

A Closer Look at Brown Staining on Archaeological Glass

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Abstract

The role of manganese compounds in the staining of archaeological glass is reviewed. Faces and cross sections of several shards of brown stained medieval archaeological glass are analysed using scanning electron microscopy, energy dispersive X-ray analysis (SEM-EDX), stereomicroscopy and light-optical microscopy. This reveals that elements and materials other than manganese compounds are associated with staining. Chief amongst these is iron. A catalogue of staining phenomena with corresponding analytical data is provided

Introduction to Brown Staining in Archaeological Glass

Black and brown staining as corrosion phenomena within archaeological glass has been observed and extensively reported in conservation literature (Geilmann 1956, Green and Hart 1987, Hunter 1987, Alten 1988, Cox and Ford 1989, Cronyn 1990, Cooper et al. 1992, Cox and Khooli 1992, Macquet and Thomassin 1992, Cooper et al. 1993, Cox and Ford 1993, Knight 1996, Loukopoulou and Watkinson 1999, Römich 1999, Freestone 2001, Davison 2003). Dark

staining has also been reported for in situ window glasses, which, through accumulation of manganese compounds, have lost their transparency (Müller et al. 1980, Fitz 1981, Müller et al. 1986, Pinto 1991, Müller et al. 2002).

Geilmann (1956) offers the most extensive documentation of staining in archaeological glass. Within the thirteenth to sixteenth century glass that he examined he observed two kinds of staining. The first followed corrosion features like pits and produced concentric ring-shapes, while the second provided separate stain features within layers of laminar corrosion and produced circular deposits on the glass surface, which he termed dendrites. Dark layers, spots, stars, dendrites and feathering formed by staining of lamellar corrosion layers, cracks, pits and plugs have been reported by other authors (Cox and Ford 1989, Cronyn 1990, Macquet and Thomassin 1992, Cooper et al. 1993, Knight 1996, Watkinson et al. 2005). While stain features have been extensively described in the literature, they have received limited photographic documentation.

Reported analyses of archaeological glass identify the black-brown discolourations as containing high concentrations of manganese as Mn (IV) dioxide (hydrated as $\text{MnO}_2 \cdot n\text{H}_2\text{O}$) and Mn (III) hydroxide (MnOOH) (Geilmann 1956, Alten 1988, Cox and Ford 1989, Cooper et al. 1992, Macquet and Thomassin 1992, Cooper et al. 1993, Knight 1996, Römich 1999, Freestone 2001, Davison 2003). Similar identifications resulted from analysis of blackened window glass (Müller et al. 1980, Pinto 1991, Müller 2002). Although staining has mostly been attributed to manganese compounds, iron compounds were often reported in association with the manganese (Geilmann 1956, Cronyn 1990, Knight 1996, Davison 2003). Consequently, the commonly used term “manganese staining” does not take the role of iron into account and as a generic term seems inappropriate (Müller et al. 1986, Pinto 1991, Torge et al. 1996). Both manganese and iron are common compositional components in medieval glass. Manganese was used as a colourant (Henderson 1985) and a decolouriser (Pollard and Heron 1996), as well as being present as an impurity (Geilmann and Brückbauer 1954), while iron was usually introduced to the glass melt within the sand that acts as the silica source for the glass former (Pollard and Heron 1996). Since both manganese and iron are common soil components, both internal and external sources of manganese and iron could be responsible for the black or brown staining of buried archaeological glass (Watkinson et al. 2005). Whatever the source of the manganese and iron ions, the high pH produced by the corroding glass precipitates them as dark insoluble compounds (Knight 1996, Watkinson et al. 2005). Additionally, staining by lead sulfide (Davison 2003) and humic acids (Geilmann 1956) have been reported.

The Study

This study formed part of a diploma thesis at the State Academy of Art and Design Stuttgart in 2005. Initially its focus was to investigate methods to either remove or reduce brown staining in archaeological glass and thereby increase its transparency. A number of archaeological samples were examined to record and investigate the staining. The staining phenomena or features were grouped into categories and documented by photography and microphotography to produce a catalogue for interpretation of discoloured glass. Analyses by SEM-EDX revealed that many brown stains were caused by substances other than manganese or iron. These results are the focus of discussion here.

Sample Material

Sample Provenance

- (I) Nineteen fragments (named FRA1 to 19) from the latrine of a medieval estate (“Limpurger Gasse”) in central Frankfurt excavated in 1989 from waterlogged conditions. Archäologisches Museum, Frankfurt (courtesy of Ms. Martins).
- (II) Five fragments (named ULM1 to 5, excavated 2003 from a medieval latrine in the “Neue Straße” in Ulm. Archäologisches Landesdenkmalamt Baden-Württemberg, Esslingen (courtesy of Ms. Lerch).
- (III) Twenty-two fragments (named SC1d to t; SC2; SC3a to d) of waterlogged painted window glass dated to the sixteenth century from Stafford Castle. These samples have been stored in water since their excavation in 1986. University of Wales College, Cardiff (courtesy of D. Watkinson):
- (IV) One waterlogged fragment (named WH1) from Wood Hall, a medieval manor house surrounded by a wet moat excavated in 1993. University of Wales College, Cardiff (courtesy of D. Watkinson).

Method

Samples of glass were examined both on their flat face and in cross section. Cross sections prepared for the SEM were slowly air-dried (if previously waterlogged) and embedded in cold curing epoxy resin (Epofix[®]). Once fully hardened the mounts were ground to reach the depth of a representative cross-section through the stain features being examined and polished to a 4000 silicon carbide finish. The samples were made conductive by vacuum coating with carbon using an Emitech K450x vacuum carbon coater.

The Analytical Procedures Employed to Examine the Staining

Stereomicroscopy (Leica MZ12 and Wild M3C) and a research microscope (Carl Zeiss Axiophot) in reflected and transmitted light were used to investigate both staining morphology and colour patterns, which were recorded as microphotographs (cameras AxioCam HRc, Nikon Coolpix 4500 and Canon EOS 300D). Both top view and cross-sections were examined using darkfield illumination as necessary. Some samples were investigated in the wet state if they had been stored in water.

SEM-EDX analysis was carried out at Cardiff University using a CamScan MaXim fitted with a low vacuum chamber and a Link ISIS (Oxford Instruments) AN 10000 energy dispersive analyser with a 148eV resolution. It has a secondary electron detector for SEI and a four-quadrant backscatter electron detector for BEI. Elemental EDX maps were acquired as speed-maps of several elements simultaneously. The quantitative measurements over a region of interest used average composition, rather than localised measurement.

SEM-EDX was used to examine the morphology and chemical composition of both stained areas and bulk glass. Corrosion was evidenced by the occurrence of features like lamellar systems within the glass morphology and compositional changes such as depletion of the alkali ions and silica enrichment (Cox and Ford 1993, Weber 2002, Watkinson et al. 2005). Both manganese and iron, as well as some of their compounds can be recorded using SEM-EDX (Cox and Ford 1993, Loukopoulou 1995, Watkinson et al. 2005).

The cross sectional morphology of staining features was recorded using one example for each characteristic feature. Qualitative analysis of the elements comprising the various staining features was carried out to verify the expected presence of manganese and/or iron (Weber 2002, Watkinson et al. 2005). Other elements present were also detected by EDX elemental mapping (Figure 2). Within these maps a high density of white dots indicates a high concentration of the element being scanned, whereas black areas indicate its absence. This technique had been used successfully in earlier laboratory experimental work to determine the distribution of manganese and/or iron in glass (Weber 2002, Watkinson et al. 2005).

Results

Staining Features

By microscopy it was possible to establish and record the following categories of stain features on the sample glasses:

A	brown layer over entire shard, slightly transparent
A*	whole brown layer
B	brown puff shapes
C	individual spot, homogenous
C*	several spots form a flower
Cb	spot, concentric rings (Figure 3 Right)
D	stars (Figure 3 Left)
E	diffuse lines
F	feathering (Figure 4)
G	plane ring systems (Figure 1)
H	circular deposits
K	dendrites (Figure 6)

These could be attributed to staining conforming to the morphology of a glass corrosion feature (categories A-G) or separate stain features within layers of laminar corrosion (categories H and K). Top and cross-sectional views of each feature listed above are provided as micrographs in the diploma thesis of Weber (2005).

Staining Elemental Composition and Distribution

In total twenty-three samples were analysed by SEM-EDX. Selections from these analyses are provided here.

Frankfurt Samples

Sample FRA5 is a fragment of a flask spout. The bulk glass was not analysed. The outer surface of the sample is covered with a pattern of filigree black-brown concentric rings, which are contained within the surface layer of the glass. This thin layer is extensively cracked and slightly corroded (Figure 1).

The analysis revealed that manganese is not responsible for this staining. A slight enrichment of iron was detected and a significant sulfur presence. Potassium, calcium, and sulfur have accumulated in similar lines. Silicon is strongly enriched in the corroded area, which emphasises its extensive corrosion (Figure 2).

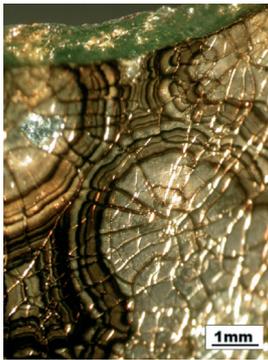


Figure 1. Stereo-micrograph of the FRA5 staining feature (transmitted light, top view) Note the thin but extensively cracked corrosion layer.



Figure 3

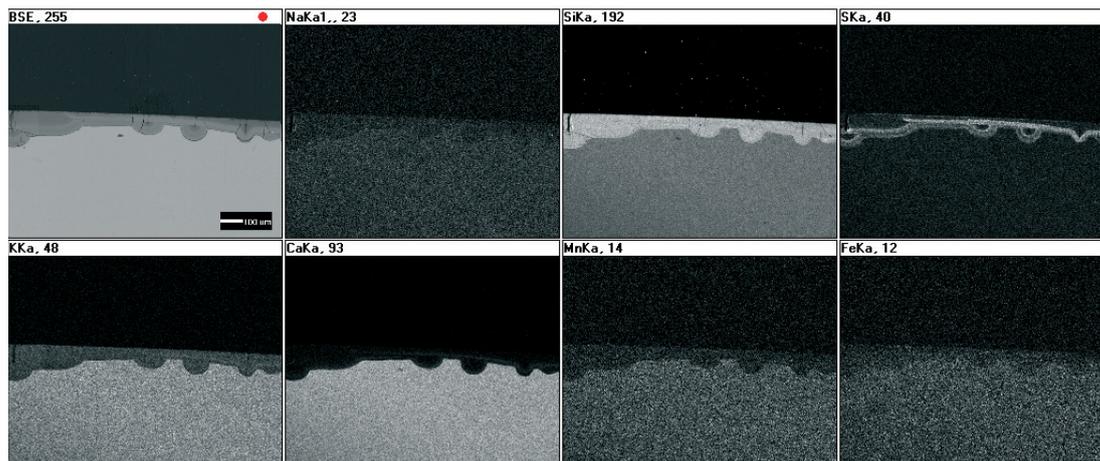


Figure 2

Figure 2. EDX map of the cross-section of the stained feature on FRA5.

Figure 3. Left: Stereo-micrograph of the star-shaped brown staining on FRA13 (reflected light, top view). Right: Stereo-micrograph of the spot-shaped staining feature on ULM4 (reflected light, top view). Note the outer red-brown staining and the blackish stain along the radial crack

Sample FRA13 is a potash glass with high calcium content. The glass is locally covered by star-shaped red-brown to yellow-brown translucent staining (Figure 3 Left). The staining is clearly defined as localised star-shaped corrosion that reaches approximately 400 μm into the sound bulk glass.

EDX elemental mapping did not reveal the presence of manganese in this type of staining. Both silicon (silica enrichment) and aluminium network formers are enriched. While all the alkalis and manganese are leached out as compared to the bulk glass composition. Within the star cross-section both sulfur and iron, which is unevenly distributed, are present.

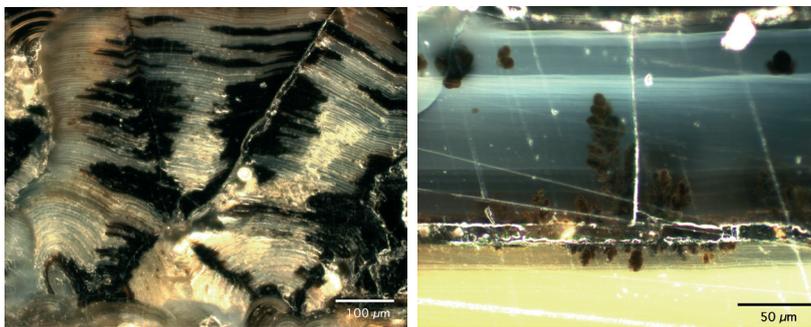


Figure 4

Figure 6.

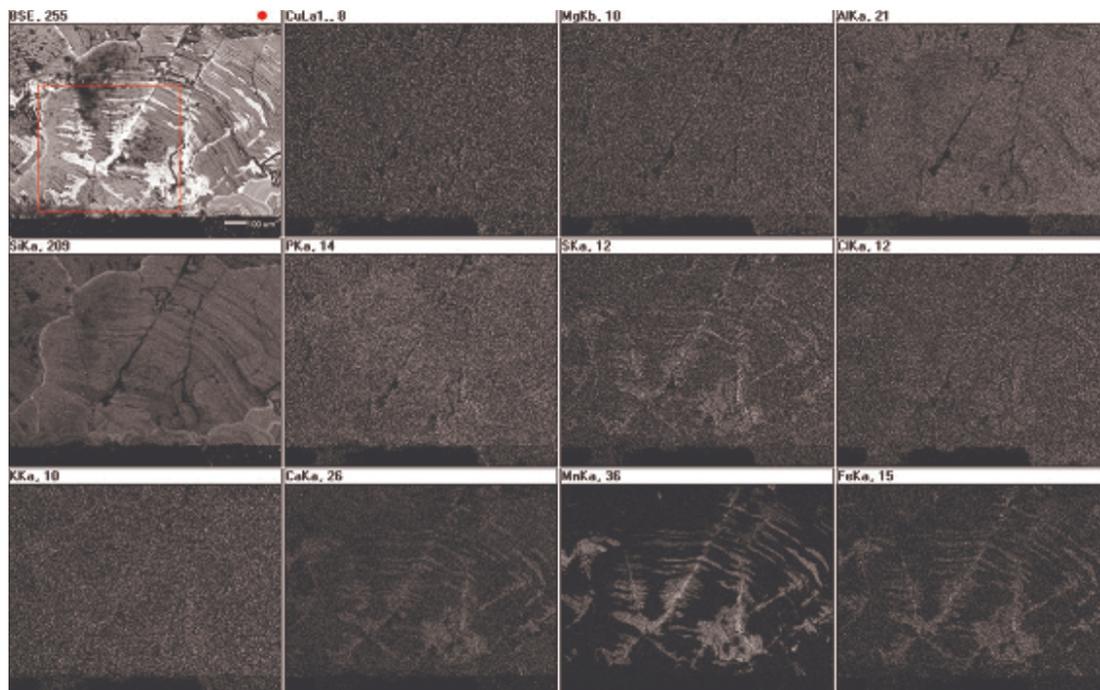


Figure 5.

Figure 4. Microphotograph of a cross-section through SC1d (darkfield illumination) of area indicated by red square in EDX map (Figure 5).

Figure 5. EDX map of staining feature of SC1d as indicated in Figure 4.

Figure 6. Microphotograph of a cross-section through SC2a (darkfield illumination) showing brown dendrites.

Ulm Samples

ULM4 was identified as a potash glass with high lime (calcium) content. On the underside of the fragment there are circular spots (Cb) (Figure 3 Right), which in cross-section are revealed as hemispherical red-brown corrosion pits. One or two cracks run directly through the centre of the hemisphere and divide it into two or three parts. While the overall colour of the hemisphere is red-brown, the crack is surrounded by a blackish “halo” with a bluish hue according to the incident light. Using the optical microscope to examine the cross section reveals a dark layer along the interface of the pit and the sound glass.

EDX mapping of the pit profile revealed that manganese had been leached out, while silicon and aluminium were enriched. The central crack across the pit had localised and concurrent raised concentrations of iron and phosphorus, which might indicate the bluish compound vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$). Similarly superimposed enrichment of sulfur and calcium had occurred both near the crack and as a thin lining of the pit bottom. This may likely be calcium sulfate (CaSO_4).

Stafford Castle Samples

The SC1d shard is weak and soft throughout. All samples appear entirely black-brown stained and opaque while wet. In cross-section black staining is distributed along cracks and lamellae resulting in a feathered staining pattern (F) (Figure 4).

EDX mapping revealed manganese in all stained areas (Figure 5). This coincided with iron in most cases. It was therefore assumed that the SC1 and 3 samples exhibited what may be termed typical “manganese staining”.

SC2a retains a sound glass layer at its core, but both the upper and lower surface of the glass shard are black-brown stained and predominately opaque. Examination of the cross-section reveals that half of the fragment’s thickness consists of clear uncorroded glass with a green tinge. The remaining half shows yellowish discoloured corroded glass. Most striking are brownish tree-like entities, so-called dendrites, which grow perpendicularly into the corroded layer (Figure 6). EDX maps of a dendrite show enrichment of manganese.

Summary of the Observations

EDX-mapping revealed the brown-black patterns on the Cardiff samples (SC1 to 3) have manganese enrichment, which is concurrent with iron enrichment in many instances. These results correlate well with the observation of other authors and therefore deserve to be recognized as manganese and iron staining. However, analyses of twenty-three samples from all sources revealed enrichment of other elements in stained areas. For several samples manganese and iron enrichment overlapped with calcium and sulfur enrichments. Such simultaneous enrichment of manganese, iron and calcium has also been observed by other authors (Cox and Ford 1989, 1993, Loukopoulou 1995, Loukopoulou and Watkinson 1999), who also reported the presence of phosphorus in these areas. Cox and Ford (1989) detected correlation of manganese with calcium phosphates (e.g. hydroxyapatite) as well as calcite (Cox and Ford 1993). The overlapping of iron and phosphorus enrichments was also detected on two samples. On two samples (Figure 2) a significant concentration of sulfur was detected.

Discussion

In clear contrast to the Stafford Castle samples, most Frankfurt and Ulm samples showed no iron or manganese precipitation patterns. Their absence in the stained area, despite being present in the bulk glass, might be electrochemically explained by either reducing or acidic conditions of the burial environment (Geilmann 1956, Cox and Ford 1993), which allowed both elements to migrate away as mobile ions. This is supported by the fact that both the Frankfurt and Ulm excavation sites are latrines that normally provide reducing deposits due to absence of oxygen. The latrine environment might have caused the sulfur accumulation in FRA5.

Other causes of staining that may fail to produce enrichment patterns of elements like iron or manganese could be the accumulation of organic substances. These are not identifiable by EDX mapping. Geilmann identified humic acids as the reason for brown-yellow staining (1956). Although attempts to identify organic substances with FTIR and Raman spectroscopy (the latter carried out at the Smithsonian Museum Conservation Institute by O. Madden) failed to produce conclusive results.

Geilmann in his study (1956) also assumes the staining material of yellow-brown areas to be silica gel with varying water contents. According to his colorimetric analyses the hydrated silica gel layers or areas also contain iron and aluminium apart from silicon. The black-blue stain visible on ULM4 displayed overlapping of iron and phosphorus concentrations on the EDX mapping. Bluish vivianite was identified in few cases also by Geilmann (1956). Vivianite is only stable in strongly reducing conditions over a very specific pH range (Geilmann 1956, Scott and Eggert forthcoming). Such conditions might have prevailed in the Ulm latrine.

Conclusion

The staining on the Cardiff glasses (SC1-3) can be attributed to manganese and iron compounds, with calcium, phosphorus, and sulfur also forming part of the staining material. The non-manganese staining could result from hydrated silica with or without iron hydroxides or absorbed iron species and/or to the presence of humic acids. The black-blue stain on ULM4 may be vivianite produced by the reducing conditions during burial. A concise discussion of staining material identification cannot be covered in this short article and will be developed elsewhere. Further analysis is necessary to determine whether organic material is present and to detect the presence of crystalline or amorphous compounds, which can then be used to further develop the corrosion model.

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