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An Overview of Germanic Grisailles through the Stained-Glass Collection at Pena Palace

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Abstract: The lack of studies reporting the characterisation of Germanic grisaille is evident, despite the recent interest of researchers in this glass painting material. This work consists of the first assessment of Germanic grisaille' chemical composition on a wide chronology (14th–19th centuries), that was only possible through the unique stained-glass collection of King Ferdinand II of Portugal. From the considerable amount of panels produced in Germanic territory and assembled by Ferdinand, twenty-two panels were characterised, and some trends of glass support typical composition and grisaille recipes were verified through this case study. A copper-based grisaille appears to have been the preference up to the 18th century. The 19th century shows higher diversity in composition, with new compounds (such as Co, Cr, Mn) appearing as colourising materials. However, with a limited number of analyses, and dispersed throughout time and different geographic locations, the results of this study are unprecedented, by being able to present the first overview on grisaille composition in Germanic stained glasses.

Keywords: grisaille; stained glass; chemical composition; Germanic productions; 14th–19th centuries

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1. Introduction

Grisaille was the first glass-based paint used in stained-glass windows, usually for the creation of contours and shadows with dark colours (brown or black) [1–4]. Grisailles are typically produced with a mixture of high-lead base-glass and metal oxides of iron and/or copper used as pigments [1]. This mixture is applied to the glass substrate after being combined with a vehicle agent (e.g., vinegar or water) and a temporary binding agent (e.g., Arabic gum). The glass-paint is fired at temperatures between 650 °C and 700 °C, forming a thin (10–100 µm) and uneven layer on the top of the substrate [2].

The study of grisaille paint has been the subject of interest for professionals and scholars throughout the years; this interest has increased very recently [2,5]. However, it was only possible to find a few publications where the Germanic grisailles' composition was quantitatively characterised [6–11]. One of the published examples is the work from 1991 authored by J. M. Bettembourg, where grisailles from five different sites were studied and characterised, one sample from the 13th century Church of St. Cosmos and Damian in Goslar, three samples from the 14th century from the Cathedrals of Regensbourg, Fribourg and Augsbourg and a 15th century sample from the Speyer Cathedral [6]. Other example is the 1996 paper by H. Marschner where forty different samples dated from the 15th century from the Saviour Church in Munich were characterised [7]. From W. Müller it is possible to give three examples: the 1996 paper where three grisaille compositions are presented from the St. Catherine Church in Oppenheim dated between 1330 and 1340 and also four compositions from 19th century replacement grisailles fragments from restoration works in the same Church [8], a 1999 work where the composition from 19th century grisailles from St. Paul Church in Schwerin is described [9] and the 2004 work in collaboration with M. Torge and K. Adam where Medieval grisailles (1380–1420) from the St. Mary Cathedral in Erfurt were characterised [10]. Finally, the last example is from M. Veritá that was published in 2009 in a paper where he studied three samples from the Cologne Cathedral dated from the 14th century [11].

The lack of studies reporting the characterisation of Germanic grisailles is evident from the few examples mentioned. Moreover, the analysis of glass compositions of Germanic stained-glass productions is not the subject of extensive attention from researchers, with some exceptions (e.g., Brill [12], Drachenberg et al. [13], Brill [14], Müller et al. [15], Sterpenich and Libourel [16], Wedepohl and Simon [17], Adlington et al. [18] and references therein). On the contrary, the production of stained glass along the centuries in Germanic territory is unquestionable—from the earliest examples of stained glass windows currently known, present in the Augsburg Cathedral [19], to prolific religious manifestations during the Holy Roman Empire [20], or even in other private and public fruition contexts after the Reformation [20,21]. German stained glass has long been targeted and explored in depth in the field of Art History (just a few examples are within references [20–22]), deserving the special attention of the *Corpus Vitrearum Medii Aevi* (e.g., "*Die mittelalterlichen Glasmalereien in …*" series of publications). Many of these Germanic stained glasses have been removed from their original architectural contexts and incorporated into collections since the late 18th century and all through the 19th century [23,24], as was the case of the subject of this study.

1.1. Case Study: The Collection of Ferdinand II

The unique stained-glass collection of Ferdinand of Saxe-Coburg-Gotha (1816–1885)—married to Queen Maria II (1819–1843), becoming Ferdinand II of Portugal (1836–1885)—includes a considerable number of panels produced in Central and Western Europe (namely, in the territories of modern Germany, Switzerland and the Netherlands). These panels were originally installed in churches, monasteries, manor houses and artisans' workshops and were later acquired for the king´s collection during the 19th century [25]. Ferdinand II kept his collections in the two residences where he spent longer periods of time: the official royal residence, the Palace of Necessidades (located in Lisbon), and the summer residence, the Pena National Palace (PNP, located in Sintra), an adaption from the ruins of the 16th century cloister of Pena [25,26]. At Necessidades Palace, the main group was displayed in the Dinning Room during the 19th century. These were dismantled after the end of the monarchy and were later kept in the storage of PNP, having been recently exhibited in the Stag Room (*Sala dos Veados*). The group consists nowadays of 37 panels and 90 *Fernsterbierscheiben*. The former are a highly diverse set with wide chronology (14th to 18th centuries) that were randomly grouped together, whereas the latter (literally translated as 'window beer panels') are small rectangular glass pieces with glass paint, produced to celebrate the opening of a house or an important family event, such as a wedding, popular among rural communities in Northern Germany, mainly from the mid-17th to the late 18th century [25–27]. The main group originally mounted for the PNP is displayed at the Great Hall of this Palace and consists of three windows with a larger set of panels, also mounted with similar aesthetic choices [28]. A set of four stained-glass panels was also set in the Pena Palace's Chapel, specially commissioned by Ferdinand II in the 19th century during the conversion of the old Monastery into the summer Palace.

The group of Germanic panels is, not surprisingly, by far the largest within the collection, also taking into consideration the art market and the dealers to whom the acquisitions were commissioned [28].

1.2. Main Objectives

This work aims to contribute by providing the first assessment of the Germanic grisailles' chemical composition on a wide chronology (14th–19th centuries), made possible through the large number of representatives within the stained-glass collection of King Ferdinand II of Portugal. A considerable number of these panels were produced in the Germanic territory and have wide chronological and geographical spans. Focusing on this unique case study, this work analyses twenty-two panels (Figure 1) using the non-destructive and non-invasive micro Energy Dispersive X-ray Fluorescence (μ-EDXRF) and Proton induced X-ray Emission (PIXE) techniques; this has allowed for the first overview of possible typical composition and/or grisaille recipes being applied from the 14th to the 19th centuries in German stained glass.

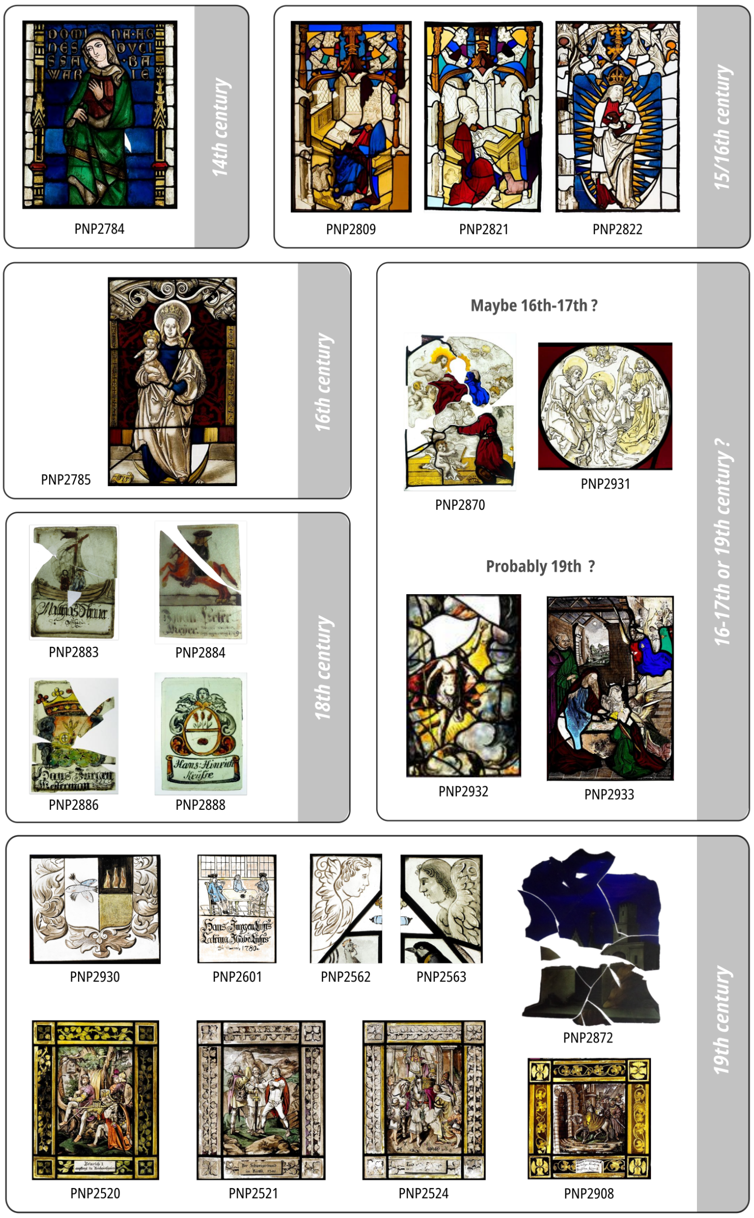

Figure 1. Stained glass panels from Pena National Palace (PNP) collection, identified by the reference number, grouped by attributed production date.

2. Materials and Methods

2.1. Panels

Twenty-two Germanic panels from the collection of the Pena National Palace—comprising both panels from the Great Hall and the Palace of Necessidades temporarily exhibited in Sala dos Veados—were accessible to be analysed by micro-energy dispersive X-ray fluorescence (µ-EDXRF) in situ and/or by micro-particle-induced X-ray emission (µ-PIXE). These 22 panels constitute the current case study and are shown in Figure 1. The studied panels originating from different locations in the territory of modern Germany date from the 14th until the late/mid 19th century, and their geographical and chronological distribution is represented in Figure 2. In this paper, only the results obtained for the glass thought to be from the original production of the panels are presented, as well as the associated grisaille painting material. This was performed through a previous stylistic and art-historical assessment of each panel. Examples can be found in some of the authors' works published elsewhere [25,27,28].

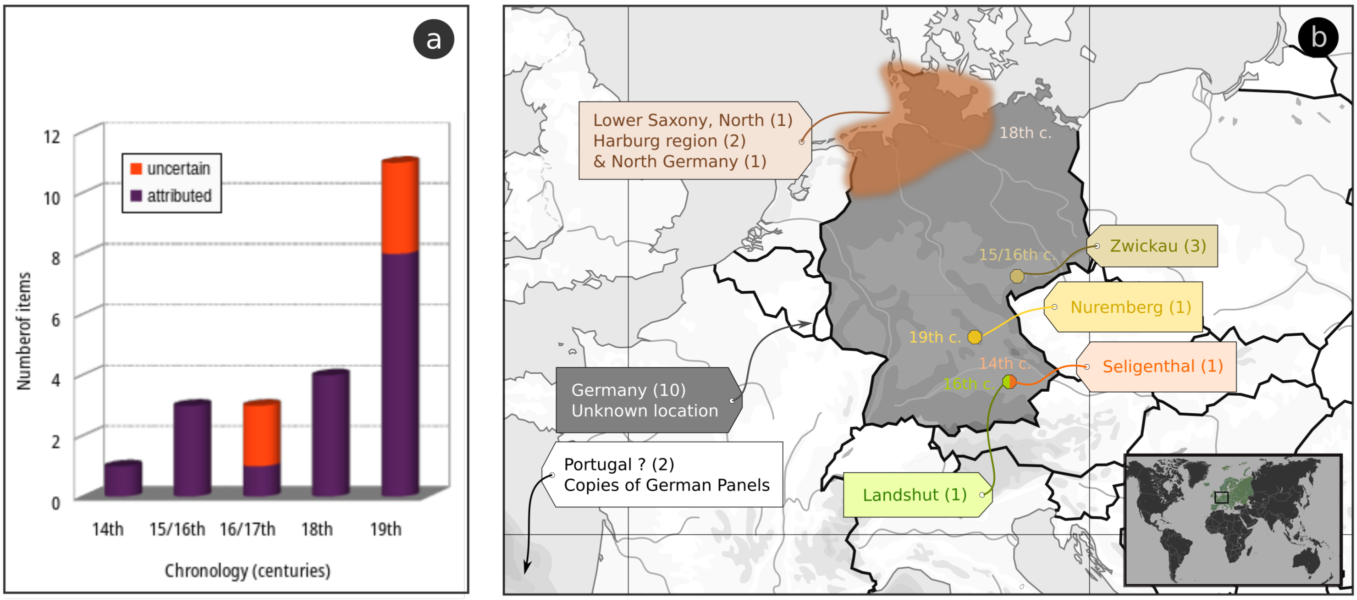

Figure 2. Chart with the number of analysed panels from each date/period (**a**) and map showing the place of origin of the studied panels, with the number of panels attributable to each location (**b**).

The oldest panel of the case study represents *Lady Agnes of Bavaria* (PNP2784), and it dates back to the 14th century (1314–1320), previously part of a window from the Seligenthal monastery [26]. The areas analysed correspond mainly to the face of Lady Agnes. Dated from late 15th/early 16th century are the three panels *Saint Gregory* (PNP2809), *Saint Ambrose* (PNP2821) and *Virgin of the Apocalypse* (PNP2822), that were already proposed to have the same manufacturer and were probably attributed to the *Marienkirche* at Zwickau [25], which was determined due to them sharing common elements in the architectural design illustrated within each panel and their similar chemical composition. The areas analysed are in accordance with the fragments considered 'original', also already published elsewhere [25]. The panel *Virgin with Child* (PNP2785) is dated from the early 16th century (1515) according to its own inscription in the bottom left-hand corner. Moreover, in this case, fragments of the face of Mary and Child were analysed. The panels of the *Virgin's Ascension* (PNP2870) and the *Baptism of Christ* (PNP2931) may also date from the 16th/17th centuries, but this attribution is uncertain due to the uncommon aesthetics of PNP2870 and due to the apparent low quality of the applied paint and poor detail on the PNP2931 panel. Many doubts exist aroudn the attribution of the panels of the *Resurrection of Christ* (PNP2932) and *Birth of Christ* (PNP2933), despite exhibiting some iconographic parallels with 16th/17th century representations, and it would be more likely that these actually belong to the 19th century. In panel PNP2933, the fragments depicting the faces of Mary or the donor and the window with the landscape were considered as potentially the earlier parts of the panel—on the contrary, many other fragments were considered as most likely replacements. The group of four *Fernsterbierscheiben* panels, PNP2883, PNP2884, PNP2886 and PNP2888, is attributed to the 18th century, whereas the remaining one (PNP2601) is already dated from the 19th century, both by their clear aesthetic differences, and by their chemical composition [27]. All other studied stained glass panels fall into the 19th century's chronology, which include the panels titled *King Henry I* (PNP2520), *The Rütlischwur* (PNP2521), *Theoderic the Great* (PNP2524), *Constantine the Great* (PNP2908), two panels representing *Cherubim angels* (PNP2562 and PNP2563), one panel depicting a coat of arms (PNP2930) and one panel from the Pena Palace's Chapel (PNP2872), the latter known to be commissioned of the Kellner workshop in Nuremberg (in 1840) [29].

2.2. Analysis

Due to the a priori limitation of no-sampling and the constraints related to moving the stained-glass panels installed in the windows at PNP, the in situ non-invasive µ-EDXRF analysis allowed the characterisation of the great majority of these panels, which are mounted in their original wood frames. The analyses were performed directly on the surface. Limitations of accessibility due to the display of the panels made it only possible to have access to one side of the glass in most cases. PIXE analyses were performed only when possible, in the case of fragments and dismantled panels. A set of four panels kept in storage/temporarily dismounted was analysed. In these panels, cross-sectional analysis of the most uniform and apparently clean and fresh fractured surfaces was preferred, in an attempt to obtain the bulk-glass composition with minimum possible surface corrosion interference. The grisaille was analysed directly on the surface of these panels. All spectra were compared.

For the results interpretation, qualitative spectral data were considered as the first approach. Semi-quantitative data obtained through the two superficial techniques (µ-EDXRF and µ-PIXE) were used for data systematisation, representation and better interpretation due to the large amount of information retrieved. Data limitations were taken into consideration, namely major element compositions that are usually lighter elements. Differentiation of compositional groups (soda lime, potash-rich, etc.) and colourants used in glass and grisailles took into consideration the presence/absence of elements or oxides and their relative amounts in terms of content. This discrimination is known to be possible even for less accurate portable equipment [30]. The influence of diffused elements from grisaille to glass [31] and the leaching of light elements from glass by either outdoor or indoor environmental factors [32] are phenomena well known to the authors, hence these were also considered. All quantitative results presented (appended) are intended to be indicative of the relative amounts of the typical oxides present in grisailles, and the authors are cautious in their interpretations.

2.2.1. µ-EDXRF

Concerning the chemical characterisation, 20 of the 22 panels (Figure 1) were accessible to be analysed by µ-EDXRF 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 µm by means of a polycapillary X-ray mini lens. The spectrometer was operated at 40 kV, 0.6 mA, under a He flow atmosphere to optimise the detection of light elements with an acquisition time of 360 s. At least three different measurements were carried out on each different material. Depending on the element and on the matrix under analysis, the typical probing of the equipment can go from a few micrometers' (ca. 30 µm, e.g., lead-based glass) to some millimeters' (ca. 2–3 mm, e.g., borossilicate) depth.

Quantitative analyses were carried out with the AXIL 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 ⩾ 13, thus making detection of sodium and magnesium impossible. The concentration of these elements was calculated by the method of 'matrix by difference' [33]. 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. Whenever the glass types under study were found not to be soda-glass (which makes the distinction of the glass types harder), the drawbacks of the approach in the present case were reduced. Nonetheless, some 19th century stained glasses had higher limitations in terms of the offered results and their interpretation with the current analytical method. For the quantification of the Pb-rich materials, such as the grisailles, lighter elements (Na, Mg) were excluded and a semi-quantification was again considered. The error associated with the analysis of grisailles was indirectly calculated for BaO, CuO and ZnO, and was below 1%; the calculated error for K_2O and PbO was below 3%, and for CaO, CoO, Fe_2O_3 and NiO was below 11%. For the lighter elements such as SiO_2 the error was below 20%. This was verified by analysing standard glasses (Corning C was used as reference for grisailles as the closest standard material) under the same experimental conditions as the samples and calculating experimentally the concentration values of the certified samples. The error associated with the grisaille material itself can not be directly assessed, hence all the quantitative result interpretations takes into consideration this limitation. The error associated with the analysis of the glass supports was also calculated and is already published elsewhere [25].

2.2.2. μ-PIXE

In order to obtain the quantitative chemical composition and elemental mapping of grisaille and glass, micro-particle-induced X-ray emission analysis was performed on a set of 4 fragmented panels that were in storage, PNP2884, PNP2886, PNP2888 and PNP2872. The fragments were analysed in cross section for glass composition, as well as directly on the surface for both glass and grisaille, and the grisaille composition was retrieved. The μ-PIXE ion beam analytical technique was performed using an Oxford Microbeams OM150-type scanning nuclear microprobe set up with external beam configuration. A 2 MeV proton beam focused down to dimensions of 70 × 70 μm was used for generating characteristic sample elemental X-rays that were collected with a silicon drift detector with 145 eV resolution. Beam scanning over a sample area of 1 × 1 mm^2 allowed for properly defining the area of analysis through the obtained elemental distribution mapping. A He flow through the detector path with 2 L/min was used in order to be able to detect elements down to Na. The results typically probe a sample depth of 10–20 μm, hence the superficial limitations are known, especially in the presence of heavy elements, such as lead [30], and in the heterogeneous materials as the grisailles. A semi-quantification is therefore considered. The OMDAQ software code was used for operation and basic data manipulation, including the mapping of the elemental distribution [34]. Quantitative analyses were performed with the GUPIX software [35]. For detailed system setup information, see Corregidor et al. [36]. Each sample was analysed in three different zones, and the results in oxide-weight-percentage form were normalised to 100 wt%. In order to validate the obtained concentration results, the glass reference standard (Corning C) was also analysed. For glass, standards Corning A, B, C and D were also analysed.

3. Results

The chemical composition of all the support glasses was also assessed for a better comprehension of each of the stained-glass panels, as well as to better compare the different grisaille paints over the different support glasses. The classification of the glass-support compositions is plotted in Figure 3 (see also Appedix B, Table A3). For this classification, the diagrams of Schalm et al. [37], Dungworth [38], Girbal and Dungworth [39] were considered.

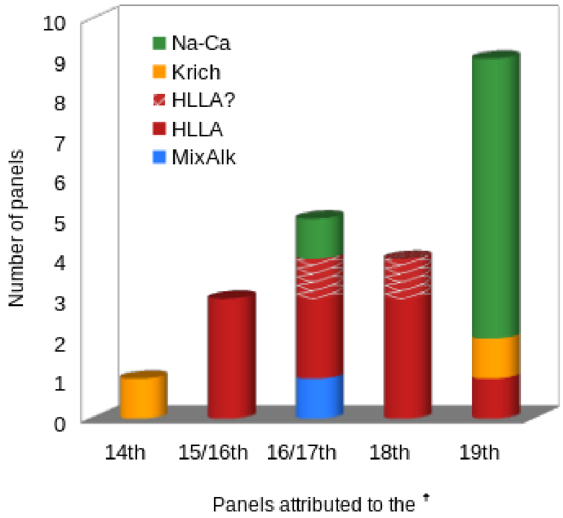

Figure 3. Distribution of the glass compositions of the panels analysed and attributed to the represented range/chronology. Legend: Na-Ca = soda-lime silicate glass, K-rich = potash silicate glass, HLLA = high-lime low alkali glass, MixAlk = mixed-alkali silicate glass.

With the exception of the glasses rich in potassium oxide (K-rich) found in the 14th century glass painting of *Lady Agnes of Bavaria* (PNP2784), there is a predominance in the use of high-lime low-alkali (HLLA) glass from the 15th to the 18th century, or so it seems from the collected data. The soda-lime (Na-Ca) and the mixed-alkali (MixAlk) glasses from the panels originally attributed to the 16th/17th centuries—PNP2870 and PNP2933—seem to possibly be related to later productions. It is very likely that these two could be 19th century productions with earlier iconographic motifs. If this is the case, the HLLA glass could indeed be the preferred formulation for the whole 15th–18th century chronology in terms of glass sheets' production in Germanic territories.

Moreover, the identified HLLA glass type in the one panel (PNP2563) attributed to the 19th century presents P_2O_5 and Fe_2O_3 content that is compatible with an earlier production (see Appendix B, Table A3). If that were the case, the panels could have been produced in the previous century to the attributed one. During the 19th century, from the gathered compositional information, glass sheet production was already incorporating the use of more purified materials, such as synthetic soda; this is in good agreement with the literature data from other European counterparts (e.g., Pradell et al. [3], Dungworth [38], Girbal and Dungworth [39]). Hence, a lower content (almost none) of potassium, magnesium aluminum and phosphorous oxides would be expected [3].

Concerning the chemical analysis of the grisailles under study, the results allowed us to retrieve the main element constituents of the colouring agent, as well as of the base glass, as is shown in Table 1.

Most of the grisailles show a predominance of the copper as the main pigment, in particular among the panels attributed to the 14th to the 18th century. Concerning this period, the range of CuO and Fe_2O_3 on the analysed grisailles is shown in Figure 4a. In turn, the 19th century grisailles possess a more diverse composition, with the likely deliberate introduction of Cr, Co and Mn, as is visible in Table 1 and Figure 4b. Elements such as Zn and As were also detected, and these can relate either to the pigment components or to the base-glass composition, which will be further discussed. The panels PNP2870 and PNP2933 seem to fit well among the diversity of the latter chronology, where the main colourant is also iron oxide.

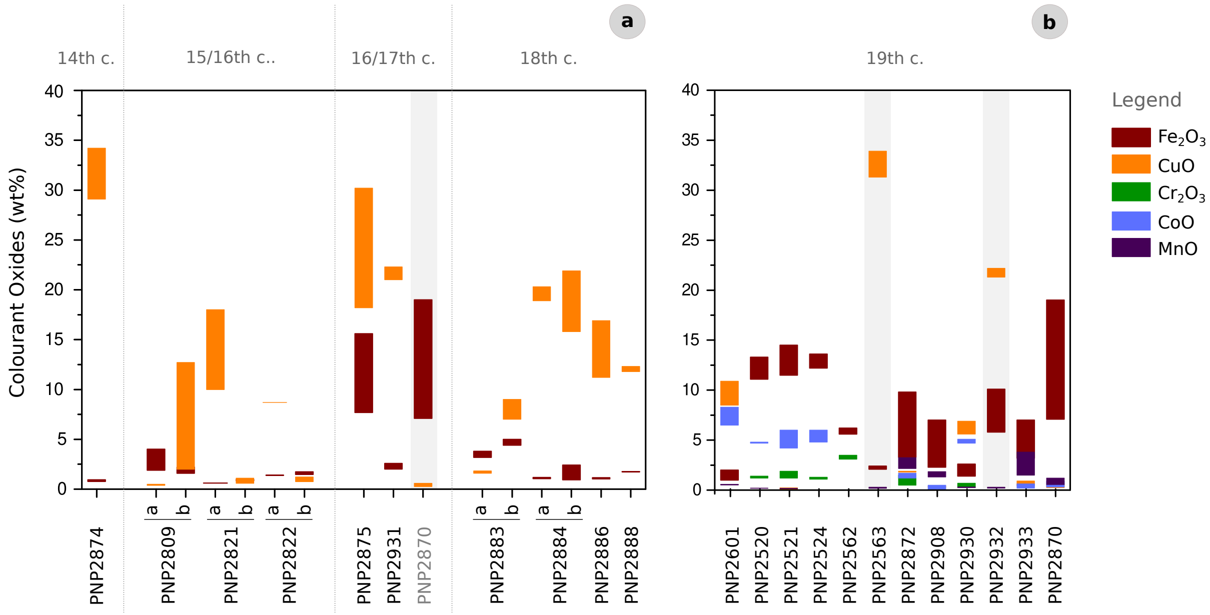

Figure 4. Range of colourant oxides (pigments) in the grisailles analysed from the panels attributed to (**a**) the 14th–18th centuries (CuO and Fe_2O_3) and to (**b**) the 19th century (grisailles/black paints). Grey areas correspond to the outliers discussed below.

Table 1. Summary of the main elements detected in the analysed grisailles related to the colouring agent (pigment), as well as to the base glass. Dominant pigment oxide is marked in red, and the Zn content in either pigment *or* base-glass is marked in gray. (a) and (b) correspond to two different compositional types encountered (see Appendix A, Tables A1 and A2).

Chronology	Inv. Nr.		Pigment								Base Glass		
			Cu	Fe	Mn	Zn	Co	Ni	As	Cr	Pb	Si	Zn
14th	PNP2784		• (red)	•							•	•	
15/16th	PNP2809	(a)	•	• (red)							•	•	
		(b)	• (red)	•							•	•	
	PNP2821	(a)	• (red)	•							•	•	
		(b)	• (red)	• (red)							•	•	
	PNP2822	(a)	• (red)	•							•	•	
		(b)	• (red)	• (red)							•	•	
16/17th	PNP2785		• (red)	•							•	•	
	PNP2870		•	• (red)	•		•	•			•	•	
	PNP2931		• (red)	•		•					•	•	
18th	PNP2883	(a)	•	• (red)							•	•	
		(b)	• (red)	•							•	•	
	PNP2884		• (red)	•							•	•	
	PNP2886		• (red)	•							•	•	
	PNP2888		• (red)	•							•	•	
19th	PNP2601		• (red)	•	•	•	•	•	•		•	•	
	PNP2520			• (red)		• (gray)	•	•		•	•	•	• (gray)
	PNP2521			• (red)		• (gray)	•	•		•	•	•	• (gray)
	PNP2524		•	• (red)	•	• (gray)	•	•		•	•	•	• (gray)
	PNP2562		•	• (red)		• (gray)			•	•	•	•	• (gray)
	PNP2563		•	• (red)		• (gray)					•	•	• (gray)
	PNP2872		•	• (red)	•	• (gray)	•		•	•	•	•	• (gray)
	PNP2908		•	• (red)	•	• (gray)	•	•			•	•	• (gray)
	PNP2930		• (red)	•		• (gray)	•	•		•	•	•	• (gray)
	PNP2932		• (red)	•							•	•	
	PNP2933		•	• (red)	•	• (gray)	•				•	•	• (gray)

When considering the grisailles with a later chronology, it is important to mention that, since light elements were not detectable through the µ-EDXRF technique applied, those elements—such as boron—were not able to be considered in the semi-quantification results. Hence, it is necessary to be aware of the possibility that some of the grisailles produced from the 17th century onward could have had borax ($Na_2B_4O_7 \cdot 10H_2O$) in their composition (considering data from other counterparts [3]), for which this study cannot provide proof. This possibility will also be further discussed in a possible theoretical way.

4. Discussion

4.1. Cu-Fe Pigment Grisailles (14th to 18th Century Panels)

4.1.1. 14th Century: A Singular Case

The panel of *Lady Agnes of Bavaria* (PNP2784) dated from the 14th century clearly presents the use of a copper-coloured grisaille (Figure 4 and Table A1, Appendix A—as a quantitative/qualitative guideline) over a potassium-rich support glass (Table A1). Despite potassium glass types sometimes presenting problems in terms of identification—quantification limitations of XRF techniques as elsewhere published [39,40]—the results obtained show consistency with this classification and with coeval compositions. Lead diffusion into the glass surface could also affect these results [30]; however, the K_2O:CaO proportion was revealed to be above 1, which supports a K-rich classification, even if potassium is being underestimated at the surface. The fact that the glass surface demonstrated very few corrosion symptoms can influence a semi-quantification not so compromised in this case as in others. This glass composition would be expected based on the chronology and central location of the glass manufacture [15–17,41]. When looking at the ranged values in Table A3, used for guidance when considering the grisaille composition, the ratio Fe_2O_3:CuO shows an approximate 1:32 proportion (about 3% Fe_2O_3 to 97% CuO), denoting the preference for the use of copper as the colourant. There is only one case study from the 14th century, hence there is no possibility of comparison within the rest of the collection. When relating this observation with the only known historical reference of grisaille recipes for an approximate chronology in Germany (*"De diversis artibus"* by Theophilus, a monk living in Germany in the 12th century), which is also the earliest known source to address the production of stained glass windows [1,42], it may seem reasonable to consider that the glass painters in the region could well be following the written source's instructions. In addition to the Germanic source, another coeval Italian written document (*"Secreti per lavorar li vetri secondo la dottrina de Maestro Antonio da Pisa"* by Antonio da Pisa, 14th century) seems to have mentioned the use of copper for the production of grisaille paint materials [1,43].

4.1.2. 15th/16th Century: Three for One

The three panels studied from the 15th/16th centuries (*Saint Gregory*, PNP2809; *Saint Ambrose*, PNP2821; *Virgin of the Apocalypse*, PNP2822) were recently attributed to the same workshop [25], hence it could be presumed that they would share the same grisaille recipe. The support glass (colourless glass) has a high-lime low-alkali (HLLA) composition, also preferred for the production of certain colours, such as deep blue, but some other coloured glasses on the panels possess higher potassium contents, possibly also contributing to obtaining other hues (see Table A3 and Rodrigues et al. [25]). Nonetheless, concerning the analysed grisailles, this group actually shows some complexity in the interpretation of the analytical results, due to the difficulties in analysing the thin paint layers and the dispersion of the compositional data obtained (see Table A3). The panels present some contours in thick lines (*grisaille à contourner*) but mostly shadows, where a thin and watery layer was applied (*grisaille à modeler*) [1]. Most of the accessible areas were thinner layers. It seems the analyses reveal that the grisailles on the three panels fall within the use of iron and copper together, similar to what was identified in other Eastern European countries [2]. Ratios of Fe_2O_3:CuO of 1:1 or 1:2 [2] seem to be consistent with some of the results presented for the three panels in this study. Only when the influence of the glass support or the amount of base-glass increases, does the amount of iron oxide seem to be dominant. In this case, a more cautious approach is necessary in terms of interpreting such results. Additionally, the proportion between the base glass and the colouring agents is also comparable with the literature reporting that, between the 15th and 17th centuries, the grisailles could have presented up to 80% of base glass (to 20% colouring agents) [2], and this could be the reason for the latter's increase in the SiO_2 content (Table A3). Another interpretation could be to consider some influence of the support glass on the analysis of thin grisaille layers.

4.1.3. 16th/17th Century: A More Complex Interpretation

Concerning the panels attributed to the period from the 16th to the 17th century by their iconographic characteristics, the chemical composition results seem to lead to a more complex interpretation.

The panel of the *Virgin with Child* (PNP2785) offers no doubts regarding its attribution; the support glass is classified as HLLA. As was previously mentioned, as well as according to the main part of the literature reporting post-medieval colourless glass compositions, this seems to have become the most commonly found composition of glass from Germanic territories after the Middle Ages and upon the use of wood-ash-lime glass compositions (i.e., with lower K_2O content) [17]. Additionally, when looking at the grisaille composition, it is again verified that a copper-rich grisaille seems typical for the location where it has been produced (Landshut, same as *Lady Agnes of Bavaria*, PNP2784). However, similarly as was observed for the previous 15/16th century group of three panels, the mixture of 1:2 parts of Fe_2O_3:CuO (see Appendix A, Table A1) seems to exist and again be in accordance with the literature [2].

The support glass of the panel representing the *Baptism of Christ* (PNP2931) is a HLLA glass. Moreover, it also presents a grisaille with a pigment rich in copper. Based on a possible lower quality of production—as could be observed by the aesthetics of the panel and of the applied paint layers, through the art historical assessment prior to the analysis—some doubts existed around the attribution to the 16th/17th centuries. However, both the base-glass and most importantly the type of grisaille applied seem to be consistent with this chronology. In this case, the Fe_2O_3:CuO is different from panel PNP2785. Additionally, the use of a different source of copper seems evident from the higher content in ZnO, suggesting the use of brass [2,31].

Contrarily, the support glass of the panel representing the *Ascension of the Virgin* (PNP2870) can be classified as a soda-lime (Na-Ca) silicate glass, and, by the absence of higher concentrations of the oxides of elements such as P, Mn and Fe, it can be very likely determined to be a later production. The probable chronology of the analysed glass is in fact the 19th century (ca. 1870–1930), where synthetic soda, among other purer raw materials, was already in use [38,39], since this panel is actually from a later chronology, and the grisaille or back-painting material show different characteristics (e.g., higher contents of Mn, Fe and Ni and very low Cu oxides, see outlier in Figure 4a). Hence, this panel, along with its respective grisaille, will be further analysed with the 19th century group.

From the observation of the results obtained for this case-study, a pattern seems to emerge from the analysis of the assembled panels, i.e., the possible existence of a preference to use copper as colourant for the production of the grisaille-paint, at least in the Southeastern part of Germany up until the 17th century. This practice could perhaps also extend to the West; however, only the panel PNP2931 could perhaps be attributed to the Western side of Germany, and neither the attribution nor the practice can be ascertained.

4.1.4. 18th Century: A Homogeneous Group

The 18th century group of panels consists of four Fensterbierscheiben, which present an overall similar glass–support composition (HLLA glass), which was confirmed by PIXE and EDXRF quantifications (see Table A3, Appendix B). The four Fensterbierscheiben panels represent a homogeneous group since this type of production was very restricted to the North of the Germanic territory, in addition to the already observed trend in the use of rather similar chemical compositions for the production of glass sheets [27]. These four panels represent slightly different chronologies and origins of production: the panel PNP2883 is attributed to Lower-Saxony North, ca. 1700–1750; the panel PNP2888 an unknown region of Northern Germany, also from the first half 18th; and the two panels PNP2884 and PNP2886 are attributed to the region of Harburg, ca. 1760–1780. These production origins do not necessarily relate to the glass support, but more importantly they concern the painting/representation that allows the attribution through the art-historical point of view and, therefore, by consequence of the grisailles material applied.

The 18th century grisailles characterised by PIXE mapping clearly show the dominance of Cu as the colourising element—Figure 5. The grisaille of PNP2884 (same for PNP2886 and PNP2888 analysed) can be easily perceived from Figure 5 as painted layer with an homogeneous distribution of Cu (colourant). The sharp line observed between the paint and the glass substrate clearly shows the differences in composition from glass to grisaille paint. The grisaille is not significantly richer in Fe compared to the glass substrate. This is in perfect accordance with the grisaille composition observed up to the 18th century in the panels from this study (see Appendix A, Table A1).

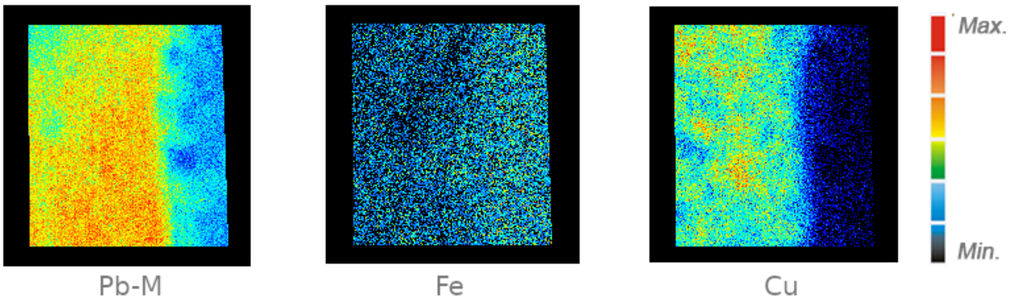

Figure 5. PIXE map of panel PNP2884 in the grisaille/glass border (surface analysis) for the elements Pb, Fe and Cu.

In addition to the interesting observation that HLLA glass supports were still preferred in this region during the 18th century, contrary to the changes already observed in other counterparts (e.g., United Kingdom [38,39]), copper-rich grisaille also appears to have been maintained. It is unfortunate that the data from Southern and Northern Germany in this collection do not allow a direct comparison, since they do not belong to the same chronology. However, the spread of data once more seems to suggest that, even if different recipes were being used, the grisailles up to the 18th century seem to show a predominant use of copper as the colourising element.

4.2. 19th Century Panels: Grisailles vs. Other Black-Paint Materials

During the 19th century, a diversity of materials seems to have started to be used in the production of both the support glass and the painting materials. Concerning the grisailles paints, the spread of the use of dark enamels seems to have increased the risk of mis-attributions [2,5]. The introduction of other colourising elements in black painting materials (Zn, Co, Cr, Mn) increases between the 19th and the 20th centuries [2,3,5,44–47]. These elements (e.g., Co, Cr oxides) are not identified in recipes for the production of grisailles but are rather more typically in enamels [2,3,48]. Prior to the 19th century, the addition of MnO as a grisaille pigment seems to appear only in two recipes (Part II, Chap. LX and LXI) of the treatise *Ars Vitraria Experimentalis* by Johannes Kunckel (17th century) [1,2,49]. Due to the diversity in the 19th century grisailles' compositions, Figure 6 presents a schematic view of the semi-quantified results—interpretation considers data limitations.

In fact, concerning the complexity of the results and the lack of information on light elements such as boron, from this point onward it is important to bear in mind the possibility of the presence of an enamel-based material whenever we talk of 'grisaille' as the back paint in these 19th century panels. The differences rely on the use of a dark enamel as a substitute for the colourless base glass used in previous centuries or even the total substitution of the grisaille paint for black enamel. In the latter case, however, we are dealing with a translucent paint material, instead of an opaque one (a main characteristic of the grisailles paint layers).

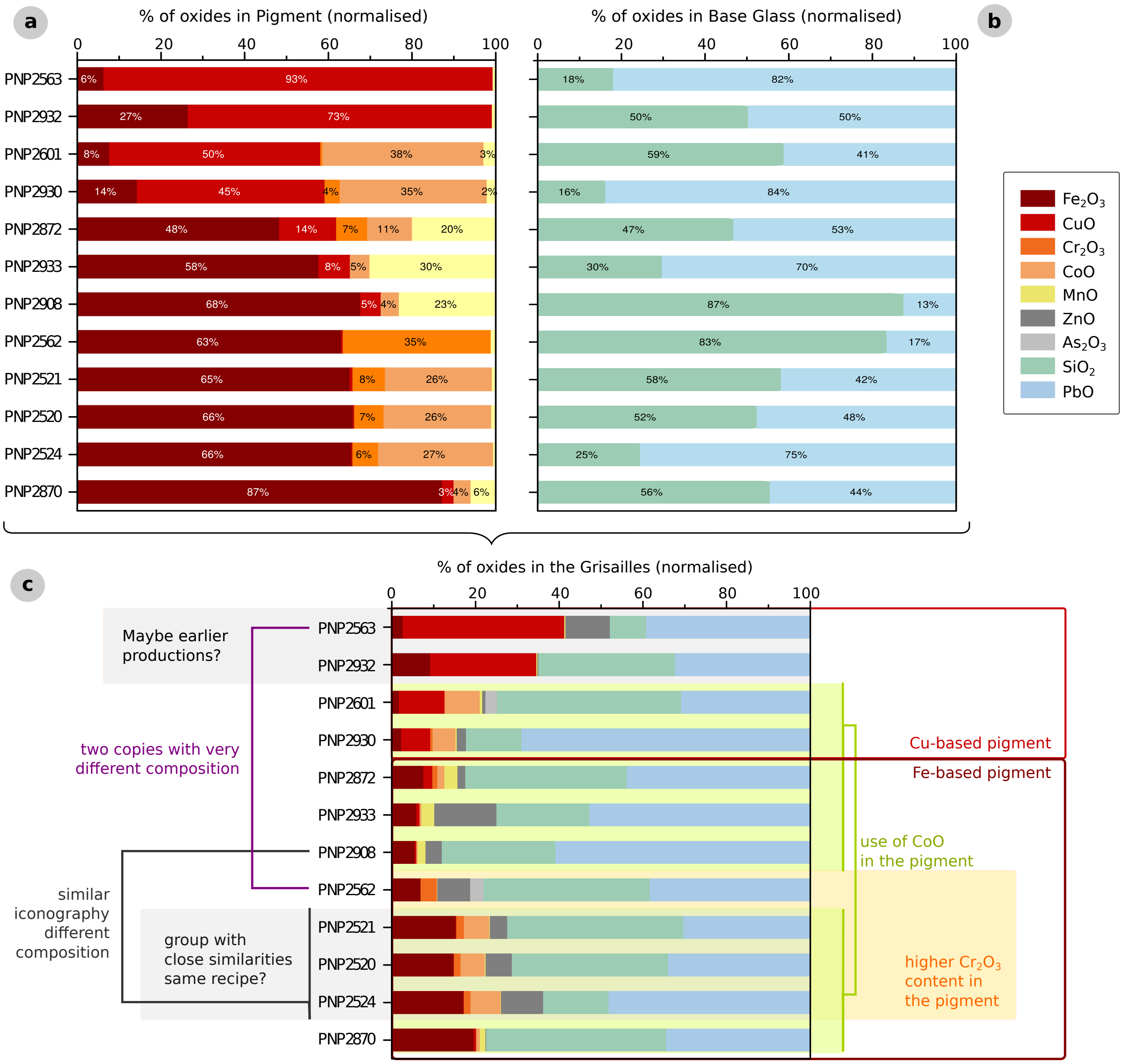

Figure 6. Normalised distributions of (**a**) the metal oxides used as pigment, (**b**) the lead-silica base-glass (other possible light elements could not be considered) and (**c**) the overall grisailles' composition in oxides of the panels attributed to 19th century chronology.

At first glance, two obvious differences can be observed in Figure 6: some of the panels presented more copper-based pigments, and other panels were richer in iron oxide among a larger diversity of colourising elements. A second clear observation is the relationship between the iconography (see Figure 1) and chemical composition (Tables A2 and A3, in Appendices A and B) of some groups of panels (e.g., PNP2520, PNP2521 and PNP2524), or the opposite behaviour between other panels (e.g., PNP2562 and PNP2563).

4.2.1. Group 1: *Historische Memorabilien* Panels

The group of panels representing *King Henry I* (PNP2520), *The Rütlischwur* (PNP2521), *Theoderic the Great* (PNP2524) and *Constantine the Great* (PNP2908) were drawn based on illustrations provided by Peter Johann Nepomuk Geiger (1805–1880) for the volumes of the *Historische Memorabilien* published by Anton Ziegler in 1840 [50]; hence, the dating of these panels is almost certainly from about 1850s, meaning that the mounting on the PNP windows occurred during the 1860s [28]. Considering the support-glass composition, a separation seems to exist between *(i)* the group of panels PNP2520, 2521 and 2524 and *(ii)* the panel PNP2908, since the former are likely using synthetic-soda (Na-Ca glass, probably, as observed for other coeval panels [15]) and the latter seems to be rich in potassium (K-rich). Different types of glass sheets were therefore used for the production of each set. The black paint material also seems to support a different production between *(i)* the group and *(ii)* the isolated PNP2908 panel: in *(i)*, the presence of Cr, Co, Ni and Zn oxides accompanies the high Fe oxide content, and low amounts of As oxide seem to be detectable; whereas, in *(ii)*, there is a slightly higher content of MnO, as well as CuO, present; there is a predominance of Fe oxide as colourant, apparently; much lower contents of Co, Ni and Cr (traces) can be observed; and Zn oxide also appears in this case, but no As was detected, contrarily to BaO. The high content of ZnO could perhaps be related to two sources: the use of cobalt ores [48,51] and/or the use of an enamel made of a lead-zinc borosilicate glass, such as the ones being used in coeval counterparts [39]. The first option seems less likely due to the larger amount of ZnO compared to the amount of CoO in the pigment (Figure 6), whilst a similar amount would be expected [51]. Here, it is important to recall the black enamel possibility, such as the ones used in coeval counterparts [5].

4.2.2. Group 2: The Two *Cherubim Angels*

The two panels representing the *Cherubim angels* (PNP2562 and PNP2563) were already visibly attributed as two different productions, one proposed as possibly being a Portuguese copy in order to maintain the symmetry on the windows' display. The very different composition of the two glass supports (Table A3, Appendix B)—one is probably a Na-Ca silicate glass (PNP2562) and another HLLA (PNP2563)—reinforced this difference. The fact that the grisaille is also visibly different in the two panels perhaps points to two different moments in time and may in fact suggest a possible later copy symmetric to PNP2563. The grisaille of the HLLA panel (PNP2563) is actually a copper-based grisaille (Figure 6), much in accordance with earlier production, as was observed in the previous '14th–18th centuries' section. On the contrary, both the glass support composition and the grisaille of the panel PNP2562 point to a later production. In the latter case, the grisaille shows differences from all other panels' grisailles; in the pigment, Fe and Cr are the dominant oxides (likely from the use of chromite as in black pigments [52]), and the presence of Zn and As oxides could not be related with the use of cobalt ores [48,51], since this one is absent in this case. The question of whether the recipe and the copy are local (Portuguese), is, however, rather difficult to answer, due to the lack of analysis for comparison, being the only published panels that are quite different and originate in the 20th century [46,53].

4.2.3. Group 3: Uncertain Attributions

Concerning the panels with uncertain chronological attributions (PNP2932 and PNP2933), two very different observations can be made from the compositional results obtained.

The support glass of the panel representing the *Birth of Christ* (PNP2933) can be classified as a mixed-alkali composition (or even borossilicate), due to the presence of oxides of K, B/Na/Mg (calculated by difference) and Ca in about the same wt% (Appendix B). The low contents of P, Mn and Fe point to the very likely attribution to the 19th century. The grisaille composition of this panel also points in the direction of 19th century chronology, especially due to *(i)* the fact that the pigment applied is richer in iron than copper oxide, opposing to the majority of other analysed grisailles attributed to between the 14th and the

18th centuries; and *(ii)* the presence of higher concentrations of elements such as Mn, Zn, Co and Ni [2,3,5,47] (see Table A2, Appendix A).

In turn, the support glass of the panel representing the *Resurrection of Christ* (PNP2932) presented some difficulties in quantification. It is possible that an alkali-corroded surface may be present. Additionally, the grisaille composition is rather different from PNP2933 (see Table A2, Appendix A), and seems more in accordance with 16th–17th century grisailles (see PNP2875 and PNP2931 in Table A1, Appendix A), with which chronology an iconographic relationship may be drawn. It is therefore possible that the panel corresponds to an earlier production. However, despite a trend that has been verified along this study, the sole information on the grisaille may be too little to support such conclusion.

4.2.4. Group 4: Ungrouped Items

In addition to the aforementioned groups with some relationship among each other, an individual interpretation of all other panels attributed to the 19th century is necessary due to the wide diversity of grisaille compositions observed (Figure 6).

Contrary to what was previously observed in panel PNP2932, where a probable attribution to the 19th century was initially considered, the opposite idea emerges from the panel representing the *Ascension of the Virgin* (PNP2870). This panel shows a grisaille with different characteristics from the chronology of the 16th/17th centuries. The contents of Fe, as well as small amounts of Mn, Co and Ni oxides seem to fit well within the 19th century group (Tables in Appendix A).

The Fensternbierscheiben panel PNP2601 was already verified as presenting a different support-glass composition from other panels with the same typology in the Ferdinand II collection [27]. When looking at the grisaille composition, the copper pigment is still dominant, as it was in the 18th century panels analysed here (PNP2883, PNP2884, PNP2886 and PNP2888), but a clear change is observable with the addition of cobalt and manganese, as well as the presence of arsenic oxides—indeed, this is in accordance with the 19th century practise [2,3,54,55].

The panel PNP2930 represents a coat of arms typical for 17th century iconography, hence the possibility of a Portuguese local copy was also considered in this case. A similar heraldic panel exists in this collection (PNP2920), disposed in a vertically symmetric position [28], with an earlier chronology attributed. The composition of the glass support, being a Na-Ca glass with a high purity of raw materials (Table A3, Appendix B), leaves no doubt regarding a 19th century attribution. The grisaille composition itself reinforces the attribution. Interestingly, this grisaille is also copper-rich, with the addition of CoO, Cr_2O_3 and MnO. Even though it does not have the same composition as the grisaille in PNP2601 at all, the similarities in the use of a Cu-rich pigment could perhaps indicate that this panel was produced within a close chronology and region to the former. The 17th century panel PNP2920 in the collection is attributed to the Lower Rhine province, which is not far from the Northwestern region which produces the Fernsterbierscheiben panels, which could include PNP2601. The Cu-based pigment relationship could perhaps open the possibility of a copy from Northern Germany, if the trend was to be verified in this region up to the 19th century. However, great advances in the characterisation of 19th century grisailles from Northern Germany ascertained productions would be necessary to verify this slim-chance hypothesis in the future.

The panel PNP2872 is the only one that can be attributed to a known workshop and date, since it was commissioned by the Palace's Chapel from the Kellner workshop in Nuremberg in 1840. The characterisation performed in this study can therefore offer valuable information on this specific case. Soda-lime silicate glass sheets were used as support glass, and the grisaille composition was indeed no longer a Cu-based pigment, but instead a Fe-rich pigment, which was also rich in many other elements (Co, Cr, Mn, and Zn). The fact that this grisaille recipe is quite different from the rest perhaps points to none of the other panels with no specific location attribution being produced in Nuremberg.

4.3. Literature Comparison

As mentioned previously, it was only possible to find a few studies reporting the characterisation of Germanic grisailles in the literature [6–8,10,11]. These studies mainly cover samples from the 13th to the 15th centuries, therefore making it easier to perform direct comparisons with the samples from the more recent chronology studies in this paper. The comparisons between the literature data and the results obtained for the 14th to 18th century panels are plotted in a ternary graph (Figure 7), reuniting the major constituents of the grisailles: the base-glass (SiO_2+PbO) and either the iron's or the copper oxides' contribution to the pigment colour. The data described in Verità [11] was not considered for the representation in Figure 7, since only the mean chemical composition of the glassy phase of the grisailles is presented in that study. The 19th century samples will be discussed latter, as this group presents a more complex composition.

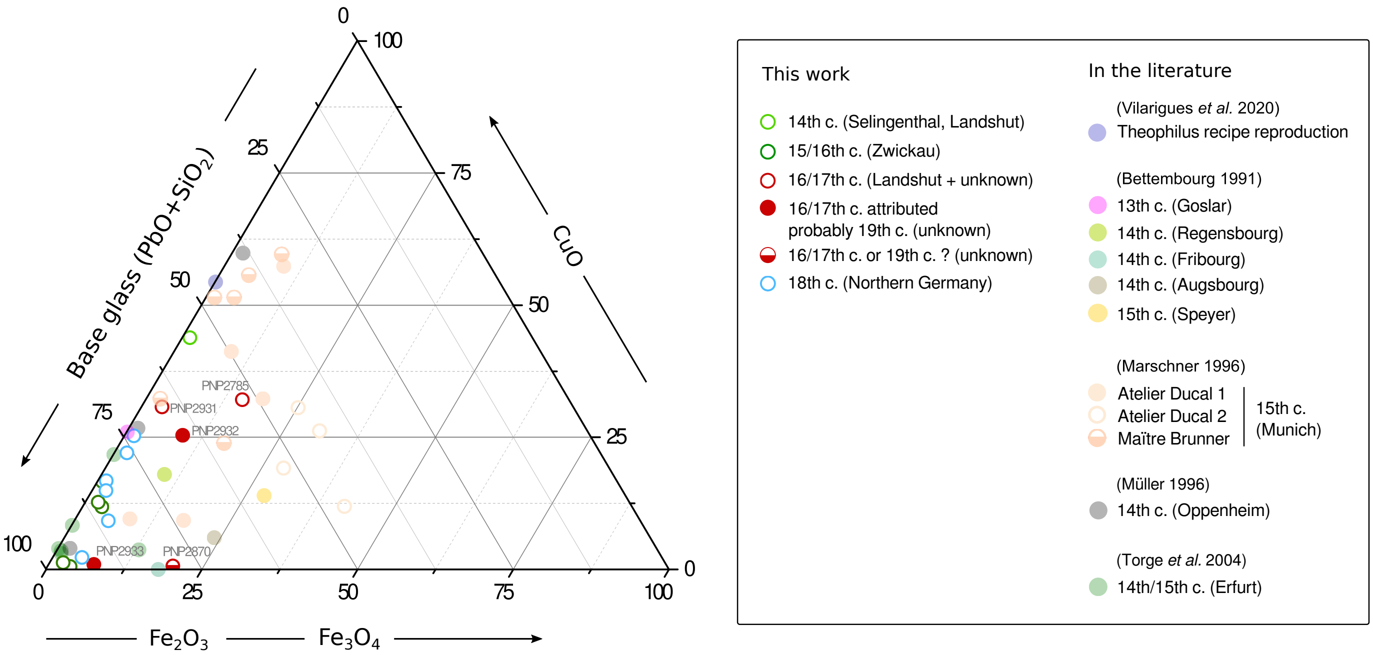

Figure 7. Ternary plot of the base-glass (SiO_2+PbO) versus iron oxide versus copper oxide concentrations showing the dispersion of the grisailles analysed in this study and comparison with the literature data [6–8,10,56].

The comparison represented in Figure 7 shows the dispersion of the results regardless of chronology and provenance, indicating a wide variety of grisaille compositions. Nevertheless, with the literature results, the general preference, as mentioned previously, to use higher amounts of copper as a colourising material instead of iron is also visible. This preference is more or less transversal throughout the different chronologies and shows the direct influence of the known 12th century Germanic written source *"De diversis artibus"* by Theophilus, where he described the grisaille as being made with copper [42].

Furthermore, Figure 7 also shows the overall increase of the base glass in the analysed samples when compared with most of the samples from the literature, with the exception of the grisailles from the Erfurt Cathedral [10]. This increase is probably related to the difficultly related to the methods of access to the panels for the analysis, which in some cases were only possible to be made on a thin grisaille layer (*grisaille à modeler*), leading to potential interference and influence from the glass support composition.

When comparing the Germanic grisailles with the European reality, it is possible to understand this as a particular case. In general, iron was the main colourant used in grisailles throughout the centuries and countries, being identified as major component (>50%) in the Iberian, French and Belgium grisailles, for instance [2]. However, higher concentrations of copper are also perceptible in the samples from the Czech Republic studied by Cílová et al. [57] originating between the 13th and 15th centuries from the Richter's House (Prague), Church of Saint James in Zbraslav (Prague) and Church of St.James the Greater (Zebnice) and the Italian samples studied by Verità [11] dated between the 13th (San Francesco in Assisi and Orvieto Cathedral) and the 14th centuries (Santa Croce in Florence). This can indicate a preference for the use of copper as a colouring agent in grisailles formulation not only in Germany, but also in the Central and South-Central European countries, although to prove this a higher sample representative with more analysis is required.

Looking to the 19th century samples, despite the more complex compositions and the greater variety of formulations, it is possible to compare and see similarities with other stained-glass panels, both with German 19th century published results and from different European contexts. This change in the production of 19th century grisailles sees its first approach in the 1868 book *Guide du Verrier* by George Bontemps, where he describes the use of ochre and earth pigments in the grisailles formulations [58]. The general predominance of the iron oxide as a colourant with the presence of Co, Cr, Ni, Zn, as in the group of panels representing *King Henry I* (PNP2520), *The Rütlischwur* (PNP2521) and *Theoderic the Great* (PNP2524), can find similarities among the grisailles characterised in Germanic counterparts, such as the ones in St. Paul Church em Schwerin (19th century additions) [9], in Spain, from the Church of San Severino in Balmaseda attributed to the French 19th century workshop of P. Degrand [59], and in the Alcala de Henares from unknown authorship [3].

Other similarity is found between the fragment PNP2872, produced in Nuremberg by the Kellner workshop, and the grisailles from Belgium studied by Schalm et al. [44] and Vilarigues et al. [60], where the use of iron with cobalt and manganese with small additions of copper, nickel and barium was identified in grisaille and black-painting material compositions.

The results of the 19th century grisailles of the soda-lime glass replacement material in St. Catherine's church in Oppenheim—where the analysis of some of the grisailles revealed interesting results regarding the use of copper-based pigments [8]—further demonstrate the complications related to the understanding of some of the 19th century cases (e.g., PNP2932). Therefore, as mentioned before, the complexity of the grisailles' compositions in the 19th century is also demonstrated in the literature, despite the scarcity of published results. For more conclusive considerations regarding the technology of production, more studies need to be carried out.

5. Conclusions

Through this work and unique case study, the lack of studies reporting the characterisation of Germanic grisailles was addressed, and the first overview of their composition was performed. Even as a case study, the 22 analysed panels from a single collection with a good dispersion in time and space provided this pioneer study that reached farther than any other on the materiality of these glass paints.

From the results obtained, as expected and in accordance with the literature, the 14th century glass support was K rich, and the grisaille material presented a copper-rich pigment, close to what the treatise of the compatriot Theophilus monk from the 12th century indicates. On the other hand, a correlation between a predominance of the use of a HLLA glass support between the 15th and 18th centuries and the maintenance of the use of copper-based grisailles also during this period in the Germanic territory was observed. The preference for the use of copper as a colouring agent until the 18th century does not find many similarities with other European regions, with few exceptions in Central and South-central Europe. On the contrary, in the 19th century, the generalised use of synthetic soda for glass-sheet production seems to have been adopted, as well as a greater variety of grisaille (or black-paint) compositions, mainly with the appearance/use of Co, Cr, Mn, Zn and As, among a few other metal oxides. In the latter chronology, the direct relationship between this study's results and those found in the literature is made clearer, in particular by the appearance of those new colourants in grisailles and enamels. The trends observed through this work in the grisailles' formulation are worthy to be subject of more research in the future, with a higher number of representatives and where more in-depth analysis could also be performed.

For the first time, this work enables a better chronological and geographic overview of the grisaille paint materials produced in the Germanic territory and promotes solid ground for further comparison and research on this subject.

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Appendix A. Grisaille Composition

The following semi-quantitative results aim at serving the reader as a guide to the interpretation of the major, minor and trace elements' oxides in each grisaille or glass. It is important to bear in mind that qualitative interpretation was given greater importance than quantitative interpretation, due to the relatively low accuracy of the presented values, especially in terms of lighter elements and of the very low contents obtained for some oxides, even when the respective elements were detected in the spectra. In all interpretations, the authors were aware of the limitations of the obtained data. Values are presented in ranges when it was necessary to demonstrate the heterogeneity of the material.

Table A1. Composition of the grisailles analysed on the surface of the panels attributed to the 14th to the 18th centuries. Semi-quantitative (indicative) results obtained by µEDXRF or PIXE (when indicated).

Panel (Grisaille)		Info	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	CoO	
PNP2874	Agnes of Bavaria		8.8–13.7	15.5–24.0	0.06–0.10	n.d.	0.02–0.04	0.78–0.94	traces	
PNP2809	St. Gregory	Type (a)	57.0–59.3	5.4–10.3	0.16–0.26	n.d.	0.49–0.89	1.9–4.0	traces	
		Type (b)	14.3–30.1	5.4–7.0	0.11–0.21	n.d.	0.61–2.07	1.6–2.2	n.d.	
PNP2821	St. Ambrose	Type (a)	12–30	8–12			0.2	0.6	n.d.	
		Type (b)	45.7–51.8	7.1–15.9	0.10–0.13	n.d.	0.13–0.47	0.84–0.96	traces	
PNP2822	Virgin of Apocalypse	Type (a)	15.2	14.0	0.09	n.d.	0.48	1.39	traces	
		Type (b)	41.5–43.1	10.0–10.2	0.16	n.d.	0.77–1.20	1.47–1.73	traces	
PNP2785	Virgin with Child		6.2–14.6	12.8–25.5	0.04–0.12	n.d.	0.03–0.28	7.7–15.6	traces	
PNP2870	Ascension of the Virgin		10.9–46.5	18.1–25.9	0.05	n.d.	0.55–1.21	7.1–19.0	0.31–0.90	
PNP2931	Baptism of Christ		25.0–27.3	12.4–21.6	0.16–0.23	n.d.	0.35–0.49	2.02–2.57	traces	
PNP2883	Bierscheiben	Type (a)	58.2–63.7	16.3–20.2	0.30–0.40	n.d.	0.72–0.94	3.2–3.8	n.d.	
		Type (b)	18.6–38.9	4.8–12.1	0.06–0.10	n.d.	0.23–0.25	4.4–5.0	n.d.	
PNP2884	Bierscheiben	PIXE	9.9–16.6	7.1–8.3	0.08–0.11	0.01	0.14–0.23	1.05–1.18	traces	
		EDXRF	24.3–29.9	3.9–11.7	0.02–0.10	n.d.	0.11–0.51	0.94–2.41	traces	
PNP2886	Bierscheiben	PIXE	38.4–43.1	4.5–10.5	0.07–0.11	n.d.	0.23–0.33	1.03–1.15	n.d.	
PNP2888	Bierscheiben	PIXE	20.2–21.3	3.4–4.6	0.08	n.d.	0.07–0.11	1.73–1.77	traces	
continuation		Info	**NiO**	**CuO**	**ZnO**	**SrO**	**As_2O_3**	**BaO**	**PbO**	**Fe/(Cu+Fe)**
PNP2874	Agnes of Bavaria		0.12–0.17	29.1–34.2	0.12–0.13	n.d.	n.d.	n.d.	28.0–36.8	3/100
PNP2809	St. Gregory	Type (a)	0.04–0.07	0.37–0.49	0.12–0.16	0.06	n.d.	0.16–0.24	18.6–23.3	86/100
		Type (b)	0.02–0.10	2.0–12.7	0.26–0.29	0.09–0.11	n.d.	0.11–0.45	20.2–40.1	34/100
PNP2821	St. Ambrose	(a)		10–18					23–30	4/100
		(b)	0.06–0.08	0.58–1.10	0.07–0.07	0.03–0.04	n.d.	0.08–0.14	21.7–33.4	51/100
PNP2822	Virgin of Apocalypse	(a)	0.08	8.7	0.42	0.12	n.d.	0.14	49.9	14/100
		(b)	0.05–0.08	0.75–1.23	0.25–0.29	0.11–0.13	n.d.	0.18–0.25	31.5–32.5	62/100
PNP2785	Virgin with Child		0.09–0.38	18.2–30.2	0.15–0.21	0–0.07	n.d.	0.01–0.10	25.0–33.3	31/100
PNP2870	Ascension of the Virgin		0.35–1.10	0.25–0.58	0.03–0.20	n.d.	n.d.	0.11–0.19	9.4–36.6	100/100
PNP2931	Baptism of Christ		0.10–0.13	21.0–22.3	1.91–2.56	0.09–0.10	n.d.	n.d.	16.3–25.5	10/100
PNP2883	Bierscheiben	Type (a)	0.02–0.09	1.59–1.83	0.25–0.34	0.05–0.07	n.d.	0.19–0.25	8.4–9.8	67/100
		Type (b)	0.16	7.0–9.0	0.51–1.13	0.04–0.05	n.d.	0.03–0.06	37.7–51.2	36/100
PNP2884	Bierscheiben	PIXE	0.03	18.9–20.3	0.23–0.34	0.12–0.15	traces	0.05	41.1–46.0	5/100
		EDXRF	0.21–0.22	15.8–21.9	0.24–0.25	0.04–0.11	b.d.l.	0.05–0.10	32.2–43.5	9/100
PNP2886	Bierscheiben	PIXE	0.02–0.03	11.2–16.9	0.16–0.20	0.05–0.08	traces	0.05–0.09	23.8–32–1	8/100
PNP2888	Bierscheiben	PIXE	0.02–0.03	11.8–12.3	0.13	0.04–0.08	n.d.	0.02–0.03	45.7–47.1	13/100

Table A2. Composition of the grisailles analysed on the surface of the panels attributed to the 19th century. Semi-quantitative results.

Panel (Grisaille)		Info	SiO_2	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	CoO	NiO
PNP2601	Bierscheiben		29.9–48.3	2.3–7.8	0.13–0.25	~0.1	0.51.0.57	0.99–1.99	6.5–8.3	1.5–2.1
PNP2520	King Henry I		27.5–34.0	7.0–9.2	0.06–0.07	1.2–1.4	0.17–0.19	11.1–13.3	4.7–4.8	5.4–5.6
PNP2521	The Rütlischwur		28.2–43.4	2.8–8.0	0.03–0.08	1.2–1.9	0.13–0.18	11.5–14.5	4.2–6.0	4.7–6.9
PNP2524	Theoderic the Great		10.6–12.9	1.5–19.0	0.04–0.15	1.1–1.3	0.10–0.11	12.2–13.6	4.8–5.7	5.3–6.2
PNP2562	Angels?/Querubins?		26.4–41.7	6.1–9.2	0.18–0.27	3.1–3.5	0.09–0.11	5.6–6.2	traces	0.08–0.11
PNP2563	Angels?/Querubins?		4.0–10–6	4.5–11.8	0.18–0.22	n.d.	0.17–0.28	2.1–2.4	n.d.	0.31–0.38
PNP2872	Fragment from Chapel		30.1–36.3	2.0–2.7	0.05–0.07	0.5–1.5	2.15–3.25	3.3–9.8	1.2–1.7	0.96–1.70
PNP2908	Constantine the Great		17.4–28.5	4.4–11.1	0.06–0.12	traces	1.32–1.84	2.3–7.0	0.1–0.5	0.05–0.41
PNP2930	Coat of Arms		8.2–15.6	2.2–2.7	0.07–0.11	0.3–0.7	0.24–0.32	1.4–2.6	4.7–5.1	1.29–1.34
PNP2932	Resurrection of Christ		27.0–29.1	6.9–8.4	0.06–0.09	n.d.	0.20–0.28	5.8–10.1	traces	0.26–0.27
PNP2933	Birth of Christ		7.6–30.9	7.8–10.4	0.05–0.16	n.d.	1.5–3.8	3.2–7.0	0.21–0.62	0.24–0.49
Continuation		Info	**CuO**	**ZnO**	**SrO**	**As_2O_3**	**BaO**	**PbO**	**Colourants**	
PNP2601	Bierscheiben		8.5–10.9	0.43–0.87	n.d.	2.2–2.7	n.d.	17.6–37.1	Cu,Co	
PNP2520	King Henry I		0.04–0.07	3.9–6.5	n.d.	traces	n.d.	25.8–30.1	Fe,Co,Cr	
PNP2521	The Rütlischwur		0.04–0.23	2.7–4.3	n.d.	traces	n.d.	19.4–32.1	Fe,Co,Cr	
PNP2524	Theoderic the Great		0.03–0.07	6.5–8.6	n.d.	traces	n.d.	30.3–42.1	Fe,Co,Cr	
PNP2562	Angels?/Querubins?		0.03–0.05	4.9–8.6	n.d.	2.6–2.9	0.17–0.33	25.6–40.1	Fe,Cr	
PNP2563	Angels?/Querubins?		31.3–33.9	7.5–10.5	0.09–0.11	n.d.	n.d.	31.7–34.5	Cu,Fe	
PNP2872	Fragment from Chapel		1.8–1.9	1.9–2.0	n.d.	1.9	n.d.	37.5–38.0	Fe,Mn,Cu,Co	
PNP2908	Constantine the Great		0.26–0.41	1.2–5.4	n.d.	n.d.	0.18–0.47	42.1–61.0	Fe,Mn	
PNP2930	Coat of Arms		5.6–6.9	1.5–2.4	n.d.	n.d.	0.08–0.22	57.7–65.6	Cu,Co,Fe	
PNP2932	Resurrection of Christ		21.3–22.2	0.20–0.26	0.04–0.05	n.d.	0.10–0.13	25.9–29.6	Cu	
PNP2933	Birth of Christ		0.42–0.91	1.9–18.0	0–0.01	n.d.	0.42–0.67	32.5–58.7	Fe	

Appendix B. Support Glass Composition

Table A3. Composition (major elements) of the glass support (colourless glass) of each panel studied. When PIXE analyses were performed, cross-sections were analysed, and the oxides marked with * apply. In all other cases, the value (between the two columns) corresponds to 'light elements, Z < 13'. For PNP2883, only the possible classification is presented due to quantification limitations.

Panel (Glass)		Analysis	SiO_2	Al_2O_3	P_2O_5	CaO	K_2O	MnO	Fe_2O_3	Na_2O *	MgO *	Classification
PNP2874	Agnes of Bavaria	EDXRF	49.3	<1.8	0.9	17.4	21.3	0.96	0.38	8.0		K-rich
PNP2821	St. Gregory	EXDRF	57.2	2.8	1.6	23.0	4.7	1.29	0.49	7.6		HLLA
PNP2809	St Ambrose	EXDRF	55.7	2.7	2.6	21.6	4.7	1.25	0.49	7.1		HLLA
PNP2822	Virgin of the Apocalypse	EXDRF	56.5	2.1	0.3	22.7	4.8	1.30	0.51	7.7		HLLA
PNP2785	Virgin with Child	EDXRF	54.4	<2.0	6.5	24.2	4.9	1.41	0.52	6.4		HLLA
PNP2870	Ascension of the Virgin	EDXRF	72.7	2.8	0.6	13.0	1.8	0.32	0.55	7.6		Na-Ca
		PIXE	75.5	1.7	0.2	7.9	3.9	0.11	0.34	7.9	0.24	Na-Ca
PNP2931	Baptism of Christ	EDXRF	68.2	<2.5	2.7	19.1	3.5	0.44	0.50	b.q.l.		HLLA
PNP2932	Resurrection of Christ	EDXRF	86.0	2.1	<0.2	9.9	0.7	0.04	0.29	b.q.l.		HLLA?
PNP2933	Birth of Christ	EDXRF	67.3	<1.4	<0.1	5.3	14.2	0.05	0.13	10.8		Mixed alkali
PNP2883	Bierscheiben	EDXRF	–	–	–	–	–	–	–	–	–	HLLA?
PNP2884	Bierscheiben	PIXE	60.0	4.0	2.3	20.8	1.6	0.61	1.4	4.7	3.2	HLLA
PNP2886	Bierscheiben	PIXE	61.6	3.7	2.1	20.0	1.4	0.55	1.3	5.2	2.9	HLLA
PNP2888	Bierscheiben	PIXE	61.7	4.0	1.9	19.2	2.4	0.81	1.2	4.9	2.7	HLLA
PNP2601	Bierscheiben	EDXRF	67.0	<2.5	<1.0	8.3	0.3	0.01	0.1	21.7		Na-Ca
PNP2520	King Henry I	EDXRF	74.5	<2.9	<1.5	11.5	3.2	0.12	0.37	13.7		Na-Ca
PNP2521	The Rütlischwur	EDXRF	75.7	<2.7	<1.3	8.9	2.2	0.06	0.26	11.1		Na-Ca
PNP2524	Theoderic the Great	EDXRF	68.0	<2.5	<1.0	9.4	3.8	0.11	0.23	16.2		Na-Ca
PNP2562	Angels?/Querubins?	EDXRF	71.3	<2.5	<1.0	9.0	0.3	0.01	0.08	15.5		Na-Ca
PNP2563	Angels?/Querubins?	EDXRF	62.3	<2.5	2.3	26.0	4.0	0.91	1.15	b.q.l.		HLLA
PNP2872	Fragment from Chapel	PIXE	66.0	1.3	0.04	8.8	1.1	0.00	0.55	17.3	0.28	Na-Ca
PNP2908	Constantine the Great	EDXRF	78.0	2.2	<0.7	5.5	14.1	0.01	0.08	b.q.l.		K-rich
PNP2930	Coat of Arms	EDXRF	63.0	<1.8	<0.2	8.6	0.3	0.02	0.11	25.3		Na-Ca

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