The *Waldglas* Project– Combining Instrumental Analysis for the Examination of Post-Excavation Corrosion on Archaeological Glass

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Introduction and project scope

Complex corrosion processes and the fragility of medieval archaeological potassium-rich glass requests high demands on conservation practice and on field archaeology. Several research projects have explored the degradation process of historical and archaeological glass [Römich et al. 2004; Sterpenich et al. 2006, Brinkmann et al. 2013]. Still, the chemical and physical reaction during burial is poorly understood. Therefor the behavior of corroded glass artifacts after excavation and lifting is difficult to predict. In addition, improper excavation methods as well as inadequate treatments influence the state of conservation of archaeological glass effectively, not only leading to severe damages but also to an increase of conservation needs and expenditures. The *Waldglas* project unites an interdisciplinary team of conservators, scientists and archaeologists to explore supportive lifting methods and preventive first-aid measurements, as well as sensitize for accelerated glass corrosion during excavation.

Immediately after lifting, archaeological glass shows traces of drying processes, which can be recognized already on a macroscopic scale: changes in appearance (colour and gloss) and loss in stability. Although, controlled drying also might lead to alterations, these objects will show greater stability, specifically within the corrosion layers. To explore potential structural differences in glass corrosion resulting from inadequate lifting, treatment, and drying procedures, a range of glass samples were observed, using and combining different instrumental analysis. Although each technique showed limitations in some way, the results are still worth mentioning. The choice of techniques and results are discussed in this paper.

Study material and methodical approach

The *Waldglas* project's study material comprises of potassium-rich glass from a glass factory of the Weserbergland region in the northwest of Germany, which dates to the 14th century and produced flat glass and glass vessels likewise [Stephan 2014]. The state of conservation differs enormously, and shows transparent glass sherds with only slight corrosion as well as completely corroded material. Analysis was performed on flat glass samples, showing a variety of colors, forms and corrosion states. Prior to analysis, all samples were examined using light and electron microscopy, which already revealed microstructural modifications due to inadequate drying processes. Instrumental analysis included µ-XRF[1], ESEM-EDX[2] and LA-ICP-MS[3]. To begin with, rather classical methods like X-ray fluorescence and X-ray spectroscopy were performed to identify the glass composition. Subsequently, the results were compared to measurements from other laboratories as well as from the literature, and showed congruency for most parts of the components. In order to observe and to characterize

[1] X-ray fluorescence was performed at HTW Berlin using Bruker ARTAX 400 XRF; anode: Rh; optic: collimator 0,200; live time: 60 s, Dead time: 0,1 %, current: 700 µA, no filter, performed in air atmosphere

[2] All ESEM-EDX measurements were performed at Bundesanstalt für Materialprüfung Berlin using an EDAX device, that is standardized on 100; BSE- detector, low vac 0,3 Torr, 15kV

[3] All LA-ICP-QMS was performed by the Institute for Inorganic Chemistry of Leibniz-University Hannover using Thermo X7; massfilter: Quadrupol, elektronmultiplier detector; ns-laser: UP-213-2078, Nd-YAG-laser, 213 nm; laser ablation software version 1.5.3.3 NewWave; linescan: 100% (2,8J/cm2), spot 40µm, 4hz, 10nm/s

corrosion layers, and in particular potential differences resulting from drying processes, advanced methods were necessary. For this purpose laser ablation in combination with mass spectrometry was also performed on the samples.

Examination of gel layers using SEM/ ESEM

An observation of polished cross-sections by SEM / ESEM is counted among the standards of archaeological glass research. However, the polished surfaces of the corrosion layers can only be examined with the BSE detector. Embedded samples also show traces from to the polishing process of the resin, which interfere with the identification of details in corrosion layers. Therefore, unprepared and recently fractured samples were examined in SEM and ESEM as well, and enabled to observe the stratigraphy of corrosion more precisely than prepared samples. In specific, these samples show the lamellar microstructure of the gel layer. Although already described in SCHALM et al. 2015 or STERPENICH 1998, the conservation approach of this observation seems to be of interest: are the lamellar microstructures more vulnerable towards mechanical strains or changes due to improper drying processes?

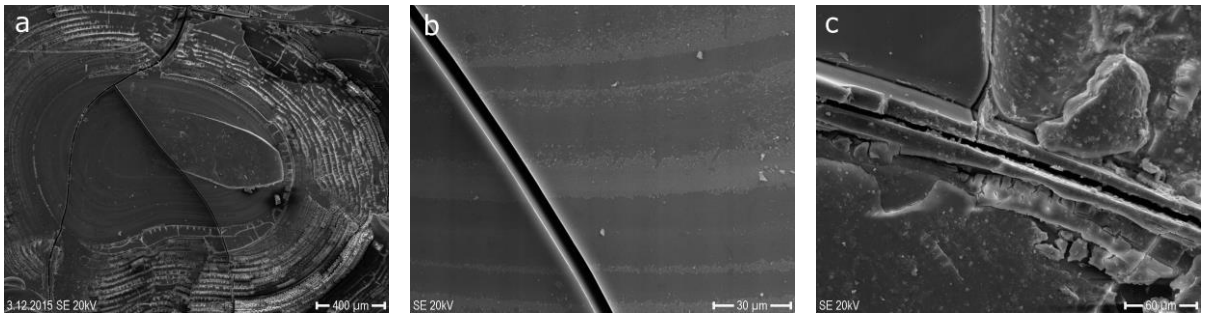


Figure 1: Sample FN1369_Ob62; SEM- examination of gel layer, which has separated as a compact lamellar network from the glass matrix. a) inner areas of gel layer, originally connected to the glass matrix; b) cracks forming independently from lamellar network; c) cracks at the border zone of lamellar networks, which also show different structural directions.

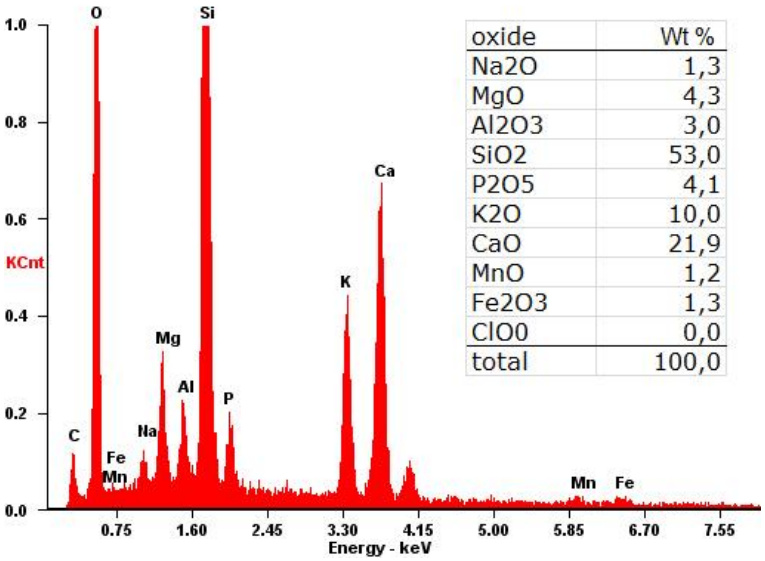
However, the results from SEM showed, that the *lamellae* are stacked securely within a stable network (Fig. 1a), and that cracks will rather occur between the alteration layer and the glass matrix. Even intense drying at high vacuum of SEM does not separate *lamellae*, but causes cracks independently of the lamellar network. Intense drying also enlarges already existing fissures (Fig. 1b-c).

Examination of gel layers and glass matrix using EDX

The examination of sample FN933_Ob65 shows the advantages of EDX analysis as well as the limitations of this method for the research on archaeological glass. The blue glass sample represents potassium-lime-glass with high contents of phosphor and magnesium. Although the literature states alkali-lime-glasses to be more stable than woodash glasses [Wedepohl 2003], this particular sample shows heavy degradation and corrosion layering. The layers consist of numerous *lamellae*, which also show brow and black staining. Unfortunately, the EDX analysis cannot trace the additives causing the blue coloration of the glass matrix, since the concentration of these elements falls below the detection limit (Fig. 2). However, the examination of the gel layer of this sample still resulted in interesting data: these areas were detected with high concentrations of metal ions, in particular cobalt and copper. The high concentrations seem to accord to the brown stains of the corrosion. A similar observation was also stated by STERPENICH 1998.

The deficiencies of EDX analysis within the *Waldglas* project became obvious, when trying to examine fresh samples in low pressure, which due to security reasons was not possible. The samples might have imploded and destroyed parts of the device. On the other hand, there was no sense in

drying samples and trying to examine stabilized layers, since they would not represent the direct post-excavation state of conservation.



oxide	Wt %
Na2O	1,3
MgO	4,3
Al2O3	3,0
SiO2	53,0
P2O5	4,1
K2O	10,0
CaO	21,9
MnO	1,2
Fe2O3	1,3
ClO0	0,0
total	100,0

Figure 2: EDX-spectrum of sample FN933_Ob65 showing the glass composition (Average of three-point measurement within the glass matrix). Despite an intensive blue coloration of the sample, no additives were detected.

Examination of gel layers using µ-XRF

Unfortunately the diameter of Bruker‘s ARTAX XRF measurement point (300µm) overlaps the gel layer thickness. Therefore, X-ray fluorescence also turns out to be unsuitable for the examination of glass corrosion, especially gel layers. Nonetheless, XRF was applied to the samples in the *Waldglas* project, since it specifically traces heavy elements, like cobalt, nickel, copper and zinc[4]. Some of these elements had already been detected in the gel layer of sample FN933_Ob65 by EDX analysis. The analysis with XRF showed that coloration metal ions are also present in the glass matrix.

Examination of corrosion layers using LA-ICP-MS

The elemental composition of the glass matrix as well as the gel layers has been observed with LA-ICP-MS. Laserablation more and more represents a standard method in glass research, given that it allows a precise detection of the glass composition, including trace elements. While it delivers a high resolution on the measurement point, which seems especially suiteable for the examination of corrosion layers, the sample area stays visible and can be examined and compared with light or electron microscopic results. The effort of sample preparation is comparably low and the method also allows to analyse damp or wet samples, which seemed extremely important for the *Waldglas* project’s approach. However promising, also laserablation showed it’s limitations. In order to examine cross-sections within the line scan mode, the surface needs to be very even. Therfore, embedded samples are more suiteable than unprepared glasses.

Likewise, a systematic examination of the corrosion layer, starting at the surface of the sample and running all the way down into the glass matrix, is also difficult to realize – especially when applied to damp or wet samples. Again, a comparison of uncontrolled dried samples and fresh material, which would have been interesting to the scope of the project, was not possible to execute. Still, the line scan provided the most promising and interesting results. It was applied on samples FN933_Ob65 and

[4] These elements are very characteristically for the coloration of historical blue glass.

FN933_Ob66. Both spectra show the structural differences in the corrosion layer, which were already observable in light microscopy. The scan also reflects the observations generated from EDX analysis, specifically the accumulation of coloring additives like Co, Ni, Cu, and Zn in the gel layer (Fig. 3). These layers correspond exactly with the manganese enrichment within the blackened areas, while they are almost completely absent in the white layers of the lamellae. Summing up, the line scan mode showed distinctive ion-exchange movement during corrosion, illustrating the distribution of elements in deteriorated glass.

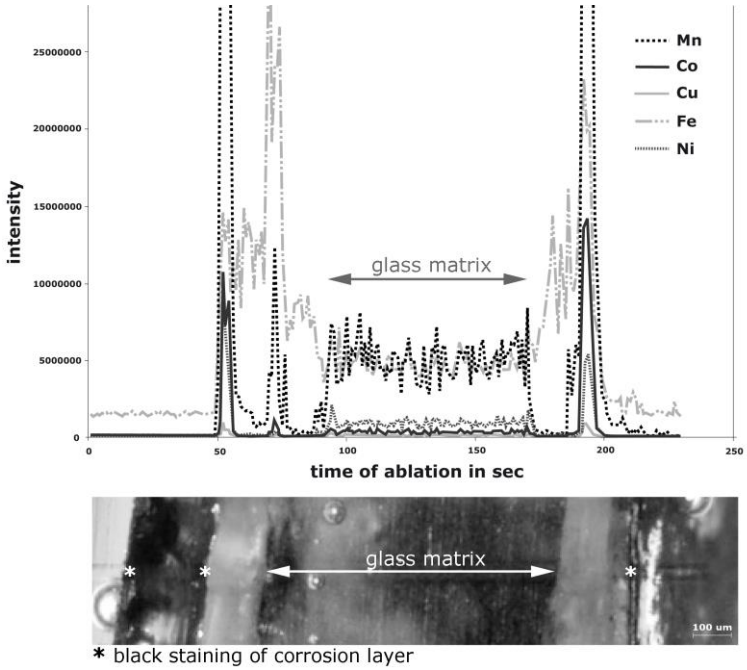


Figure 3: Sample FN933_Ob66; Intensity profile of laser ablation line-scans applied on a cross-section of the glass sample. While the scan detected accumulation of coloration elements Co, Ni, Cu, and Zn in those areas of the gel layer, which show back staining by manganese enrichment, the light areas of the gel layer were analysed with a lack of coloring elements.

Conclusion

Instrumental analysis offers a high potential for the study of archaeological glass. Already optical methods, like electron and light microscopy do result in precise data concerning the state of conservation, while numerous X-ray devices contribute to the study of glass composition and components. In combination, all they can also contribute to a better understanding of corrosion layers.

Only when applied to archaeological originals, which are often damp or freshly excavated, most instrumental analysis meet constrains. Either the devices are too sensitive against particles from rather soiled objects, or the methods do not meet the requirements of non-destruction.

For both reasons, parts of the *Waldglas* project remain unresolved. Unfortunately, it was not possible to examine inadequately dried glass samples, and compare the data with those from controlled treatment. Nonetheless, results from the project are promising.

Therefore, the evaluation and combination of instrumental analysis for the examination of archaeological glass should be continued. Especially post-excavation corrosion processes need to be further investigated, resulting in the development of adequate lifting and first-aid methods, and appropriate staff guidelines for handling the material on site.

Acknowledgements
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