

Unlocking the secrets of ancient glass technology using ToF-SIMS

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Introduction

A precursor to glass composed of a combination of ground quartz and glass, faience, was produced as early as 4500 BC. The earliest true glass dates back to *ca* 2500 BC and is thought to have been manufactured in northern Mesopotamia, modern day northern Syria and Iraq. About 1000 years later, the first glazes and enamels were in use and the first (core-formed) vessels were made (e.g. Figure 1). The investigation of these ancient vitreous materials has benefited in a number of ways from the use of scientific techniques. Compositional and phase information has been produced using techniques such as X-ray fluorescence, X-ray diffraction, electron-probe microanalysis, scanning-electron microscopy (SEM), atomic absorption spectroscopy, ICP-AES (Inductively-Coupled Plasma Atomic Emission Spectroscopy), Raman spectroscopy, PIXE (Particle-induced X-ray Emission) and, more recently, LA-ICP-MS (Laser Ablation ICP-Mass Spectrometry) and stable isotope determinations (using thermal ion mass spectrometry and LA-ICP-MS). These techniques have provided evidence for the existence of both conservative production technologies, sometimes continuing for several hundred years, and for innovation with new raw materials during periods of experimentation and change. Furthermore, these techniques have quite recently provided information about production and distribution zones; such information can contrib-



Figure 1. Decorated glass vessel in the shape of a fish excavated from Tel el-Amarna (Egypt, ancient Akhenaten), dated 14th century BC. © Copyright The Trustees of The British Museum (EA 55193).

ute to ancient models of trade in both ancient raw glass and glass objects. This has only become a realistic possibility because of the discovery of archaeological sites where glass was fused from raw materials. The scientific analysis of the glass made at these sites in the Middle

East has provided "base-line" compositions against which to compare contemporary objects; thus potentially providing a provenance for them.

The earliest glass artefacts, made in Mesopotamia and Egypt, were almost exclusively made from opaque soda-

Table 1. Composition of raw materials for making ancient pre-800AD glasses, from Reference 1.

Ingredients	Soda $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + \text{NaCl}$	Lime (CaCO_3)	Silica (SiO_2)
Raw materials	Mainly plant ash before and minerals after 8 th century BC (Natron)	Shell fragments in sand, Ca in plant ash	Sand, quartz pebbles
Common impurities	Plant ash: Metabolised elements, esp. Mg, K, Ca Minerals: substantially less Mg	Depending on specific source, e.g. Sr	(Trace) minerals such as Fe, Cr, Ti, Al

lime glasses (Table 1). Crystalline opacifiers were either added as a mineral-rich colorant, or the glass was heat-treated in order to precipitate them out of solution. For example, crystals of metallic copper and of cuprous oxide produce opaque red colours, calcium antimonate crystals produce an opaque white colour (when formed in a turquoise matrix the result is an opaque turquoise colour) and lead antimonate crystals produce an opaque yellow colour.¹ The smallest inclusions can be below the spatial resolution of commonly applied analysis techniques.

Whilst the bulk compositional (major and minor) characteristics of ancient glasses, enamels and glazes down to trace levels can provide one level of information, a detailed characterisation of the opacifying crystals themselves can provide another—and this

is where Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), could come into its own. It is the only technique which, in principle, is capable of chemically analysing and mapping the major, minor and trace levels of components *within* opacifying and other crystals, whilst at the same time providing isotopic information. SEM can provide distributional information but the energy-dispersive (ED) spectrometers often attached to such machines are 10–100 times less sensitive than ToF-SIMS, so the detection of trace elements is impossible, and no isotopic information is obtained. ICP-AES and LA-ICP-MS are both very sensitive techniques, but in the former case samples are dissolved so that distributional information is lost and in the latter case, though spot analyses are carried out, inclusions cannot be

imaged. Another technique, the scanning proton micropobe, can image opacifiers in scanning mode, but the depth from which X-rays are generated (of up to 40 µm in lead-rich glasses) makes it difficult to know whether an analysis is a combination of crystal(s) and matrix. Therefore potentially vital information about the differential association of trace impurities with specific crystalline opacifiers and glass matrices can uniquely be obtained using ToF-SIMS.

This kind of information has the potential to characterise ancient glass technologies in new ways. For example, it could provide a means of distinguishing between the use of “the same” opacifier from different sources. Lead antimonate ($Pb_2Sb_2O_7$) occurs naturally as bindheimite and the use of two different mineralogical sources would bring



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with it different impurities. White calcium antimonate crystals do not occur naturally as a mineral but are formed out of solution as a result of heat-treating the glass. Therefore, whilst X-ray diffraction combined with ED-X-ray fluorescence in an SEM would provide unambiguous evidence for the use of calcium antimonate crystals, neither technique can pick up the impurities included in the crystals when they were formed out of solution. The impurity patterns both in precipitated and deliberately added crystals, as gleaned from the co-localisation of specific elements, could therefore provide a means of detecting the use of different sources and contribute to our knowledge of the organisation of the glass industry.

ToF-SIMS (time-of-flight secondary ion mass spectrometry)

In this ultra-high vacuum surface analysis technique a beam of energetic positively charged *primary* ions, is used to eject (sputter) material from the sample. Roughly 1% of the sputtered particles, which range from single atoms to very large clusters, carry a positive or negative charge. These *secondary* ions can be extracted into a mass spectrometer. In the work presented here the primary ion beam is pulsed and the mass spectrum produced by measuring the flight time of the secondary ions, accelerated to the same energy, in a drift tube. Mass separation takes place with the lighter ions arriving at the detector first. This is an extremely efficient process as the whole spectrum is effectively collected in parallel. In the case of element detection the technique is highly sensitive, capable of ppm detection levels, or better, within the sampled depth. Modern ToF spectrometers are capable of achieving a mass resolution $m/\Delta m$ of 10^4 , providing a means of confirming the identity of spectral peaks (fragment composition) based on accurate mass analysis.

Most of the detected ions originate from the uppermost two monolayers of the sample and the mass spectra of organic materials (positive or negative ions) are as characteristic of the material as is the case for conventional organic

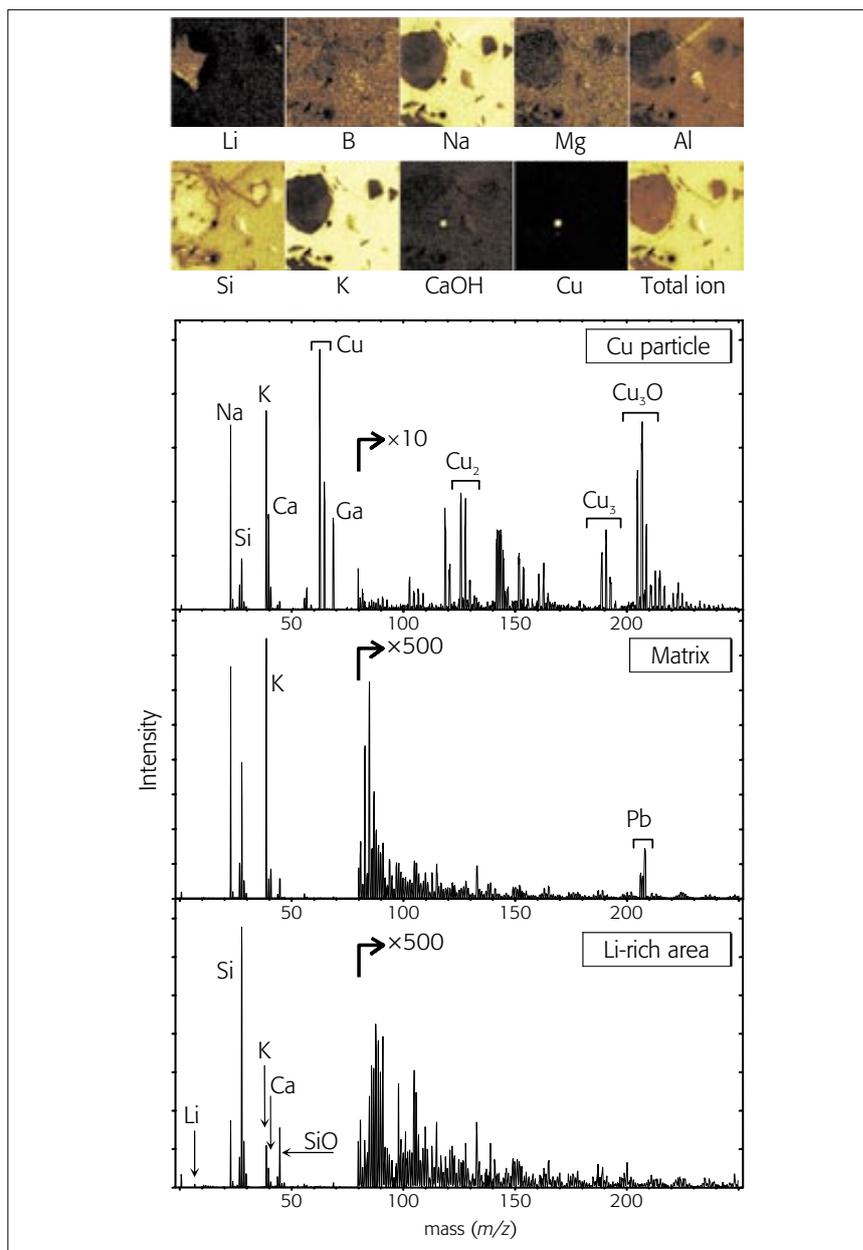


Figure 2. SIMS analysis of opaque red glass bead found at Frattresina, Italy (Po-river valley, northern Italy), dated 10th century BC. Top pane: chemical maps of selected positive ions ($80 \times 80 \mu\text{m}^2$). Lower pane: spectra generated from RDS for opacifier particle, matrix and Li-rich area.

mass spectrometry. The same is also true for inorganic species where the cluster ions similarly reflect the bonding arrangements in the sample surface.

The primary ion beam can be highly focused, allowing a spatial resolution of $<1 \mu\text{m}$ in imaging mode, when the ion beam is digitally rastered over the surface. Such experiments are best carried out using the raw data stream

(RDS) approach in which the full spectrum is acquired at each image pixel. This RDS can then be used to generate a total ion image by summing the intensity at each pixel: the contrast in this image is dominated by topographic or major chemical differences so it provides a useful visualisation of the scanned area. Alternatively, a total (or average) spectrum can be generated by summing

the spectra in all pixels. From the total ion image a region of interest (group or groups of pixels) can be selected and the spectrum reconstructed from the RDS (retrospective microanalysis). Similarly, by selecting a peak or group of related peaks of interest in the total spectrum, a chemical image can be generated from the RDS (retrospective chemical imaging). ToF-SIMS is now a well-established technique and more details are available in Reference 2.

Experimental

All images were acquired on a ToF-SIMS IV time-of-flight secondary ion mass spectrometer (Ion-ToF GmbH, Münster, Germany) using gallium ions with an energy of 25 kV. The primary ion beam was focused to a spot size of ca 300 nm diameter and rastered over an area of 80×80 μm² to acquire a total of 65,536

datapoints (each of which is associated with a spectrum!) per image. To prevent sample charging due to the incoming positive gallium ions, the sample was exposed to 20 eV low energy electrons between primary ion pulses.

Samples were prepared by embedding in 12×12 mm² blocks of epoxy resin and subsequent polishing down to 0.5 μm using diamond paste in a well-established procedure developed for conventional microprobe analysis, removing weathered layers in the process. No further steps were required prior to insertion in the SIMS analysis chamber other than wiping with a lens tissue moistened with high purity hexane to remove ubiquitous silicone contamination.

Analysis of samples prepared in this manner revealed spectra typical of adventitious hydrocarbon contamination. The extremely limited sampling

depth of SIMS, ca 1–2 nm, necessitated removal of these contaminants to expose materials of interest, which was achieved by briefly exposing the sample to an intense primary ion beam. Most organic contaminants could thus be removed very effectively, leaving only slight traces of aromatic species as a result of the ion bombardment-induced damage. The effectiveness of this cleaning procedure was verified throughout using high mass resolution spectrometry, allowing for the unambiguous identification of hydrocarbons from inorganic materials with the same nominal mass.

Case studies

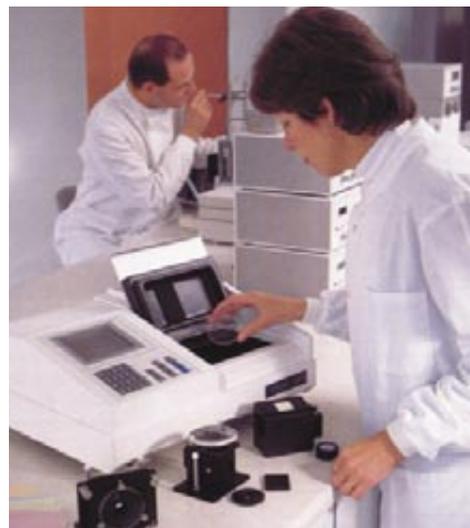
The following samples were selected so as to highlight the potential of the technique:

- (1) A sample of opaque red glass bead from the 10th century BC industrial

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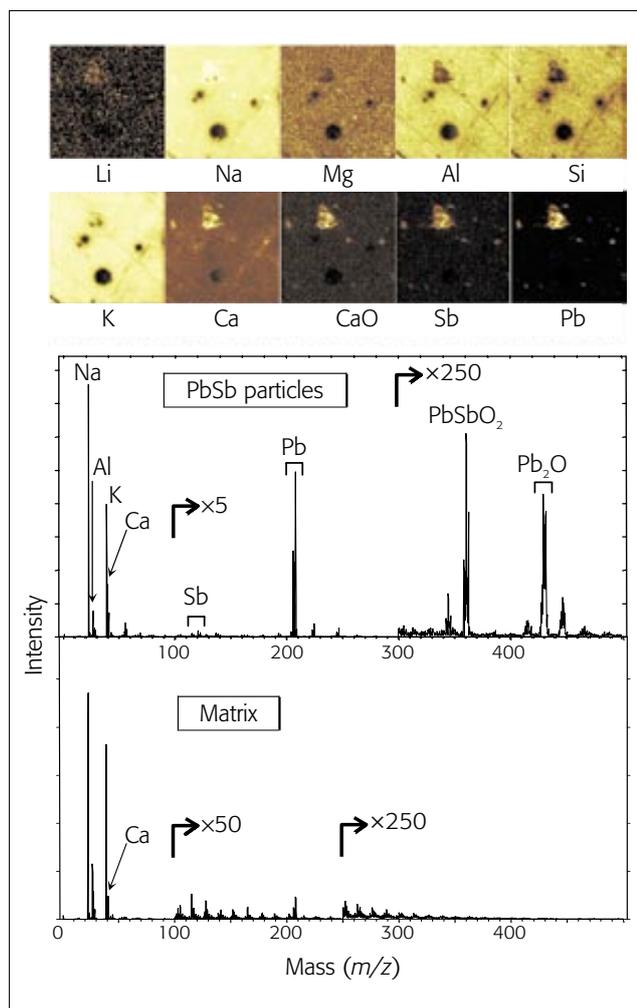


Figure 3. SIMS analysis of a fragment of opaque yellow from a glass vessel found at Tel el-Amarna, Egypt, dated 14th century BC. This glass is similar to the yellow glass in the fish-shaped vessel in Figure 1. Top pane: chemical maps of selected positive ions ($80 \times 80 \mu\text{m}^2$). Lower pane: spectra generated from RDS for opacifier particles and matrix.

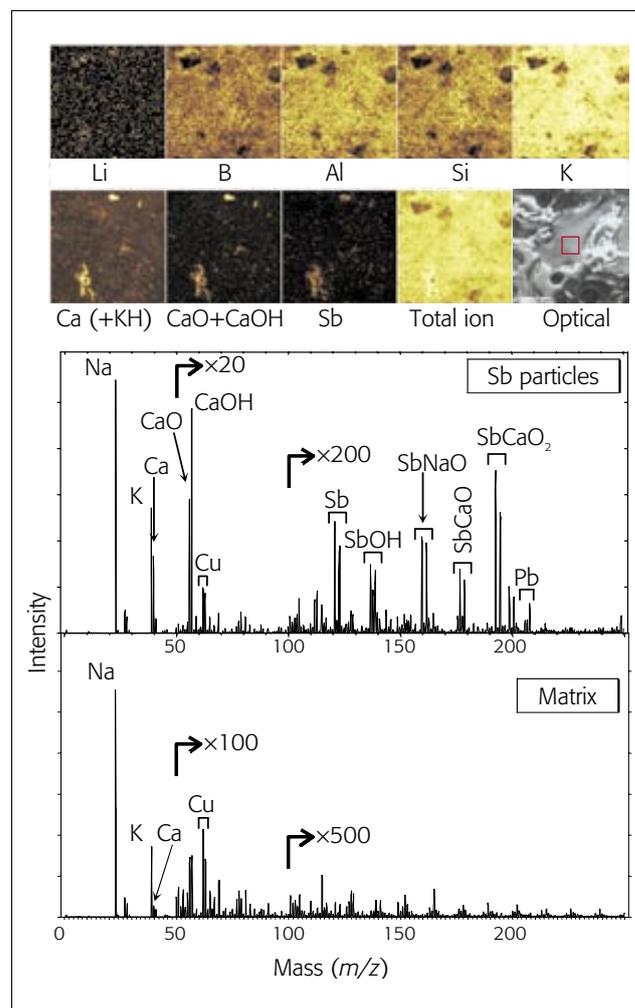


Figure 4. SIMS analysis of opaque turquoise glass from a bead found at Pella, Jordan (Jordan valley), dated 14th century BC. Top pane: chemical maps of selected positive ions and *total positive ion signal* ($80 \times 80 \mu\text{m}^2$). Bottom right image displays a visual image (*ca.* $1 \times 1 \text{mm}^2$) of the sample, with the red square denoting the area depicted in the SIMS images. Lower pane: spectra generated from RDS for opacifier particles and matrix.

site of Fratessina in the Po valley, northern Italy;

- (2) an opaque yellow sample from a decorated polychrome vessel fragment excavated at the 14th century BC Egyptian site of Tel el-Amarna;
- (3) a 14th century BC opaque turquoise sample of a glass bead from Pella in Jordan.

Case 1

Figure 2 displays the distributions of a selection of important secondary ions from a small region of the opaque red Fratessina bead, in which a copper-

containing inclusion with a diameter of *ca.* $3 \mu\text{m}$ was detected. These images were reconstructed from the raw data stream (RDS) as described above. The *thermographic* intensity scale ranges from black at zero intensity through red, orange and yellow to white at the maximum intensity for that particular ion. Clearly a number of chemically distinct areas are identified in the matrix as well as the opacifying particle. The associated spectra in Figure 2 were reconstructed from the RDS. The spectrum from the region of high copper intensity is shown to be due to metallic copper from the appearance and rela-

tive intensities of the copper cluster ions (Cu_2 , Cu_3). The related O-containing clusters are attributed to surface oxidation of the sectioned metal particle following sample preparation. The surrounding matrix displays a spectrum expected from a mixed alkali glass and is almost totally devoid of copper. Lead, a potential impurity in the copper, is clearly only associated with the matrix, whilst calcium, which is frequently present in the matrix (Table 1) is co-located with the copper. A lithium-rich area can also be identified, which is unusually associated with low levels of other alkalis (Na,

K). Boron, another interesting trace element, is detected throughout the matrix.

Case 2

Figure 3 shows data from a small region of the opaque yellow Tel el-Amarna glass, which appears to contain several small, micron-sized inclusions as well as an agglomerate of inclusions of similar composition. The spectrum of this agglomerate shows fragments consistent with lead antimonate (based on the appearance of spectra generated from iron antimonate and the precursor iron and antimony oxides³). Co-located are lithium, sodium and calcium. Depleted in this phase are the primary matrix elements aluminium, silicon, potassium and again boron (not shown).

Case 3

Figure 4 shows data from a small region of the opaque turquoise Pella bead. Small particles and agglomerates rich in antimony and calcium are detected and the spectrum from the agglomerate suggests the presence of calcium antimonate (note the generic similarity with the lead antimonate spectrum in Figure 3). Traces of lead and copper are detected, but whereas the lead is primarily in the inclusions (see spectra), the copper is present in both phases with possible enrichment in the antimonate phase compared to the matrix.

Conclusions

Even though the opacifying inclusions in these examples are typically only a few microns in size and of low density in the polished cross-sections, ToF-SIMS not only detects them but also provides spectroscopic identification of the chemical state. It should also be noted that only positive ion data have been utilised so far, and that negative ion data are equally powerful.

In all cases impurities were sought and found within the crystallites in each sample. Any impurities detected provide a new way of characterising the glasses: a distinction in impurities and their levels between the glasses found in Egypt and Jordan could ultimately provide much-needed scientific answers to the question whether Egypt manufactured its own glass from raw materials or imported ready made raw glass from the Middle East (Mesopotamia), where it is known that the first glass was manufactured. Fratessina has produced a large amount of evidence for the working, and perhaps the fusion, of the first European glass from its raw materials.¹ The characterisation of the red glass from the site in a new way contributes to the understanding of an important area of innovation with raw materials in this relatively new technology for Europe.

The samples studied were originally prepared for electron probe microanalysis. Because ToF-SIMS has such a shallow sampling depth, the cross-sectional area of an inclusion exposed by polishing will only be optimal when the polished surface coincides with the maximum dimension(s) (e.g. the full diameter of a spherical particle). This is an inherently low probability occurrence! By contrast the sampling depth in electron probe or SEM/EDX analysis (typically 5 µm) allows a major fraction, if not all, of an inclusion to be analysed. It is clear from these preliminary studies that optimisation of sample preparation, and particularly

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the polishing process, specifically for ToF-SIMS analysis could dramatically improve the situation.

A further issue to be addressed is the fact that SIMS intensities are not directly amenable to quantification because of matrix effects on secondary ion yields. This limits the ability to quantify relative impurity levels, unless the matrices are the same (or very similar). However, this problem can be overcome by using specially prepared standards, as the success of SIMS in trace analysis of semiconductor materials so amply demonstrates.⁴

Overall, the application of ToF-SIMS to ancient glasses has the potential to provide important new information about the occurrence and distribution of trace impurities in inclusions, which cannot be obtained using any other technique. This will hopefully enable us to differentiate

between glass production technologies, aid the determination of provenance of this important and prestigious material and hence increase our knowledge of the glass trade in the ancient world.

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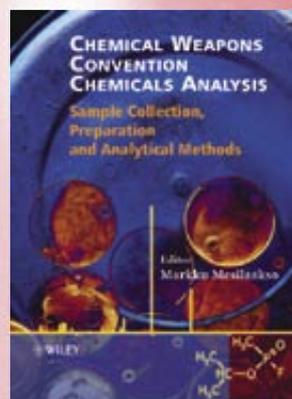
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