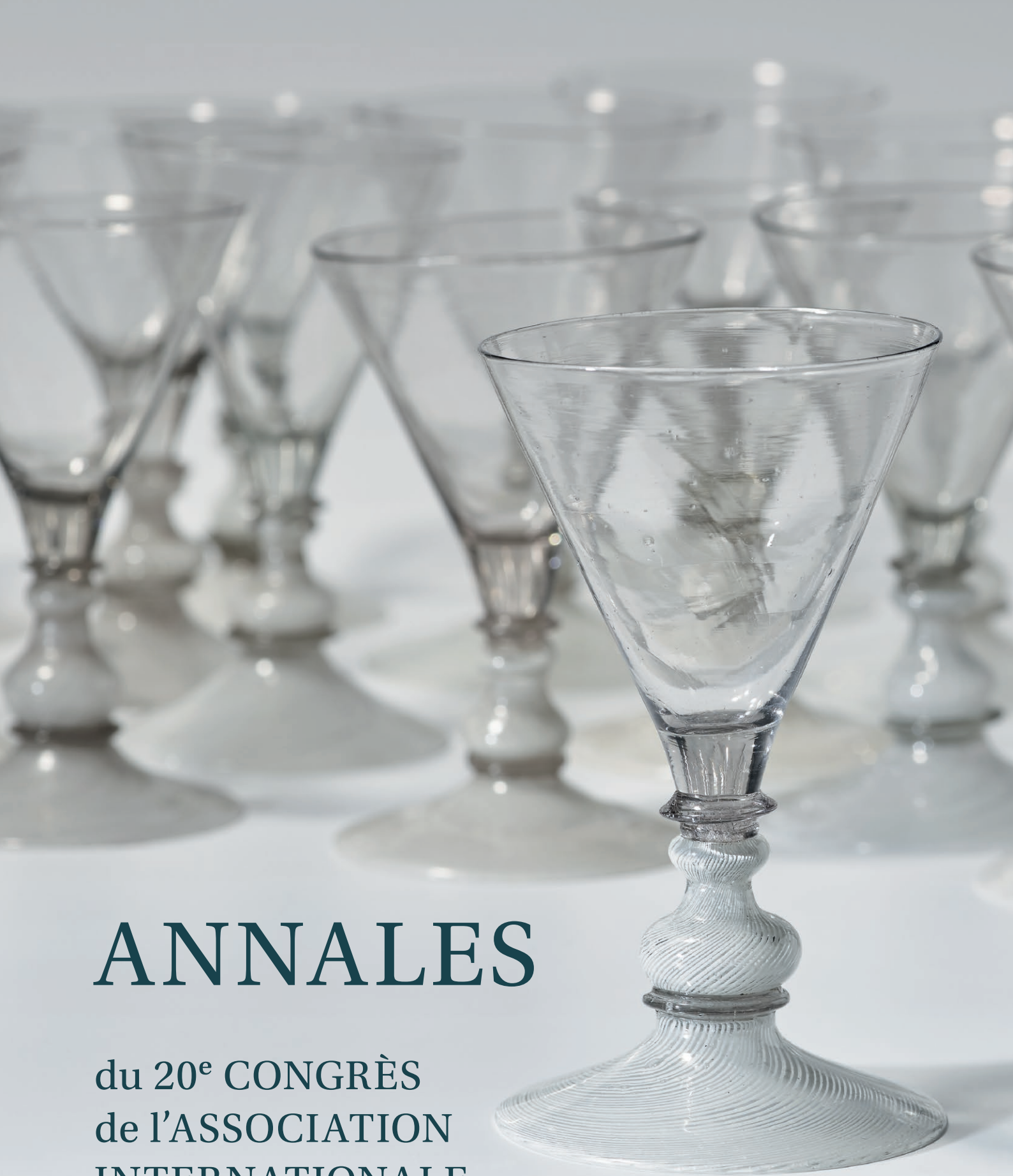

ANNALES

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SUR LE VITRAIL ET LES ARTS DU VERRE
SCHWEIZERISCHES FORSCHUNGSZENTRUM
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FOR STAINED GLASS AND GLASS ART

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SCHWEIZERISCHES MUSEUM
FÜR GLASMALEREI UND GLASKUNST
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Cover illustration
Goblets with white filigree decoration, produced in Swiss glasshouses, late 17th to early 18th century. From different Swiss public and private collections. For a detailed discussion see: Erwin Baumgartner, Reflets de Venise, Bern 2015, p. 254–272, 322–328 and the contribution of Christophe Gerber in the present volume, page 564.

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SWISS *KABINETTSCHEIBEN* FROM A 19TH CENTURY PORTUGUESE COLLECTION. STUDY AND CHEMICAL CHARACTERISATION

Andreia Machado, Alexandra Rodrigues, Mathilda Coutinho, Luís C. Alves, Victoria Corregidor, Rui C. da Silva, Vincent Serneels, Ildiko Katona Serneels, Sophie Wolf, Stefan Trümpler, Márcia Vilarigues

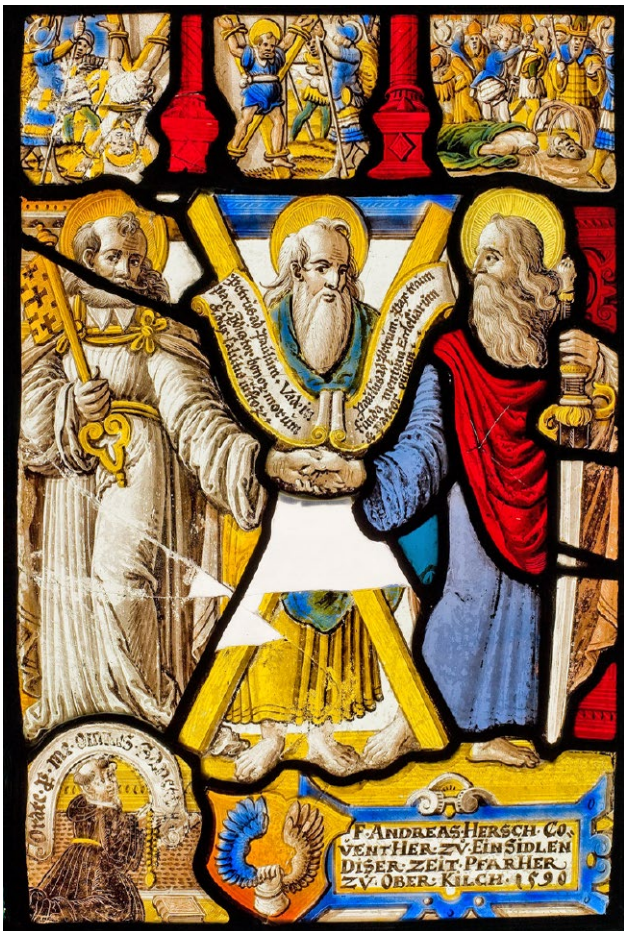

Fig. 1: Swiss stained-glass panels from Pena National Palace collection: (a) Saint Andre, Saint Peter and Saint Paul, 1590 (inscribed) (PNP2858). H: 34 cm, W: 23 cm; (b) Heraldic panel with the coat of arms of Niedersimmental, 17th century (PNP2860). H: 43 cm, W: 33 cm; (c) Heraldic Panel with the coat of arms of the canton of Luzern, 1688 (inscribed) (PNP2808). H: 51.5 cm, W: 59.5 cm. © Parques de Sintra – Monte da Lua, S.A. Photos: Luis Pavão.

The private collection of King Ferdinand II (1816–1885), currently on display at the Pena National Palace in Portugal, is composed of stained-glass panels from the 14th century to the 19th century, with fine examples from Germany, the Low Countries and Switzerland (figure 1). The set of Swiss stained-glass panels from Pena National Palace includes a group of small-scale art works designed to be viewed up close, whether in a religious or civil context. Common themes that are depicted on those panels are, for example, the coat of arms of the family donating the panel and scenes demonstrating an alliance or friendship between two

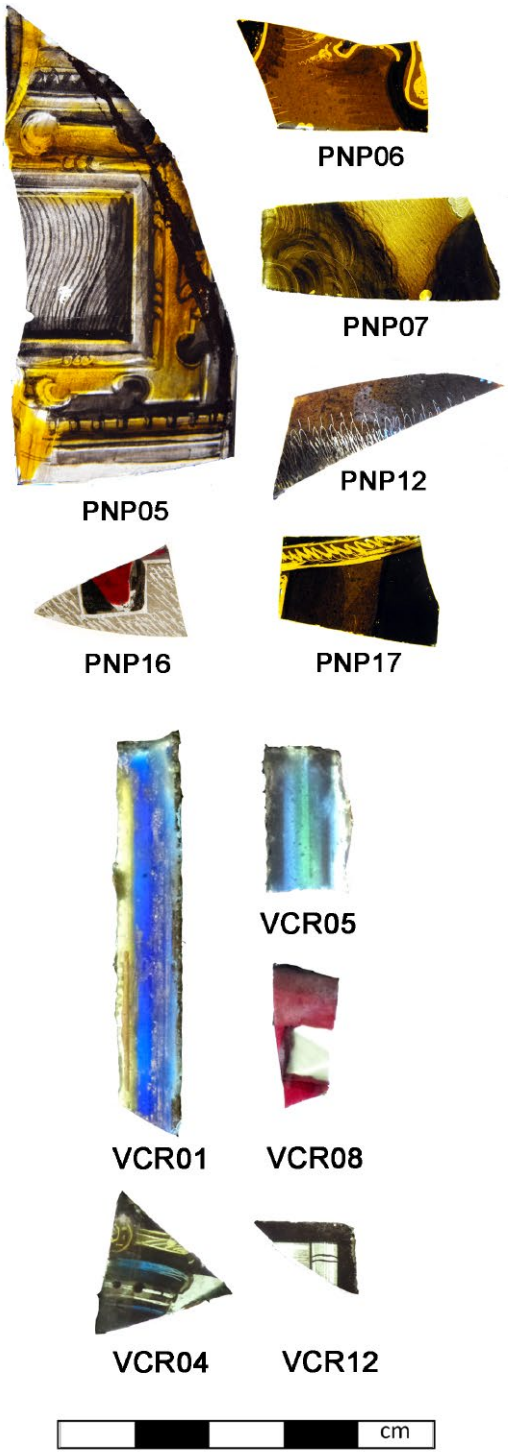

Fig. 2: Some of the stained-glass fragments from Pena National Palace (PNP) and from Vitromusée Romont (VCR) used in the analysis. © authors.

houses.[1] The stained-glass panel PNP2860 (see figure 1b) is an example for a restored panel where missing or broken pieces have been replaced in the past with glass pieces from other panels; the added pieces may have come from contemporary stained glass or from panels of a later period. Other stained-glass panels from the collection have been restored in a similar way.

Collected as well as inherited by the King, the panels were placed in the dining room of the Necessidades Palace in Lisbon. In 1947, they were transferred to the Ajuda National Palace and there put into storage until 1949. They were then transferred to the Pena National Palace, where they were also kept in storage until their display in the current exhibition.[2]

With the aim of shedding light on this unique collection, stained-glass *in situ* as well as stained-glass fragments not incorporated in the exhibition were being studied in detail from historical, archival, analytical and preservation perspectives. In this context, the chemical composition of six Swiss stained-glass fragments, which date to between the 16th and 17th centuries and were not incorporated in the exhibition, was determined by particle-induced X-ray emission (μ-PIXE). The compositions (PNP set, figure 2) were compared with those of 15 coeval Swiss stained-glass fragments from the Vitromusée Romont; they are part of the legacy of the stained-glass painter Hans Meyer, who worked in Zurich between 1893 and 1961 (VCR set, see figure 2). Both sets include stained-glass samples of colourless glass painted with blue enamels and grisaille. The VCR set comprises also a group of painted and unpainted colourless glass, red flashed glass, as well as purple glass, which is composed of blue and red flashed glass.

In addition to the chemical analysis of the glass and glass paints by μ-PIXE, the morphology and the composition of the paint layers were analysed using a scanning electron microscope coupled with energy-dispersive X-ray spectroscopy for microanalysis (SEM-EDS).

RESULTS AND DISCUSSION

Base glass

With exception of two samples, PNP06 and VCR06, the stained-glass fragments from Pena National Palace (PNP) and Vitromusée Romont (VCR) fall into two compositional groups: a high lime-low alkali glass (HLLA) and a potassium-rich glass with high calcium content (figure 3).[3]

The HLLA group has a K_2O / CaO ratio between 0.2 and 0.4. In this group, the K_2O concentration varies between 3.4 wt. % and 7.3 wt. %, CaO ranges from 17.4 wt. % to 22.3 wt. %, and Na_2O concentration is between 0.7 wt. % and 3.0 wt. %. The glass of the second group has a K_2O / CaO ratio between 0.6 and 1.2, with K_2O-concentrations varying between 9.8 wt. % and 15.2 wt. %. CaO is ranging between 12.1 wt. % and 18.8 wt. % and Na_2O between 0.4 wt. % and 1.9 wt. %.

With the exception of samples VCR03, VCR06, PNP06 and PNP07, the colourless glass from both sets, painted or unpainted, has a HLLA-type glass composition. Also the red-flashed glass of fragments VCR07 and VCR08 is a HLLA-type glass. The rest of the coloured glass as well as two painted fragments (VCR03 and PNP07) belong to the potassium- and calcium-rich glass group.

1 Boesch 1955, 51; Hasler and Trümpler 1998, 31.
2 Martins 2011, 10.
3 Schalm et al. 2007; Wedepohl 2010.

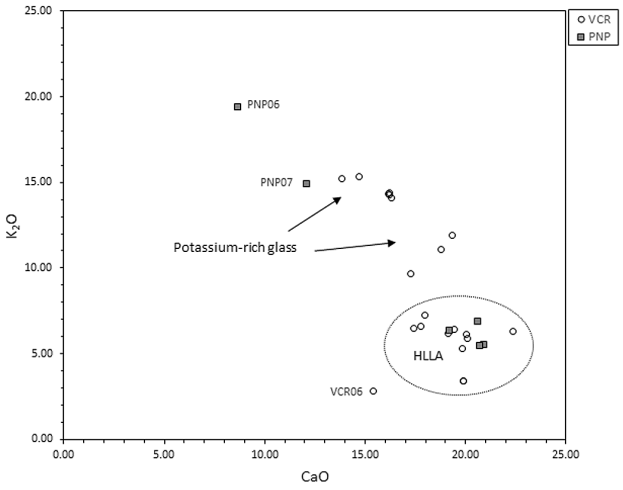

Fig. 3: Biplot CaO vs. K_2O (given in wt.%) for all samples analysed, showing elements mainly associated with the flux. © authors.

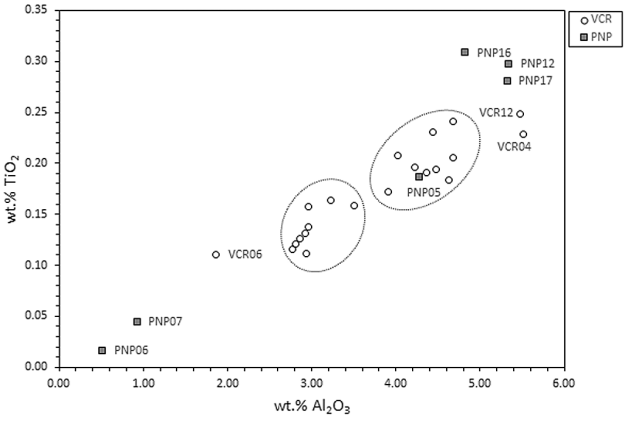

Fig. 4: Biplot Al_2O_3 vs. TiO_2 for all samples analysed, showing elements associated with the silica source. © authors.

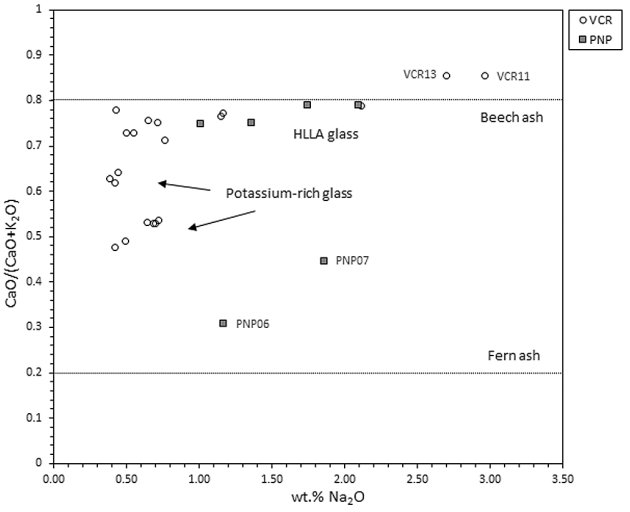

Fig. 5: Biplot Na_2O vs. CaO / ($CaO+K_2O$) for all stained-glass samples analysed. © authors.

Sample PNP06 is a potassium-rich glass with potassium and calcium concentrations of 19.4 wt. % and 8.6 wt. % respectively. The high content of potassium, together with a low content of phosphorous (0.23 wt. % P_2O_5) suggests the employment of potash (leached wood ash) for the production of this glass.[4] VCR06 is a sodium-rich glass with a Na_2O-concentration of 8.0 wt. % and a K_2O / Na_2O ratio of 0.3.

Apart from samples PNP06 and PNP07, all other glass from the PNP set has a composition similar to that of 15th–17th century glass from the late medieval and early modern period published by Schalm and co-authors.[5]

The positive correlation between titanium and alumina contents could indicate that both glass groups were made from a similar sand (figure 4). The chemical similarity of most of the fragments from the VCR set, with exception of samples VCR04, VCR06 and VCR12, even suggests that this glass was made from sand of the same source. The observed smaller changes in the relation between TiO_2 and Al_2O_3 might be an indication for the use of different glass batches in the production of these panels. With the exception of PNP05, which was made from the same sand as the VCR set, the glass of the PNP set was probably made from sand coming from a different sand source in the same (geological) region. The low TiO_2 and Al_2O_3 contents of the colourless glass of PNP06 and PNP07 are consistent with those of Venetian glass, which might be an indication for the employment of quartz pebbles instead of sand for the production of this glass.[6]

According to the data shown in figure 5,[7] both groups are made from wood ash. The observed CaO / ($CaO+K_2O$) ratio in the HLLA glass that ranges between 0.7 and 0.9 is similar to that of beech ash. The potassium values for beech ash, however, seem to be very variable. Similar ratios are also given for other types of wood ash, such as pine and spruce.[8] It is therefore not possible to determine, which type of wood ash was employed. The CaO / ($CaO+K_2O$) ratio for the potassium-rich group lies between 0.3 and 0.6. Similar ratios are obtained for beech and birch ash.[9] Again, the ratios do not really allow to decide which type of ash was used in the production.

In summary, the glass compositions of both groups are similar in terms of the silica sources and type of flux, wood ash, employed. This suggests the existence of glass production centres that worked with similar raw materials, and possibly in the same region.

Glass paints

The enamel paints have a more heterogeneous morphology when compared with the base glass (figure 6a). They show different glass phases and several silicon- and aluminium-rich inclusions, suggesting the presence of quartz and

4 Stern and Gerber 2009.
5 Schalm et al. 2007.
6 Veritià 2013, 528.
7 Van der Linden 2005, beech and fern ash data from Velde 1989.
8 Ratios calculated from data given by Stern and Gerber 2004; Cílová 2012.
9 Ratios calculated from data given by Stern and Gerber 2004; Cílová 2012.

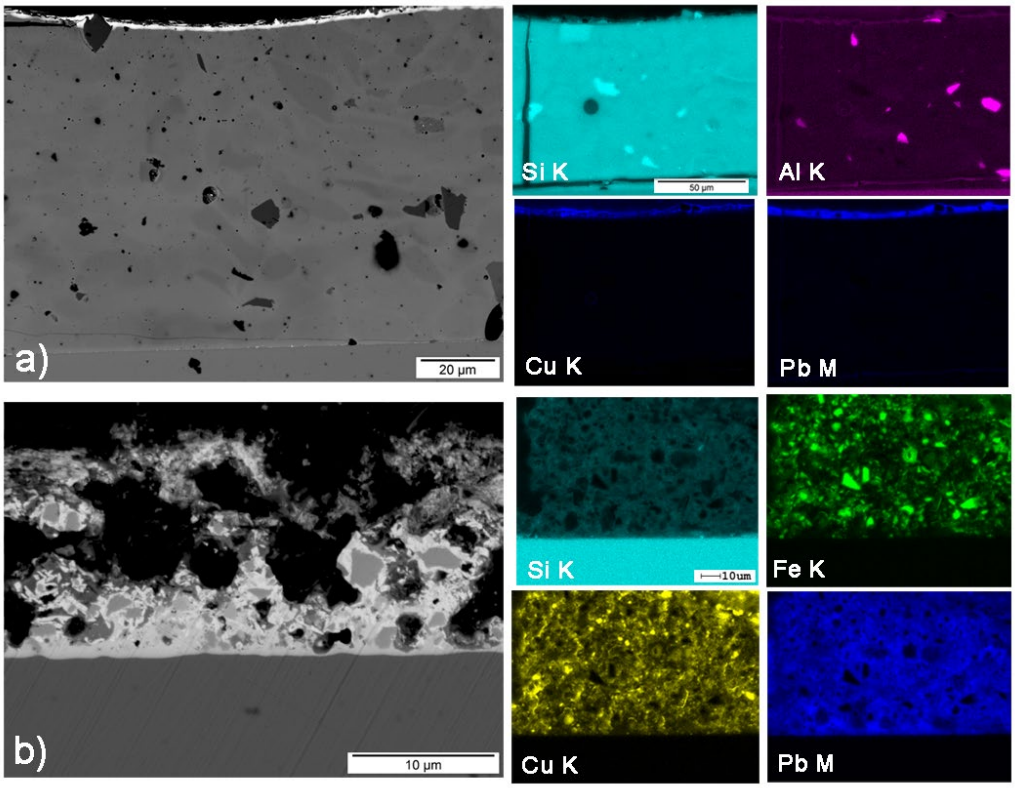

Fig. 6: Backscattered electron images and elemental maps (SEM-EDS) for (a) blue enamel paint on sample VCR01 and (b) grisaille on sample VCR05. © authors.

feldspar. The thickness of the enamel paint layers ranges between approximately 30 µm and 80 µm; thicknesses can vary throughout the layer. According to the results of µ-PIXE analysis, the cobalt content lies between 0.3 wt. % and 3.5 wt. % for all enamel layers analysed. The amount of lead is low with no more than 5.1 wt. %. An area enriched in copper and lead indicates the presence of a grisaille layer over the enamel layer (figure 6a).

The grisaille paintings analysed by SEM-EDS revealed that the thickness of the grisaille layer varies between approximately 20 µm and 50 µm. Analysis for the grisaille of sample VCR05 by µ-PIXE provides concentrations of 17.5 wt. % for Fe_2O_3, 4.7 wt. % for CuO and 31.7 wt. % for PbO, whereas sample VCR12 has 6.4 wt. % Fe_2O_3, 18.5 wt. % CuO and 42.8 wt. % PbO. Both grisailles show a diffuse interface between grisaille and base glass, suggesting an extended lead diffusion with a good adherence of the paint layer and the glass. This is an indication that the grisaille painting was properly melted onto the glass.[10] The elemental mapping (SEM-EDS) of sample VCR05 reveals a great dispersion of iron grains of different sizes, whereas copper is more evenly distributed (see figure 6b). The production process of a grisaille explains this morphology. The grisaille paint layers are fired at temperatures between 600 °C and 750 °C. At these temperatures lead is totally fused, whereas metals such as copper or iron (with much higher melting temperatures) are dispersed as grains.[11]

Conclusions

The aim of this study was the characterisation by means of µ-PIXE and SEM-EDS analysis of a group of Swiss stained-glass fragments belonging to a set of stained-glass panels from Pena National Palace collection and dating to between the 16th and 17th centuries. This set was compared to a group of stained-glass fragments from the Vitromusée Romont attributed to Switzerland and dating to the same period.

The analysed samples consist of glass of HLLA and potassium- and calcium-rich composition. The majority of the stained-glass fragments from VCR set was made from a similar silica source. It was possible to identify the use of different batches of glass in the production of the window panes of this set. One stained-glass sample from the PNP set (PNP05) can be related with this group. The other glass from the PNP set was made from a different sand, but possibly produced in the same region as indicated by linear correlations between sand-related elements. Wood-ash was the flux in all glass fragments analysed. At present, it is not possible to identify the wood species of the ash used in the production of the glass.

The paint layers of the analysed fragments, in particular the grisaille, are of very good quality as shown by the good adherence between glass paint and glass. They are composed of a lead-rich silicate matrix and pigments containing iron and copper. The enamel layers are relatively heterogeneous and characterized by the presence of various glassy phases, bubbles and inclusions rich in silicon and aluminium, suggesting the presence of quartz and feldspar.

10 Carmona, Villegas and Navarro 2006.
11 Vilarigues and Silva 2004.

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