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Boron isotopic composition as a provenance indicator for the flux raw material in Roman natron glass

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ABSTRACT

Boron is a trace element present in natron glass, which largely enters the glass via the flux. Therefore, the B isotope ratio is targeted as a means of provenancing this flux. In this work, 33 Greco-Roman natron glasses and 18 natron samples were analysed for their B isotopic composition (expressed as $\delta^{11}B$). All glasses, except one of mixed flux origin, show a $\delta^{11}B$ value close to the average value of +29‰. 11 natron samples from the Wadi Natrun show an average $\delta^{11}B$ of +29.8‰, while the sample from al-Barnuj shows a $\delta^{11}B$ of +28.5‰, the average for 4 Fezzan samples from Libya is +25.3‰ and that for the 2 samples from Lake Pikrolimni in Greece +10.5‰. There is an influence of the sand on the $\delta^{11}B$ of natron glass, complicating the picture, but in general, the silica source will slightly lower the $\delta^{11}B$ of the glass compared to that of the natron source. The high melting temperature has no significant effect on the B isotope ratio. It can be concluded that Greco-Roman natron glasses show a rather homogenous $\delta^{11}B$. The Wadi Natrun salts analysed fit a model in which the $\delta^{11}B$ of the glasses is somewhat lower than that of the natron source due to the input of low $\delta^{11}B$ sand. The samples from Lake Pikrolimni in Greece analysed in this study show too low $\delta^{11}B$ values to be used in glass making according to this model.

1. Introduction

Provenancing the raw materials used for the manufacturing of natron glass in the Greco-Roman world, has received much attention in recent archaeometrical research. Glass is a relatively common find in excavations, but it has proven difficult to provenance. The major elemental composition is fairly homogeneous for Roman natron glass (Freestone, 2006; Wedepohl et al., 2011), making elemental analysis unsuitable for detailed provenancing. Since the 1970's Pb and O isotope ratios (Brill, 1970) have been investigated as possible provenance indicators. Later on, the isotopic composition of Sr became commonly used for characterising and provenancing the lime source (Degryse et al., 2006, Degryse et al., 2009; Wedepohl and Baumann, 2000) used in natron glass, and even more recently, Nd isotope ratios in combination with the trace element composition have shown to be promising indicators for the origin of the silica source of natron glass (Brems, 2012; Brems et al., 2013; Degryse and Schneider, 2008). Recently, also isotopic analysis of Sb, used in glass manufacturing as an opacifier or (de) colorizer, was reported on for the first time (Lobo et al., 2013). However, no suitable provenance indicator has been developed to trace the source of the natron flux in this type of glass.

Natron glasses were widespread in the Mediterranean and the Levant between the second half of the first millennium BC and the ninth century AD (Freestone et al., 2002). Natron is an evaporitic deposit of alkaline lakes, which is also referred to as *natrun* (Shortland, 2004). These deposits are mostly a mixture of different minerals containing natron ($Na_2CO_3.10H_2O$), trona (Na_2CO_3.-$NaHCO_3.2H_2O$), burkeite ($Na_6CO_3.2SO_4$) and/or halite (NaCl) in varying proportions. A detailed description of the possible minerals present in the natron mixture can be found in Shortland (2004). The source of the natron used in Roman glass production, is supposed to be the evaporitic deposits of Wadi Natrun in Northern Egypt, located 100 km northwest of Cairo (Shortland, 2004). This is mainly based on

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the writing of Pliny the Elder (*Natural History* 31, 46). However, Pliny also mentions other sources, which are interpreted as al-Barnuj in Egypt and current Lake Pikrolimni in Greece (Dotsika et al., 2009). Other possible sources, mentioned in Shortland et al. (2006) are at-Tarabiya in the Eastern Nile delta, al-Kab in Upper Egypt or Bi'r Natrun on the route to Darfur in Sudan. Outside Egypt, next to Lake Pikrolimni in Greece, also Lake Van in Turkey and al-Jabbul in northern Syria are possible candidates. However, no unambiguous evidence exists for the use of a single or of several sources of flux during Roman glass production. Since isotopic systems for provenancing raw materials have already proven useful, efforts were made to develop a method for provenancing the flux. Only a few minor and trace elements enter the glass mainly by the flux, namely Cl, S and B. Of these, B seems most promising due to the limited solubility of Cl and S in the glass melt (Freestone, 2006; Tanimoto and Rehren, 2008). Boron has 2 stable isotopes ^{11}B and ^{10}B with a natural ^{11}B/^{10}B ratio of approximately 4. The isotope ratio is expressed as δ^{11}B in ‰ relative to the isotopic reference material NIST SRM 951 boric acid. The B isotopic composition varies due to natural isotope fractionation (Vanhaecke and Kyser, 2012) and it can span a range of −20 to +40‰. As a consequence, different geological places might have different B isotopic signatures, and Swihart et al. (1986) and Vengosh et al. (1992) showed that provenancing evaporites is possible based on the B isotopic composition. Consequently, the B isotope ratio might be used to differentiate multiple sources of flux. The aims of this research paper are (i) to look for variation in δ^{11}B in natron glasses and natron samples, (ii) to find out whether the δ^{11}B of a glass matches the δ^{11}B of the flux, (iii) to assess the influence of B in the silica source and (iv) to evaluate the influence of melting on the glass δ^{11}B.

2. Reagents, samples and methodology

In this work, 33 natron glasses, 18 natron samples and 17 sand samples were analysed for their B isotopic composition. A detailed description of the dissolution, separation and measurement procedures can be found in Devulder et al. (2013). It has to be noted that all results are expressed as delta values in pemil (‰) relative to the B isotopic reference material NIST SRM 951 (^{11}B/^{10}B = 4.0436 (Catanzaro et al., 1970)) and are calculated according to Equation (1).

$$\delta^{11}\mathrm{B} = \left(\frac{\left(^{11}\mathrm{B}/^{10}\mathrm{B}\right)_{\mathrm{sample}}}{\left(^{11}\mathrm{B}/^{10}\mathrm{B}\right)_{\mathrm{NIST-SRM951}}} - 1\right)*1000 \tag{1}$$

Glass samples originate from Sagalassos (Turkey), dating between the 1st and 7th century AD, Oudenburg (Belgium), dating between the 3rd and the 5th century AD, Kelemantia (Slovakia), dating between AD 175 and 179, and Crandcourt Farm (UK), dating between the 4th and the 1st century BC. The colours are very diverse, varying from colourless, yellow, yellow/green, blue/green over pale yellow to blue, dark blue and brown. A detailed description of the samples is given in Table 1. This table also shows the results obtained for the δ^{11}B and the B concentration, as well as reference data when available from previously published data. All glasses are natron glasses, except KEL2, which has higher MgO, K_2O and P_2O_5 levels and may have a mixture of natron and plant ash as a flux (Degryse et al., 2009; Degryse and Shortland, 2009).

The natron samples investigated comprise 11 samples from Wadi Natrun (Egypt), one from al-Barnuj (Egypt), two samples from

Table 1
Information on glass samples analysed such as colour, date, place found as well as the δ^{11}B (‰) and the B concentration, the εNd and the reference where this can be found. The expanded uncertainty on the δ^{11}B results is 1.6‰ ($k = 2$).

Sample	Colour	Date	Place found	δ^{11}B (‰)	[B] (ug.g^{-1})	εNd	Reference
SA-2007-VL-358	Colourless	Second half 2nd century	Sagalassos	30.1	195.3	−6.3	(Lauwers, 2008)
SA-2007-VL-1161	Yellow	1st–7th century AD	Sagalassos	32.6	253.1	/	Previously unpublished
SA-2007-VL-744	Colourless	1st–7th century AD	Sagalassos	29.7	139.1	/	Previously unpublished
SA-2007-VL-678	Colourless	1st–7th century AD	Sagalassos	30.2	161.4	/	Previously unpublished
SA-2007-VL-219	Colourless	1st half 4th century AD	Sagalassos	28.7	162.1	/	Previously unpublished
SA-2007-VL-135	Colourless	2nd half 4th century, 1st half 5th century AD	Sagalassos	28.7	149.9	/	Previously unpublished
SA-2007-VL-539	Yellow/green	1st–7th century AD	Sagalassos	29.4	237.9	/	Previously unpublished
SA-2007-VL-115	Colourless	1st–7th century AD	Sagalassos	29.7	148.0	/	Previously unpublished
SA-2007-VL-88	Colourless	1st–7th century AD	Sagalassos	28.4	160.3	/	Previously unpublished
SA-2007-VL-211	Colourless	1st–7th century AD	Sagalassos	27.3	151.2	/	Previously unpublished
SA-2007-VL-304	Pale yellow	1st–7th century AD	Sagalassos	27.1	158.4	/	Previously unpublished
SA-2006-VL-7	Colourless	End 5th century AD/6th century AD	Sagalassos	28.8	210.1	−5.2	(Lauwers, 2008)
SA-2007-VL-26	Dark blue	1st–7th century AD	Sagalassos	30.1	162.9		Previously unpublished
SA-2005-VL-31	Brown	1st–7th century AD	Sagalassos	31.0	170.6	/	Previously unpublished
SA-2007-VL-1167	Pale green	1st–7th century AD	Sagalassos	27.1	176.9	/	Previously unpublished
SA-2007-VL-1085	Colourless	1st–7th century AD	Sagalassos	27.7	166.5	/	Previously unpublished
SA-2007-VL-1095	Yellow	1st–7th century AD	Sagalassos	32.2	290.6	/	Previously unpublished
8933	Pale blue/green	4th – 5th century AD	Oudenburg	28.7	159.6	/	(Ganio et al., 2012)
8926C	Pale blue/green	3rd century AD	Oudenburg	29.7	136.3	/	(Ganio et al., 2012)
71310	Pale blue	3rd century AD	Oudenburg	28.2	154.1	−5.61	(Ganio et al., 2012)
23993	Pale blue/green	4th–5th century AD	Oudenburg	28.7	159.6	−6.09	(Ganio et al., 2012)
2960	Pale blue	4th–5th century AD	Oudenburg	27.4	193.7	−6.54	(Ganio et al., 2012)
SA-2006-VL-05	Yellow/green	1st–7th century AD	Sagalassos	27.4	264.7	/	Previously unpublished
SA-2007-VL-136	HIMT	1st–7th century AD	Sagalassos	26.3	192.9	/	Previously unpublished
SA-2007-VL-137	HIMT	1st–7th century AD	Sagalassos	27.7	198.6	/	Previously unpublished
SA-2007-VL-138	HIMT	1st–7th century AD	Sagalassos	26.9	187.6	/	Previously unpublished
SA-2007-VL-205	HIMT	1st–7th century AD	Sagalassos	29.0	218.8	/	Previously unpublished
KEL2	Pale blue	Between 175 and 179 AD	Kelemantia	−4.4	31.1	−7.3	(Degryse and Shortland, 2009)
KEL3	Pale yellow	Between 175 and 179 AD	Kelemantia	29.0	108.3	−6.1	(Degryse and Shortland, 2009)
KEL4	Colourless	Between 175 and 179 AD	Kelemantia	29.9	152.7	−9	(Degryse and Shortland, 2009)
GF1	Dark yellow	4th–1st century BC	Grandcourt Farm	31.6	227.7	−4	Previously unpublished
GF4	Colourless	4th–1st century BC	Grandcourt Farm	34.0	101.3	−4	Previously unpublished
GF5	Dark blue	4th–1st century BC	Grandcourt Farm	30.5	109.4	−12	Previously unpublished