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The use of oxygen, strontium and lead isotopes to provenance ancient glasses in the Middle East

J. Henderson[a,*], J.A. Evans[b], H.J. Sloane[b], M.J. Leng[b], C. Doherty[c]

[a] *Department of Archaeology, University of Nottingham, University Park, Nottingham NG7 2RD, UK*
[b] *NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham NG12 5GG, UK*
[c] *Research Laboratory for Archaeology and the History of Art, Oxford University, 6 Keble Road, Oxford OX1 3QJ, UK*

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Abstract

It is sometimes possible to discriminate between glasses made at different factory sites by using chemical analysis. However, this is not necessarily a means of provenancing them unambiguously because glass of slightly different compositions may have been fused using different proportions of the same raw materials. The determination of oxygen, strontium and lead isotopes can provide the possibility of linking the geological sources of the glass raw materials to the production sites on which the glass was fused. Here we consider the possible isotope contributions made to the raw materials thought to have been used in the manufacture of plant ash and natron glasses found at 8th–9th century al-Raqqa, Syria. The isotopic data from al-Raqqa are compared with published results from other Middle Eastern and German glasses. We show that strontium isotopes, in particular, provide a reliable means of distinguishing between the sources of plant ash glass raw materials and that oxygen and lead isotope signatures are less discriminatory.

Keywords: Isotopes; Oxygen; Strontium; Lead; Glass; Islamic; Raqqa; Provenance; Raw materials

1. Introduction: ancient glass making and the problem

Glass is created by fusing three basic components and then cooling them quickly to create a super-cooled liquid which is waterproof, transparent/translucent, brittle and can be fashioned into an enormous variety of shapes and forms for practical and decorative purposes. The three basic components of glass are a *former*, a *flux* and a *stabilizer*. The former is the main component of glass and is normally silica or quartz (SiO_2). Fluxes are added to the former to lower the melting temperature of the silica. Soda (Na_2O) and potash (K_2O), both alkalis, are common fluxes. Lime (CaO) is used as a stabilizer and makes the glass more durable. The main sources of these raw materials comprise sand and quartz pebbles (SiO_2), natron, desert plant ash or marine plant ash (Na_2CO_3), potash (K_2O), generally from trees, and lime ultimately from marine shells and plant ashes ($CaCO_3$). These raw materials can contain impurities such as magnesium, aluminium, phosphorus and iron.

The chemical analyses of ancient glasses provide clear evidence of use of different raw materials. Isotopes have the potential to distinguish between different sources of the main glass constituents (i.e. the sources of formers, fluxes and stabilizers) and thereby refine the current understanding of glass production. By suggesting the raw materials used in glass production from chemical analyses and linking these to their isotope signatures, it

* Corresponding author. Tel.: +44 115 951 4840; fax: +44 115 951 4812.
E-mail address: julian.henderson@nottingham.ac.uk (J. Henderson).

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Table 1
Mean and standard deviation values for chemical compositions of natron and plant ash glasses from 8th–9th century al-Raqqa

	Natron glass ($n=66$)		Plant ash glass ($n=36$)	
	wt %	s.d.	wt %	s.d.
SiO_2	71.17	1.67	67.55	1.46
Na_2O	13.82	0.88	13.7	1.11
CaO	9.07	1.09	8.51	1.02
MgO	0.73	0.35	3.55	0.33
K_2O	0.61	0.21	2.47	0.19
Al_2O_3	3.19	0.28	1.17	0.17
Fe_2O_3	0.39	0.09	0.52	0.22
TiO_2	0.05	0.01	0.06	0.01
MnO	0.04	0.04	1.2	0.62
P_2O_5	0.1	0.05	0.29	0.04
Cl	0.73	0.11	0.79	0.16
SO_3	0.09	0.06	0.18	0.07
Totals	100		100	

may be possible to trace technological developments of the industry in a new way.

Using major element chemistry we know that ancient glasses fall into two broad categories (e.g. Table 1) [21]. The first type is thought to have combined a soda-based flux and lime derived from plant ash with quartz pebbles as the silica source. The second type is a soda-based flux of natron with a sand source for the silica and seashells providing the stabilizer ($CaCO_3$). These two glass types will be referred to from here on as plant ash glass and natron glass respectively [12, p. 25–26].

In this study we concentrate on a single plant ash glass type from a range of three found at al-Raqqa and on natron glass [15,16]. Isotope analysis has the potential to define the sources of raw materials from around the al-Raqqa glass making site, to compare them with the two main glass types found at the site and to test the hypothesis that the raw materials were locally derived.

The isotope systems of oxygen, strontium and lead all provide possible discriminates for glass manufacture. Brill [3] suggested that oxygen isotopes could be used to detect the source of silica in glass as there is a natural range in isotopes values of silica depending upon the geological conditions of quartz formation. Sand, via the erosion of a particular type of granite, would give low $\delta^{18}O$ values (typically c. 10–12‰) whereas low temperature metamorphic quartz, typical of vein quartz would have higher values, perhaps up to 20‰. The isotope ratio of strontium depends upon the age and Rb content of the parent rock. As strontium generally substitutes for calcium, it will provide data on the source and nature of the lime sources. In particular lime from old marine limestones can be distinguished from modern-day sea shell sources. Plants take up strontium and their $^{87}Sr/^{86}Sr$ ratio is a reflection of the underlying geology on which the plants grow [8,23]. This means that the Sr isotope compositions of plant ash glasses provide information about the geological/surfical environment in which the plants used to make them grew. Although lead is not a major constituent of most glass, lead isotopes can provide a comparison of the average Pb isotope composition of the raw materials.

2. Previous work on the isotope composition of ancient glass

As mentioned above, Brill and Brill et al. [3,4] noted that oxygen isotopes could be used to source silica because there is a natural range in isotope values which is dependant on the geology. They suggested that the oxygen isotope composition of archaeological glass is strongly dependent on the oxygen isotope composition of the raw ingredients, especially the silica, since silica is the predominant component. Variations in the melting times and temperatures (within certain limits) had no measurable effect on the final $\delta^{18}O$ of the glass. Wedepohl and Baumann [26] have shown that the $^{87}Sr/^{86}Sr$ isotope composition of late fourth century Roman glasses from the Eifel region (Western Germany) are characteristic of the calcium source used. Six glass samples with Sr concentrations of between 388 and 447 ppm have $^{87}Sr/^{86}Sr$ ratios within the range 0.7087–0.7090 which is just below the Sr isotope ratio of modern day seawater (0.7092). They concluded that the Roman glass factories used modern marine molluscan shells as the main source of Sr, with possibly a small Sr contribution from natron sources which might provide the slightly less radiogenic Sr needed to bring the glass values below modern day seawater. Recent work by Freestone et al. [10] using strontium isotopes, has shown that it is possible to distinguish between natron glasses made in Egypt (Tel el Ashmunein) and those made in Israel. This distinction is possible because the calcium source in the Egyptian glass is likely to have been Tertiary limestone whereas that used in the Israeli glass is thought to have been modern marine shells.

Lead isotopes of a range of archaeological glasses have been determined, mainly by Brill and co-workers [1,6,7]. These studies have shown that it is possible to distinguish, in general terms, using $^{208}Pb/^{206}Pb$ vs $^{207}Pb/^{206}Pb$ between the sources of lead in archaeological objects (including glass) from, for example China and Egypt. However, leads from Spain, Wales and Sardinia fall into the same grouping as do leads from England, Italy and Turkey. Wedepohl et al. [27] have been able to link lead isototope characteristics of medieval glass to lead ore deposits in Germany. A much larger number of lead isotope determinations taken from artifacts from a relatively small area has underlined the complexities of recycling and other parameters in attempting to source metal used in artifacts [20]. No such study has yet been attempted