TITLE

High-Boron and High-Alumina Middle Byzantine (10th-12th century CE) Glass Bracelets: A Western Anatolian Glass Industry

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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 suggest that glass making was not limited to the traditional glassmaking regions of the Levant and Egypt, and a production origin in or near western Anatolia is proposed. Glass bracelets from Ḥiṣn al-Tīnāt in southern Turkey 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; Ḥiṣn al-Tīnāt; chemical composition; LA-ICPMS

INTRODUCTION

Recent analytical work on Byzantine glass from Anatolia has provided evidence that the origin of the raw glass used in the Byzantine world may not have been limited to the traditional glassmaking 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 and 1999b, 2002, and 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 Ḥiṣn 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 glassmaking 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 Ḥiṣn al-Tīnāt boron glasses may 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 Ḥiṣn al-Tīnāt has recovered 1,031 glass vessel fragments and 43 fragments from glass bracelets. Although this is a relatively small collection, it is a highly important one because it is one of the few glass assemblages dating to the 8^{th}-12^{th} centuries in Anatolia to be studied in full (Swan in review). A total of 135 vessel fragments and 40 bracelets were chemically analyzed in two separate campaigns in 2010 and 2015. The chemical data for the glass vessels from Ḥiṣn 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 Ḥiṣn al-Tīnāt

Ḥiṣn al-Tīnāt is a small, early medieval fortified settlement on the Mediterranean coast of south-central Anatolia (Figure 1). In the medieval period, this region was a border zone between Byzantium to the north and the Islamic caliphates to the southeast. The area consequently changed political hands several times during this period, controlled in turn by the Umayyads, ‘Abbāsids, Byzantines, Armenians, Seljuks, and Crusaders. Ḥiṣn 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 Ḥawqal (ca. 978 CE) describes Ḥiṣn al-Tīnāt as a timber depot and port involved in Mediterranean trade to Syria and Egypt (Eger 2010).

Three short excavation seasons in 2008, 2010, and 2011 at Ḥiṣn al-Tīnāt revealed five phases of construction dating primarily to the mid-8th to the early-12th centuries CE (Eger in preparation). Phases V and IV date to the mid-8th to 10th centuries CE (Early Islamic), Phase III is 10th century CE (likely 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 Ḥiṣn 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 Ḥiṣn al-Tīnāt glass bracelet compositions largely correspond to the color, 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 9th century CE (Parani 2005; Antonaras 2012). The widespread fashion for glass bracelets during the Middle Byzantine period is strongly 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 1989; Mănucu-Adameşteanu and Poll 2012)—and also by contemporary artistic representations in paint and mosaic media (Parani 2005). The popularity of bracelets was likely 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 2005: 153). This 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 in 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 2009; e.g. Bulgaria, see Borisov 1989: 292), and might therefore be considered an element of material culture that is specifically characteristic of the Middle Byzantine period.

Out of the 43 total bracelet fragments recovered from the excavation of Ḥiṣn al-Tīnāt, 40 were analyzed for their chemical composition (Table 1 and Figure 2). The fragments come from different areas of the site, including areas within and just beyond the corner towers and walls of the fortified structure, as well as within the extramural building to the south of the fort. Only one complete bracelet was recovered (Figure 2.N); although it was not possible to chemically analyze the complete bracelet, this object demonstrates how irregular in shape and thickness glass bracelets can be. The stratigraphic phasing and associated ceramic finds at Ḥiṣn al-Tīnāt indicate the bracelets as a group generally 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 ca. 1020-1150 CE using Radiocarbon accelerator mass spectrometry (Laboratory number Beta-316435). Stylistically, the bracelet repertoire of Ḥiṣn al-Tīnāt is simple in both color and decorative manipulation. The majority of the bracelets are monochrome blue-green, dark blue, purple, or colorless-to-purple glass. One bracelet is made from two different glasses (colorless 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 spiral twists. “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 at the site but in more limited numbers.

Analytical methods

A tiny snip of glass (less than $5mm^3$ 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 seconds. 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 ^{29}Si 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 0.01-1 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: 153-155 and Tables 1-3).

RESULTS

The bracelets form three distinctive compositional groups (Table 1, Figures 3 and 4); all are either soda-lime or soda-alumina glass with K_2O 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 2012a). Group 2 and Group 3 are high-boron glasses with elevated lithium, the former containing very high alumina and the latter very high lithium and strontium (Swan 2012b). Interestingly, *none* of the vessels sampled from Ḥiṣn 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% K_2O, 2.5 wt% MgO, and 0.41 wt% P_2O_5. Their boron and lithium concentrations are around 60 to 100 ppm and 5 to 10 ppm, respectively (Table 1), in line with published plant ash glasses from the Late Bronze Age (e.g., Shortland et al. 2007) as well as the Islamic period (e.g. Henderson et al. 2016). Group 1 includes all of the bracelets made from purple and colorless glass and five bracelets described as naturally aqua or light green. The bracelets in this group include those with plain circular sections as well as those with spiral twists and 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 profile, fits within the Group 1 type but is somewhat different both 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 likley the result of a colorant—perhaps a leaded bronze—and variations in the trace elements include lower strontium and titanium, as well as 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 levels of manganese, ranging from 0.75 to 2.8 wt% MnO. The high manganese content of the aqua bracelets of this group (0.75-1.5 wt% MnO) is noteworthy, given the low iron content of these samples.

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

This group consists of 11 samples (HT_020 to HT_030) with very high levels of both boron (averaging 1660 ppm) and lithium (averaging 110 ppm), and very high level of alumina (averaging 9.8 wt% Al_2O_3). Group 2 glass has the lowest levels of silica (averaging 56.4 wt% SiO_2) and lime (averaging 4.3 wt% CaO) as well as the highest levels of soda (averaging 19.5 wt% Na_2O), potash (averaging 4.2 wt% K_2O), 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% P_2O_5) 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 glasses of the two other groups, possibly indicating a complex mineral assemblage to provide the flux, rather than plant ash (Rehren in preparation).

The common decorative features of this group of bracelets are striking: this group includes the majority of the spirally-twisted and peaked bracelet types, and notably all of the intensely-colored dark blue fragments found at the site. The dark blue color is due to cobalt and copper (c. 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. 1992; Henderson 1998). 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 (2013), which also has elevated zinc, manganese, and REE concentrations, as well as higher alumina than contemporary copper-blue or colourless glasses. However, there is no elevated nickel associated with the Ḥiṣn al-Tīnāt glass bracelets that could suggest the cobaltiferous alums of Egypt were used as a colorant (e.g. Kaczmarczyk 1986; Shortland et al 2006; Abe et al 2012). 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% Al_2O_3. This glass type has a comparatively low potash level (averaging 1.6 wt% K_2O) and low phosphate (averaging 0.11 wt% P_2O_5), 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 11.1 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 as well (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 then 30 ppm in all other samples in this group) and barium (c 120-140 ppm Ba, compared to less than 100 ppm in all others). HT_033 is also the only one in this group with 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 contents are similar to the Group 1 glasses, although the soda level is higher (16.1 wt% Na_2O). The glass has comparatively low potash and magnesia levels (1.2 wt% K_2O and 1.7 wt% MgO); the lime, iron, and alumina contents 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 levels are lower than is common for glasses made with plant ash, but this does not necessarily indicate that 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 color of the glass derives from its iron content (1.5 wt% FeO) as well as trace amounts of cobalt and copper (c. 500 ppm Co and 800 ppm Cu); elevated levels of lead are also present, which is similar to the blue glasses of Group 2.

DISCUSSION

Approximately half of the bracelet fragments excavated at Ḥiṣn al-Tīnāt are made from a plant ash soda glass that is similar in composition to the glass vessels used at the site (Figure 3), while the other half is made from two varieties of glass containing elevated levels of boron and lithium (Figure 4A), one of which is also characterized by very high alumina (Figure 4B), 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 match closely 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 ca. 1025 CE Serçe Limanı shipwreck (Brill 2009). The Group 2 glasses have even higher levels of magnesia and potash than Group 1, but their high boron, lithium, and alumina levels 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 contents (1.6 wt% K_2O and 2.7 MgO) are above 1.5 wt% (Sayre and Smith 1961; Brill 1970; Henderson 2000), although their phosphate content is extremely low (averaging 0.11 wt% P_2O_5) 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 glassmaking 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% B_2O_3; 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% B_2O_3 (Brill 1968: 51; Brill 2002: 16), equivalent to about 25-100 ppm B. High boron levels in glass, therefore, mark 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 glass to be those with 0.04 wt% B_2O_3 (equivalent to about 125 ppm B) or more, for the purposes of this paper we limit discussion to those samples with 0.1 wt%

B_2O_3 (300 ppm B) or more. Brill's samples come from contexts dating from the 6th/7th century to the 12th century CE (Brill 1999a, 2002, 2005); interestingly, these high boron glasses all have connections with regions within or immediately neighboring the Byzantine world (Figure 1 and Table 2), as they were excavated in modern Turkey, Cyprus, Greece, and northern Italy. These include vessel fragments and cullet from 6th/7th-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-4th-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 likely dates to the 11th/12th or 13th/14th centuries (for this debate see Weinberg 1940, McDonald et al. 1983, Whitehouse 1991 and 1993, and Parani 2005). Brill's samples also 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 particularly intriguing considering the dark blue color of many Ḥiṣn 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 sub-groups (Rehren et al. 2015: 275): the first subgroup is termed HBAl and is characterized by high boron (averaging 1000 ppm B) and high alumina (averaging 9 wt% Al_2O_3), as well as higher soda, iron, titania, phosphate, and arsenic; the second subgroup is termed HLiBAl and is characterized by high lithium (averaging 300 ppm Li), high boron (averaging 1500 ppm B), and high alumina (averaging 5 wt% Al_2O_3) as well as much higher lime, sulphate, rubidium, and strontium. In terms of boron, lithium, and alumina the Ḥiṣn al-Tīnāt glass Group 2 and Group 3 fit somewhat with the two Pergamene high boron subgroups (Table 2). Group 2 is similar to HBAl, and Group 3 is similar to HLiBAl. However, unlike the Pergamene glasses, Ḥiṣn 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 also still quite high; Group 2 also has much higher potash and magnesia than the Pergamene HBAl type. In addition, Ḥiṣn al-Tīnāt Group 2 and 3 glasses have higher boron contents 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 Ḥiṣn al-Tīnāt; the dates of the Pergamene samples also differ, the majority being identified as early Byzantine or dating to the 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 Ḥiṣn 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% Al_2O_3. However, significant discrepancies exist in the levels of some trace elements, including barium, boron, and strontium.

At the site of Djadovo in Bulgaria, 808 glass bracelet fragments were recovered from the 11^{th}-12^{th} 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% B_2O_3), and they are very similar in terms of their style, decorative technique, weathering patterns, and chemistry to the two painted bracelets from Ḥiṣn al-Tīnāt (HT_032 and HT_037). Unfortunately, no trace element data are avalable to further compare these analyses to the above-mentioned bracelets.

High alumina glasses

The very high alumina content of a large number of the high boron glasses from Ḥiṣn al-Tīnāt and Pergamon is also of key interest. Soda-lime-silica glasses—both the mineral and plant ash soda types—typically contain between 1 and 3 wt% Al_2O_3 (e.g. Freestone 2006: 203, table 2), and a glass containing more than 4 wt% Al_2O_3 is normally considered to be a "high alumina" type (Dussubieux et al. 2010). Although high alumina glasses are common on archaeological sites in South and Southeast 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% Al_2O_3) 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, Southeast 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 Ḥiṣn 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 excavated from Middle Byzantine occupation levels at Sagalassos, 11 were analyzed (Lauwers et al. 2010); one (SA07VL96) stands out from the rest with its extremely high alumina and very low lime (10.2 wt% Al_2O_3 and 4.6 wt% CaO). The color 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 the fragment was dark blue—then the chemical and typological similarities with the Ḥiṣn 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 of these is a twisted bracelet of dark blue glass (sample 1978/1) made from plant ash soda, while 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), with the majority of the samples being soda-lime-silica glass (~85%); nine have high levels of alumina (4.7-11.1 wt% Al_2O_3) and the flux used to produce these is identified as mixed natron-plant ash, and plant ash soda in two cases; we are awaiting trace element analyses of these Romanian bracelets to see whether they are indeed high-boron glasses similar to those from Pergamon and Ḥiṣn al-Tīnāt.

Interpreting raw material sources and fluxing technology

A comparison of the Ḥiṣn 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 likely reflects variations in the precise type and source of raw materials, glassmaking 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 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% B_2O_3, citing the toxicity of boron to plants (Miwa et al. 2007 and 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, 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 (Helvaci and Alonso 2000; Helvaci 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 Ḥiṣn 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 characterisation 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-HCO_3-type hot springs could indeed have been a source of the alkali flux for locally-produced glass. The high-boron glasses from Ḥiṣn al-Tīnāt fit well with this hypothesis: the average Na/B ratio is 92 for Ḥiṣn al-Tīnāt Group 2 and 43 for Group 3, 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 Ḥiṣn 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 unpublished 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 Ḥiṣn al-Tīnāt glass bracelet samples there is a frequent link between the style of the bracelets (cross-section shape, glass colors, 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 colorless 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: reflecting the products of different local or regional workshops; indicating that glassworkers within a workshop used different raw glass—intentionally or not—when producing a batch of bracelets in a particular style (for example, ribbed bracelets); or another combination of factors entirely. Overall, the glass bracelets from Ḥiṣn 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 on 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 10^{th}-13^{th} centuries CE come from sites in modern Turkey and Bulgaria, which reinforce Brill's suggestion as to the geographic 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-HCO_3-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 later Iznik ware of Ottoman Turkey (Raby 1989; 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 Ḥiṣn al-Tīnāt. The compositional information provided by the Ḥiṣn al-Tīnāt bracelets is valuable for the technical history of glassmaking technology, but the socio-cultural 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 Ḥiṣn 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 colors 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 programs? 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 here?

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 dataset 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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LIST OF FIGURE CAPTIONS

Figure 1: Map showing the location of Ḥiṣn al-Tīnāt and the findspots of high-boron glasses (≥300 ppm B, equivalent to ≥0.10 wt% B_2O_3) mentioned in the text (base map: Esri, USGS, NOAA).

Figure 2: Examples of the cross-section and decorative types of the Ḥiṣn al-Tīnāt glass bracelets. (Drawings: Carolyn Swan and Serkan Demir; photographs: Carolyn Swan and Marie-Henriette Gates. Courtesy of Kinet Project archives.)

Figure 3: Potash vs. magnesia scatterplot of the Ḥiṣn al-Tīnāt bracelets, compared with vessel glass from the site (Swan unpublished data).

Figure 4: Scatterplots of the Ḥiṣn al-Tīnāt bracelets, (A) lithium vs. boron and (B) alumina vs. lime.

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

Table 2: Average chemical compositions for published high-boron glasses (≥300 ppm B, equivalent to ≥0.10 wt% B_2O_3) dating from the $6^{th}/7^{th}$ to $13/14^{th}$ centuries CE contexts (data from Borisov 1989, Brill 1999b, and Rehren et al 2015). Values are wt% oxide for major and minor compounds, and ppm for the trace elements B, Rb, Li, Sr, and Zr (na = not analysed).