Investigating Ion Depletion in Unstable Historic Glass Samples Using Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry and Ion Chromatography

ABSTRACT

This paper presents results of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) elemental depth profiling of unstable historic glass, in combination with ion chromatography (IC) analysis of ions extracted from these samples. Three historic glass samples from the Corning Museum of Glass are used in this research. Depth profiles were obtained for 55 elements before the samples were immersed in deionized water to extract ions from the glass. The depth profiles indicate the depletion of sodium, potassium, and lithium from the top layer of the glass, while no calcium depletion is observed. The thickness of the alteration layer of one sample was measured using scanning electron microscopy and compared to the LA-ICP-MS depth profile. In the leachates, only sodium and potassium were identified with IC. The ratio of sodium to potassium was lower in the leachates than in the bulk glass, indicating that relatively more potassium than sodium is leached out of the glass.

KEYWORDS

Glass deterioration · Leaching · Depth profiles · Ion chromatography · LA-ICP-MS · SEM

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INTRODUCTION

The atmospheric moisture-induced chemical deterioration of glass in museum collections is a problem for conservators and curators as it can dramatically and irreversibly change the appearance and structural integrity of an object. It would therefore be beneficial to be able to identify unstable glass objects in early stages of deterioration in order to implement conservation strategies tailored to these vulnerable objects. Recent research has focused on the development of an early warning system (EWS) for unstable glass in museum collections, using ion chromatography (IC) as the main analytical tool (Verhaar 2018). This EWS is based on the notion that the concentration of ions on the surface of an unstable glass object is indicative of the chemical stability of the glass. This research comprised the first use of a validated protocol for the quantification of ions leaching from the bulk glass of museum objects. Studies of glass collections confirmed that a distinction between stable and unstable glass could be made based on the nature and amount of salts on glass surfaces.

The changes in composition occurring as a result of atmospheric deterioration of glass have been well studied and reviewed (Alloteau et al. 2017; Fearn, McPhail, and Oakley 2004 and 2005; Kunicki-Goldfinger 2008). Depth profiling of sodium for artificially aged glass surfaces using secondary ion mass spectrometry (SIMS) has demonstrated that the depletion of sodium strongly depends on the relative humidity (RH) of the surrounding environment (Fearn, McPhail, and Oakley 2005). Studies concerning the formation of moist films and salts have primarily focused on the chemical identity of these salts, but had, until the development of the EWS, not concerned the complete quantification of the ions constituting these films. Despite the ability to now investigate the amount of ions accumulating on glass surfaces, it is as yet unclear which proportion of ions can be attributed to the chemical deterioration of glass and which ions may originate from another source, such as atmospheric aerosols (Verhaar, Van Bommel, and Tennent 2016). In order to better understand glass deterioration processes, the relative contribution of ions, in particular cations, leached from the glass, compared to ions originating from another source requires further investigation.

It has been well established that cations can leach from glass when immersed in aqueous solutions. The extraction of ions from the glass strongly depends on the composition of the glass, the condition of the glass, and the nature of the solution. It has been observed that calcium is extracted in acid solutions, but usually not in other aqueous solutions (El-Shamy et al. 1975; Schreiner et al. 1999). The rate of ion depletion depends on the time that the glass has been exposed to a harmful environment. Studies have investigated the depletion of ions from glasses in solution but primarily focus on the influence of glass composition and use freshly prepared replica glasses, which are often ground to a fine powder to maximise the exposed surface area during extraction (Douglas and El-Shamy 1967; El-Shamy et al. 1975; Rohanová et al. 2012). In contrast, we aim to study the extraction of ions from naturally aged glass samples that already include an altered surface layer. This enables the evaluation of extracted ions in relation to the EWS, which targets intact objects in museum collections.

This paper presents the results of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and IC analysis for comparison of, respectively, compositional changes within unstable glass and the quantity of ions leached from the glass during degradation. The value of ion chromatography for the study of the deterioration of historic artefacts has been demonstrated in other studies, with a recent emphasis on historic glass (Eremin et al. 2005; Tennent et al. 1992; Verhaar 2018). The combination of IC and LA-ICP-MS allows for the evaluation of the IC protocol used in the EWS and for the identification of marker ions for glass instability. LA-ICP-MS achieves the quantitative multi-element analysis of the glass composition, from major to minor to trace elemental levels, and has, for example, been used in drilling mode in the study of deteriorated historic artefacts to produce elemental depth profiles (Panighello et al. 2015). New developments in the application of LA-ICP-MS to investigate the ion-depletion process by the construction of glass pseudo cross-section elemental concentration profiles are presented here for the first time. Accordingly, a quantitative comparison of different techniques to measure ion depletion is accomplished, thus enabling better refinement of the EWS and a better understanding of the deterioration processes.

METHODS

Samples

Three fragments of unstable glass objects from the Corning Museum of Glass were used in the experiments. These samples had been previously investigated in an important paper on crizzling by Robert Brill (1975). Table 1 provides a selection of the atomic absorption spectrometry compositional data provided by Brill (1975), as well as more information on the samples. It should be noted that Brill (1975) also mentions the presence of oxides, including lithium oxide (Li_2O), in varying trace levels. All samples are of unstable composition with clear crizzling patterns on the surfaces. Historic glass samples were chosen over model glasses to account for their more complex composition and the potentially unexpected properties which can originate from minor differences in composition.

SAMPLE	DESCRIPTION	COMPOSITION (wt.%)			
		SiO_2	Na_2O	K_2O	CaO
CMG 449	Wineglass, French, ca. 1750	76	0.89	18.7	0.22
CMG 1050	Wineglass, French, ca. 1600-50	70.7	17.7	3.42	1.53
CMG 4011	Engraved goblet, Silesian, ca. 1710-30	73.5	0.39	16.6	1.61

Table 1. *Overview of studied samples with elemental oxide concentrations in wt.% as determined by Brill (1975)*

Pseudo cross-sectional analysis

LA-ICP-MS was used for analysis of 55 elements in a system comprising a 193 nm ArF* excimer laser ablation system, Analyte G2 from Teledyne Photon Machines Inc., Bozeman, MT, coupled to a quadrupole ICP-MS instrument, Agilent 7900x from Agilent Technologies, Santa Clara, CA. Ablation took place in a HelEx 2-volume ablation cell and the mass spectrometer was used in time-resolved analysis mode, measuring one point per mass and acquiring the 55 masses of interest. Elemental depth profiles in the glass samples were obtained by performing 150 consecutive laser ablation passes on the same line, each line approximately 1.8 μm deeper than the previous one, calibrated according to a procedure presented in the results and discussion section, while focusing the laser to the appropriate depth every ten lines. Each line was scanned using the following LA-ICP-MS conditions: beam size, 80 μm (square mask); repetition rate, 20 Hz; scanning speed, 160 $\mu m\ s^{-1}$; duty cycle time, 0.5 s with dwell times for individual elements equally distributed. For quantification of each pixel of the resulting pseudo cross-sectional image, a total of 12 glass standards were used, i.e. NIST SRM 610 and 612, P&H DLH 6, 7, and 8, SGT 2, 3, 4, and 5, and CMG B, C, and D, in combination with a sum normalization calibration protocol as developed earlier (Van Elteren, Tennent, and Šelih 2009), summing all 55 elements as their oxides to 100 weight percent (wt.%). The ensuing pseudo cross-sectional maps for each of the 55 elements consisted of 40 × 150 pixels and had a size of 3,200 × ~270 μm^2, width × height; the height represents the maximum depth reached.

IC analysis

A Dionex ICS-1100 ion chromatography system was used for cation analysis. The IC system consisted of a Dionex Ionpac CS12-A 2 mm × 250 mm analytical column protected by a Dionex CG12-A 2 mm × 50 mm guard column. The system was equipped with a Dionex DS6 conductivity detector. A 20 mM methane sulfonic acid solution was used as the eluent at a flow rate of 0.25 ml per minute. The IC setup achieves the quantification of lithium, sodium, ammonium, potassium, magnesium, and calcium ions in solution.

Solution ICP-MS analysis

Solution ICP-MS was carried out using an Agilent 7900x ICP-MS instrument. The samples were diluted 200 times using a 2 percent (v/v) solution of nitric acid. A Merck Multi IV multi-elemental standard solution was used to prepare calibration solutions. The following elements were measured: lithium, boron, sodium, magnesium, aluminium, calcium, chromium, iron, cobalt, nickel, copper, zinc, gallium, strontium, silver, cadmium, indium, barium, thallium, lead, and bismuth.

SEM analysis

A JEOL JSM-5910lv scanning electron microscope (SEM) was used for the examination of a cross-section of sample CMG 449. The software used was Thermo Scientific NSS. A voltage of 20 kV was used in a low vacuum of 30 Pa.

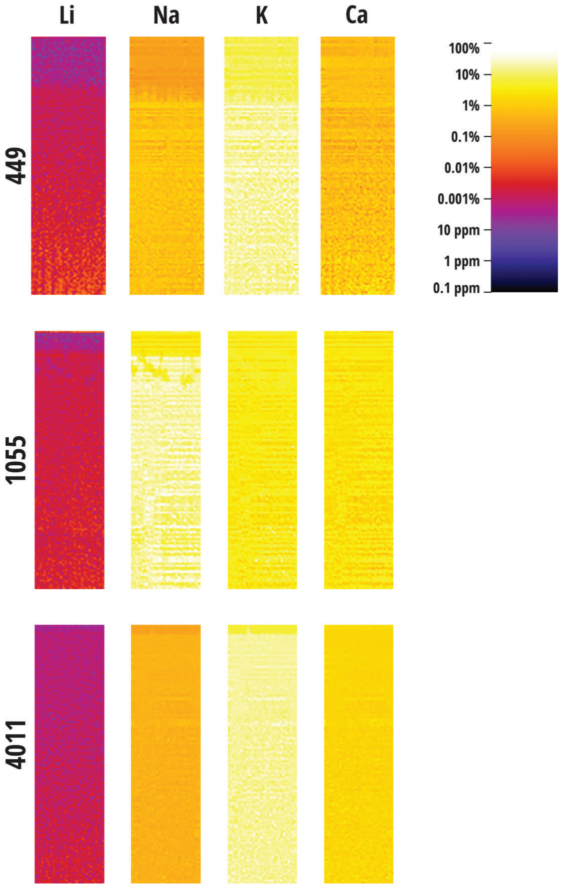

Figure 1. *LA-ICP-MS pseudo cross-sectional element maps of Li, Na, K, and Ca, with log concentration values for samples CMG 449, 1050, and 4011; the maps are not to scale, i.e., width = 3,200 µm and height (representative of depth) = 270 µm*

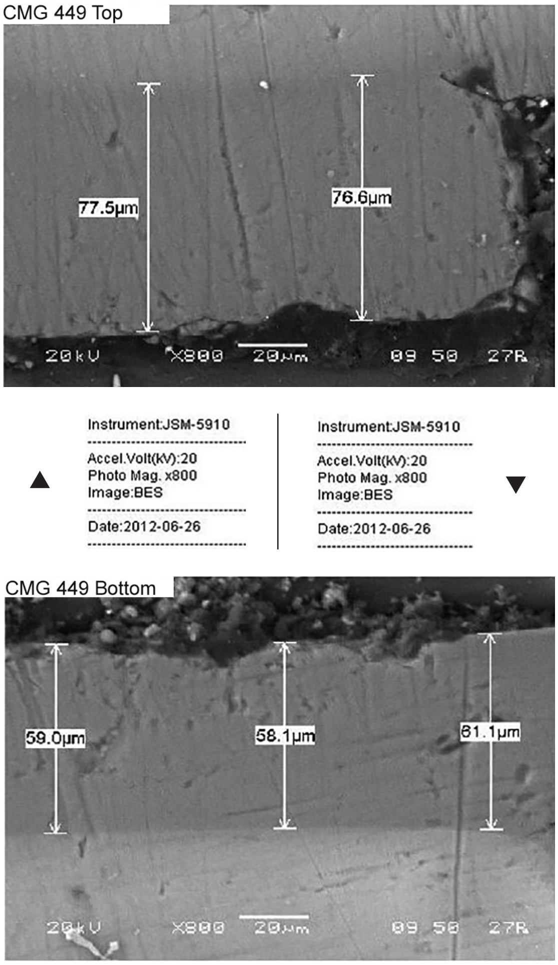

Figure 2. *Scanning electron micrographs of an embedded cross-section of sample CMG 449*

SAMPLE	**COMPOSITION**									
	Li_2O (ppm)		Na_2O (wt.%)		K_2O (wt.%)		CaO (wt.%)		SiO_2 (wt.%)	
	Bulk	Altered	Bulk	Altered	Bulk	Altered	Bulk	Altered	Bulk	Altered
CMG 449	15.6	3.5	0.85	0.21	19.7	8.9	0.6	0.6	76.7	87.8
CMG 1050	20.9	1.7	21	2.23	3.4	3.4	2.6	3.2	70	86.3
CMG 4011	6.8	3.8	0.42	0.22	17.8	6.5	1.6	1.6	70.1	80.5

Table 2. *Elemental oxide concentrations in wt.% of the bulk glass and altered layer of the investigated samples as determined by LA-ICP-MS*

Extraction experiments

Small fragments of the glass samples were immersed in deionized water to extract ions from the glass. The solutions were analysed using IC and solution ICP-MS. Two extraction experiments were conducted. In the first experiment, a fragment of each sample was placed in a polypropylene vial and 250 µl of deionized water was added to extract ions from the samples at room temperature. After 24, 122, and 429 hours, 50 µl of liquid was removed from each vial, and diluted with 200 µl deionized water, for IC analysis. In the second experiment, another fragment of each glass was placed in a glass vial and 500 µl of water was added for extraction. These vials were placed inside an oven set at 60 °C to promote ion leaching from the samples. After 168 hours, 50 µl of liquid was removed from each vial and diluted with 200 µl of deionized water for IC analysis. After 240 hours, 100 µl was removed from each vial and diluted in 200 µl deionized water to increase the amount of ions in solution in case ions were present below the detection limit in the first sampling round. The obtained concentrations were corrected for differences in extraction and sampling volume. The remaining solution was used for solution ICP-MS analysis. Blanks consisted of vials containing deionized water and were exposed to the same conditions as the samples.

RESULTS AND DISCUSSION

Pseudo cross-sectional analysis

The use of LA-ICP-MS depth profiling allows for the investigation of 55 elements and their concentrations at different depths of the sample. We report the depth profiles of three element oxides mainly associated with the deterioration of glass: sodium oxide (Na_2O), potassium oxide (K_2O), and calcium oxide (CaO). Additionally, the pseudo cross-sectional maps for lithium oxide are shown (Figure 1).

From these pseudo cross-sections, it is evident that sodium is leached from the top layer for all samples. Potassium is leached from samples CMG 449 and CMG 4011, but surprisingly, no potassium depletion is observed in sample CMG 1050. No calcium depletion is observed for any of the samples, and the concentration of silica is higher in the alkali depleted layer than in the bulk glass. The depth profiles were used to determine the average elemental concentrations of Li_2O, Na_2O, K_2O, CaO, and silicon dioxide (SiO_2) in both the altered glass layers and the bulk glass for the three samples (Table 2).

The thicknesses of the alteration layers for the three different samples are 37 pixels for CMG 449, 16 pixels for CMG 1050, and 6 pixels for CMG 4011. For sample CMG 449, a cross-section was prepared and investigated using SEM (Figure 2). The thickness of the sample's altered layer was measured to be 66.5 ± 8.7 µm, which provides an estimated average depth of 1.8 µm for each of the 150 laser ablation passes on the glass samples.

Depletion of lithium, similar, as anticipated, to the depletion of the other alkali metals, sodium and potassium, was observed for all samples. The presence of lithium oxide in trace levels was mentioned by Brill (1975), but the depletion of lithium from historic glass has not been previously described. Other trace elements showing depletion profiles include beryllium, nickel, zinc, and europium (see Appendix A for all pseudo cross-sections). These observations require further investigation, outside of the scope of the current work.

Extraction experiments

The extraction experiments addressed three issues. Firstly, the influence of temperature during ion extraction was investigated. Secondly, solution ICP-MS and IC analyses were compared in order to support the use of IC as an analytical tool for the early detection of glass deterioration. Thirdly, the glass compositional analyses described above were compared to the ions extracted from the glass, providing insight into the detection and significance of the ions on unstable glass surfaces.

The effect of temperature on the depletion of ions from the glass was investigated in two extraction experiments. Ion extraction from the glass samples at elevated temperatures was carried out to extract as high an amount of ions from the glass as possible, particularly to assay for the presence of lithium and calcium in the leachate. Figure 3 shows the effect of temperature on the amount of ions extracted as determined by IC. Only sodium and potassium were detected at both temperatures. Since the extraction at 60 °C was performed in glass vials, there is a contribution of the blank in the sodium measurement, whereas

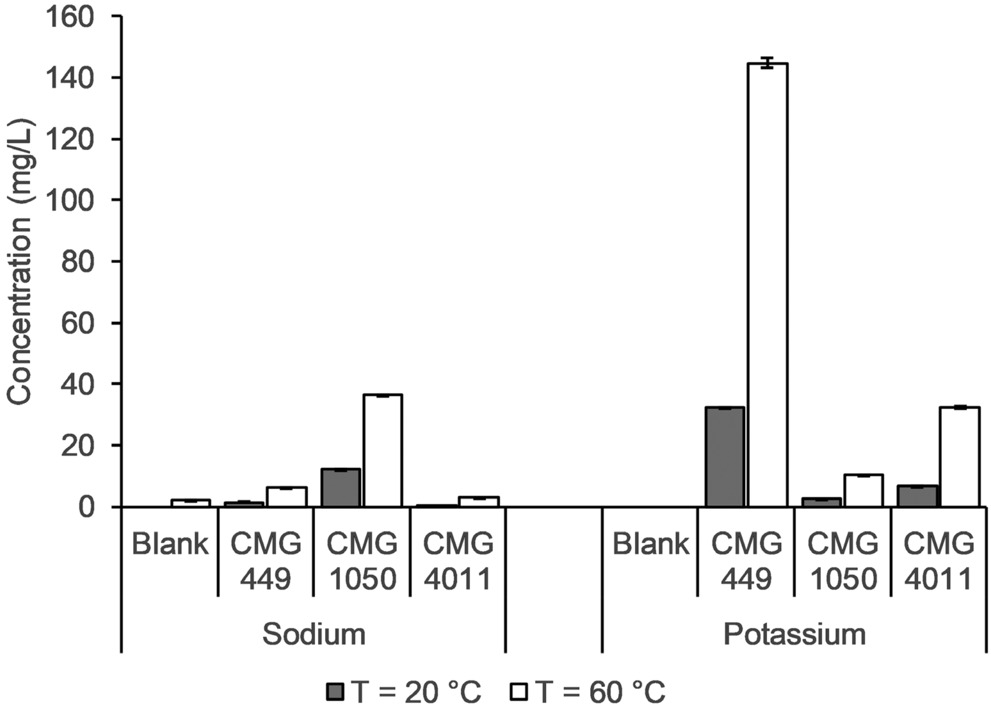

Figure 3. *Sodium and potassium concentrations in leachates after aqueous extraction at 20 °C and 60 °C as determined by IC*

potassium was not detected in the blanks. The two samples with the most comparable extraction times, namely, 122 hours for the room temperature extraction and 168 hours for the elevated temperature extraction, were evaluated.

Extraction at elevated temperature increases the extraction of ions. No calcium was detected in any of the extracted solutions. This corroborates the depth profiles, which show no calcium depletion. As previously mentioned, calcium is not extracted from glass in pH-neutral aqueous solutions, but extraction in acid will cause calcium depletion (El-Shamy et al. 1975); this observation was confirmed in the study of replica samples of medieval stained-glass compositions (Schreiner et al. 1999). Interestingly, the depletion of calcium from the surface layer has been noted in laboratory situations simulating the effect of atmospheric moisture on museum glass (Fearn, McPhail, and Oakley 2005). However, the depletion of calcium from aged glass replicas was not observed in a separate SIMS study (Rodrigues et al. 2018). In contradiction with general observations, another extraction study indicated the depletion of calcium from glass at 37 °C in distilled water (Rohanová et al. 2012). Importantly, all of the aforementioned studies were carried out on freshly prepared and artificially aged replica glasses. We studied naturally aged samples from historic artefacts, the compositions of which are more complex than the binary or ternary replica glasses used in previous laboratory studies; this factor has the potential to affect the release of ions into solution (Kunicki-Goldfinger 2008; Rohanová et al. 2012) and further investigations are therefore warranted.

Sodium and potassium were detected in the extracted solutions from all samples. This reflects the composition of the glass: all investigated samples contain sodium and potassium, with samples CMG 449 and CMG 4011 being high in potassium and low in sodium, while sample CMG 1050 is high in sodium but low in potassium. Surprisingly, no potassium depletion was observed for sample CMG 1050 in the pseudo cross-sections obtained with LA-ICP-MS. Currently, no satisfactory explanation has been found for this result, but future experiments will address this issue. No lithium was detected in the leachates, either by IC or by solution ICP-MS. It is to be expected that leaching of the trace amounts of

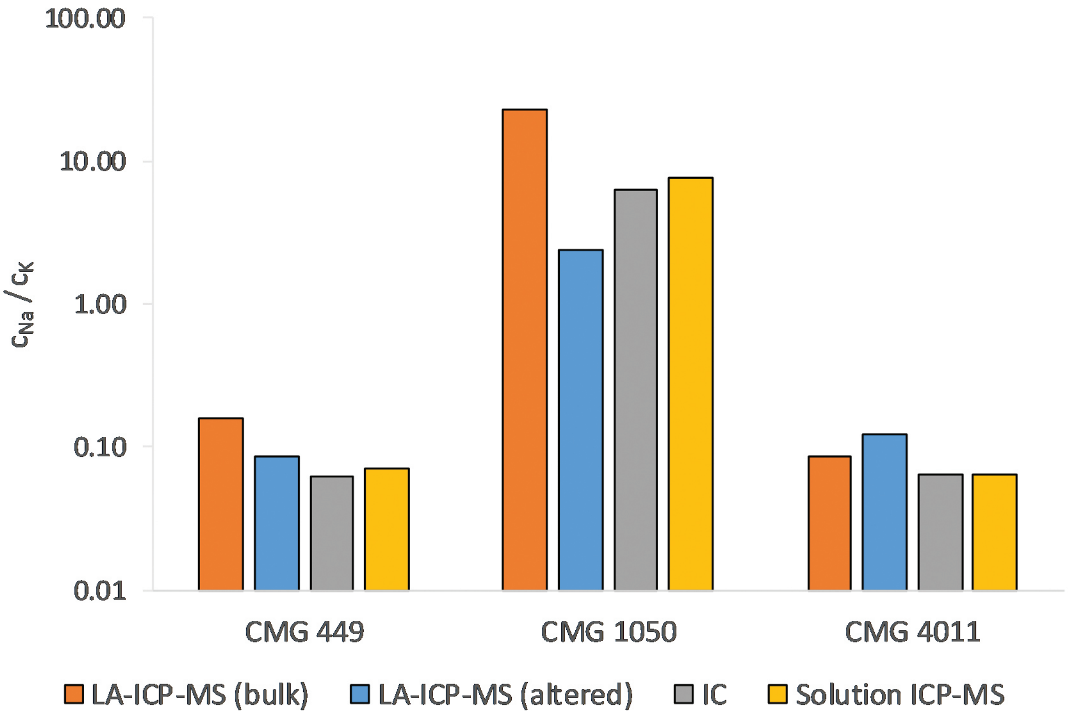

Figure 4. *The molar concentration ratios of sodium over potassium (C_{Na}/C_K) for the samples CMG 449, 1050, and 4011, measured for the bulk glass and the altered layer with LA-ICP-MS and for the extract with IC and ICP-MS, all corrected for the blank*

lithium from the glass would result in solution concentrations below the detection limits of these analytical techniques.

In order to investigate the leaching behaviour of sodium and potassium in the glass samples, the molar concentration ratios of sodium to potassium (C_{Na}/C_K ratio) were determined at the end of the extraction experiments at 60 °C: in the bulk glass and altered layer, by LA-ICP-MS; and, in the extracts, by IC and ICP-MS (Figure 4). The C_{Na}/C_K ratio of the leached layer is different from that of the bulk glass, implying preferential leaching of one of the ions. For samples CMG 449 and CMG 1050, relatively more sodium was leached out of the glass sample, leading to a surface layer depleted in sodium, resulting in a lower C_{Na}/C_K ratio. For sample CMG 4011, relatively more potassium was leached out of the glass sample, and, for sample CMG 1050, no depletion of potassium was observed in the depth profiles, hence the dramatic decrease in the C_{Na}/C_K ratio.

Comparing the C_{Na}/C_K ratios of the bulk glass and altered layer to that of the leachates, it follows that the relative amounts of sodium and potassium extracted from the glass are not the same as their C_{Na}/C_K ratio in the glass itself. For all samples, the C_{Na}/C_K ratio is lower in the leachate than it is in the bulk glass, implying that a larger proportion of potassium is extracted from the glass. Since all the samples under investigation aged naturally for several hundred years before the start of these experiments, this observation can be explained by the fact that most of the sodium has already been depleted from the glass prior to the experiments. Sodium moves out of sodium-rich glass more rapidly than other glass constituents in the early stages of aging, after which a protective layer is formed on the surface, slowing down the leaching rate after the initial stage. Conversely, potassium-rich glass dissolves congruently, and glass constituents are leached at a similar rate (Rohanová et al. 2012). Since a large proportion of the sodium has already been depleted from the glass during the early stages of deterioration, relatively more potassium remains available for extraction, leading to a lower C_{Na}/C_K ratio in the leachates. This will most likely also be the case for historic objects, as these objects will have already undergone the initial stage of severe sodium depletion. However, in absolute amounts, the sodium-rich glass, CMG 1050, still shows a much higher sodium concentration in the leachate.

Importantly for the EWS, the C_{Na}/C_K ratio obtained with leachate analysis using solution ICP-MS is in agreement with the results of IC analysis. The IC setup utilised was not suitable for aluminium analysis, but solution ICP-MS analysis quantified very low amounts of aluminium as the only other element in the leachates. However, the LA-ICP-MS pseudo cross-sectional maps show no depletion of aluminium prior to aging (Appendix A). Possibly, the more aggressive extraction procedures have caused the leaching of a small amount of aluminium from the glass.

CONCLUSIONS

In the context of research into the relationship between the glass composition and the leaching of ions from within the glass into solution, the results demonstrate the value of the combined use of IC and LA-ICP-MS.

Sodium and potassium ions were found in the leachates, and their molar ratios differ from the ratios in the glass, with relatively more potassium than sodium leached. No other ions were identified in the leachates using IC; additionally, aluminium was found using solution ICP-MS. LA-ICP-MS pseudo cross-sectional maps showed the depletion of trace elements, including lithium. No evidence was found that indicates depletion of calcium from the historic glasses studied under natural or accelerated aging.

LA-ICP-MS depth profiles have been shown to make a significant contribution for obtaining and presenting quantified compositional data on the leaching of ions from historic glass in order to gain a better understanding of the extent of release of ions at different stages of the degradation process. Future work involving the combination of LA-ICP-MS depth profiles and IC analysis of ions on the surface will be vital in providing crucial information on the degradation process in relation to the development of storage guidelines for unstable glass.

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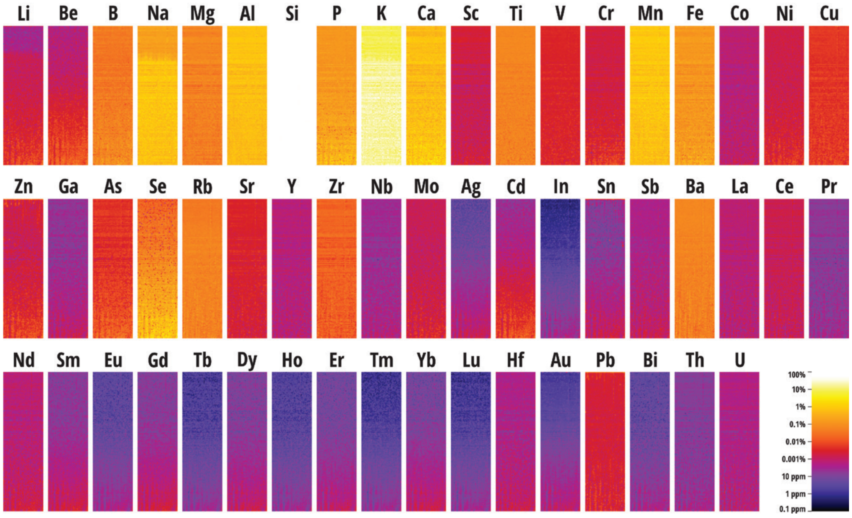
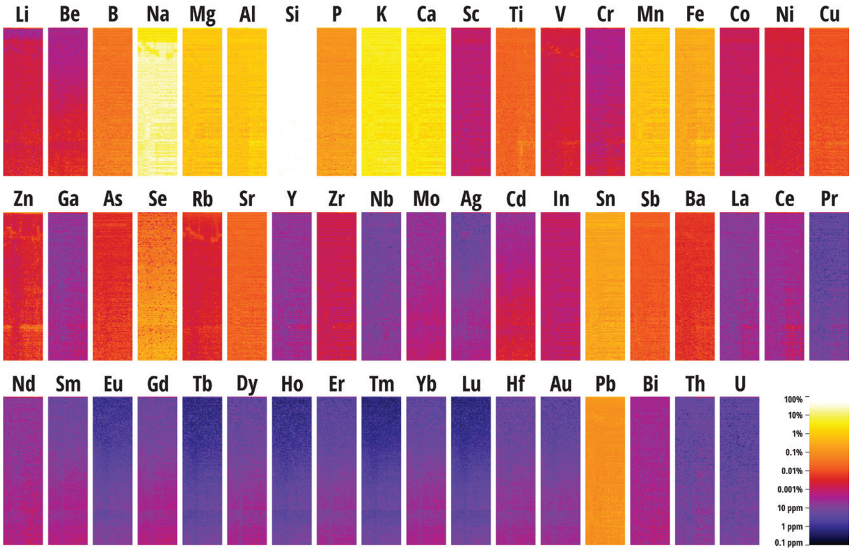
APPENDIX A

Oxide content (log) pseudo cross-sections for 55 elements

sample 449 - oxide content (log) pseudo cross-sections



sample 1055 - oxide content (log) pseudo cross-sections



sample 4011 - oxide content (log) pseudo cross-sections