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Glass in Byzantium –
Production, Usage, Analyses

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Produktion, Verwendung, Analysen

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R | G | Z | M

Jörg Drauschke, Daniel Keller (eds)

**GLASS IN BYZANTIUM –
PRODUCTION, USAGE, ANALYSES**

International Workshop organised by the
Byzantine Archaeology Mainz, 17th-18th of January 2008
Römisch-Germanisches Zentralmuseum

**GLAS IN BYZANZ –
PRODUKTION, VERWENDUNG, ANALYSEN**

Internationaler Workshop der
Byzantinischen Archäologie Mainz, 17.-18. Januar 2008
Römisch-Germanisches Zentralmuseum

GLASS IN BYZANTIUM – PRODUCTION, USAGE, ANALYSES

The products of Byzantine glass-making workshops are found throughout the whole of the Mediterranean area and were also distributed into regions far beyond the borders of the Empire. Research into glass production and distribution in Byzantium has made enormous progress, especially in the last years. Thanks to state of the art scientific methods and a number of recent discoveries, it is not only possible today to identify centres of raw glass production, but also to trace additional trade routes to secondary workshops. Furthermore the results of this research have revealed details of the formulas used in glass production, the source of the raw products and the technologies employed.

The current state of this research was the subject of discussion at an international workshop hosted in January 2008 by the »Byzantine Archaeology Mainz«. Contributions to this conference dealt with a geographical area between North Africa, the Balkans, Asia Minor and the Near East. The focal point of the workshop was formed on the one hand by recent results of scientific analyses of glass and on the other hand by studies of regionally-specific expressions of Byzantine forms of glass. Thus research into Byzantine glass manufacture has once again produced highly interesting findings and permitted an insight into the diverse possibilities of modern analytical methods.

GLAS IN BYZANZ – PRODUKTION, VERWENDUNG, ANALYSEN

Die Erzeugnisse byzantinischer Glaswerkstätten finden sich im gesamten Mittelmeerraum und erreichten auch weit entfernte Regionen jenseits der Reichsgrenzen. Die Erforschung der Glasproduktion und -verbreitung in Byzanz hat gerade in den letzten Jahren enorme Fortschritte erzielt: Dank modernster naturwissenschaftlicher Methoden und vielen Neufunden ist es heute möglich, Zentren der Rohglasherstellung zu identifizieren und den weiteren Vertriebsweg an sekundäre Werkstätten nachzuvollziehen. Die Ergebnisse geben darüber hinaus Auskunft über die verwendeten Glasrezepturen, die Herkunft der Rohstoffe und die angewandten Glastechnologien. Der aktuelle Stand der Forschung wurde im Januar 2008 bei einem von der »Byzantinischen Archäologie Mainz« veranstalteten internationalen Workshop diskutiert. Die Beiträge der Tagung behandeln einen geographischen Raum zwischen Nordafrika, Balkan, Kleinasien und dem Nahen Osten. Den Schwerpunkt bilden einerseits aktuelle Ergebnisse naturwissenschaftlicher Glasanalysen, andererseits Studien zur regionalspezifischen Ausprägung byzantinischer Glasformen. So liefert die Erforschung der byzantinischen Glaskunst immer wieder hochinteressante Erkenntnisse und gibt einen Einblick in die vielfältigen Möglichkeiten moderner Untersuchungsverfahren.

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TECHNOLOGY AND PROVENANCE OF LEVANTINE PLANT ASH GLASS USING SR-ND ISOTOPE ANALYSIS

Recent work has shown that the isotopes of strontium and neodymium may be particularly useful in the investigation of the provenance of natron glass (Freestone et al. 2003; in press; Henderson et al. 2005; Degryse / Schneider 2008). The present study addresses the utility of this system in the investigation of some glasses made using plant ash as the main source of flux.

A number of studies have analysed plant ash glass from the eastern Mediterranean dating from the 9th to the 11th century A.D. These include raw glass from the primary production sites of al-Raqqa, Syria (Henderson et al. 2005) and Tyre, Lebanon (Freestone 2002) as well as raw glass and cullet from the secondary production site of Baniyas, present Israel (Freestone / Gorin-Rosen / Hughes 2000) and from the ship wreck found at Serçe Limanı, Turkey (Brill 1999). These plant ash glasses fall into relatively discrete compositional production groups in terms of their major element compositions (Freestone 2002; Henderson 2003), suggesting it can be possible to group plant ash glasses according to their production location (Freestone 2006). Plant ash as a flux, however, is a complex and heterogeneous material and it is still not entirely clear how the composition of a plant ash glass corresponds to that of a raw material batch (Freestone 2006; Tanimoto / Rehren 2008). Thus the meaning of differences in major or trace element composition may not always be clear. Major and trace element analysis may therefore be useful techniques but new approaches may be needed to source plant ash glasses.

Sr-Nd isotopic analysis is a relatively new technique used in archaeometry to provenance primary glass production. Strontium (Sr) in ancient glass is mainly incorporated with the lime bearing material. However, minor influences may be attributed to feldspar or heavy minerals in the silica source (Degryse et al. 2006; Freestone et al. in press). In the case of plant ash glass, the silica source is typically low in lime in order to produce a balanced composition with the lime-bearing plant ash flux (Freestone / Gorin-Rosen 1999). In such cases the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio of the glass reflects that of the plant ash which was in itself derived from the bio-available Sr in the soil where the plant grew; this is likely to reflect the local geology in most cases (Freestone et al. 2003 and references therein; Henderson et al. 2005). The neodymium (Nd) content of glass is likely to have originated from the accessory minerals in the silica-bearing raw material. Nd isotopes are regularly used as an indicator of the provenance of siliciclastic sediments in the earth sciences (Banner 2004). The isotopes of Nd are particularly useful indicators of the origin of glass, because glass-making sands from the eastern Mediterranean coast carry a distinctive signature related to their derivation from the Nile. Freestone and others (in press) inferred an Egyptian origin of HIMT (natron) glass, on the basis of an eastern Mediterranean Nd isotopic signature. On the other hand, Degryse and Schneider (2008) showed that 1st to 3rd century A.D. natron glass could not exclusively originate from the known region of primary glass production in Syro-Palestine and Egypt, as the Nd signature of some of their glass samples corresponded to a western Mediterranean or north-western European signature. The coincidence of one of the ancient world's most productive glassmaking areas with an isotopically distinctive geochemistry is proving a fruitful testing ground for isotopic studies of glass.

Sr-Nd isotopic studies on plant ash glasses have remained limited up till now. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic analysis of glass from al-Raqqa (Henderson et al. 2005) and Baniyas (Freestone et al. 2003) showed that the plant ashes

sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	CoO	CuO	ZnO	total
TYRE 3	62.37	0.09	1.77	0.45	1.64	3.66	11.93	12.91	2.56	0.43	0.11	0.62	<0.05	<0.05	<0.05	98.54
TYRE 8	62.60	0.10	1.78	0.46	1.67	3.53	12.06	13.02	2.56	0.43	0.14	0.60	<0.05	<0.05	<0.05	98.96
TYRE 9 glass	74.01	0.10	1.71	0.30	0.54	2.03	5.14	10.89	2.84	0.40	0.12	0.67	<0.05	<0.05	<0.05	98.74
TYRE 12	65.60	0.07	1.77	2.60	0.66	2.68	9.04	12.57	2.74	0.42	0.12	0.70	0.07	0.21	0.06	99.30
TYRE 13	64.33	0.09	1.76	0.47	1.95	3.88	9.11	14.17	2.63	0.44	0.15	0.74	<0.05	<0.05	<0.05	99.73
BAN 49	67.59	0.13	1.77	0.53	1.49	3.35	9.77	11.38	2.51	0.29	0.59	0.66	nd	nd	nd	100.06
BAN 51	70.98	0.11	1.27	0.40	0.85	2.59	8.42	12.01	2.01	0.23	0.32	0.82	nd	nd	nd	100.01
BAN 61	70.70	0.13	0.91	0.46	0.95	2.76	7.83	12.77	1.92	0.28	0.30	0.89	nd	nd	nd	99.90
BAN 62	71.70	0.19	0.87	0.33	0.95	2.71	7.61	12.76	1.84	0.27	0.27	0.88	nd	nd	nd	100.38
BAN 63	68.94	0.10	1.00	0.39	0.93	2.64	10.19	12.57	1.81	0.33	0.28	0.78	nd	nd	nd	99.96
BAN 58	68.95	0.12	0.87	0.21	0.93	2.81	9.69	13.06	1.46	0.30	0.58	0.85	tid	nd	nd	99.83

Tab. 1 Major and minor elements in samples analysed.

used were derived from different regions. Data for Tyre (Leslie et al. 2006), however, fell within the Raqqa range and have led to speculation that plant ashes from the same area may have been used in both instances, reflecting an early medieval trade in Syrian plant ash for glassmaking (Freestone 2006). $\delta^{18}\text{O}$ isotopic measurements confirmed that Raqqa and Tyre glasses were made using different silica sources and probably therefore in different locations (Leslie et al. 2006).

In the present study we have investigated chunk glass samples from the primary workshop at Tyre and the secondary workshop at Baniyas in attempt to address a number of questions. The Tyre glasses originated in large tank furnaces, melting up to 30 tonnes of glass in one firing and excavated by Aldsworth and others (2002). However, the elemental composition of any sand used in their manufacture was very different from the sands used in natron glass from the coastal areas of Palestine. Not only are the sands used to manufacture the Tyre plant ash glasses likely to have been low in lime, as indicated above, but also their alumina contents were much lower than those of Levantine I and II natron glasses, which are typically around 3% (Freestone / Gorin-Rosen / Hughes 2000); the Tyre glasses on the other hand contain only around 1% Al₂O₃ (Freestone 2002). Thus were the Tyre glassmaking sands from the coast? Furthermore, do they carry the typical Nd isotopic signature of other Levantine coastal glass? Our second area of enquiry concerns the Baniyas glass. Was the primary glass from inland Baniyas transported from the coast, or was it made at an inland site, such as Raqqa, or somewhere more local to Baniyas itself? In addition there were a number of issues pertinent to the individual sites which we anticipated isotopic data might be used to address.

SAMPLES

Eleven samples, five from Tyre and six from Baniyas, were analysed for their Sr-Nd isotopic composition. Major element compositions, after Freestone, Gorin-Rosen and Hughes (2000) and Freestone (2002), are presented in **table 1**. All Tyre plant ash glass samples (TYRE 3, 8, 12-13) are from unworked lumps or chunks of glass (Freestone 2002). One sample (TYRE 9) was a lump of raw glass, partly fused, with the silica material still visible and accessible for sampling. Of this sample, both the glassy and silica-rich regions were analysed. SEM examination of this sample reveals that the large lumps of silica visible in the hand specimen are in fact aggregates of fine sand grains in a matrix of glass (Freestone 2006). The Tyre glasses are variable particularly in their lime and soda contents, ranging respectively from 5.14% to 12.06% and 10.89% to

sample	$^{143}\text{Nd}/^{144}\text{Nd}$	2s	conc. Nd (ppm)	1000/Nd	e Nd (t = 0)	$^{87}\text{Sr}/^{86}\text{Sr}$	2s	$\delta^{18}\text{O}^*$
BAN 49	0.512345	0.000007	5.9	169.43	-5.7	0.70778	0.000020	NA
BAN 51	0.512377	0.000010	4.5	223.41	-5.1	0.70766	0.000004	NA
BAN 61	0.512354	0.000010	3.6	278.60	-5.5	0.70762	0.000020	12.40
BAN 62	0.512382	0.000008	3.6	280.00	-5.0	0.70773	0.000010	12.60
BAN 63	0.512326	0.000009	3.6	275.28	-6.1	0.70770	0.000004	12.89
BAN 58	0.512380	0.000010	3.8	263.06	-5.0	0.70802	0.000006	NA
TYRE 3	0.512350	0.000010	5.3	187.14	-5.6	0.70812	0.000006	11.90
TYRE 8	0.512389	0.000006	5.8	171.30	-4.9	0.70812	0.000004	11.79
TYRE 9 glass	0.512361	0.000010	5.2	192.52	-5.4	0.70817	0.000006	NA
TYRE 12	0.512441	0.000009	5.2	191.94	-3.8	0.70846	0.000009	NA
TYRE 13	0.512473	0.000010	5.6	180.17	-3.2	0.70811	0.000008	12.37
TYRE 9 quartz	0.512296	0.000012	5.6	178.63	-6.7	0.70824	0.000007	NA

Tab. 2 Isotopic data. – * Oxygen data from Leslie et al. 2006.

14.17 %, which Freestone (2002) interpreted as reflecting the variability in the composition of the plant ash used. Silica and alumina are fairly constant, indicating a reasonably homogeneous silica source. To glasses TYRE 3, 8 and 13 manganese oxide has been added to counter the effects of the iron present, so that the blue-greenish tint of the material was modified to close to colourless (Freestone 2002). Sample TYRE 12 is a deep blue glass coloured with cobalt.

The Baniyas glass is variable in its SiO_2 and Al_2O_3 contents, varying between 67.59 % to 71.70 % and 0.87 % to 1.77 % respectively. The lime, soda, magnesia and potash content are fairly constant. It is particularly notable that the sum of the latter oxides, attributable to the plant ash component, is inversely proportional to the sum of the components typically attributed to the silica source, pointing to a failure to control closely the ratio of silica to ash, or a failure to fully homogenise the ingredients during mixing and melting of the primary batch. MnO_2 was added to the Baniyas glass to counteract the effects of iron oxides. Although from a secondary production site, the Baniyas glass is considered to represent a single primary production centre (Freestone / Gorin-Rosen / Hughes 2000). However, samples BAN 49 and BAN 58 studied here were selected because they are somewhat different in elemental composition. Moreover, sample BAN 58 is a purple glass, less common in the Baniyas context.

ANALYTICAL METHODOLOGY

For isotope analysis, samples were weighed into Teflon screw-top beakers and dissolved in a 3:1 mixture of 22 M HF and 14 M HNO_3 on a hot plate. Solutions were dried and dissolved in aqua regia. Aliquots of these solutions were spiked with a highly enriched ^{84}Sr and ^{150}Nd tracer for separate concentration analyses by isotope dilution, whereas unspiked aliquots were used for determination of isotope ratios. For separation of Sr and Nd from the same sample solutions, sequential extraction methods developed by Pin and others (1994) were utilized and slightly modified. Sr and REE were separated using 2 M HNO_3 on coupled miniaturized Teflon columns containing 50 μl of EICHRON Sr and TRU resin, respectively, and eluted with deionized H_2O . For separation of Nd, the REE cut was further passed through a column containing 2 ml EICHRON Ln resin. For this, the column was washed with 5.5 ml 0.25 M HCl after adding the sample. Nd was then stripped off using 4 ml 0.25 M HCl.

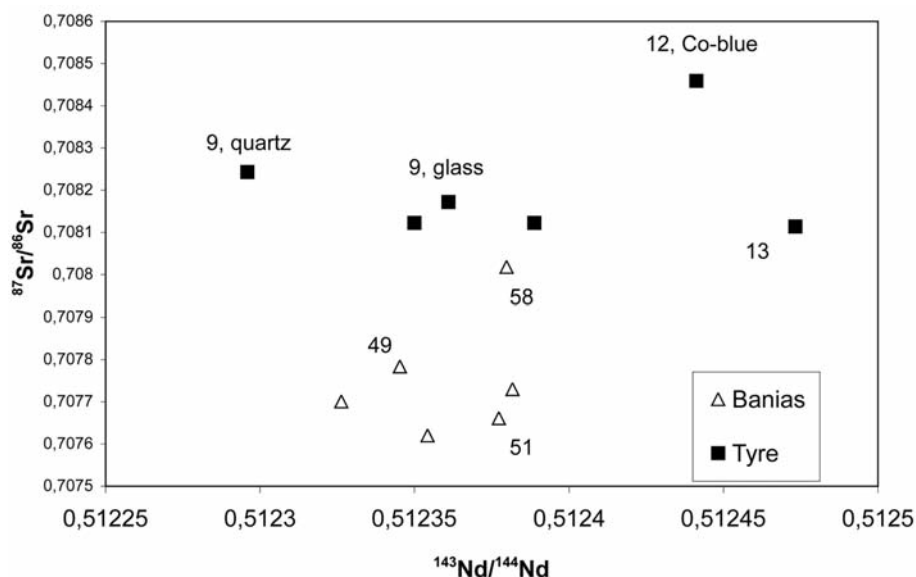


Fig. 1 Results of isotopic analyses.

All measurements were performed on a six-collector FINNIGAN MAT 262 thermal ionization mass spectrometer (TIMS) running in static multicollection mode. Sr isotopic ratios were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, Nd isotopic ratios were normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Repeated static measurements of the NBS 987 standard over the duration of the study yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71025 ± 2 (2σ , $n = 22$). Repeated measurements of the La Jolla Nd standard yielded $^{143}\text{Nd}/^{144}\text{Nd} = 0.511848 \pm 0.000009$ (2σ , $n = 8$). Total procedural blanks ($n = 6$) did not exceed 30 pg Sr and 50 pg Nd and were found to be negligible.

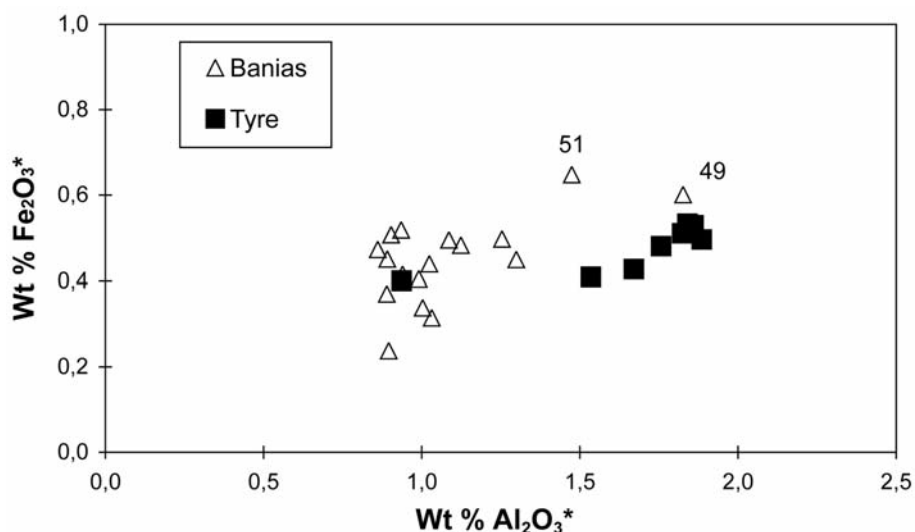
RESULTS

Analytical results are presented in **table 2** and summarized in **figure 1**. Major element analyses are taken from Freestone, Gorin-Rosen and Hughes (2000) and Freestone (2002), and available $\delta^{18}\text{O}$ measurements for selected samples are from Leslie and others (2006). All Banias glass except sample BAN 58 show a homogeneous isotopic composition of $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.70762 and 0.70778 and $^{143}\text{Nd}/^{144}\text{Nd}$ between 0.512326 and 0.512382, or an ϵ Nd (a normalization of the $^{143}\text{Nd}/^{144}\text{Nd}$, see Degryse / Schneider 2008) between -5.0 and -6.1 . Sample BAN 58 has a divergent $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70802 but a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512380 (ϵ Nd -5.0) similar to the other Banias samples. The Tyre glass samples show a more heterogeneous isotopic composition, with $^{143}\text{Nd}/^{144}\text{Nd}$ ranging between 0.512350 and 0.512473 (ϵ Nd between -3.2 and -5.6) and $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.70811 and 0.70842. The silica taken from sample TYRE 9 has a $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512296 (ϵ Nd -6.7) and a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70824.

DISCUSSION

In a general sense the Tyre results indicate unequivocally that the primary glass there was made using coastal sand with the characteristic high ϵ Nd of natron glasses made in Palestinian tank furnaces (Freestone et al. in press) and of Levantine coastal sand (Degryse / Schneider 2008). Furthermore, this result

Fig. 2 Relationship between Baniyas and Tyre glasses in terms of major elements.



strongly suggests that plant ash glasses made from Levantine coastal sands have Nd isotopic signatures essentially unmodified by the use of plant ash. The site of Tyre comprises an isthmus with a very large amount of sand which has accumulated against the causeway built by Alexander's forces some 2300 years ago (Emery / George 1963; Nir 1996). By the 11th century A.D. this would have provided a very abundant material for glassmaking. Given the size of the furnaces on Tyre, the transport of sand from a long distance seems most improbable and we must assume for the present time that differences in ϵ Nd reflect variation in local sand compositions.

The variation in ϵ Nd for the Tyre glass, from -5.6 to -3.2 , is of interest, as it suggests that a primary production site using a (presumably) common source of sand may generate a relatively wide range of ϵ Nd. In the case of Tyre, this may reflect the geomorphological situation, with strata of different composition available in the substantial sedimentary deposits. Changes in the heavy mineral and isotope composition of the Nile load due to the effect of climate change of the supply of material from the source areas are well known (Foucault / Stanley 1989; Krom et al. 2002) and we might expect these to be reflected in the composition of rapidly accumulated sediment such as that at Tyre. The limited oxygen isotope data (tab. 2) support this view, as of the three samples analysed by Leslie and others (2006), sample TYRE 13 which has highest ϵ Nd (-3.2) also has highest $\delta^{18}O$. Thus as expected, oxygen isotope composition is also a reflection of sand source.

The Baniyas glass has a more homogenous Nd isotopic composition, but is remarkably consistent with Mediterranean beach sands (Degryse / Schneider 2008) and the primary glass made of it in the 4th to 8th century natron glass producing facilities of Syro-Palestine, the so-called Levantine I and II glass groups as defined by Freestone and collaborators (Freestone / Gorin-Rosen / Hughes 2000; Freestone et al. in press). This may give an indication of the geographic primary production location of the Baniyas plant ash glass, though the use of lime rich beach sands such as used for natron glass does not appear possible, due to the lime content of plant ash (see above). Even so, although found inland, the Baniyas glass was clearly derived from coastal sand and hence from furnaces located near to the coast. This provides the first unequivocal analytical evidence for a long distance trade in raw plant ash glass.

Figure 2 shows the relationship between Baniyas and Tyre glasses in terms of their major elements (Freestone 2002). The separation between the two groups is clear, but two samples from Baniyas have higher

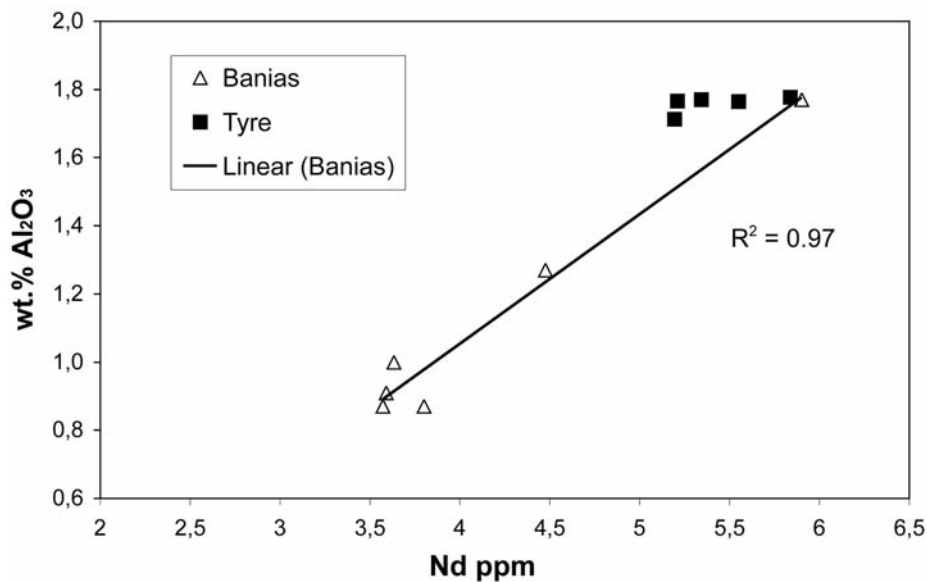


Fig. 3 Correlation between Al₂O₃ and Nd content in Banias and Tyre glasses.

Al₂O₃ and lie as close to the Tyre group as to the centre of the cluster of Banias glass. We analysed these glasses (BAN 49, 51) isotopically to determine whether they were genuinely affiliated to Banias or if they might indicate that some Banias glass had been manufactured in the Tyre furnaces. The clear separation of the Banias and Tyre groups in terms of ⁸⁷Sr/⁸⁶Sr (fig. 1) indicates that these outliers in terms of major element composition are indeed closely affiliated to the Banias glasses. This suggests that major element analysis is not always unambiguous in determining the specific origin of individual samples.

Some evidence for the origin of the Nd in plant ash glass is found from the Banias glass where the concentration of elemental Nd correlates with iron and titanium but is particularly well correlated with alumina (fig. 3). In Mediterranean coastal sediments alumina and iron are strongly correlated and this is related to the presence of a fine grained component in the sand; the same would appear to be the case here. Interestingly ε Nd does not show any correlation with alumina, again suggesting that only one source of Nd was present in the glass raw materials, and that this was probably the sand.

It is intriguing that the Nd signature of the quartz-rich component in sample TYRE 9 is different from that of the rest of the Tyre glass analysed, while the glass analysed from the same sample, has an Nd signature consistent with the rest of the Tyre glass (fig. 1). There are a number of possible explanations for this process. Perhaps most likely is that the inconsistency between silica and glass may be due to preferential melting of some minerals into the glass phase, leaving the silica analysed with only a partial fraction of the total Nd in the glass batch. This would be corroborated by the high silica content of this glass (sample Tyre 9), differing from the general main element chemistry of the Tyre glass. The possibility that some influence of silica processing contaminates the glass, for example grinding in mortars or on rock, as suggested for Bronze Age glass by Rehren (2008) can probably be ruled out, as it is inconsistent with the similar total Nd in both glass and the silica in sample TYRE 9, just above 5 ppm. In addition the rounded and well sorted nature of the sand grains in the sample (fig. 4) indicates that the sand was not milled. Finally, a contribution from the plant ash cannot be completely discarded. Then, the Nd signature of the glass would be a mixture of the Nd in the plant ash and in the silica source. However, analysis of plant ashes by Barkoudah and Henderson (2006) suggests that the Nd contents of plant ashes are generally insignificant relative to those of sands.

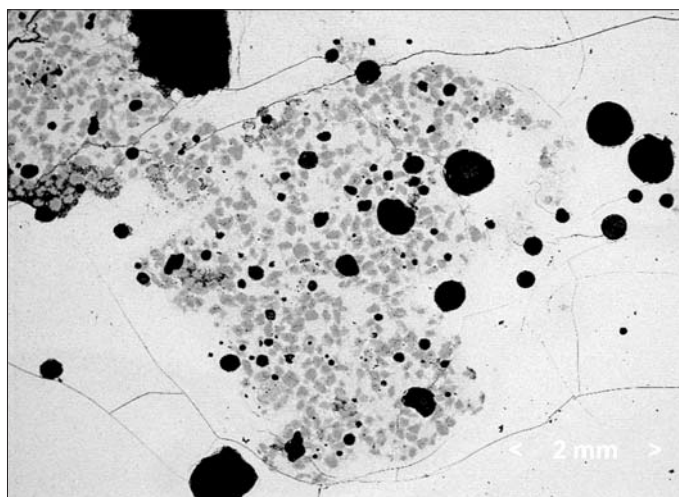


Fig. 4 Matrix of sample TYRE 9 with rounded and well sorted sand grains.

The blue glass found at Tyre was from the redeposited remains of tank lining that had been dumped in a »pit« cut through one of the larger tanks manufacturing colourless or weakly coloured primary glass. Blue glass sample TYRE 12 has a slightly different $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from the other Tyre glasses, indicating the use of a different plant ash. Furthermore, it has ϵ Nd of -3.8 , which is significantly higher than some of the other Tyre samples and suggests a different sand. With the archaeological evidence, this suggests that the Co-blue glass of Tyre was made in a later campaign of melting from the uncoloured glasses. Indeed its major element composition is particularly close to that of glass from the Serçe Limanı wreck, with which it was compared by Freestone (2002). Furthermore, it lies just outside the interquartile range of $^{87}\text{Sr}/^{86}\text{Sr}$ for glass from the Serçe Limanı wreck, reported by Brill and Fullager (2009). It seems possible that some of the Serçe Limanı glass originated in the Tyre furnaces, although Nd isotope analysis on the Serçe Limanı glasses is ideally required to test this.

The purple sample BAN 58 has significantly higher $^{87}\text{Sr}/^{86}\text{Sr}$ than the other Baniyas glasses, suggesting that it was indeed a product of a different batch of glass, using different plant ash, and where furnace conditions were more oxidising, encouraging the development of the purple colour.

CONCLUSIONS

Sr-Nd isotopic analysis has shown that plant ash glass made from Levantine coastal sand carries the characteristic high ϵ Nd of Levantine natron glass. The Baniyas glass seems to have been made on the Levantine coast, like that of Tyre, but the two productions used the ashes of plants from different locations. Unless further analysis of Tyre glass extends markedly the range of compositions produced there, we must assume that there was more than one production centre on the Mediterranean coast producing large quantities of raw plant ash glass between 9th and 11th centuries A.D. These findings have broader implications. With further work the Sr-Nd approach will allow the significance of the eastern Mediterranean coast in supplying raw glass in Medieval times to be evaluated. Finally the Sr-Nd analyses have been extremely useful in allowing us to resolve several issues arising for the previous major element studies – the relationship of coloured glasses and of compositional outliers to the other glasses.

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REFERENCES

- Aldsworth et al. 2002: F. Aldsworth / G. Haggarty / S. Jennings / D. Whitehouse, Medieval glassmaking at Tyre, Lebanon. *JGS* 44, 2002, 49-66.
- Banner 2004: J. L. Banner, Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. *Earth Science Reviews* 65, 2004, 141-194.
- Barkoudah / Henderson 2006: Y. Barkoudah / J. Henderson, Plant ashes from Syria and the manufacture of ancient glass: ethnographic and scientific aspects. *JGS* 48, 2006, 297-321.
- Brill 1999: R. H. Brill, *Chemical analyses of early glasses* (Corning, New York 1999).
- Brill / Fullagar 2009: R. H. Brill / P. D. Fullagar, Strontium-isotope studies of historical glasses and related materials: a progress report. *Annales du 17^e Congrès de l'A.I.H.V., Antwerp 2006* (Antwerp 2009) 552-557.
- Degryse / Schneider 2008: P. Degryse / J. Schneider, Pliny the Elder and Sr-Nd isotopes: tracing the provenance of raw materials for Roman glass production. *Journal of Archaeological Sciences*, 35, 2008, 1993-2000.
- Degryse et al. 2006: P. Degryse / J. Schneider / U. Haack / V. Lauwers / J. Poblome / M. Waelkens / Ph. Muechez, Evidence for glass recycling using Pb and Sr isotopic ratios and Sr-mixing lines: the case of early Byzantine Sagalassos. *Journal of Archaeological Science* 33, 2006, 494-501.
- Emery / George 1963: K. O. Emery / C. J. George, The shores of Lebanon. *Miscellaneous Papers in the Natural Sciences* 3 (Beirut 1963).
- Foucault / Stanley 1989: A. Foucault / D. J. Stanley, Late quaternary palaeoclimatic oscillations in East Africa recorded by heavy minerals in the Nile Delta. *Nature* 339, 1989, 44-46.
- Freestone 2002: I. C. Freestone, Composition and affinities of glass from the furnaces on the island site, Tyre. *JGS* 44, 2002, 67-77.
- Freestone 2006: I. C. Freestone, Glass production in Late Antiquity and the Early Islamic period: a geochemical perspective. In: M. Maggetti / B. Messiga (eds.), *Geomaterials in Cultural Heritage*. Geological Society of London Special Publication 257 (London 2006) 201-216.
- Freestone / Gorin-Rosen 1999: I. C. Freestone / Y. Gorin-Rosen, The great glass slab of Bet Shearim – an early Islamic glass-making experiment? *JGS* 41, 1999, 105-116.
- Freestone / Gorin-Rosen / Hughes 2000: I. C. Freestone / Y. Gorin-Rosen / M. J. Hughes, Primary glass from Israel and the production of glass in Late Antiquity and the Early Islamic period. In: M.-D. Nenna (ed.), *La route du verre. Ateliers primaires et secondaires du second millénaire av. J.C. au Moyen Âge*. Travaux de la Maison de l'Orient Méditerranéen 33 (Lyon 2000) 65-82.
- Freestone et al. 2003: I. C. Freestone / K. A. Leslie / M. Thirlwall / Y. Gorin-Rosen, Strontium isotopes in the investigation of early glass production: Byzantine and early Islamic glass from the Near East. *Archaeometry* 45, 2003, 19-32.
- Freestone et al. in press: I. C. Freestone / P. Degryse / J. Shepherd / Y. Gorin-Rosen / J. Schneider, Neodymium and Strontium Isotopes Indicate a Near Eastern Origin for Late Roman Glass in London. *Journal of Archaeological Science*, in press.
- Henderson 2003: J. Henderson, Glass trade and chemical analysis: a possible model for Islamic glass production. In: D. Foy / M.-D. Nenna (eds.), *Echanges et commerce du verre dans le monde antique*. Actes du colloque de l'Association Française pour l'Archéologie du Verre, Aix-en-Provence, Marseille 2001. *Monographies Instrumentum* 24 (Montagnac 2003) 109-124.
- Henderson et al. 2005: J. Henderson / J. A. Evans / H. J. Sloane / M. J. Leng / C. Doherty, The use of oxygen, strontium and lead isotopes to provenance ancient glasses in the Middle East. *Journal of Archaeological Science* 32, 2005, 665-673.
- Krom et al. 2002: M. D. Krom / D. J. Stanley / R. A. Cliff / J. C. Woodward, Nile River sediment fluctuations over the past 7000 yr and their key role in sapropel development. *Geology* 30, 2002, 71-74.
- Leslie et al. 2006: K. A. Leslie / I. C. Freestone / D. Lowry / M. Thirlwall, Provenance and technology of near Eastern glass: oxygen isotopes by laser fluorination as a compliment to Sr. *Archaeometry* 48, 2006, 253-270.
- Nir 1996: Y. Nir, The city of Tyre, Lebanon and its semi-artificial tombolo. *Geoarchaeology* 11, 1996, 235-250.
- Pin et al. 1994: C. Pin / D. Briot / C. Bassin / F. Poitrasson, Concomitant separation of strontium and samarium-neodymium for isotopic analysis in silicate samples, based on specific extraction chromatography. *Analytica Chimica Acta* 298, 1994, 209-217.
- Rehren 2008: Th. Rehren, A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides. *Journal of Archaeological Science* 35, 2008, 1345-1354.
- Tanimoto / Rehren 2008: S. Tanimoto / Th. Rehren, Interactions between silicate and salt melts in LBA glassmaking. *Journal of Archaeological Science* 35, 2008, 2566-2573.

ABSTRACT / ZUSAMMENFASSUNG / RÉSUMÉ

Technology and provenance of Levantine plant ash glass using Sr-Nd isotope analysis

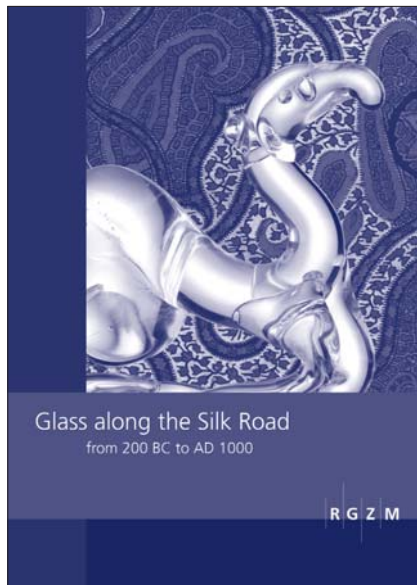
Measuring the isotopes of strontium (typical for the lime source in a glass) and neodymium (typical for the silica source) has been shown to be particularly useful in the investigation of the primary provenance of natron glass. The present study addresses the utility of this system in the investigation of glasses made using plant ash as the main source of flux. The isotopic analysis performed on primary chunk plant ash glass from the primary workshop at Tyre and the secondary workshop at Baniyas showed that both glass types were made from Levantine coastal sand (with a characteristic high ϵ Nd) but the two productions used the ashes of plants from different locations (showing a different $^{87}\text{Sr}/^{86}\text{Sr}$ signature). Hence, more than one centre on the Mediterranean coast produced raw plant ash glass between 9th and 11th centuries A.D., raising the significance of the eastern Mediterranean coast as a supplier of raw glass in Medieval times.

Technologie und Herkunft von levantinischem Pflanzenascheglas anhand Sr-Nd Isotopenanalysen

Die Messung der Strontium-Isotope, die typisch für die Kalkquelle im Glas sind, und der Neodymium-Isotope, die typisch für die Sodaquelle sind, hat sich als besonders hilfreich für die Untersuchung der primären Herkunft von Natron-Glas herausgestellt. Die vorliegende Studie befasst sich mit der Brauchbarkeit dieses Systems bei der Untersuchung von Gläsern, die unter Verwendung von Pflanzenasche als Hauptquelle des Flussmittels hergestellt wurden. Die Isotopenanalyse, die an Rohglasbrocken von Pflanzenaschenglas aus der primären Werkstätte in Tyros und aus der sekundären Werkstätte in Baniyas vorgenommen wurde, zeigte auf, dass beide Glastypen aus levantinischem Küstensand mit einem charakteristisch hohen ϵ Nd-Anteil hergestellt wurden, dass aber die beiden Produktionen Pflanzenaschen von verschiedenen Orten benutzten, was sich in einer unterschiedlichen $^{87}\text{Sr}/^{86}\text{Sr}$ -Signatur zeigt. Daher produzierte mehr als ein Herstellungszentrum an der Mittelmeerküste zwischen dem 9. und 11. Jahrhundert Pflanzenaschen-Rohglas, was die Bedeutung der östlichen Mittelmeerküste als Lieferant von Rohglas im Mittelalter vergrößert. D. K.

Techniques et provenance des verres du Levant utilisant des cendres à plantes utilisant Sr-Nd de l'analyse isotopique

La mesure de l'isotope du Strontium, typique du calcaire dans le verre, et l'isotope du Neodymium, typique de la soude, se sont montrés particulièrement utile dans la recherche de l'origine primaire du verre au bicarbonate. La présente étude se concentre sur l'utilité de ce système dans la recherche des verres, qui sont fabriqués avec l'utilisation de cendre de plantes comme source principale du flux. L'analyse isotopique, qui a été entrepris sur des morceaux de verre brut de cendres de plantes de verre des ateliers primaires à Tyr et d'ateliers secondaires à Baniyas, nous montre, que les deux types de verre fabriqués avec du sable des plages levantines ont été produits avec une teneur élevée en ϵ Nd caractéristique. Mais que les deux utilisent des cendres de plantes de lieux différents, ce qui se détermine par la signature $^{87}\text{Sr}/^{86}\text{Sr}$ différente. C'est pourquoi plus d'un centre de production en mer méditerranée entre le 9^e et le 11^e siècle produisait du verre brut à base de cendres de plantes, ce qui amplifie l'importance des côtes méditerranéennes comme fournisseur en verre brut au Moyen Age. E. L.



B. Zorn · A. Hilgner (eds)

Glass along the Silk Road from 200 BC to AD 1000

International conference within the scope of the »Sino-German Project on Cultural Heritage Preservation« of the RGZM and the Shaanxi Provincial Institute of Archaeology, December 11th-12th 2008

Since Antiquity the routes of the so-called Silk Road formed an important network for commercial, cultural and technological exchange and connected the East to the West. Since glass never played a significant role in Far Eastern cultures, glass finds from Far Eastern sites provide evidence for far-reaching trade relationships and imply cross-fertilization with other cultures. Thus the contributions in this volume deal with a wide geographical area covering a chronological range from 200 BC to AD 1000. The conference focused on recent results of scientific analyses of glass and on archaeological questions. The possibility of interdisciplinary research was one of the focal points of the conference and hence of this volume, as well as questions concerning workshops, raw material, technology and trade. One goal was to provide the participants with an insight beyond their own immediate concerns. By means of presenting studies of regionally specific glass forms and techniques as well as current methods and discoveries, even when not directly connected to the Silk Road, a broader perspective is offered.

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