84 ± 0.53
total mean alkali	16.47	14.66	17.48	16.76	17.22

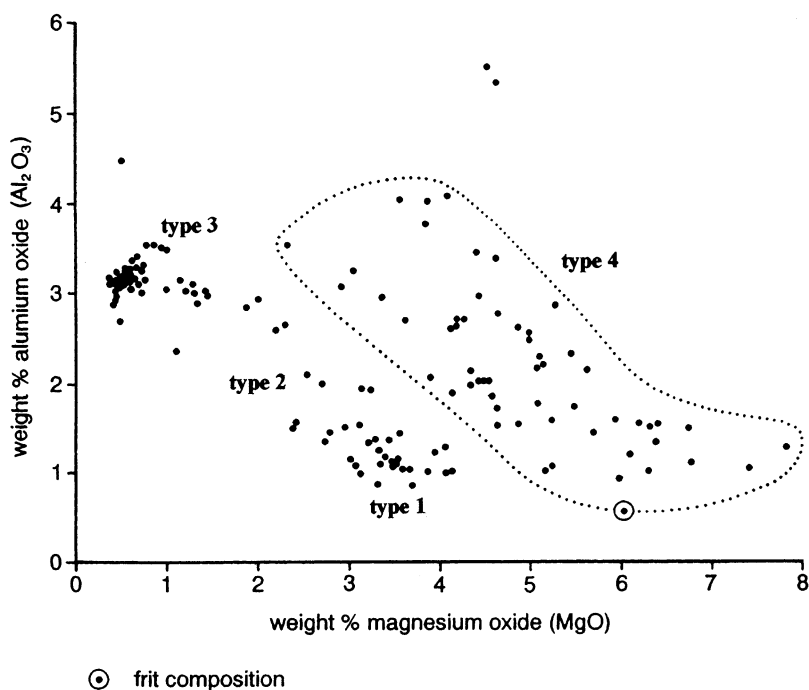


FIGURE 4. Bi-plot of weight % Al₂O₃ vs weight % MgO in Islamic glasses from al-Raqqā, northern Syria, dating from the late 8th to early 9th centuries A.D. The composition of the vitreous component of the frit is shown as an encircled spot.

material needed to melt the glass,⁴⁰ and that it would have been used in large quantities, the switch to a plant ash source of alkali clearly had an economic advantage to the glass-making industry, quite apart from making it easier to blow the glass produced.

However, a study of glass chemical compositions reveals that the switch to the use of a plant ash was not simply a change from one definable glass composition to another. A much wider range of glass compositions was found in the 8th–9th century glass workshop in al-Raqqā (Table 3, where there is early evidence for the use of plant ash to make glass,⁴¹ than amongst the natron glasses found in the Roman and Byzantine glass workshops at Jalame and Bet Eli’ezzer, respectively (Table 1). First, high alumina, high calcium oxide natron glasses discussed above (type 3 in Figure 4 and Table 1, al-Raqqā) were detected. These are the Islamic version of the natron–sand glass identified at Dor and Apollonia by Freestone et al., but they are distinguishable by their generally lower soda levels (Figure 3, Table 1). Second, glasses with a low alumina, high magnesia plant ash–quartz/chert composition (type 1 in Figure 4, Table 3, al-Raqqā type 1) were detected. Glasses of this general composition were set to become the principal Islamic glass type for the next 600 years. Third, a mixture of these two compositions is represented by samples which plot between these two types in Figure 4 labeled type 2 (see Table 2). Presumably, another strategy for dealing with the decreasing amounts of natron was to extend stocks of natron glass (which had known glass-working properties) by mixing it with plant ash glass, producing glasses with a mean total alkali of 17.28%. It is almost unique to be able to illustrate analytically that glass recycling has occurred; it is only possible here because there was such a radical change in

the use of raw materials which produced distinctively different compositions.

In addition to the plant ash glass compositions labeled type 1 in Figure 4 with 3–4% MgO, a fourth compositional type containing far higher MgO levels of up to 7% and low alumina occurs (Figure 4, type 4). These higher magnesia glasses suggest that a different (second) species or genus of plant has been ashed in order to provide the alkali raw material (Table 3, type 4, “lo Al”). There is analytical evidence that this highest magnesia-containing type 4 glass composition was fritted on site (see Figures 4 and 5) from primary raw materials,⁴² possibly including bone ash in order to augment the calcium content which was evidently lower in the new plant ash used (see Table 3 and Figure 5). The chemical analyses of al-Raqqā type 4 glasses show very clearly that we are dealing with a range of chemical compositions which can be linked to distinct combinations of raw materials and glasses.⁴³ The glass compositions fall on a (second) negative correlation running between two “end members” from very high magnesia (~7%) and low alumina (~1%) (see Figure 4, type 4; Table 3, al-Raqqā type 4, “lo Al”) to glasses containing lower levels of magnesia (~3.5%) and high alumina (~4%) (see Figure 4, type 4; Table 3, al-Raqqā type 4, “hi Al”).

These plant ash glasses, of al-Raqqā type 4, first appear in the 9th and 10th centuries and seem to disappear after the 11th century, at which point, according to the currently available analytical data, almost all Islamic glass was manufactured using plant ash glass of type 1 represented by type 1 in Figure 4 and Table 3, al-Raqqā *subtype* 1. The high alumina al-Raqqā type 4 glass was made with sand (containing alumina-rich impurities) and plant ash. This



FIGURE 5. Scanning electron micrograph of a sample of overheated frit from al-Raqqa, northern Syria, of late 8th to early 9th century date, showing inclusions of silica and a calcium-rich raw material which is probably bone.

combination of raw materials is an important new variation from the long-established combination of sand and natron.

To produce glasses with higher mean total alkali contents shortly after or at the point of change to a plant ash, this experimentation with new combinations of raw materials led to the production of al-Raqqa types 2 and 4 (Tables 2 and 3). It appears that, in the manufacture of type 4 glasses, the same silica source (sand) that had been used in the Levant for hundreds of years may have been used first, to which the “new” plant ash source of alkali was added. This glass composition (Table 3, type 4, “hi Al”) is also characterized by low silica (a mean of 63.5%), which would have counterbalanced its relatively high melting temperature imposed by the levels of alumina and calcium oxide. In this case, therefore, we can suggest tentatively that the sand and plant ash glass was a half-way stage on the road to producing plant ash–quartz/chert glass, forming part of the experimental process. Those type 4 plant ash glasses containing the highest magnesia levels also contain the lowest levels of calcium and alumina oxide levels and therefore represent a total break from the Levantine “Christian” natron tradition. For glasses plotted in Figure 4, containing progressively lower alumina and higher magnesia levels, glass-makers were mainly experimenting with different proportions by weight of fully fused glasses (rather than raw materials) of the two variants (Table 3, al-Raqqa type 4, “lo Al” and “hi Al”) in order to exert the degree of control shown by the spread of compositions. The same degree of control is apparent for other pairs of associated oxides in these glasses.⁴⁴ This appears to be the first time that experimentation with

ancient glasses and raw materials has been demonstrated analytically.

Compositional evidence for the relatively unusual combination of sand and plant ashes has been found in 9th–10th century Islamic glasses from Nishapur, Iran,⁴⁵ and also in the great glass slab from Bet She’arim, Israel, which was recently re-dated as Islamic.⁴⁶ The difference between the Bet She’arim glass composition and those from Nishapur and al-Raqqa of this type is that the last two contain significantly lower calcium oxide levels (which would have been introduced both in plant ashes and in sea shell fragments in sand), presumably because some of the shell fragments were removed from the sand by filtration or centrifuge prior to making up the batch. This new data from al-Raqqa tends to confirm that new plant ash–sand glasses were the result of successful experiments, whereas the Bet She’arim glass melt was unsuccessful.

Conclusions

It is clear that glass produced between 800 B.C. and 800 A.D. mainly used a combination of the mineral alkali, natron, sand and shell fragments with only restricted compositional variations. This period saw the introduction of glass-blowing by the Romans in the 1st century B.C. that was ultimately to transform ancient glass-making leading to mass production of vessels and consequent reduction in the value of some. It is against this background of the conservative use of raw materials that any evidence for the processes of innovation in glass production is generally obscured. During this period, it is clear

that once the artisans had produced glass with suitable working properties, they did not normally attempt to experiment with new raw materials. In rare instances, there is evidence of distinct glass types being used for molding and for blowing glass vessels.⁴⁷ However, in general this is not the case.

One of the compositional characteristics of Roman Levantine natron soda–lime–silica glasses between the 1st and 4th centuries A.D. is that, with time, soda levels start to fall off slightly (Table 1). The soda levels in Byzantine natron glasses between the 5th and 7th centuries sometimes also exhibit the same trend, with those from Bet Eli'ezer and many glasses from Apollonia containing relatively low soda levels. There is evidence for an initial "shock" realization that the soda source (natron) was becoming less easy to obtain and that higher glass melting points had to be accommodated. Once this was clear ca. 7th–8th centuries A.D., it became critical to find a new alkali raw material. This led to a period of experimentation, perhaps in a number of production centers.

The response was a (re-)introduction of halophytic plant ash alkalies in the late 8th and 9th centuries in many areas (after a break of nearly 1600 years)—with a result that mean total alkali levels rose from ~12–14.5% to 16–17.5%, reducing the melting temperature of the glasses. It is the "accommodation" of this new alkali source in an existing glass recipe that led to experimentation with a range of raw materials and which, for once, can be proven analytically. One result is that an unusually wide range of glass compositions has been found at the 8th–9th century Islamic glass factory of al-Raqqa, Syria, compared to, for example, the 4th century Roman factory at Jalame and the 6th–7th century Byzantine glass factory at Bet Eli'ezer, where no such experimentation apparently occurred.

This experimentation with raw materials would have impacted on the working properties of the glasses with a reduction in their melting points, a need for less fuel, and the ability to blow glass at lower temperatures. In order to control and monitor the changes in glass working and melting temperatures, so critical to blowing glass, part of this experimentation is likely to have involved the mixture of glasses rather than their raw materials which could introduce compositional variations, leading to unpredictable glass working properties. One thing that is difficult to explain, however, is that during the period after we have evidence for the production of new "experimental" glass in the Middle East, glass-makers ignored the "results" of these experiments. Between the 11th and 14th centuries they reverted to making glass from the alternative plant ash. This introduced lower magnesia levels and in al-Raqqa glasses, at least, the lower levels of mean total alkali (Table 3, subtype 1) found in natron glasses of the pre-experimental phase, causing an increase in the melting temperature of the glass.

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