European Materials in Crusader Window Glass from Acre

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Acknowledgments: We are extremely grateful to Centre for British Research in the Levant (CBRL) and Arts and Humanities London Partnership (LAHP) for funding this research. An anonymous referee made helpful comments and suggestions on the manuscript.

Painted glass windows in the style of northern and western Europe have been found in several Crusader buildings in the Latin East, for example, at the Crusader fortress at Montfort, where window style has been considered consistent with the French tradition of stained-glass windows of the thirteenth century.[1] Chemical analysis of the Montfort glass suggested it was produced in the Levant, but the windows were decorated and fabricated by French artists working in the Levant.[2]

We present here the surprising insights provided by a preliminary study of the composition of colored window glasses from the Crusader city of Acre (Fig. 1). Acre was conquered by the Crusaders in 1104 and quickly became the main harbor of the Latin East. Lost to Saladin's army in 1187, it was soon recovered and remained in Crusader hands until the final conquest by the Mamluks in 1291.

[1] Whitehouse and others 2017.
[2] Whitehouse and others 2017.

The glass analyzed was found mostly in the Hospitaller Compound and the Church of St. John in the Old City of Acre during large-scale excavations by the Israel Antiquities Authority, between 1991 and 1998.[3] Around four hundred fragments of decorated and undecorated window glass have been studied.[4] As at Montfort, the great majority of the windows were colorless or naturally colored; some were produced from colored glass, including purple, amber, green, blue, and red. Ten samples were analyzed to include representatives of the different colors (Fig. 1). Where preserved, painted decoration is consistent with French stained glass of the mid-thirteenth century.

Small millimeter-sized fragments of glass were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at IRAMAT-CEB (Institut de Recherche sur les ArchéoMATériaux – Centre Ernest Babelon) in Orlèans (Loiret, France), using the standard procedure.[5]

The composition of the window glasses

The majority of the samples show a soda-rich plant ash signature (Table 1), but the translucent red (Acre 009) is a potash-lime-silica composition with low levels of soda (Na_2O < 2%). All soda plant ash glasses, except the amber, contain manganese oxide in quantities above those naturally present in sand and ash, indicating that it was added intentionally to the melt as a decolorizer.[6] The amber color is likely due to the presence of the ferri-sulphide chromophore, which forms under reducing conditions, and the low concentration of the

[3] Stern and Abu-'Uqsa 2010.
[4] Ganor 2015.
[5] Gratuze 2016.
[6] Sayre 1963.

manganese oxidizing agent is consistent with this.[7] Manganese was added in relatively high amounts (between 1.5 wt% and 2.7 wt%) to produce the two pink glasses, while two brown glasses are probably a combination of manganese red and iron green. The two green glasses contain high copper (CuO > 3%) and iron oxides (Fe_2O_3 > 1%). A translucent blue fragment (Acre 005) was colored using around 1000 ppm cobalt and has elevated amounts of zinc, lead, copper, tin, and indium, which are impurities associated with the cobalt ore used.

When considering those components which are commonly associated with the plant ash, such as alkali and alkaline earth metals (e.g., Na_2O, CaO, MgO, K_2O), the soda ash glasses appear rather homogeneous (Table 1), suggesting that a similar type of ash was used. Conversely, those components believed to have been introduced with the silica source, such as aluminium, titanium, zirconium, and hafnium,[8] present more variability (Table 1). The wide compositional variability of the soda ash glass, for example, in Zr and Ba contents (Fig. 2), suggests that several silica sources were used, indicating that the colored glasses are likely to have several different origins.

[7] Sayre 1963.
[8] Brems and Degryse 2014.

TABLE 1
LA-ICP-MS Data for the Glasses Analyzed
Major and Minor Elements in Weight Percent and Selected Trace Elements in ppm

		wt%											ppm										
Sample	Color	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Ba	La	Zr	Hf	Th	Cu	Co	Ni	Zn	In	Sn	Pb
Acre 001	Colorless	11.2	3.11	1.46	68.5	0.34	0.77	2.72	10.6	0.06	0.75	0.37	234	5.85	32.0	0.83	0.75	14.0	4.02	10.9	30.4	0.24	0.98	
Acre 002	Colorless/ Light Pink	11.0	3.36	1.50	67.5	0.49	0.76	3.75	9.24	0.12	1.52	0.67	251	6.67	60.3	1.51	1.08	70.9	16.2	13.8	91.3	1.76	4.18	81.9
Acre 003	Brown	11.5	3.22	1.50	69.1	0.26	0.86	2.73	9.45	0.06	0.76	0.34	229	5.83	30.9	0.83	0.72	13.9	3.16	9.70	30.2	0.09	5.58	38.0
Acre 004	Green	14.2	3.36	0.98	64.2	0.34	0.70	2.58	8.15	0.07	0.63	1.17	71.2	6.46	58.9	1.53	1.24	26011	25.2	21.6	63.3	1.05	1253	984
Acre 005	Blue	11.8	2.98	1.68	68.6	0.30	0.85	2.22	9.68	0.08	0.30	0.82	205	6.60	36.6	0.96	0.89	1137	1010	16.3	1531	123	129	721
Acre 006	Amber	15.1	3.38	0.69	67.8	0.24	0.77	2.11	9.24	0.12	0.03	0.33	57.7	4.19	149	3.66	0.84	8.54	3.89	5.58	19.3	0.01	1.38	491
Acre 007	Light Pink	10.1	3.24	1.74	67.2	0.50	0.83	3.36	9.34	0.12	2.70	0.62	362	7.33	65.7	1.54	1.31	23.3	11.7	21.5	80.4	0.04	0.59	
Acre 008	Brown	11.8	3.19	1.47	69.3	0.25	0.88	2.72	8.95	0.06	0.96	0.33	237	5.77	28.6	0.77	0.70	12.2	2.57	11.1	33.0		0.24	
Acre 009	Red	1.17	5.44	1.50	57.6	3.09	0.60	16.12	12.1	0.18	0.92	0.64	1179	43.0	114	2.90	3.10	1319	8.61	12.5	307	0.81	2.23	
Acre 009b	Red	1.14	5.60	1.49	57.1	2.93	0.56	15.86	12.6	0.18	0.93	0.66	1205	42.3	111	2.93	3.12	4949	8.31	14.0	278	0.02	5.10	19.3
Acre 010	Green	14.2	3.19	0.94	64.4	0.32	0.75	2.52	7.99	0.07	0.63	1.15	71.5	6.62	60.1	1.51	1.28	27116	27.1	23.8	54.6	1.33	1322	1055

On the other hand, the red window glass (sample 009) is of the K_2O-CaO-SiO_2 type (Table 1), typical of the so-called medieval "forest glass" produced in central and northern Europe.[9] The composition of the Acre red window glass is consistent with glass production in northwestern France and therefore with the northern Europe tradition, and it is most likely French in origin .[10]

Medieval "ruby red" window glass was colored by the production of nanoparticles of copper. Two main categories are recognized depending upon their micromorphology.[11] The Acre red is of the striated type, comprising numerous micrometer thick striations and presents a layered structure (Fig. 3). The sample has been analyzed at two different points to reflect its striated nature, and their compositional differences are related exclusively to different copper contents (and associated elements), suggesting that an almost pure copper source was added to the glass and incompletely dispersed.

Procuring colored glass from Europe and the Levant

The presence of a red glass showing a European signature suggests that "special" glasses were imported for Crusader building projects. The production technology of this type of red glass was extremely complex, and it was likely mastered by only a small number of glassmakers. To date, the "ruby red" window glass from Acre is the furthest easterly known example of this striated red glass. It was probably imported as a flat sheet, as the final color could have been damaged by the reworking of the glass. Both its composition and grisaille patterns[12] suggest it is an import from northwestern France, implying that the glazier must

[9] Wedepohl and Simon 2010.
[10] Adlington and others 2019.
[11] Kunicki-Goldfinger and others 2014.
[12] Whitehouse and others 2017, 187–188.

have almost certainly been French and conveyed the glazing techniques to the craftspeople.

The composition of the cobalt-blue glass fragments further confirms a link with European glass technology. Cobalt with high zinc and indium as its main impurities is typically associated with European cobalt ores, extracted in the Erzgebirge in Germany from the end of the twelfth to the end of the fifteenth century.[13] No source of cobalt with high indium is known from the medieval Islamic world.[14] Our data therefore represent the first archaeological evidence of trade in cobalt colorants from Europe to the Crusader Levant. The import of European colorants to Frankish ports is attested by several documents and trade manuals.[15] At the time, cobalt was either imported as pigment or as colored glass to be reworked. Glass with a composition similar to the Levantine one was also produced in Venice,[16] a major glassmaking and trading center which played a crucial role in the Crusades, and therefore a potential source for glass. The composition of the base glass of the blue fragment has been compared with that of a group of medieval Venetian glasses (twelfth to fifteenth centuries), revealing a different trace-element signature (Fig. 4). It shows similarities with Levantine glass probably made in the region of Tyre (Fig. 4). This suggests that European glaziers commissioned the Levantine glassmakers to make the blue glass but brought their own materials with them.

The high compositional variation of the Acre assemblage makes a single production center for all the glasses unlikely. Some of the samples resemble glass made in the Levant, while others are more similar to the Egyptian and Syrian compositions (Fig. 4). The amber glass, with exceptionally high Zr and Hf, may originate elsewhere. This preliminary study

[13] Gratuze and others 2018.
[14] Gratuze and others 2018.
[15] Jacoby 2018.
[16] Verità 2013.

suggests both that the range of colors required was not available from a single supplier and that some workshops may have specialized in particular colors.

Conclusions

All of the glass windows analyzed, except a red fragment, were made using Levantine plant ash and likely came from different areas in the eastern Mediterranean. The analysis suggests that the compositional differences encountered are related to the colors of the windowpanes, pointing to the presence of color-specific workshops.

The most striking result is the evidence of the import of European pigments and glass. The data indicated the presence of a red window glass imported from France as well as of a cobalt-blue pigment imported from Europe and likely added to a Levantine base glass. It thus seems that the Crusaders brought with them from Europe colorants, luxury glass, and possibly even specialists in window painting.

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FIGURE CAPTIONS

FIG. 1. *Examples of window glasses from Acre. (Photo: courtesy Israel Antiquities Authority)*

FIG. 2. *LA- ICP-MS data for the plant ash glasses analyzed, showing different sand sources. (Graphic: Veronica Occari)*

FIG. 3. (a, b) *The red glass sample with a thick, weathered layer and an internally zoned structure (dimensions: 4.5x3cm);* (c) *Sample as seen under the microscope (magnification 20x)(Photos by the authors).*

FIG. 4. *La/Th vs Hf (ppm) of the samples analyzed compared with "Levantine" glass (the Tyre type; Phelps 2016, 2018), glass from Syria (al-Raqqa, Damascus; Henderson and others 2016), Egypt (Scibille and others 2019), Beirut (Henderson and others 2016), and Khirbat al-Minya (Henderson and others 2016), and medieval glass from Venice (authors' unpublished data). (Graphic: Veronica Occari)*