<u>High-boron and High-alumina Middle Byzantine (10th–12th Century ce) Glass Bracelets:</u> <u>A Western Anatolian Glass Industry</u>

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***Note: Table 1 has been added using an image capture tool, and is non-compatible with screen reader software programs.

Abstract:

The trace element boron is present in most ancient glasses as an impurity, and high boron(≥300 ppm) marks raw material sources that are geologically specific and relatively uncommon. Recent analyses of Byzantine glass with high boron contents suggest that glass-making was not limited to the traditional regions of the Levant and Egypt, and a production origin in or near western Anatolia is proposed. Glass bracelets fromHişn al-Tīnāt in southernTurkey give fresh evidence for the production and circulation of high-boron glasses that closely correlates with object typology. The patterning of findspots suggests that high-boron glass was closely connected to the Byzantine world

Keywords: High-boron glass | High-alumina glass | glass bracelets | anatolia | middle byzantine period | Hisn al-Tīnāt | chemical composition

Article:

Introduction

Recent analytical work on Byzantine glass from Anatolia indicates that the origin of the raw glass used in the Byzantine world may not have been limited to the traditional glass-making regions of the Levant and Egypt (Schibille 2011; Rehren *et al.* 2015). Robert Brill was the first to notice that Byzantine glasses linked to Greece, Cyprus and Turkey often have a high concentration of the trace element boron (Brill 1968, 1999a,b, 2002, 2005). Despite these early

publications, boron is only now recognized as a key discriminator for a hitherto-unrecognized glass compositional group, found primarily at Pergamon in western Turkey (Schibille 2011; Rehren *et al.* 2015). Glass samples from the small fortified settlement of Hisn al-Tīnāt, located in southern Turkey on what was once the Byzantine/Islamic frontier (*al-thughūr*), provide new evidence for the wider use of boron-rich glass, supporting the identification of an Anatolian-based primary glass production zone that could be located in or near the western borate district of modern Turkey.

The purpose of this paper is to refine and expand the glass-making narrative for the Late Antique and early medieval Eastern Mediterranean region. We give fresh evidence for compositional groups of soda–lime–silica glasses that have only recently been identified, through the analysis of glass bracelets with high levels of boron and/or alumina. While these high-boron glasses are similar to those identified at Pergamon, the Hisn al-Tīnāt boron glasses suggest the existence of object-specific, specialized industries that employed different types of raw glass—evidence that could help provide a more nuanced understanding of the issues of ancient glass production, circulation and use. We then review the presence of high-boron glass elsewhere in the wider Byzantine world, identifying an international distribution and significance of this glass composition.

Materials and methods

The excavation of Hisn al-Tīnāt has recovered 1031 glass vessel fragments and 43 fragments from glass bracelets. Although a relatively small collection, it is a highly important one, because it is one of the few glass assemblages dating to the eighth to 12th centuries in Anatolia to be studied in full (Swan forthcoming). A total of 135 vessel fragments and 40 bracelets were chemically analysed in two separate campaigns in 2010 and 2015. The chemical data for the glass vessels from Hisn al-Tīnāt will be presented elsewhere. This paper focuses only on the glass bracelets, because their unique chemical profile gives important new evidence for high-boron glass production groups.

Archaeological and historical background to Hisn al-Tīnāt

Hişn al-Tīnāt is a small, early medieval fortified settlement on the Mediterranean coast of south-central Anatolia (Fig. 1). In the medieval period, this region was a border zone between Byzantium to the north and the Islamic caliphates to the south-east. The area consequently changed political hands several times during this period, controlled by the Umayyads, 'Abbāsids, Byzantines, Armenians, Seljuks and Crusaders. Hişn al-Tīnāt functioned as a waystation on the main overland route between Anatolia and Syria, with its fortifications serving as a means of safeguarding the local trade products (Eger 2015); Ibn Hawqal (c. 978 ce) describes Hişn al-Tīnāt as a timber depot and port involved in Mediterranean trade to Syria and Egypt (Eger 2010).



Figure 1. A map showing the location of Hisn al-Tīnāt and the findspots of high-boron glasses (\geq 300 ppm B, equivalent to \geq 0.10 wt% B2O3) mentioned in the text (base map: Esri, USGS and NOAA).

Three short excavation seasons in 2008, 2010 and 2011 at Hisn al-Tīnāt revealed five phases of construction dating primarily to the mid-eighth to early-12th centuries ce (Eger <u>forthcoming</u>). Phases V and IV date to the mid-eighth to 10th centuries ce (Early Islamic), Phase III to the 10th century ce (probably Early Islamic, pre-conquest), Phase II to the late-10th to early-12th centuries ce (Middle Byzantine), and Phase I to the post-12th century ce (Late Byzantine and later).

At Hisn al-Tīnāt, the bracelets are high-boron glass, while vessel glasses conform to more typical mineral soda and plant ash soda compositional groups. This pattern associates the chemical composition of a glass object to its formal or stylistic elements, as the Hisn al-Tīnāt glass bracelet compositions largely correspond to the colour, cross-section shape and decorative techniques used to make the bracelets. Glass bracelets conceivably represent cultural tastes and style more readily than do everyday household vessels, precisely because they are objects of personal adornment; as such, they are highly important examples of material culture.

Glass Bracelets

In the Byzantine Empire, bracelets became especially popular after the ninth century ce (Parani 2005; Antonaras 2012). The widespread fashion for glass bracelets during the Middle Byzantine period is supported by the archaeological record—bracelets of metal and glass are a typical find,

especially for female burials, in the 10th–12th centuries ce (e.g., Borisov <u>1989</u>; Mănucu-Adameșteanu and Poll <u>2012</u>)—and also by contemporary artistic representations in paint and mosaic media (Parani <u>2005</u>). The popularity of bracelets was probably a response to changing clothing fashions: by the mid-11th century ce, dresses with trumpet-shaped sleeves were worn by women of all classes, where 'the lower, pointed end of the sleeves are pulled back and tied in a knot between the shoulder blades, leaving the arms not only unhampered but also visible' (Parani <u>2005</u>, 153). The new fashion provided an opportunity for personal adornment by means of bangles, single or stacked, on the forearm or upper arm. A decline in the popularity of bracelets during the Late Byzantine period is also attested to by the archaeological record and in artistic representations; depictions from the 14th century ce, similar in artistic content and iconography to those of earlier centuries, now depict women with bare arms. Painted or metallic-stained glass bracelets were widespread between the 10th and mid-12th centuries in parts of the Byzantine world (Ristovska <u>2009</u>; e.g., Bulgaria, see Borisov <u>1989</u>, 292), and might therefore be considered an element of material culture that is specifically characteristic of the Middle Byzantine period.

Of the 43 total bracelet fragments recovered from the excavation of Hisn al-Tīnāt, 40 were analysed for their chemical composition (Table 1 and Fig. 2). Only one complete bracelet was recovered (Fig. 2 n); although it was not possible to chemically analyse the complete bracelet, this object demonstrates how irregular in shape and thickness glass bracelets can be. The stratigraphic phasing and associated ceramic finds at Hisn al-Tīnāt indicate that the bracelets as a group date to the late-10th to early-12th centuries ce; the context of one dark blue, tightly twisted bangle from Phase II can be more closely dated to c. 1020–1150 ce using radiocarbon accelerator mass spectrometry (laboratory number Beta-316435). Stylistically, the bracelet repertoire of Hisn al-Tīnāt is simple in colour and decorative manipulation. The majority of the bracelets are monochrome blue-green, dark blue, purple or colourless-to-purple glass. One bracelet is made from two different glasses (colourless glass with an internal purple thread) and two bracelets are decorated with a painted or stained geometric pattern on the exterior surface. The most common cross-section shape is circular to oblong, and almost half of the fragments with this shape are further decorated by twisting. 'Peaked' bracelets (those having a triangular section), 'ribbed' or ridged bracelets (those having a flat inner surface with a horizontally ribbed outer surface), and oblong bracelets with a central depression are also present, but in more limited numbers.

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	SiO ₂	Na ₂ O	K20	MgO	Al ₂ O ₃	CaO	FeO	P ₂ O ₅	MnO	Li	Be	В	Sc	Ti	V	Cr	Со	Ni	Си	Zn	As	Rb	Sr	Y	Zr	Nb	Мо
HT_001	Naturally aqua Circular section, loosely twisted	Group 1	69.2	11.3	2.31	2.16	2.00	10.65	0.65	0.52	0.75	5.4	0.5	63	2.7	377	16	17	3.7	10	19	27	3.5	13	532	6.6	37	2.5	2.0
HT_002	Colorless and purple Oblong section, flat interior and ribbed exterior	Group 1	67.7	11.4	2.56	2.75	2.09	9.76	0.63	0.42	1.93	7.5	0.6	64	2.9	235	19	18	8.1	16	1404	33	0.0	15	522	8.2	46	2.7	4.5
HT_003	Colorless and purple Circular section, twisted w/ internal purple thread	Group 1	70.5	12.1	2.26	2.78	1.68	8.10	0.49	0.41	1.16	4.7	0.5	66	3.1	279	14	11	3.6	8.4	40	25	0.0	14	389	6.0	33	2.1	2.9
HT_004	Naturally aqua (bluish) Oblong section, flat interior and ribbed exterior	Group 1	70.3	11.8	2.79	1.95	1.07	7.72	0.56	0.46	0.04	16	0.7	70	2.3	139	11	39	5.3	36	13251	45	75	8.8	248	5.5	34	1.6	1.4
HT_005	Colorless Circular-squared section, twisted	Group 1	71.2	10.6	2.63	2.49	1.99	9.21	0.54	0.43	0.90	4.3	0.4	74	2.7	452	14	13	3.6	11	30	27	0.0	11	553	6.6	35	2.0	2.2
HT_006	Purple Oblong section, flat interior and ribbed exterior	Group 1	65.5	12.9	2.79	2.67	2.08	9.86	0.58	0.46	2.35	5.6	0.5	75	2.5	403	23	12	11	32	42	29	4.1	13	520	6.6	34	2.0	9
HT_007	Purple Circular section, loosely twisted	Group 1	67.2	12.3	2.62	2.50	2.07	8.81	0.64	0.43	2.80	6.0	0.5	76	3.1	311	27	22	25	36	250	45	12	12	586	7.5	40	2.3	9
HT_008	Purple Oblong section, flat interior and ribbed exterior	Group 1	69.6	11.6	2.36	2.90	2.16	8.28	0.58	0.38	2.02	5.7	0.5	76	2.3	453	16	16	10	35	119	32	0.0	13	536	6.5	39	2.3	4.6
HT_009	Purple Oblong section, flat interior and ribbed exterior	Group 1	64.4	13.4	2.94	2.83	2.00	10.11	0.61	0.49	2.47	5.7	0.3	76	2.3	437	16	14	11	13	118	37	4.6	14	538	6.2	35	2.2	4.2

Table 1. Analytical results: major and minor oxides (in w%) and trace elements (in ppm)

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	SiO ₂	Na ₂ O	K20	MgO	Al_2O_3	CaO	FeO	P ₂ O ₅	MnO	Li	Be	В	Sc	Ti	V	Cr	Со	Ni	Си	Zn	As	Rb	Sr	Y	Zr	Nb	Мо
HT_010	Light green Circular-squared section, loosely twisted	Group 1	68.7	11.2	2.38	2.30	2.10	10.50	0.57	0.44	1.52	5.5	0.2	76	1.8	379	15	12	6.5	14	62	32	3.2	14	705	7.8	46	2.7	3.2
HT_011	Purple Circular section, twisted	Group 1	70.2	11.4	2.33	2.52	2.26	8.51	0.61	0.40	1.47	5.6	0.6	77	2.5	459	19	15	12	15	589	41	0.0	12	521	6.5	38	2.1	4.5
HT_012	Purple Circular section	Group 1	69.0	11.9	2.33	2.46	2.05	8.95	0.52	0.39	1.66	5.3	0.3	80	2.0	380	18	14	12	17	167	30	0.0	13	536	7.0	38	2.2	6.5
HT_013	Light green Circular section	Group 1	70.7	10.6	2.03	2.32	2.30	9.51	0.61	0.35	1.24	5.1	0.3	83	1.5	378	14	16	10	84	382	47	12	14	612	7.9	50	2.6	3.2
HT_014	Purple Circular section	Group 1	66.7	12.6	2.46	2.96	1.99	10.13	0.51	0.40	1.51	6.1	0.4	84	2.1	355	15	15	6.8	14	76	28	3.5	13	476	6.0	34	1.8	5.1
HT_015	Purple Circular section	Group 1	66.8	14.7	1.89	1.91	2.37	8.98	0.59	0.31	1.76	5.8	0.5	86	2.8	297	23	25	20	18	418	48	0.6	12	497	7.1	40	2.1	5.6
HT_016	Purple Rectangular to circular section	Group 1	68.9	12.5	2.07	2.18	2.04	8.45	0.57	0.34	2.29	5.4	0.6	94	2.9	289	22	19	14	20	287	42	1.0	12	523	7.0	40	2.1	10
HT_017	Purple Circular section, loosely twisted	Group 1	66.7	12.9	2.17	2.15	2.33	9.49	0.70	0.40	2.16	5.5	0.4	96	2.5	431	22	18	17	59	543	43	5.2	12	569	6.8	40	2.3	8.4
HT_018	Naturally aqua Circular-squared section, irregularly twisted	Group 1	66.4	14.0	2.67	2.94	1.88	9.08	0.54	0.37	0.93	11	0.4	97	2.6	277	13	18	19	16	4572	153	6.8	14	497	6.2	39	2.0	2.7
HT_019	Purple Circular section	Group 1	63.9	15.4	1.95	1.95	2.56	10.27	0.69	0.34	1.86	7.9	0.4	111	2.5	445	25	27	20	18	517	43	5.4	12	519	7.2	43	2.1	6.2
HT_020	Dark blue Circular section	Group 2	61.1	18.4	4.38	1.94	9.68	2.14	1.24	0.11	0.07	85	3.4	1079	2.4	252	4.9	4.2	213	10	1054	314	7.0	148	84	23	74	20	3.7
HT_021	Dark blue Circular section, loosely twisted	Group 2	59.9	19.8	4.48	1.25	10.55	1.69	1.45	0.29	0.03	91	3.8	1190	2.7	213	3.8	5.3	296	12	1169	376	4.6	196	63	31	96	28	4.6

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	SiO ₂	Na2O	K20	MgO	Al_2O_3	CaO	FeO	P ₂ O ₅	MnO	Li	Be	В	Sc	Ti	V	Cr	Со	Ni	Си	Zn	As	Rb	Sr	Y	Zr	Nb	Мо
HT_022	Dark blue Circular section, tightly twisted	Group 2	53.0	20.3	4.14	4.46	10.07	6.01	1.27	0.22	0.08	110	2.6	1319	5.1	409	12	6.8	482	15	518	94	5.3	115	285	42	126	31	5.1
HT_023	Dark blue Circular section,	Group 2	58.5	21.3	4.38	2.12	9.55	2.00	1.50	0.17	0.03	108	4.0	1333	2.3	263	3.7	3.5	327	12	1264	286	0.0	169	88	26	79	24	3.8
HT_024	Dark blue Circular section,	Group 2	54.3	20.8	3.96	4.10	9.46	5.10	1.41	0.26	0.09	112	2.5	1677	4.7	490	12	9	568	18	735	134	4.9	112	246	39	116	29	5.9
HT_025	Light blue Circular section,	Group 2	57.2	17.9	3.98	4.63	8.59	5.68	1.44	0.26	0.04	115	3.1	1820	2.9	365	7.7	7.3	103	13	1040	72	0.0	119	243	22	73	18	3.0
HT_026	Dark blue Peaked section	Group 2	54.5	19.1	4.13	4.47	10.47	5.15	1.37	0.30	0.08	114	3.2	1883	4.9	361	11	5.7	535	21	816	112	12	104	216	37	108	26	5.0
HT_027	Dark blue Peaked section	Group 2	59.1	16.8	4.82	2.86	10.76	3.28	1.40	0.25	0.12	91	3.5	189 2	5.1	449	11	6.7	430	17	805	127	2.6	97	150	35	92	25	5.3
HT_028	Light blue Peaked section	Group 2	52.6	20.3	3.79	5.21	9.29	6.44	1.38	0.35	0.14	129	2.1	1996	4.6	497	15	15	284	24	688	95	4.8	84	271	29	93	22	4.0
HT_029	Dark blue Circular section, tightly twisted	Group 2	54.3	18.9	3.94	5.06	9.76	5.88	1.37	0.34	0.11	125	2.9	2016	4.7	396	14	16	657	27	743	132	11	93	241	33	101	23	4.8
HT_030	Dark blue Peaked section	Group 2	55.4	21.1	4.23	3.36	9.49	4.10	1.25	0.26	0.09	117	2.9	2069	3.9	494	8.5	7.5	278	20	486	87	4.1	93	175	32	91	22	3.4
HT_031	Naturally aqua (greenish) Slightly peaked	Group 3	64.2	13.8	1.75	2.74	2.62	11.72	2.68	0.11	0.04	493	2.0	2148	4.4	275	28	79	7.9	89	17	29	58	104	2366	11	32	4.3	1.7
HT_032	Naturally aqua Circular section; opaque yellow ground, brownish chains with red dots in centre	Group 3	62.5	15.2	1.67	2.83	2.93	12.43	1.94	0.10	0.05	464	1.6	2261	4.7	337	26	73	8.0	83	22	23	39	84	2274	9	34	4.1	1.2

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	SiO ₂	Na ₂ O	K20	MgO	Al ₂ O ₃	CaO	FeO	P ₂ O ₅	MnO	Li	Be	В	Sc	Tī	V	Cr	Со	Ni	Си	Zn	As	Rb	Sr	Y	Zr	Nb	Мо
HT_033	Naturally aqua (light blue) Oblong section, slight central depression on exterior	Group 3	68.0	13.5	1.57	2.78	2.91	9.00	1.57	0.08	0.23	397	1.1	2362	3.5	518	20	53	125	58	760	191	0.0	60	1630	5.5	32	3.3	2.4
HT_034	Naturally aqua Oblong section	Group 3	66.4	13.4	1.47	2.76	2.78	10.75	1.87	0.12	0.05	442	1.7	2509	4.2	407	24	73	8.7	78	30	25	49	79	1955	7.8	30	3.7	1.3
HT_035	Naturally aqua (greenish) Oblong section, slight central depression on exterior	Group 3	62.3	15.7	1.60	2.80	2.80	12.25	2.03	0.11	0.06	489	1.0	2545	4.6	391	25	68	7.4	76	21	23	35	81	2195	8.9	32	3.7	1.2
HT_036	Naturally aqua Circular section	Group 3	65.1	15.2	1.63	2.34	2.63	10.56	2.07	0.11	0.05	462	1.3	2637	3.8	487	21	60	6.6	61	21	22	36	67	1490	9	29	3.1	1.0
HT_037	Naturally aqua Oblong, opaque yellow ground with red diagonal hashes	Group 3	64.4	14.4	1.56	2.55	2.46	12.47	1.59	0.18	0.04	496	1.0	2652	3.4	387	19	67	6.0	56	18	25	41	73	2439	6.9	37	3.3	0.8
HT_038	Naturally aqua Oblong section	Group 3	65.4	15.9	1.70	2.55	2.46	9.69	1.88	0.08	0.05	495	1.3	2698	4.0	337	21	63	8.6	69	26	27	28	72	1748	6.5	26	3.3	0. 9
HT_039	Naturally aqua (light blue) Rectangular to circular section, partially hollow	Group 3	65.7	14.5	1.45	2.61	2.41	10.97	1.78	0.08	0.02	456	1.0	2767	3.1	456	20	57	118	63	925	210	22	81	1858	4.9	28	3.5	1.8
HT_040	Blue Oblong section	Outlier	67.8	16.1	1.22	1.69	2.01	8.06	1.54	0.27	0.50	45	0.6	571	3.1	290	18	20	513	24	786	130	37	16	390	5.6	36	2.2	3.7

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	Ag	Sn	Sb	Cs	Ba	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Та	W	Au	Pb	Bi	Th	U	Na/B
HT_001	Naturally aqua Circular section, loosely twisted	Group 1	0.1	1.9	0.4	0.1	228	5.9	11	1.5	5.6	1.1	0.3	1.0	0.1	1.0	0.2	0.6	0.1	0.5	0.1	1.0	0.1	0.2	0.0	39	0.0	0.9	0.5	1320
HT_002	Colorless and purple Oblong section, flat interior and ribbed exterior	Group 1	0.5	10	1.7	0.2	277	6.4	12	1.5	6.2	1.4	0.2	1.4	0.2	1.0	0.2	0.6	0.1	0.5	0.0	0.9	0.1	0.7	0.0	187	0.1	0.9	0.3	1335
HT_003	Colorless and purple Circular section, twisted w/ internal purple thread	Group 1	0.0	0.5	0.1	0.1	195	5.1	11	1.4	5.1	1.0	0.3	0.9	0.2	0.9	0.2	0.5	0.1	0.5	0.1	0.8	0.1	0.3	0.1	4.1	0.0	0.7	0.3	1359
HT_004	Naturally aqua (bluish) Oblong section, flat interior and ribbed exterior	Group 1	8.0	3286	21	0.2	37	5.0	10	1.2	4.6	1.0	0.2	0.9	0.1	0.8	0.2	0.4	0.1	0.5	0.1	1.0	0.1	0.1	0.2	9031	2.6	1.6	1.7	1245
HT_005	Colorless Circular-squared section, twisted	Group 1	0.0	1.8	0.2	0.1	193	5.2	10	1.3	5.0	1.1	0.3	1.0	0.1	0.9	0.2	0.5	0.1	0.4	0.1	0.7	0.1	0.2	0.0	26	0.0	0.6	0.3	1064
HT_006	Purple Oblong section, flat interior and ribbed exterior	Group 1	0.1	1.7	0.7	0.1	288	5.7	11	1.4	5.3	1.1	0.3	1.1	0.2	1.0	0.2	0.6	0.1	0.5	0.1	0.9	0.1	0.3	0.0	44	0.0	0.8	0.5	1275
HT_007	Purple Circular section, loosely twisted	Group 1	0.3	24	5.4	0.2	360	7.2	13	1.8	7.1	1.5	0.4	1.4	0.2	1.3	0.3	0.8	0.1	0.6	0.1	1.4	0.1	0.4	0.0	1548	0.1	1.2	0.8	1207
HT_008	Purple Oblong section, flat interior and ribbed exterior	Group 1	0.1	8.4	1.6	0.2	364	6.3	12	1.6	6.0	1.3	0.3	1.1	0.2	1.0	0.3	0.6	0.1	0.6	0.1	1.1	0.1	0.4	0.0	1223	0.0	0.9	0.5	1133
HT_009	Purple Oblong section, flat interior and ribbed exterior	Group 1	0.1	4.5	1.0	0.1	393	5.4	12	1.4	5.4	1.1	0.3	1.0	0.1	0.9	0.2	0.5	0.1	0.4	0.1	0.8	0.1	0.4	0.0	178	0.0	0.8	0.4	1300

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	Ag	Sn	Sb	Cs	Ba	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Hf	Та	W	Au	Pb	Bi	Th	U	Na/B
HT_010	Light green Circular-squared section, loosely twisted	Group 1	0.2	37	4.9	0.1	465	8.5	17	2.2	8.6	1.8	0.5	1.6	0.2	1.5	0.3	0.9	0.1	0.8	0.1	1.6	0.2	0.4	0.1	843	0.1	1.4	0.8	1092
HT_011	Purple Circular section, twisted	Group 1	0.5	43	28	0.2	281	5.7	11	1.4	5.1	1.1	0.3	1.0	0.2	0.9	0.2	0.5	0.1	0.5	0.1	0.9	0.1	0.3	0.0	1361	0.1	0.8	0.4	1097
HT_012	Purple Circular section	Group 1	0.8	4.9	3.8	0.2	344	7.1	13	1.9	7.3	1.5	0.4	1.5	0.2	1.3	0.2	0.7	0.1	0.6	0.1	1.3	0.2	0.4	0.1	2 11	0.0	1.1	0.6	10 <mark>97</mark>
HT_013	Light green Circular section	Group 1	0.9	24	16	0.2	441	8.9	17	2.2	8.8	1.9	0.5	1.8	0.3	1.6	0.3	0.9	0.1	0.8	0.1	1.9	0.3	0.5	0.1	1019	0.1	1.6	0.7	949
HT_014	Purple Circular section	Group 1	0.1	8.7	0.8	0.2	256	5.4	11	1.4	5.6	1.1	0.3	1.0	0.2	1.0	0.2	0.6	0.1	0.4	0.1	0.9	0.1	0.3	0.0	372	0.0	0.8	0.4	1112
HT_015	Purple Circular section	Group 1	0.6	33	67	0.1	258	6.5	12	1.7	6.3	1.3	0.4	1.3	0.2	1.2	0.2	0.6	0.1	0.6	0.1	1.2	0.1	0.4	0.1	1214	0.1	0.9	0.7	1270
HT_016	Purple Rectangular to circular section	Group 1	0.5	24	41	0.2	291	6.6	12	1.7	6.4	1.4	0.4	1.3	0.2	1.3	0.3	0.7	0.1	0.6	0.1	1.3	0.1	0.4	0.0	1444	0.1	1.1	0.8	982
HT_017	Purple Circular section, loosely twisted	Group 1	0.6	49	67	0.1	365	6.5	13	1.7	6.3	1.3	0.3	1.2	0.2	1.1	0.2	0.6	0.1	0.6	0.1	1.2	0.1	0.4	0.2	687	0.1	0.9	0.7	996
HT_018	Naturally aqua Circular-squared section, irregularly	Group 1	2.7	91	16	0.4	228	5.7	11	1.5	5.9	1.1	0.3	1.1	0.2	1.0	0.2	0.6	0.1	0.4	0.1	1.1	0.1	0.3	0.1	378	0.6	1.0	0.5	1072
HT_019	twisted <i>Purple</i> Circular section	Group 1	0.5	33	67	0.3	267	6.3	12	1.6	6.1	1.3	0.4	1.2	0.2	1.0	0.2	0.6	0.1	0.5	0.1	1.1	0.1	0.3	0.0	1078	0.1	0.9	0.6	1029
HT_020	Dark blue	Group 2	0.3	5.8	3.5	4.5	36	15	33	3.9	13	3.1	0.1	2.9	0.5	3.5	0.8	2.3	0.4	2.7	0.4	3.3	1.6	2.1	0.0	149	0.2	32	8.2	127
HT_021	Dark blue Circular section, loosely twisted	Group 2	0.5	7.9	3.8	5.9	26	19	38	4.3	14	3.6	0.0	3.6	0.6	4.1	0.9	2.5	0.4	3.0	0.5	3.9	1.9	2.2	0.1	82	0.2	37	9	124
HT_022	Dark blue Circular section, tightly twisted	Group 2	0.2	2.9	0.9	2.0	249	28	58	6.9	24	6.2	0.9	5.6	0.9	6.2	1.3	3.8	0.5	4.0	0.5	3.8	1.3	1.6	0.1	47	0.1	21	5.2	114

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	Ag	Sn	Sb	Cs	Ba	La	Се	Pr	Nd	Sm	Еи	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Та	W	Au	Pb	Bi	Th	U	Na/B
HT_023	Dark blue Circular section,	Group 2	0.2	7.0	4.0	5.5	32	15	34	4.1	14	3.6	0.1	3.6	0.6	4.3	0.9	2.7	0.4	3.2	0.5	3.9	2.1	2.7	0.0	94	0.3	37	10	119
HT_024	Dark blue Circular section,	Group 2	0.3	3.5	1.3	2.1	241	27	57	6.6	23	5.7	0.8	5.1	0.9	5.8	1.2	3.5	0.5	3.6	0.6	3.5	1.4	1.6	0.1	49	0.2	19	5.0	92
HT_025	Light blue Circular section, twisted	Group 2	0.2	2.7	1.0	2.8	43	12	25	3.0	10	2.5	0.1	2.4	0.4	2.8	0.6	1.8	0.3	2.0	0.3	2.6	1.2	1.7	0.0	32	0.2	21	5.6	73
HT_026	Dark blue Peaked section	Group 2	0.3	2.7	1.8	1.9	216	26	52	6.2	22	5.6	0.8	5.0	0.8	5.6	1.1	3.4	0.5	3.4	0.5	3.4	1.3	1.4	0.1	24	0.2	19	4.7	75
HT_027	Dark blue Peaked section	Group 2	0.4	3.9	3.7	2.0	237	25	53	6.4	22	5.4	0.8	5.1	0.8	5.7	1.2	3.4	0.5	3.6	0.5	3.4	1.2	1.6	0.0	180	0.1	18	5.1	66
HT_028	Light blue Peaked section	Group 2	1.3	4.4	2.1	1.4	207	22	44	5.1	17	4.1	0.7	3.8	0.6	4.3	0.9	2.6	0.4	2.8	0.4	3.0	1.0	1.4	0.1	35	0.1	16	4.0	76
HT_029	Dark blue Circular section, tightly twisted	Group 2	0.3	4.0	1.7	1.8	202	23	47	5.5	19	4.6	0.8	5.3	0.7	5.0	1.1	3.1	0.6	3.2	0.4	3.0	1.2	1.7	1.1	52	0.3	17	4.4	69
HT_030	Dark blue Peaked section	Group 2	0.3	2.9	1.2	1.8	215	23	48	5.9	20	5.0	0.7	4.9	0.8	5.4	1.1	3.3	0.5	3.2	0.5	3.4	1.3	1.4	0.0	44	0.2	18	4.6	76
HT_031	Naturally aqua (greenish) Slightly peaked section	Group 3	0.1	1.3	56	63	96	8.4	18	2.1	7.3	1.6	0.3	1.6	0.2	1.6	0.4	1.2	0.2	1.2	0.2	0.9	0.3	0.7	0.9	3.2	0.6	2.9	2.0	48
HT_032	Naturally aqua Circular section; opaque yellow ground, brownish chains with red dots in centre	Group 3	0.3	1.5	31	52	84	7.6	15	1.7	6.3	1.4	0.3	1.5	0.2	1.3	0.3	0.8	0.1	0.9	0.1	1.0	0.2	0.6	0.0	2.3	0.0	2.8	1.3	50

Sample No.	Glass colour(s) Bracelet shape, decoration	Chemical group	Ag	Sn	Sb	Cs	Ba	La	Се	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Та	W	Au	Pb	Bi	Th	U	Na/B
HT_033	Naturally aqua (light blue) Oblong section, slight central depression on exterior	Group 3	2.2	3.5	40	38	138	7.1	13	1.7	6.2	1.2	0.2	1.0	0.2	1.0	0.2	0.5	0.1	0.5	0.1	0.9	0.2	0.5	0.0	37	0.0	2.5	1.3	43
HT_034	Naturally aqua Oblong section	Group 3	0.4	2.1	39	47	88	7.2	15	1.8	6.3	1.3	0.2	1.1	0.2	1.2	0.3	0.7	0.1	0.8	0.1	0.9	0.2	0.6	0.0	4.5	0.0	2.7	1.5	40
HT_035	Naturally aqua (greenish) Oblong section, slight central depression on exterior	Group 3	0.3	1.4	34	49	86	7.2	14	1.7	6.3	1.6	0.3	1.6	0.3	1.9	0.4	1.0	0.2	1.3	0.1	0.9	0.2	0.7	0.3	4.0	0.0	2.6	1.4	46
HT_036	Naturally aqua	Group 3	0.1	0.7	43	41	75	6.3	12	1.5	5.6	1.2	0.3	1.3	0.2	1.4	0.3	1.0	0.1	1.0	0.1	0.7	0.2	0.4	0.0	4.8	0.0	2.3	1.2	43
HT_037	Naturally aqua Oblong, opaque yellow ground with red diagonal hashes	Group 3	0.1	1.1	29	47	76	6.3	12	1.5	5.3	1.1	0.2	0.9	0.2	1.2	0.2	0.6	0.1	0.7	0.1	0.9	0.2	0.7	0.0	1.9	0.0	2.4	1.0	40
HT_038	Naturally aqua Oblong section	Group 3	0.6	1.3	45	48	85	7.0	14	1.8	6.1	1.3	0.3	1.2	0.2	1.3	0.3	0.7	0.1	0.8	0.1	0.8	0.2	0.5	0.0	7.1	0.0	2.5	1.5	44
HT_039	Naturally aqua (light blue) Rectangular to circular section, partially hollow	Group 3	0.3	2.1	57	67	124	8.2	17	2.0	7.2	1.5	0.3	1.2	0.2	1.1	0.2	0.7	0.1	0.6	0.1	1.1	0.3	0.7	0.1	28	0.0	3.3	1.8	39
H1_040	Oblong section	Outher	0.3	30	11	3.9	149	4.7	9	1.2	4.4	0.9	0.2	0.8	0.1	0.8	0.2	0.5	0.1	0.5	0.1	0.9	0.2	0.4	0.1	326	0.1	1.1	1.9	209



Figure 2. Examples of the cross-section and decorative types of the Hisn al-Tīnāt glass bracelets: (a)–(n) (drawings by Carolyn Swan and Serkan Demir; photographs by Carolyn Swan and Marie-Henriette Gates; courtesy of Kinet Project archives). [Colour figure can be viewed at wileyonlinelibrary.com]

Analytical Methods

A tiny snip of glass (less than 5 mm3 in size) was removed from each bracelet fragment. Chemical analysis was conducted in the Elemental Analysis Facility at the Field Museum in Chicago. Analyses were made using a high-sensitivity Analytik Jena quadrupole inductively coupled plasma - mass spectrometer (ICP-MS) connected to a New Wave Nd: YAG deep UV [213 nm] laser ablation system; a 55–80 µm laser beam pulsed at 15 Hz and 70% output for approximately 60 s. Four analyses were made for each sample and the average of these measurements was calculated. The analysed data is reported as wt% for major and minor oxides and as ppm for trace elements using an Excel macro designed by Laure Dussubieux and based on the procedures and formulas outlined by Bernard Gratuze (Gratuze 1999; Gratuze et al. 2001). For full quantification, the isotope 29Si was used as an internal standard as well as synthesized glasses and certified reference materials as external standards; the latter included Corning Reference Glasses B, C and D (Brill 1999b) for major and minor components, and the National Institute of Standards and Technology's SRM 610 and SRM 612 for trace elements (Pearce et al. 1997). The detection limits range from 0.01 to 1 ppm for most of the elements. Accuracy and precision range from 5% to 10% depending on the elements and their concentrations; a more detailed account of the performance of this technique is described in Dussubieux et al. (2009), 153 - 5 and tables 1 - 3).

Results

The bracelets form three distinctive compositional groups (Table <u>1</u> and Figs <u>3</u> and <u>4</u>a-b; for complete archaeological context, see supplemental <u>Table S1</u>); all are either soda–lime or soda–alumina glass, with K2O and MgO > 1.5% and variable concentrations of boron and lithium, except for one outlier that has low potash and magnesia and relatively high boron. Group 1 is made from a soda-rich plant ash glass similar to the glass used to produce the majority of the vessels at the site (Swan <u>2012a</u>). Groups 2 and 3 are high-boron glasses with elevated lithium, the former containing very high alumina and the latter very high lithium and strontium (Swan <u>2012b</u>). Interestingly, *none* of the vessels sampled from Hişn al-Tīnāt were made using high-boron glass.

Group 1: soda-lime glass with low B and low Li

Almost half of the bracelet samples (samples HT_001 to HT_019) have a typical plant ash glass composition, averaging 2.4 wt% K2O, 2.5 wt% MgO and 0.41 wt% P2O5. Their boron and lithium concentrations are around 60–100 ppm and 5–10 ppm, respectively (Table 1), in line with plant ash glasses from the Islamic period (Henderson *et al.* 2016). Group 1 includes all of the bracelets made from purple and colourless glass and five bracelets described as naturally aqua or light green. The bracelets in this group include those with plain circular sections and those with twisted or ribbed exteriors. Bracelets with ribbed exteriors are only made from the Group 1 glass. Sample HT_004, a bluish-aqua bangle with a ribbed exterior, fits within the Group 1 type but is somewhat different stylistically and chemically: this bracelet is narrower in width than other examples of the ribbed type and it also has the smallest number of ribs; elevated copper, tin and lead are probably the result of a colourant—perhaps a leaded bronze—and variations in the trace elements include lower strontium and titanium, much lower barium, and much higher lithium and chromium than the rest of the glasses in this group. With the exception of HT_004, all of the

fragments in this group have elevated manganese, ranging from 0.75 to 2.8 wt% MnO. The high manganese content of the aqua bracelets in this group (0.75 - 1.5 wt% MnO) is noteworthy, given the low iron of these samples.



Figure 3. Scatterplot of potash versus magnesia for the Hisn al-Tīnāt bracelets, compared with vessel glass from the site (Swan unpubl. data). [Colour figure can be viewed at wileyonlinelibrary.com]

Group 2: soda-alumina glass with high B and high Li

This group includes 11 samples (HT_020 to HT_030) with very high levels of boron (averaging 1660 ppm) and lithium (averaging 110 ppm), and very high levels of alumina (averaging 9.8 wt% Al2O3). Group 2 has the lowest levels of silica (averaging 56.4 wt% SiO2) and lime (averaging 4.3 wt% CaO), as well as the highest levels of soda (averaging 19.5 wt% Na2O), potash (averaging 4.2 wt% K2O) and magnesia (averaging 3.6 wt% MgO). These high potash and magnesia levels could indicate that the Group 2 samples are plant ash soda glasses, although the phosphate levels (averaging 0.25 wt% P2O5) are lower than those of Group 1; it may be that these components derive at least partly from a silica source rich in accessory minerals rather than a plant ash flux. Group 2 also has lower strontium and higher rubidium, zirconium, niobium and REE than the two other groups, possibly indicating a complex mineral assemblage to provide the flux rather than plant ash.



Figure 4. Scatterplots of the Hisn al-Tīnāt bracelets: (a) lithium versus boron; (b) alumina versus lime. [Colour figure can be viewed at wileyonlinelibrary.com]

The common decorative features of these bracelets are striking: this group includes the majority of the spirally twisted and peaked bracelet types, and notably all of the intensely coloured dark blue fragments found at the site. The dark blue colour is due to cobalt and copper (~100–650 ppm Co and ~500–1300 ppm Cu), and iron (> 1.2 wt% FeO). Slightly higher zinc may indicate the use of a zinc-rich cobalt source (Gratuze *et al.* <u>1992</u>; Henderson <u>1998</u>). This combination of relatively low cobalt and intermediate copper levels resembles the Late Bronze Age cobalt–copper blue glass recently discussed by Smirniou and Rehren (<u>2013</u>), which also has elevated zinc, manganese and REE concentrations, as well as higher alumina than contemporary copper-blue or colourless glasses. There is no elevated nickel associated with the Hişn al-Tīnāt glass bracelets that would suggest the use of cobaltiferous alums from Egypt (e.g., Kaczmarczyk <u>1986</u>; Shortland *et al.* <u>2006</u>). Two of the bracelet fragments in this group (HT 025 and HT 028)

were visually described as light blue glass, in line with their somewhat lower levels of cobalt and copper.

Group 3: soda-lime glass with high B, Li and Sr

Nine of the bracelet fragments (samples HT_031 to HT_039) are characterized by extremely high levels of boron and lithium (averaging 2500 ppm B and 470 ppm Li), as well as extremely high strontium (averaging 2000 ppm Sr). Unlike Group 2, the alumina level is not high, averaging 2.7 wt% Al2O3. This glass type has comparatively low potash (averaging 1.6 wt% K2O) and low phosphate (averaging 0.11 wt% P2O5), which might indeed suggest the use of a mineral soda flux, although the magnesia content (averaging 2.7 wt% MgO) is more in keeping with plant ash soda fluxes. This glass type also has the highest levels of lime (averaging 1.1 wt% CaO) of the groups described here.

All of the Group 3 samples are naturally aqua glasses with a relatively high iron and low manganese content (averaging 1.9 wt% FeO and 0.07 wt% MnO). Two samples have elevated amounts of cobalt and copper (HT_033 and HT_039, with 120–125 ppm Co and 750–925 ppm Cu), which are associated with elevated zinc (around 200 ppm Zn, compared to less than 30 ppm in all other samples in this group) and barium (~120–140 ppm Ba, compared to less than 100 ppm in all others). HT_033 is also the only one in this group with an elevated managese content. The majority of the bracelets made with the Group 3 glass type have oblong and rounded cross-sections, and one fragment has a slightly peaked section. The two bracelets with a central depression and the two bracelets decorated with painted or stained designs are also made from this glass type.

Outlier: soda-lime glass with relatively high B

The chemical composition of sample HT 040, a light blue bracelet with a plain oblong cross-section, does not quite fit within the three groups defined above. The silica, alumina and lime are similar to the Group 1 glasses, although the soda level is higher (16.1 wt% Na2O). The glass has comparatively low potash and magnesia (1.2 wt% K2O and 1.7 wt% MgO); the lime, iron and alumina are similar to the Egyptian II mineral soda glasses, but the glass has much lower titanium and zirconium than does the Egyptian II glass composition. The glass also has elevated lithium, arsenic, rubidium, strontium, uranium and molybdenum, as well as lower hafnium. The potash and magnesia are lower than is common for glasses made with plant ash, but this does not necessarily indicate that the glassmakers used a mineral soda flux; it may represent the mixing of two different glass types, one of which was possibly a high-boron glass. The boron content of HT 040 is 571 ppm B, roughly a third of the amount in the Group 2 glasses and a fifth of the Group 3 glasses, but it is still five times greater than that of the Group 1 glasses. The lithium content of HT 040 is similarly distinctive (45 ppm Li), being higher than that of Group 1 glasses but still lower than that of Groups 2 and 3. The blue colour of the glass derives from its iron content (1.5 wt% FeO) and raised amounts of cobalt and copper (~500 ppm Co and ~800 ppm Cu); lead is also elevated, similar to the blue glasses of Group 2.

Discussion

Approximately half of the bracelet fragments excavated at Hisn al-Tīnāt are made from a plant ash soda glass that is similar in composition to the glass vessels used at the site (Fig. <u>3</u>), while the other half is made from two varieties of glass containing elevated boron and lithium (Fig. <u>4</u>a), one of which is also characterized by very high alumina (Fig. <u>4</u>b) and the other by very high strontium. The high-boron glasses can be linked to the primary production of glass in western Anatolia, while the close correlation between composition and stylistic features suggests the occurrence of an object-specific industry tied to Middle Byzantine material culture.

Plant ash soda glasses

The Group 1 bracelet glasses are identified as plant ash glasses because of their magnesia, potash and phosphate content. These components resemble contemporary Levantine vessel glasses made using plant ash as a flux; for example, glass from the 10th–13th century ce secondary workshop at Banias (Freestone *et al.* 2000), the 10th–11th century ce furnace at Tyre (Freestone 2002) and the *c*. 1025 ce Serçe Limani shipwreck (Brill 2009). The Group 2 glasses have even higher magnesia and potash than Group 1, but their high boron, lithium and alumina clearly set them apart from typical plant ash soda glasses; the Group 3 glasses could also have been made using plant ash soda as a flux, as their average potash and magnesia (1.6 wt% K2O and 2.7 MgO) are above 1.5 wt% (Sayre and Smith 1961; Brill 1970; Henderson 2000), although their phosphate is extremely low (averaging 0.11 wt% P2O5) even for mineral soda glasses. On balance, we consider it more likely that a significant part of the potash and magnesia of Groups 2 and 3 could possibly derive from minerals in the silica source rather than from plant ash used as a flux. It is not entirely clear whether the single outlying sample is made using plant ash soda, as its high boron and lithium yet again set it apart from more commonly encountered types of soda glasses and it is possible that a mixture of glass types was used.

High-boron glasses

Boron is a trace element that is present as an impurity of the glass-making raw materials, and it is thought to enter the glass largely via the fluxing agent (Devulder *et al.* 2014). Additionally, boron can enter the glass as part of the mineral tourmaline, which contains around 10 wt% B2O3; it is an accessory mineral in certain granites and immature sands derived from them. The boron content of ancient and medieval glasses is normally no greater than 0.01 - 0.03 wt% B2O3 (Brill 1968, 51; Brill 2002, 16), equivalent to about 25–100 ppm B. High boron in glass, therefore, marks raw material sources that are geologically highly specific and relatively uncommon.

High-boron glass was not widely produced: amongst the more than 3000 analyses of ancient and medieval glass published by Brill over 40 years, he notes that only two dozen or so contain elevated levels of boron (Brill 2005, 217). The elevated boron is sometimes associated with elevated lithium and strontium as well (Brill 2002, 2005). While Brill considered high-boron glasses to be those with 0.04 wt% B2O3 (equivalent to about 125 ppm B) or more, for the purposes of this paper we limit discussion to those samples with 0.1 wt% B2O3 (300 ppm B) or more. Brill's samples come from contexts dating from the sixth to seventh century up to the 12th century ce (Brill 1999a, 2002, 2005); interestingly, these high-boron glasses all have connections

with regions within or immediately neighbouring the Byzantine world (Fig. 1 and Table 2), as they were excavated in modern Turkey, Cyprus, Greece and northern Italy. These include vessel fragments and cullet from sixth-to-seventh-century Aphrodisias, vessel and bracelet fragments from unspecified (Lydian, Roman or Early Byzantine) contexts at Sardis, as well as vessels, windows and tesserae from 12th-century Constantinople in Turkey; vessel glass from 12th-century Paphos in Cyprus; vessel fragments, cullet and wasters from a medieval glass workshop in the Corinth Agora and a Roman industrial site at the port of Corinth, mid-fourth-century opus sectile from Kenchreai, and tesserae from the mid-11th-century Hosios Loukos monastery in Greece; and 12th-century tesserae from Venice, Ravenna and Rome in Italy. The phasing of the Corinth glass workshop is unclear but probably dates to the 11th–12th or 13th-14th centuries (Weinberg 1940; McDonald et al. 1983; Whitehouse 1991, 1993; Parani 2005). Brill's samples include many examples of dark blue glass, some of which come from a type of tall cylindrical vessel with gilded and painted or enameled decoration (Brill 2002; Ristovska 2009). The reoccurring association of cobalt-blue glass with a high-boron glass in Brill's studies is intriguing considering the dark blue colour of many Hisn al-Tīnāt bracelets, even though the Group 2 objects have a different chemical composition than the glasses analysed by Brill (Table 2).

A recent study of glass from the city of Pergamon (Schibille 2011; Rehren *et al.* 2015) documented 28 high-boron glass fragments falling into two chemical subgroups (Rehren *et al.* 2015, 275): HBAI is characterized by high boron (averaging 1000 ppm B) and high alumina (averaging 9 wt% Al2O3), as well as higher soda, iron, titania, phosphate and arsenic; HLiBAI is characterized by high lithium (averaging 300 ppm Li), high boron (averaging 1500 ppm B) and high alumina (averaging 5 wt% Al2O3), as well as much higher lime, sulphate, rubidium and strontium. In terms of boron, lithium and alumina, the Hişn al-Tīnāt glass Groups 2 and 3 fit somewhat with the Pergamene glasses (Table 2). Group 2 is similar to HBAI, and Group 3 is similar to HLiBAI. However, unlike the Pergamene glasses, Hişn al-Tīnāt Group 2 does not have higher iron, titania and arsenic than Group 3 and the lithium content of Group 2 (averaging 109 ppm Li) is still quite high; Group 2 also has much higher potash and magnesia than the Pergamene HBAI type. In addition, Hişn al-Tīnāt Group 2 and 3 glasses have higher boron than the Pergamene glasses.

Of the seven bracelet fragments from Pergamon that were analysed (Rehren *et al.* 2015), six were identified as HBAl and one as HLiBAl. The HBAl bracelets are black olive, brownish red and yellowish green, which is notably different from the repertoire of glass bracelets found at Hisn al-Tīnāt; the dates of the Pergamene samples also differ, the majority being identified as early Byzantine or 12th–13th century. A single HLiBAl Pergamene bracelet (Per 041) is described as bluish green and Byzantine in date, which is typologically similar to the Hisn al-Tīnāt Group 3 glasses. Although not a perfect match, Per 041 is also chemically similar to Group 3 in terms of its major and minor oxides; for example, containing 2.6 wt% Al2O3. However, significant discrepancies exist in the levels of some trace elements, including barium, boron and strontium.

 Table 2. Average chemical compositions for published high-boron glasses (≥ 300 ppm B, equivalent to ≥0.10 wt% B2O3) dating from 6th–7th to 13th–14th century ce contexts; data from Borisov 1989 (Djadovo), Brill 1999b (Corning Museum of Glass collection), and Rehren et al. 2015 (Pergamon). Values are wt% oxide for major and minor compounds, and ppm for the trace elements B, Rb, Li, Sr and Zr (na = not analysed)

Site, country Samples (count = n)	Object types (colour)	Date (c. CE)	SiO2	Na2O	CaO	K2O	MgO	Al2O3	FeO	В	Rb	Li	Sr	Zr
Hişn al-Tīnāt, Turkey Group 2 (n=11)	bracelets (dark blue)	10th-12th	56.4	19.5	4.31	4.20	3.59	9.79	1.69	1661	121	109	188	96
Hişn al-Tīnāt, Turkey Group 3 (n=9)	bracelets (aqua, light blue-green)	10th-12th	64.9	14.6	11.09	1.60	2.66	2.67	2.39	2509	78	466	1995	31
Ḥişn al-Tīnāt, Turkey <i>Outlier (n=1)</i>	bracelet (blue)	10th-12th	67.9	16.1	8.10	1.22	1.69	2.01	1.54	571	16	45	390	36
Pergamon, Turkey <i>HBA1</i> type (n=16)	vessels and bracelets (black olive, yellowish olive, olive green, yellowish green, brownish green, yellowish brown, reddish brown, dark red)	4th-13th	59.1	17.6	5.18	1.56	1.43	9.19	1.34	971	36	35	263	270
Pergamon, Turkey BLiBAl type (n=12)	vessels and bracelets(olive green, yellowish green, bluish green, reddish brown, colorless)	1st-13th	64.8	15.0	9.50	1.56	1.01	4.54	0.86	1413	87	323	3029	55
Sardis, Turkey Nos. 1093, 1094, 1522, 3220, 3221 (n=5)	vessel, flat fragments, and bracelets (yellowish olive, purple, green, black, red)	uncertain	61.2	17.7	5.83	1.47	1.61	8.03	2.07	528	na	54	380	231
Aphrodisias, Turkey Nos. 590, 591, 1110, 1111, 1112, 1113, 1114 (n=7)	vessels and cullet (aqua, green)	6th-7th	68.8	15.5	7.98	1.45	2.73	1.65	0.46	2893	na	664	1362	42
Constantinople, Turkey (Hagia Sophia) <i>No. 2788</i> (<i>n</i> =1)	tessera (red)	uncertain	63.8	14.3	9.39	1.54	1.88	2.06	2.92	932	na	139	844	37

Table 2 (Continued)														
Site, country Samples (count = n)	<i>Object types</i> (colours)	Date (c. CE)	SiO2	Na2O	CaO	K2O	MgO	Al2O3	FeO	В	Rb	Li	Sr	Zr
Constantinople, Turkey (Zeyrek Camii) Nos. 132, 134, 141, 143, 145, 246, 541, 1575, 1576, 2501, 2502, 2504, 2505 (n=13)	vessels and windows(aqua, amber, emerald green, olive green, dark blue, purple, colorless)	12th	65.1	15.1	9.86	1.72	2.31	1.62	0.87	1245	na	107	493	222
Paphos, Cyprus No. 2309 (n=1)	vessel (dark blue)	12th	65.9	14.0	9.03	1.81	2.46	1.97	1.85	559	na	74	371	74
Djadovo, Bulgaria <i>Nos. 1 and 2</i> $(n=2)$	bracelets (painted)	11th-12th	65.0	15.4	9.09	2.32	3.13	1.77	2.13	404	na	na	na	na
Corinth, Greece Nos. 3278, 3281, 3285, 3286, 3290, 3320 (n=6)	vessels, cullet, and waste glass (dark blue and green)	12th or 14th	67.2	14.3	8.96	2.01	1.96	1.90	1.42	947	na	52	700	123
Kenchreai, Greece Nos. 757, 758, 769, 973, 974, 976, 977, 981, 982, 983, 984, 985, 986, 1145, 1146, 3066 (n=16)	<i>opus sectile</i> (yellow, white, green, blue, red, "flesh")	mid-4th	66.9	16.3	6.43	0.86	1.35	1.83	1.04	314	na	na	2015	na
Hosios Loukos, Greece Nos. 2793, 2794 (n=2)	tesserae (light blue and dark blue)	mid-11th	77.0	12.3	4.97	0.89	1.20	1.22	1.39	388	na	72	253	74
Venice, Italy (San Marco) No. $2800 (n=1)$	tessera (red)	12th	56.9	16.8	2.39	0.33	0.35	0.89	2.76	311	na	23	42	37
Ravenna, Italy Nos. 2336, 2337, 2342, 2345 (n=4)	tesserae (amber, blue, green)	uncertain	59.8	15.0	4.54	2.08	0.16	0.58	1.32	1863	na	10	243	74
Rome, Italy (San Clemente) No. 2726 $(n=1)$	tessera (dark blue)	12th	63.6	15.7	3.26	2.00	0.14	1.33	0.48	621	na	46	na	37

At the site of Djadovo in Bulgaria, 808 glass bracelet fragments were recovered from the 11th–12th century ce settlement and necropolis, and four samples underwent chemical analysis (Borisov 1989). Two of these are high-boron glasses (both with 0.13 wt% B2O3), and they are very similar in terms of their style, decorative technique, weathering patterns and chemistry to the two painted bracelets from Hisn al-Tīnāt (HT_032 and HT_037). Unfortunately, no trace element data are avalable to further compare these analyses.

High-alumina glasses

The very high alumina content of a large number of the high-boron glasses from Hisn al-Tīnāt and Pergamon is also of key interest. Soda–lime–silica glasses—both mineral and plant ash soda types—typically contain between 1 and 3 wt% Al2O3 (e.g., Freestone 2006, 203, table 2), and a glass containing more than 4 wt% Al2O3 is normally considered to be a 'high-alumina' type (Dussubieux *et al.* 2010). Although high-alumina glasses are common at archaeological sites in South and South-East Asia, they are relatively rare to the west of these regions and can even be surprising: in a survey of the chemical composition of Roman and medieval glasses from Bulgaria, the high alumina content (7–11.2 wt% Al2O3) of four samples from the First Bulgarian capital of Pliska was considered to be an analytical error (Kuleff and Djingova 2002, 102), but in light of the data presented here, it is possible that this data is correct.

Of the five high-alumina mineral soda glass groups defined by Dussubieux and colleagues (Dussubieux *et al.* 2010), only one group was found exclusively outside of India, South-East Asia and Sub-Saharan Africa (m-Na-Al 5): these samples include 12th–14th century ce bracelets, tesserae, windows and raw glass from Sardis in Turkey; notably, two bracelet samples from Sardis with high alumina also contain high boron (Brill 1999b). While the magnesia and potash levels of Hisn al-Tīnāt Group 2 are high enough to suggest a plant ash soda flux, their high alumina, low lime and low strontium are very similar to the m-Na–Al Sardis glasses.

Some recent studies of glass bracelets from Middle Byzantine period sites in Anatolia and the Balkans have also identified high-alumina glass; although boron, rubidium, lithium and strontium have not been measured in these studies, it is possible that the glasses contain high levels of these diagnostic trace elements as well. Out of 113 glass bracelets from Middle Byzantine occupation levels at Sagalassos, 11 were analysed (Lauwers et al. 2010); one (SA07VL96) stands out with its extremely high alumina and very low lime (10.2 wt% Al2O3 and 4.6 wt% CaO). The colour and decorative style of the bracelet are not described, but spirally twisted cobalt blue bracelets were found at Sagalassos; if SA07VL96 is one of these-the iron content as well as elevated amounts of copper and cobalt suggest that the fragment was dark blue-then the chemical and typological similarities with the Hisn al-Tīnāt Group 2 glasses might suggest that the Sagalassos fragment, too, is made from high-boron glass. From the analysis of 12 bracelets from the 10th-13th century ce Byzantine site of Nufăru in Romania (Bugoi et al. 2012), two samples stand out with high alumina levels (9.3 and 10.0 wt%); one is a twisted bracelet of dark blue glass (sample 1978/1) said to be made from plant ash soda, and the other is an opaque dark green glass interpreted as a mixed natron - plant ash glass that has yellow painted decorations (sample 1981/16). Three different glass compositional groups were observed among the 78 sampled bracelets dating to the 10th–13th centuries from the site of Isaccea in Romania (Bugoi et al. 2016); nine have high levels of alumina (4.7–11.1 wt% Al2O3) and the flux used to produce these is identified as mixed natron – plant ash and plant ash soda—we await trace element analysis to see whether they are indeed high-boron glasses.

Interpreting raw materials sources and fluxing technology

A comparison of the Hisn al-Tīnāt glasses with the other published examples of high-boron glass underscores the notion that there may be several compositional subtypes of glass characterized by elevated boron (Table 2). This probably reflects variations in the precise type and source of raw materials, glass-making recipes and production processes, including aspects such as furnace contamination or cullet mixing and recycling.

Brill was the first to hypothesize that high-boron glass can be linked with Turkey, 'or more precisely, [made] from some batch material originating in Turkey' (Brill 2002, 17), and he suggested that the high boron levels possibly derive from plants harvested in the area of western Turkey, where boron is mined from colemanite deposits. Schibille (2011) has argued that it is doubtful that plant ashes could contain enough boron for the glass to reach levels of 1.0 wt% B2O3, citing the toxicity of boron to plants (Miwa *et al.* 2007; Camacho-Cristóbal *et al.* 2008); she instead proposes that the high-boron glasses from Pergamon were made from an evaporitic mineral soda source rich in boron, lithium and strontium, which was used to flux an alumina-rich silica source (Schibille 2011, 11–12).

One of the largest borate reserves in the world is located in western Anatolia (Fig. 1), including Ca-borate (colemanite), Na-borate (borax), Na-Ca-borate (ulexite), Mg-borate and Sr-borate deposits located at Emet, Bigadiç, Kestelek and Kırka. Geological studies have shown that these deposits often contain increased lithium and strontium (Helvacı and Alonso 2000; Helvacı et al. 2004), although the ratios and concentrations of lithium and strontium in these deposits are highly variable (Schibille 2011, 12). The variable concentrations of lithium and strontium within the high-boron Hisn al-Tīnāt Group 2 (80–130 ppm Li and 60–290 ppm Sr) and Group 3 (390-500 ppm Li and 1490-2400 ppm Sr) glasses appear to agree with Schibille's characterization of the Anatolian borate deposits. A recent comparison of the Na/B ratios of high-boron Byzantine glasses from Pergamon, Sagalassos and Aphrodisias with those of hot spring waters from western Turkey has shown a good match with the waters from Afyon-Gazlıgöl, Urganlı, Alaşehir and Salihli (Tite et al. 2016); this suggests that soda-rich salts produced by evaporating water from Na-HCO3-type hot springs could indeed have been a source of the alkali flux for locally produced glass. The high-boron glasses from Hisn al-Tīnāt fit well with this hypothesis: the average Na/B ratio is 92 for Hisn al-Tīnāt Group 2 and 43 for Group 3 (Table 1), which potentially matches the hot spring waters of Afyon-Gazlıgöl and Urganlı.

Object typology and glass technology

One of the most intriguing aspects of the Hisn al-Tīnāt glass assemblages is that bracelets alone are made from high-boron glasses. The sampled glass vessels from the site do not contain high boron (Swan unpubl. data), although it is clear that high-boron glass was being used to produce vessels during this time as well (Schibille 2011; Rehren *et al.* 2015). Moreover, for the Hisn al-Tīnāt glass bracelet samples there is a frequent link between the style of the bracelets (cross-section shape, glass colours and decorative manipulations) and the composition of the

glass itself. The clearest patterns are the dark blue spirally twisted and peaked bracelets made from a soda–alumina glass with high boron and lithium (Group 2); the naturally aqua bracelets with a central depression and those with painted designs made from soda–lime glass with high boron, lithium and strontium (Group 3); and the purple and colourless bracelets, as well as all those with ribbed exteriors, made from a glass without elevated boron or alumina (Group 1). These patterns might be explained in a number of ways, for example reflecting the products of different local or regional workshops, or indicating that glassworkers within a workshop used different raw glass—intentionally or not—when producing a batch of bracelets in a particular style (e.g., ribbed bracelets). Regardless, the glass bracelets from Hisn al-Tīnāt provide strong evidence for a close relationship between object typology and composition in ancient glass production.

Glass bracelets dating to the 10th–12th centuries ce are very common at sites in modern Turkey, Greece, Macedonia, Bulgaria, Romania, Serbia and Russia. Published analytical data for glass bracelets is unfortunately not as plentiful as it is for glass vessels, and trace element data for this period and region is particularly scarce. However, at least nine other high-boron glass bracelets dating to the 10th–13th centuries ce come from sites in modern Turkey and Bulgaria, which reinforces Brill's suggestion as to the geographical and cultural associations of high-boron glasses, while high-alumina (and potentially high-boron?) glass bracelets from the Middle Byzantine period have also been noted in Turkey and Romania.

Conclusions

A type of ancient glass characterized by very high levels of boron and lithium, and often very high levels of alumina or strontium as well, is increasingly being recognized and investigated. From the evidence currently available for high-boron glasses, there appears to be a very strong link between the findspots of this unique chemical type and the core regions of the Byzantine world, especially Anatolia and the Balkans. The pattern that has been observed—high-boron glasses excavated from sites in present-day Turkey, Greece, Cyprus, northern Italy and Bulgaria—suggests that this glass type largely circulated in regions culturally connected to the Byzantine world. Moreover, the presence of an extensive borate district and the evidence from Na–HCO3-type hot springs in western Anatolia do seem to support the interpretation of the primary production of glass in this region, as does documentary and chemical evidence for high-boron glazes being used to produce the Iznik ware of Ottoman Turkey (Tite *et al.* 2016). It is therefore highly likely that high-boron glass was the product of a local Anatolian manufacturing operation.

Glass bracelets have a great potential to make significant contributions to the investigation of high-boron glass in general, and of Byzantine glass technology and production in particular. Of the 108 published examples of high-boron glass containing 300 ppm B or more (Table 2), 32 are bracelets and 21 of these come from Middle Byzantine contexts at Hisn al-Tīnāt. The compositional information provided by the Hisn al-Tīnāt bracelets is valuable for the technical history of glass-making technology, but the sociocultural implications are exciting as well. Just over a century ago, it was believed that the Byzantines did not have a glass industry of their own (Henderson and Mango 1995; Keller 2010), and until very recently there was little typological and chemical study of glass dating to the Middle Byzantine period. Glass bracelets were a very popular form of material culture in Byzantium and the people living in the small frontier

settlement of Hisn al-Tīnāt, located on the southern border between Byzantium and the Islamic caliphal territories, were clearly keeping up with the latest fashion trends of the Byzantine world: bracelets of various colours and decorations (including those with painted designs) were either worn by the inhabitants themselves, or were used as items of trade and exchange. If the high-boron glass types were indeed being produced in Anatolia, as seems likely from the patterns in the chemical data discussed here, then bracelets as a marker of Byzantine material culture may help shed light on the production and circulation of glass in Byzantium and beyond.

An important question remains: why the slow recognition of this unique high-boron glass technology? Does it reflect a general lack of interest in the study of Byzantine glass, or the availability of glass samples for chemical analyses? Is it a result of the limited inclusion of trace elements in previous analytical programmes? Is it due to the fact that this was not a widely produced or circulating glass type? Or do more than one of these factors come into play? It is hoped that this study will interest more scholars in the technology of Byzantine glasses and encourage a regular inclusion of trace elements—especially boron, rubidium, lithium and strontium—in the chemical analysis of glass. With an increased data set of high-boron glasses, future analytical work can focus on further defining the high-boron glass type and refining its subgroups, in order to understand the raw materials and specific technologies as well as the provenance and circulation of these glasses.

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