Analytical Plan for Roman Glasses

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SUMMARY

Roman glasses that have been in the sea or underground for about 1800 years can serve as the independent "experiment" that is needed for validation of codes and models that are used in performance assessment. Two sets of Roman-era glasses have been obtained for this purpose. One set comes from the sunken vessel the Iulia Felix; the second from recently excavated glasses from a Roman villa in Aquileia, Italy. The specimens contain glass artifacts and attached sediment or soil. In the case of the Iulia Felix glasses quite a lot of analytical work has been completed at the University of Padova, but from an archaeological perspective. The glasses from Aquileia have not been so carefully analyzed, but they are similar to other Roman glasses.

Both glass and sediment or soil need to be analyzed and are the subject of this analytical plan. The glasses need to be analyzed with the goal of validating the model used to describe glass dissolution. The sediment and soil need to be analyzed to determine the profile of elements released from the glass. This latter need represents a significant analytical challenge because of the trace quantities that need to be analyzed. Both pieces of information will yield important information useful in the validation of the glass dissolution model and the chemical transport code(s) used to determine the migration of elements once released from the glass.

In this plan, we outline the analytical techniques that should be useful in obtaining the needed information and suggest a useful starting point for this analytical effort.

CONTENTS

Acronyms

ESI-MS	Electro-spray ionization mass spectroscopy
FIB	Focused ion beam
FIB/SEM	Focused ion beam/scanning electron microscope
GC-MS	Gas chromatography mass spectroscopy
ICP-MS	Inductively coupled plasma – mass spectroscopy
LA-ICP-MS	Laser ablation-ICP-MS
PIXE	Particle-induced X-ray emission
PNNL	Pacific Northwest National Laboratory
SEM	Scanning electron microscope
TEM	Transmission electron microscope
ToF-SIMS	Time of flight – secondary ion mass spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

WASTE FORMS CAMPAIGN
ANALYTICAL PLAN FOR ROMAN GLASSES

1. Introduction

Ancient glasses (manmade) that have been buried for about 2000 years offer some of the best possibilities for validation of models used for performance assessment and for calculating the dissolution of silicate-based glasses. To validate these codes or models, independent experiments are needed. When ancient glasses were discarded, buried with a person as part of ritual, or went under water as the result of a shipwreck, long-term experiments were started. These experiments have been ongoing for periods of approximately 4000 y (Jackson, and Nicholson 2010). With advanced analytical techniques such as trace element analyses (Jackson, and Nicholson 2010), isotope ratios (Longinelli et al. 2004), and others, the provenance (origin) of these glasses and other factors surrounding their history are becoming known. This means that there are fewer unknowns in these long-term experiments; the experiments are becoming better constrained.

Two glasses have become available for study as part of an effort to validate models associated with performance assessment and calculation of glass dissolution. One set of glass specimens was recovered from the Iulia Felix, a Roman ship that sunk approximately 1800 years ago off the northern coast of Italy, near the present town of Grado. These glasses were contained in a large wooden keg. The glass shipment consisted of broken articles, such as plates, cups, works of art, etc., that were being shipped to a glass melter to be melted and formed into useful articles or works of art again. These glasses are described by Silvestri and coworkers (Silvestri 2008; Silvestri, Molin, and Salviulo 2008). Since closing of the Iulia Felix project some 5 or so years ago, many of the artifacts have been in storage and preparations are being made for an exhibit. Another set of three glass specimens were recently recovered from a Roman villa in the Italian town of Aquileia, just north of Grado. These glass specimens were recovered still embedded in the surrounding soil with which they have been in contact since being discarded some 1800 years ago.

2. Purpose

The purpose of this analytical plan is to review the analytical methods that can best be used to determine the distribution of elements released from the glass in the soil or sediment. Additionally, information will be obtained from the glass artifacts that can be used to develop more detailed insight on the relative dominance of various release mechanisms.

While the Iulia Felix glasses have been studied quite well, the studies were aimed at obtaining archaeological information. Additional analytical studies are needed to obtain data more targeted to nuclear waste disposal purposes. For example, the colorless glass from the Iulia Felix had corrosion layers consisting of an opaque white crust (largely silica), while the colored glasses had layers consisting of complex, but repeating layers or lamellae (Silvestri, Molin, and Salviulo 2005a). The difference between the compositions of these glasses is basically about 2 mass% CaO and 0.5 mass% Al_2O_3 (Silvestri, Molin, and Salviulo 2005a). These glasses were corroded at a nearly constant temperature of about 15 °C and plenty of water. Analyses of these alteration layers, along with the changes within the adhering sediment, should also yield information that can be used to resolve some of the remaining areas of scientific uncertainty about the kinetic mechanism by which glass dissolves.

The glass specimens recovered from the Aquileia site have not been studied, having just been recovered, but they present the potential to obtain different experimental information. Since they are contemporaneous with the Iulia Felix glasses, and it is becoming clear that the Roman glasses as a class

of materials are well constrained, i.e. there were very few Roman melters (Longinelli et al. 2004; Silvestri, Longinelli, and Molin 2010), comparisons of the different corrosion environments are expected to be quite valid. Although the glass specimens recovered from Aquileia are expected to have similar compositions to the glasses found on the Iulia Felix, the compositions are as yet unknown and, therefore, we do not know if they fit in the colored or colorless classification. However, they have been in contact with the soil for much of the 1800 years. Therefore, although only a small amount of glass has corroded, some of the elements from the glasses are in the soil. How much of these elements have been released from the glass gives us information on the glass dissolution mechanism, while the profile of these elements in the soil gives us a check on our ability to calculate this profile with existing coupled chemistry and transport codes and, hence, validate these codes.

3. Analytical approach

The analysis of both specimen types will, of necessity, be evolutionary. There are nuances about these specimens that will come to light when the analytical team and Dr. Silvestri have sufficient time to interact. We will start with a careful review of the existing data and move on to complementary and more extensive targeted characterization. In each glass type, three key steps must be accomplished to facilitate the acquisition of the desired data: consolidation, preparation, and characterization

3.1 Consolidation

The Aquileia artifacts specimens contain both glass and soil. To preserve the orientation of the glass and soil, a consolidation technique is needed. Thus, one of the biggest challenges is the handling and sampling of the soil surrounding the object while ensuring that the spatial information is not lost. None of these techniques have been attempted, so the methodology has to be developed. Fortunately, we collected and made up several simulated glass plus soil specimens with which we can develop the consolidation technique. These simulated specimens were made with actual Roman glass artifacts and soil from the Roman villa at Aquileia.

Some of the Iulia Felix specimens contain both glass and sediment. Attempts are being made to obtain specimens that contain both glass and sediment and have not been heretofore examined. These may contain sea water residuals and be as close as possible to being a freshly obtained specimen. In these specimens, the sediment near and to some 10s of millimetres from the glass is cemented by a secondary growth of calcite (Silvestri, Molin, and Salviulo 2005b) or magnesian-calcite (calcite containing up to 50 mol% $MgCO_3$ or $(Mg,Ca)CO_3$). Initial X-ray diffraction analyses suggest that the difference between modern and Iulia Felix sediments is the presence of magnesian-calcite in the sediment surrounding the Iulia Felix glass. This suggests that the magnesian-calcite formation occurred due to the glass dissolution. This is an important clue to the dissolution mechanism because of the role that alteration products play in the dissolution of the glass. To confirm this conclusion, we are attempting to obtain some sediment from the areas in the Iulia Felix that were not located near glass. Additional information can be obtained from element profiles, such as that from Cl that exist only in the sea water or Sb that exist only in the glass. Because the sediment in the Iulia Felix specimens is cemented, they are partly consolidated. However, the sediment is still fragile and crumbles easily. Therefore, they also need to be properly consolidated to make them suitable for further manipulation and analyses, particularly if spatial resolution of the cemented region is desired.

Several consolidation techniques are under consideration. It may be possible to embed the entire sample in hot gelatin or agar, as is commonly done in soil analysis. The specimen can then be frozen in liquid nitrogen and the surface polished so that it is ready for surface analysis. Alternatively, the specimen can

be carefully and slowly dried, for example at 40 °C. Then, a single-component light-curing resin, like Technovit 2000LC (Heraeus Kulzer GmbH, Hanau, Germany) can be used for consolidating the soil and glass artifact. This can be followed by polishing since the soil plus resin would be solid at room temperature. In addition, the simplicity of the resin composition would provide the least interference with the sensitive compositional analyses planned for the samples. In any event, the consolidation would render the specimen amenable to various sample preparation techniques.

3.2 Sample Preparation

Once consolidated, the key areas of each sample must be sectioned and prepared for analysis. Spatial resolution is of critical importance, so several preparation techniques which can be done at small scale are under consideration. In addition, the relatively small amount of glass combined with the necessity to minimize destructive analysis means that the most efficient sectioning techniques are desirable. The site specific nature of the following sample preparation techniques provides a means by which to probe any number of interfaces in the glass samples.

A coring technique may be the simplest way to obtain sections of the area of interest without compromising the rest of the consolidated sample. This would be done with small diameter coring needles, which can be as small as 0.5 mm. Micro-cores can be obtained at the same distance from the glass surface and parallel to the face of the glass artifact. Some of these micro-cores can be dissolved and analyzed or dissolved followed by special procedures to isolate the trace elements of interest.

Additional spatial resolution can be obtained through the use of the ultra-microtome. With an ultra-microtome, the core specimens can be sectioned along the core axis, thereby revealing new layers to be analyzed. Thus, while the micro-core would have about 1 mm resolution, the use of the microtome would allow a resolution of about 10 μm. In addition to the compositional analysis, micro X-ray diffraction (XRD) can be utilized to get structural and phase information (if there is any) on these small samples. Phases on the order of a few micrometres can be spatially identified.

Even more detailed sections can be obtained through the use of focused ion beam (FIB) sample preparation techniques. Three focused ion beam/scanning electron microscopes (FIB/SEM) are available at PNNL. It is possible to remove small (10-20 μm wide by 10 μm deep by ~100 nm thick) foils for TEM analysis in one of these instruments.

3.3 Characterization

A variety of characterization techniques (described more completely later) will be performed on the samples, mainly focusing on compositional and phase identification with high spatial resolution. Cores will be examined in a scanning electron microscope (SEM), while the smaller microtome and FIB samples are more suited for transmission electron microscopy (TEM). Samples can be prepared for the analysis of buried interfaces and boundaries between grains and phases utilizing atom probe tomography (APT). They can be washed to remove soluble salts for elemental and organic analyses, although the elements released from the glass are expected to be inorganic. Other candidate methods for spatially resolved compositional analysis include inductively coupled plasma mass spectroscopy (ICP-MS), gas chromatography mass spectroscopy (GC-MS), electro-spray ionization mass spectroscopy (ESI-MS), laser ablation ICP-MS (LA-ICP-MS), particle induced X-ray emission (PIXE), X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ionization mass spectroscopy (ToF SIMS), and Raman spectroscopy.

Techniques with very low limits of detection are the most desirable, particularly for the Aquileia glass with soil samples. Since only a few tens of micrometres of the Aquileia glass have been corroded, the amount of elements from the glass that are in the soil is very small and the profile of these elements in the soil is likely to be relatively steep from that in the glass to less than detectable. Additionally, some of the main glass elements are the same as those in the soil. Results from these techniques may also indicate how many compounds related to elements released from the glass through dissolution still remain locally present in the soil.

Hyperspectral X-ray imaging is a technique in which the full X-ray spectrum is obtained at each point of analysis. This yields a full three dimensional map of each element of interest. Often, two or more spectroscopies are combined, e.g. X-ray fluorescence and cathodoluminescence, (Brewer et al. 2008; Edwards, Martin, and Lee 2007; Lee et al. 2005; Macrae et al. 2005). The use of this technique could yield directly the elemental profile in the soil. It is unclear at this point what the resolution and sensitivity are of this technique, especially when applied to the whole specimen, although resolutions on the order of several micrometres have been reported (Lee et al. 2005).

Once prepared, the analytical TEM can be utilized to determine morphology, crystallography, and chemistry of interfaces between glass and alteration products and between alteration products and soil or sediment. Either a JEOL 2010F with Oxford INCA energy dispersive spectrometer (EDS) System or a FEI Titan high resolution TEM/STEM with an aberration probe corrector and a monochromator will be used for these experiments.

Particle induced X-ray emission (PIXE) is a vacuum technique that can be used on dry or frozen specimens. Under most conditions, sensitivities on the order of parts per million can be expected for most of the elements above Na in the periodic table. Other than visually undetectable ion beam damage, PIXE is nondestructive. Thus, this should be a useful technique to get some information from the glass and soil specimens. Like most probes involving X-rays, the information comes from about 2-3 μm depth from the surface. The amount of an element is a total in the excitation volume, but the quantification is accurate. Lateral resolution is 10-20 μm. The accelerator facility at PNNL can be utilized for these measurements.

X-ray photoelectron spectroscopy can be performed if we want to know the chemical state information of the elements. This technique is very surface sensitive, with a penetration depth of about 4-6 nm. X-ray absorption spectroscopy capabilities such as X-ray absorption near edge spectroscopy at the Advanced Light Source (Lawrence Berkeley National Laboratory) or the Advanced Photon Source (Argonne National Laboratory) can be effectively used to determine the chemical state of the elements in the bulk. In combination with the micro-core and ultra-microtome techniques, a very good depth profile of elemental composition with their chemical state is expected.

Although quantification is not as accurate as for other analytical techniques, use of the time of flight SIMS (ToF-SIMS) technique can yield elemental depth profiles with high spatial and depth resolution. The sensitivity is little higher in comparison to PIXE. Combination of ToF SIMS and PIXE (and probably energy dispersive spectroscopy) should provide useful information from these specimens, especially if combined such as in a hyperspectral approach.

Microstructural analyses with APT are also being developed for oxide materials. Atom probe tomography is a very powerful technique, returning a fully 3-dimensional elemental map of a small, FIB-prepared section. This allows careful examination of the buried interfaces and microstructures, i.e., grain boundaries. The use of this technique on insulating materials has been demonstrated, but requires great care.

Solid-state NMR spectroscopy is an isotopically-selective probe that can be utilized to determine the local environment of NMR sensitive nuclides including ^{1}H, ^{13}C, ^{23}Na, ^{27}Al, ^{29}Si, and others that are present in bulk glasses, altered layers, and soil components. Core samples may be analyzed with a combination of simple one-pulse experiments for quantifying changes in bonding environments and more complex cross-polarization experiments that provide spatially localized spectra. Cross-polarization experiments exploit the presence of ^{1}H nuclei in leached layers (and their absence in the bulk glass) and are used in the study of alteration products on glass surfaces (Tsomaia et al. 2003). Changes in the coordination and next-nearest neighbor environments of ^{29}Si and ^{27}Al species are observable with these methods and the magnetic resonance facility at PNNL contains a variety of ultrahigh field NMR spectrometers capable of performing these experiments with the high resolution and sensitivity enhancements afforded by working at extremely high magnetic fields (> 14 tesla).

Data analysis and integration is the next challenge. Some of the techniques outlined above require extensive computing capabilities and data storage. Fortunately, both exist at PNNL. Statistical analysis such as clustering information and classifying gradients are needed.

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