Non-destructive redox quantification reveals glassmaking of rare French Gothic stained glasses

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Striped-glass throughout medieval Europe

The extended color palette of glass, detailed painting, complex engraving and high number of rare glasses used in the rose of the apocalypse comply with the precious royal aura of the Saint-Chapelle in Paris and at the same time demonstrate the range of perfection and mastery achieved by glassmakers and glaziers at the end of the Middle Ages. Among the precious rare glasses used in the rose, one can find striped glasses, which consist in colorless glass with colored stripes (Figure S-1).

The most ancient striped glasses have been found in Austria. In France, during the 15th and 16th centuries, most of the striped glasses show only red stripes and were found in Parisian monuments: Saint-Merry church (window 114, circa 1540), Saint-Gervais church (window 16 of the Wisdom of Salomon, 1531), Saint-Etienne-du-Mont church (Saint nom de Jésus window, 1540) and Saint-Germain-l'Auxerois church, or other in French cities: Madeleine church in Troyes (Passion window, circa 1494), Sainte-Marie cathedral in Auch (window 8, Saint-Louis chapel, 1513) and Saint-Pierre church in Dreux).

Triple-colored striped glasses are exceptional and were only found in: the rose of the Apocalypse of the Sainte-Chapelle in Paris (Figure S-1.a-f), the *bourreau de la Flagellation* (Figure S-1.g), Cluny Museum (Paris, circa 1490), Saint-Gervais church in Paris (window 9 of Sainte Isabelle of France, circa 1510) as well as in Switzerland (Saint-Christophe window, museum of Basel, circa 1510/1525).[1] The later has been assigned to an Alsatian glazier by Hans Baldung Grien or Nuremberg.[1,2] The small number of striped glasses known today, together with the narrow period of production might suggest a common origin for these glasses.

The usage of the word "Venetian" was defined by the art historian Jean Lafond according to the Swiss Saint-Christophe window for such glasses, in which the very thin stripes resemble the filigree glasses made in Murano's workshops at the same period.[3] The Venetian origin of the striped glasses found in the Sainte-Chapelle in Paris is refuted in this work according to the chemical composition (see main text). It seems that the usage of such striped-glasses stopped after ca. 1550.

The name "Venetian glass" is an echo to the naming "*à-la-façon-de-Venise*" used to define the glassware produced in Europe from the 16th century and imitating the filigree glass *Venitian cristallo*. This "*à-la-façon-de-Venise*" glassware was produced by Venetian glassmakers who escaped from Murano island and developed their own business in Northern Europe. This was unraveled from finds in Antwerp (Belgium), Amsterdam (the Netherlands) and London (UK).[4] However, the chemical composition of this "*à-la-façon-de-Venise*" glassware is very different: soda-lime silicate glass (>10 wt % of Na_2O). Surprisingly, window glass produced from 14th to 17th centuries in Belgium present significantly different chemical composition from the glassware production technology.[5] As a consequence, the results of the present study, revealing potash-lime silicate glasses, strongly support that the striped glass of the present work was not produced using the imported Venetian glassmaking skills and therefore should not be named "Venetian glass" nor "*à-la-façon-de-Venise*".

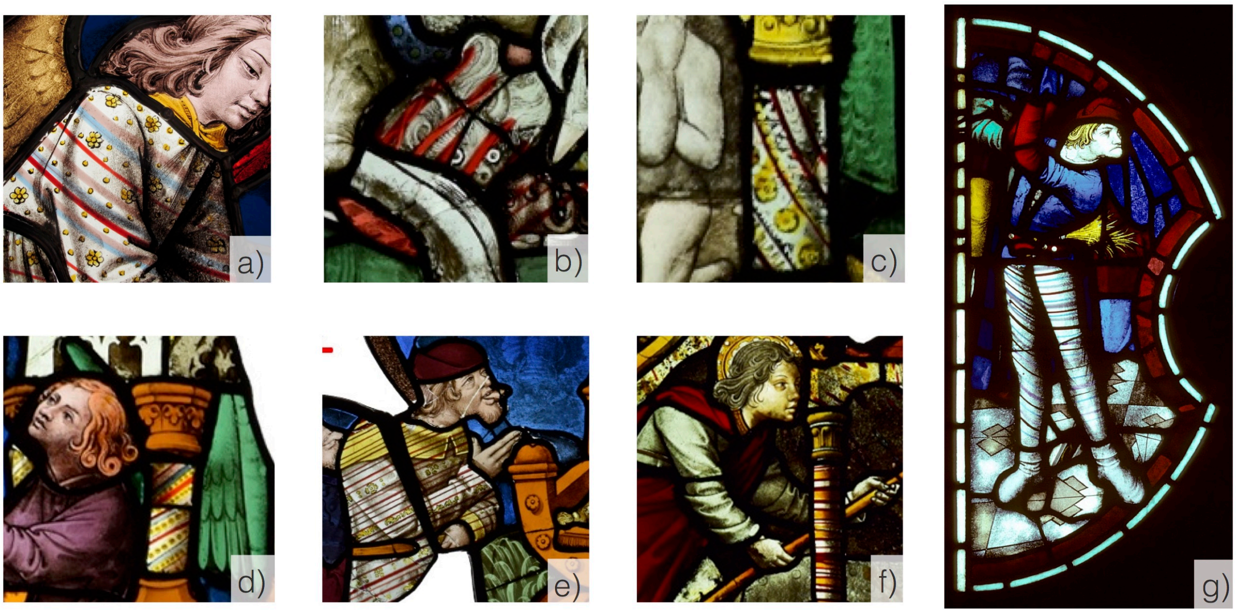

Figure S-1: Striped glasses in the stained glass windows of the apocalypse rose of the Sainte-Chapelle in Paris: details of panels a) T9, b) E2, c) F2, d) M2, e) O2, f) T1; g) *Bourreau de la flagellation,* Cluny Museum (Paris, France), circa 1490. Courtesy of Michel Hérold, Centre André Chastel.

Chemical compositions of the glasses

The composition of ancient glasses has been extensively used to determine geographical and temporal origins. However, the melting process induces the loss of the information about the origin of the chemical species and blurs chemical correlations. Since some chemical components could be added on purpose while others added as impurities from the raw materials, a major questioning concerns the intentional mastering of the chemical composition and thus the control of the final resulting color by the medieval glassmaker (i.e. the glass recipe). To relate the chemical composition to a place and time of production, it is necessary to determine how they influence the variation of the chemical composition. The chemical concentrations (Table S-1) are given in mass percentages of total oxides for major elements and part per million of total oxides for minor and trace elements. For each glass area (based on their color difference), the concentrations are obtained by integration over the total area of the colored stripe. The standard deviations are calculated for each area from five sub-maps of equal areas. As a consequence these standard deviations include the variation due to the statistical error and the heterogeneities on the glass.

Indoor vs outdoor faces of the glass

We distinguish here the side of the glass that is on the outside of the window and undergo atmospheric weathering: “outdoor” face, from the side that is inside the building: “indoor” face.

The chemical composition extracted from the PIXE-PIGE mappings of each face is given in Table S-1. In the base glass, we observe that the concentration of sulphur is much higher and heterogeneous (4.95 ± 1.70 wt % SO_3) on the outdoor face of the glass than on the indoor face (0.56 ± 0.06 wt % SO_3). This might be assigned to atmospheric pollution although the glass had been restored.

Table S-1: Chemical compositions extracted from each area of the PIXE-PIGE mapping.

		Base glass	inside	Base glass	outside	Blue stripe		Purple Stripe		Red stripe		Silver Yellow	paint	Grisaille	paint	Brill D
		mapping average	standard deviation	mapping average	standard deviation	mapping average	standard deviation	mapping average	standard deviation	mapping average	standard deviation	mapping average	standard deviation	mapping average	standard deviation	mapping average
Major oxides (wt%)	Na_2O*	1.08(5)	0.06(3)	1.09(7)	0.03(7)	0.81(8)	0.03(1)	0.99(0)	0.03(1)	0.94(1)	0.01(4)	1.07(1)	0.03(5)	0.87(7)	0.09(2)	1.38(7)
	MgO	4.04(4)	0.11(2)	3.67(7)	0.22(8)	4.16(0)	0.07(5)	3.39(8)	0.09(7)	3.94(0)	0.03(8)	3.95(8)	0.18(5)	0.72(1)	0.33(6)	3.52(5)
	Al_2O_3	2.37(1)	0.02(6)	2.66(8)	0.05(9)	2.62(8)	0.04(2)	2.71(7)	0.03(7)	2.62(3)	0.08(0)	2.67(2)	0.04(4)	2.18(6)	0.47(0)	5.18(4)
	SiO_2	53.35(1)	0.47(7)	51.90(6)	1.14(9)	53.34(6)	0.28(2)	51.27(1)	0.32(6)	54.48(5)	0.52(4)	52.75(5)	0.56(3)	34.09(7)	9.60(9)	55.98(9)
	P_2O_5	3.94(6)	0.03(3)	3.63(1)	0.10(8)	3.92(8)	0.06(4)	3.59(8)	0.03(9)	3.87(5)	0.07(4)	3.78(8)	0.06(2)	2.18(9)	0.45(1)	3.67(7)
	SO_3	0.56(9)	0.06(9)	4.95(0)	1.70(2)	1.14(0)	0.30(0)	2.41(4)	0.56(8)	1.20(6)	0.40(6)	2.93(6)	0.87(5)	3.03(9)	4.12(9)	0.25(7)
	Cl	0.29(0)	0.01(3)	0.26(8)	0.01(4)	0.18(6)	0.00(8)	0.18(7)	0.00(8)	0.23(6)	0.00(7)	0.25(7)	0.01(1)	0.55(6)	0.05(7)	0.15(7)
	K_2O	16.54(1)	0.17(0)	14.66(4)	0.65(4)	15.81(1)	0.17(0)	14.10(4)	0.21(1)	16.64(0)	0.07(8)	15.23(1)	0.24(8)	8.78(5)	4.52(7)	11.46(6)
	CaO	14.57(1)	0.27(9)	14.26(7)	0.30(5)	13.51(3)	0.11(1)	11.97(7)	0.23(4)	12.58(1)	0.21(6)	14.14(4)	0.10(2)	9.34(3)	3.21(8)	14.49(3)
	TiO_2	0.15(5)	0.01(0)	0.15(5)	0.01(2)	0.15(0)	0.00(5)	0.16(2)	0.01(1)	0.15(2)	0.05(6)	0.15(3)	0.00(6)	0.22(6)	0.03(3)	0.46(3)
	MnO	1.19(8)	0.02(0)	1.20(2)	0.03(6)	1.28(4)	0.05(7)	7.18(6)	0.28(0)	0.96(6)	0.02(8)	1.28(2)	0.07(3)	0.90(4)	0.34(2)	0.59(2)
	Fe_2O_3	1.02(3)	0.18(9)	0.76(6)	0.02(6)	1.60(5)	0.02(7)	0.92(2)	0.09(9)	0.75(9)	0.01(8)	0.78(8)	0.03(4)	25.56(0)	9.50(5)	0.53(9)
	CuO	0.09(4)	0.02(1)	0.05(4)	0.00(8)	0.25(7)	0.00(5)	0.16(5)	0.00(9)	1.06(1)	0.03(9)	0.09(8)	0.00(7)	1.91(8)	0.68(3)	0.40(0)
Minor oxides (ppm)	V_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		97	52	134
	Cr_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		51	33	18
	CoO	20	15	20	15	3906	96	239	61	18	10	255	88	n.d.		230
	NiO	44	3	41	1	2068	40	168	37	100	4	158	47	168	48	524
	ZnO	454	10	503	35	429	10	427	12	332	11	455	14	845	292	1021
	Ga_2O_3	8	2	n.d.		n.d.		n.d.		n.d.		n.d.		110	41	n.d.
	As_2O_5	n.d.		n.d.		156	13	313	26	n.d.		n.d.		199	83	404
	Rb_2O	435	24	388	16	332	16	386	18	392	25	397	11	865	392	46
	SrO	986	29	912	21	1052	16	1058	24	1049	49	939	24	719	396	631
	Y_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		860	720	20
	ZrO_2	88	13	83	24	75	21	82	28	65	17	80	14	n.d.		132
	MoO_3	n.d.		n.d.		119	12	18	8	n.d.		n.d.		538	737	8
	Ag_2O	n.d.		n.d.		n.d.		n.d.		44	20	2718	1059	n.d.		98
	In_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		89	0	n.d.
	SnO_2	409	159	76	38	113	111	170	123	123	51	130	93	2329	2881	736
	Sb_2O_5	n.d.		21	9	n.d.		n.d.		n.d.		n.d.		247	132	9082
	BaO	2657	178	2717	153	2407	66	4951	215	2037	156	2609	95	3234	474	3409
	La_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		490	79	n.d.
	Nd_2O_3	n.d.		n.d.		35	36	96	77	37	57	49	22	208	27	n.d.
	PbO	2378	572	1108	173	981	47	1149	78	1128	69	838	149	84957	46954	2221
	Bi_2O_3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.

n.d. : not detected

* PIGE analysis

Manganese-barium correlation

Although manganese can be an impurity associated to the sand used for the glass, it is well known from ancient (Theophilus's treatise[6]) and modern (Georges Bontemps's treatise[7]) glassmakers, and has been assessed by successive studies, that manganese was added on purpose to counterbalance the redox equilibrium of iron and correct the greenish color that ferrous iron impurities give to the glass; also known as the "glassmakers soap". A typical earth-abundant mineral known to be used as a source of manganese is pyrolusite (MnO_2). Here, the concentration of manganese is correlated (Figure S-2) with the presence of barium, which suggests that psilomelane ($(Ba,H_2O)_2Mn_5O_{10}$) was also present in the ore used as a source of manganese.

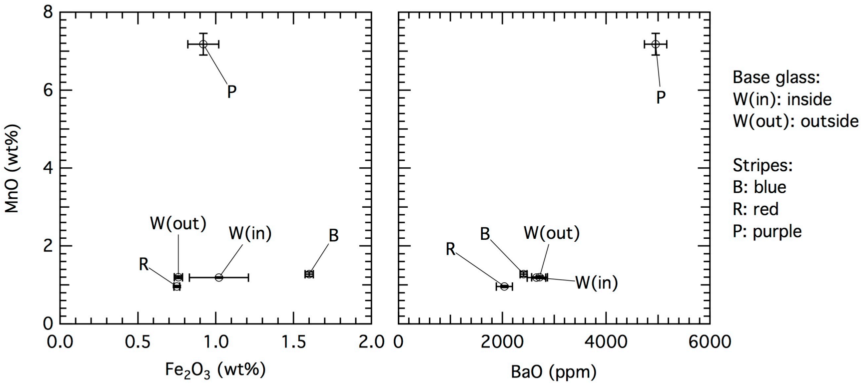

Figure S-2: Manganese concentration as a function of the iron (left) and barium content (right). All oxide concentrations are given in wt % of total oxide. The error bars correspond to the standard deviations (Table S-1).

Manganese in red flashed-glasses

The measured lower concentration of MnO in the red-stripe glass compared to the base glass is consistent with the necessity of minimizing i) in favor of ii). This effect is confirmed in majority by the chemical compositions published in the work of Kunicki-Goldfinger *et al.*[8] (Figure S-3): we observe that for a majority of the glass samples, the iron concentration is slightly higher in the red layer than in the colorless layer (72% of the samples) and that the manganese concentration is slightly lower in the red layer than in the colorless layer (61% of the samples).

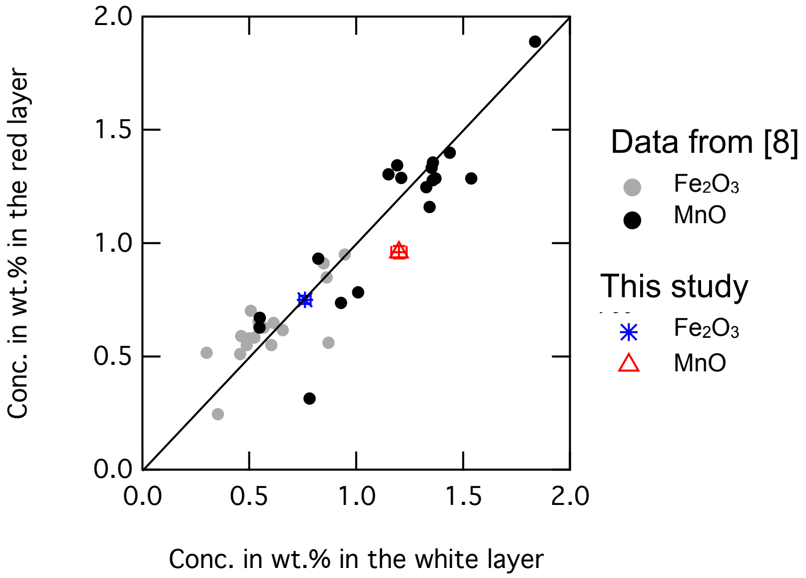

Figure S-3: Concentration of chemical element in the red layer as a function of the concentration of the same chemical element in the base glass layer. Data from Kunicki-Goldfinger *et al.*[8] compared to this study (error bars have the same size as the markers). The diagonal line draws the 1:1 ratio.

As an *aparte*, here we would like to underline the importance of obtaining the chemical compositions from the two layers of one glass, as this is the only case where one can be certain that both glasses were made in the same place, at the same time, and therefore, enables detailed discussion on the composition variations in terms of recipe.

Composition mappings of black opaque staining

The *grisaille* is an opaque brown-black vitreous painting used to make black drawings to prevent transmission of light. The mappings for the internal side of the glass are shown below in Figure S-4. The iron and copper elemental maps of the internal face reveal the shape of the flower painted with *grisaille* opaque paint, which follows the shape of the flower painted on the external face of the glass with yellow-silver paint. The extracted chemical composition and standard deviations are given in Table S-1.

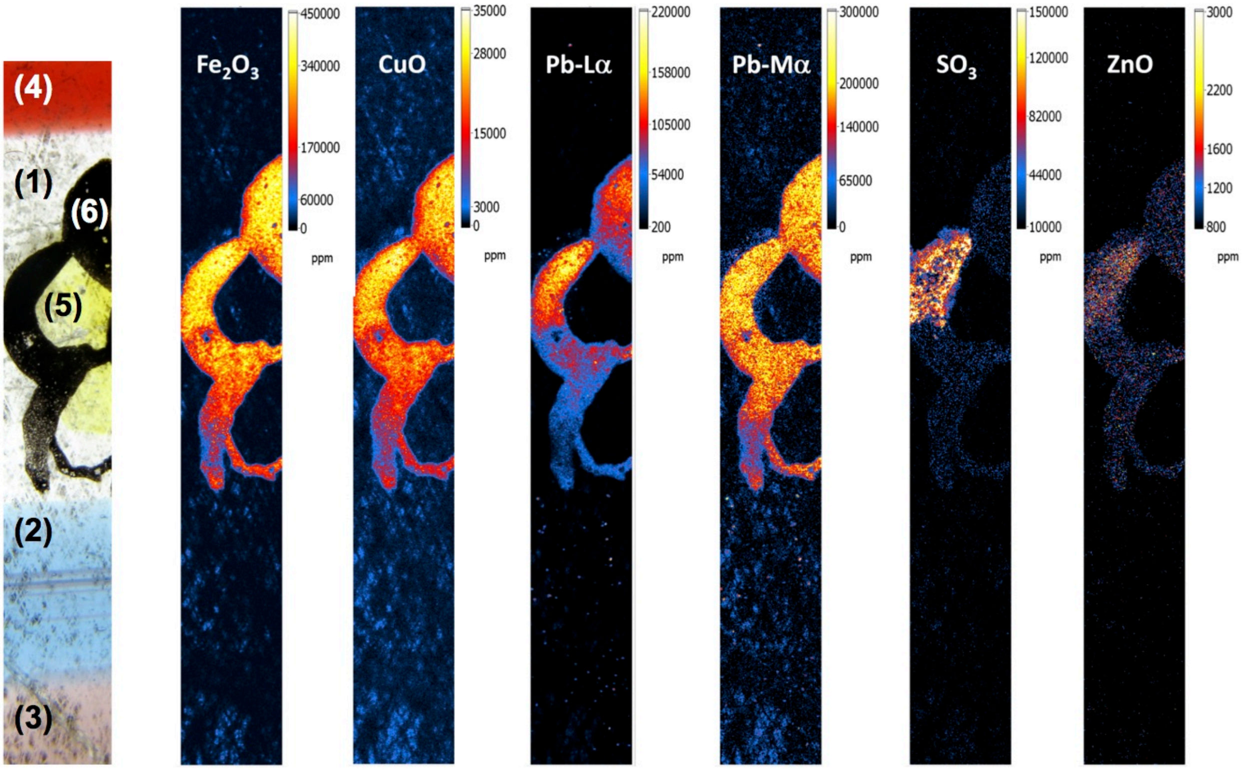

Figure S-4: Chemical quantitative mapping of the oxides concentrations of the internal side of the glass, revealing the flower-shape of the black *grisaille* paint.

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