

# Chemical characterisation of Glass Waste and crucible fragments from the late 17<sup>th</sup> - early 18<sup>th</sup> century Scottish glass manufacturing site at Morison's Haven, East Lothian

Helen M. Spencer\*, Jim Buckman, Alan M. Forster, Craig J. Kennedy

School of Energy, Geoscience, Infrastructure and Society, Heriot Watt University, Edinburgh, Scotland, United Kingdom, EH14 4AS

\* Corresponding Author. Email: [hms1@hw.ac.uk](mailto:hms1@hw.ac.uk)

## Abstract

Glass waste and crucible fragments from the late 17<sup>th</sup> – early 18<sup>th</sup> century Scottish glass furnace at Morison's Haven, East Lothian was characterised using a range of analytical techniques (SEM-EDX, p-XRF, LA-ICP-MS and micro-XRF). Morison's Haven is the earliest excavated glass furnace in Scotland. The glass working waste provides a unique opportunity to compare the actual composition of some of the glass produced with the documentary records of raw materials used at the site and the types of glass artefacts produced. The work provides new technological and economical insights into the nature of glass production in the early 18<sup>th</sup> century in Scotland.

Fourteen samples of glass working waste and three crucible fragments were examined. Two types of mixed alkali glass were found to be produced at the site neither being of a HLLA type as suggested by initial visual analysis. The first was a high quality soda-rich glass made with barilla and a pure sand source. The second type of glass was a range of lower quality mixed alkali glass at least partially fluxed with kelp ashes and using a range and mixture of less pure sand sources. This was most likely used to make windows or lower quality vessels. LA-ICP-MS analysis suggests that sand from two different sources were selected to make the two types of glass.

This work is the first attempt to chemically characterize glass waste from a Scottish glass manufacturing site and adds to the known documentary and archaeological evidence to provide more knowledge pertaining to the early glass manufacturing industry in Scotland.

## Keywords

Glass waste, post-medieval, Scotland, furnace, mixed alkali

## Highlights

- Glass working waste was chemically characterized from the earliest glass manufacturing furnace to be excavated in Scotland, situated at Morisons Haven, East Lothian
- Two main types of glass were identified. The first was a high quality soda-rich glass made with barilla and a pure sand source. The second type of glass was a range of lower quality mixed alkali glass at least partially fluxed with kelp ashes and using a range and mixture of less pure sand sources.
- LA-ICP-MS analysis confirms that different sand sources were used to make the two different types of glass

## 1. Research Aim

The aim of the work was to undertake analysis of glass waste from a Scottish post-medieval glass manufacturing site. Whilst limited in scale, the importance of this site as the earliest Scottish glass furnace to be excavated cannot be over emphasized. This analysis provides a valuable insight in to the early indigenous production, materials and technologies of Scottish glass.

## 2. Introduction

The growth of the post-medieval glass manufacturing industry and the development of recipes used to produce different glass products during this period in England has been the subject of a number of archaeometric studies. Following the analysis of window glass from numerous sites (both archaeological and window glass still in situ), a generalised model was developed that can be used to characterise and date window glass found on archaeological sites (Dungworth, 2012a, Dungworth and Loaring, 2006). Similar work was also carried out to chart the changing composition of bottle glass manufacture in England (Dungworth, 2012b).

A sudden change occurred in the composition of glass manufactured in England around 1567. Prior to this date glass had been made using plant ashes that were high in potassium oxides and termed 'forest glass'. Immigrant glass workers from the continent brought with them a recipe to make glass known as high lime low alkali (HLLA), which contain increasing amounts of calcium oxides and lower potassium oxides. The introduction of coal fired furnaces in the early 17<sup>th</sup> century brought about a further compositional change with glass produced containing much lower manganese oxide levels (>0.2%). An expanding range of glass recipes were developed throughout the 17<sup>th</sup> and 18<sup>th</sup> centuries for the production of bottles, vessels, windows and plate glass. By the turn of the 18<sup>th</sup> century the window glass was being made using a mixed alkali recipe rather than a HLLA recipe which continued to be used for bottles. The particular qualities desired in high quality window and vessel glass, such as transparency, lack of coloured tints and fewer bubbles meant that different raw materials were chosen from those used in bottle production, where the glass could be more opaque and highly coloured.

Of particular interest is the start of the use of kelp ash as a flux to manufacture vessel, bottle and window glass which has implications in terms of dating window glass. The use of kelp was identified by increased strontium oxide levels in the glass and its origin from kelp was confirmed by complementary strontium isotope analysis (Dungworth et al., 2009). Dungworth (2009) suggested that the introduction of kelp as a flux is tied to the reintroduction of the crown glass technique in England for making windows. Glass workers in Normandy, France appear to have continued crown glass manufacture when cylinder glass was the preferred method in most other places in Europe and a mixed alkali kelp fluxed glass was thought to have been produced in France for window and mirror glass in the Palace of Versailles during the mid-late 17<sup>th</sup> century (Velde, 2013).

Strontium oxide at levels greater than 0.2% were found in glass waste at Silkstone, England dated to around 1660 which was thought to have been used to produce vessels (Dungworth, 2005) and kelp was thought to have been used to make window glass, as part of a mixed alkali recipe, in England from around 1700 (Dungworth, 2012a). Recent analysis of window glass from Scottish contexts has however found the use of kelp as at least one component of the flux to make a HLLA glass dated to the mid-late 17<sup>th</sup> century (Spencer, 2018) and there is unpublished evidence that kelp was also used in part to make some English manufactured HLLA window glass in the later 17<sup>th</sup> century (Dungworth, pers comm). A more radical change to the composition of vessel glass also occurred with the invention of lead-crystal glass in 1674 (Brain and Dungworth, 2006, Dungworth and Brain, 2013).

Until 1610 A.D. there is no confirmed physical or documentary evidence that glass was manufactured directly from its raw materials in Scotland.

Turnbull (2001) chronicles the early glass production in Scotland drawing on evidence from a variety of documentary sources. The first patent for Scottish glass production was issued to Sir George Hay in 1610. Following the patent, a number of glass furnaces were established on the east coast of Scotland in the early 17<sup>th</sup> century, primarily along the shores of the Firth of Forth, in the counties of East Lothian and Fife. Many of the sites were recorded, either through patent applications and other primary documentary evidence sources such as financial records and contracts. Regrettably these sites, can be no longer physically identified, either being obscured through changes in the natural coastline or subsequent industrial and domestic developments located on earlier sites. It is thought that most of these furnaces were short lived enterprises due in part to the glass manufacturers that struggled to produce glass of sufficiently high quality and quantity to compete with English glass houses. Creating context for the embryonic industries, economic stimulus was fostered, including a ban on the importation of foreign glass at various points in the 17<sup>th</sup> century as well as an exemption from duty of the import of raw materials. This quasi subsidy mechanism aimed to establish a profitable glass industry north of the border.

The earliest glass furnace to have been excavated in Scotland is at Morison's Haven. The site was investigated and subsequently excavated as part of a community archaeology project organised by East Lothian Council (Cressey et al., 2012). Morison's Haven is situated on the current Prestongrange Industrial Museum, which lies between the towns of Prestonpans and Musselburgh. The site sits on the coast of the Firth of Forth and only ten miles from the capital city of Edinburgh and the major Medieval and Post-Medieval port of Leith (figure 1).



Figure 1 Map of Scotland showing the location of Morisons Haven, East Lothian

This site was excavated with subsequent investigation being an integral part of a community archaeology project. In addition to glass production, the site was associated with other regional industrial activities that were better known. These included, extensive pottery and salt manufacture in the 18<sup>th</sup> and 19<sup>th</sup> Centuries (salt panning from which the town of Prestonpans derived its name). Due in part to the multi layering of archaeological industrial processes this glass manufacturing site has been ostensibly overlooked.

Scientific analysis of glass manufacturing waste from similar sites in both England (Dungworth, 2005, Dungworth, 2006, Dungworth, 2007, Dungworth and Mortimer, 2005) and Ireland (Farrelley et al., 2014), have been carried out, but this is the first time glass manufacturing waste has been characterised from a 17<sup>th</sup>/18<sup>th</sup> century Scottish glass furnace. The glass working waste provides a unique opportunity to compare the actual composition of some of the glass produced with the documentary records of raw materials used at the site and the types of glass artefacts produced. Targeted analysis from this work include the identification of the recipes used to make glass in Scotland at this period, identify if local raw materials such as kelp, that could be used as an alkali flux, were being exploited, and how the manufacturing process may have differed from the rest of the United Kingdom during the same period.

### 3. Documentary Evidence

There is a significant amount of documentary evidence for the manufacture of glass at Morison's Haven throughout the 17<sup>th</sup> and early 18<sup>th</sup> century which is discussed in detail by Turnbull (2001). Glass production started at the site before 1623 and, apart from a hiatus between 1627 – 1635, continued to around 1647 following which glass manufacturing transferred to the nearby site at West Pans and further along the coast in Newhaven and Leith. There is no archaeological evidence of glass working on the site from this period

Glass making at Morison's Haven is known to have been re-established in the late 1690's. The 'Act of Ratification in favors of the Glass Manufactory at Morisons Haven' by the Scottish Parliament allowed William Morison of Prestonpans to operate a glass works at the site in 1697 (APS 10, 180). The Act grants that they were supplying bottles and '*severall other sorts and species of glasses which were never heretofore manufactured within this Kingdome such as mirror and looking glasses, plate coach glasses, moulded glasses and window panes*'. The products were said to be 'as good, or better and as cheap or cheaper as has been imported any time heretofore' (Turnbull, 2001). Morison was granted a monopoly for nine years to manufacture all items of glass, apart from bottles, although bottles were still likely to have been a product of the glass house as they would have provided the most regular income. In the ensuing thirty years, the glass works underwent periods of financial difficulty, forcing it to close and re-open under new ownership several times. In 1708 there were two furnaces described as being present on the site – a large and a small one – although in a state of disrepair (Turnbull, 2001).

Documentary records also show that different fluxes were imported into Morison's Haven docks during this period. Over 20 thousand pounds of barilla were imported from Amsterdam in 1700. Kelp was supplied as a raw material to the glass house, in addition to wood ash and 'soap and light ashes' to a total of 219 tons in 1706. There are also records of soap ash, kelp and barilla ashes being stored on site when the glass house was sold in 1708. In the 1720's there are records of both barilla and 'English sande' being imported for use at Morisons Haven for the production of high quality plate glass. However it is thought that production of glass at Morison's Haven ceased by 1727 when the York Company moved their glass production to nearby Port Seton (Turnbull, 2001).

#### 4. Archaeological Evidence

A community archaeology project organized by East Lothian Council was established with the aim of investigating and partially excavating some areas of the Prestongrange industrial complex. Initial surveying and field walking of the area was carried out in 2004 and this was followed by limited excavations in 2005-2007 (Cressey et al., 2012). During these excavations an area of a glass furnace was excavated (figure 2).

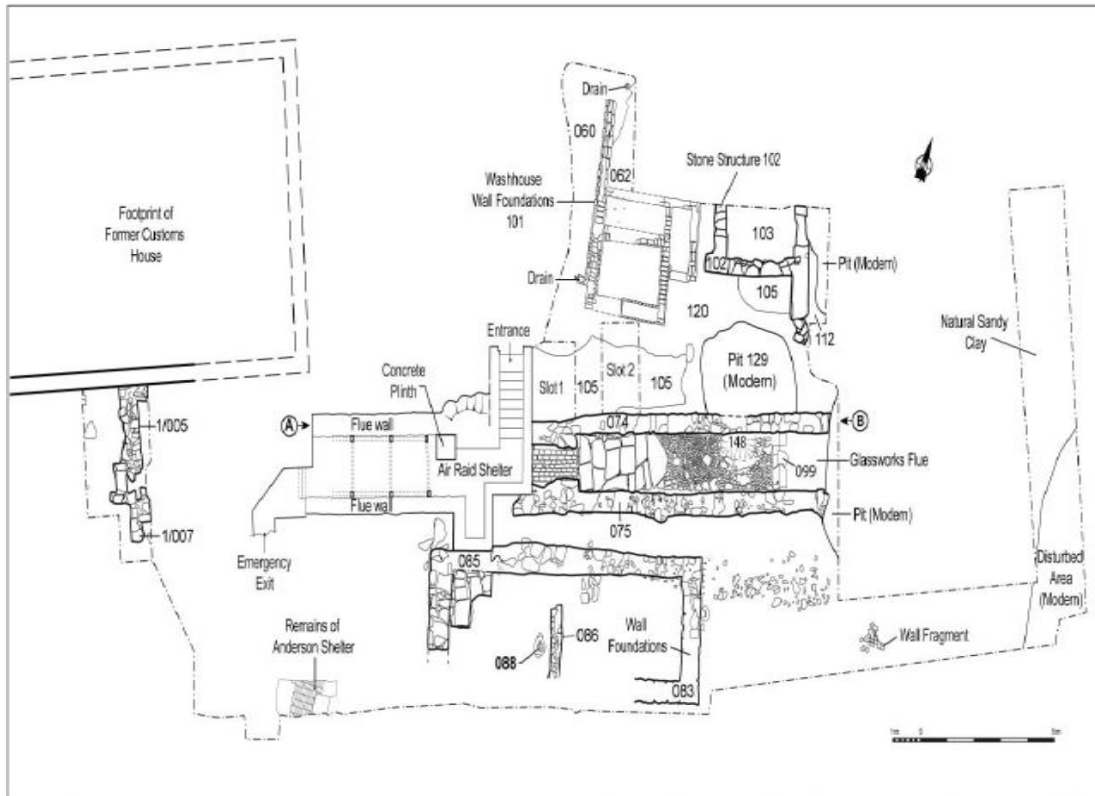


Figure 2 Plan of excavated glass furnace at Morisons Haven (Cressey et al., 2012)

A glass flue was excavated which has been dated to the latter period of glass manufacture at the site between 1697 – 1727, due to its similarity with the design of furnaces found at Catcliffe (Yorkshire) and Kimmeridge (Crossley, 1987).

A range of glass and glass working waste was found on the site – just under 1.5 kg in weight. A variety of bottle, vessel and window glass fragments were found in topsoil or un-dateable deposits, which were mostly identified as 19<sup>th</sup>/20<sup>th</sup> century. However 0.75kg of glass waste was found which was in contexts associated with the glass flue. The majority derived from a context which was a coal ash layer associated with the flue. Figure 2 shows a plan of the excavated furnace

The waste was undiagnostic, with no clear blowing waste, such as moils or overblows, but consisted of a range of sizes of lumps. The majority of the assemblage was large pieces of slag and frit comprising of partially melted silica and alkali phases which had not yet been fully fused. Pieces of fuel ash, gall and slag were also found. However, some of the glass had been melted and was fully formed pot metal ready to be used to for blowing. There were also a small number of drips.

Wilmott (2006) visually identifies the glass to be of a high-lime low-alkali (HLLA) type glass due to the green colour of the pot metal. He suggests it is of a type most suitable for wine bottle making.

Three fragments of crucible were also found which had evidence of glass on the inner surfaces.

## 5. Methodology

Thirty four bags of glass making waste were examined. Most of this waste was opaque, bubbly or contained un-melted granules of silica and was interpreted as being either frit or 'altered glass' which had fallen onto the fuel pit. These were not suitable for analysis as they were very heterogeneous in nature and their composition would not be similar to the final glass produced on site. However, sixteen samples of homogenous glass waste were analysed. Thirteen of these were lumps of melted glass, while one of them was a 'drip' of glass (Figure 3).



Figure 3 Selection of glass waste fragments from Morisons Haven

In addition the three crucible samples were chosen for analysis.

### *Portable X-ray fluorescence (p-XRF)*

The surface of each sample were manually abraded and polished using as series of silicon-carbide papers and diamond polish to  $3\mu\text{m}$  to provide a clean flat surface for analysis.

Portable X-ray fluorescence (p-XRF) analysis of the samples was undertaken using a Bruker Tracer III-SD with a Rhodium X-ray tube. Two sets of analysis were carried out the first at 40kV  $11\mu\text{A}$  with a 'yellow filter' and the second at 7kV  $55\mu\text{A}$  with no filter under helium flushed vacuum to allow for better detection of the lighter elements. The calibrations used for quantitative analysis were made in Bruker



S1pXRF software using a Compton method for normalization. This produced 'empirical' calibrations and validated the concentration of the elements in the samples that were within the range of elements present in the standards. Twenty two glass standards were used to create this calibration including Corning, Pilkington, NIST and Society of Glass Technology.

#### *Scanning Electron Microscopy and Energy Dispersive X-ray analysis (SEM-EDX)*

Small samples of approximately 1-3mm<sup>2</sup> were taken from each of the 17 samples and three crucibles to enable cross sections to be mounted for analysis. In order to overcome the potential of surface contamination due to association with the furnace fabric, the crucible and fuel vapour or ash only areas of fully fused glass, taken from the interior of a sample were analysed. A cross sectional sample was mounted in silicon moulds, using two-part Tiranti™ clear casting resin. The mounted samples were then ground and polished using a series of silicon-carbide papers and diamond polish to 3µm.

The samples were then analyzed using a XL30 LaB<sup>6</sup> ESEM equipped with Oxford Instruments X-Max 80mm EDX detector. The ESEM was operated in low vacuum mode. The samples were placed on a stage inside the chamber with the pressure set to 10 Pa. Samples were viewed using the Back-Scattered (BSE) detector to determine the most appropriate areas to analyse. Areas were selected to be analyzed were homogenous in appearance and in the centre of the cross section and away from the visible corroded surfaces. The EDX was set at an operating voltage of 20 kV. The working distance was set to 10 mm and the spot size set to 4.2. The area was analyzed for 10 live sec. The area analyzed each time was approximately 100 µm. Each sample was analyzed three times, choosing a different area for each analysis. Standards were pure oxides and minerals and quantification was carried out using the ZAF correction software. The accuracy of the measurements were assessed by comparison with the measurement of known glass standards (NIST, Corning D). Oxide weight percentages were calculated stoichiometrically. The average and standard deviations for the three measurements calculated.

#### *Laser-Ablated-Inductively coupled Mass Spectrometry*

Four of the mounted samples were analysed by LA-ICP-MS to assess and quantify the presence of trace and rare earth elements.

An ESI New Wave Research 193 ArF excimer laser system was used in conjunction with an Agilnet 7700x ICP-Q-MS. The mounted SEM cross sections were mounted on a Perspex plate which was placed on a floating stage. The stage was flushed with He to collect and carry the analyte to the ICP-MS at 400 ml/min. A laser was pulsed at 10Hz with a fluence of 3.5J/cm<sup>2</sup>. Ablation spots were 100 µm in diameter. The ICP-MS used Argon Plasma gas flow at the rate of 1.1 l/min and the analysis carried out for 60 s. Gas blanks of 30 s were used in each analysis. Data was recorded using in-house software. The quantification was checked in comparison with the primary reference standard NIST 612 and secondary reference standard NIST 610. The calibration standards were analysed after every 12 analyses. Each sample was analysed 5 times and the averages and standard deviations calculated.

The SEM-EDX data for calcium was used to standardise the readings. Concentrations for major elements were calculated assuming that the sum of their concentrations in weight percent in glass is equal to 100% (Gratuze 1999). Concentrations for the trace elements are reported in ppm/ppb.

## 6. Results

The major and minor elemental composition as determined by SEM-EDX and p-XRF of the seventeen glass waste samples is shown in table 1. The SEM-EDX and p-XRF measurements alongside the manufacturer's (Pilkington and DDG) guidance levels of elements in the glass standards used are listed as percentage of oxides and shown in table 2. The trace element and REE composition for four samples as determined by LA-ICP-MS is shown in table 3 (see appendices).

The results of the scientific analysis showed that the glass made on the site was all of a mixed alkali composition. While some samples have trace amounts of lead, there was no evidence that lead-crystal vessel glass was produced at this furnace. Neither could any of the glass waste be characterized as being HLLA. There is a more complex picture with a wide range of mixed alkali glass composition being identified. This would be expected when analyzing glass waste as none of the samples are likely to represent the composition of the finished article, but of glass part way through the melting process.

The glass waste from Morison's Haven has a significant amount of both sodium oxide (3-11%) and potassium oxide (3-6%). Magnesium oxide is present between 3-5% and phosphorus oxide between 0.2-1.5 %. All samples have less than 11% calcium oxide showing they were not HLLA as had previously been thought from visual inspection and that all the glass waste can be categorized as a mixed alkali type.

Whilst there appears to be a continuum of glass compositions, the glass waste has been split into two potential groups based on a number of criteria (table 1 and figure 4).

<b>Type 1 (8 samples)</b>	<b>Type 2 (7 samples)</b>
Sodium > 8%	Sodium < 8%
Sodium + Potassium > 13%	Sodium + Potassium < 13%
Phosphorous < 0.6%	Phosphorus > 0.6%
Calcium > 9%	Calcium < 9%
Strontium < 0.15%	Strontium > 0.15%

Table 1 Summary of the characteristics of the two groups of glass waste identified

The eight samples of type 1 glass waste have the highest sodium oxide levels of 8-11%, calcium oxide between 9-11% and low phosphorus oxide (<0.6%) and contain <0.15% strontium oxide. Five samples have phosphorus oxide levels below 0.3% which might suggest a synthetic soda glass produced later than 1835, but the potassium oxide and calcium oxide levels show that the glass is a mixed alkali glass type and consistent with the late 17<sup>th</sup> and early 18<sup>th</sup> century. Three of these samples form a tight group and are made with a flux with both the highest soda and lowest strontium oxide contents. The low levels

of phosphorus oxide and other minor elements therefore suggest that highly purified ashes, probably barilla, were used to make this high quality glass (Van der Linden et al., 2005).

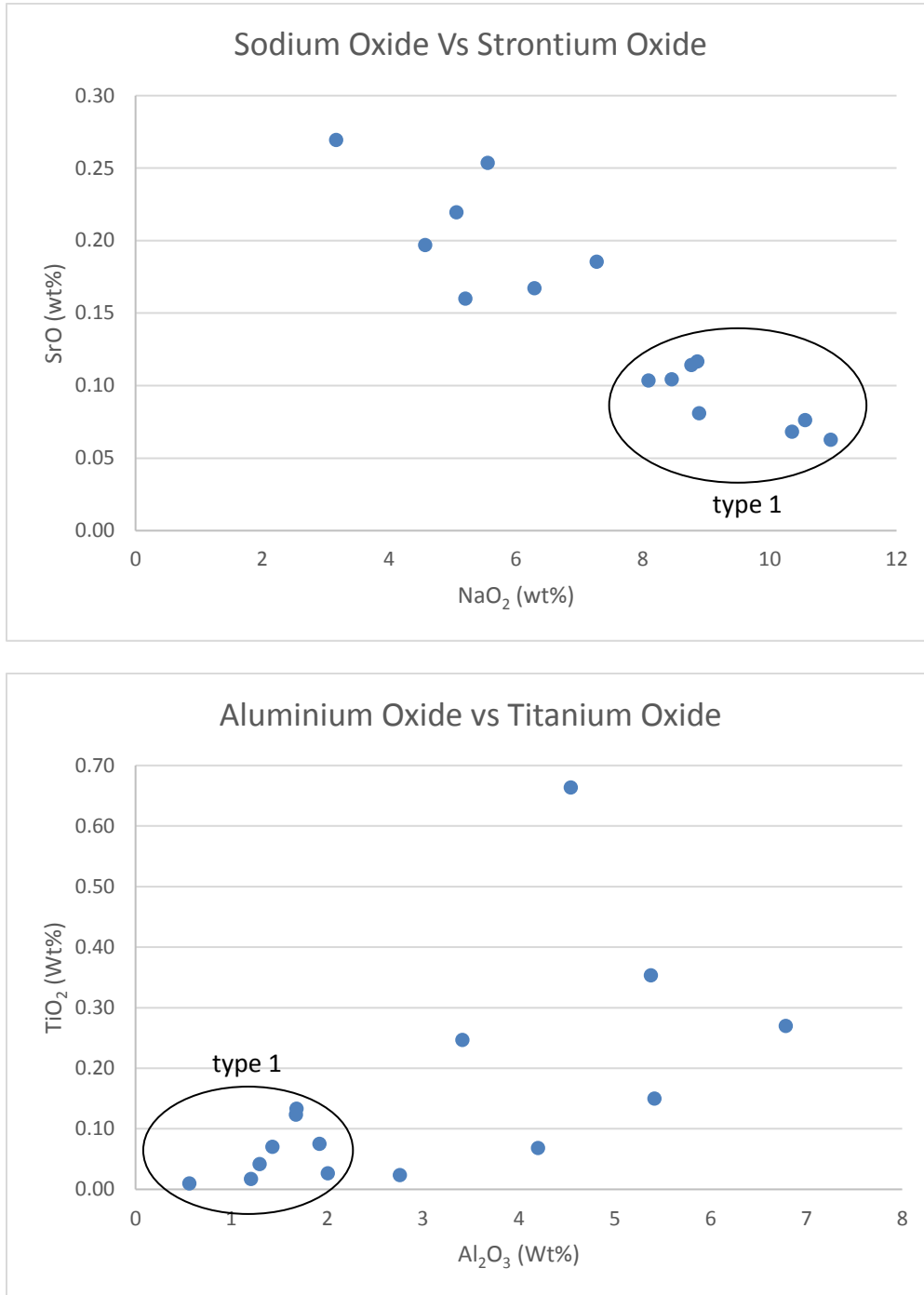


Figure 4 Graphs showing the comparison between elemental oxides related to the flux (sodium and strontium oxides) and the sand source (aluminium and titanium oxides).

Seven of the samples, have been categorized into a different group, Type 2. This group has a more diverse composition and most probably represents a continuum of glass compositions. While having lower sodium and calcium oxides, they all have strontium present at levels greater than 0.15%. Strontium oxide at this level is an indicator that kelp ash was at least one ingredient used in the glass. These samples also had higher aluminium, phosphorus and iron oxides alongside increased trace elements compared to type 1 glass waste. This would suggest that a less pure sand source was used to make these glasses. The waste shows a continuum of compositions and the diversity in the composition of particularly this second group shows there is likely to have been experimentation on site where glass was made using the most available fluxes and sands. The addition of mixed glass cullet would also result in broadening the range of glass compositions made at the site.

The drip (MH14) is a high soda, low strontium oxide type 1 glass waste. Dungworth (2006) highlights the difficulty when analysing this type of glass waste. He contends that as the glassworkers made the glass they would test it by pulling out small amounts of glass to inspect it either for bubbles or viscosity. The glass drips may represent tests like this before the glass was fully formed – and may have still required remelting or refining.

Glass on the surface of three crucible samples was analysed. The crucible fabrics were visibly very different. MH55 crucible was of a mid-beige colour and was made from a high aluminium, titanium and iron clay. MH56 and MH59 were both made from a whiter coloured clay, which was richer in silica and lower aluminium. The glassy layer on the surface of the crucible is likely to have been heavily contaminated by the crucible fabric it is less representative of the final glass composition than the lumps of waste. The glass residue on MH55 has the highest sodium oxide levels and low strontium oxide levels, more akin to the Type 1 glass. MH 56 and MH59 has almost equal amounts of sodium and potassium oxides. Discussion

## 7. Discussion

The analysis suggests that at least two different types of glass were being produced at Morison's Haven when this furnace was in use at some point between 1698 and 1727. Neither glass was of a high lime low alkali (HLLA) type as suggested by initial visual analysis.

The first type of glass with low phosphorus oxide, could be considered a high quality mixed alkali glass, because it was made using purified ashes and a silica rich sand with few impurities. Glass analysed from the 17<sup>th</sup> century in the Low Countries also showed similar low phosphorus oxide levels suggesting that a method had been developed to purify the ashes by as early as 1650 (Van der Linden et al., 2005). It is known that in the year 1700, 20,700 pounds of barilla ashes were recorded as being imported to Morisons Haven direct from Amsterdam (Turnbull, 2001), and this analysis confirms the use of this to make a high quality glass. This glass is unlikely to have been used to make bottles or windows and may have been used to make either mould blown vessels or plate glass, which is recorded as a possible product of the glass house at this time. The parliamentary act granted to William Morison to allow him to set up the glass furnace at Morison's Haven states that he intended to produce high quality plate

glass and more unusual glass items such as mirror or looking glasses, watch glasses and spectacle glasses (NAS GD 109/3945). The glass waste confirms that glass of this quality was attempted to be produced on this site and confirms the documentary evidence that the glass house was supplied with barilla and 'English sand'.

The second 'type' of glass, whilst still a mixed alkali type, appears to be made from a mixture of flux sources including both kelp and soap ashes, suggested by the higher potassium oxide. A wider range of cullet may also have been added to the glass melt and will also account for the more diverse final glass composition. It is suggested that the glass samples in this group were subject to less quality control and were used to make lower quality glass than the high soda type 1 samples.

Dating models have been developed for the change in recipes of English window glass (Dungworth and Girbal, 2011) and for English bottle glass (Dungworth, 2012b). It is suggested that mixed alkali glass in England in the late 17<sup>th</sup> and early 18<sup>th</sup> centuries was being used for windows rather than for bottle manufacture, which still used HLLA glass. Sodium oxide levels above 5% were not identified in the chemical analysis of English bottles until the mid-19<sup>th</sup> century (Dungworth, 2012b). If the recipes were similar in Scotland this would also suggest that the type 2 glass waste identified at Morison's Haven was produced to make windows or possibly table-ware, rather than bottles.

As no other glass working waste from furnace sites has been investigated in Scotland the closest comparison can be made with sites excavated and waste analysed in England. A number of late 17<sup>th</sup> and early 18<sup>th</sup> C sites have been investigated including sites in Bristol (Dungworth and Mortimer, 2005, Dungworth, 2007), London (Dungworth, 2006, Cable, 2006, Mortimer, 1995) and Yorkshire (Dungworth, 2005).

Analysis of glass working waste from St Thomas Street, Bristol (Dungworth, 2007) found that both HLLA and mixed alkali glass was being produced there at the same time. The St Thomas Street mixed alkali glass was 'virtually indistinguishable' from glass produced at the nearby Bristol site of Cheese Lane (Dungworth and Mortimer, 2005) suggesting that they were using the same raw materials and recipes. The bottle glass was made from HLLA while documentary evidence suggests that window glass may have been produced from the mixed alkali glass. The mixed alkali glass analysed at St Thomas Street, all had higher in strontium oxide (>0.3%) than the glass waste from Morisons Haven.

In comparison, mixed alkali glass excavated from Vauxhall, London had very low strontium oxide levels (<0.1%) so kelp was unlikely to have been used as a flux at this glasshouse (Dungworth, 2006). The mixed alkali glass waste at Vauxhall could be further separated into three groups by the lead oxide concentration which in 16 samples was >2%. None of the Morison's Haven samples have lead concentrations above trace levels. This suggests that neither lead-glass cullet was used at Morison's Haven nor were lead vessels used for the purification of plant ashes used as fluxes (Brill and Hanson, 1976).

The site of Silkstone in Yorkshire is particularly interesting as there are a number of phases of glass working, using different recipes of glass, which can be tightly dated (Dungworth, 2005). In phase 1 (1655-70) there is production of both a HLLA glass and a high strontium oxide (0.27 +/- 0.01) mixed alkali

glass. However in the later period of 1670-80 they are replaced by the use of a mixed alkali glass that has low strontium oxide levels (0.05 +/- 0.01). The composition of the mixed alkali glass from phase 1 at Silkstone is very similar to type 2 samples from Morisons Haven samples which have strontium oxide levels of >0.15%.

The two samples MH14 and MH66 are both type 1 mixed alkali glass and appear to have been made from the same sand source when the proportion of aluminium and titanium oxides are plotted in respect to silica oxides (figure 5). The other two samples are made to a type 2 recipe, but made from different sand sources. MH62 is made from an aluminium rich sand source. However, MH54, while being a glass of similar bulk composition was made from a sand much richer in titanium and lower in aluminum oxides. The plot of REE profile confirms the different sand used in the production of MH54 to the other three samples. Local sand may have been used, but sand was likely specially selected and imported for the higher quality type 1 glass.

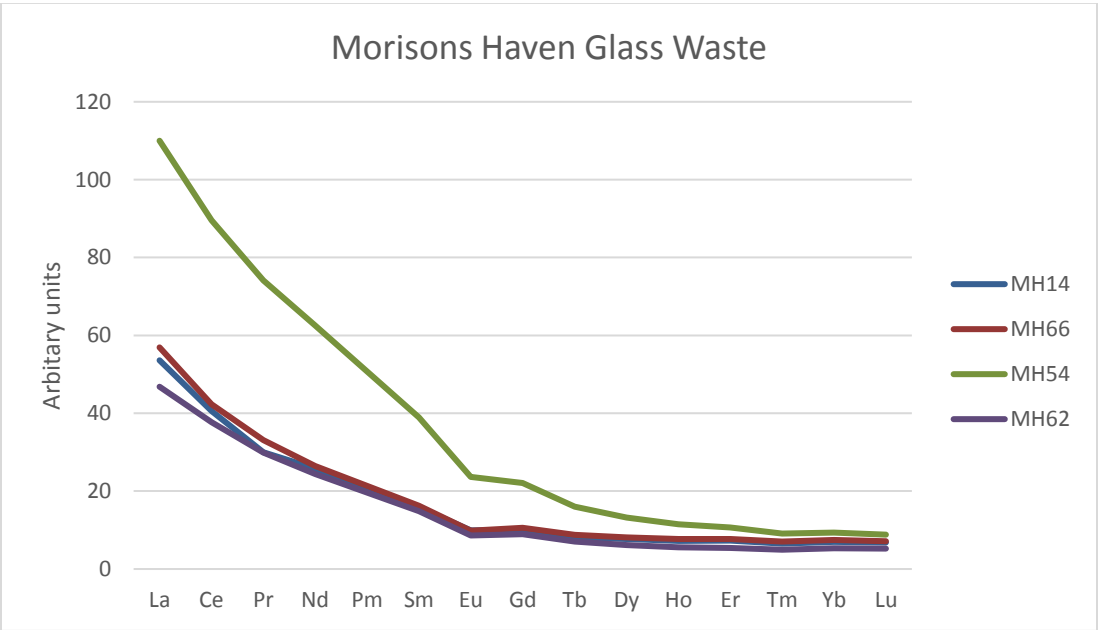
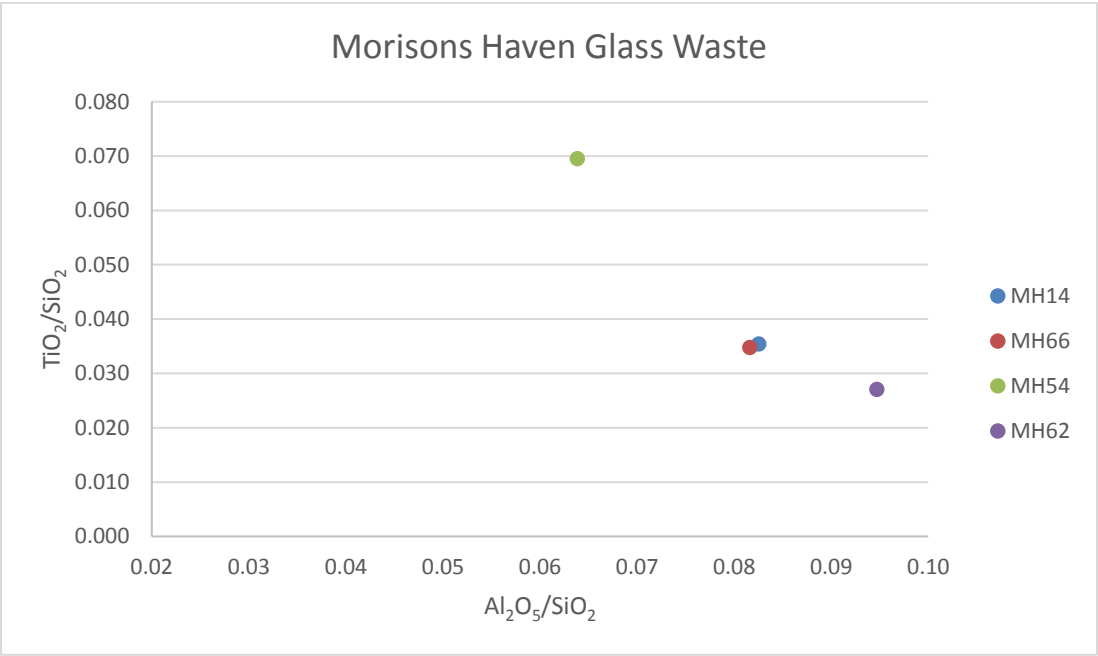


Figure 5 Graphs showing the aluminium and titanium oxide content of the four glass waste samples (in proportion to silica) analysed by LA-ICP-MS and the chondrite normalized REE profile of the four samples

## 8. Conclusions

The glass waste identified is consistent with glass documented as being produced between 1697 and 1727, the final period of glass making at Morison's Haven. The analysis shows that glass was made from a range of raw materials and different glass recipes were used for special products.

A glass was made with sodium rich purified ashes – likely to have been a mixture of imported purified barilla and soap ashes and a sand chosen with fewer impurities as can be seen by the REE and trace element results. This higher quality glass was likely to be used for vessels or plate glass and the production of mirrors by the broad glass technique.

A second type of mixed alkali glass made in part using kelp ashes with strontium (>0.15%) was made for either window, vessel or bottle production. The high level of sodium oxide >5% and low levels of calcium oxide <11% suggest windows were being made from this glass. It is likely that recipes were continually being manipulated to make the best use of available resources. It is possible that using kelp alone as a flux did not produce the desired quality of glass, so kelp was used as one of a number of alkali sources along with soap ashes for instance.

The waste analysed provides no evidence for bottle manufacture using a HLLA recipe using this furnace. However, this does not preclude the making of bottles elsewhere on the site in a different furnace at this time. Indeed the records show that at least two furnaces (large and small) operated on the site before 1708 (Turnbull, 2001) and documentary evidence for the supply of chopkin and mutchkin bottles (NAS AC9/219).

The period from the late 17<sup>th</sup> – early 18<sup>th</sup> century was a time of innovation and development in the Scottish glass industry. The documentary evidence shows that the glass manufacture was not continuous at Morison's Haven during this period but stopped and started again as the money to continue the venture ran out and new glass makers took over the tack of the site. There would have been a great deal of experimentation to produce the high quality glass that was desired to be made locally in Scotland at the time, and to make it to the required standard and cost to compete with imports. There would have been a compromise to be made between the use of cheaper local ingredients, such as kelp, and the use of more expensive imported materials such as barilla, in order to produce the specialist glass that was purported to be made at Morisons Haven during this time.

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Table 1: Composition of glass waste from Morisons Haven determined by SEM-EDS (to CaO) and p-XRF (from TiO<sub>2</sub>) – normalized weight % oxides

SAMPLE	type	NaO	MgO	Al2O3	SiO2	P2O5	SO3	Cl	K2O	CaO	TiO2	MnO	Fe2O3	As2O3	Rb2O	SrO	ZrO2	PbO
MH26	Waste	10.96	3.61	0.56	66.49	0.22	0.29	1.41	6.12	10.24	0.01	0.01	0.35	0.01	0.0033	0.06	0.01	0.09
MH66	Waste	10.35	3.50	1.67	67.07	0.18	0.21	0.93	5.92	9.93	0.12	0.01	0.61	n.d.	0.0036	0.07	0.01	0.07
MH50	Waste	8.77	4.06	1.20	69.59	0.60	0.22	n.d.	4.85	9.45	0.02	0.03	0.56	n.d.	0.0032	0.11	0.02	0.08
MH51	Waste	8.09	3.12	2.01	67.20	0.20	0.40	n.d.	6.45	10.89	0.03	0.02	0.44	n.d.	0.0040	0.10	0.01	0.11
MH52	Waste	8.89	3.39	1.43	69.66	0.28	0.19	1.26	5.14	9.77	0.07	0.03	0.91	0.01	0.0034	0.08	0.01	0.01
MH53	Waste	8.45	3.91	1.29	69.31	0.38	0.21	1.33	5.88	9.29	0.04	0.03	0.54	n.d.	0.0040	0.10	0.01	0.11
MH54	Waste	6.29	3.56	4.20	69.30	0.66	0.17	0.68	5.62	8.61	0.07	0.04	1.01	n.d.	0.0050	0.17	0.02	n.d.
MH58	Waste	8.86	3.77	2.76	67.69	0.35	0.06	1.31	4.65	9.33	0.02	0.03	0.95	n.d.	0.0035	0.12	0.02	0.05
MH57	Waste	5.20	3.85	5.38	69.91	0.94	0.18	0.44	5.23	7.39	0.35	0.03	0.89	n.d.	0.0045	0.16	0.02	n.d.
MH60	Waste	3.16	2.04	6.78	76.56	0.80	0.13	0.33	3.87	3.53	0.27	0.06	1.29	n.d.	0.0038	0.27	0.03	n.d.
MH62	Waste	5.55	5.06	1.68	74.01	1.03	0.25	1.14	3.30	7.72	0.13	0.07	0.82	n.d.	0.0028	0.25	0.03	n.d.
MH63	Waste	4.57	4.28	5.41	72.06	1.19	0.11	0.45	3.71	6.81	0.15	0.05	1.57	n.d.	0.0039	0.20	0.02	n.d.
MH64	Waste	7.27	3.49	3.41	72.25	0.79	0.27	0.82	5.29	5.60	0.25	0.05	1.08	n.d.	0.0086	0.19	0.02	n.d.
MH65	Waste	5.06	2.25	4.54	74.60	0.86	0.10	0.10	4.14	4.28	0.66	0.05	2.61	n.d.	0.0053	0.22	0.03	n.d.
MH14	drip	10.56	3.56	1.92	66.81	0.25	0.17	1.04	5.65	9.74	0.08	0.05	1.01	n.d.	0.0042	0.08	0.01	0.14
MH55	Glass layer	6.16	3.26	10.09	66.24	0.66	0.15	n.d.	3.95	6.84	0.04	0.01	2.73	n.d.	0.0033	0.12	0.03	n.d.
	Crucible																	
MH56	Glass layer	3.92	0.68	4.38	80.04	n.d.	n.d.	0.04	4.61	2.71	0.21	n.d.	2.73	n.d.	0.0023	0.10	0.03	n.d.

Crucible

MH59	Glass layer	4.10	0.69	6.88	76.80	0.06	0.13	n.d.	4.41	3.98	0.45	0.02	1.64	n.d.	0.0053	0.09	0.02	n.d.
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Crucible

Table 2 Manufacturer's (Pilkington and DDG) guidance levels of elements in the glass standards alongside p-XRF and SEM-EDX measurements for comparison. Values listed as percentage of oxides.

Sample	Analysis	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	CoO	NiO	CuO	ZnO	As <sub>2</sub> O <sub>3</sub>	BaO	PbO	SrO	ZrO <sub>2</sub>
76C144	<b>Manufacturers Guidance</b>	<b>0.10</b>	<b>0.04</b>	<b>3.9</b>	<b>43.6</b>				<b>29.50</b>	<b>20.60</b>	<b>0.10</b>	<b>0.05</b>	<b>2.10</b>						<b>0.20</b>		<b>0.02</b>	
	p-XRF			3.48	47.81			0.02	29.29	18.18	0.18	0.06	2.18						0.29	0.01	0.02	
	SEM-EDX	0.19	0.11	3.38	45.62	0.02	0.37	0.13	26.58	21.39	0.20	0.00	2.38									
76C145	<b>Manufacturers Guidance</b>		<b>0.05</b>	<b>3.80</b>	<b>40.70</b>				<b>24.90</b>	<b>29.40</b>		<b>0.10</b>			<b>0.10</b>		<b>0.50</b>	<b>0.04</b>		<b>0.16</b>	<b>0.02</b>	
	p-XRF			1.38	23.78		0.15	0.25	19.16	32.87		0.09	0.03		0.10		0.48	0.04		0.16	0.02	
	SEM-EDX	0.40	0.07	4.22	49.70	0.00	0.10	0.15	22.34	23.47	0.05	0.00	0.14									
76C147	<b>Manufacturers Guidance</b>	<b>0.10</b>	<b>0.05</b>	<b>3.80</b>	<b>48.70</b>				<b>14.60</b>	<b>30.10</b>	<b>0.50</b>					<b>1.80</b>	<b>0.07</b>				<b>0.10</b>	<b>0.10</b>
	p-XRF			3.83	55.88			0.04	15.75	30.30	0.44		0.02			1.97	0.07				0.12	0.09
	SEM-EDX		0.03	3.97	52.04	0.01	0.01	0.09	14.58	27.23	0.63	0.14	0.13			1.95						
76C148	<b>Manufacturers Guidance</b>		<b>0.05</b>	<b>3.9</b>	<b>53.8</b>				<b>14.60</b>	<b>25.90</b>		<b>0.20</b>	<b>0.40</b>		<b>0.08</b>	<b>0.07</b>		<b>0.02</b>		<b>0.90</b>	<b>0.02</b>	
	p-XRF			3.51	60.15			0.05	15.20	25.19		0.20	0.40		0.08	0.08				1.15	0.02	
	SEM-EDX		0.03	3.92	57.11		0.06	0.07	14.61	24.14	0.02	0.13	0.37									
76C149	<b>Manufacturers Guidance</b>	<b>0.10</b>		<b>4.20</b>	<b>56.80</b>				<b>14.30</b>	<b>21.50</b>	<b>0.22</b>	<b>1.80</b>	<b>0.00</b>	<b>0.24</b>		<b>0.90</b>					<b>0.02</b>	
	p-XRF			4.33	69.83			0.02	15.21	20.81	0.26	1.99		0.22		0.97						0.02
	SEM-EDX	0.00	0.24	4.19	58.62	0.01		0.13	14.23	20.15	0.05	1.67	0.13	0.20		0.93						
76C150	<b>Manufacturers Guidance</b>	<b>9.50</b>	<b>6.60</b>	<b>4.30</b>	<b>55.40</b>				<b>1.50</b>	<b>21.90</b>			<b>0.30</b>	<b>0.09</b>			<b>0.10</b>				<b>0.02</b>	<b>0.20</b>
	p-XRF		5.29	3.62	61.97			0.05	1.51	22.82			0.31	0.08			0.10				0.02	0.18
	SEM-EDX	8.37	6.52	3.60	55.05	0.00	0.00	0.10	1.65	24.33	0.14	0.33	0.55									
76C151	<b>Manufacturers Guidance</b>	<b>5.00</b>	<b>3.20</b>	<b>3.90</b>	<b>56.0</b>	<b>3.90</b>			<b>7.20</b>	<b>19.00</b>	<b>0.20</b>	<b>0.50</b>	<b>0.31</b>			<b>0.10</b>		<b>0.08</b>		<b>0.70</b>	<b>0.02</b>	

	p-XRF		2.76	3.45	65.1	4.00		0.07	7.06	18.03	0.15	0.48	0.27		0.10	0.05	0.91	0.02	
	SEM-EDX	5.40	3.43	3.45	57.0	4.52	0.27	0.02	7.46	17.08	0.25	0.62	0.59						
<b>76C158</b>	<b>Manufacturers Guidance</b>		<b>0.06</b>	<b>3.80</b>	<b>42.60</b>				<b>24.20</b>	<b>28.40</b>		<b>0.11</b>		<b>0.10</b>	<b>0.50</b>	<b>0.05</b>	<b>0.14</b>	<b>0.02</b>	
	p-XRF			4.56	52.58			0.02	26.63	28.83		0.14	0.02	0.11	0.55	0.04	0.18	0.03	
	SEM-EDX	0.13	0.08	3.82	45.36	0.00	0.05	0.05	24.33	26.42	0.00	0.10	0.00						
<b>76C159</b>	<b>Manufacturers Guidance</b>		<b>0.07</b>	<b>3.90</b>	<b>44.00</b>				<b>14.50</b>	<b>34.90</b>	<b>0.50</b>	<b>1.00</b>	<b>0.11</b>		<b>0.50</b>		<b>0.50</b>	<b>0.03</b>	
	p-XRF			4.90	56.84			0.11	15.04	32.17	0.43	1.04	0.13	0.48			0.56	0.03	
	SEM-EDX	0.10	0.02	4.44	53.01	0.06	0.14	0.30	13.94	26.56	0.58	1.11	0.17						
<b>77C33</b>	<b>Manufacturers Guidance</b>	<b>21.70</b>		<b>4.10</b>	<b>48.70</b>				<b>0.00</b>	<b>22.60</b>	<b>0.12</b>	<b>0.05</b>	<b>2.50</b>				<b>0.20</b>	<b>0.02</b>	
	p-XRF			3.41	57.73			0.13	0.03	24.87	0.19	0.06	2.69				0.14	0.02	0.03
	SEM-EDX	19.07	0.32	5.01	51.86	0.00	0.02	0.00	0.23	21.23	0.25	0.09	2.26						
StandardGlas II	<b>Manufacturers Guidance</b>	<b>13.78</b>	<b>3.40</b>	<b>0.10</b>	<b>72.26</b>	<b>0.27</b>	<b>0.00</b>	<b>0.00</b>	<b>10.05</b>	<b>0.03</b>	<b>0.02</b>								
	p-XRF		1.67	0.00	73.08	0.41	0.08	0.01	9.67	0.03	0.05								
	SEM-EDX	12.20	3.31	0.05	74.07	0.27	0.00	0.04	10.13	0.02	0.04								
Standard Glas I	<b>Manufacturers Guidance</b>	<b>14.95</b>	<b>4.18</b>	<b>1.23</b>	<b>71.72</b>	<b>0.44</b>	<b>0.00</b>	<b>0.38</b>	<b>6.73</b>	<b>0.14</b>	<b>0.19</b>								
	p-XRF	0.00	2.21	0.67	73.58	0.63	0.09	0.33	6.53	0.12	0.18								
	SEM-EDX	14.61	4.32	1.44	72.67	0.48	0.00	0.35	6.04	0.09	0.20								

Table 3 Trace element composition of four samples analyzed by LA-ICP-MS (ppm)

	MH14	MH66	MH54	MH62
59Co	14.0	12.0	20.0	16.0
60Ni	48.0	40.0	61.0	43.0
63Cu	33.0	27.0	44.0	11.0
66Zn	34.0	42.0	77.0	57.0
69Ga	8.0	7.9	12.0	4.9
72Ge	2.6	3.5	2.9	1.5
75As	10.0	9.4	26.0	41.0
85Rb	25.0	26.0	30.0	11.0
88Sr	639.0	611.0	1447.0	2214.0
89Y	10.0	9.2	14.0	6.4
90Zr	57.0	57.0	77.0	78.0
93Nb	3.4	3.3	3.9	2.6
95Mo	1.5	1.5	0.8	0.3
107Ag	0.0	0.0	0.0	0.1
111Cd	0.1	0.1	0.1	0.1
118Sn	2.5	3.5	4.0	6.0
121Sb	0.3	0.3	0.4	0.5
133Cs	0.5	0.5	1.0	0.2
137Ba	102.0	95.0	137.0	70.0
139La	11.0	9.9	19.0	8.2
140Ce	21.0	19.0	40.0	17.0
141Pr	2.5	2.3	5.1	2.0
146Nd	9.7	8.9	21.0	8.2
147Sm	1.9	1.8	4.2	1.6
153Eu	0.5	0.4	1.0	0.4
157Gd	1.7	1.6	3.2	1.3
159Tb	0.3	0.2	0.4	0.2
163Dy	1.6	1.5	2.4	1.1
165Ho	0.3	0.3	0.5	0.2
166Er	1.0	0.9	1.3	0.6
169Tm	0.1	0.1	0.2	0.1
172Yb	0.9	0.9	1.1	0.6
175Lu	0.1	0.1	0.2	0.1
177Hf	1.5	1.5	2.0	2.0
181Ta	0.2	0.2	0.2	0.2
182W	0.5	0.5	0.3	0.1
208Pb	11.0	19.0	34.0	53.0
209Bi	1.2	1.0	2.2	1.5
232Th	2.0	2.0	3.0	1.6
238U	2.8	2.4	4.9	5.2





