Regional patterns in medieval European glass composition as a provenancing tool

L. W. Adlington*[1], I. C. Freestone[1], J. J. Kunicki-Goldfinger[2], T. Ayers[3], H. Gilderdale Scott[3], A. Eavis[4]

*Corresponding author laura.adlington.12@ucl.ac.uk

[1] Institute of Archaeology UCL, 31-34 Gordon Square, London WC1H 0PY

[2] Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

[3] Department of History of Art, University of York, Heslington, York, YO10 5DD

[4] English Heritage, The Engine House, Fire Fly Avenue, Swindon SN2 2EH

Keywords

Medieval glass, legacy data, elemental analysis, stained glass window, glass mirror.

Highlights

- Regional compositions of medieval glass systematically established for the first time
- Simple diagrammatic provenancing tools based upon major element composition
- Provenancing of window glass now feasible
- Change in source of glass used in England by 1400 CE
- Explanation offered for dominance of German mirror glass

This article has been accepted for publication to the Journal of Archaeological Sciences and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the published version. Please cite this article as DOI: 10.1016/j.jas.2019.104991

Abstract

A legacy dataset of 1329 major element analyses of medieval glass (12^{th}-15^{th} centuries) has been compiled and analysed for geographical distribution of compositional characteristics. Three regional compositional types may be distinguished using simple elemental plots, associated with glass production in northwestern France, in the region around the Rhine, and in central Europe. Distribution maps are presented to aid interpretation and use of the data. The application of the approach is illustrated through three case studies. Late thirteenth-early fourteenth century medieval stained glass from York Minster (n=91), late fourteenth-century stained glass from New College Oxford (n=79) and a single medieval mirror found in Egypt were analysed using scanning electron microscopy–energy dispersive analysis. The York coloured and white glasses were identical and consistent with an origin in NW France. In the late fourteenth century, the coloured glass samples from Oxford were from the Rhenish region, while the white glass is consistent with an origin in NW France or England. The mirror glass from Egypt is of central European origin, and similar mirror glass is known from Italy. The apparent dominance of German mirror production may reflect an advantage of the glass, which is low in iron. The meta-analysis of the legacy data shows significant potential for developing an understanding of the production and movement of medieval glass.

1 Introduction

Glass production in the medieval period was a large industry; in central Europe alone, it has been estimated that about 40,000 tonnes of glass were produced between 1250 and 1500 (Wedepohl, 2003). The demand for glass was in large part due to a dramatic increase in church building during the Gothic period, an architectural style that was characterised by large openings for windows to maximise light (Bony, 1983; Nussbaum, 2000; Philippe, 1998; Scott, 2003; von Simpson, 1962; Wilson, 1990). The sources of window glass and other artefacts are often not evidenced in documentary sources. An understanding of the compositions of medieval window glass and other glass artefacts can lead to important information about technology and trade during the medieval period.

Medieval treatises describe the recipe of sand and the ashes of trees and terrestrial plants such as ferns (Theophilus in Hawthorne and Smith, 1979; Eraclius in Merrifield, 1967), which results in a glass characterised by high potassium and calcium, relatively low silica, and moderate concentrations of sodium, magnesium, phosphorus, manganese, alumina, and iron (Freestone, 1992). Compositions of this "forest glass" are highly variable relative to the variability of the soda-lime-silica glasses of the Mediterranean and Middle East, reflecting the high variability in the composition of wood ash.

Numerous factors affect the ash composition; one of the foremost of these is the underlying substratum upon which the plant grew (Drobner and Tyler, 1998; Meiwes and Beese, 1988; Sanderson and Hunter, 1981; Stern and Gerber, 2004; Turner, 1956). Other factors also impact the composition of the wood ash, including the plant species (such as different types of tree, or the use of fern or bracken), as well as time of harvest (seasonally and year to year) and the part of the tree/plant used (for example, trunk versus bark; Jackson et al., 2005; Jackson and Smedley, 2008, 2004; Stern, 2017; Turner, 1956; Wedepohl, 1998; Wedepohl and Simon, 2010). Regional variations in glassmaking technology also affect the glass composition; for example, Cilová and Woitsch (2012) argue that addition of refined potash to the batch was practiced in Bohemian glass production.

In light of this, it seems likely that regional geology, regional availability of different plant species (requiring variations on the basic recipe) and regional technological traditions may result in identifiable regional patterns in forest glass composition. Characterisation of such trends would be a powerful tool for provenancing glass; this is particularly the case for a region such as England where the absence of evidence for local production of coloured glass, coupled with documentary evidence for glass importation, has led to the view that all coloured glass was imported from Europe (Marks, 1993). Furthermore, there is likely to have been inter-regional exchange of glass in continental Europe; potash rich glasses of northern character are found in southern regions (e.g. Alonso et al., 2007). Therefore, an elucidation of regional trends in glass composition is likely to have wide application. Some observations on regional variations have been made previously: most notably, Barrera and Velde (1989) published a detailed study of French compositions, looking at both regional and chronological trends; Wedepohl (2003) observed differences between French and German glass; and Brill and Pongracz (2004) noted similarities between glass from French contexts and glass found in England. In spite of these important contributions, no formal synthesis of European glass compositions exists to our knowledge, and the constraints of modern national borders on research agendas may have confused current understanding as the situation in the medieval period was very different.

This paper provides a synthesis of data from a range of sources to form a picture of regional characteristics of the potash-rich forest glass typical of production north of the Alps during the medieval period. As a demonstration of the application of this approach, three previously unpublished case studies involving different types of medieval glass are presented, comprising two English stained glass window campaigns and a glass mirror found in Egypt.

2 Regional variation in glass compositions

2.1 Meta-analysis of legacy data

The making of forest glass marks a change in glass-making technology that occurred in northern Europe around the end of the first millennium, with technological changes that saw not only a shift in raw materials from soda-rich natron to potash-rich wood or fern ashes, but also changes in production location, furnace design and types of products (Charleston, 1978; Jackson and Smedley, 2008; Thorpe, 1949). The present meta-analysis of legacy data focuses on forest glass of the 12th through the 15th centuries, a period which coincides with the development of Gothic architecture and the related surge in glass production through to the end of the medieval period (Philippe, 1998; Wedepohl, 2003). Compositional data for forest glass predating this period are more scarce and it is less well-defined chemically (Barrera and Velde, 1989; Wedepohl and Simon, 2010; for early forest glass data, see also Sterpenich and Libourel, 2001; Van Wersch et al., 2016) and archaeological evidence for glass production is similarly comparatively scarce before the 12th century (Foy, 2000; Philippe, 1998).

Regional studies on glass compositions in Germany (Wedepohl and Simon, 2010), Bohemia/Czechia (Smrček, 1999), France (Barrera and Velde, 1989) and Belgium (Schalm et al., 2007) have noted similar chronological changes during the period of interest: silica concentrations increase slightly, potash concentrations drop, and lime contents increase (or increase relative to potash concentrations). The early fifteenth century appears to be a particularly transitional period for medieval glass-making technology; two of these studies (Schalm et al., 2007; Wedepohl and Simon, 2010) use the year 1400 to divide chronological glass types, while Barrera and Velde (1989) use the year 1450. This transition towards the widely recognised high lime low alkali (HLLA) glass type is a technological development that became increasingly established in the post-medieval period. Aside from the recognition in the legacy data of the HLLA type, defined here as glass with $CaO/[CaO+K_2O]$ greater than about 0.75, and with less than about 10% alkali (K_2O+Na_2O; e.g., Type I in Brill and Pongracz, 2004; Schalm et al., 2007, 2004; Wedepohl and Simon, 2010), chronological changes in composition are not specifically addressed in this paper due to the widely varying precision of dating in the published sources.

2.2 Methods

Major element data for forest glass of the 12th through the 15th centuries (*n*=1329) were gathered from 36 sources (Table 1). Data with Na_2O greater than 6% (following Barrera and Velde, 1989) or with PbO higher than 2% were excluded. The data include both archaeological glass (including window glass, vessels, and production waste) and *in situ* windows in Europe (with a focus on areas north of the Alps). For English contexts, only data for white glass (i.e., colourless or unintentionally tinted glass) from archaeological glass-making sites were included, due to the current understanding that coloured glass was not being made in this country during the medieval period (see above). Some of the data were originally published as mean values, and therefore had only general provenance; for example, Schalm (2007) published mean values for different groups of glass from various buildings in Belgium.

Visual inspection and graphical analysis of the dataset suggested that it includes three major compositional groupings; key differences between these were explored and discriminatory thresholds for individual elements or simple oxide ratios determined. These thresholds were used in the spatial exploration of the data, but are not intended as definitive boundaries for defining compositional typologies; we seek only to acknowledge regional patterns or trends.

Data are displayed as pie charts to show the proportion of glass with different characteristics (e.g., high or low phosphate contents) at different sites, constructed using QGIS software and Natural Earth Vector data (naturalearthdata.com). Data from sites in close proximity were combined into a single locality for better visualisation and to minimise overlap, to give a total of 78 localities each representing a city, a site or a cluster of sites. The number of samples at each locality was scaled logarithmically (base 10) to allow for the disparity in the numbers (from 1 to 223), and the size of the pie charts on the maps was based on this scaling.

Compositional trends of different regions are also presented in scatterplots, and so the distortion of the results due to unequal sample numbers at different localities was a concern. Three localities in particular offer very high numbers of samples: two localities in Belgium (Raversijde, *n*=223, and various unspecified sites, *n*=135) and Paris (*n*=213). The data from the Belgian localities were published as groups/types defined by the authors, with only the mean composition for each group reported (Schalm et al., 2007, 2004); the sample numbers given in Table 1 and used to scale the pie charts reflect the total number of samples at those sites. However, the scatterplots show only the reported means of the eight groups from Raversijde and the four groups from various Belgian sites. The Paris locality, on the other hand, reflects a cluster of several sites within Paris and the nearby vicinity with data from seven published sources and dates spanning several centuries. The Paris sites were initially examined separately to ensure the high number of data points would not distort trends in scatterplots, and no differences were observed between the Paris locality and the surrounding region of NW France (see next section). Therefore, distortion of the results due to unequal sample numbers at different localities is expected to be minimal.

2.3 Regional patterns in composition

Three regional compositions of forest glass were identified (Fig. 1): the western and central area of northern France (in keeping with Barrera and Velde, 1989); the region surrounding the Rhine and its tributaries, and to the East, central Europe including much of modern Germany. Glass produced in England tends to have similar characteristics to glass found in NW France, but potentially distinguishing trends are noted below. Magnesia and phosphate contents were found to be most diagnostic of regional provenance, although there are observable trends in lime, silica, soda and potash contents (Figs. 2-4).

Magnesia and lime contents show an inverse relationship, with a *low-lime high-magnesia* group (LLHM) and a *high-lime low-magnesia* group (HLLM). These groups have been recognised previously (Freestone et al., 2010; Kunicki-Goldfinger et al., 2014) but the present analysis indicates that they are strongly related to geographical findspot (Fig. 2, using a cut-off of MgO/CaO = 0.24), with the LLHM type concentrated in NW France and England, and the HLLM type concentrated in the Rhenish region and central Europe.

Phosphate concentrations are also strongly related to geographical findspot, with glass in NW France, England, and the Rhenish region typically showing phosphate concentrations greater than about 2% P_2O_5, while glass found in central Europe has less than about 2% P_2O_5 (Fig. 3). Within the high phosphate grouping, it is also observed that the majority of glass found in the Rhenish region and in England tends to have less than 4% P_2O_5, while glasses found in NW France have up to 6% P_2O_5. Glass found in central Europe is also characterised by lower silica (most with less than 50% SiO_2 (Fig. 3).

Glass found in NW France and England generally has higher concentrations of soda, ranging from about 0.5% to 4% Na_2O, while Rhenish glass and glass in central Europe generally have less than 1% Na_2O (Fig. 4). The exception here is HLLA glass, which is often found to have Na_2O contents in excess of 1%, perhaps added as sodium chloride to offset the low alkalinity of the potash-poor recipe (Gerth et al., 1998; Kunicki-Goldfinger et al., 2009; Schalm et al., 2007; Wedepohl and Simon, 2010). Glass found in central Europe has high potash contents, above about 17% K_2O and up to about 27%, while most of the glasses found in NW France, England and the Rhenish region have less than 20% K_2O (Fig. 4), a situation which may be explained by the addition of potash to the batch in central Europe (Cílová and Woitsch, 2012; Stern, 2017).

3 Provenancing medieval glass: case studies

3.1 Analytical Methods

The three case studies we explore are based upon standardised energy dispersive X-ray analysis in the scanning electron microscope. Although currently less favoured in archaeometric studies because of its high detection limits and the consequent narrow range of elements measurable, SEM-EDS is easily accessed, inexpensive, rapid and can yield accurate major element data suitable for regional studies such as this one. Small fragments were removed from each glass piece, mounted in epoxy resin and polished down to 0.25 µm diamond. They were vacuum coated before insertion in the SEM for analysis.

The window glasses were analysed in the Department of Archaeology, Cardiff University in a CamScan 2040 SEM equipped with an Oxford Instruments ISIS or INCA energy dispersive X-ray spectrometer (SEM-EDS). Analyses were carried out using a beam in raster mode at 500X magnification with a dimension of about 400µm across for 100s with 20kV accelerating voltage. Cobalt optimisation was around 4000 cps. Quantification was carried out by the ZAF method using pure oxide and mineral standards, and oxide weight percents were calculated by stoichiometry. Totals were 98-102% and were normalised to 100% for comparative purposes. Secondary standards Corning D (Adlington, 2017; Brill, 1999) and the ESF-funded medieval glass standards prepared by Pilkington Brothers Ltd for Newton (1977a) were analysed to assess data quality of the analyses; analyses were typically within 6% relative of the accepted compositions and CaO and SiO_2 better than 1%.The mirror glass was analysed in 1994 in the British Museum research laboratories using a JEOL JSM 840 scanning electron microscope equipped with an Oxford Instruments LINK Systems 860 energy dispersive spectrometer. Operating conditions were 35^{o} take-off angle, 15kV accelerating potential and 200s counting livetime with and a beam current of 1.7nA. Quantification was carried out using pure elements, oxides and compounds of known composition. Results on Corning D, analysed at about the same time using the same equipment and conditions, are given by Binski and Freestone (1995), and agreement is good.

The mean results of groups identified are reported with standard deviations in Table 2 and full data for the windows are given in Supp. Table S1.

3.2 *The Chapter House Vestibule Windows, York Minster, UK*

The glazing of the York Minster Chapter House and its vestibule include the earliest known examples in England of the so-called band window, which would become popular in the first half of the fourteenth century (Marks, 1993). Although no documentation survives which describes the construction of the chapter house or its windows, heraldic and stylistic evidence suggests the windows were glazed in the 1290s and 1300s, with the vestibule usually dated to 1300-1307 and the chapter house to the 1290s (Brown, 2003; Marks, 1993).

Two windows in the vestibule (CHn9, CHs7; Fig. 5) were conserved in 2008-2009 by the York Glaziers Trust, during which time 91 pieces of glass were sampled for analysis, including a range of colours (white, amber, yellow, blue, green, murrey, and red).

Excluding four HLLM glasses (two of which are HLLA) that are likely to have been later repairs, all of the analysed colours from the Chapter House vestibule appear to have a similar base glass recipe, with about 6-8% MgO and 13-17% CaO, with high phosphate mostly above 4% P_2O_5 and around 1% Na_2O (Table 2). These are LLHM glasses indicating an origin in NW France or England (Fig. 2). The scatterplots (Fig. 6) confirm this interpretation.

3.3 *Chapel Windows, New College, University of Oxford*

The original windows in the chapel of New College at the University of Oxford were made *c.* 1385 by Thomas Glazier, and commissioned by William of Wykeham, Bishop of Winchester and Chancellor of England (Marks, 1993; Woodforde, 1951). Wykeham, a wealthy patron of high status, is considered to be one of the most important figures in the patronage of medieval stained glass in England (Marks, 1993), and the glass is likely to have been of the highest quality available although the purchase records are not extant. Wykeham is documented to have employed Thomas Glazier for this and the glazing of Winchester College Chapel. Other glass has been related to these sites on stylistic grounds.

Conservation of the medieval glazing began in 2008-2009, during which time 79 pieces of glass from window n6 (Fig. 5) were sampled for analysis, including white, blue, red, pink and yellow glass.

The white and coloured glass pieces from New College have different base glass compositions (Table 2, Fig. 7). The coloured glass pieces are HLLM, with 21-26% CaO and 4-5% MgO. Phosphate contents range from about 2-5% P_2O_5, and soda contents ranging from 0.4-1.5% Na_2O (Fig. 7). The compositions of the coloured glass are broadly consistent with those of glass from the Rhenish region, although some of the phosphate and soda contents are higher: the Rhenish legacy data generally contain 2-4% P_2O_5 and less than 1% Na_2O. However, HLLM glass with 4-5.5% P_2O_5 are also represented in the Rhenish region (Fig. 8). The reds are coloured by simple flashing (Type B, in Kunicki-Goldfinger et al., 2014).

The white glass may be subdivided into two groups, based particularly on phosphate, soda and potash contents. The larger group has lower phosphate (2.8-3.7% P_2O_5), soda (1.9-2.7% Na_2O) and potash (10-14% K_2O), while the smaller group has about 4.7-5.3% P_2O_5, 3.2-3.8% Na_2O and 15.2-16.6% K_2O (Table 2, Fig. 7, Supp. Table S1). On the basis of their magnesia and potash contents, both groups are of the LLHM category, and consistent with an origin in NW France or England. The larger group, however, is also consistent with the trends shown by English glass, in particular in terms of its phosphate, soda and potash concentrations (compare Figs. 2-4 and Fig. 7). We have no final explanation for this grouping at present; it is known, however, that the window was repaired several times in the early fifteenth century. Two HLLA glass pieces were also analysed (one white, one blue, with about 4.2% K_2O, 20.3% CaO, and 3% Na_2O, see Supp. Table S1) and, given the late dating of this glass type, are unlikely to be original to the windows.

3.4 Glass mirror from Egypt

A glass mirror (British Museum 1902,0529.18-19, Fig. 9) with two convex glasses in a hinged pewter case, was acquired by the British Museum in 1902 from Henry Wallis. The provenance of the mirror was listed as el-Azam, in Asyut, Egypt (Kahl, 2007), and dated to the 13th-14th centuries. The mirror and case were studied in 1994 at the request of Dr. Ingeborg Krueger to determine their composition and manufacture (Freestone and Stapleton, 1994, British Museum Department of Science file no. 6343). The openwork case is decorated with a lion and griffin underneath a tree; the glass was backed with molten lead (as in Krueger, 1993) and then painted with minium to create a red background for the openwork of the case (Freestone and Stapleton, 1994).

The composition of the mirror glass is reported in Table 2 and Fig. 10. It is characterised by a notable high potash content of 24.0% K_2O, a low MgO/CaO ratio with 18.5% CaO and 3.3% MgO and low phosphate (1.3% P_2O_5) and silica (47.7%). Its chemical characteristics are therefore closely paralleled by glass found in central Europe.

4 Discussion

4.1 Regional variations

The two western groups we have identified correspond more-or-less to the regions likely to have been supplied by the well-known sources of medieval glass in Normandy (NW France) and somewhere in the Rhenish area, while the East appears related to the traditional glassmaking area centred on Bohemia. Archaeological evidence for glass-making sites in early medieval Europe is rare until about the 12th century, which could be due in part to the operation of production models other than the forest-based glass-house that was dominant in the later medieval period, such as itinerant glass-making, temporary workshops in association with major building works, and production associated with monasteries (Foy, 2000). In France, archaeological finds and archival documentation put Normandy (northwestern France), in particular in the Lyons Forest, at the forefront of the glass-making industry from about the 13th century, which has been linked to the local intensity of royal and ecclesiastical construction (Philippe, 1998). In our Rhenish region, an early, intensive industry is also evidenced in the Argonne Forest, situated in northeastern France and accessible to the river Meuse leading to the Rhine-Meuse-Scheldt delta in the Netherlands (Philippe, 1998). In the forested hills of Bramwald (in Lower Saxony, accessible to the river Weser), a glass-house has been uncovered that dates to the early 13th century and another in the Spessart Mountains (in Bavaria and Hesse, with access to the Rhine) dates to at least 1300 (Schmid et al., 1996; Wedepohl and Simon, 2010). In Bohemia, the earliest archaeological evidence shows glass-making from at least the mid-13th century in mountainous areas such as the Ore Mountains bordering modern-day Germany and Czechia (Černá and Frýda, 2010). Notably, the well-known early 15th century illustration of glass-making from Sir John Mandeville's *Travels* is set in Bohemia (British Library Add. 24189f.16; e.g. Rehren and Freestone, 2015). In England, the two primary areas for glass production during the medieval period (from at least the 13th century) were the Weald and in Staffordshire (Kenyon, 1967; Thorpe, 1949; Welch, 1997); however, the production of coloured glass is not evidenced during the medieval period (see next section).

The regional differences in glass composition observed here reflect the ash components of the glass: K_2O, CaO, MgO and P_2O_5, with the possibility of some variation due to the addition of common salt as an additional fluxing agent. As suggested above, there are a number of potential influences on vegetal ash compositions, including geology, species and technological choice but current understanding supports the view that the major variations reflect different technologies or communities of practice. The high K_2O and low P_2O_5 contents of central European glass are consistent with the addition of refined potash as a third component to the more widely recognised ash-sand recipe, as is documented from at least the eighteenth century and suggested, for example, by Cilova and Woitsch (2012) and also by Stern (2017). The differences between the HLLM glasses of the Rhenish area and the LLHM glasses of France are less easy to interpret but might reflect the dominance of the ashes of different species: for example bracken in France and England (Smedley and Jackson, 2006, 2002) as opposed to beech in the Rhenish region (Theophilus; Hawthorne and Smith, 1979). The higher lime content of the HLLM glass would have required higher melting temperatures (Jackson and Smedley, 2004) and it seems possible that the medieval ceramic industries of the Rhineland, renowned for the production of salt-glazed stoneware (Gaimster, 1997) and high-fired refractory crucibles (Martinón-Torres et al., 2008), provided the pyrotechnological framework within which it was developed. However, whatever the origins of the compositional differences observed, they are reasonably consistent over a single region and the logical explanation is that this reflects the characteristics imparted by the dominant manufacturing process and raw materials used in each region. Therefore we may use these regional variations to make sensible suggestions about the regions of origin of the glass analysed.

The results of the meta-analysis of legacy data appear robust; the number of sites is relatively large so that, should we have missed several sites in regional literature to which we do not have easy access, the fundamental pattern should not be substantially affected. However, this research will benefit from further investigation, as the number of data is quite small and there was no distinction between archaeological kiln sites, window glass and vessels. Furthermore, there are likely to be chronological changes in composition which our approach has obscured; we do not expect these to affect the overall regional pattern, but as more data are added it will be possible to add a more detailed chronological dimension to the analysis.

A further observation is the low degree to which trade disseminated the regional types, in particular between NW France and the other regions. This may have been due to access (and the use of a nearby glass producer) and/or a result of the political landscape of Europe at the time. It is worth noting that the boundary imposed for the purposes of this paper between NW France and the Rhenish region is close to the western border of the Holy Roman Empire during this period (Fig. 1).

4.2 English windows of the thirteenth and fourteenth centuries

The current consensus on the origins of stained glass in English churches is that all coloured glass was imported from continental Europe during the later medieval period. A 1449 patent to John Utynam for making coloured glass and teaching others the craft states "the said art has never been used in England" (Marks, 1993, p. 30). No evidence of coloured glass production has been found at archaeological kiln sites, although the production of white glass (i.e., colourless or unintentionally tinted) was practiced in both the Weald in south-eastern England and further north in Staffordshire (Midlands) from at least the fourteenth century (Kenyon, 1967; Marks, 1993; Welch, 1997). The limited historical documentation available indicates that England's two principal sources for coloured window glass were "Rhenysh", or glass from areas along the Rhine and its tributaries and which was transported along it to the North Sea, and Normandy glass, which was exported from Rouen (Knowles, 1936; Marks, 1993). Normandy glass appears to have been regarded as superior to Rhenish glass: it was more expensive and, for example, ordinances of the Saint Luke guild in late fifteenth century Antwerp dictated that only glass from Normandy was to be used by its members for stained glass windows, presumably because of its higher quality (Caen et al., 2006; Marks, 1993).

Both the coloured and the white glass of c.1300 from the Chapter House vestibule at York have compositions consistent with production in NW France or England and are most likely French in origin. Close comparison of the position of the Chapter House glasses in Fig. 6 with the glasses from English production sites shown in figs 2, 3 and 4, indicates that the

York glasses have higher phosphate and lower silica and are more consistent with the French glass. The relatively narrow range of compositions (Fig. 6) is consistent, in our present state of understanding, with a single source and the importation of one or more consignments of glass from a single supplier.

The results from the New College window, constructed about one hundred years later in the late fourteenth century, are very different. There is a marked compositional difference between the white glasses, which are of the LLHM type, corresponding to a French or English origin, and the coloured glasses, which are HLLM with high phosphate and therefore probably Rhenish (Fig. 7, Fig. 8). Although the data are not an exact parallel for the majority of the Rhenish glass, they are consistent with a small subset of HLLM glass found in the Rhenish region with 4-5.5% P_2O_5 and moderate concentrations of Na_2O (Fig. 8). The date of the New College window (c. 1385) appears to fall at a transitional period in English window glass compositions, which may suggest a chronological explanation for the compositional deviations. Previously published data of English window glass, from various buildings but primarily from York, Canterbury, Oxford and Coventry (Brill, 1999, 1970; Freestone et al., 2010; Gillies and Cox, 1988; Kunicki-Goldfinger et al., 2014; Newton, 1977b, 1976; Pollard, 1979) show a general change from LLHM to HLLM coloured glass in England around the end of the 14^{th} century (Fig. 11), while the white glasses retain the earlier LLHM composition. At about the same time, the technology of the red glass changes from multi-layered to simple flashing, leading to the suggestion that these changes reflected two technological changes in European glassmaking (Kunicki-Goldfinger et al., 2014). However, the current findings point to a more complex situation.

The continuation of LLHM glass in Normandy and England in the form of white (uncoloured) glass, does not suggest a blanket technological change, but that the main source of coloured glass switched in the late fourteenth century from Normandy to the Rhenish area. Political upheavals associated with the Hundred Years War and the accessibility of Norman glass offer one possible explanation. Another possibility is that the combination of the devastation of the Black Death and the pressures exerted by the War (e.g., Gottfried, 2010) caused a major downturn in glass-making in Normandy and perhaps a loss in skills and/or access to colourant materials such as cobalt, which was obtained from Saxony (Gratuze, 2013; Gratuze et al., 1995). In the 14^{th}-15^{th} centuries, a relative “boom” of production in the Rhenish region is suggested by the enormous and steady increase in the number of glass-houses documented from century to century, especially in the Lorraine (Philippe, 1998). The intensity of glass-making activity, for coloured glass production in particular, seems to have shifted to areas near the Rhine, perhaps Lorraine or the Argonne Forest. This topic requires further study.

Turning to the origins of the white glass in the New College window, it has been observed that it falls into two groups, the larger of which is consistent with the products of English glass houses. It is tempting to see a complete shift away from glass made in Normandy so that coloured glass was imported from the Rhenish region and white glass obtained from English sources. This possibility again requires more detailed investigation, but would be consistent with the increase in white relative to coloured glass which occurs in English windows in the latter part of the fourteenth century (Marks 1993).

4.3 Mirror glass

Although found in Egypt, the composition of the medieval mirror glass is unlike contemporary glass being produced in the Mediterranean, which was made with the soda-rich ashes of marine plants (e.g., Fenzi et al., 2009; Foy, 1985); instead it resembles compositions found in central Europe, which would be consistent with documentary evidence for a widespread demand for glass mirrors from Germany (Krueger, 1993, 1990). The production of glass mirrors was organised within the guild system in Nuremberg by 1373, and German mirrors were exported widely, as evidenced by Venetian regulations on the importation of the mirrors in 1446 (Krueger, 1993, 1990; Schechner, 2005). Close parallels in composition can be found in small decorative glass mirrors used by the painter Giotto (end of 13th century to the early 14th century) in various works in Padua, Florence and Assisi (Santopadre et al., 2002). The glass mirrors of this period were usually convex, made by blowing large glass bubbles, coating the inside with molten lead, and then allowing the glass and metal to harden before cutting (Krueger, 1993, 1990). Ethnographic parallels are known from India (Kock and Sode, 2002).

The popularity of these mirrors suggests that there were skills involved that were specific to German glass-makers, perhaps in spreading the thin lead layer, or that there was some chemical property inherent in the glass that made it better suited to the purpose. One possible explanation is that central European glasses tend to have lower concentrations of iron compared to the other regions producing forest glass (Fig. 12, Table 3). Elevated concentrations of iron result in a green or blue tint even in so-called "white" or "colourless" glass and would furthermore reduce the transmission of light, overall ruining the desired effect of the mirror. It may be that German glass mirrors were preferred as the glass was nearly colourless.

An attempt by Venetian glass-makers to learn the craft of mirror making from a German master craftsman was recorded in 1318, however this enterprise failed (Schechner, 2005). Although the details of why it failed are unknown, it is possible that the low iron content of the central European glass could not be replicated, even with the selection of the same plant species and the same technical processes carried out, due to regional variation in composition that was outside the control of the medieval glass-maker. It was not until about 1500, by which point Venetian glass-makers had developed the highly clear and colourless *cristallo* glass, that they began to produce Venetian flat glass mirrors, surpassing the German products (McCray, 1998; Schechner, 2005).

5 Conclusions

This survey of the compositions of medieval forest glass has allowed the discrimination between three compositional groups of glass that correspond to the three main known regions of medieval glass production, NW France and England, the Rhine and its environs, and Central Europe. These groups may be differentiated by the major components associated with vegetal ash: the oxides of Ca, K, Mg, P and Na.

Three case studies have demonstrated the likely dependence of glazing c.1300 upon coloured glass from France; a major switch in the source of coloured glass to the Rhenish area in the fourteenth century, and the greater reliance on white window glass made in England by this time. In addition, we have shown that a mirror found in Egypt originated in Central Europe, and we suggest that mirror glass in frescoes by Giotto in Italy is also Central European. The data suggest that one reason for this apparent dominance of German mirrors may be the lower iron content of the glass.

This analysis of legacy data allows a wide range of questions about medieval glass production and sourcing to be addressed and for the first time places the study of medieval glass composition in a systematic context. We have depended upon major elements in our analysis. While trace elements and isotopes will be required to test some of these ideas and explore them in more depth, it appears that data obtained using relatively accessible methods are sufficient to address the wider issues. In this context, we have previously demonstrated that the discrimination between HLLM (Rhenish) coloured glasses and LLHM (French/English) white glass is readily attainable with standardised handheld pXRF (Adlington and Freestone, 2017), using a few elements such as Rb, Sr and Zr, which opens up the possibility of large scale survey of in situ medieval window glass.

This approach provides a tool for archaeologists, historians and art historians interested in medieval industries and the medieval economy. Furthermore, it is potentially important for art-historical investigations as many windows in museums and collections have been repaired with medieval glass taken from other windows, frequently of very diverse origins and it will allow this to be recognised. Finally, it offers a tool to further understanding of why windows in different locations corrode at very different rates and will be of value in preventive conservation.

Acknowledgements

This work was funded by a UCL Graduate/Overseas Research Scholarship to L W Adlington and a Leverhulme Trust Project grant to I C Freestone and T Ayers. We thank the British Museum for permission to publish the analysis of the mirror. We are grateful to the Dean and Chapter of York Minster for permission to analyse the York Minster glass, and Mr Nick Teed and the staff of the York Glaziers Trust for their help in sampling. The referees are thanked for their helpful comments, which allowed us to improve the paper.

References

Adlington, L.W., 2017. The Corning Archaeological Reference Glasses: New Values for "Old" Compositions. Pap. from Inst. Archaeol. 27, 1–8.

Adlington, L.W., Freestone, I.C., 2017. Using handheld pXRF to study medieval stained glass: A methodology using trace elements. MRS Adv. 2, 1785–1800. https://doi.org/10.1557/adv.201

Alonso, M.P., Capel, F., Valle Fuentes, F.J., De Pablos, A., Ortega, I., Gómez, B., Respaldiza, M.A., 2007. Caracterización de un vidrio rojo medieval procedente de las vidrieras del Monasterio de las Huelgas de Burgos. Bol. La Soc. Española Cerámica Y Vidr. 48, 179–186.

Barrera, J., Velde, B., 1989. A study of french medieval glass composition. Archéologie Médiévale XIX, 81–130.

Binski, P., Freestone, I.C., 1995. The technique of the Westminster Retable: a preliminary report with an analysis of the glass components, in: Malmanger, M., Berczelly, L., Fuglesang, S.H. (Eds.), Norwegian Medieval Altar Frontals and Related Material. Giorgio Bretschneider, Rome, pp. 59–69.

Bony, J., 1983. French Gothic Architecture of the Twelfth and Thirteenth Centuries. University of California Press, Berkeley.

Brill, R.H., 1999. Chemical analyses of early glasses. Corning Museum of Glass, Corning, NY.

Brill, R.H., 1970. Scientific Studies of Stained Glass: A Progress Report. J. Glass Stud. 12, 185–192.

Brill, R.H., Pongracz, P., 2004. Stained glass from Saint-Jean-des-Vignes (Soissons) and comparisons with glass from other medieval sites. J. Glass Stud. 46, 115–144.

Brown, S., 2003. 'Our Magnificent Fabrick': York Minster: An Architectural History c. 1220-1500. English Heritage, Swindon, UK.

Caen, J., De Munck, B., De Laet, V., 2006. Technical Prescriptions and Regulations for Craftsmen in the Southern Netherlands during the Sixteenth, Seventeenth and Eighteenth Centuries. A Confrontation of Archival and Material-Technical Information regarding Glazing and Stained-Glass Windows, in: Lagabrielle, S. (Ed.), Verre et Fenêtre Del'antiquité Au 18e Siècle: Actes Du Premier Colloque International de l'association Verre et Histoire (Paris-La Défense / Versailles, 13-14-15 Octobre 2005).

Verre et Histoire, Paris.

Calligaro, T., 2008. PIXE in the study of archaeological and historical glass. X-Ray Spectrom. 37, 169–177. https://doi.org/10.1002/xrs

Carmona, N., Villegas, M.A., Navarro, J.M.F., Ferna, J.M., 2006. Study of glasses with grisailles from historic stained glass windows of the cathedral of León (Spain). Appl. Surf. Sci. 252, 5936–5945. https://doi.org/10.1016/j.apsusc.2005.08.023

Černá, E., Frýda, F., 2010. Sklo vrcholného středověku – současný stav a perspektivy studia historických technologií. Archaeol. Hist. 35, 335–357.

Charleston, R.J., 1978. Glass furnaces through the ages. J. Glass Stud. 20, 9–33.

Cílová, Z., Woitsch, J., 2012. Potash - A key raw material of glass batch for Bohemian glasses from 14th-17th centuries? J. Archaeol. Sci. 39, 371–380. https://doi.org/10.1016/j.jas.2011.09.023

Cílová, Z.Z., Kučerová, I., Knížová, M., Trojek, T., 2015. Corrosion damage and chemical composition of Czech stained glass from 13th to 15th century. Glas. Technol. Eur. J. Glas. Sci. Technol. Part A 56, 153–162. https://doi.org/10.13036/17533546.56.5.153

Drobner, U., Tyler, G., 1998. Conditions controlling relative uptake of potassium and rubidium by plants from soils. Plant Soil 201, 285–293. https://doi.org/10.1023/A:1004319803952

Fenzi, F., Mendera, M., Vigato, A., 2009. Technology of medieval and renaissance glass in Tuscany (Italy): an interdisciplinary approach to the study of production indicators, in: Janssens, K. (Ed.), Annales Du 17e Congrès de l'Association Internationale Pour l'Histoire Du Verre, Anvers 2006. pp. 326–332.

Foy, D., 2000. Technologie, géographie, économie: les ateliers de verriers primaires et secondaires en Occident. Esquisse d'une évolution de l'Antiquité au Moyen Âge, in: La Route Du Verre. Ateliers Primaires et Secondaires Du Second Millénaire Av. J.-C. Au Moyen Âge. Colloque Organisé En 1989 Par l'Association Française Pour l'Archéologie Du Verre (AFAV) Lyon : Maison de l'Orient et de La Méditerranée Jean Pouilloux. pp. 147–170.

Foy, D., 1985. Essai de typologie des verres medievaux d'apres les fouilles provencales et languedociennes. J. Glass Stud. 27, 18–71.

Freestone, I.C., 1992. Theophilus and the composition of medieval glass, in: Vandiver, P.B. (Ed.), Materials Issues in Art and Archaeology III: Symposium Held April 27-May 1, 1992, San Francisco, California, U.S.A. Materials Research Society, pp. 739–745.

Freestone, I.C., Kunicki-Goldfinger, J.J., Gilderdale-Scott, H., Ayers, T., 2010. Multidisciplinary Investigation of the Windows of John Thornton, Focusing on the Great East Window of York Minster, in: Shepherd, M.B., Pilosi, L., Strobl, S. (Eds.), The Art of Collaboration: Stained-Glass Conservation in the Twenty-First Century. The International Committee of the Corpus Vitrearum for the Conservation of Stained Glass, London, pp. 151–158.

Freestone, I.C., Stapleton, C.P., 1994. Report on the Examination of a Medieval Mirror [Unpublished Report, British Museum Department of Science file 6343].

Gaimster, D., 1997. Stoneware production in medieval and early modern Germany, in: Freestone, I.C., Gaimster, D. (Eds.), Pottery in the Making: World Ceramic Traditions. British Museum, London, pp. 122–127.

Garcia-Vallès, M., Gimeno-Torrente, D., Martínez-Manent, S., Fernández-Turiel, J.L., 2003. Medieval stained glass in a Mediterranean climate: Typology, weathering and glass decay, and associated biomineralization processes and products. Am. Mineral. 88, 1996–2006.

Gerth, K., Wedepohl, K.H., Heide, K., 1998. Experimental melts to explore the technique of medieval wood ash glass production and the chlorine content of medieval glass types. Chemie der Erde 58, 219–232.

Gillies, K.J.S., Cox, G.A., 1988. Decay of medieval stained glass at York, Cantebury and Carlisle. Part 1: Composition of the glass and its weathering products. Part 2: Relationship between the composition of the glass, its durability, and the weathering products. Glas. Berichte 61, 75–84 & 101–107.

Gimeno, D., Garcia-Valles, M., Fernandez-Turiel, J.L., Bazzocchi, F., Aulinas, M., Pugès, M., Tarozzi, C., Riccardi, M.P., Basso, El., Fortina, C., Mendera, M., Messiga, B., 2008. From Siena to Barcelona: Deciphering colour recipes of Na-rich Mediterranean stained glass windows at the XIII-XIV century transition. J. Cult. Herit. 9, 10–15. https://doi.org/10.1016/j.culher.2008.08.001

Gottfried, R.S., 2010. Black Death: Natural and Human Disaster in Medieval Europe. The Free Press, New York.

Gratuze, B., 2013. Provenance Analysis of Glass Artefacts, in: Janssens, K. (Ed.), Modern Methods for Analysing Archaeological and Historical Glass. John Wiley & Sons, Chichester, UK.

Gratuze, B., Soulier, I., Barrandon, J.-N., Foy, D., 1995. The origin of cobalt blue pigment in French glass from the thirteenth to the eighteenth centuries, in: Hook, D.R., Gaimster, D.R.M. (Eds.), Trade and Discovery: Scientific Study of Artefacts from Post-Medieval Europe and Beyond, British Museum Occasional Paper. British Museum, London, pp. 123–133.

Hawthorne, J.G., Smith, C.S., 1979. Introduction, in: On Divers Arts: The Foremost Medieval Treatise on Painting, Glassmaking and Metalwork. pp. xv–xxxv.

Jackson, C.M., Booth, C.A., Smedley, J.W., 2005. Glass by design? Raw materials, recipes and compositional data. Archaeometry 47, 781–795.

Jackson, C.M., Smedley, J.W., 2008. Medieval and post-medieval glass technology: Seasonal changes in the composition of bracken ashes from different habitats through a growing season. Glas. Technol. Eur. J. Glas. Sci. Technol. Part A 49, 240–245.

Jackson, C.M., Smedley, J.W., 2004. Medieval and post-medieval glass technology: Melting characteristics of some glasses melted from vegetable ash and sand mixtures. Glas. Technol. Eur. J. Glas. Sci. Technol. Part A 45, 36–42.

Kahl, J., 2007. Ancient Asyut: The first synthesis after 300 years of research. Harrassowitz Verlag, Wiesbaden.

Kenyon, G.H., 1967. The Glass Industry of the Weald. Leicester University Press.

Knowles, J.A., 1936. Essays in the History of the York School of Glass-Painting. Macmillan, New York.

Kock, J., Sode, T., 2002. Medieval glass mirrors in southern Scandinavia and their technique, as still practiced in India. J. Glass Stud. 44, 79–94.

Krueger, I., 1993. Glass-mirrors in medieval times, in: Annales Du 12e Congrès de l'Association International Pour l'histoire Du Verre. pp. 319–332.

Krueger, I., 1990. Glasspiegel im Mittelalter: Fakten, Funde und Fragen. Bonner Jahrbucher 190, 233–313.

Kunicki-Goldfinger, J.J., Freestone, I.C., McDonald, I., Hobot, J.A., Gilderdale-Scott, H., Ayers, T., 2014. Technology, production and chronology of red window glass in the medieval period - rediscovery of a lost technology. J. Archaeol. Sci. 41, 89–105. https://doi.org/10.1016/j.jas.2013.07.029

Kunicki-Goldfinger, J.J., Keirzek, J., Freestone, I.C., Małożewska-Bućko, B., Nawrolska, G., 2009. The composition of window glass from the cesspits in the old town in Elbląg, Poland, in: Ignatiadou, D., Antonaras, A. (Eds.), Annales Du 18e Congrès de l'Association Internationale Pour l'Histoire Du Verre, Thessaloniki 2009. ZITI Publishing, Thessaloniki, pp. 395–400.

Kunicki-Goldfinger, J.J., Mester, E., Freestone, I.C., 2013. The chemical composition of glass from the Hungarian glasshouses and glass utilized in Hungary from the 14th century to the 17th century, in: Michalik, J., Smułek, W., Godlewska-Para, E. (Eds.), Annual Report 2012. Institute of Nuclear Chemistry and Technology, Warszawa, pp. 73–75.

Kunicki-Goldfinger, J.J., Pańczyk, E., Dierżanowski, P., Waliś, L., 2008. Trace element characterization of medieval and post-medieval glass objects by means of INAA and EPMA. J. Radioanal. Nucl. Chem. 278, 307–311. https://doi.org/10.1007/s10967-008-0507-z

Lagabrielle, S., Velde, B., 2005. Evolution of French stained glass compositions during the Middle Ages - Analyses and observations made on the Cluny Collection, in: Annales Du 16e Congrès de l'Association Internationale Pour l'Histoire Du Verre, Nottingham UK 2003. AIHV, pp. 341–346.

Lombardo, T., Loisel, C., Gentaz, L., Chabas, A., Verita, M., Loisel, C., Gentaz, L., Chabas, A., Verita, M., Lombardo, T., Loisel, C., Gentaz, L., Chabas, A., Verita, M., 2010. Long term assessment of atmospheric decay of stained glass windows. Corros. Eng. Sci. Technol. 45, 420–424. https://doi.org/10.1179/147842210X12710800383800

Marchesi, B., Negri, E., Messiga, B., Riccardi, M.P., 2006. Medieval stained glass windows from Pavia Carthusian monastery (northern Italy). Geomaterials Cult. Herit. 257, 217–227. https://doi.org/10.1144/GSL.SP.2006.257.01.17

Marks, R., 1993. Stained Glass in England during the Middle Ages. Routledge, London.

Martinón-Torres, M., Freestone, I.C., Hunt, A., Rehren, T., 2008. Mass-Produced Mullite Crucibles in Medieval Europe: Manufacture and Material Properties. J. Am. Ceram. Soc. 91, 2071–2074. https://doi.org/10.1111/j.1551-2916.2008.02383.x

McCray, W.P., 1998. Glassmaking in Renaissance Italy: the innovation of Venetian Cristallo. JOM J. Miner. Met. Mater. Soc. 50, 14–19.

Meek, A., Henderson, J., Evans, J., 2012. Isotope analysis of English forest glass from the Weald and Staffordshire. J. Anal. At. Spectrom. 27, 786. https://doi.org/10.1039/c2ja10364h

Meiwes, K.J., Beese, F., 1988. Ergebnisse der Untersuchung des Stoffhaushaltes eines Buchenwaldökosystems auf Kalkgestein. Berichte Forschungszentrum Waldökosysteme B9, 1–142.

Merrifield, M.P., 1967. Medieval and Renaissance Treatises on the Arts of Painting: Original Texts with English Translations. Dover Publications, New York.

Molina, G., Murcia, S., Molera, J., Roldan, C., Crespo, D., Pradell, T., 2013. Color and dichroism of silver-stained glasses. J. Nanoparticle Res. 15, 1–13. https://doi.org/10.1007/s11051-013-1932-7

Müller, W., Bochynek, G., 1989. Possibilities of approximate dating of medieval glasses using their chemical composition, in: Mazurin, O. V. (Ed.), Proceedings of the XVth International Congress on Glass, Leningrad. pp. 47–52.

Newton, R.G., 1977a. Simulated medieval glasses. CV News Lett. 25, 3–5.

Newton, R.G., 1977b. More Analytical Results. Corpus Vitr. Newsl. 24.

Newton, R.G., 1976. Chemical Analyses of Medieval Window Glasses - Part 1. Corpus Vitr. Newsl. 21, 9–16.

Nussbaum, N., 2000. German Gothic Church Architecture. Yale University Press, New Haven.

Philippe, M., 1998. Naissance de la verrerie moderne XIIe-XVIe siècles: Aspects économiques, techniques et humains. Brepols, Turnhout.

Piñar, G., Garcia-Valles, M., Gimeno-Torrente, D., Fernandez-Turiel, J.L., Ettenauer, J., Sterflinger, K., 2013. Microscopic, chemical, and molecular-biological investigation of the decayed medieval stained window glasses of two Catalonian churches. Int. Biodeterior. Biodegradation 84, 388–400. https://doi.org/10.1016/j.ibiod.2012.02.008

Pollard, A.M., 1979. X-Ray Fluorescence and Surface Studies of Glass, with Application to the Durability of Mediaeval Window Glass. University of York.

Rehren, T., Freestone, I.C., 2015. Ancient glass: from kaleidoscope to crystal ball. J. Archaeol. Sci. 56, 233–241. https://doi.org/10.1016/j.jas.2015.02.021

Sanderson, D.C.W., Hunter, J.R., 1981. Composition variability in vegetable ash. Sci. Archaeol. 23, 27–30.

Santopadre, P., Vallotto, M., Verità, M., 2002. Il vetro di Giotto. Riv. della Stn. Sper. del Vetro 2, 25–33.

Schalm, O., Caluwé, D., Wouters, H., Janssens, K., Verhaeghe, F., Pieters, M., 2004. Chemical composition and deterioration of glass excavated in the 15th–16th century fishermen town of Raversijde (Belgium). Spectrochim. Acta Part B At. Spectrosc. 59, 1647–1656. https://doi.org/10.1016/j.sab.2004.07.012

Schalm, O., Janssens, K., Wouters, H., Caluwé, D., 2007. Composition of 12–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings. Spectrochim. Acta - Part B At. Spectrosc. 62, 663–668. https://doi.org/10.1016/j.sab.2007.03.006

Schechner, S.J., 2005. Between Knowing and Doing: Mirrors and Their Imperfections in the Renaissance. Early Sci. Med. 10, 137–162.

Schmid, B., Krüger, I., Wedepohl, K.H., 1996. Das Fundmaterial zweier mittelalterlicher Latrinen aus Mainz, Tritonplatz. Mainzer archäologische Zeitschrift 3, 127–131.

Schreiner, M.R., 1984. Verwitterungserscheinungen an mittelalterlichen Glasgemälden österreichischer Provenienz, in: Vendl, A., Pichler, B., Weber, J. (Eds.), Wiener Berichte Über Naturwissenschaft in Der Kunst. Hochschule für Angewandte Kunst in Wien, Lehrkanzel für Technische Chemie, Wiener Arbeitskreis für Naturwissenschaft in der Kunst, Vienna, pp. 96–117.

Scott, R.A., 2003. The gothic enterprise: A guide to understanding the medieval cathedral. University of California Press, London.

Sedláčková, H., Rohanová, D., Lesák, B., Šimončičová-Koóšová, P., 2014. Medieval glass from Bratislava (ca 1200–1450) in the context of contemporaneous glass production and trade contacts. Památky Archeol. CV 215–264.

Smedley, J.W., Jackson, C.M., 2006. Medieval and post-medieval glass technology: Bracken as a sustainable resource for glassmaking. Glas. Technol. Eur. J. Glas. Sci. Technol. Part A 47, 39–47.

Smedley, J.W., Jackson, C.M., 2002. Medieval and post-medieval glass technology: A review of bracken in glassmaking. Glas. Technol. 43, 221–224.

Smrček, A., 1999. Batch and composition of typical Bohemian glasses from the 14th to 19th centuries, in: Proceedings of the 5th ESG Conference. pp. 1–9.

Stephan, H.-G., Wedepohl, K.H., Hartmann, G., 1997. Mittelalterliches Glas aus dem Reichskloster und der Stadtwüstung Corvey: Mit einem Nachtrag zu den Analyseergebnissen von Gläsern aus dem Kloster Brunshausen. Germania 75, 673–723.

Stern, W.B., 2017. Phosphate: a neglected argument in studies of ancient glass technology. Swiss J. Geosci. https://doi.org/10.1007/s00015-016-0242-3

Stern, W.B., Gerber, Y., 2004. Potassium - calcium glass: New data and experiments. Archaeometry 46, 137–156.

Sterpenich, J., Libourel, G., 2001. Using stained glass windows to understand the durability of toxic waste matrices. Chem. Geol. 174, 181–193.

Theophilus, n.d. On Divers Arts: The foremost medieval treatise on painting, glassmaking and metalwork. Translated from the Latin with introduction and notes (1979).

Thorpe, W.A., 1949. English Glass. Adam and Charles Black, London.

Topić, N., Bogdanović Radović, I., Fazinić, S., Skoko, Ž., 2016. Analysis of medieval and post-medieval glass fragments from the Dubrovnik Region (Croatia). Archaeometry 58, 574–592. https://doi.org/10.1111/arcm.12191

Turner, W.E.S., 1956. Studies of Ancient Glass and Glass-making Processes. Part V. Raw Materials and Melting Processes. J. Soc. Glas. Technol. 40, 277–300.

Van Wersch, L., Loisel, C., Mathis, F., Strivay, D., Bully, S., 2016. Analyses of Early Medieval Stained Window Glass From the Monastery of Baume-Les-Messieurs (Jura, France). Archaeometry 58, 930–946. https://doi.org/10.1111/arcm.12207

Vassas, C.D., 1971. Etude chimique, thermographique et physique de verres de vitraux du Moyen-Age, in: International Congress on Glass IX, Versailles, France, 1971. pp. 241–306.

Velde, B., Barrera, J., 1986. Composition of medieval blown glass fragments found at Orleans.pdf. Archéologie Médiévale XVI, 93–103.

von Simpson, O., 1962. The Gothic Cathedral. Harper and Row, New York.

Wedepohl, K.H., 2003. Glas in Antike und Mittelalter: Geschichte eines Werkstoffs. Schweizerbart'sche Verlagsbucchandlung, Stuttgart.

Wedepohl, K.H., 1998. Mittelalterliches Glas in Mitteleuropa: Zusammensetzung, Herstellung, Rohstoffe. Nachrichten der Akad. der Wissenschaften Göttingen. 2, Math. Klasse, 1.

Wedepohl, K.H., Simon, K., 2010. The chemical composition of medieval wood ash glass from Central Europe. Chemie der Erde - Geochemistry 70, 89–97. https://doi.org/10.1016/j.chemer.2009.12.006

Welch, C.M., 1997. Glass-making in Wolseley, Staffordshire. Post-Medieval Archaeol. 31, 1–60. https://doi.org/10.1179/pma.1997.001

Wilk, D., Kamińska, M., Walczak, M., Bulska, E., 2017. Archaeometric investigations of medieval stained glass panels from Grodziec in Poland, in: Targowski (Ed.), Lasers in the Conservation of Artworks XI, Proceedings of LACONA XI. NCU Press, Torún, pp. 263–278. https://doi.org/10.12775/3875-4.19

Wilson, C., 1990. The Gothic Cathedral: The Architecture of the Great Church, 1130-1530. Thames and Hudson, London.

Woodforde, C., 1951. The Stained Glass of New College. Oxford University Press, Oxford.

Table 1 Data sources providing city/site, date range and number of analyses. The source of the data is numbered and corresponds to the list on the next page. Some of the dates given in this table exceed the range of 12th-15th centuries; these data were assigned a broad date range (continued next page)

City/Site	Century	*n*	References	City/Site	Century	*n*	References
Ebriach, Austria (CE)	14	3	27	Marseille/Rougiers, France	12-14	12	4,9
Kremsmunster, Austria (CE)	15	1	21	Montpellier, France	13	2	4
Spitz, Austria (CE)	14	1	27	Saint-Jean-des-Vignes, France	13-16	47	2
St Martin im Muhlkreis, Aust. (CE)	14	5	21	Cologne, Germany (R)*	14	31	14, 34
Strassengel, Austria (CE)	14	12	21, 24	Frankfurt/vicinity, Germany (R)*	12-15	8	4, 21, 30, 34
Vienna/vicinity, Austria (CE)	12-15	22	4, 21, 22, 24, 27	Freiburg, Germany (R)	13-14	12	4
Raversijde, Belgium (R)*	15-16	223	25	Lautenbach, Germany (R)	15	1	4
(Various), Belgium (R)*	12-17	135	26	Höxter/vicinity, Germany (R)	11-16	42	4, 8, 29, 34
Dunave, Croatia (CE)	14-15	1	31	Nuremburg, Germany (R)	14-15	3	4, 32
Bohušov, Czechia (CE)	13-14	1	28	Ulm, Germany (R)	14-15	11	3, 4, 21
Brno-stred, Czechia (CE)	13-14	2	28	Altenberg/Naumberg, Ger.(CE)	13-15	17	4,14
Chrudim, Czechia (CE)	14-16	1	28	Augsburg/Munich, Ger. (CE)	14	8	4,14, 21
Moldava and Most, Czechia (CE)	14-16	12	7, 8	Braunschweig, Germany (CE)	12-13	1	28
Olomouc, Czechia (CE)	15	1	7	Budapest, Hungary (CE)*	14-18	17	13
Opava, Czechia (CE)	14-16	2	28	Erfurt, Germany (CE)	14	7	4
Plasy, Czechia (CE)	14	2	8, 28	Halberstadt, Germany (CE)	15	2	4
Prague, Czechia (CE)	13-15	6	8	Jerichow, Germany (CE)	12-16	6	20
Staffordshire, England (W)	13-14	4	35	Leck, Germany (CE)	13	1	21
Weald, England (W)	13-14	19	18	Meissen, Germany (CE)	14	1	30
Amiens, France (W)	13	11	4, 21, 32	Regensburg, Germany (CE)	13-14	4	4
Angers, France (W)	14	5	1	Wienhausen, Germany (CE)	13-15	4	21
Bourges, France (W)	13-15	6	4,15	Florence, Italy	14 -16	5	4
Brittany/Brennilis, France (W)	15	4	4,15	Orvieto, Italy	13-14	1	28
Évron (Mayenne), France (W)	14	1	4	Pavia, Italy	15	33	17
Le Mans, France (W)	13-15	1	21	St. Leonhard in Passeier, Italy	14	1	21
Orleans & Chartres, France (W)	12-16	51	1, 4, 24, 33	Heemskerk, Netherlands (R)	15-16	1	14
Paris/vicinity, France (W)	12-16	213	1, 4, 5,14,15, 21, 32	Zutphen, Netherlands (R)	14 -16	23	14
Poitiers, France (W)	11-12	2	1	Elblag, Poland (CE)	Late medieval	11	12
Provins, France (W)	15	4	15	Grodziec, Poland (CE)*	15	13	36
Rouen/vicinity, France (W)	13-16	78	1, 4,15,16, 21, 30, 32	Turuń, Poland (CE)	Medieval	1	12
Tours, France (W)	13-14	3	32, 30	Batalha, Portugal	15-16	9	4
Argonne and Metz, France (R)	14-15	62	1	Bratislava, Slovakia (CE)	13-16	4	28
Châlons-en-Champagne, Fr. (R)	12-15	10	1, 32	Avila, Spain	15	1	19
Reims, France (R)	12	1	4	Barcelona, Spain	14	23	10,11, 23
Troyes/Aube, France (R)	13-16	8	4, 21	Burgos, Spain	13	1	14
Avignon, France	14	10	3, 4	León, Spain	12-15	7	6
Chambaran, France	15	2	1	Palencia, Spain	15	1	19
Digne, France	12-13	5	30	Tarragona, Spain	14	17	10, 23
Léon, France	13-15	23	4	Bern, Switzerland (R)	15	3	4

Table 1 (continued from previous page) in the original source but were consistent with typical medieval compositions and so included. References, below, correspond to the numbered sources on the previous page. *Some data were not reported individually in the source publication, instead reported as an average. This will affect the number of data points in scatterplots. The adjusted *n* for these localities are: Raversijde 8, Various Belgium 4, Cologne 8, Frankfurt/vicinity 23, Budapest 1, Höxter/vicinity 20, and Grodzeic 1.

1 Barrera & Velde 1989
2 Brill & Pongracz 2004
3 Brill 1970
4 Brill 1999
5 Calligaro 2008
6 Carmona et al. 2006
7 Cílová & Woitsch 2012
8 Cílová et al. 2015
9 Foy 1985
10 Garcia-Vallès et al. 2003
11 Gimeno et al. 2008
12 Kunicki-Goldfinger et al. 2008
13 Kunicki-Goldfinger et al. 2013
14 Kunicki-Goldfinger et al. 2014
15 Lagabrielle & Velde 2005
16 Lombardo et al. 2010
17 Marchesi et al. 2006
18 Meek et al. 2012
19 Molina et al. 2013
20 Muller & Bochynek 1989
21 Newton 1976
22 Newton 1977b
23 Piñar et al. 2013
24 Pollard 1979
25 Schalm et al. 2004
26 Schalm et al. 2007
27 Schreiner 1984
28 Sedláčková et al 2014
29 Stephan & Wedepohl 1997
30 Sterpenich & Libourel 2001
31 Topić et al. 2016
32 Vassas 1971
33 Velde & Barrera 1986
34 Wedepohl & Simon 2010
35 Welch 1997
36 Wilk et al. 2017

Table 2 Chemical composition of the case studies, as analysed by SEM-EDS. The windows case studies are reported as mean results; full results for the windows are given in Supplementary Table S1.

	York Minster		**New College, Oxford**						**Mirror**
			White(I)		*White(II)*		*Colours*		
	$\overline{x}$	σ	$\overline{x}$	σ	$\overline{x}$	σ	$\overline{x}$	σ	
Na_2O	2.10	*0.52*	2.41	*0.16*	3.51	*0.20*	1.34	*0.33*	0.4
MgO	6.96	*0.56*	6.55	*0.46*	6.86	*0.29*	4.58	*0.29*	3.3
Al_2O_3	1.74	*0.30*	1.27	*0.24*	1.32	*0.09*	1.42	*0.19*	1.5
SiO_2	49.55	*3.16*	54.20	*1.65*	48.80	*0.76*	46.56	*1.25*	47.7
P_2O_5	6.07	*1.12*	3.28	*0.22*	5.01	*0.22*	4.29	*0.82*	1.3
SO_3	0.32	*0.07*	0.34	*0.07*	0.32	*0.07*	0.36	*0.06*	0.3
Cl	0.38	*0.08*	0.41	*0.14*	0.34	*0.04*	0.08	*0.04*	<0.2
K_2O	16.33	*2.26*	11.88	*0.96*	15.80	*0.42*	14.07	*1.99*	24
CaO	15.54	*1.44*	15.51	*0.60*	14.35	*0.28*	23.46	*1.30*	18.5
TiO_2	0.15	*0.07*	0.15	*0.06*	0.08	*0.06*	0.13	*0.07*	0.2
MnO	1.18	*0.17*	1.23	*0.08*	1.36	*0.09*	1.22	*0.26*	1.8
Fe_2O_3	0.71	*0.15*	0.70	*0.07*	0.62	*0.07*	0.90	*0.28*	0.2
CuO	0.25	0.54	0.34	0.13	0.29	0.11	0.43	0.15	*na*
ZnO	0.10	0.16	0.06	0.08	0.08	0.09	0.06	0.07	*na*
BaO	0.28	0.13	0.17	0.10	0.26	0.11	0.41	0.12	*na*
PbO	0.05	0.18	0.05	0.08	0.23	0.07	0.04	0.09	0.6
n=	*87*		*31*		*15*		*31*		

Table 3. Average composition of Fe_2O_3 in the three regions (mean, median and mode reported). Major outliers were calculated based on the entire legacy dataset, and omitted (> 1.69). The mode (marked with an asterisk*) was calculated after rounding the data to one decimal place. The glass found in Central Europe, presumably related to Bohemian glass manufacture, are generally lower in iron (see also Fig. 12).

	NW France	Rhenish	Central Europe
Mean	0.67	0.75	0.52
Median	0.61	0.80	0.46
Mode*	0.6	0.8	0.3

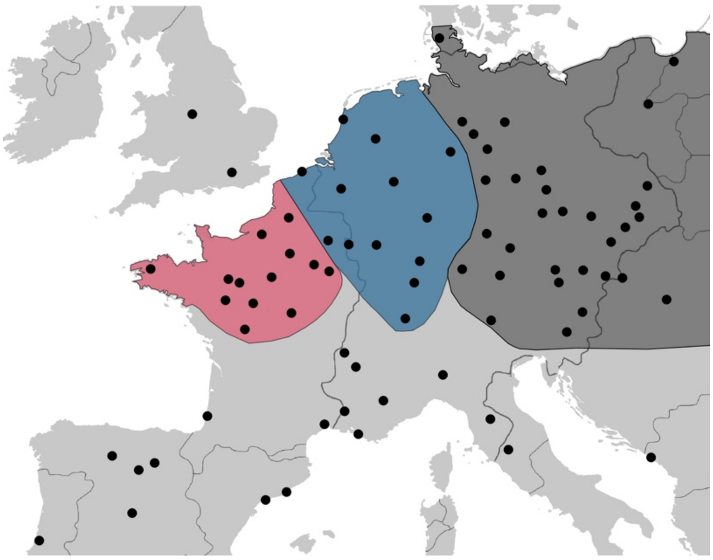

Fig. 1 Map showing the cities/sites included in this meta-analysis, with regions highlighted that correspond to the scatterplots in the subsequent figures. Red: NW France; Blue: Rhenish; Black: Central Europe. Borders are based on Europe of 1300.

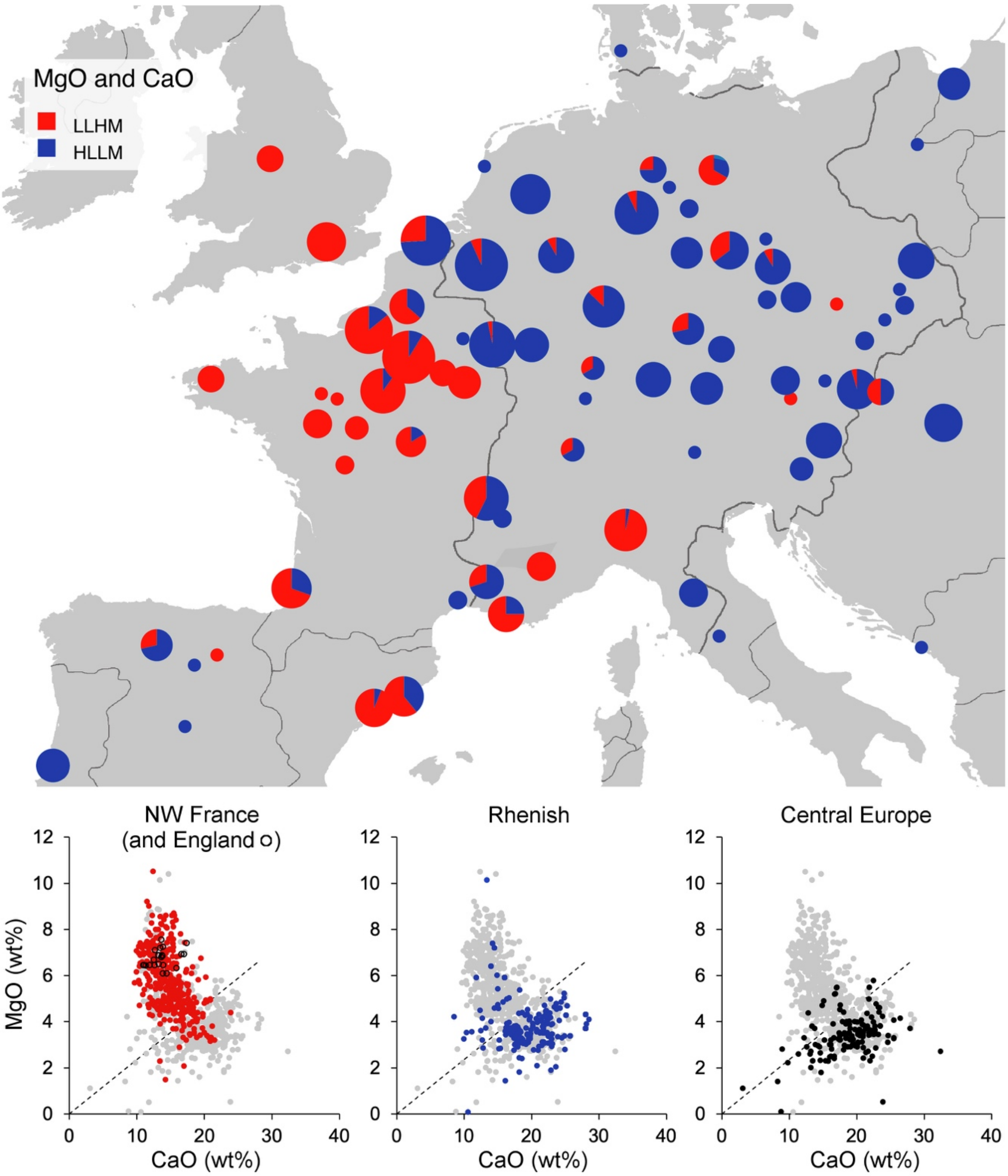

Fig. 2 Map showing the regional distribution of LLHM and HLLM glasses using a threshold of MgO/CaO=0.24, with scatterplots showing magnesia and lime contents of glass from the three regions. This threshold is established only for the purposes of the above illustration, and is not intended as a boundary for defining a compositional typology. High magnesia is characteristic of glass found in western and central parts of northern France and in England (the latter marked with an open circle, **O**, in the scatterplot). Borders are based on Europe of 1300.

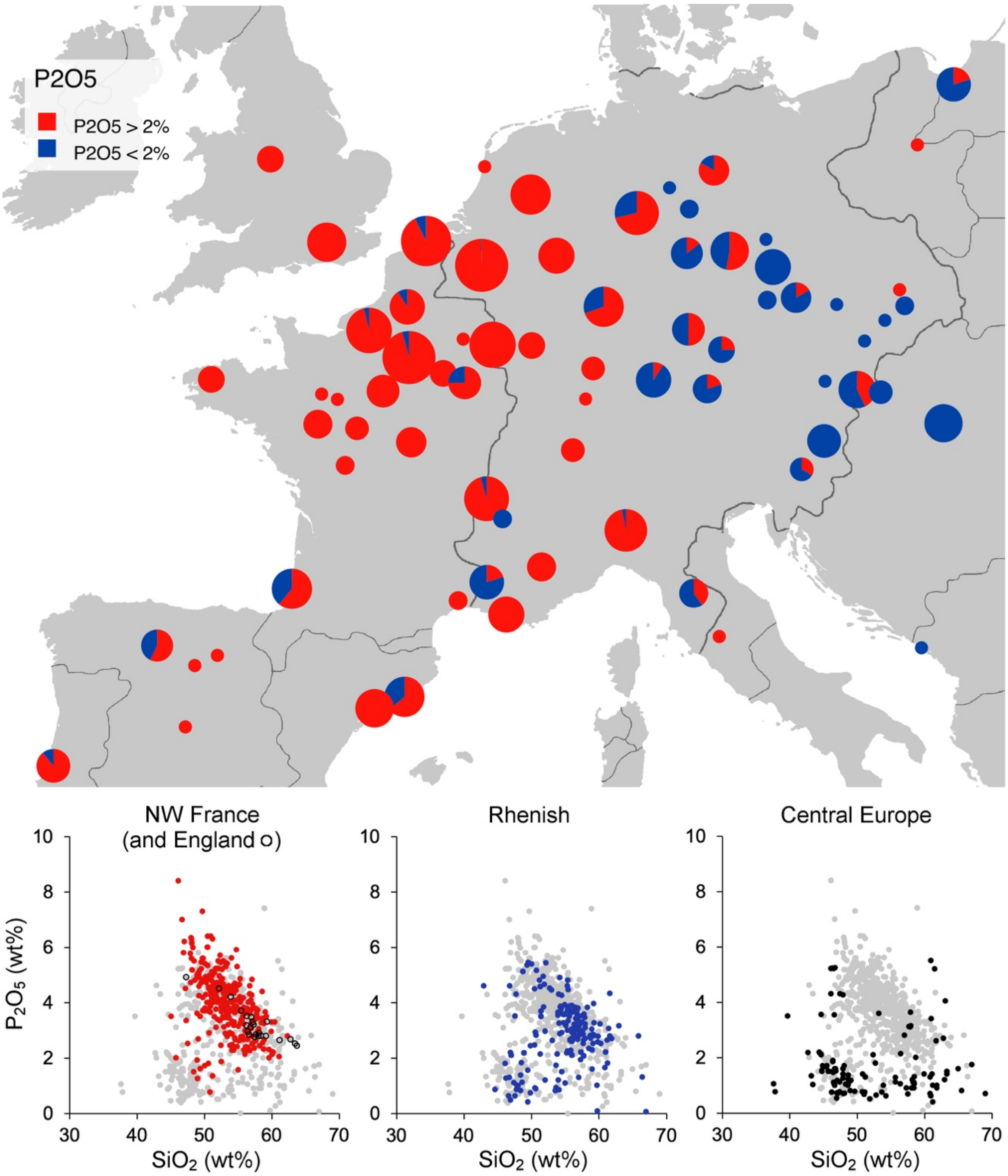

Fig. 3 Regional distribution of glass with high and low phosphate (threshold at 2% P_2O_5), and scatterplots showing phosphate and silica contents of the three regions. This threshold is established only for the purposes of the above illustration, and is not intended as a boundary for defining a compositional typology. The low phosphate type is characteristic of glass found in central Europe, excluding areas near the Rhine and its tributaries. Borders are based on Europe of 1300.

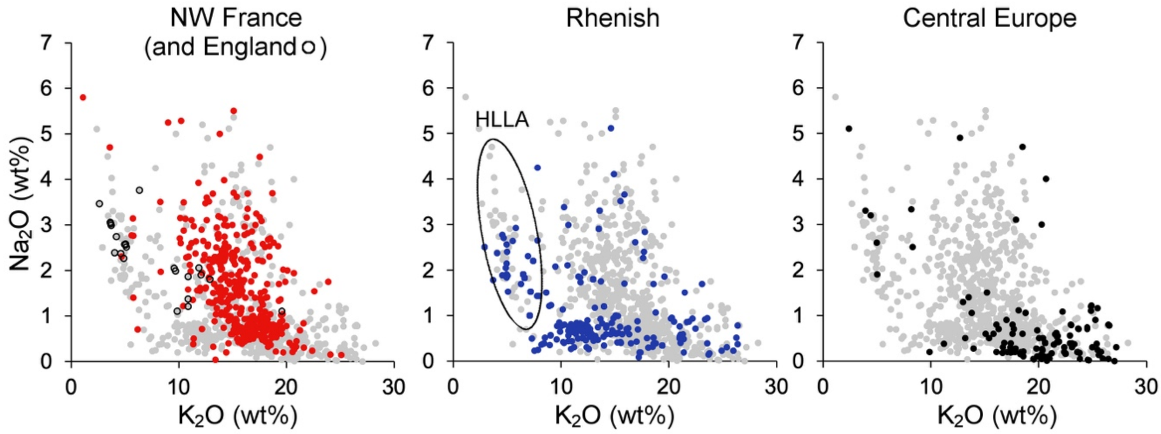

Fig. 4 Scatterplots showing the soda and potash contents of glass in the three regions.

York Minster
CHn9 panels 4-6a   CHs7 panels 5-7a

New College Chapel
n6 panel B3

Fig. 5 Panels from the two windows from the York Minster Chapter House Vestibule (CHn9 and CHs7, left) dating to the 13th century, and from a window from the chapel of New College, University of Oxford (n6, right), dating to the late 14th century. Glass pieces from several panels across each window were sampled (CHn9: 8 panels; CHs7: 13; n6: 10). *(York) Photograph: York Glaziers Trust, reproduced with the permission of the Chapter of York. (New College) © Warden & Scholars of New College, Oxford.*

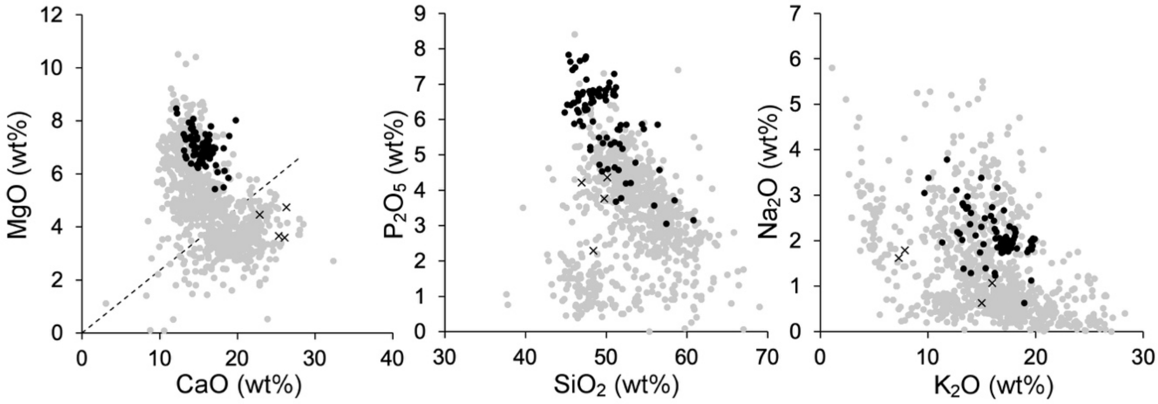

Fig. 6 The York Minster chapter house glass plotted against the synthesised data from the previous section. Most of the glass is of the LLHM type, with four HLLM glasses (marked by an "×"). Compare to regional patterns reported in Figures 2-4.

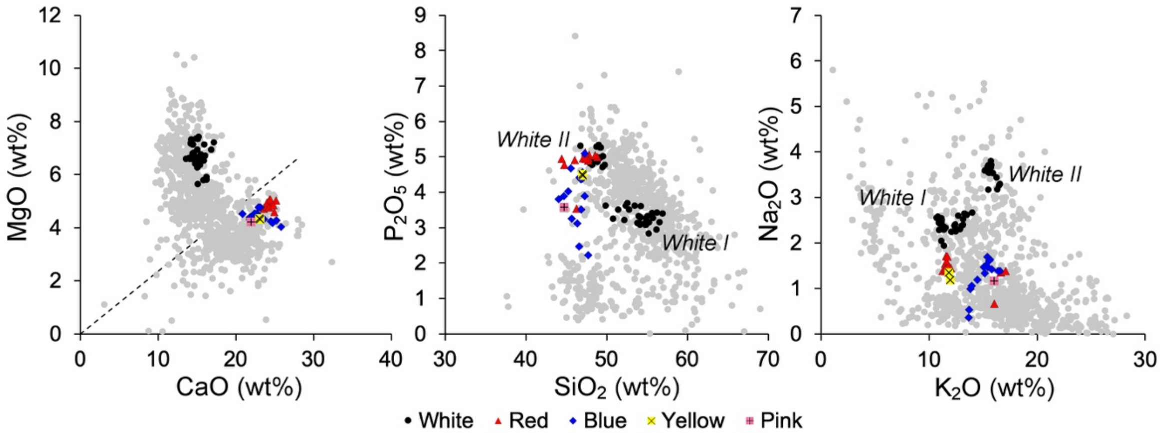

Fig. 7 The Oxford New Chapel glass plotted against the synthesised data from the previous section. The two groups of white glass are both of the LLHM type, while all of the colours are HLLM. Compare to regional patterns reported in Figures 2-4.

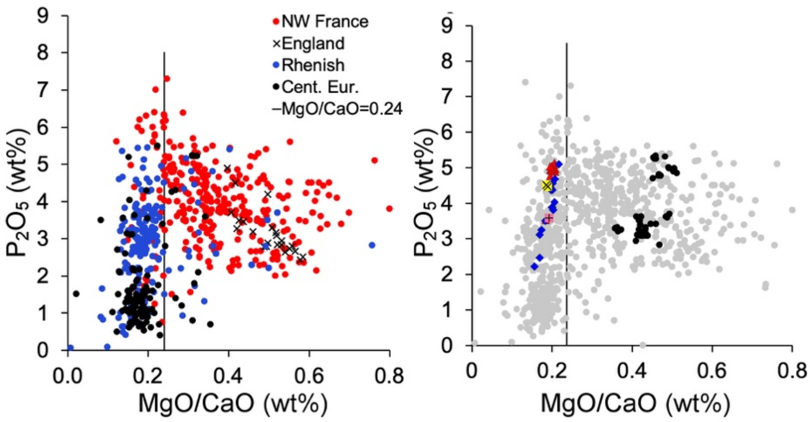

Fig. 8 Phosphate against MgO/CaO for the three regions defined in this study (left) and for the Oxford New College window glass (right, refer to legend in Fig. 7).

Fig. 9 Glass mirror found in Egypt (British Museum 1902,0529.18-19), with two convex glasses in a hinged pewter case. © *The Trustees of the British Museum.*

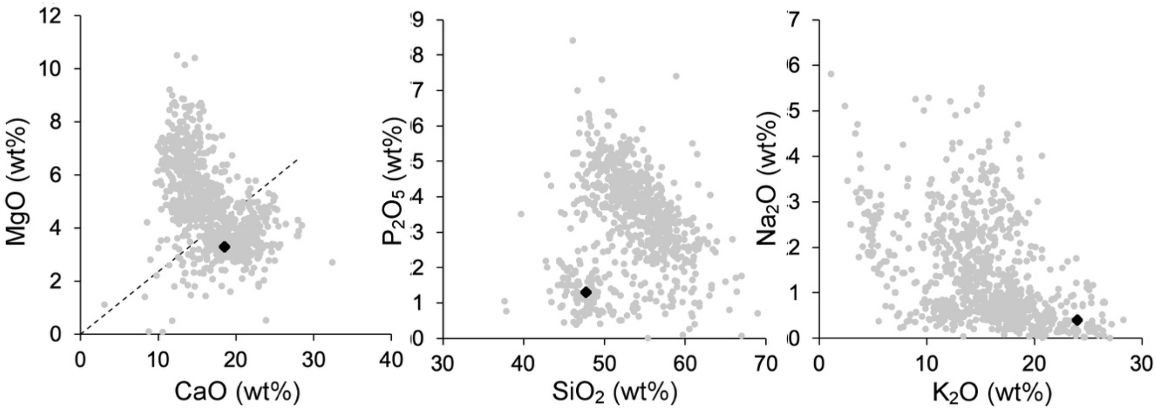

Fig. 10 Scatterplots showing the compositional characteristics of the glass mirror against the European data.

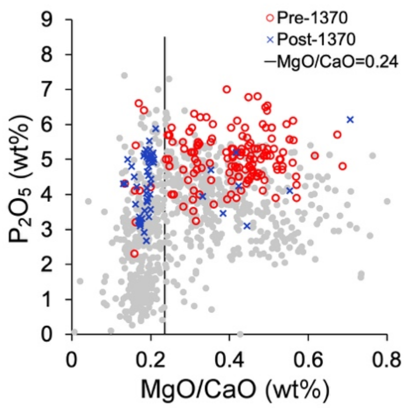

Fig. 11 Scatterplot showing P2O5 contents against MgO/CaO ratio of coloured window glass from English windows. Towards the end of the 14th century, there is a shift from LLHM to HLLM (with high phosphate) glass. Data are from several English sites including York, Canterbury, Oxford and Coventry (Brill, 1999, 1970; Freestone et al., 2010; Gillies and Cox, 1988; Kunicki-Goldfinger et al., 2014; Newton, 1977b, 1976; Pollard, 1979).

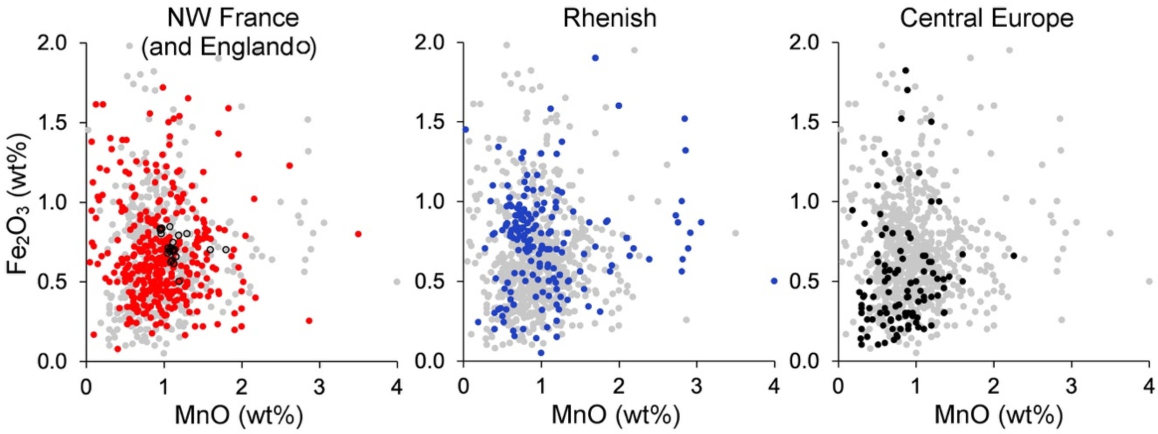

Fig. 12 Scatterplots showing iron and manganese concentrations of glass found in different regions of Europe. Glasses from central Europe tend to have lower iron contents than glass from other regions (see also Table 3).