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Evolution of glass recipes during the Early Middle Ages in France : analytical evidence of multiple solutions adapted to local contexts

Inès Pactat, Magalie Guérit, Laure Simon, Bernard Gratuze, Stéphanie Raux, Céline Aunay

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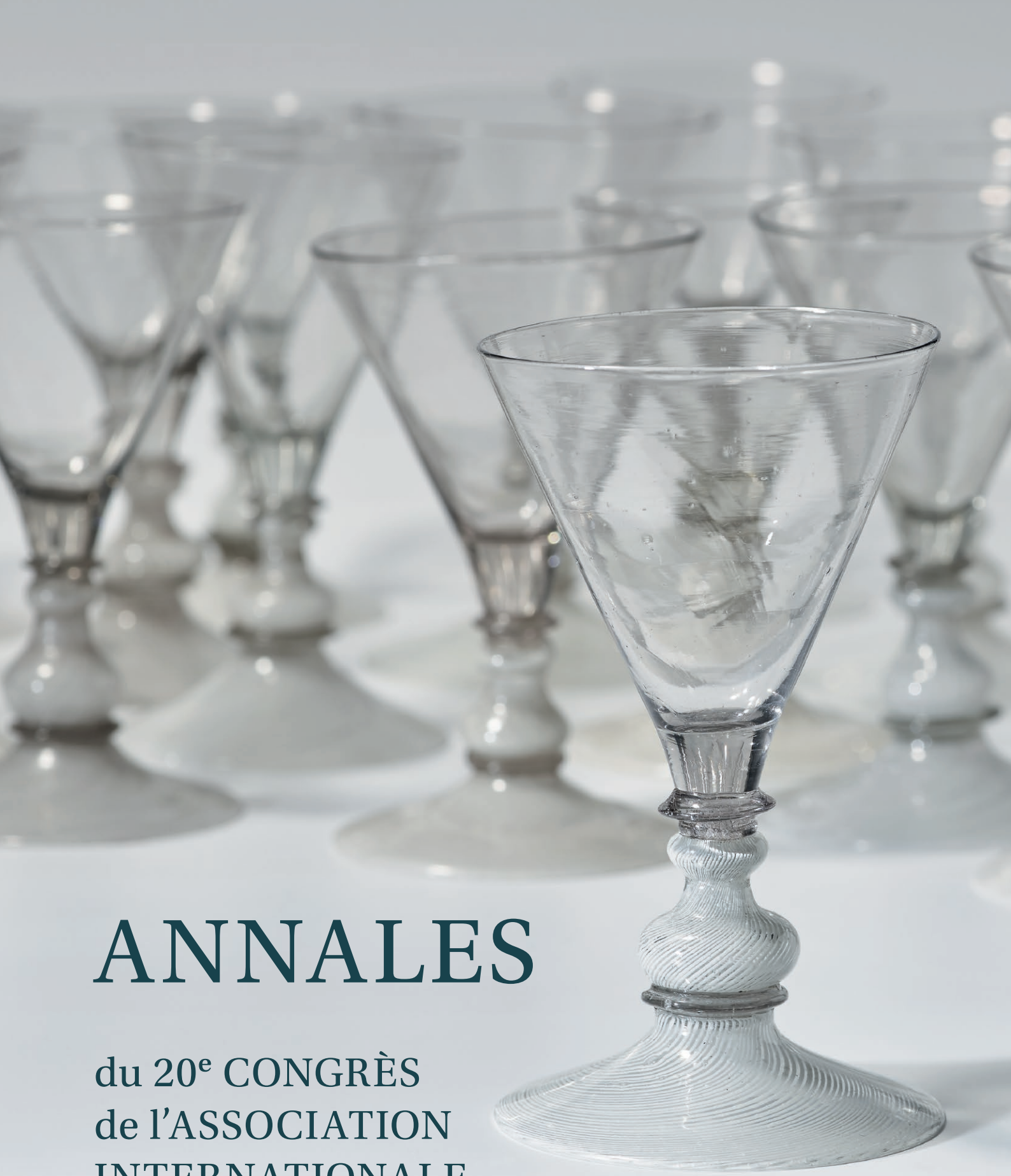

ANNALES

du 20e CONGRÈS de l'ASSOCIATION INTERNATIONALE pour l'HISTOIRE du VERRE

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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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EVOLUTION OF GLASS RECIPES DURING THE EARLY MIDDLE AGES IN FRANCE: ANALYTICAL EVIDENCE OF MULTIPLE SOLUTIONS ADAPTED TO LOCAL CONTEXTS

Inès Pactat, Magalie Guérit, Laure Simon, Bernard Gratuze, Stéphanie Raux, Céline Aunay

INTRODUCTION

This paper deals with the transition from Roman to medieval glass manufacturing processes by examining three Carolingian glass workshops in France. During the Merovingian period, the Roman production system is still in effect, but an increase of recycling soda-lime glass made from mineral soda (also called natron glass) has been observed from the 7th century onwards.[1] This phenomenon is the direct result of a progressive decline of Near Eastern raw glass imports. Similar solutions of glassmaking, based on a plant ash as fusing agent, were adopted both in the East and the West. During the 9th century, soda-lime glass made from halophytic plant ash replaced natron glass in Eastern Mediterranean and in Mesopotamia.[2] By the 12th century, it is the dominant glass type throughout the Mediterranean. In Western and Continental Europe, potash-lime glass made from wood ash develops from the end of the 8th century,[3] resulting in glass compositions characterized by high contents of magnesia, and oxides of phosphorus and manganese.[4] This type of glass, also known as wood ash glass, becomes the prevailing one in continental Europe at the end of the 10th century. However, cobalt blue natron glass is still used until the end of the 12th century for specific productions.[5] We must also point out the existence of another kind of glass, where the calco-alkaline flux is partly or totally replaced by lead oxide.[6]

As we have discussed, important changes in glass manufacturing processes occurred in Western Europe during the Carolingian period. In recent years, the increasing number of analyses carried out on Western European glass dating from this transition period has highlighted the presence of a great variety of compositions. This diversity seems to reflect the use of local raw materials, which enabled glassmakers to face the lack of both raw and recycled natron glass. Three case studies of glass workshops in France illustrate the different solutions developed during the 9th–10th centuries to maintain the glass manufacturing: Méru (Oise), La Milesse (Sarthe) and Melle (Deux-Sèvres) (figure 1). The first two are glass workshops dating from the 9th and the 10th centuries; they are located in the north and the northwest of France respectively. The third workshop is known for its glass produced from recycled metallurgical vitreous slags.

A CAROLINGIAN GLASS WORKSHOP IN MÉRU

In 2008, an archaeological evaluation conducted at Méru (Oise) has revealed a medieval glass workshop and a contemporary settlement.[7] The site was probably abandoned after a fire and has not been reoccupied afterwards. Despite its relative isolation from urban and religious centres, the workshop is located on land belonging to the abbey of Saint-Denis, and is situated on a major road, close to necessary resources (wood, clay and water). Although the site has not been fully excavated, different elements prove undoubtedly the presence of a glass workshop: vitreous slag and vitrified furnace walls, crucibles (including three complete ones), glass working waste and glass artefacts. Based on ceramics and glass vessels, the site can be dated to the first and second third of the 9th century.

Fig. 1: Location of the three studied glass workshop and the sites where the beakers from Melle have been discovered. © authors.

In order to understand which types of glass were worked and produced at Méru, 50 samples have been ana-

1 Freestone 2015; Mirti et al. 2001.
2 Whitehouse 2002.
3 Van Wersch et al. 2015; Velde 2009; Wedepohl, Winkelmann and Hartmann 1997.
4 Wedepohl and Simon 2010.
5 Brill 1999, 244; Foy 2001, 291–302; Simon-Hiernard and Gratuze 2011; Strepnich and Libourel 1997.
6 Brill 1999; Duckworth et al. 2014; Mecking 2013; Wedepohl and Baumann 1997.
7 Pactat, Gratuze and Derbois 2015.

		Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO	Fe_2O_3	TiO_2	ZnO	SrO	CoO	Rb_2O	CuO	SnO_2	Sb_2O_3	BaO	PbO
Samples	**Colour**	%																		
Crucibles																				
111-72	blue-green	17.6	0.63	2.41	67.6	0.06	0.71	8.36	0.34	0.62	0.08	0.003	0.05	<0.001	0.002	0.005	0.002	0.46	0.02	0.01
82-C1	colourless	9.48	2.62	3.10	64.4	1.04	4.01	11.2	0.78	1.29	0.19	0.05	0.05	0.002	0.007	0.74	0.07	0.10	0.08	0.34
Raw glass																				
12-61	blue-green	13.7	0.62	2.62	69.7	0.11	0.37	10.0	0.26	1.04	0.25	0.01	0.03	0.002	0.001	0.03	0.01	0.004	0.02	0.08
111-143	light yellow	11.8	0.60	2.65	69.9	0.10	0.39	10.6	1.50	1.02	0.31	0.01	0.02	0.001	0.001	0.001	0.001	<0.001	0.04	0.002
111-139	light green	13.7	1.12	3.01	68.8	0.29	1.71	8.27	0.86	1.01	0.20	0.02	0.04	0.001	0.003	0.13	0.01	0.08	0.05	0.06
111-102	purple	10.9	1.32	3.47	70.3	0.27	1.15	8.24	0.74	2.09	0.37	0.02	0.05	0.003	0.002	0.14	0.04	0.14	0.04	0.16
Wastes																				
94-33	deep green	6.85	4.06	2.39	62.5	1.71	7.60	11.8	0.64	1.01	0.18	0.03	0.05	0.001	0.01	0.21	0.04	0.05	0.09	0.18
111-156	deep green	10.7	2.04	3.29	61.9	2.48	4.05	10.2	0.66	2.16	0.27	0.05	0.05	0.004	0.007	0.47	0.14	0.12	0.08	0.64
101-47	yellow-green	4.47	4.96	2.40	57.3	2.56	11.7	12.4	0.71	1.41	0.20	0.03	0.05	0.002	0.02	0.89	0.05	0.03	0.11	0.22
111-97	green	9.11	2.94	2.69	64.0	1.28	6.06	10.6	0.60	1.11	0.21	0.05	0.04	0.002	0.01	0.37	0.05	0.06	0.08	0.17
94-29	light green	5.46	4.77	2.39	60.1	2.35	10.0	11.5	0.69	1.18	0.20	0.04	0.04	0.001	0.02	0.48	0.04	0.04	0.10	0.18
111-75	light green	10.9	2.65	2.95	63.6	1.07	4.33	10.7	0.59	1.32	0.22	0.11	0.04	0.002	0.008	0.61	0.06	0.06	0.07	0.20
111-127	light green	6.42	4.11	2.86	61.8	1.95	7.62	11.8	0.67	1.21	0.22	0.04	0.05	0.002	0.01	0.22	0.06	0.05	0.11	0.27
111-153	blue-green	16.7	0.54	2.41	68.5	0.07	0.51	6.84	0.12	0.62	0.10	0.16	0.05	0.001	0.001	1.05	0.01	0.77	0.02	0.42
111-101	cobalt blue	16.7	0.55	3.09	69.0	0.12	0.55	6.34	0.35	0.66	0.13	0.01	0.04	0.01	0.001	0.48	0.03	0.67	0.02	0.08
94-27	red	13.4	0.79	2.29	63.5	0.29	3.57	7.37	0.36	5.08	0.09	0.02	0.05	0.004	0.007	0.97	0.02	0.53	0.04	0.60
94-27	black	15.2	0.60	2.57	66.6	0.13	0.95	6.51	0.32	3.75	0.10	0.03	0.04	0.004	0.001	0.29	0.04	0.62	0.02	1.32
Tesserae																				
58-63	blue-green	13.6	0.48	2.50	63.4	0.11	0.50	6.77	0.47	0.49	0.07	0.003	0.05	0.001	0.001	1.47	0.09	0.69	0.02	8.38
111-100	blue-green	15.9	0.57	2.59	66.5	0.20	0.72	6.80	0.48	0.93	0.09	0.005	0.05	0.001	0.001	1.68	0.06	0.39	0.02	1.59
94-28	yellow	14.6	0.39	1.76	61.7	0.05	0.43	4.45	0.22	0.97	0.10	0.003	0.03	0.000	0.001	0.01	0.04	1.80	0.01	12.5
Vessels																				
55-50	deep green	8.36	3.10	2.67	62.3	1.43	6.17	11.1	0.72	1.12	0.18	0.02	0.05	0.002	0.01	1.86	0.07	0.09	0.09	0.21
48-54	light green	15.5	1.00	2.77	67.1	0.24	1.16	8.17	0.85	1.20	0.15	0.03	0.06	0.003	0.002	0.25	0.05	0.20	0.04	0.23
56-68	light green	3.62	4.85	2.44	60.2	2.37	11.0	12.1	0.75	1.33	0.24	0.03	0.04	0.001	0.02	0.14	0.04	0.02	0.14	0.20
82-11	light green	5.36	4.64	2.48	60.4	2.18	9.18	12.3	0.75	1.29	0.22	0.03	0.05	0.001	0.02	0.32	0.07	0.04	0.11	0.14
94-23	light green	14.7	0.94	2.81	68.2	0.23	0.98	8.27	0.88	1.03	0.18	0.05	0.05	0.002	0.002	0.43	0.03	0.13	0.04	0.16
111-124	light green	13.9	0.70	3.13	71.7	0.08	0.54	8.35	0.02	0.44	0.08	0.001	0.05	<0.001	0.001	0.003	0.001	<0.001	0.02	0.002
111-128	light green	7.75	3.97	2.61	62.3	1.71	6.75	11.3	0.76	1.26	0.21	0.06	0.04	0.002	0.01	0.46	0.04	0.04	0.10	0.13
111-144	light green	8.36	3.39	2.77	61.2	1.19	5.74	11.1	0.73	1.35	0.17	0.04	0.05	0.002	0.01	0.61	0.24	0.09	0.13	2.30
111-147	light green	12.7	1.24	2.33	66.5	0.32	5.04	8.54	0.84	1.01	0.14	0.02	0.05	0.002	0.004	0.12	0.04	0.15	0.04	0.16
14-59	blue-green	4.02	4.41	2.60	59.7	2.13	10.1	12.4	0.78	1.35	0.23	0.03	0.04	0.002	0.02	0.46	0.19	0.03	0.13	0.88
111-115	blue-green	3.25	5.06	2.93	59.4	2.38	9.55	13.8	0.79	1.49	0.28	0.03	0.04	0.001	0.020	0.13	0.04	0.02	0.16	0.23
94-22	light blue	12.5	0.93	2.89	70.1	0.12	0.70	10.5	0.09	1.04	0.28	0.004	0.02	0.001	0.001	0.01	0.003	0.003	0.02	0.01
94-24	light blue	16.0	0.37	2.06	71.9	0.13	0.50	6.96	0.42	0.30	0.05	0.001	0.04	0.001	0.001	0.003	0.001	0.004	0.02	0.001
111-79	light blue	6.80	4.39	2.68	61.5	2.00	8.04	11.2	0.65	1.23	0.20	0.04	0.05	0.002	0.018	0.21	0.07	0.05	0.10	0.31
111-107	light blue	15.9	0.59	2.89	69.3	0.12	0.94	8.84	0.02	0.37	0.07	0.00	0.05	<0.001	0.001	0.001	0.001	<0.001	0.02	0.003
82-3	light blue	6.57	4.18	2.42	60.9	1.88	8.92	11.6	0.66	1.16	0.20	0.06	0.05	0.002	0.016	0.50	0.06	0.05	0.10	0.21
82-3	cobalt blue	13.3	0.95	2.46	67.7	0.27	2.99	8.36	0.51	1.13	0.16	0.06	0.04	0.04	0.004	0.26	0.02	0.85	0.03	0.14
82-3	colourless	14.0	1.03	2.53	68.6	0.25	2.05	8.47	0.83	0.82	0.15	0.01	0.05	0.001	0.003	0.06	0.01	0.20	0.04	0.03
111-99	light yellow	13.6	0.56	2.56	68.3	0.09	0.37	10.3	1.59	1.06	0.30	0.01	0.02	0.001	0.001	0.002	0.001	<0.001	0.03	0.002
55-51	opaque white	8.56	2.00	2.79	54.8	0.98	3.67	9.19	0.58	1.33	0.17	0.04	0.04	0.003	0.006	0.56	10.2	0.10	0.08	4.42
55-51	black	7.15	3.00	3.52	63.4	1.28	4.66	11.8	0.68	1.65	0.24	0.03	0.05	0.002	0.010	0.37	0.75	0.06	0.11	0.85
111-149	black	5.84	3.27	3.60	61.8	1.70	5.93	12.3	0.68	2.42	0.27	0.04	0.05	0.002	0.011	0.60	0.11	0.06	0.10	0.82
Stained glass																				
82-9	deep green	6.35	3.74	2.67	61.1	1.55	6.75	11.8	0.71	1.52	0.23	0.04	0.05	0.002	0.013	2.09	0.35	0.05	0.10	0.39
82-10	light green	5.67	3.88	2.49	60.5	1.49	7.56	12.3	0.71	1.50	0.20	0.03	0.04	0.002	0.015	0.55	0.38	0.05	0.11	2.00
94-30	light green	14.8	0.85	2.64	67.3	0.62	0.98	9.11	0.92	1.09	0.15	0.01	0.06	0.002	0.002	0.13	0.04	0.20	0.04	0.12
94-37	light green	14.7	0.87	2.58	68.1	0.22	0.87	9.57	0.38	1.02	0.21	0.02	0.03	0.002	0.001	0.16	0.03	0.05	0.02	0.27
110-62	light green	6.82	4.25	2.33	61.0	1.94	8.12	12.0	0.70	1.10	0.17	0.08	0.04	0.002	0.013	0.54	0.05	0.04	0.09	0.17
111-112	light green	3.70	4.87	2.67	58.5	2.38	10.8	13.3	0.79	1.50	0.25	0.02	0.04	0.001	0.022	0.14	0.04	0.02	0.15	0.27
94-18	cobalt blue	15.2	0.69	2.63	67.8	0.15	0.77	7.64	0.38	1.17	0.10	0.02	0.05	0.05	0.001	0.56	0.04	1.58	0.02	0.36
82-8	cobalt blue	13.1	1.04	2.78	68.5	0.24	0.93	9.60	0.36	1.60	0.23	0.12	0.03	0.08	0.001	0.30	0.01	0.18	0.03	0.08
94-17	red	11.8	1.38	3.19	66.5	0.60	2.30	9.67	0.69	1.62	0.20	0.03	0.05	0.004	0.004	0.41	0.13	0.18	0.05	0.61
94-20	red	12.9	1.40	2.63	66.9	0.38	1.69	9.97	0.87	1.09	0.17	0.07	0.05	0.003	0.002	0.58	0.10	0.08	0.04	0.34
82-2	purple	13.2	1.06	2.29	68.9	0.18	1.00	9.48	1.30	1.19	0.21	0.01	0.03	0.001	0.001	0.04	0.01	0.01	0.04	0.08
82-5	purple	15.1	1.05	2.81	68.0	0.16	0.85	7.94	1.16	1.42	0.22	0.01	0.06	0.002	0.001	0.11	0.02	0.09	0.04	0.13

Fig. 2: Chemical analyses of 50 glass samples from Méru, by LA-ICP-MS. © MSHE, I. Pactat.

lysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (figure 2). They represent the whole variety of the finds: raw glass, cullet, glass working waste, glass droplets, crucibles, glass vessels and stained glass.

The analyses have revealed two main compositional groups, which correspond to two different glass recipes (figure 3). They are mainly distinguished by their levels of soda (Na_2O), potash (K_2O), lime (CaO) and phosphorus oxide (P_2O_5). The first recipe follows the Roman glass making

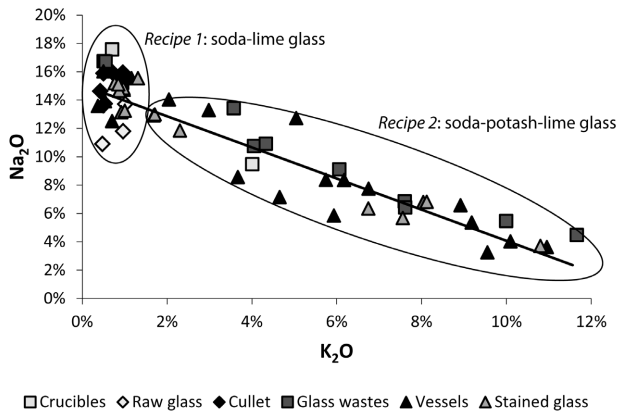

Fig. 3: Sodium and potassium oxides contents of the glass from Méru, labelled according artefact category. © MSHE, I. Pactat.

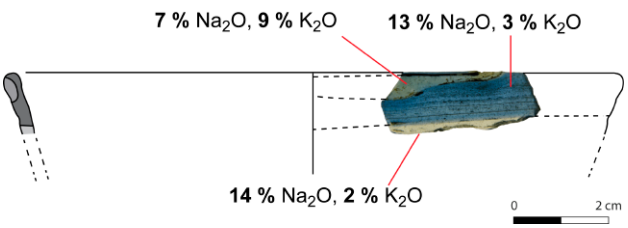

Fig. 4: Sodium and potassium contents of a composite funnel beaker from Méru. © MSHE, I. Pactat.

% oxide	Glass from La Milesse			Glassy slags and wastes from La Milesse		
	Average (14)	min	max	Average (4)	min	max
Na_2O	0.54	0.37	0.67	0.53	0.46	0.58
MgO	3.81	2.99	4.49	2.22	0.85	3.77
Al_2O_3	2.92	2.21	3.88	3.87	3.51	4.16
SiO_2	55.5	52.2	60.7	67.7	60.9	72.7
P_2O_5	2.94	2.05	3.55	1.17	0.17	3.40
K_2O	12.9	8.6	17.3	12.6	10.9	13.4
CaO	16.3	13.2	23.7	6.35	2.5	9.6
MnO	0.89	0.68	1.12	0.44	0.19	0.81
Fe_2O_3	3.03	2.14	5.76	4.08	2.69	4.67
TiO_2	0.45	0.36	0.57	0.57	0.52	0.64
ZnO	0.031	0.019	0.038	0.011	0.0019	0.032
SrO	0.052	0.044	0.076	0.027	0.012	0.047
Sb_2O_3	–	–	0.0001	–	–	–
BaO	0.0015	0.0009	0.0026	0.0019	0.0002	0.0059
PbO	0.22	0.19	0.29	0.13	0.056	0.23
SnO_2	0.0014	0.0011	0.0018	0.0017	0.0013	0.0022

Fig. 6: Composition of the glass from La Milesse, by LA-ICP-MS. © CNRS, B. Gratuze.

tradition by re-melting natron glass (figure 3, recipe 1). Some glass vessels and stained glass fragments found at Méru were produced using recycled glass like tesserae, antique beads and glassware. Small blocks of soda-lime glass were also discovered in the workshop. The second recipe is partly based on the reuse of natron glass, but the contents of potash, magnesia, and phosphorus oxide are higher. This particular feature could be interpreted either by the mixing of two different types of glass (natron and wood ash) or by the addition of an increasing amount of wood ash into a mixture of glass cullet (figure 3, recipe 2). We observe an inverse relationship between soda on the one hand, and potash, magnesia and phosphorus oxide on the other: soda decreases from 14 to 3.2 wt.% while potash increases from 1.7 to 11.7 wt.%. This corresponds to a gradual transition between natron glass and wood ash glass. Crucibles, glass working waste, glass vessels and stained glass are once again represented in the soda-potash-lime group.

Among the different glass vessels from Méru, a funnel beaker made with three different parts of glass (colourless, cobalt-blue and light-blue) is particularly interesting (figure 4). The analyses reveal that the different parts of the beaker have different soda, potash, lime and magnesia contents, which means that the two main glass recipes identified could have been partly contemporary (figure 2, sample 82-3).

In conclusion, the presence of both crucibles and glass wastes into the two main compositional groups shows undoubtedly that the transition from natron glass to potash-lime glass occurred in Méru. During this transition period, glassworkers had to adapt their methods in response to the decrease in the availability of natron glass by developing new recipes using local raw materials in order to meet the demand for glass. Evidence that stained glass and vessel glass were manufactured in the same place is provided by glass waste, such as a twisted shard of a cylinder-blown window glass, and a common chemical composition (figure 5-A).

THE 10TH CENTURY GLASS WORKSHOP OF LA MILESSE

The archaeological site of Bois Beslan at La Milesse (Sarthe) was discovered in 2012–2013. Most finds discovered at the site relate to the extraction and reduction of iron ore between the Late Iron Age and Antiquity. A glass workshop has been identified in the north-eastern part of the site.[8] Typical elements of glass-working activity have been collected in abandoned mining dumps (figure 5-B). Seven crucibles with glass or vitrified matter on their internal or external walls have been identified and more than 20 kg of waste materials have been recovered. Half of this material is related to glass working (wires and rods of drawn glass with round or flat sections, glass drops, small raw glass fragments and shapeless nodules), the other half is scoriaceous vitreous material.

The workshop can be dated to the 10th century according to glassware and ceramic typology; the dates have been confirmed by radiocarbon analyses. The most frequently found form is that of a goblet with a straight or hemmed edge, a concave bottom and an ovoid body. The goblets are decorated with horizontal or spiral trails. They are similar to specimens dating to the 9th–10th centuries.[9] The second most frequent form is that of a high goblet with a simple rounded rim and a truncated wall. Funnel beakers and hemispheric cups are each represented by one object. All the glass samples are coloured deep green.

8 Raux et al. 2015.
9 Foy and Sennequier 1989, n° 61, 145–146; Mouny 2008, n° 1, fig. 2.

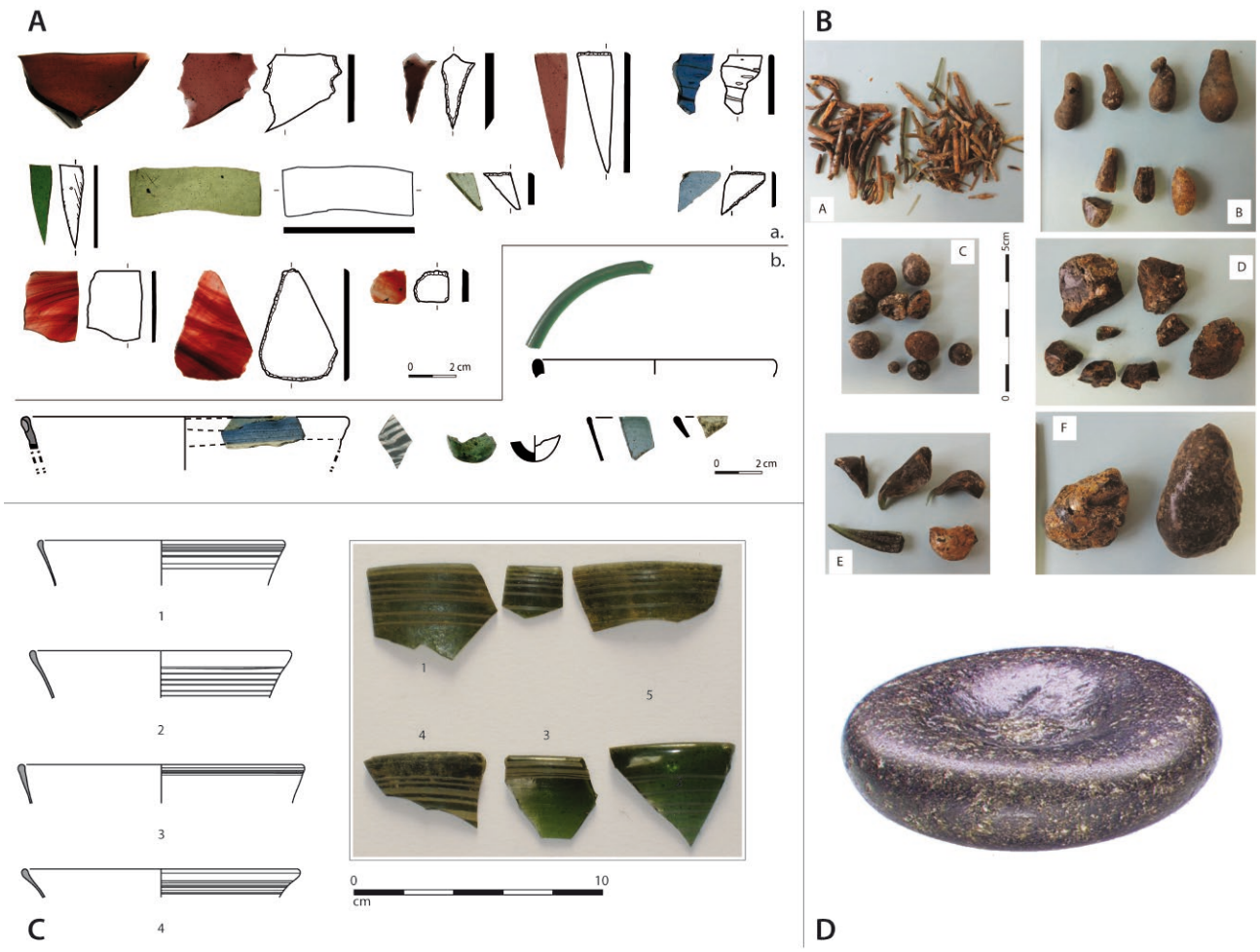

Fig. 5:

A: Méru workshop production: stained glass (a) and glass vessels (b). © Inrap, M. Derbois, St. Lancelot; MSHE, I. Pactat.

B: Glass wastes from La Milesse: wires and rods (a), glass drops (b-c), raw glass fragments (d), shameless nodules (e-f). © Inrap, St. Raux.

C: Deep green beakers with white trails from Faye-sur-Ardin. © Inrap, L. Simon.

D: Lead-rich linen smoother from Beaugency (Loiret, ø = 70 mm). © CNRS, B. Gratuze.

14 samples of crucibles, raw glass, glass wastes and vessels have been analysed using LA-ICP-MS (figure 6). They form a homogeneous chemical group of potash-lime glass. Compared to contemporaneous wood ash glass,[10] La Milesse glass contains less soda and more alumina and oxides of iron, titanium and zirconium (figure 7). Recycled natron glass was not added to the melt as evidenced by the low soda contents (0.54 +/- 0.10 wt.% Na_2O). The high iron oxide level shows furthermore that local ferrous sand was used. So, the chemical homogeneity of this group reveals primary glass production at La Milesse.

The reoccupation of an abandoned mine site represented several advantages for the glassworkers. They could benefit from local raw materials like sandstone and clay deposits to build the furnaces. In addition to the local sand (with elevated iron oxide), the fuel and plant ash required for glass production were supplied by nearby vegetation. Due to the absence of structures, it is difficult to interpret the archaeological remains, but we can suppose that the La Milesse glass workshop was very close to medieval models with a primary furnace to prepare the melting batch and a secondary one for glass blowing. The particular composition of the glass and the presence of semi-finished products and glassy slags suggest that the primary production was located near the excavated area.

THE RECYCLING OF LEAD SLAG IN THE AREA OF MELLE DURING THE CAROLINGIAN PERIOD

In 1992, Julia Scapova published an uncommon composition of a 10th century linen glass smoother discovered in Novgorod (Russia).[11] This silica-lime-alumina-lead glass contained high iron, barium and antimony. During the following decades, several linen glass smoothers with a similar composition were described in Germany, France, England[12], Ireland, Norway and, more recently, Denmark and Belgium. All these objects are dated between the end of the 8th century and the end of the 10th century. At the end of the 1990s, both chemical and lead isotopes analyses were carried out on various materials (lead ore, slag, metallic lead, silver coins…) from the Carolingian lead-silver mines

10 Unpublished data.
11 Scapova 1992.
12 Bayley 2009, 258.

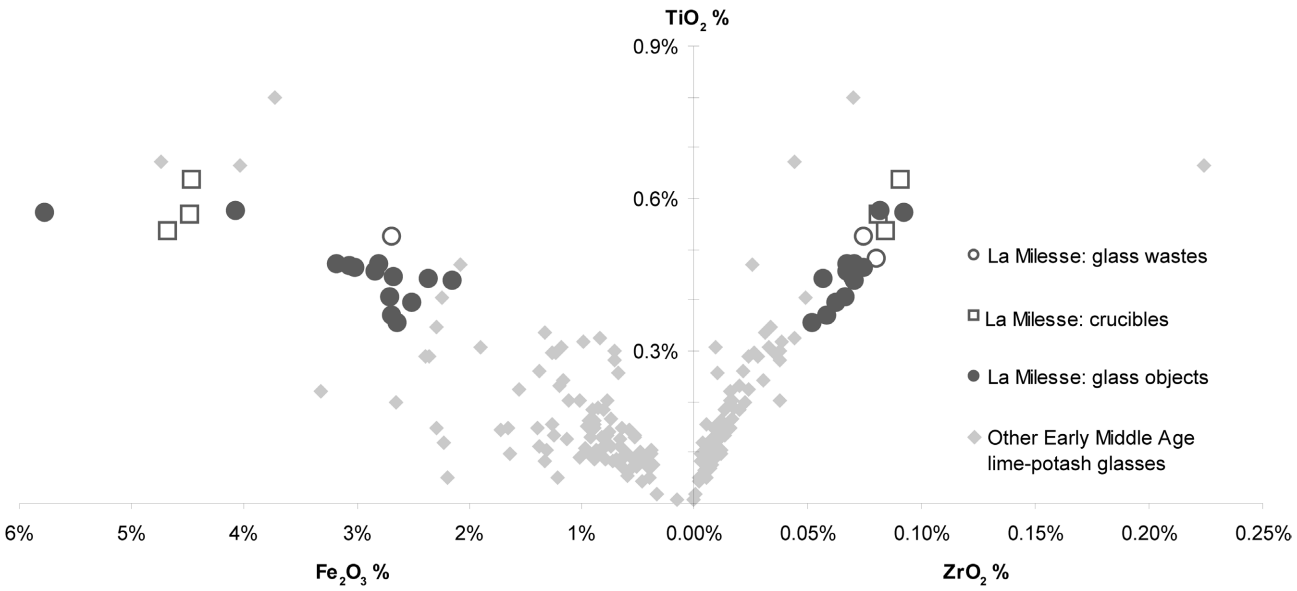

Fig. 7: Iron, titanium and zirconium oxides contents of glass from La Milesse. © CNRS, B. Gratuze.

% oxide	Melle's glass smoothers			Melle's slag		
	Average (70)	min	max	Average (35)	min	max
Na_2O	1.32	0.68	2.36	0.26	0.13	0.42
MgO	2.26	1.55	3.40	3.07	0.87	4.92
Al_2O_3	7.27	5.58	10.13	4.64	3.18	6.13
SiO_2	44.2	37.0	52.3	41.6	30.8	52.3
P_2O_5	1.87	1.02	3.00	2.28	1.11	3.81
K_2O	4.02	3.03	5.45	2.51	0.89	4.57
CaO	15.5	12.3	19.8	16.5	6.40	28.4
MnO	0.29	0.11	0.55	0.47	0.23	0.77
Fe_2O_3	3.43	1.69	4.66	10.40	5.73	20.20
TiO_2	0.25	0.18	0.42	0.28	0.21	0.37
ZnO	0.21	0.04	0.55	0.24	0.04	0.74
SrO	0.09	0.06	0.16	0.12	0.05	0.20
Sb_2O_3	0.51	0.30	0.80	0.31	0.11	0.51
BaO	1.35	0.41	3.11	4.46	0.32	12.70
PbO	17.8	8.10	26.1	12.7	3.50	37.0
SnO_2	0.0058	–	0.028	0.004	0.0004	0.018

% oxide	Faye-sur-Ardin / Bressuire / Poitiers / Pussigny					
	Deep green glass from beakers			Opaque white glass from trails		
	Average (19)	min	max	Average (9)	min	max
Na_2O	2.59	1.15	4.50	2.31	1.33	3.94
MgO	1.86	1.56	2.32	1.61	1.52	1.71
Al_2O_3	8.20	7.13	10.20	7.18	6.66	7.94
SiO_2	58.7	52.9	64.2	50.2	46.9	56.8
P_2O_5	1.34	0.94	1.94	1.39	0.89	2.28
K_2O	4.09	3.61	4.57	3.58	3.30	3.92
CaO	12.4	10.0	15.7	11.3	10.1	12.0
MnO	0.42	0.26	0.51	0.38	0.33	0.44
Fe_2O_3	3.50	2.67	5.51	3.41	2.63	4.35
TiO_2	0.25	0.21	0.30	0.24	0.21	0.29
ZnO	0.09	0.02	0.33	0.08	0.02	0.12
SrO	0.06	0.05	0.07	0.06	0.05	0.07
Sb_2O_3	0.14	0.07	0.27	0.17	0.07	0.23
BaO	0.68	0.26	1.16	0.66	0.24	0.91
PbO	5.15	1.66	10.10	10.50	5.47	14.2
SnO_2	0.31	0.02	0.69	6.66	4.24	10.2

Fig. 8: Composition of glass smoothers and slag from Melle, and composition of beakers from Bressuire, Faye-sur-Ardin, Pussigny and Poitiers. © CNRS, B. Gratuze.

of Melle (Deux-Sèvres). A connection was established between the glassy slag produced at this smelting site and the silica-lime-alumina-lead glass of the linen glass smoothers (figure 8).[13] Since 2012, several glass vessels sharing the same specific composition as the Melle's linen smoothers have been identified thanks to a systematic analysis of glass objects discovered on different Carolingian archaeological sites to the north and to the west of Melle: Bressuire, Faye-sur-Ardin, Pussigny, Poitiers and probably Perigny.[14] Most of these objects are deep green coloured beakers with a flared and rounded rim and several opaque white trails under the rim (figure 5-C). But some unidentified fragments from Faye-sur-Ardin could expand and diversify this first typology.

LA-ICP-MS analysis results shows that – like the linen smoothers – all these objects were made from recycling glassy slag, which was produced during the smelting of galena (figure 9). Comparing the chemical composition of the glassy slag, the linen smoothers and the beakers (figure 8), it appears that soda-lime glass cullet is systematically added to the melting batch: to a lesser extent in the production of the linen smoothers (1.3 +/- 0.3 wt.% Na_2O) and to a greater extent in the production of the glass vessels (2.4 +/- 1.3 wt.% Na_2O). The results also reveal that opaque white glass is locally produced by adding tin and probably lead oxides to the same base used for the glass body (figure 8).

The use of this metallurgical by-product has two main advantages. Firstly, glassy slag is a cheap raw material that was used to compensate for the shortage of natron glass. Secondly, this recipe saves significant amounts of energy. The production of wood ash glass, developed at the same time in Western Europe, requires large amounts of wood which was used as fuel and – in the form of ash – as potash-lime flux. Therefore, the use of slag significantly reduces wood

13 Téreygeol et al. 2004.
14 Gratuze et al. 2014.

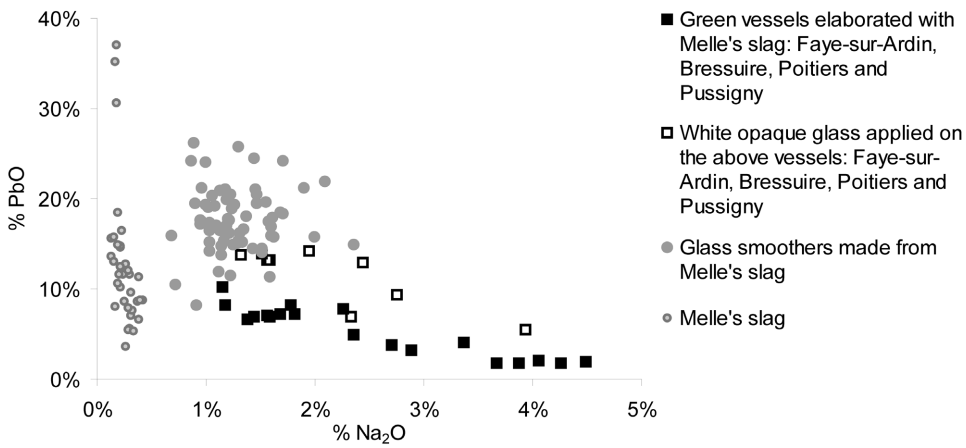

Fig. 9: Comparison of lead and sodium oxides contents of the beakers from Bressuire, Faye-sur-Ardin, Pussigny and Poitiers, and the lead-rich linen smoothers and slag from Melle. © CNRS, B. Gratuze.

needs and can be considered as an adaptation of Melle's glassworkers to the lack of natron glass across Europe. This real technological innovation does not have, as far as we know, any equivalent in the Carolingian period.

As no craft structure has yet been discovered at Melle, the workshop is consequently only known through its products (linen glass smoothers and vessels). We can, however, hypothesise that – for practical reasons – it was located close to the smelting site. The glassware production can be dated between the 9th and the 10th centuries, according to the archaeological context within which the beakers were found.

CONCLUSION

While archaeological and archaeometric data date the emergence of wood ash glass to the end of the 8th century, these three glass workshops dating from the 9th–10th centuries have shown that the transition from soda-lime to potash-lime glass was a gradual process. Indeed, the use of wood ash as flux did not happen suddenly since natron glass cullet was still used in the 9th century. The site of Méru illustrates this phenomenon on a workshop scale. But ongoing studies on Carolingian glass[15] demonstrate that Méru is not an isolated case. For example, two contemporary glass objects discovered at Vernou-sur-Brenne (Central France) fall into the transition between natron soda-lime glass and wood ash glass.[16] While the first one is a soda-lime glass containing a little wood ash (3 wt.% K_2O and 1.4 wt.% MgO), the second one is a potash-lime glass containing high soda (5 wt.% Na_2O). These two pieces were produced by an unknown glass workshop. At the same time, an original recipe recycling metallurgical waste was developed by Melle's glassworkers.

These different case studies provide the first evidence of medieval primary glass production in France. They outline local solutions to the lack of natron raw glass and they illustrate the Carolingian glassworkers's ability to adapt methods and recipes in order to maintain production volumes of vessel glass and stained glass. The transition period seems to end between the mid-10th century and the beginning of the 11th century.

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15 Gratuze, Pactat and Hilberg, forthcoming.
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