

TRACE ELEMENT ANALYSIS IN PROVENANCING ROMAN GLASS-MAKING*

D. BREMS† and P. DEGRYSE

KU Leuven, Department of Earth and Environmental Sciences, Division of Geology, Celestijnenlaan 200E, B-3001 Leuven, Belgium

In this study, the use of trace elements as a provenance indicator for Roman natron glass is evaluated. Suitable glass-making sand raw materials are analysed for their trace elemental composition and compared to glass from known production centres. It is shown that the combined use of Nd isotopic and trace element analysis can be efficient for the provenancing of Roman glass. Trace elements associated with (de)colourants of glass are only present in small concentrations in glass-making sands. Background levels introduced to the glass by the sand raw material are defined and a lower threshold for the concentrations influenced by recycling is determined.

KEYWORDS: TRACE ELEMENTS, Nd ISOTOPES, PROVENANCE STUDIES, ROMAN, NATRON GLASS, RAW MATERIALS, BEACH SAND, WESTERN MEDITERRANEAN, INAA

INTRODUCTION

After decades of research, it still remains difficult to determine the primary provenance of Roman natron glass. This type of material was made by melting three components (i.e., quartz sand, natron and lime) at temperatures of about 1100°C (Gorin-Rosen 2000). During the production of natron glass, the raw materials are completely transformed and all their visible characteristics are lost, leaving only bulk chemical data as a potential discriminating feature. Unfortunately, the compositional variation of soda–lime–silica glass is limited due to the maximum attainable furnace temperatures and the shape of the Na₂O–SiO₂–CaO ternary phase diagram (Shahid and Glasser 1972). As a result, all Roman glass is relatively uniform in its major elemental composition (Sayre and Smith 1961; Freestone 2006). On top of that, raw glass is reworked into objects in secondary workshops, which are not necessarily located close to the primary origin of the glass (Freestone *et al.* 2002b). During this process, raw glass from different sources can be mixed and colouring agents can be added, introducing a wide variety of chemical elements. Furthermore, glass fragments or cullet can be recycled at any stage. During the past few years, however, studies on the provenance determination of ancient glass have revived due to the introduction of trace element and isotope analysis (Wedepohl and Baumann 2000; Freestone *et al.* 2003; Degryse *et al.* 2006; Shortland *et al.* 2007; Degryse and Schneider 2008; Degryse and Shortland 2009; Brems *et al.* 2013a,b).

During the Late Roman and Byzantine periods, raw glass appears to have been produced exclusively in a small number of primary production centres in Israel and Egypt (Gorin-Rosen 1995, 2000; Freestone *et al.* 2000, 2002a,b). Analytical data suggest that during the Hellenistic and Early Roman periods, natron glass production also took place in the western part of the

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†Corresponding author: email dieter.brems@ees.kuleuven.be

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Roman Empire (Degryse and Schneider 2008; Brems *et al.* 2012b). However, the exact location of any primary production centres in these regions remains unknown. Recently, a limited number of potential sources of suitable glass-making sand raw materials were identified along the coasts of Spain, France and Italy (Brems *et al.* 2012a,c), indicating that the necessary materials for glass production were indeed available in these parts of the Empire. In this paper, we present the trace elemental composition of these sand raw materials, and we investigate whether a distinction can be made between these possible source areas and glass from the known primary production centres in the eastern Mediterranean on the basis of trace element geochemistry.

TRACE ELEMENTS IN ROMAN GLASS

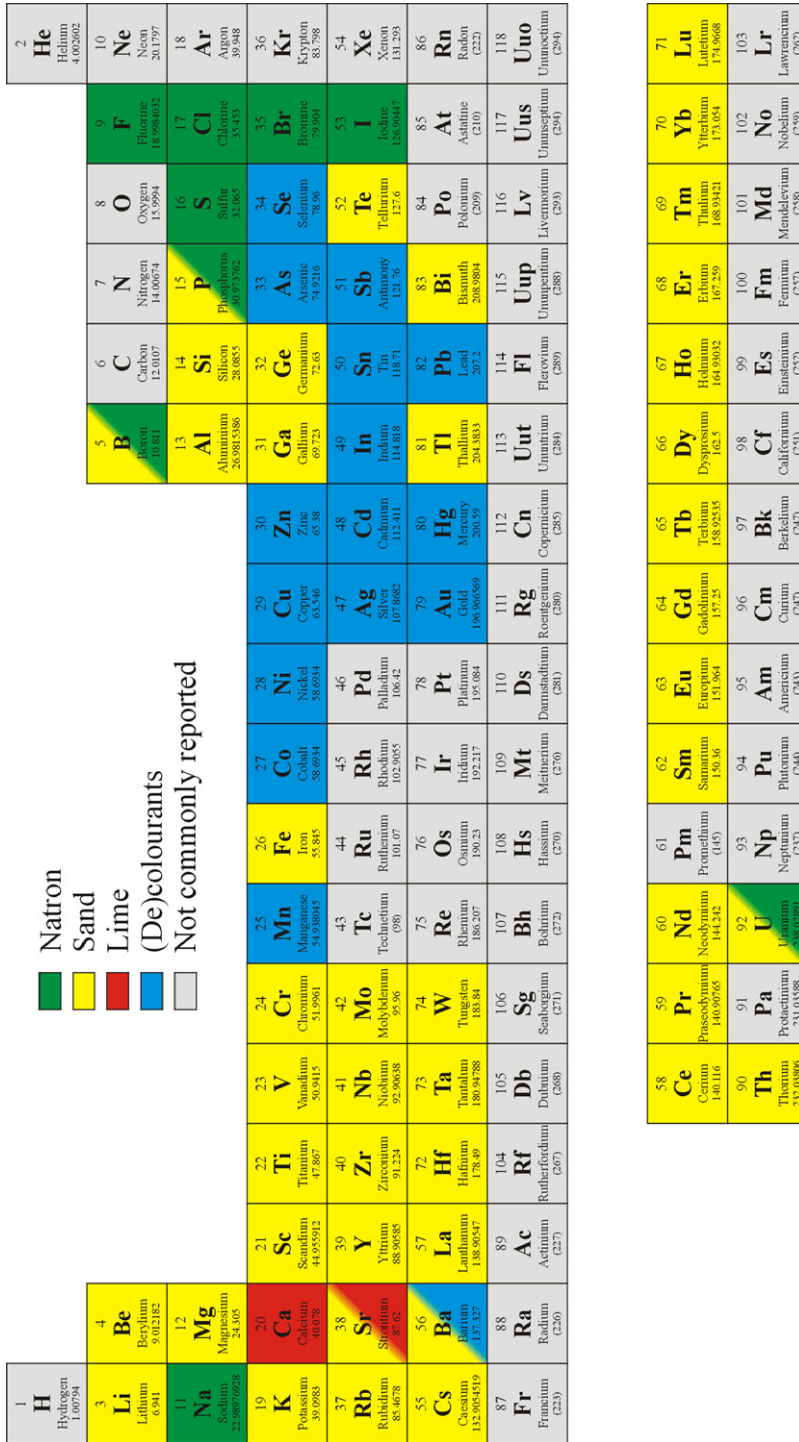
Roman natron glass can be seen as a mixture of three components: silica sand, lime-bearing material and natron as the soda-rich flux. Additionally, glass was often coloured or decoloured by adding a small amount of specific minerals. These raw materials all introduced a number of trace elements to the glass batch (Fig. 1). In particular, those solely related to the sand raw material are of interest as possible provenance indicators.

Natron

Natron was a relatively pure source of soda, found in evaporitic lakes. It was composed of sodium carbonates (trona, natron and nahcolite), sulphates (thenardite, burkeite and mirabilite), chlorides (halite) and insoluble material (quartz and clay) in varying proportions (Shortland 2004; Shortland *et al.* 2006, 2011; Currie 2008). Depending on the mineralogy of the evaporitic deposits, the concentration of elements such as Cl and S varies greatly (Brill 1999; Currie 2008; Shortland *et al.* unpublished data). These elements were probably almost entirely introduced to the glass batch by the natron flux. The concentration of Cl and S in the final glass is, however, limited by their solubility in soda–lime–silica melts (Bateson and Turner 1939; Gerth *et al.* 1998; Köpsel 2001; Shugar and Rehren 2002; Salviulo *et al.* 2004). The concentration of most other commonly measured trace elements in both modern and ancient evaporites from the Wadi Natrun is found to be very low (Currie 2008; Wedepohl *et al.* 2011b; Shortland *et al.* unpublished data). When compared with the concentration of trace elements in natron glass as given by, for example, Degryse and Shortland (2009) and Wedepohl *et al.* (2011a), only B, P, Br and U appear to occur in the same order of magnitude in both natron and natron glass. Mg concentrations are 30 times lower in the flux. The concentration of elements such as Li, K, V, Cr, Ni, Cu, Zn, Sr, Zr, Ba, Pb and the rare earth elements (REE) are between 60 and 1500 times lower in natron than in average natron glass (Currie 2008; Wedepohl *et al.* 2011b; Shortland *et al.* unpublished data).

Sand

Because of the small ionic size of Si^{4+} (0.026 nm) (Shannon 1976), only very small amounts of other elements such as Al, Ti, Fe and Ge can be incorporated into the crystal structure of quartz. Minor and trace elements in quartz-rich sands are generally concentrated in associated accessory minerals such as feldspar, pyroxene, amphibole, zircon, Fe–Ti oxides, monazite and clay minerals, among others. Sand deposits can contain different types and quantities of accessory minerals, depending on the nature of the source rocks and the local geological setting. Different mineralogical compositions of the sands will lead to different trace element signatures, which may be useful tracers for their origin.



The application of trace elements as provenance indicators for ancient glass was explored in recent studies. Roman natron glass generally contains relatively low levels of trace elements. This is attributed to the use of mineralogically mature sand, rich in quartz and relatively depleted in heavy minerals (Freestone *et al.* 2000, 2002b). HIMT glass typically contains higher concentrations of trace elements, suggesting the use of less pure quartz sands (Freestone *et al.* 2005). Promising groupings of glass could be made based on elements such as Zr–Ti (Aerts *et al.* 2003), Zr–Ti–Cr–La (Shortland *et al.* 2007; Reade 2009; Walton *et al.* 2009) and Zr–Sr–Ba (Freestone *et al.* 2000; Paynter 2006; Silvestri 2008; Silvestri *et al.* 2008). In most cases, these elements can be used to distinguish between different sand raw materials, since they are usually not related to the (de)colouring agents that could have been deliberately added to the glass batch. However, for Mn-decoloured glass, caution is in order. Mn ores are likely to introduce some minor amounts of Ba (Brill 1988; Jackson 2005; Paynter 2006; Silvestri 2008; Foster and Jackson 2010) and possibly Sr (Ganio *et al.* 2012) to the glass. Zr, together with Hf, is accumulated in the heavy mineral zircon. Trace elements such as Sc, Ti, V and Cr are generally correlated with iron oxides (Wedepohl *et al.* 2011a) or with specific heavy minerals such as rutile, ilmenite, titanite and chromite. Ba and Rb are related to alkali feldspar. Wedepohl and Baumann (2000) attributed relatively high Ba concentrations in Roman glass from Hambach to the presence of barite as a heavy mineral in the glass-making sand. Ga substitutes for Al in aluminium silicates (Wedepohl *et al.* 2011a). Other elements that are probably also related to the sand raw materials are Li, Be, Ge, Y, Nb, Mo, Te, Cs, La, Ta, W, Tl, Bi and Th (Shortland *et al.* 2007; Degryse and Shortland 2009; Reade 2009; Wedepohl *et al.* 2011a,b). B, P and U are partly derived from the silica source (Shortland *et al.* 2007), but they also come in with the natron flux. Sr is provided by both the sand (i.e., mostly feldspar and mica) and the source of lime (Brems *et al.* 2013a). In Mn-rich glasses, some of the Sr may be introduced through the Mn ore (Ganio *et al.* 2012).

Rare earth elements (REE) are generally used as provenance indicators of sediments and sedimentary rocks (e.g., McLennan 1989; Lidiak and Jolly 1996). In quartz-rich sands, these elements are mostly concentrated in the clay and silt fraction (Cullers *et al.* 1979; Tlig and Steinberg 1982; McLennan 1989; Yokoo *et al.* 2004). However, heavy mineral species can also contain significant amounts of REE. The light REE are accumulated in monazite and allanite, while the heavy REE are relatively concentrated in zircon and garnet (Gromet and Silver 1983; McKay 1989; McLennan 1989). Unlike the other REE, Eu can occur in a divalent state and as a result, it can be preferentially incorporated in plagioclase. Enrichment or depletion in plagioclase during weathering, erosion or sedimentary processes can cause positive or negative Eu anomalies in the REE patterns of sandy sediments, which in turn can be passed on to the glass (for a more extensive discussion, see also Degryse and Shortland 2009; Wedepohl *et al.* 2011b). Average REE patterns appear to be distinctly different between three major ancient glass groups; that is, soda-ash glass, natron glass and wood-ash glass (Wedepohl *et al.* 2011b). However, within the group of natron glass, REE patterns are relatively uniform (Degryse and Shortland 2009; Wedepohl *et al.* 2011b). This would indicate that the REE are derived from the clay fraction of the sand raw materials or from interaction with the furnace walls, and are of little use as a provenance indicator for Roman natron glass (Degryse and Shortland 2009; Walton *et al.* 2009).

Lime

Sr in natron glass is mostly derived from the shell or limestone introduced (whether deliberately or not) as the source of lime (Wedepohl and Baumann 2000; Freestone *et al.* 2003; Brems *et al.*

2013a). High Sr concentrations in glass suggest the use of shell fragments, while low Sr contents indicate the use of limestone. However, other mineral species in the sand raw material, such as feldspar and mica, can also introduce Sr to the glass (Degryse *et al.* 2006; Brems *et al.* 2013a). It has also been suggested that some of the Sr in glasses decolourized with Mn could have been introduced by the Mn ore (Ganio *et al.* 2012). The lime-bearing component of the glass batch can also introduce minor amounts of chemically related elements such as Mg, Fe and Mn. Rare earth elements and other trace elements only occur in very small concentrations in shell material (e.g., Wedepohl *et al.* 2011a,b).

(De)colourants and recycling

Pure soda–lime–silica glass, without any impurities, is essentially colourless. Most ancient glass fragments, however, contain a small amount of Fe_2O_3 . This results in a green–blue tint. This iron was usually unintentionally introduced as impurities in the sand raw material. The green–blue colour could be neutralized by the addition of Mn or Sb, which resulted in the oxidation of the Fe^{2+} to the practically colourless Fe^{3+} (Sayre and Smith 1961; Sayre 1963; Brill 1988). By adding different metals in varying concentrations and under different furnace conditions, a whole range of different colours could be achieved. Details of the effects of these different elements on the colour of glass are beyond the scope of this study and can be found in Weyl (1951), Bamford (1977), Green and Hart (1987) and Pollard and Heron (2008).

Elements commonly associated with (de)colouring in ancient glass are Mn, Co, Ni, Cu, Zn, As, Se, Ag, Cd, In, Sn, Sb, Au, Hg and Pb (Aerts *et al.* 2003; Shortland *et al.* 2007; Degryse and Shortland 2009; Reade 2009; Wedepohl *et al.* 2011a). Some of these elements do not influence the colour of the glass, but they occur as impurities in the mineral (de)colourants. Elevated concentrations of these (de)colourant-related elements (over 1000 ppm) suggest that they were deliberately added to the glass batch to influence the colour of the resulting product. Concentrations between about 100 ppm and 1000 ppm are typically interpreted as indications for glass recycling (Freestone *et al.* 2002b; Silvestri *et al.* 2005; Degryse and Shortland 2009; Foster and Jackson 2010). Remelting of a batch of colourless cullet with small amounts of coloured fragments would result in concentrations of these colouring elements not high enough to significantly alter the colour and suggest intentional addition, but too high to be explained by natural impurities in the sand raw materials. Low concentrations (<100 ppm) of trace elements such as Co, Cu, and Pb are said to suggest that the glass was produced from primary raw materials and that recycling was limited, or that recycling took place after very careful selection of cullet to avoid contamination (Silvestri 2008; Silvestri *et al.* 2008). These concentration boundaries are, however, arbitrary. Little is known about the actual background concentrations of (de)colourant-related elements in glass-making sand raw materials.

Roman natron glasses decoloured by Mn often show elevated Ba contents and a strong positive correlation between Mn and Ba (Brill 1988; Paynter 2006; Foster and Jackson 2010). This is consistent with the use of wad or a mixture of pyrolusite (MnO_2) and psilomelane ($(\text{Ba},\text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$) as the source of Mn (Jackson 2005; Silvestri 2008). Next to Ba, the Mn source may also introduce extra Sr to the glass (Ganio *et al.* 2012).

OBJECTIVES AND METHODS

The trace elemental composition of natron glass will be a combination of elements present in the sand, the natron and the lime, and possibly any (de)colourants that were added to the glass batch.

In this study, we investigate the variation in trace element signatures of 11 potential glass-making sand raw materials (Fig. 2 and Table 1). The analysed samples belong to a much larger set of 178 beach sand samples from the Mediterranean coasts of Spain, France and Italy, which were previously evaluated for their suitability for natron glass production (Brems *et al.* 2012c). The major elemental compositions of these sands were used to calculate the compositions of glass that

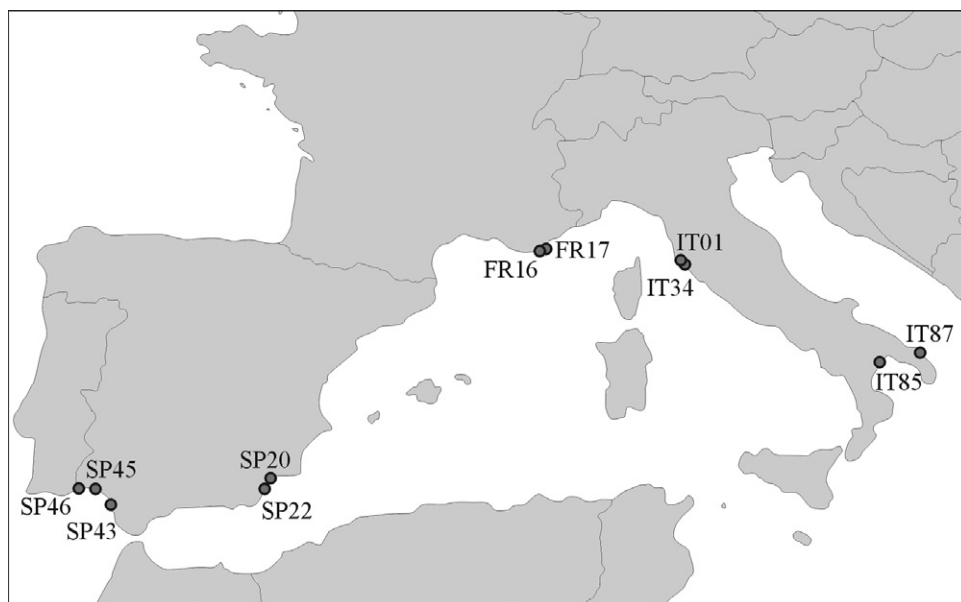


Figure 2 A map of the western Mediterranean, showing the sample locations of the beach sands analysed.

Table 1 Sampling locations of beach sands analysed in this study

Sample	Location	Latitude ($^{\circ}$ N)	Longitude ($^{\circ}$ E)
<i>Spain</i>			
SP46	Isla Canela	N37 $^{\circ}$ 10'34.08"	W007 $^{\circ}$ 21'15.58"
SP45	Mazagón	N37 $^{\circ}$ 07'44.86"	W006 $^{\circ}$ 49'29.42"
SP43	Sanlúcar de Barrameda	N36 $^{\circ}$ 46'48.43"	W006 $^{\circ}$ 21'59.54"
SP22	Las Marinas de Vera (Garrucha)	N37 $^{\circ}$ 11'50.56"	W001 $^{\circ}$ 48'44.82"
SP20	El Rubial	N37 $^{\circ}$ 24'02.10"	W001 $^{\circ}$ 35'33.26"
<i>France</i>			
FR16	Les Bormettes, La Londe-les-Maures	N43 $^{\circ}$ 07'16.69"	E006 $^{\circ}$ 15'38.86"
FR17	Cavalaire-sur-Mer	N43 $^{\circ}$ 10'57.28"	E006 $^{\circ}$ 32'28.29"
<i>Italy</i>			
IT34	Torre del Sale, Piombino	N42 $^{\circ}$ 57'14.50"	E010 $^{\circ}$ 36'00.71"
IT01	Cala Viola	N42 $^{\circ}$ 50'19.53"	E010 $^{\circ}$ 46'29.46"
IT85	Metaponto Lido	N40 $^{\circ}$ 20'34.11"	E016 $^{\circ}$ 49'23.68"
IT87	Masseria Maime	N40 $^{\circ}$ 33'27.00"	E018 $^{\circ}$ 02'36.73"
Shell	Mixture of shell fragments from southern France and north-western Italy	–	–

could be produced after the addition of pure natron. These compositions were then compared to the average composition of Roman natron glass. The 11 beach sands under investigation in the present study were found to be the most suitable for the production of natron glass, with or without the need for an extra source of lime (Brems *et al.* 2012c). Sand deposits from specific beaches in Basilicata (sand sample IT85), Puglia (IT87) and Tuscany (IT34) are suitable for the production of natron glass in their present form. Sands from particular locations in the province of Huelva (SP46, SP45 and SP43), the Murcia region (SP22 and SP20) and Provence (FR16 and FR17) contain insufficient CaO to produce a stable glass. However, after the addition of an extra source of lime, these sands can be melted into glass that would show a very close resemblance to Imperial Roman natron glass (Brems *et al.* 2012c). By determining their trace elemental composition, we can examine whether the elements commonly attributed to the sand raw material can be used to distinguish between these potential sources of natron glass and raw glass from the known primary production centres in the Levant and Egypt. The concentrations of trace elements generally associated with (de)colouring agents will provide more information about the background levels for these elements that are attributable to the sand raw materials. A mixture of shell material collected from several beaches along the Mediterranean coast of France and north-west Italy was also included in the analysis to investigate the possible influence of the addition of extra shell fragments on the final bulk trace element signature of a glass batch.

Sand and shell samples were finely crushed in an agate mortar and analysed for their trace elemental composition using instrumental neutron activation analysis (INAA) at the Interfaculty Reactor Institute of the Delft University of Technology, the Netherlands (Bode 1990; Greenberg *et al.* 2011). About 200 mg of sample material was weighed and packed in high-purity polyethylene capsules. Together with a standard and blank, the capsules containing the samples were sealed in polyethylene foil and packed in an irradiation container. This container was irradiated by bringing it near the reactor core using a pneumatic irradiation tube system. After irradiation, the samples were unpacked and the emitted gamma radiation was measured using a semiconductor gamma-ray spectrometer. Results were processed using a UNIX-based computer system.

RESULTS AND DISCUSSION

The results of the trace element analysis of the suitable glass-making sands and the shell fragments are listed in Table 2. This table also contains previously unpublished trace elemental data for a sand sample from the mouth of the River Belus, sampled by R. H. Brill in the 1960s (Brill 1999) and analysed via ICP–MS by Degryse. Table 3 shows the correlation matrix for the trace elements analysed by INAA and major and minor elements previously determined via ICP–OES (methodology and data published by Brems *et al.* 2012c). Elements for which the concentration was above the detection limit for only three samples or less were discarded. For Br, measurable concentrations were detected in only four sand samples, so any correlations found with this element must be evaluated carefully to rule out any errors due to the small amount of data points.

Natron-related elements

The elements Na, Cl, S, P, F, Br, I, B and U in natron glass are fully or partially attributed to the natron flux used (Fig. 1). Of these elements, Na and P were previously analysed via ICP–OES and discussed in Brems *et al.* (2012c). Cl, Br and I could be analysed using INAA. Cl concentrations

Table 2 The trace element analysis results of the beach sands and shell analysed. The $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and ϵ_{Nd} values are taken from Brems et al. (2013a,b). The Al_2O_3 and Fe_2O_3 data are published by Brems et al. (2012c). Elemental data for sample BRILL 674 (Brill 1999) were obtained via ICP-MS by Degryse (previously unpublished). Isotopic data for BRILL 674 are from Degryse and Schneider (2008)

	SP46	SP45	SP43	SP22	SP20	FR16	FR17	IT34	IT01	IT85	IT87	Shell	BRILL 674
Cl	(wt%)	0.15	0.12	0.34	0.11	0.17	0.16	0.01	0.01	0.10	0.14	0.12	nd
TiO ₂		0.31	0.61	0.16	0.27	0.16	0.42	0.10	0.34	0.22	0.08	<0.01	0.05
MnO	(wt%)	0.05	0.03	0.01	0.05	0.02	0.03	0.09	0.02	0.11	0.03	0.00	0.013
Li	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3
Sc	(ppm)	3.90	2.20	1.17	4.30	2.86	3.17	2.37	2.24	4.05	1.17	0.04	1
V	(ppm)	32.9	31.8	12.8	31.2	23.5	28.5	12.9	24.9	22.0	14.8	<0.64	3
Cr	(ppm)	22.6	16.8	8.2	19.1	14.7	20.2	124.9	277.0	72.2	16.2	0.93	7
Co	(ppm)	4.52	3.26	1.54	4.53	3.07	3.20	2.32	1.81	3.68	1.08	0.20	1
Ni	(ppm)	<41	<37	<26	21	<36	<37	<35	<35	<42	<26	<36	3
Cu	(ppm)	<47	<39	<41	<45	<37	<94	<30	<38	<54	<35	<33	4
Zn	(ppm)	47	84	11.7	47	32	272	16	15	15	5.3	1.2	11
Ga	(ppm)	<20	<17	<17	13	<16	<36	<26	<23	<31	<16	<15	nd
As	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	6.6
Se	(ppm)	<0.87	<0.82	<0.59	<0.91	<0.77	<0.77	<0.74	<0.79	<0.91	<0.59	<0.36	nd
Br	(ppm)	<6.4	<6.1	11.3	<6.4	3.5	<11	<9.3	<6.2	<10	5.4	5.0	nd
Rb	(ppm)	35.3	25.5	38.9	25.4	24.1	23.6	36.1	28.6	30.7	24.2	<1.2	25.0
Sr	(ppm)	84	82	94	107	32	113	192	50	196	31.5	1550	287
Y	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	7.0
Zr	(ppm)	67	170	42	<180	71	107	<68	<20	190	40	<16	13
Nb	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.8
Mo	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.3
Ag	(ppm)	<1.9	<2.0	<1.2	<2.0	<1.8	<1.7	<2.0	<2.3	0.8	<1.2	<0.6	nd
Cd	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03
In	(ppm)	<0.049	<0.045	<0.039	<0.054	0.026	<0.085	<0.067	<0.054	<0.077	<0.041	<0.034	nd
Sn	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.2
Sb	(ppm)	0.65	0.71	0.44	1.38	0.90	0.42	0.45	0.82	<0.42	0.22	0.14	29.53
I	(ppm)	<2.0	1.10	<1.4	<2.0	<1.4	<3.1	<2.8	<2.0	<3.2	<1.5	<1.2	nd
Cs	(ppm)	1.11	0.75	1.16	1.63	4.07	0.48	4.26	0.97	0.60	0.34	0.04	0.61

Ba	(ppm)	180	110	159	169	95	150	186	136	129	230	280	15	263
La	(ppm)	nd	nd	nd	nd	nd	<150	nd	nd	<140	nd	<96	nd	7.56
Ce	(ppm)	<140	<130	<120	<140	<120	<120	<120	<120	<140	<150	<96	<65	13.87
Pr	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.76
Nd	(ppm)	11.0	11.1	4.8	9.0	6.2	8.8	4.5	5.2	6.3	14.7	11.6	0.4	7.55
Sm	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.51
Eu	(ppm)	0.46	0.42	0.27	0.40	0.28	0.51	0.47	0.46	0.28	0.60	0.55	0.01	0.66
Gd	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.38
Tb	(ppm)	0.28	0.26	0.11	0.25	0.17	0.26	0.19	0.25	0.14	0.35	0.25	<0.022	0.21
Dy	(ppm)	2.01	1.75	0.81	2.04	1.54	1.79	1.46	1.52	1.33	2.60	1.73	<0.19	1.08
Ho	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.24
Er	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.60
Tm	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.09
Yb	(ppm)	0.78	0.72	0.41	0.99	0.66	0.73	0.81	0.51	0.51	1.19	0.62	0.02	0.51
Lu	(ppm)	0.13	0.11	0.06	0.15	0.10	0.12	0.12	0.07	0.09	0.18	0.09	<0.0073	0.08
Hf	(ppm)	1.80	5.07	1.38	1.94	1.82	2.45	2.81	1.01	2.18	5.35	1.10	0.03	nd
Ta	(ppm)	0.34	0.48	0.22	0.35	0.29	0.47	0.48	0.18	0.42	0.48	0.25	0.02	nd
Hg	(ppm)	<0.20	<0.26	<0.24	<0.19	<0.16	<0.19	<0.23	<0.16	<0.17	<0.70	<0.13	<0.081	nd
Tl	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.23
Pb	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	8.2
Bi	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13
Th	(ppm)	2.30	3.37	1.86	2.74	2.15	3.24	1.91	1.55	2.85	5.45	2.06	0.06	1.46
U	(ppm)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.59
$^{87}\text{Sr}/^{86}\text{Sr}$		0.71378	0.71197	0.71369	0.71222	0.71559	0.72358	0.71315	0.71034	0.71357	0.71079	0.70867	0.70915	0.71159
$^{143}\text{Nd}/^{144}\text{Nd}$		0.512229	0.512193	0.512167	0.512057	0.512035	0.512002	0.512118	0.512156	0.512184	0.512325	0.512424	0.512297	0.512393
ϵ_{Nd}		-7.99	-8.68	-9.20	-11.33	-11.76	-12.40	-10.14	-9.40	-8.86	-6.11	-4.17	-6.66	-4.80
Al_2O_3	(wt%)	3.686	1.867	2.210	3.841	2.771	4.195	7.701	2.841	3.121	2.676	1.261	0.04	3.61
$\text{Fe}_2\text{O}_3(\text{t})$	(wt%)	1.389	1.018	0.492	1.925	1.365	1.640	1.501	0.988	0.957	1.449	0.545	0.01	0.24

Table 3 The correlation matrix for the main and trace elements of the sand samples analysed

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cl	TiO ₂	MnO	Sc	V	Cr	Co	Zn	Br	Rb	Sr	Zr	Sb	Cs	Ba	Nd	Eu	Tb	Dy	Yb	Lu	Hf	Ta	Th		
SiO ₂	1.00																																	
Al ₂ O ₃	0.03	1.00																																
Fe ₂ O ₃	-0.12	0.58	1.00																															
MgO	-0.50	0.26	0.72	1.00																														
CaO	-0.90	-0.43	-0.21	0.26	1.00																													
Na ₂ O	-0.07	0.94	0.36	0.05	-0.29	1.00																												
K ₂ O	-0.10	0.05	-0.25	-0.42	0.11	0.16	1.00																											
P ₂ O ₅	-0.11	0.04	0.57	0.54	0.00	-0.08	-0.50	1.00																										
Cl	0.31	0.14	0.12	-0.23	-0.40	0.22	0.02	0.20	1.00																									
TiO ₂	0.49	0.35	0.33	-0.15	-0.58	0.29	-0.11	0.20	0.10	1.00																								
MnO	-0.76	-0.04	0.24	0.33	0.71	-0.01	0.39	0.12	-0.45	-0.20	1.00																							
Sc	-0.26	0.46	0.91	0.74	-0.01	0.23	-0.03	0.56	-0.13	0.23	0.49	1.00																						
V	0.34	0.42	0.68	0.35	-0.50	0.19	-0.25	0.46	-0.07	0.77	-0.10	0.66	1.00																					
Cr	0.09	-0.07	-0.18	-0.19	0.01	-0.11	0.27	-0.70	-0.52	-0.03	0.17	-0.09	-0.12	1.00																				
Co	-0.02	0.42	0.90	0.56	-0.23	0.20	-0.06	0.66	0.17	0.44	0.27	0.90	0.76	-0.33	1.00																			
Zn	0.31	0.20	0.42	-0.14	-0.42	0.19	-0.05	0.16	0.77	0.42	-0.25	0.13	0.26	-0.26	0.44	1.00																		
Br	0.31	0.75	0.42	-0.58	-0.49	0.99	0.66	-0.30	0.98	0.89	-0.13	0.26	0.26	-0.30	0.55	0.87	1.00																	
Rb	0.02	-0.21	-0.30	-0.36	0.06	-0.14	0.85	-0.34	0.20	-0.30	0.24	-0.13	-0.41	0.12	-0.08	0.00	0.55	1.00																
Sr	-0.80	-0.32	-0.39	0.05	0.89	-0.11	0.12	-0.17	-0.31	-0.52	0.45	-0.25	-0.52	-0.08	-0.42	-0.40	-0.37	-0.05	1.00															
Zr	-0.28	0.07	0.44	0.29	0.21	0.07	-0.02	0.64	-0.33	0.59	0.71	0.52	0.46	0.70	0.48	0.08	0.55	-0.22	-0.04	1.00														
Sb	0.19	0.17	0.38	-0.12	-0.32	0.20	0.03	0.07	0.80	0.19	-0.23	0.12	0.05	-0.16	0.34	0.96	0.89	0.09	-0.30	0.07	1.00													
Ba	-0.03	-0.14	0.05	0.16	0.07	-0.24	-0.15	0.01	-0.24	-0.45	0.16	0.03	-0.29	0.10	-0.02	-0.16	-0.48	0.16	-0.16	-0.24	-0.16	1.00												
Cs	-0.67	-0.05	-0.15	0.15	0.64	0.11	0.18	-0.03	-0.02	-0.36	0.29	-0.01	-0.24	-0.20	-0.17	-0.23	-0.13	-0.08	0.82	-0.11	-0.09	-0.55	1.00											
Nd	-0.36	-0.40	0.15	0.16	0.47	-0.39	0.00	0.44	-0.06	0.12	0.43	0.33	0.26	-0.20	0.33	0.09	-0.01	-0.14	0.39	0.51	0.12	-0.45	0.52	1.00										
Eu	-0.68	0.11	0.24	0.14	0.58	0.24	0.21	0.18	0.05	0.02	0.59	0.31	0.03	-0.26	0.28	0.22	0.32	-0.10	0.63	0.43	0.33	-0.38	0.69	0.67	1.00									
Tb	-0.60	-0.10	0.41	0.31	0.56	-0.10	0.13	0.41	-0.11	0.08	0.73	0.54	0.24	-0.21	0.53	0.21	0.26	-0.05	0.43	0.62	0.26	-0.16	0.42	0.82	0.86	1.00								
Dy	-0.35	-0.02	0.59	0.52	0.45	-0.11	-0.06	0.54	-0.17	0.11	0.66	0.73	0.42	-0.14	0.64	0.14	0.07	-0.23	0.27	0.64	0.21	-0.19	0.39	0.84	0.73	0.92	1.00							
Yb	-0.51	0.26	0.72	0.68	0.30	0.17	-0.16	0.69	-0.08	0.22	0.56	0.82	0.51	-0.26	0.71	0.09	0.18	-0.33	0.12	0.78	0.15	-0.29	0.35	0.66	0.61	0.74	0.89	1.00						
Lu	-0.42	0.28	0.76	0.66	0.20	0.16	-0.13	0.66	-0.05	0.28	0.51	0.86	0.59	-0.21	0.76	0.14	0.30	-0.31	0.03	0.75	0.20	-0.33	0.31	0.66	0.57	0.72	0.89	0.99	1.00					
Hf	-0.06	0.02	0.27	0.01	0.05	0.04	-0.08	0.48	-0.06	0.63	0.37	0.34	0.43	-0.05	0.37	0.14	0.69	-0.25	-0.09	0.99	0.10	-0.41	-0.02	0.57	0.36	0.49	0.55	0.63	0.62	1.00				
Ta	0.17	0.44	0.52	0.05	-0.34	0.40	-0.13	0.30	0.15	0.80	0.04	0.45	0.68	0.05	0.50	0.44	0.76	-0.42	-0.34	0.82	0.40	-0.59	-0.04	0.36	0.32	0.31	0.44	0.58	0.63	0.79	1.00			
Th	-0.24	-0.15	0.34	0.18	0.25	-0.15	0.01	0.42	0.02	0.30	0.49	0.45	0.27	0.09	0.38	0.20	0.79	-0.10	0.02	0.84	0.50	-0.40	0.19	0.74	0.45	0.61	0.73	0.73	0.74	0.84	0.67	1.00		

in the analysed sand samples vary between 0.01 and 0.53%. This variation is a result of the varying amounts of halite from the seawater adhering to the beach sand grains. Concentrations of Br in the beach sands range from below detection limit to 20 ppm and are strongly correlated with Cl (correlation coefficient $r = 0.984$). Iodine (I) was found to be below the detection limit for all samples analysed except for sand SP45, which contains 1.1 ppm I. Although the shell fragments were washed to remove sand and salt particles before crushing, they still contain 0.12% Cl, indicating its presence as inclusions in the shell itself. These results show that beach sand raw materials and seashell fragments can introduce some 'natron-related' elements such as Cl and Br to the glass batch.

Sand-related elements

The elements that are exclusively related to the sand raw materials are of particular interest for provenance studies of ancient glass. Two of those elements are Zr and Hf, as they are almost entirely derived from the heavy mineral zircon. The Zr contents of the sands and shell analysed range from below the detection limit to 190 ppm. It must be noted, however, that the reported detection limits are rather high: <16 ppm for the shell material and <68 to <220 ppm for the sand samples. Concentrations of Hf vary between 1.01 and 5.35 ppm in the sand. Shell material only contains 0.03 ppm Hf. Zr and Hf are very strongly correlated ($r = 0.995$) with Zr/Hf ratios between 30 and 40, typical for zircons derived from granites (Gulson 1969).

Next to Zr and Hf, TiO_2 is also generally related to the heavy mineral fraction in the sand raw materials and as a result they too are often correlated. The TiO_2 contents range from 0.08 to 0.61%. In a biplot of TiO_2 versus Zr, the expected correlation between the two elements is indeed present ($r = 0.948$; Fig. 3 (a)). Sand sample IT85, however, does not follow the same correlation and is relatively enriched in Zr, reflecting a relative enrichment of zircon with respect to the Ti-rich mineral species, such as rutile, ilmenite and/or titanite, in the sand. Sc concentrations in the sands vary between 1.17 and 4.30 ppm. The V contents lie between 12.8 and 32.9 ppm. Moderate to good correlations of these elements with Fe_2O_3 and TiO_2 suggest that they are also related to the heavy mineral fraction of the sand. The concentration of Ta in the beach sands varies between 0.18 and 0.48 ppm. Ta is relatively well correlated with other elements of group 4 and 5 of the periodic table, such as TiO_2 ($r = 0.801$), V ($r = 0.676$), Zr ($r = 0.825$) and Hf ($r = 0.786$). The most common heavy mineral containing Cr is chromite. This mineral is generally associated with ultramafic igneous rocks. The Cr concentrations in the sands analysed in this study vary widely, between 8.2 and 277 ppm.

Concentrations of Rb range from 23.6 to 38.9 ppm in the analysed sands. A correlation between K_2O and Rb ($r = 0.847$) indicates that Rb is present in K-feldspar. Cs values range from 0.34 to 4.26 ppm, with sands IT34 and SP20 having the highest values. There is no clear correlation between Cs and the other alkali elements. The Ba concentrations in the sands vary between 95 and 280 ppm. Ba is often said to be related to alkali feldspar. However, the data show no correlation between Ba and K_2O ($r = 0.182$) or between Ba and Rb ($r = -0.077$). Although not very strong, correlations are present between Ba and Sr ($r = 0.816$) and Ba and Ca ($r = 0.642$). This suggests that Ba is not exclusively related to feldspars and that it can also be derived from the carbonate fraction of the beach sands. However, the shell material analysed in this study only contains 15 ppm Ba. A connection to barite could not be investigated, since concentrations of S are not available.

Ga could only be detected in one sample, SP22, where it reaches 13 ppm. Detection limits for this element were, however, generally of the same order of magnitude. Concentrations of Th

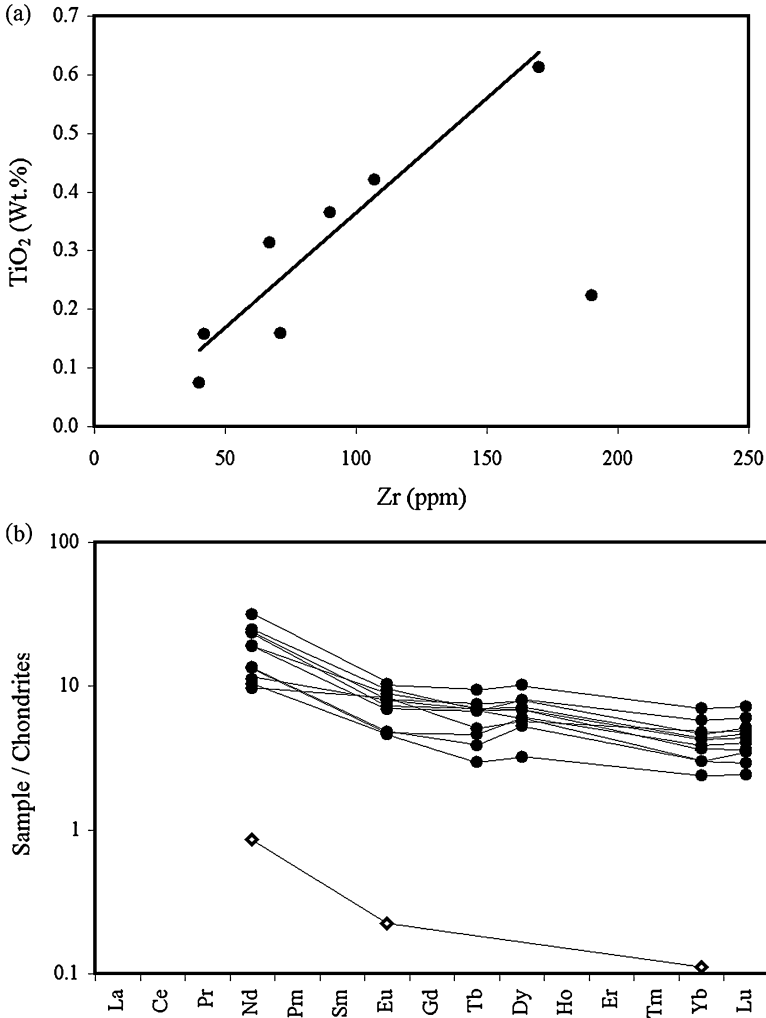


Figure 3 (a) The covariation of Zr with TiO₂ in the analysed beach sands. The trendline ($r = 0.948$) is calculated after removal of sand IT85 from the data set. (b) The chondrite-normalized rare earth element patterns of the sands and shell analysed. The black dots are the sand samples and the open diamond is the shell material.

range from 1.55 to 5.45 ppm in the sands. Th is correlated with Zr ($r = 0.839$), Hf ($r = 0.838$) and the (heavy) rare earth elements ($r = 0.726-0.739$), indicating its presence in zircon (Wang *et al.* 2011; Nardi *et al.* 2012).

Rare earth element concentrations are chondrite-normalized using the values of Sun and McDonough (1989) and the REE patterns are shown in Figure 3 (b). Only Nd, Eu, Tb, Dy, Yb and Lu could be analysed. Ce was below the detection limit in all samples. The REE patterns of the sands are relatively flat, with a slight enrichment in light rare earth elements (LREE). Only sand sample FR17 shows a small positive Eu anomaly, consistent with its relatively high feldspar content (Brems *et al.* 2012c). For the other samples analysed, no significant Eu anomalies were found. The REE concentrations in the shell fragments are more than one order of magnitude

lower than in the sands. The chondrite-normalized REE pattern of the shell material is similar to those of the sands, although possibly somewhat more enriched in LREE (Fig. 3 (b)).

Lime-related elements

The concentration of Sr in the sands analysed varies between 32 and 315 ppm, with a good correlation between Sr and Ca ($r = 0.892$). The use of Sr isotope ratios and Sr concentrations for the provenancing of Roman natron glass, and especially the source of lime used, is extensively discussed by Brems *et al.* (2013a).

Shell fragments have relatively low concentrations of most of the trace elements analysed. Only Sr is strongly concentrated in shell (1550 ppm). Cl and Br are present in concentrations similar to those found in the sands. The other elements analysed occur in concentrations at least one order of magnitude smaller than in the sand samples. Results for the REE concentrations are comparable to those reported for clam shells from the North Sea by Wedepohl *et al.* (2011b).

(De)colourant-related elements

Mn and Sb are often present in elevated concentrations in Roman natron glass (Sayre and Smith 1961; Sayre 1963; Henderson 1985; Jackson 2005; Freestone 2008; Silvestri 2008; Foster and Jackson 2009). These elements were deliberately added to the batch to make the glass colourless by oxidizing iron, or to combine with other elements to create a variety of colours. The MnO concentration in the analysed sands ranges from 0.01 to 0.11%. These values can be seen as the background level for Mn, which can be attributed to the sand raw material (see also Brems *et al.* 2012c). Concentrations of MnO higher than 0.1% in natron glass are influenced by deliberate addition or by recycling. As an impurity in the Mn decolourizing agent, extra Ba is often introduced to the glass, resulting in a strong positive correlation between the two elements (Brill 1988; Jackson 2005; Silvestri 2008). The data presented in this study show no significant correlation between MnO and Ba ($r = 0.285$). Sb contents of more than 37 500 ppm (4.99% Sb₂O₃) have been reported for natron glass (Arletti *et al.* 2006). Most of the sands analysed in this study contain low concentrations of Sb; that is, below 1.4 ppm. Only sand FR16 has higher Sb levels of 19.2 ppm. The Zn concentrations of most sands analysed vary between 5.3 and 84 ppm. Sand sample FR16, however, contains 272 ppm of Zn. The very high Zn and Sb contents in sand FR16 can be attributed to the former exploitation of a Pb–Zn–Ag deposit in Les Bormettes (Féraud 1983; Artignan and Nauchbaur 2007). Exploitation of this small-scale ore deposit had already commenced during the Gallo-Roman period and ended in 1908 (Artignan and Nauchbaur 2007). Erosion and redeposition of material from local tailings results in relatively high concentrations of metals in the local beach sand. Next to Zn and Sb, soils in the area locally contain elevated concentrations of Pb, Cd, Cu and Hg (Artignan and Nauchbaur 2007).

Of all sands analysed, only SP22 contains measurable amounts of Ni; that is, 21 ppm. Measured concentrations of Co in the sands vary between 1.1 and 4.5 ppm. The Cu, Se and Hg concentrations are below the INAA detection limit for all samples analysed. Ag is below the detection limit for all samples except for sand IT85, which contains 0.80 ppm Ag. Indium (In) is only above the detection limit in sand sample SP20, where it reaches 0.03 ppm.

TRACE ELEMENTS AS A PROVENANCE INDICATOR FOR THE SILICA SOURCE?

To determine the provenance of an archaeological glass artefact, we must find a measurable property that can link the glass to a particular production area. Most of the suitable sand raw

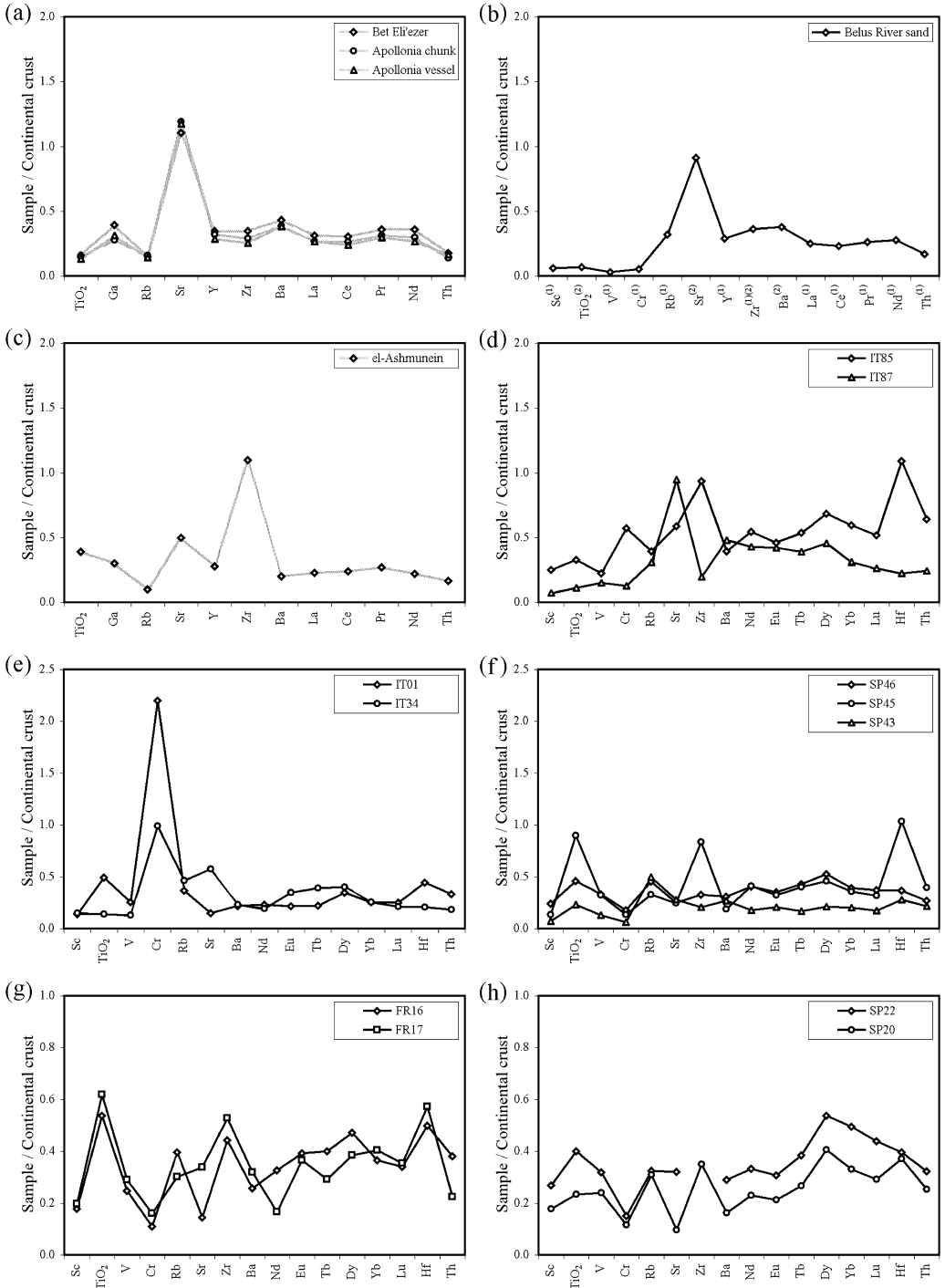
materials from the western Mediterranean can be distinguished from those from the east by relying on their Nd isotopic composition (Brems *et al.* 2013b). Raw natron glass from Egypt and Syro-Palestine has relatively homogeneous ϵ_{Nd} values between -6.0 and -5.1 (Degryse and Schneider 2008; Freestone *et al.* unpublished data). Western Mediterranean beach sands mostly have lower ϵ_{Nd} values; that is, usually lower than -8 . However, Brems *et al.* (2013b) have shown that suitable sand raw materials from two locations in the south-east of Italy (IT85 and IT87) also have relatively high ϵ_{Nd} values, which coincide with those thought to be typical for raw glass produced in the eastern Mediterranean. Differences in trace element patterns may help to resolve this problem.

To evaluate the use of trace elements as a provenance indicator for Roman natron glass, we must compare the trace elemental signature of the sands analysed in this study to those of the known glass groups and raw materials from the eastern Mediterranean. For easier comparison, trace element data are often normalized to a common reference. In glass studies, this is usually the average continental Earth's crust (Freestone *et al.* 2002b; Wedepohl *et al.* 2011a,b). In this study, we use the average continental crust values of Wedepohl (1995).

Selected trace element data for raw natron glass and glass vessels from the Byzantine–Islamic primary workshops at Bet Eli'ezer and Apollonia on the coast of Israel are given by Freestone *et al.* (2000). Their compositional profiles (Fig. 4 (a)) are relatively uniform, indicating the geochemical homogeneity of the sand sources along the Levantine coast (Freestone 2006). Average trace element patterns for Belus River sands are indeed very similar in shape (Fig. 4 (b); Brill 1988, 1999; Degryse previously unpublished; Table 2). Glasses from a workshop at Tel el-Ashmunein, Egypt, show a very different trace element distribution (Fig. 4 (c)). They are readily distinguished from the Syro-Palestinian glasses by their lower Sr and Ba, and higher Zr concentrations (Freestone *et al.* 2000). The different origins of these glass groups was confirmed by Sr isotopic analysis, which suggested the use of shell-bearing beach sands for the production of the Syro-Palestinian glasses, and inland sand and limestone for the Egyptian glass (Freestone *et al.* 2003). Trace elemental compositions similar to those of the Syro-Palestinian raw glass were also found in glasses from Cyprus and Anglo-Saxon England (Freestone *et al.* 2002b; Freestone 2008). Other glasses—for example, from Carthage—have both high Sr and Zr, indicating that their primary origin lies elsewhere (Freestone *et al.* 2000).

Sand raw material IT87 has an ϵ_{Nd} value of -4.17 (Brems *et al.* 2013b). This is higher than the ϵ_{Nd} values of -6.0 to -5.1 characteristic of raw natron glass from Israel (Degryse and Schneider 2008; Freestone *et al.* unpublished data). However, ϵ_{Nd} values as high as -1 have been reported for sands 400 m south of the mouth of the Belus River (Degryse and Schneider 2008) and Nile River sediments (Goldstein *et al.* 1984; Weldeab *et al.* 2002; Scrivner *et al.* 2004). Therefore, it is very likely that a suitable sand source with such high ϵ_{Nd} values also exists along the Syro-Palestinian coast. Sand raw material IT85 has an ϵ_{Nd} value of -6.11 (Brems *et al.* 2013b). Trace element signatures of these Italian sands are shown in Figure 4 (d). The two trace element patterns are markedly different. Sand IT87 generally has the lower concentration of trace

Figure 4 (following page) Trace element concentrations normalized to the mean abundances in the Earth's continental crust (Wedepohl 1995). The black lines are sand samples and grey lines represent glass samples. (a) Syro-Palestinian raw glass chunks from Bet Eli'ezer and Apollonia, and glass vessels from Apollonia (Freestone *et al.* 2000); (b) Belus River sand (superscripts in parentheses: 1, Degryse previously unpublished; 2, Brill 1988, 1999); (c) Egyptian glass from Tell el-Ashmunein (Freestone *et al.* 2000); (d) sand samples IT85 and IT87; (e) sand samples IT01 and IT34; (f) sand samples SP46, SP45 and SP43; (g) sand samples FR16 and FR17; (h) sand samples SP20 and SP22.



elements. Only Sr and Ba are relatively elevated. Concentrations of TiO₂, Cr and Zr are very low. Sand sample IT85 generally contains higher concentrations of heavy minerals and the associated trace elements TiO₂, Cr, Zr, Hf and REE. When comparing Figures 4 (a), 4 (b) and 4 (d), the trace element pattern of sand IT87 appears to be very similar to those of Syro-Palestinian raw glass and Belus River sands. However, IT87 is even more depleted in Zr. Another important difference lies in the characteristically low Al₂O₃ content of sand IT87, which resulted in Al₂O₃ contents lower than 1.5% in the glass (see Brems *et al.* 2012c). This is significantly lower than the Al₂O₃ concentrations of 2.2–3.2% in Belus River sand (Brill 1988, 1999) and 2.5–4.0% generally found in the Syro-Palestinian glass made from that sand (Freestone *et al.* 2000). Sand raw material IT85 can be easily distinguished from Belus River sand by its higher TiO₂, Cr and Zr contents, and lower Sr. Sand IT85 has ⁸⁷Sr/⁸⁶Sr isotope ratios higher than the modern seawater value, while Egyptian glass has relatively low Sr isotopic signatures (Freestone *et al.* 2003; Brems *et al.* 2013a; Fig. 5).

Other suitable sand raw materials along the coasts of the western Mediterranean all have significantly lower ε_{Nd} values (Brems *et al.* 2013b). These sand sources can be further separated on the basis of their ε_{Nd} values and trace element signatures (Fig. 5). Italian sands IT01 and IT34 have similar Nd isotopic signatures as suitable (low lime) sand raw materials from the south-west of Spain (SP46, SP45 and SP43). The ε_{Nd} values of these sands all lie between –9.40 and –7.99 (Brems *et al.* 2013b). IT01 and IT34 can be distinguished from each other by their different TiO₂ and Cr contents (Fig. 4 (e)). Sand IT01 is also much lower in Sr, a result of the very low calcium carbonate content of this sand. After the addition of extra shell fragments as a source of lime, glasses produced from these two sands would have similar Sr concentrations (Brems *et al.* 2013a). Trace element signatures of the Spanish sands vary according to their heavy mineral contents (Fig. 4 (f)). Sample SP43 is the most pure quartz sand and has very low concentrations of, for example, TiO₂, Zr, Hf and REE. Sands SP46 and especially SP45 contain more heavy minerals and have relatively elevated TiO₂, Zr, Hf and REE. The most distinguishing feature between the Italian and Spanish sands is the Cr content. The Italian sand samples contain on average 12 times more Cr than the Spanish sands.

Suitable glass-making sand raw materials from south-eastern Spain (SP22 and SP20) and south-eastern France (FR16 and FR17) all have ε_{Nd} values lower than –10 (Brems *et al.* 2013b). Trace element signatures of the French sands are shown in Figure 4 (g). Sand sample FR17 has slightly higher concentrations of most trace elements. Rb and Th, however, are higher in FR16 and also the REE pattern is somewhat different, with an enrichment of Eu in FR17. Sand samples SP22 and SP20 have trace element patterns with very similar shapes (Fig. 4 (h)). The pattern of SP22 is generally shifted to higher concentrations. This sand also contains relatively elevated Fe₂O₃ and Al₂O₃ levels. SP20 shows two pronounced peaks for Zr and Hf, indicating a relative enrichment of the heavy mineral zircon. These peaks are absent in the SP22 trace element pattern. The two sand samples from the south-east of France contain, on average, higher concentrations of TiO₂ and also the TiO₂/V ratio is different, with 0.014–0.016 for French sands and 0.006–0.009 for Spanish sands.

CONCLUSIONS

In this study, we have evaluated the use of trace elements as a provenance indicator for Roman natron glass. It was shown that the combined use of Nd isotopic signatures, major elements (particularly Al₂O₃) and trace element patterns makes it possible to distinguish between the different possible sources of suitable sand raw materials in the regions under investigation. The

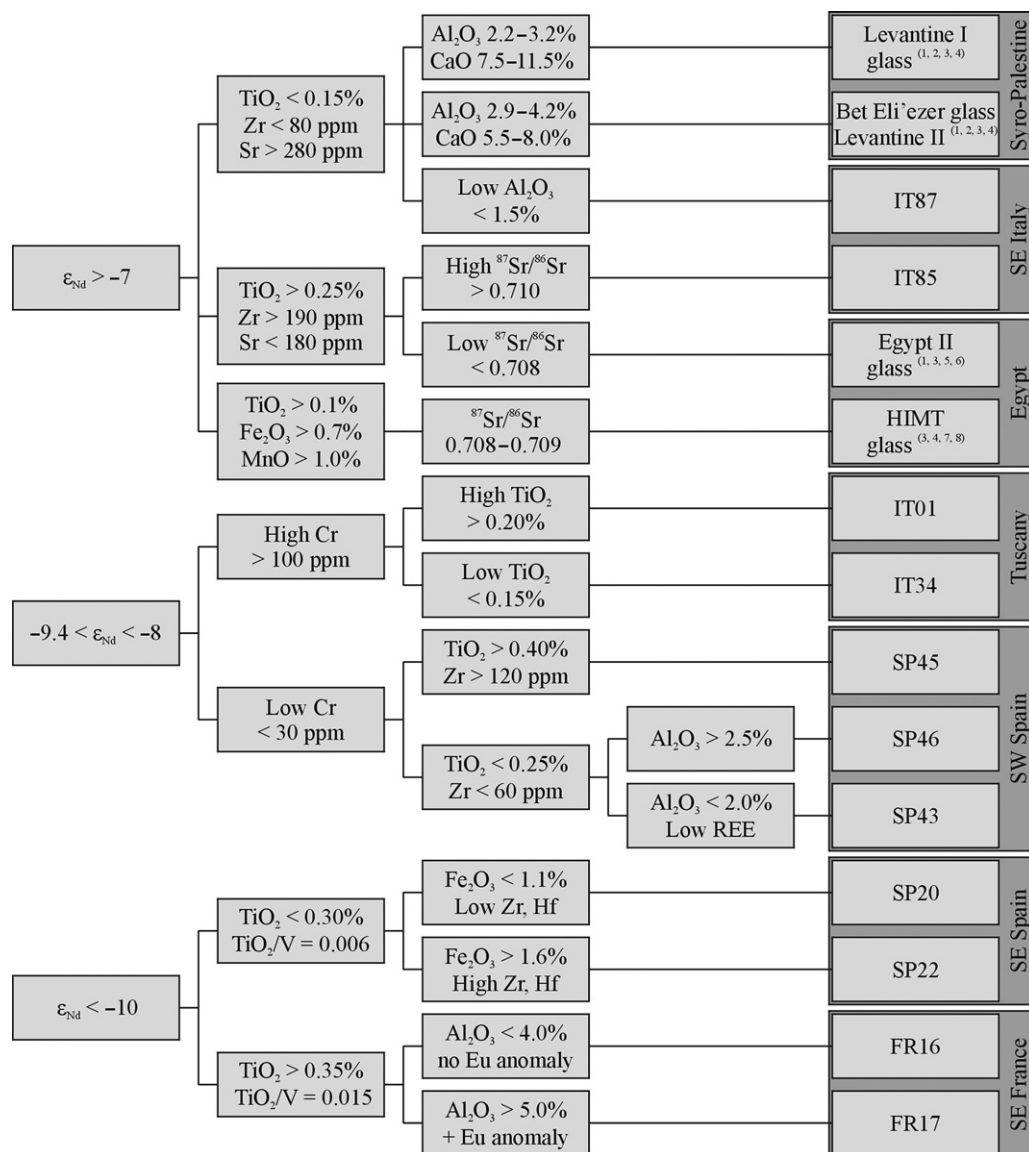


Figure 5 A flowchart for determining the provenance of natron glass (superscripts in parentheses: 1, Freestone et al. 2000; 2, Freestone 2006; 3, Degryse and Schneider 2008; 4, Freestone et al. unpublished data; 5, Gratuze and Barrandon 1990; 6, Freestone et al. 2003; 7, Freestone et al. 2005; 8, Foster and Jackson 2009).

trace elements that proved to be the most diagnostic are Ti, Cr, Sr, Zr and Ba. Apart from Ba (and possibly Sr), which is often associated with Mn decolourants, these elements are seldom influenced by the addition of colouring agents or recycling, and should provide direct information about the nature of the silica source used. However, since data for possible sand sources from areas such as Corsica, Sardinia, North Africa, Greece, Turkey and Cyprus are not yet available,

the existence of competing Roman glass producers with overlapping elemental and isotopic characteristics in these areas cannot be excluded nor confirmed.

Slightly elevated concentrations in glass of trace elements commonly associated with colouring agents, such as Mn, Co, Ni, Cu, Zn, Sb and Pb, are often interpreted as the result of recycling of glass cullet. The analysis of these elements in suitable glass-making sands provides a good idea of the background levels that can be attributed to impurities in the source of silica. The current data set suggests that for the two most commonly used decolourizers, MnO and Sb, these background levels are 0.1% and 30 ppm respectively. The presence of higher amounts of these elements in Roman glass would indicate their deliberate or accidental (due to recycling of cullet) addition. Additional detailed analysis of a wider range of trace elements in suitable sand raw materials can only provide further insights into the influence of the different raw materials on the composition of ancient natron glass. Also, trace elemental data of materials typically used as colourants in antiquity are essential to evaluate their contribution to the final trace elemental composition of the glass. In particular, their influence on the concentration of elements commonly attributed to the sand source should be investigated to make sure that these elements are indeed only derived from the sand raw material and are therefore potentially useful as provenance indicators. To our knowledge, data of this kind are not available at the moment.

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