Isotopic investigation into the raw materials of Late Bronze Age glass making

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ABSTRACT

This paper discusses Sr-Nd-Sb isotopic analysis of Late Bronze Age glass to investigate the origin and nature of the mineral raw materials used in early glass making. Sr—Nd isotopic analysis characterizes the flux and silica component of the glass raw material mixture. This technique has been successfully applied to separate Egyptian from Mesopotamian glass signatures, also identifying the use of at least two distinct flux-silica mixtures in Mesopotamian glass making. Sb isotopic analysis is presented as a novel technique to examine the raw material used to opacify the earliest glass. It is demonstrated that Egyptian and Mesopotamian glass factories likely used an identical source of Sb, possibly originating from the Caucasus. This suggests a steady supply and long distance exchange or trade of this material during the Late Bronze Age.

1. Introduction

As with any invention, someone, somewhere made the first artificial glass. Tracking this moment down temporally and geographically in an archaeological record that is at best partial is extremely difficult, if not impossible. Man-made glass only becomes common in Syria-Mesopotamia and Egypt in the Late Bronze Age (LBA), after the fifteenth century BCE glass revolution (Peltenburg, 1987). During this period, an explosion in the amount, colors and types of glass occurs. Scattered finds of earlier man-made glass objects, however, mainly in the form of beads, demonstrate the existence of glass throughout Egypt, Mesopotamia, Syria and Anatolia from the late third millennium BCE onwards (Beck, 1934; Moorey, 1994; Peltenburg, 1987).

Early glass was a strongly coloured high-status material, resembling semi-precious stones. Glass in the Late Bronze Age was made by melting a mixture of ground, relatively pure quartz(ite) pebbles (as a glass network former), plant ashes (as a flux) and colorants/opacifiers. A suite of (sometimes uncommon) elements are used as colorants and opacifiers. Dark-blue glass is obtained by the addition of cobalt, whereas generally the addition of copper results in a lighter blue glass. Antimony gives the earliest glass its opacity, with or without the addition of lead (Shortland, 2002a) (Fig. 1). The colouring elements are added as separate constituents, potentially in the form of ores, minerals or metal alloys, either in their primary form or processed in some way. The use of metals such as Cu, Sb and Pb has led to the speculation that the development of glass technologies was closely related to the metal production 'industries' (Peltenburg, 1987; Shortland, 2012). Long-

	None	**Ca$_2$Sb$_2$O$_7$**	**Pb$_2$Sb$_2$O$_7$**	**Cu$^+$**
None	colourless			
Cu^{2+}				na
Co			na	na
Mn		na	na	na

Fig. 1. Phases common in early glass, and their colouring effect.

distance exchange and trade in metals began long before the second millennium BCE in the Old World with copper and tin (Muhly, 1988). If the working of native copper is seen as premetallurgical, metallurgy really begins with smelting, the earliest evidence of which for copper is dated to 5000 BCE in both Serbia (Radivojević et al., 2010) and Iran (Frame, 2009, 2012). This is contemporary with the first use of lead and antimony (as Cu–Sb alloy) in the late sixth to fifth millennium BCE (Killick, 2001; Killick and Fenn, 2012; Moorey, 1988; Thornton, 2007; Shalev and Northover, 1993; Ussishkin, 1980).

By applying isotopic analysis protocols, especially developed for ancient glass and its possible raw materials, the nature and origin of glass as a material can be investigated. While elemental analysis of glass objects will allow the identification of the glass technology used (in particular the flux and colorant/opacifier type), Sr–Nd isotopic analysis may provenance the constituents mixed to make the base glass (Degryse and Schneider, 2008; Degryse et al., 2010a). In this paper, Sr–Nd isotopic analysis of LBA glass is combined with Sb isotopic analysis. In this way, also the source of the antimony used to opacify the earliest glasses may be traced (Lobo et al., 2012). By sourcing the raw materials used in the earliest glass making, exchange networks of raw materials can be mapped, and possibly minerals and metals used jointly in the earliest glass and metal pyrotechnologies can be identified or compared.

2. Materials and methods

2.1. Materials

Glass from five sites, Amarna and Malkata in Egypt, and Nuzi, Nippur and Tell Brak in Mesopotamia (Tables 1 and 2), all dating to the 14th to 13th century BCE, was selected for Sr-Nd-Sb isotopic analysis. Additional samples of a white opaque glassy material, described as antimony slag from Sagebis Dsiri (Georgia) and a metallic antimony bead from Jerablus Tahtani (Syria) were also analysed. The isotopic data obtained were compared to a database of glass making sands and antimony ores (Brems et al., 2012; Lobo et al., 2012, Table 3).

2.2. Analytical methodology

Chemical mapping was undertaken using a JEOL 840A SEM with an accelerating voltage of 20 kV. Images, maps and elemental spectra were obtained using an attached EDAX Genesis microanalysis system.

For Sr–Nd isotopic analysis, 100 mg of powdered sample was weighed into a Savillex screw-top beaker and digested in a 3: 1 mixture of 22 M HF and 14 M HNO$_3$ on a hot plate. The digest thus obtained was dried and the residue re-dissolved in *aqua regia*. After digestion was completed, the sample was evaporated to near-

dryness and the residue was taken up into 7 M HNO$_3$. The concentrations of Sr and Nd were determined using a quadrupole-based Perkin–Elmer SCIEX Elan 5000 ICP-MS instrument. An internal standard (In) was used to correct for matrix effects, signal drift and instrument instability, and calibration was performed against an external standard containing known amounts of the elements to be determined.

For Sb isotopic analysis, 10–50 mg of sample was used. Prior to digestion, each glass sample was cleaned by immersion in 1.4 M HNO$_3$ at 100 °C for 3 h, rinsed with Milli-Q water and dried in an oven. Then, the glass was crushed in an Agate mortar. Digestion was performed in a two-step procedure. First, 2.5 ml of a 3:2 mixture of 28.9 M HF and 14 M HNO$_3$ was added to the powdered glass and the mixture was kept at 110 °C in a closed Savillex® beaker for 48 h. The solution was then evaporated to dryness at a temperature of 90 °C, to prevent Sb losses by evaporation. Subsequently, 2.5 ml of *aqua regia* was added and the closed beaker was subjected to heating at 110 °C for another 48 h. Finally, the *aqua regia* was evaporated at 90 °C and the residue re-dissolved in 10 ml of 0.14 M HF. The digest was analysed for its Sb content by quadrupole-based ICP-MS (Thermo Scientific X Series II) using Ru as internal standard. Similar to the Sr and Nd isotopic analysis, external calibration was relied on to determine the Sb concentrations in glass samples.

After digestion, chromatographic isolation of Sr, Nd and Sb was performed prior to isotopic analysis. Sr and Nd ratios for all samples from Tell Brak, Malkata and samples 1930.82.17, 1930.82.50 and 1930.66.90b from Nuzi were determined using a six-collector Finnigan Mat 262 thermal ionization mass spectrometer (TIMS), running in multi-collection mode. Sr isotope ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$, and Nd isotope ratios to $^{146}Nd/^{144}Nd = 0.7219$. Repeated static measurements of the NIST SRM 987 isotopic reference material over the duration of the study yielded an average $^{87}Sr/^{86}Sr$ ratio of 0.71025 ± 0.00002. Repeated measurements of the La Jolla Nd standard yielded $^{143}Nd/^{144}Nd = 0.511848 \pm 0.000009$. In this case, Sr and Nd isolation was carried out using the protocol developed by Pin et al. (1994) using coupled miniaturized Teflon columns containing 50 ml of Eichrom Sr Spec and TRU Spec resin, respectively. Matrix components were removed from the resin using 2 M HNO$_3$, while Sr and the REE were eluted with de-ionized H$_2$O. For the isolation of Nd, the REE cut was further passed through a column containing 2 ml of Eichrom Ln Spec resin. This resin was washed with 5.5 ml of 0.25 M HCl after adding the sample, after which Nd was stripped off using 4 ml of 0.25 M HCl.

Sr and Nd isotope ratios for all samples from Nippur and the other samples from Nuzi were obtained with a Thermo Scientific Neptune multi-collector inductively coupled plasma - mass spectrometer (MC-ICP-MS), equipped with a micro-flow PFA-50 Teflon nebulize and a double spray chamber, consisting of a cyclonic and a Scott-type sub-unit for sample introduction, and running in static multi-collection mode. A concentration-matched solution of NIST SRM 987 SrCO$_3$ isotopic reference material was used as an external standard ($^{86}Sr/^{88}Sr = 0.1194$) to correct for instrumental mass discrimination (sample-standard bracketing). To correct for the interference from Kr at an m/z of 86, the intensity obtained for ^{83}Kr was used. On average, $^{87}Sr/^{86}Sr$ isotope ratios were measured with an internal precision (2s) of 0.000044. For Nd, instrumental mass discrimination correction was performed using JNdi-1 reference material (Geological Survey of Japan, $^{143}Nd/^{144}Nd = 0.51515$, $^{146}Nd/^{144}Nd = 0.7219$). The intensity obtained for ^{147}Sm was used to correct the intensities obtained at m/z 144 for spectral interference from Sm. On average, $^{143}Nd/^{144}Nd$ isotope ratios were measured with an internal precision (2s) of 0.000022. Sr isolation (De Muynck et al., 2009) was accomplished using a BioSpin column (BioRad) packed with 400 ml of Sr spec resin (Eichrom). After loading the