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A transparent dialogue between iconography and chemical characterisation: a set of foreign stained glasses in Portugal

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Abstract

This work presents the first results of the iconographic study and analytical characterisation of a set of four stained-glass panels that are part of the collection of National Palace of Pena (Sintra, Portugal). These panels were collected by the King Ferdinand II in the mid-nineteenth century, for his main residence the Palace of Necessidades (Lisbon, Portugal), and only first presented to the general public in 2011. This study contributes with the knowledge of Technical Art History and Heritage Science to a better and deeper understanding of their history, materials and techniques used in the production, where an art-historical and a scientific approach are applied to attribute their origins. Based on the analysis of the formal and stylistic characteristic of the panels, it is proposed that the drawings used for the production of three of these panels may be based on the design and painting being carried out in the same workshop, and that the four panels have the same provenance (Germany). The composition of the glass and grisaille was determined and colourising elements were identified. Through this approach, conclusive correlation between the analysed glasses was possible: all are calcium rich or calcium–potassium rich types, and the results also suggest that the same source of silica was used for their production. A typical mixture of glass and lead oxide was found in the grisaille applied on the painted panels. However, less usual was the use of a copper oxide pigment for the black grisaille. All these findings support the proposals made regarding provenance and production period (fifteenth century).

Keywords: Stained glass, Iconography, Chemical composition, μ-EDXRF, UV–vis spectroscopy, PCA

Introduction

The art of stained glass has always sought to interact with the surrounding space by creating architectural planes that allowed illumination while transforming the experience of light into one specific and meaningful to the purpose of a building [1]. From the beginning, production of stained glass developed side by side with economic, social and cultural innovations. In the Middle Ages, stained glass gained an important role with the construction of cathedrals, reaching its peak in the fifteenth century with Gothic architecture. During the Renaissance period, single glass sheet panels and roundels showing themes of family and local interest brought stained glass into a more intimate and domestic setting with highly personalised imagery. From the eighteenth century onwards, medieval and later stained-glass panels were collected in order to decorate private houses and chapels [1–3], often bought in the art market and/or through an intricate network of dealers which grew throughout the nineteenth century [4]. This was the case with Ferdinand

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II's stained-glass collection, housed today at the Pena National Palace (PNP) [5]. These stained-glass panels—produced in Central and Western Europe (namely, in the territories of modern Germany, Switzerland and the Netherlands)—had been originally installed in churches, monasteries, manor houses, and artisans' workshops, prior to their installation in the Portuguese Palaces, which is merely a short chapter in their long history [5].

The history of this unique stained-glass collection begins with King Ferdinand II (1816–1885)—born and raised in Vienna, married to Queen Maria II (1819–1843) since 1836, and King of Portugal since 1837 [6]—, who dedicated part of his life to collecting and financing works of art, and his vast collection of glassware and stained glass was a source of pride for him [5].

Ferdinand II kept the greater part of the objects acquired in Portugal and overseas—collections of paintings, armour, sculptures, porcelain and others—in his royal residence, the Palace of Necessidades (located in Lisbon). These collecting activities included a group of stained-glass panels of different origins and sizes, with which he decorated the windows of the Palace's dining room, very much in the style of the other Saxe-Coburgs' castles [5, 6]. Later in his life, he lived in the old cloister of Pena (restored and turned into a Palace), where he also ordered to be mounted another group of stained-glass panels in the windows of the Great Hall [6]. The choice for the use of stained-glass windows in the openings of the main rooms of residences reflected a central and northern European tradition [6]. It is known that the King bought a large number of stained-glass panels on the German art market between 1850 and 1860, in order to decorate his summer palace in Sintra [7, 8], but as recent investigations suggests, the mainly foreign stained glasses arriving during that period have likely been set on display at the Palace of Necessudades due to the early death of the Queen [8].

Unlike the windows installed in the main hall of Pena Palace's, the stained-glass windows first located in Palace of Necessidades remained unknown to the general public until very recently. As such, the transference of the panels to PNP is a story in and of itself [6]. The stained-glass windows were transferred by 1949, since during the Republic (after 1910), the Palace of Necessidades was handed over to the Ministry of Foreign Affairs and its contents were stored and gradually dispersed. It was in 1949 that, after being requested by the conservator of PNP, the '*eight wooden frames with stained-glass windows*' arrived at this Palace. Unfortunately, their poor state of preservation required an intervention before they could be installed, and so they were to lie forgotten in the storeroom for the next sixty years [6]. It was only in 2010–2011 that this important and unique group of stained glass panels was restored and displayed [6]. The collection's main group currently consists of thirty-seven panels, to which ninety *Fernsterbierscheiben* (window beer panels, i.e. small rectangular glass pieces painted to celebrate the opening of a house or an important family event, such as a wedding) have been added. This is a highly diverse set of stained-glass panels, produced between the fourteenth and eighteenth centuries, which were randomly grouped together [7].

This study aims to contribute to the knowledge of the history, materials, and techniques used in the production of a group of four panels within this collection. In the present work, a relation between the stylistic, formal and iconographic studies, and the chemical characterisation of some of the glass fragments allowed us to attribute the set to the same origins, highlighting the ability of already widely recognised and here employed scientific heritage studies to resolve complex historical questions (e.g. [9, 10]). Combining the tools and procedures from the fields of Art-History and Archaeometry (Technical Art History) as was done here, is increasingly proving to be an indispensable methodology when studying medieval stained-glass. Micro Energy Dispersive X-Ray Fluorescence (μ-EDXRF) was used in order to obtain a non-destructive characterisation of the composition the glass and grisaille used in the production of three of the panels (*Virgin of the Apocalypse*, *Saint Ambrose*, *Saint Gregory*). This information was, in turn, used to help establish the origins, art schools and artistic trends involved in the manufacture of the panels, as well as its recently established relation with the fourth element (*Sigmund von Schönfels coat of arms*).

Materials and methods

Visual observation and art-historical approach

The four panels under study are currently held by PNP (acc. nrs. PNP2809, PNP2810, PNP2821 and PNP2822) (Figs. 1 to 2). These stained glasses were observed with the aim of understanding their production technology and evaluating their state of conservation. An iconographic analysis (an art historical analysis) was also made, interpreting what could be seen in the glassworks under study. On the basis of these observations, the objects were related to other primary sources (images and texts). This art historical interpretation is published elsewhere [11], and it will herein be used as single reference, providing it is an authoritative secondary source.

Chemical analyses and statistical methods

Energy dispersive X-ray fluorescence

Concerning the chemical characterisation, several fragments of the panels of *Virgin of the Apocalypse*, *Saint Ambrose*, *Saint Gregory* (Fig. 1) were accessible to be

Fig. 1 Photographs of the panels under study: (left) Saint Ambrose (PNP2821), (middle) Virgin of the Apocalypse (PNP2822), and (right) Saint Gregory (PNP2809). Bellow, details of the faces of the depicted figures (Photograph credits ©PSML—Luís Pavão)

analysed by μ-EDXRF. The analyses were carried out using an ArtTAX, Intax®spectrometer, equipped with an air-cooled low-power X-ray tube with a Mo target and Xflash®Peltier cooled silicon drift detector. The primary X-ray beam is focused to a diameter of 70 micrometers by means of a polycapillary X-ray mini lens. The spectrometer was operated at 40 kV, 0.6 mA and 360 s acquisition time, in a He atmosphere. At least three different measurements were made in each glass fragment selected, based on their visual aspect (colour, etc.). Mapping of the data points is added in Additional file 1: Figure S1.

Quantitative analyses were carried out with the WinAXIL program, making use of spectra obtained from CMOG A, B, C and D glass standards. The analytical capability of the equipment is limited to elements with atomic number $Z \geq 13$, thus making detection of sodium and magnesium impossible. The concentration of these elements was calculated by the method of 'matrix by difference' [12]. This is a less rigorous method, because it is not possible to separate both elements from other light elements that may also exist in the glass composition. Nonetheless, given the fact that the glass types under study were found not to be soda-glass—for which distinction of the glass typology would be more difficult—, the drawbacks of the approach in the present case are in this way reduced. The error associated with the analysis was calculated for SiO_2, K_2O, BaO and CoO, and is below 5%. Calculated error for CaO, Fe_2O_3, MnO and SrO is below 10%. For the remaining elements or oxides, Al_2O_3, CuO, PbO, Sb_2O_5, SnO_2, TiO_2 the error is below 25%,

Fig. 2 Photograph of the panel depicting Sigmund von Schönfels' coat of arms (PNP2810) (Photograph credits ©PSML—Luís Pavão)

which was verified by analysing standard glasses (Corning A, B, C and D) under the same experimental conditions as the samples, and calculating experimentally the concentration values of the certified samples. P_2O_5 and other light elements standard deviations calculated by the same method were much higher, and therefore this is considered to be a semi-quantitative method.

In this paper, only the results obtained for the glass thought to be from the original production of the panels are presented (mapping of acquisitions spots in Additional file 1: Figure S1). Nevertheless, in all four panels several modern glass insets (probably introduced during the nineteenth century in the assemblage of the windows) were found.

Principal Component Analysis

The chemometric study was performed through the statistical treatment of the data collected on the μ-EDXRF spectra, using Principal Component Analysis (PCA). This technique was applied to the peaks of the identified elements obtained through the μ-EDXRF analysis. PCA is known to be useful in reducing the dimensionality of the datasets, increasing interpretability and at the same time minimising information loss [13]. As elemental peak intensity variations from sample to sample result from the variation of their chemical composition, these were used in PCA in order to identify groups based on the glass chemical composition. The freeware R-statistica under the terms of Free Software Foundation's GNU General Public License and Statistica from StatSoft (Dell software) were used to accomplish the statistical analyses.

UV–visible spectroscopy

UV–visible absorption spectroscopy (UV–vis) was used to confirm the presence of the transition metal ions responsible for the colours on the glass fragments. An Avantes AvaSpec-2048 fibre optic spectrometer with a 300 lines/mm grating was used. The operational range used was between 200–800 nm and the instrument has a FWHM resolution of 2.4 nm. The light transmitted was measured using a 200 μm transmission probe (Avantes FC-UV600-2).

Results and Discussion

The iconographic analysis: from questions to answers

Of the four panels under study—*Virgin of the Apocalypse*, *Saint Ambrose*, *Saint Gregory* and *Sigmund von Schönfels' coat of arms*—the former three are proposed to have the same manufacturer, due their formal and stylistic characteristics (Fig. 1). The three panes *Virgin of the Apocalypse*, *Saint Ambrose*, *Saint Gregory* share common elements in the architectural design illustrated within each panel. The framing seen in the lateral and upper level uses Gothic arches of stone and wood and respective uprights. Several details also suggest that perhaps the same artist could have painted the entire series; specifically, the hair and eye-brows, and the vestments. It is well known that stained-glass workers could design and produce panels by copying a cartoon made by an artist or by being inspired by famous engravings within the iconographic program ordered by the commissioner [1]. In the present case, it is proposed that the design of these three panels may be based and strongly influenced by the works of German engravers active in the Upper Rhine—namely Master E.S., known to be active between 1450 and 1467 based on the monogram on eighteen of his surviving prints. Master E.S. was a very well known engraver and influenced many others, and some similarities between these panels and several of his prints may be found [14], as further presented. Simultaneously, an influence from Nuremberg artists seems also to be present, such as the works from the Era of Dürer [15]. The forth panel, *Sigmund von Schönfels' coat of arms* (Fig. 2), was recently directly related with the glazing of the windows of the *Marienkirche* at Zwickau [11], presenting itself as the link between the acquisition of Ferdinand II in the nineteenth century and the Medieval origins of these four panels. The study and interpretation of the iconographic program, the stylistic features and the design of the panels were the first ways to tackle the several unanswered historical questions.

Panel of the virgin of the apocalypse

This panel, recovered after a complex restoration, shows a way of representing the Virgin that was highly popular in the late fifteenth century. The iconography is taken from a passage in the Book of Revelation that describes 'a woman clothed with the sun, and the moon under her feet, and upon her head a crown of twelve stars' [Revelation 12:1]—the signs of the Apocalyptic woman were later transferred to the Virgin Mary [11, 16]. In this panel the Virgin holding the Child is represented inside an altarpiece with a late-Gothic architectural design, dressed in a red tunic symbolising her great love, a white robe that symbolises Purity, and a blue background of truth [17]. We might easily recognise the depiction of sunlight as a surrounding brilliance (to compensate for the inability to portray a garment of sun), as well as the moon under her feet and the crown over her head. On the contrary, the twelve stars that usually ornament the crown and 'the wings of a great eagle' offered to 'the woman clothed with the sun' [Revelation 12:14] are absent in this representation [16, 18]. The absence of some of the attributes and the simplicity of the depictions is one of the main peculiarities of the three stained glass panels here compared.

Panel of Saint Gregory

This panel depicts Saint Gregory, a Father of the Latin Church. The depiction of the four Fathers in the same series is usual [15]. Saint Gregory is sitting on a bench at a desk, writing in a book in a very similar architectural space to that of Saint Ambrose and with the same iconographic characteristics. The papal red tunic together with a blue robe, a bordeaux lining, and the papal tiara are his most recognisable attributes, together with a crosier with the double cross. At his feet lies what appears to be an eagle. His special attribute is the dove; in ancient pictures this symbol is never far from his ear, sometimes apparently whispering to him, or hovering about his head and shoulders [17].

The eagle is thought to be the representation of Saint John the Evangelist using this symbol. The depiction of this Doctor of the Church associated with Saint John, or his symbol, is uncommon to find but it may be seen for example in the frescos of the ceiling of Basilica San Giulio in Piedmont, Italy, dating from 1500. In sixteenth century German stained-glass representations, Saint Gregory is usually depicted associated with St. Matthew the Evangelist (or his symbol, the angel) [15].

Panel of Saint Ambrose

In this panel, Saint Ambrose is thought to be represented. Like the previously described panels, this one is also illustrated in an architectural space: under the roof of a small late-Gothic chapel, the Saint is sitting at a desk, on a bench which is decorated with quatrefoil, similar to the one that he wears on his collar. The scene recalls a *scriptorium*, girded with a bay window and an ambience that is created by the three small windows shown in background, arranged in a diamond shape. The saint wears a white tunic, a red robe with a blue lining, and an Episcopal white mitre. He writes with the right hand on one folio of an open book and leans his left hand on the previous folio. At his feet lies what seems to be an ox. Although it is depicted without wings, it is thought to be the symbol representing Saint Luke the Evangelist, a symbol for him that became common during Romanesque and Gothic eras [19]. In front, we see a small depiction of the Virgin holding the Child on a damask background. She wears a white robe, which also covers the Child, and the small dimensions of the figures suggests perhaps a Marian apparition.

Saint Ambrose's representation in this panel is a direct reference to his comments drawn from the Gospel of Saint Luke; he is surrounded by attributes related to Saint Luke the Evangelist including the image of the Virgin and Child, books and the ox [19]. The depiction of Saint Ambrose associated with Saint Luke the Evangelist, more precisely his symbol the ox, may be seen in several sixteenth century German stained glasses [15].

Panel with Sigmund von Schönfels' coat of arms

This panel does not belong to the iconographic group as do the other three, but it is the only one that has survived and can directly be related with the glazing of the windows of the *Marienkirche* at Zwickau. The rectangular field shows the coat of arms of the Saxon family of Schönfels, a slanted silver bar in black, within a frame of columns and above them—later added—an arch. When the pane came to Portugal, the panels were restored and the black background was incorrectly replaced with blue glass [11]. The panel is dated from 1517, and in the inscription can be read '*Sigmund von Schönfels 151?*'. Not much is known about Sigmund, the founder of the coat of arms—a noble from a family that owned several properties near the town since the fourteenth century, and inhabited the Schönfels Castle, southwest of Zwickau. Why Sigmund, who died in 1519, started a window foundation in the *Marienkirche* remains a mystery. However, the donated panel and its inscription is nowadays the connection with the church documents and the testimony of Lorenz Wilhelm (Zwickau cantor), which in

1633 refers to this stained-glass window—and in the documents, the inscribed year is '*1517*' [11].

The other three panes—the *Madonna* and the two Church fathers—were made together and part of a set, something that seems clearly evidenced by technology, composition and style.

According to written sources, a total of six other stained-glass windows were sold to Silesia in 1819/20, including the coat of arms of Sigmund von Schönfels. There are short descriptions of the panels sold, but unfortunately when Crown Prince Friedrich August became chairman of the Royal Saxon Antiquities Association in 1825, and realised the mistake made with the sale, reacquisition negotiations undertaken between 1839–40 failed. Thus, for the next 170 years, nothing was known about the whereabouts of the panels sold [11], and attribution was lacking one final link.

Chemical characterisation and chemometrics approach

The three panels—*Virgin of the Apocalypse*, *Saint Ambrose*, *Saint Gregory*—could be chemically analysed by μ-EDXRF. The identified medieval colours of the coloured glass fragments were two red hues, light purple, blue, two brown hues, yellow and colourless glass. All the other coloured fragments are thought to have been been added later, probably when the whole collection was gathered in the window sashes of Palace of Necessidades. The ancient fragments were easily recognisable, as a result of their very even thickness and the presence of fine design work in the grisaille painting. Almost all of them were found in a good state of preservation in terms of the corrosion process, showing no significant signs of iridescence, and few signs of corrosion products despite the poor storage conditions under which these panels remained for six decades.

By observation of the production defects (e.g. bubbles), we can deduce that these stained-glass panels were fabricated by first blowing cylinders of coloured glass, and then cutting and flattening those under heat. because the bubbles in the glass tend to be elongated (see Additional file 1: Figure S2). This elongation air bubbles in the molten glass, presents in a technique widely used for making flat glass sheets in the Middle Ages. The hot glass gathered on the pipe is first blown into a spherical shape, is then reheated, stretched and then blown into a tall cylindrical mould. It is known that the long axes of the bubbles indicate the direction of the original cylindrical axis [20].

Glass composition: unveiling similarities

As can be seen in Fig. 1, the majority of the analysed glasses are coloured. As aforementioned, in the present case, six different colours can be distinguished: a bright red, two types of brown (hereafter Types 1 and 2), a dark hue of yellow, light purple and a dark red or bordeaux, and blue glass. It is well known that glass was produced by melting a silica-rich material as a network former (e.g. quartz sand), a fluxing agent (e.g. coastal plants or wood ashes), and a stabiliser (usually deriving from either a calcareous sand or from plant ash), and that coloured glass was obtained by adding one or more colouring materials (metal oxides) [1].

The evaluation of the major set of results obtained on the panels *in situ* or to ascertained glass fragments by μ-EDXRF was performed by PCA using the main elements' peaks from the μ-EDXRF spectra. In Fig. 3, the resulting plot of the two first components allow the interpretation of the variance among data points, explaining approximately 92% of the results. On PC1 axis, the variance is mainly explained by Ca and Fe contents opposed to K (or the corresponding oxides in the glass matrix), suggesting an axial distinction of two compositional groups. The later seem to be related in all cases with the different fragments' colours. PC2 axis presents the inverse correlation between K (with greater influence), Rb and Sr oxides, and Mn and Fe oxides, which mainly seems to represent the spread among colours used (or the element oxides associated with the production of colour).

The variance of the associated elements indicated by the arrows in Fig. 3 is in accordance with what would be expected for different glass types, where two different fluxes or recipes were applied. The influence of the silica (inferred through the Si peak) and alumina (inferred through the Al peak) seems to be rather small, which suggests the use of the same silica source. Ca and K represent both the most variable elements (corresponding to their respective oxides in glass composition) and the most common leachates (even low degree corrosion can produce small variations in light elements). Given the spreading of the data points associated with the same fragment of each panel through a diagonal line (scores plot, Fig. 3), the relation between the similarly-coloured fragments seems clear. Despite using μ-EDXRF analysis, a technique which only allows surface analysis, data points were acquired on both sides of the glass fragments (and cross-section whenever possible) and no significant differences were found, allowing one to assume that alkali leaching (associated to corrosion processes) had few consequences on the currently performed comparison [21].

Analysing the relationship between panel (Fig. 3), it is clear that clusters are being formed based on mainly two compositional groups, which in turn seem to group by sets of fragments' colours. Glass compositional data presented in Table 1 suggest that the flux used was probably wood ash (e.g. bracken, oak and beech) [22]. The glass of the analysed samples can be classified in two

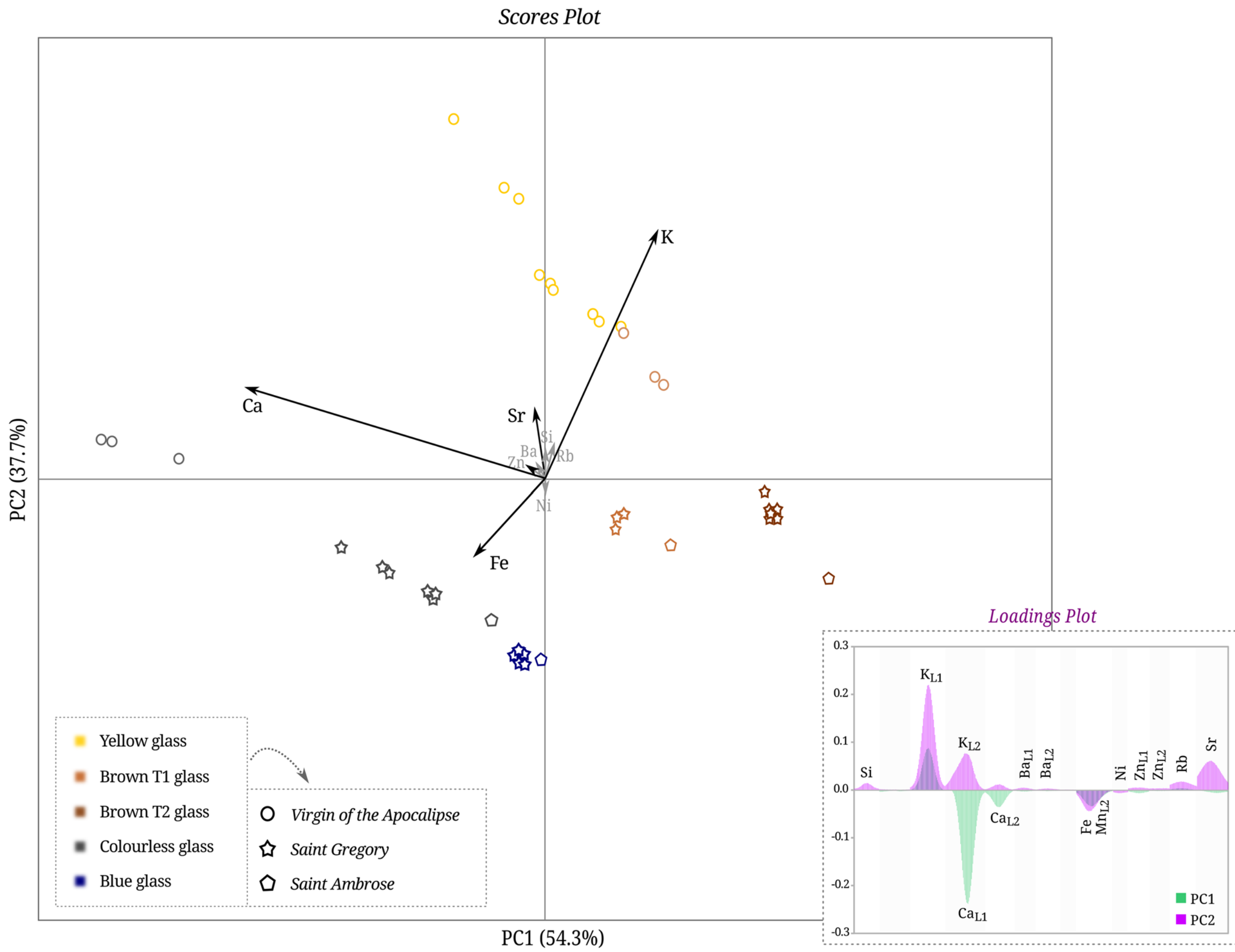

Fig. 3 Principal component analysis (XRF data—scores plot) of the three panels analysed and grouping of the several coloured glasses, explained by variations of elements according to the presented arrow and the down-right loadings plot

compositional groups: (i) high-lime low-alkali (HLLA) or (ii) K–Ca-rich silica type (with mixture of alkali: K and Na). For the classification of these glasses, the authors considered that Na_2O content is lower than 6 wt%, since an amount of MgO between 3 and 4 wt% (associated with the chlorophyll) is expected in wood ash glass [22]. Thus, the colourless, red and blue glasses are HLLA glasses, following Schalm et al. [23] classification (the ratio between K_2O and Na_2O is, in that case, under 0.5). The purple/bordeaux, yellow and brown glasses are then considered Ca–K-rich glasses, since they have high contents of K_2O and the ratio between this and CaO is higher than 0.5 [23]. The concentration of P_2O_5 of about 2 wt% points to the use of unrefined wood ash [23].

Overall (*cf.* Table 1), glasses revealed contents of SiO_2 from *ca.* 52–60 wt%, K_2O from *ca.* 4.7–6 wt% in a first group (HLLA), and *ca.* 10–13 wt% in a second group (K–Ca-rich), (Na_2O + MgO) from *ca.* 6.6–9.5 wt% in the HLLA type, and *ca.* 7.2–9.8 wt% in the K–Ca-rich type, and CaO from *ca.* 19–25 wt% in the HLLA type and *ca.* 13–19 wt% in the K–Ca-rich type. The interpretation of the compositional groups based on the K/Ca oxide concentration ratio is supported by the equivalent grouping of Rb/Sr oxide concentration ratios (see Additional file 1: Table S1), as has been reported in the literature [24]. The latter elements characteristic X-rays are more energetic and detected from inner glass areas, being able to corroborate the absence of data distortion by the presence of alteration layers in this case. As already mentioned, the panels were in fair state of preservation and no significant differences were found when comparing polished cross sections with surface compositions.

Raw materials and the origins of production

The semi-quantitative chemical composition of the studied glasses obtained by μ-EDXRF analysis, illustrated in

Table 1 Average chemical compositions, and corresponding standard deviations of the glass of fragments of the three panels 'Saint Ambrose', 'Saint Gregory' and 'Virgin of the Apocalypse' obtained by μ-EDXRF (minimal data points = 3), expressed wt% of the corresponding most common oxides present in glass

Oxides:	SiO_2	Al_2O_3	P_2O_5	CaO	K_2O	MnO	Fe_2O_3	CoO	CuO	Cl
Panel of Saint Ambrose										
Colourless	57.2 ± 0.8	2.8 ± 0.2	1.6 ± 0.1	23.0 ± 1.7	4.7 ± 0.5	1.29 ± 0.09	0.49 ± 0.03	n.d.	0.01 ± 0.00	0.26 ± 0.08
Red	58.0 ± 1.7	3.3 ± 0.6	2.00 ± 0.00	23.0 ± 0.0	5.3 ± 0.2	0.98 ± 0.04	0.57 ± 0.02	n.d.	0.4 ± 0.1	0.37 ±0.04
Brown T1	58.0 ± 1.1	2.5 ± 0.2	1.1 ± 0.1	18.2 ± 0.9	10.1 ± 0.2	0.52 ± 0.02	0.64 ± 0.03	n.d.	0.02 ±0 .00	0.11 ± 0.03
Brown T2	60.0 ± 0.5	2.4 ± 0.3	1.1 ± 0.1	13.8 ± 0.7	11.9 ± 0.8	1.05 ± 0.04	0.26 ± 0.01	n.d.	0.04 ± 0.03	0.2 ± 0.1
light Purple	59.2 ± 0.5	2.8 ± 0.3	1.03 ± 0.05	17.3 ± 0.1	12.8 ± 0.4	1.25 ± 0.01	0.28 ± 0.00	n.d.	0.02 ± 0.01	0.11 ± 0.02
Blue	58.3 ± 1.7	2.9 ± 0.1	1.4 ± 0.1	20.5 ± 1.5	5.8 ± 0.8	0.99 ± 0.05	0.8 ± 0.2	0.24 ± 0.07	0.05 ± 0.01	0.24 ± 0.04
Panel of Saint Gregory										
Colourless	55.7 ± 0.6	2.7 ± 0.3	2.60 ± 0.04	21.6 ± 0.1	4.73 ± 0.03	1.25 ± 0.01	0.49 ± 0.01	n.d.	0.02 ± 0.00	0.29 ± 0.02
Red	57.0 ± 0.4	1.8 ± 0.4	3.1 ± 0.6	22.2 ± 0.1	6.13 ± 0.06	0.91 ± 0.01	0.51 ± 0.01	0.01 ± 0.00	0.17 ± 0.01	0.20 ± 0.02
Blue	60.1 ± 0.4	1.6 ± 0.3	2.9 ± 0.3	19.7 ± 0.2	5.20 ± 0.00	1.01 ± 0.01	1.07 ± 0.01	0.32 ± 0.01	0.07 ± 0.00	0.18 ± 0.01
Bordeaux	52.0 ± 1.0	1.7 ± 0.5	3.7 ± 0.6	19.4 ± 0.4	13.1 ± 0.1	1.84 ± 0.03	0.19 ± 0.01	0.01 ± 0.01	0.03 ± 0.01	0.05 ± 0.02
Panel of the Virgin of the Apocalypse										
Colourless	56.5 ± 0.7	2.13 ± 0.07	0.27 ± 0.06	22.7 ± 0.6	4.8 ± 0.1	1.30 ± 0.00	0.51 ± 0.02	n.d.	0.01 ± 0.00	0.25 ± 0.01
Yellow	57.2 ± 1.2	1.4 ± 0.4	1.1 ± 0.3	15.9 ± 0.5	12.8 ± 0.4	0.40 ± 0.02	0.36 ± 0.01	n.d.	0.01 ± 0.00	0.08 ± 0.02
Brown T1	56.2 ± 2.7	1.4 ± 0.2	0.27 ± 0.06	16.7 ± 0.6	13.2 ± 0.4	0.42 ± 0.02	0.37 ± 0.02	n.d.	0.01 ± 0.00	0.08 ± 0.01

Oxides:	BaO	PbO	SnO_2	SrO	TiO_2	ZnO	NiO	Rb_2O	Na_2O +MgO
Panel of Saint Ambrose									
Colourless	0.72 ± 0.07	0.04 ± 0.02	0.11 ± 0.01	0.09 ± 0.01	0.10 ± 0.01	0.04 ± 0.01	Trace	Trace	7.6 ± 1.6
Red	0.51 ± 0.03	0.03 ± 0.00	0.13 ± 0.02	0.09 ± 0.00	0.12 ± 0.00	0.03 ± 0.00	n.d.	Trace	7.1 ± 0.4
Brown T1	0.64 ± 0.03	0.07 ± 0.01	0.09 ± 0.02	0.16 ± 0.01	0.15 ± 0.01	0.03 ± 0.00	Trace	0.01 ± 0.00	7.7 ± 0.2
Brown T2	0.50 ± 0.04	0.13 ± 0.13	0.05 ± 0.01	0.06 ± 0.00	0.07 ± 0.01	0.03 ± 0.00	Trace	0.02 ± 0.00	8.6 ± 0.8
Light Purple	0.68 ± 0.03	0.05 ± 0.03	0.10 ± 0.01	0.10 ± 0.00	0.11 ± 0.01	0.03 ± 0.00	Trace	0.02 ± 0.00	7.24 ± 0.08
Blue	0.63 ± 0.03	0.04 ± 0.01	0.09 ± 0.01	0.09 ± 0.02	0.09 ± 0.02	0.03 ± 0.01	0.05 ± 0.01	Trace	7.7 ± 0.7
Panel of Saint Gregory									
Colourless	0.67 ± 0.06	0.06 ± 0.02	0.14 ± 0.02	0.10 ± 0.01	0.11 ± 0.01	0.04 ± 0.00	n.d.	0.01 ± 0.00	9.5 ± 0.8
Red	0.47 ± 0.03	0.04 ± 0.00	0.14 ± 0.01	0.10 ± 0.00	0.13 ± 0.01	0.02 ± 0.00	0.01 ± 0.00	Trace	6.6 ± 0.7
Blue	0.50 ± 0.00	0.06 ± 0.02	0.12 ± 0.00	0.08 ± 0.00	0.14 ± 0.01	0.02 ± 0.00	0.07 ± 0.00	Trace	6.6 ± 0.1
Bordeaux	0.83 ± 0.06	0.07 ± 0.01	0.12 ± 0.01	0.10 ± 0.00	0.05 ± 0.01	0.03 ± 0.00	n.d.	0.02 ± 0.00	7.3 ± 0.8
Panel of the Virgin of the Apocalypse									
Colourless	0.53 ± 0.06	0.06 ± 0.03	0.16 ± 0.04	0.10 ± 0.00	0.13 ± 0.01	0.04 ± 0.00	n.d.	Trace	8.6 ± 1.9
Yellow	0.51 ± 0.03	0.09 ± 0.08	0.16 ± 0.05	0.20 ± 0.01	0.13 ± 0.00	0.03 ± 0.00	0.01 ± 0.00	0.03 ± 0.00	9.8 ± 1.6
Brown T1	0.57 ± 0.06	0.02 ± 0.00	0.18 ± 0.02	0.21 ± 0.01	0.13 ± 0.00	0.03 ± 0.00	0.01 ± 0.00	0.04 ± 0.02	6.7 ± 2.6

Glass classified as HLLA is highlighted in italic, whilst glass classified as K–Ca glass is shown in bolditalic. 'n.d.'—not determined; trace—wt% $<$ 0.01

Table 1, are helpful in the interpretation of the raw material sources used.

The plot K_2O vs. CaO (Fig. 4a) shows a general disposition of compositional groups similar to that of PCA in Fig. 3. As will be presented, there is a good correspondence between the multivariate statistical and geochemically based analyses. It is possible to assume that two different glass compositions were used—one with a higher content of potash (K–Ca-rich) and another with a lower content of potash (HLLA)—from these two consistent results, providing strong evidence that the PCA groups are robust. The two different batches may be associated with two different recipes, or different raw materials used for the same recipe.

The high-lime levels in the HLLA samples compared to a lower level in proportion to the increase in K_2O could result from: (i) the use of a mixture of a high-lime ash with a high-potash ash (either by using different parts of the same wood, where differences in the ratio K_2O/CaO are expected to occur [22], or by mixing different species), (ii) the use of a lime-containing silica source or (iii) a separate addition of lime, such as by adding limestone. It is difficult to determine from compositional data whether the groups here formed are due primarily to the variability of the raw materials, the choice of specific raw materials by the glassmaker, or the use of these sources in different recipes, or a combination of these factors.

The binary plot in Fig. 4b—showing the relations between Sr, Ba and Ca—was used to clarify the differences observed, and it becomes clear that two different lime sources were applied. The elements Ba, Cu, Rb are known to accompany K in beech-tree trunks, whilst P, Mn, Ba and Sr are related to Ca in the bark. Ba is accumulated in both trunks and bark in almost equal proportions [22]. A high CaO/Sr is observed for HLLA glasses (low in Sr), whilst Ca–K glass has higher Sr and Ba contents (according to the lower Ca/Sr or Ba ratios, Fig. 4b). This trend seems contradictory with the use of different parts of the same tree, since Sr contents are higher in the K-rich glasses.

It is also known that ashes were mixed for glassmaking, still for unclear purposes, being assumed that perhaps they were in short supply or that different combinations produced a desired colour or working property [25], and being the most typical wood beech, oak, birch and bracken [22, 25, 26]. The use of fern as a source of K_2O is also mentioned, but it is still unclear if or why glassmakers actually made use of this source [27, 28]. Higher Ca:K proportions follow the trend oak > birch > beech > bracken > fern, whilst the Si and Sr contributions follow the opposite trend; and Ba content is usually higher in birch > beech > oak > bracken [26, 29, 30]. Fig. 4d, e present higher values of iron oxide and alumina in HLLA glass. Whilst in the first case (Fe_2O_3) it seems to be related with the higher content in CaO, the increase in alumina seems independent of this factor, being similar to the Ca–K-rich glass. This could suggest a contribution of the K-rich ashes in Ca–K glass to the SiO_2 content, but not for alumina. In the current scenario, the expected proportions upon mixture of two wood ashes [26] only do not correspond to the observed trends in Fig. 4b. Since interpretation should be made with caution and taking into account the great number of variables involved and the analytical technique applied, a mixture of wood-ashes may still be a plausible hypothesis.

The use of calcareous sand or the separate addition of lime is here also considered. In Fig. 4e, the ratios of TiO_2/Al_2O_3 vs. Al_2O_3/SiO_2 are plotted against the SiO_2/CaO ratio. The former ratios are extremely powerful in identifying production groups, since they relate the chemical composition to the glassmaking sands mineralogy (silica from quartz, alumina from the feldspars and titania from heavy minerals in the silica source) [31]. It is possible to observe in Fig. 4e that the silica-lime and titania/alumina ratios are similar in the two glass types, despite the division of the two groups by the higher alumina/silica ratio in HLLA glass, as in Fig. 4d. Hence, this suggests that only one source of silica was used in the manufacture of the analysed glasses. Additionally, there is no clear relation between the contents of CaO and Al_2O_3, which may indicate the use of non-calcareous sand in both glass types. Instead, it appears more plausible to consider the separate addition of lime. External sources of lime included travertine (high in Sr and low in Ba, P, Cu, and Rb) [22], limestone (low in Sr and Ba) [32, 33], and even dolomitic limestones are mentioned to have been used in the medieval period [34]. In the current case, limestone would probably increase the Ca/Ba and Ca/Sr ratios if mixed with sand and ash. According to Wedepohl [35] a transition from wood-ash to wood-ash-lime glass occurred in Germany after about 1400, which reflected the shortage of wood-ash due to its increasing demand. Wood-ash-lime glass seems to have been produced by the addition of quartz, lime and soda-ash (or Na-glass cullet), and probably with the simultaneous replacement of beech by spruce due to its higher productivity [35]. Proportions of 1:1 or 1:2 (sand:ash) [26, 35] in wood-ash-glass and 1:1:3 (ash:limestone:sand) in the transitional wood-ash-lime (Hartmann 1994 *apud* [36, 37])—later HLLA—have been suggested. Both the just described possible recipe-modifications or the mixture of different wood-ashes seem reasonable possible reasons for the variations in oxides content observed between the two glass types.

Finally, the relatively high Cl concentration, predominantly in HLLA glass (see Fig. 4f), suggests that the low

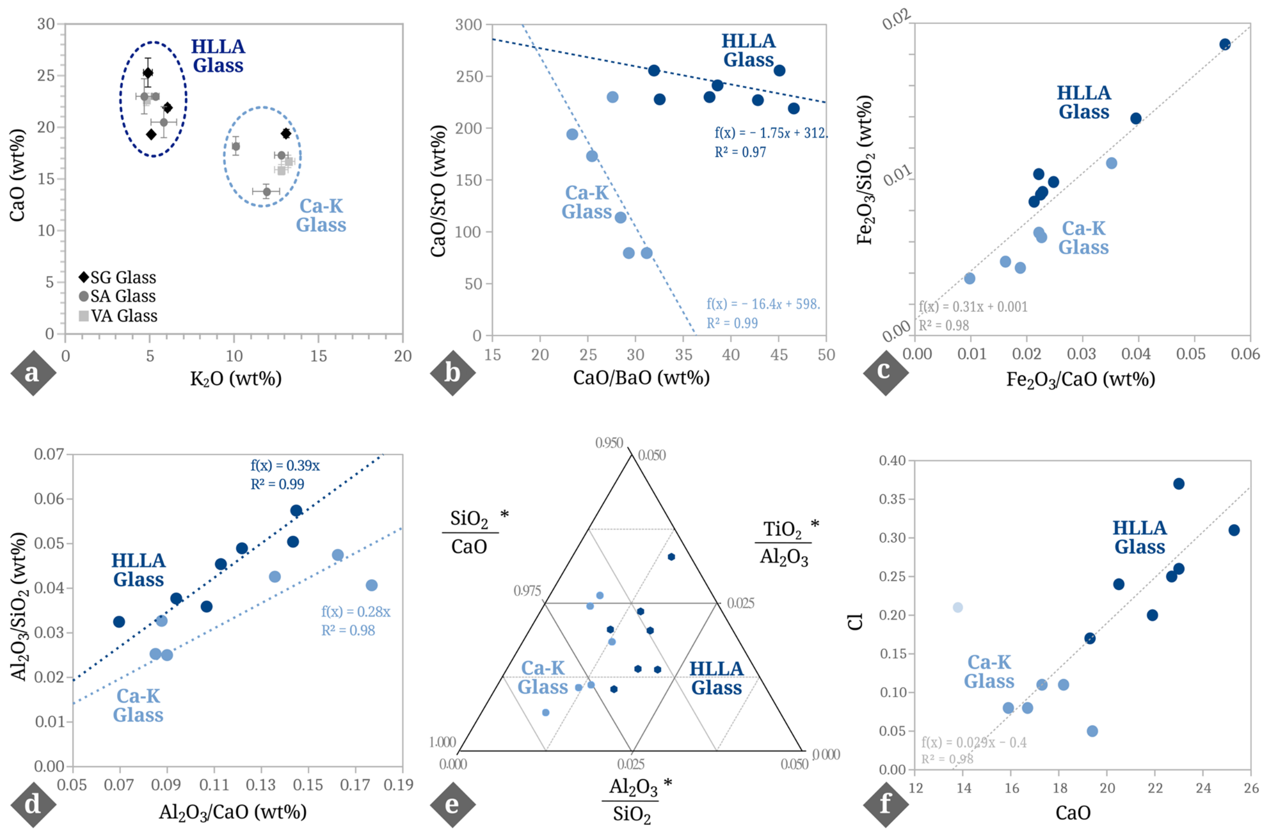

Fig. 4 Binary/ternary plots showing the relations between the concentration (in weight percent of oxides) of **a** K_2O vs. CaO, **b** CaO/BaO vs. CaO/SrO, **c** Fe_2O_3/CaO vs. Fe_2O_3/SiO_2, **d** Al_2O_3/CaO vs. Al_2O_3/SiO_2, **e** normalised ratios Al_2O_3/SiO_2 vs. TiO_2/Al_2O_3 vs. SiO_2/CaO and **f** Cl vs. CaO

K_2O as alkali flux in this case was supplemented by NaCl, similarly to cases reported elsewhere [23].

Colours and painting techniques: helpful tools for provenance and dating

According to the resulting compositions, manganese oxide (MnO) is present in all analysed glasses in concentrations from *ca.* 0.4–1.8 wt%. This oxide could have been added either as a decolourising agent, to neutralise the colour given by iron contaminations (e.g. sand, crucible), or with the purpose of altering the hue of a colour. Batch composition and combustion atmosphere are the key parameters determining the oxidation state. In the case of light purple and bordeaux glass, MnO seems to have been added as a colourant to a K–Ca-rich glass (see Table 1), and the glass was produced in a kiln with an oxidising atmosphere, since Mn^{3+} (identified through UV–vis as shown in Fig. 5a) is usually the ion responsible for purple colour in glass [38, 39]. The case of the bordeaux colour of the robes in the panels of *Saint Gregory* and *Virgin of the Apocalypse* and the light purple of the ox in the panel of *Saint Ambrose* are different hues obtained by the addition of MnO in oxidising environments—MnO in different concentrations (Table 1), hence the different UV–vis intensities (Fig. 5a).

The brown colours in glass could be obtained by changing the proportions of MnO and iron oxide. A yellowish hue is present in Brown T1, (the lighter brown used in the bench and desk of the Church Fathers) and a deeper brown hue can also be observed (Brown T2, as in the architectural elements), all sharing a similar composition (see Table 1). It is likely that the same colouring strategy was used for these colours by the glassmaker, and that different equilibria of the oxidising states are found in the two hues produced, as is suggested by the different intensities of the Fe^{2+} bands the UV–vis spectra in Fig 5b, combined with the spreading of the yellow-brown fragments in Fig. 3 plot, which are directly related to a different K_2O/CaO and Fe_2O_3/MnO ratios (Table 1). High alkaline glasses favour a closer bond of the Fe_2O_3 with the alkali, which means the formation of ferrites. Ferrite corresponds to the presence of iron with coordination number 4 ($Fe^{3+}O_4$), with a strong absorption in the ultraviolet region, which extends into the blue, so that brown colour results. At the same time, MnO in a glass batch acts an oxidising agent changing FeO to Fe_2O_3. An increase in MnO content as in Brown T2 (Table 1) decreases the infrared absorption and increases the absorption in the violet and blue, corresponding to an increase in Fe^{3+} ions also resulting in a brown colour [38, 39].

The blue colour is given by cobalt Co^{2+} in a tetrahedral environment [39] (as identified in Fig. 5c), since cobalt oxide is present only in the composition of the blue glass analysed (Table 1), which distinguishes it from the similar colourless glass composition (as can be observed in the colourless and blue fragments cluster in Fig. 3 and the data on Table 1). In the glasses where cobalt is present, Ni and Fe were also detected (in higher amounts than other cases where Fe is also present—c.f. Table 1), most probably because they coexist in the mineral from which cobalt is extracted. According to comparative studies, performed by Gratuze [40], the association of Co and Ni indicates the use of cobalt extracted from the mines of Erzgebirge, Germany.

Consistent with analytical studies on historical red glass in the panel of *Saint Ambrose*, this colouration was probably produced by nanoparticles of metallic copper dispersed in the glass matrix [39]. The red glass composition has a CuO content varying from *ca.* 0.2 to *ca.* 0.50 wt%, which is much higher than in any other analysed glass (as can be observed in Fig. 1). This, together with the correlated UV–vis absorption bands presented in Fig. 5d, is an indication that copper is the element responsible for red colour in the glasses.

Following a similar approach to other authors [41], a visual comparison of the results of μ-EDXRF and UV–vis techniques for colour attribution is shown in Fig. 6. The colour attribution mainly overlaps in terms of the formed colour groups in all three panels analysed and discussed.

The absence of silver staining for yellow and brown hues, and the use of iron coloured glass fragments instead (Fig. 5b), points to dating these panels to the period before the dissemination of the practice of silver staining [1, 42]. A time gap between the beginning and third quarter of the fifteenth century is consistent with the iconographic program and the typical glass compositions being produced in the Germanic region [35, 43].

Grisaille For the three panels here compared, the same painting technique applied; the lines and shading were executed in grisaille grisaille upon the glass surface to complex designs, lines and shadows of the iconographic representation, and darker and lighter hues were used—see Additional file 1: Figure S3. In the specific case of the the panels analysed, the darker grisaille composition was very heterogeneous, having SiO_2 content varying from 12 wt% to 30 wt%, PbO between 23 wt% and 30 wt%, CaO from 8 wt% to 12 wt% and K_2O content of about 1 wt%. The most significant characteristic of this grisaille is the fact that no relevant amount of iron oxide was detected. This oxide is normally responsible for the black/dark-brown colour of grisaille [1, 44]. However, in this case the iron oxide was replaced by copper oxide (see Fig 7), present in a concentration varying between 10 wt% and 18 wt%. To the best of our knowledge, this composition of grisaille was only reported fashionable in the stained-glass panels of Central Europe during the fifteenth century [45], such as the church of *Salvatorkirche* in Munich [46], in St. James' Church, Prague [47], as well as in Batalha Monastery in Portugal [48], where it is known that a German glass-manufacturer, probably originating from Nuremberg, settled and worked on the production of the stained-glass windows in Batalha Monastery during this period [49].

It is worth mentioning that the two grisailles in Fig. 7 were compared with a Nuremberg *Schwarzlot* painting on hollow glass signed with the monogram of Johann Schapper (dated from the seventeenth century), also in Ferdinand II's collection. It emerged that the Nuremberg painting is similar to the darker grisaille in the choice of black colourising agent (copper oxide, instead of iron as is typical and is observed in the white grisaille, Fig. 7).

Tackling the remaining historical questions

Through the combination of an art-historical and an archaeometric approach, these four late-medieval windows are now being attributed to the *Marienkirche* (Saint Mary's Church) in Zwickau, in the German state of Saxony. *Sigmund von Schönfels' coat of arms* is undoubtedly correlated, and the three other panels relation to this site seems very likely.

Documents attest that the Zwickau panels were sold about 200 years ago, and a correlation with the acquisitions of Ferdinand II in the nineteenth century may be made [11]. Some authors, such as Michael Kühn (*apud.* [11]), suspected that Albrecht Dürer has designed at least one of the glass paintings of the cathedral, but it seems now confirmed that the windows were placed in Zwickau a few years after the altar, which the Nuremberg-based Michael Wolgemut created around 1479, and where, interestingly, the young Dürer had worked. However, dismissing that tantalising possibility, the church documents attest to the commission for the '*window fillings*' of the '*liberey*' and '*new chapel*' being given to a '*glazier*' named '*Jacoff*' (Jakob) on October 21, 1481, who received the '*princely*' sum of 75 guilders for the job. Jakob was probably settled on site with his workshop, which productions and commisions perhaps covered the entire area around Zwickau. Because of the increase of silver mining in the area, an influx of stained glass manufacturers and artisans ensued, which in turn, during the second half of the fifteenth century, resulted in the construction of a number of new churches and stained-glass commissions

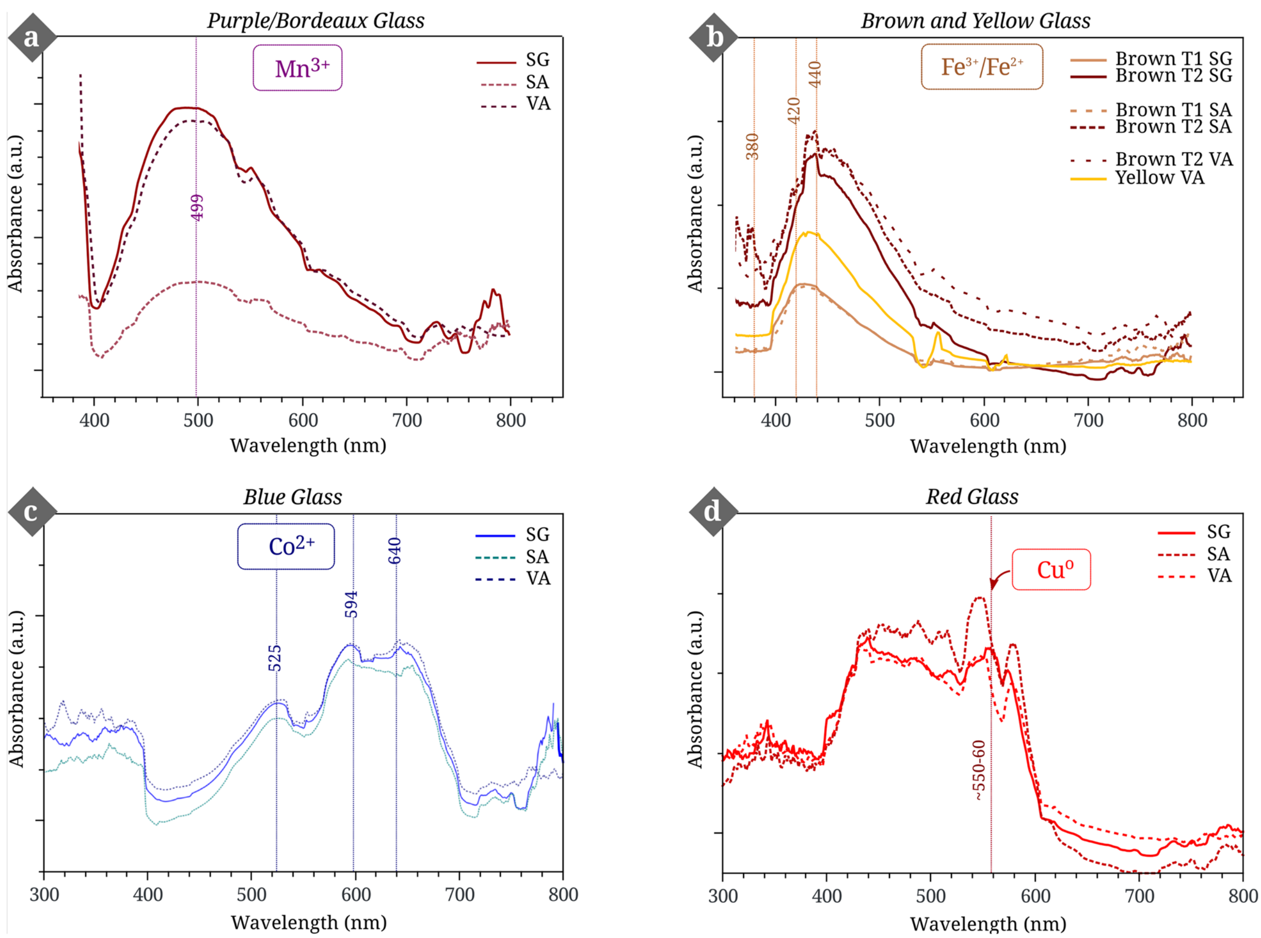

Fig. 5 The **a** purple glass, **b** brown and yellow glass fragments, **c** blue glass and **d** red glass UV–vis absorbance spectra plots for the three analysed panels (*SG* panel of Saint Gregory, *SA* panel of Saint Ambrose, *VA* panel of the Virgin of the Apocalypse)

[11]. The influence of the already mentioned Masters and glass-artisans (Wolgemut, Dürer, Master E.S.) in the three stained-glass panels here considered seems clear. Additionally, these panels also seem to be in line with the iconographic program of Zwickau's cathedral, since: (i) the Virgin Mary appears as an apocalyptic woman and present a close relation with the *Ecclesia*, (ii) and at the same time, the Church Fathers stand for the teaching authority of this very Church, being represented on their *scriptoria*; both of which would be attuned with their placement in the library [11].

Together with the art-historical interpretation, the attribution of an almost certain relationship between the four panels and a *Zwickauer* provenance can now also be reinforced with the results of their chemical analysis. The fact that both Ca–K-rich and HLLA glasses (or wood-ash and wood-ash-lime glass classification [35]) were being used in the three analysed panels supports a probable dating of these windows of 1481, such as should have been the ones at Zwickau according to the documentation [11], since the period of interest (the course of the fifteenth century) saw the transition towards the widely recognised HLLA glass, a technological development which became increasingly established in the regions of Germany and Bohemia/Czechia, [22, 23, 43, 50]. Both types are known to have been used simultaneously during the transitional period [35].

The two hypothesis related to flux raw materials also provide interesting connections to the Zwickau site. The use of mixed wood ashes (beech, oak, and spruce were abundant in the region) and used in the glasshouses situated there during the fifteenth century [51]). The addition of lime through an external source to produce HLLA also points to the Zwickau region because limestone was being extracted in the nearby Ore Mountains [52, 53], and curiously dolomitic limestone was even used in the mortar of the *Mariekirche* itself [54]).

Fig. 6 Classification of glass colours (constituent fragments) based on **a** μ-EDXRF and **b** UV–vis results—false colour maps. Gray areas represent modern glass insets (probably introduced during the nineteenth century)

Finally, the colouring agents in the glass and glass paints also support the relationship here established. The chemical results point to the use of a cobalt-rich mineral extracted from the mines of Erzgebirge, so that establishing a link because of the proximity to the production site (either nearby Zwickau or Nuremberg) is very tempting. Nonetheless, it is well known that the mineral was in use around 1500, and exported to other sites in Europe [40]. Contrariwise, the use of copper in the black grisaille may be a regional trend—an hypothesis derived from the previously presented examples of Batalha's grisailles, where possibly a Nuremberg artist worked [48], or the later application of *Schwarzlot* on tri-dimensional glass, a technique that became famous in the seventeenth century at Nuremberg. It is possible to correlate this information with the 'southern German, Franconian influences' on the handwriting of the glassmaker Jakob, and to the close relationship between Zwickau and Nuremberg in the late-15th and early-16th centuries [11]. The use of copper in colouration of the black grisaille may be a strong indication of the production of these panels in that same region as the proposed *Marienkirche*.

Deeper research would be necessary to definitively attribute the production to a Zwickau-based workshop solely on a chemical basis—perhaps with the use of more invasive chemical analyses that would provide information regarding trace- and rare earth elements (e.g. Laser Ablation Inductively Coupled Plasma Mass Spectrometry, La-ICP-MS). However, to the authors present knowledge, the composition of local raw-materials used for glassmaking has not yet been sufficiently studied to allow the definite establishment of direct correlations.

Conclusion

The study of the four medieval panels in the collection of Ferdinand II of Portugal making use of a multidisciplinary approach (art historical and chemical characterisation) strongly points to a common provenance—now attributed to Zwickau's cathedral in Germany. The current results suggest all panels belong to the same group, three of them sharing common design elements. Those common design elements indicate that those three panels are the work of the same artist, probably influenced by coeval artists such as Master E.S., or the young Albrecht Dürer, at the time working in the workshop of the Nuremberg based Michael Wolgemut, who provided the great altarpiece of Zwickau's *Marienkirche*. The iconographic program also indicates production of the panels during the late 15th to early sixteenth century.

Results from the glass composition analysis are in accord with the proposed date and, most likely, provenance. The glass of the analysed samples is of HLLA or Ca–K-rich silica type, coloured with manganese, iron, cobalt and copper. The panels are all painted with a black grisaille of peculiar composition, in which copper oxide was the coloring agent instead of iron oxide. The possible regional use of copper-based black paints, might perhaps strengthen the relationship established with a Nuremberg-master or a workshop in proximity, such as in the Zwickau area.

As a result of art historical research, stylistic similarities and chemical analysis, it thus becomes evident that the origins provenance of these stained glasses most likely corresponds to the one here proposed, being attributed to the same manufacture and region of production, as well as to the *Marienkirche* site.

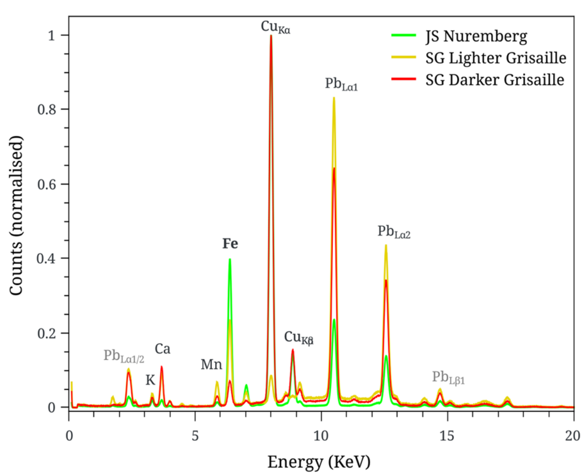

Fig. 7 EDXRF spectra of the two types of grisailles (representative spectra were chosen from Saint Gregory—SG—panel) compared with the spectrum of a Nuremberg *Schwarzlot* painting on hollow glass signed with the monogram of Johann Schapper, also in Ferdinand II's collection. Values normalised between lighter and darker grisaille by the Ca peak, whilst the whole spectra is normalised to the maximum peak, in the present case being the Cu peak

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40494-021-00480-w.

Additional file 1. Supplementary figures and tables—**Figure S1.** Mapping of the analysed spots by μ-EDXRF in the three panels (left to right: 'Saint Ambrose', 'Virgin of the Apocalypse' and 'Saint Gregory'). **Figure S2.** Bubbles in the studied glass tend to be elongated—it can be deduced that these stained-glass panels were produced with coloured blown flat glass, obtained with cylinder glassmaking. **Table S1.** K/Ca and Rb/Sr oxide ratios illustrating the similar trend found and the corroboration of the classification of the fragments into two compositional groups. **Figure S3.** The two grisailles analysed in the panels (Saint Gregory is represented), darker and lighter hues, and their location.

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Authors' contributions

First and corresponding author (AR) has worked on the conception, design, acquisition, analysis and interpretation of data and main contributor in writing the manuscript. Second (MC) and third (AM) authors have made substantial contributions to the acquisition, analysis, and interpretation of data. MC has contributed for the manuscript revision. Forth author (BM) substantially contributed to the art-historical interpretation. Fifth (LCA) and sixth (FM) authors contributed the acquisition and analysis, and FM has substantially revised this work. Sixth and last author (MV), as scientific responsible for the funded project and this work, has made substantial contributions to the work design, data acquisition, interpretation and manuscript revision. All authors read and approved the final manuscript.

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Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare that they have no competing interests.

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