Journal of Archaeological Science 62 (2015) 55–65

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

Roman and late-Roman glass from north-eastern Italy: The isotopic perspective to provenance its raw materials

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ARTICLE INFO

Article history:
Received 27 February 2015
Received in revised form
19 June 2015
Accepted 6 July 2015
Available online 17 July 2015

Keywords:
Glass
Roman
Late-Roman
North-eastern Italy
Strontium
Neodymium
Oxygen
Isotopes
Provenance
Raw materials

ABSTRACT

In this study, the strontium, neodymium and oxygen isotopic composition of Roman (1st–3rd century AD) and late-Roman glass (4th–6th century AD) from Adria and Aquileia, two of the most important archaeological sites of north-eastern Italy, is discussed.

The majority of glass analysed, independent from age, shows values of strontium isotope ratios close to that of modern seawater, indicating that the source of lime in the glass was marine shell, and likely coastal sands were used in its production. The Nd signature of all late-Roman glasses from Aquileia and of the majority of the Roman ones from Adria, independent from their chemical composition, is homogeneous and higher than −6 εNd, supporting the hypothesis of an eastern Mediterranean origin, probably located on Syro-Palestinian coast. However, the composition of late-Roman samples with HIMT signature, with lower $^{87}Sr/^{86}Sr$ values correlated to higher contents in Fe_2O_3, TiO_2, MgO and lower contents in CaO, suggests an area of origin for this glass on the Egyptian coast. In addition, the different Nd signatures of two Adria Roman glasses ($\varepsilon Nd < -7$) suggest their primary production in western Mediterranean. Oxygen isotopes proved to be a further diagnostic method to discriminate natron and soda plant ash glass, and different silica sources, in the case of the soda plant ash glass. The combination of isotopic and chemical data supports the hypothesis of an eastern Mediterranean origin for late-Roman glass, which may be produced in few primary workshops on the Syro-Palestinian and Egyptian coast, although not necessarily in the same *ateliers* as have been identified so far. In the case of the Roman glass investigated, although the majority of data suggests an eastern Mediterranean origin, on the basis of Nd isotopes and chemical compositions, the existence of other primary glass producers located in the western Mediterranean can be suggested.

1. Introduction

Provenance determination of archaeological and historical artefacts relies on the assumption that there is a scientifically measurable property that will link an artifact to a particular source or production site (Degryse et al., 2009a). In this context, mineralogical, petrographical or elemental chemical analyses are the techniques most often used to try to identify where inorganic artefacts were produced. In ancient glass provenancing, chemical composition may provide indications on the glass raw materials, which may then suggest a specific source of supply, although direct relationships between mineral raw materials and the artefacts made from them can be lost at high temperatures (Degryse et al., 2009a). In many recent studies, new questions about glass provenance have been addressed using radiogenic and stable isotopes (e.g., Degryse et al., 2009b, 2010a, 2010b, 2010c; Henderson et al., 2005; Silvestri et al., 2010; Ganio et al., 2012a, 2012b, 2013; Degryse, 2014), since transformations as melting have little effect on the isotopic ratios in glass. In particular, the heavy isotopes of e.g. strontium and neodymium are, due to their relatively high masses at low internal mass differences (Faure, 1986), not

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http://dx.doi.org/10.1016/j.jas.2015.07.004

fractionated during technical processes. The isotopic composition of the artefact will hence be identical, within analytical errors, to the raw materials of which it was derived, while the signatures of different raw materials used, and hence the resulting artefacts, may differ (Brill and Wampler, 1965; Gale and Stos-Gale, 1982). Conversely, variations in many stable isotope ratios reflect different geological origins, due to different formation processes. The isotopic composition of a raw material is thus largely dependent on the geological age and origin of that material (Brill et al., 1999).

The application of strontium isotopes to the interpretation of ancient glasses depends primarily upon the assumption that the bulk of the strontium of many glasses is incorporated with the lime-bearing constituents in the glass (Wedepohl and Baumann, 2000). These lime-bearing components are likely to be, on one hand, shell or limestone, and, on the other, plant ash, which is usually lime-rich (e.g., Brill, 1970; Verità, 1985). Where $CaCO_3$ was derived from Holocene beach shell, the $^{87}Sr/^{86}Sr$ ratio should reflect that of modern seawater and be close to 0.7092. If, on the other hand, the strontium was incorporated in the glass in the form of limestone, then it will have an isotopic signature that reflects that of the environment at the time the limestone was deposited, modified by any diagenetic alteration that might have occurred to the limestone over geological time (Freestone et al., 2003). For a glass made using plant ash, the $^{87}Sr/^{86}Sr$ value will reflect the bioavailable strontium from the soils on which the plants grew (Degryse et al., 2010b). It has been assumed that the contribution of natron to the strontium balance of glass is negligible, and minor contributions may be attributed to feldspars or heavy minerals in the silica raw material (Freestone et al., 2003; Degryse et al., 2006a). However, recent study on sand raw materials from the western Mediterranean shows that, in some cases (e.g., for glass produced using sand from the western Mediterranean with high Al_2O_3 and an Al_2O_3/CaO ratio higher than 0.25), the Sr isotopic signature of the lime source may be overshadowed by the influence of the Sr from the silicate fraction in the sand (Brems et al., 2013a).

The introduction of neodymium isotopes in glass studies is recent. Nd in glass is likely to have originated partly from the clay mineral content and partly, but principally, from the non-quartz mineral content of the silica raw material (Degryse et al., 2006b; Degryse and Schneider, 2008). The effect of recycling on the Nd isotopic composition of a glass batch is not significant, apart from mixing sources, and neither is the effect of colourants and opacifiers (Freestone et al., 2005). This offers a great potential in tracing the origins of primary glass production. In this context, a database of Nd isotopic compositions of possible sand raw materials from the western Mediterranean was recently published (Brems et al., 2013b; Degryse, 2014) and this, together with previous data on the Nd pattern of the eastern Mediterranean sediments (e.g., Freydier et al., 2001; Tachikawa et al., 2004; Brems et al., 2012a), constitutes a useful mean of comparison for the growing number of isotopic data on ancient glass. Nd isotopic signatures of the beach sands show, in fact, a decrease in εNd from east to west of Mediterranean basin, ranging from −12.4 for Spanish sands to −3.3 at the mouth of the river Nile (Brems et al., 2013b). Previous studies, carried out on glass dated from Roman to early Byzantine period (e.g., Degryse et al., 2006b; Degryse and Schneider, 2008; Degryse and Shortland, 2009; Ganio et al., 2012a, 2012b; Freestone et al., in press) suggested a primary provenance for most of the glass analysed in the Syro-Palestine area and in Egypt. However, some Roman glass showed “exotic” Nd isotopic compositions, which did correspond well to sediments from the western Mediterranean, suggesting that during the Roman era primary production may also be located outside the Near East.

Oxygen was the first isotope to be used to investigate the provenance of ancient glass. Its potential was pioneered by Brill and co-workers (Brill, 1970, 1988; Brill et al., 1999), which showed that stable isotopes of oxygen have characteristic ranges for certain glass groups. For a typical soda–lime–silica glass, the bulk of the oxygen is about 45 wt%, and approximately 70% of it enters the glass as a component of the silica. Even in strongly coloured glasses, the bulk of the oxygen is derived from the major components of the base glass (Leslie et al., 2006). For this reason, the oxygen isotopic composition of ancient glass mainly depends on the silica source, with minor influences of flux and stabilizer (Brill, 1970; Brill et al., 1999). In addition, it was experimentally demonstrated that variations in melting time and temperature had no measurable effects on the final oxygen signature of the glass (Brill et al., 1999). Therefore the isotopes of oxygen could be expected to be useful discriminants of raw material sources. In spite of its apparent promise and the important pioneering works of Brill and co-workers, oxygen isotope analysis has not been widely applied in the investigation of glass. Only recently Henderson et al. (2005), Leslie et al. (2006), Silvestri et al. (2010) and Degryse et al. (2010c) have contributed to amplify the database of oxygen isotope data for various archaeological glass samples and possible raw materials.

In this study, isotopic compositions of strontium, neodymium and oxygen are obtained on Roman and late-Roman glass coming from north-eastern Italy, which, because of its particular position, had a central role in trade as commercial hub between the Mediterranean and the Padan and Transalpine area. The combined use of Sr, Nd and O isotopic analyses of glass allows different raw materials (sand and/or flux) used for their primary production to be distinguished and characterised. The isotope ratio data obtained for the glass are compared to the sand database, which includes relevant sands from the eastern and western Mediterranean, and with isotopic data on coeval glass, already published in literature. These comparisons allow us to advance further hypotheses on location and supply of raw materials and on trade routes during the Roman and late-Roman period.

2. Materials and methods

In the present work, 38 samples were selected for the analysis of Sr and Nd isotopes, and the same with the addition of two plant ash glasses (for a total of 40) for O isotope. They are Roman (1st–3rd century AD) to late-Roman in date (4th–6th century AD) and come from north-eastern Italy, in particular from Adria and Aquileia, the two most important sites in the period and in the area considered. The selection was carefully conducted, in order to represent the various archaeological types, colours and the different compositional groups identified and detailed in Gallo et al. (2013, 2014).

In particular, 22 samples were selected from Adria, all Roman (1st–3rd century AD) in date. 12 samples come from compositional group AD/N1, composed of the transparent Adria samples. They are light blue, light green, amber, purple, blue, olive green and Mn-colourless and form an homogeneous group with chemical composition close to that of the “typical” Roman glass of the 1st–3rd cents. AD found in the Western provinces (e.g., Nenna et al., 1997; Silvestri, 2008). 4 samples were taken from group AD/N2, all Sb-colourless glasses and forming a distinct group, produced with a high purity sand, poorer in calcite and feldspars than that used for the ‘typical’ Roman production. 3 samples belong to group AD/A (sample AD-VE-2 for Sr, Nd and O isotopes, plus samples AD-VE-3 and AD-VE-4 for the only O isotopes), composed of glasses produced with a soda plant ash as flux. In the Roman period, soda ash glass was uncommon and generally only used to produce particular colours, such as emerald green and black, as in these Adria samples, and its provenance is still debated. Additionally, three other samples, defined as Outliers 1, 2, 3, were analysed.