An archaeometric study of Archaic glass from Rhodes, Greece: Technological and provenance issues

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ABSTRACT

In the present study, a set of 86 beads, of various colours, dating to the Archaic period (640–600 BCE) and excavated on Rhodes island, Greece is investigated using a range of analytical techniques such as SEM/EDX, mXRF and LA-ICP-MS. The role of Rhodes in ancient glassmaking is undoubtful and has been attested by various scholars. Its favourable geographical position being a node between mainland Greece and Asia Minor, Cyprus and consequently the Levantine coast and Middle East enhanced its trading activities and its cultural influences.

The main aim of this study is to shed light to the technological features of Archaic glass and in a second stage and through the comparison with already published analytical data of coeval, earlier and later glass samples, to investigate thoroughly the provenance of the Rhodian assemblage.

The scientific data demonstrates that there is no continuity in the technology used for the Archaic glass and glass of the subsequent centuries in Rhodes in terms of the basic glass composition. It seems that the technology shifts both in terms of the silica raw materials towards other possible sources and in alkali raw material towards the use of a mineral source rather than plant ash.

Relating to the provenance of the Archaic beads, both major-minor and trace elements analysis show that there are strong indications for a Mesopotamian origin. As it is demonstrated in various biplots there is higher correlation between the majority of Archaic samples from Rhodes with samples from Mesopotamia.

1. Introduction

Analyses of glass artefacts dating to the Archaic period (about 800 to 480 BCE (Shapiro, 2007)) from modern Greece are scarce in the literature (Oikonomou et al., 2008; Zacharias et al., 2008; Sokaras et al., 2009; Beltsios et al., 2012; Oikonomou, 2012; Oikonomou et al., 2012a; Oikonomou et al., 2012b; Oikonomou et al., 2014; Blomme et al., 2016, 2017). Glass research tends to focus either on prehistoric periods, mainly Mycenaean (Nikita and Henderson, 2006; Walton et al., 2009; Henderson et al., 2010; Polikreti et al., 2011; Smirniou et al., 2012; Triantafyllidis and Karatasios, 2012; Möncke et al., 2013; Zacharias et al., 2013; Zacharias et al., 2018), or on Classical and Hellenistic times (Brill, 1999, 2012; Triantafyllidis, 2000a, 2000b; Rehren et al., 2005; Triantafyllidis et al., 2012; Oikonomou, 2018).

It is now well established by the scientific community that both plant ashes and minerals was used to flux the silica raw materials (sand or quartzite pebbles) to produce glass during antiquity (Henderson, 2013 and references therein). Early glass was made using halophytic plant ashes while the mineral form of flux, natron, was probably introduced during the beginning of 1st Millennium BCE. Some of the earliest examples of natron glass are dated to the 10th c. BCE (Schlick-Nolte and Werthmann, 2003) and according to Sayre and Smith (1961), natron glass was established by 800 BCE in wider areas of the

Mediterranean and western Europe. The transition between the two traditions coincides with major sociopolitical/economic changes of the period such as the collapse of Bronze Age civilizations, Dark Ages and at the same time the introduction of iron in past societies (Henderson, 2013).

The present study of archaic glass from Rhodes aims to shed light on various aspects of Archaic glass in Greece such as:

- the technology of the selected glass samples from Rhodes
- the identification of raw materials used
- the changes in glass technology in terms of the raw materials used (if any) and
- the provenance of the primary glass

Rhodes island (Fig. 1), located in the south west part of Aegean sea, played an important role in glassmaking during the first millennium BCE because of its favourable geographic location being a node of trade activities in close proximity to the Asia Minor, Cyprus and consequently to the Levantine coast (Triantafyllidis, 2002a, 2002b). Many scholars believe due to archaeological evidence that there was primary and secondary glassmaking activity on the island of Rhodes as early as the 6th c. BCE (core formed vessels) (Harden, 1981; McClelan, 1984; Grose, 1989; Stern and Schlick-Nolte, 1994) while we may assume that there

Fig. 1. Map showing the position of Rhodes in south east Mediterranean (Oikonomou et al., 2014).

Fig. 2. Characteristic samples from Kamiros, Rhodes island (Oikonomou et al., 2014).

was a significant activity also in earlier periods (Triantafyllidis and Karatasios, 2012). In addition, research in the city of Rhodes clearly indicates the presence of glassmaking at least during late Classical and early Hellenistic period in the newly founded Rhodian *asty*, which is regarded as one of the largest ancient glassworking centers in the Mediterranean (Triantafyllidis, 2000a). The archaeological research revealed an underground complex in close proximity to the Hellenistic workshop Weinberg excavated in 1966–67 (Weinberg, 1966). Within the complex, huge deposits of quartz sand, calcium materials, glass frits and raw glass were found (Triantafyllidis, 2000a). The importance of Rhodes island in glass industry during the first Millennium BCE is well attested in various studies (Triantafyllidis, 2000a, 2000b, 2002a, 2002b, 2003; Weinberg, 1966, 1969, 1983, 1992 and references therein). Furthermore, there are archaeological indications of small-scale industries for other materials as well such as ivory, gold and faience showing the technological advancement of the island (Filimonos et al., 2006). According to the excavation record an impressive total of 10,000 glass objects was found in the Geometric (8th–7th c. BCE) and early Archaic tombs (late 7th–6th c. BCE) of Ialysos and Kamiros and also in the sacred deposits of the large sanctuaries in Ialysos, Kamiros, and Lindos (Triantafyllidis, 2006).

In addition, the contents of graves and artefacts from the depository in the temple of Athena in Kamiros, which blossomed mainly during the Archaic period (680–480 BCE), testify to the fact that during the 7th and the 6th c. BCE commercial relations existed between Kamiros and mainland Greece, along with Asia Minor and the southeast Mediterranean.

In the present study a total of 85 samples excavated in Kamiros are studied systematically with a combination of analytical techniques.

2. Materials and methods

A set of 85 semi-cut glass beads (Fig. 2), excavated at the ancient city of Kamiros, is a small subset of a large number of glass ornaments-beads on the order of 6000, mostly necklace beads, which were found as offerings in the great sanctuaries of Rhodes or as grave artefacts in the cemeteries of Ialysos and Kameiros. The samples considered here were found at the archaic depository of the sacred sanctuary of Athena on the acropolis of Kameiros during the Italian occupation of Rhodes (1912–1943) (Jacopi, 1932) and were excavated from within an oinohoe (*oenokhoē*, wine vessel) of the wild goat style, which dates back to the late Archaic period (ca. 640–600 BCE) (Triantafyllidis, 2006). The samples were analyzed by means of SEM-EDX, mXRF and LA-ICP-MS. The peculiar/precise breakage of the beads might suggest fault during the manufacturing process rather than accidental breakage (due to usage). Therefore, this might be a solid evidence of secondary glassmaking in Rhodes as early as the 7th c. BCE.

One of the broken surfaces of each bead was selected and polished using a hand-drill bearing a silicon carbide head followed by cleaning with garnet paper of various grits (600, 800, 1000, 1200 and 1500 grits). The samples were then embedded in acetone solution and dried with compressed air to remove any remains from the mechanical treatment, a process that resulted in a clean, flat, and uncorroded surface suitable for SEM-EDX and mXRF analysis. A subset of 20 selected samples were analyzed by LA-ICP-MS. Small pieces (< 1 mm) were mounted in a resin block which was ground with silicon carbide paper of various grits (600, 800, 1200, 2500) and then polished using diamond paste of 6–3 and 1 μm. The accuracy of the techniques is shown in

Table 1
The accuracy of the techniques after the analysis of standard reference materials. For more information about the mXRF and SEM/EDX can be found in (Sokaras et al., 2009). c.v. certified values.

Oxides/ elements	mXRF		SEM/EDX		Elements	LA-ICP-MS	
	NIST620	c.v.	NIST614	c.v.		NIST 612	c.v.
Na₂O (wt%)	n.d.	14.39	13.67	14	Ni (ppm)	39.1	38.8
MgO (wt%)	n.d.	3.69	–	–	Sr (ppm)	78.8	78.4
Al₂O₃ (wt%)	1.32	1.80	2.27	2	Zr (ppm)	38.8	37.9
SiO₂ (wt%)	72.4	72.08	73.05	72	Sb (ppm)	33.4	34.7
K₂O (wt%)	0.36	0.41	–	–	Ba (ppm)	39.5	39.3
CaO (wt%)	7.55	7.11	11.01	12	La (ppm)	36.4	36
Fe (ppm)	306	302	–	–	Nd (ppm)	35.1	35.5
As (ppm)	484	426	–	–	Ni (ppm)	39.1	38.8

Table 1.

Major and minor oxides were detected using a FEI Quanta Inspect D8334 scanning electron microscope equipped with an energy dispersive X-ray analyzer (EDX). All samples were attached to sample holders with carbon glue in order to enhance conductivity and to achieve better imaging. At least three measurements were conducted on each sample due to electron beam size; then the mean value and standard deviation of each measurement was calculated. Measuring conditions involved accelerating voltage of 25 kV, while the fluorescence X-rays were detected through a SUTW Si(Li) detector at 35° with respect to sample surface. Quantitative analyses were corrected with a ZAF routine.

Trace elements were detected using an in house developed milli-XRF facility. The facility with beam dimension of ~3 mm on a sample surface consists of a Rh-anode side-window low power X-ray tube (50 W, 50 kV, 75 μm Be window), a Si-PiN diode X-ray detector (XR-100CR, Amptek Inc.) with a 500 μm nominal crystal thickness (165 eV FWHM @ Mn-Kα) and a digital signal processor (PX4, Amptek Inc.). A filtered high energy excitation mode (high voltage set at 40 kV) probed trace elements above $Z = 20$. Each measurement was conducted for at least 3000 s in order to have good statistics to detect trace elements. Quantitative analysis was performed using WinQxas software (Sokaras et al., 2009).

A full range of trace elements for the subset of the 20 samples were detected using an LA-ICP-MS instrument with a NewWave UP193FX excimer (193 nm) laser system coupled to an Agilent 7500 series ICP-MS. Laser ablation craters were set at 70 μm, the laser being fired for 45 s at 10 Hz and a typical fluence of 2.8 J cm^{-2}. Data was collected in a time resolved analysis mode, with a gas blank being measured before a series of ablations on glass samples, calibration standards and quality control standards, were carried out. Calibration standards bracketed the samples and QC over a period of 1 h or less. Calibration of the system was performed using NIST SRM610 trace element glass standard while NIST SRM612 was used for quality control purposes.

3. Chemical analysis of Archaic Rhodian samples

The glass bead collection from Rhodes is of soda-lime-silica type (Sayre and Smith, 1961). The major and minor oxides which detected in all samples are: Na_2O, MgO, Al_2O_3, SiO_2, Fe_2O_3, SO_3, Cl, K_2O, CaO (Table 2). In most of the samples trace elements of Sr, Zr and Sb were detected using mXRF. Furthermore, in selected samples a full range of trace elements were detected by means of LA-ICP-MS. Maximum, minimum and average values are shown in the end of Table 3.

The average value of SiO_2 is 68.0 wt% with min. and max. value of 57.7% and 75.1 wt% respectively. Major alkali component is Na_2O with values varying from 10.4% to 23.5 wt% with average value of 18.5 wt%, while K_2O is the secondary alkali with much lower values (min. 0.1%, max. 4.5% and average 1.4 wt%). Major alkaline earth oxide is CaO with min. and max. value of 2.3% and 9.9 wt% respectively and average value of 5.3 wt%, while the corresponding values for the secondary alkaline earth oxide, MgO, are 0.5%, 7.1% and 3.7 wt% respectively. Al_2O_3 varies from 0.5% to 3.1 wt% with average value of 1.1 wt%, while SO_3 and Cl were detected with average values of 0.6 wt% and 0.8 wt% respectively. Raw materials usually contain respectable amounts of S and Cl,[1] but these typically decrease to around 1% due to solubility limitation (as defined from heating temperature and total composition). In all samples Fe_2O_3 is detected with min. and max. value of 0.1 wt% and 1.0 wt% respectively. Fe_2O_3 is associated with sand impurities, but amounts over 0.5 wt% can reflect deliberate addition to achieve certain colours (e.g. black or red depending on the oxidation state of Fe) (Henderson, 2000).

According to the elevated amounts of both MgO and K_2O the majority of the samples from Rhodes belong to a plant ash tradition, i.e. plant ashes were used to flux the sand raw material. However, there are 7 samples (see Table 2 samples R.13, R.30, R.34, R.38, R.43, R.60 and R.83), showing low concentrations of both oxides (lower than 1 wt%), suggesting use of a mineral form of flux, such as natron, indicating a totally different glassmaking tradition.

Regarding the coloration of Rhodian samples the samples there is a variety in colours. In particular, the majority of the samples (60 out of 85) bear green colour in various hues (green, lemon-yellow green, deep olive-green) which is attributed to the presence of Fe_2O_3 in the sand raw material; therefore, it can be assumed that are naturally coloured. The different hues might be also a result of the combination of other mineral rich colourants or/and furnace conditions (Henderson, 2013). Furthermore, there are seven turquoise samples because of the presence and elevated amount of copper (averages at 7846 ppm). There are also few samples (7 out of 85) having a lemony yellow colour which are transparent. They do not exhibit any elevated content of colourant elements and probably lemon-yellow colour is due to the presence of antimony (Sb averages at 2141 ppm) even though usually it was used in the form of lead antimonate ($Pb_2Sb_2O_7$) to give an opaque yellow colour in glass. For these lemon-yellow samples no Pb was detected. Moreover, the colourless glass samples (9 out of 85), which are also transparent, show substantial amount of Sb (Sb averages at 2290 ppm). It is worth noting that among the colourless glass samples, sample R.86 has no Sb content, but instead shows elevated values of Mn (11,951 ppm). Therefore, we may assume that Mn acted as decolourizer for R.86 sample. Finally, there are two amber samples without any noticeable values of colourant elements such as Fe, Mn, Cu. Paynter and Jackson (2017) suggest that natron is a key to amber colour development in combination with low iron concentrations and very controlled furnace atmosphere, but this is not the case in these samples since they are both plant ash with 0.48 wt% average Fe_2O_3 content (which is rather normal). Therefore, we may assume that their coloration is probably due to varied furnace atmospheres (Henderson, 2000).

4. Interpretation of the data

One of the basic archaeological questions that can be addressed through the application of scientific methods - except from questions pertaining to technology - is provenance. Provenance studies have received increased attention over the past few decades, as they provide indication for the movement or raw material and goods via trade and other forms of exchange (Shortland et al., 2007; Degryse and Schneider, 2008; Degryse et al., 2009a, 2009b; Henderson, 2009; Degryse et al., 2010; Henderson et al., 2010). The main aim of the present study is to try and identify the provenance of archaic glass from Greece which has not received much attention by the scientific community.

Basic glass composition in antiquity involved the combination of at least 2 (maybe 3) raw materials. These raw materials were the source of its main component, silica, which could be either sand or quartz pebbles (Turner, 1956), while the source of alkalis could be either of phytogenic or mineral origin (Beretta, 2004). The last major component was lime, which was either deliberately added to the glass batch in form of shells, bones and dolomitic limestone, or was accidentally added as a part of impurities in sand (Henderson, 2013). Biplots of various oxides and elements (Figs. 3–10) are presented here to compare the Rhodian glass samples with already published data (see Table 2) in order to investigate possible similar raw materials/technology and provenance. The major-minor compositional data of this study are directly compared to two distinct data sets (Figs. 3–4 and 9–10): first, with data from Rhodes dating to later periods, i.e. Classical and Hellenistic (Brill, 1999; Triantafyllidis, 2000a, 2000b; Triantafyllidis et al., 2012), and second, with roughly contemporary samples from other regions, such as

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[1] Natron samples (no. 655, 657 and 658) analyzed by Brill (1999) show average values of SO_3 and Cl 7.1 and 21.1 wt% respectively while for plant ash samples (no. 1331, 1380 and 1381) the average values of SO_3 and Cl are 5.0 and 9.3 wt% respectively.

Table 2
Information about the published data used in this paper.

Sample name	Dating	Glass type	Reference
Rhodes 5th–1st c. BCE	5th–1st c. BCE	Core formed vessels	Triantafyllidis et al., 2012
Rhodes 4th–2nd c. BCE	4th–2nd c. BCE	Cast vessels	Triantafyllidis, 2000a, 2000b
Rhodes 3rd–2nd c. BCE	3rd–2nd c. BCE	Beads and cullets	Brill, 1999
Thebes 7th–6th c. BCE	7th–6th c. BCE	Beads	Beltsios et al., 2012
Nimrud 7th c. BCE	7th c. BCE	Bowls and inlays	Brill, 1999
Lisht 12th–9th c. BCE	1200–900 BCE	Core formed vessels, canes and cullet	Brill, 1999
Mesopotamia LBA	14th–13th c. BCE	Pendants, ingots, vessels and beads	Shortland et al., 2007
Egypt LBA	1390–1352 BCE	Rods	Shortland et al., 2007
Tiryns LBA	1400–1300 BCE	Mycenaean beads	Walton et al., 2009
Pylos LBA	1600–1300 BCE	Beads	Polikreti et al., 2011
Thessaly LBA	1400–1300 BCE	Mycenaean beads	Smirniou et al., 2012

mainland Greece (Thebes) (Oikonomou, 2012) or Mesopotamia (Nimrud) and Egypt (Lisht) (Brill, 1999). In addition, regarding the trace element compositional data (Figs. 5–8) the 7th c. BCE samples (this study) is compared with earlier LBA glass from Mesopotamia, Egypt (Shortland et al., 2007), Tiryns (Walton et al., 2009), Pylos (Polikreti et al., 2011) and Thessaly (Smirniou et al., 2012).

5. Silica source

The distinction between silica raw materials (sand or quartz pebbles) can be done through the investigation of the correlation of SiO_2 and Al_2O_3 as it can be seen in Fig. 3. Silicon oxide (SiO_2) is the main component of either sources and aluminum oxide (Al_2O_3) is present as an impurity in sands (Jackson et al., 2003; Nikita, 2004).

Different groups of samples are formed in the plot of SiO_2 against Al_2O_3 (Fig. 3). Archaic glass samples from Rhodes contain Al_2O_3 with a mean value of 1.02 wt% excluding four samples which have Al_2O_3 > 1.5 wt% (R.13: 3.04%, R.34: 3.09%, R.66: 1.93%, R.68: 1.96%; average 2.51 wt%) either because of a deliberate addition of Al_2O_3 from an unknown source or use of another sand as a raw material. The majority of the Archaic samples were manufactured using a sand raw material rather than quartz pebbles, even though the low amount of Al_2O_3 detected could suggest use of a quartz silica source. In addition, when quartz pebbles are used the amount of neodymium (Nd) trace element is lower than 2 ppm (Henderson, 2013) and in general quartz, as a mineral, contains virtually no Nd (Brems et al., 2014), while in our case the Nd content of selected samples (see below in trace element analysis, especially Fig. 7), has min and max values of 1.92 and 5.54 ppm respectively and averages at 3.2 ppm. Therefore, it may be assumed that the samples from Rhodes were manufactured with a rather pure sand source exhibiting low concentrations of Al_2O_3 impurities.

Values of Al_2O_3 > 1.5% and with mean value close to 2.5% are characteristic of glasses using sand as the main source of silica of later periods, e.g. Classical, Hellenistic and Roman period (Degryse, 2014). Samples from Rhodes from the 5th–1st c. BCE, 4th–2nd c. BCE and 3rd–2nd c. BCE present mean values of Al_2O_3 2.68 wt%, 2.13 wt% and 1.84 wt% respectively and form different groups as shown in Fig. 4. Samples from Thebes Greece, contemporary with the 7th c. BCE samples from Rhodes, form two distinct groups with mean values of Al_2O_3 of 0.97 wt% and 2.83 wt% respectively. Theban samples exhibit evidence of deliberate addition of Al_2O_3 (Beltsios et al., 2012). As it is shown on the plot (Fig. 3) the majority of Rhodian samples have the tendency to coincide better with samples from Thebes (the low Al_2O_3 ones), Nimrud (average of Al_2O_3 0.82 wt%, excluding 6 samples having Al_2O_3 > 1.5 wt%) and Lisht (average of Al_2O_3 0.74 wt%).

In addition to aluminum oxide, iron oxide (Fe_2O_3) is also mainly associated with impurities of sand used in ancient glassmaking. Plant ashes also contain Fe_2O_3, but in lower values (e.g. the average composition of Fe_2O_3 in plant ashes according to Barkoudah and Henderson (2006) is 0.25 wt%). Typical value of Fe_2O_3 found in 1st Millennium

BCE glass and mainly Roman glass is around 0.50 wt%. Values above this mean could reflect deliberate addition of Fe_2O_3 for coloring purposes (dark green, brown or black colour). The colour depends on two additional factors: the furnace atmosphere (oxidizing or reducing) and the presence of bivalent or trivalent iron (Fe^{+2} and Fe^{+3}) (Henderson, 2000).

In Fig. 4 the values of Fe_2O_3 against Al_2O_3 are plotted for the total of the analyzed samples. Samples form a number of groups which overlap slightly but can be easily distinguished. Archaic glass from Rhodes forms a solid group, with the exception of four samples having elevated values of Al_2O_3, as mentioned above. Rhodian samples of this study have the same values of both oxides as the majority of the samples from Nimrud (with the exception of 4 Nimrud samples with values of Fe_2O_3 > 2.5 wt% and 6 samples with values of Al_2O_3 > 4 wt%). In this plot Rhodian 7th c. BCE samples and Mesopotamian glasses from Nimrud are clustered together, while it seems that there is no clustering with samples from other regions and dates.

On top of that, the correlation between the concentrations of Zr with Sr, Ti and Nd are investigated in the corresponding plots (Figs. 5–7). Due to the lack of published data of trace elements of the Archaic period, Rhodian samples are compared with Late Bronze Age glass from Mesopotamia (Nuzi and Tel Brak referred as "Mesopotamia LBA"), Egypt (Malkata and Amarna referred as "Egypt LBA") [both data sets published by Shortland et al., 2007] and Mycenaean glass from Greece and more specifically from Pylos [data referred as "Pylos LBA" published by Polikreti et al., 2011], Tiryns [data referred as "Tiryns LBA" published by Walton et al., 2009] and Kazanaki Thessaly [data referred as "Thessaly LBA" published by Smirniou et al., 2012].

These trace elements are expected to have regional variability (or differences) making them suitable for provenance studies for two main reasons: first, they are non-volatile and not affected from firing conditions and second, they vary accordingly to the geochemistry of every region. Furthermore, they are often used as compositional discriminants in igneous geochemistry (Shortland et al., 2007). Strontium (Sr) and zirconium (Zr) are often considered as markers for tracing and distinguishing between possible sand sources (Silvestri et al., 2008; Degryse, 2014), since Zr is expected to be primarily present as zircons in sands, while Sr is connected with the presence of Ca which derives from shells (aragonite) or/and limestone (Henderson, 2013; Oikonomou et al., 2016). According to Freestone these elements provide information about the geochemistry of the sand that has been used in glassmaking (Freestone et al., 2000). In general, glasses that were manufactured using Mediterranean sands have typically low values of Zr (~60 ppm) and high values of Sr (~400 ppm) due to the presence of shells in the sand (Silvestri et al., 2008; Degryse, 2014). Furthermore, Nd in glass is likely derived from the non-quartz minerals fraction in the silica raw materials (Gallo et al., 2015; Ganio et al., 2013; Degryse et al., 2009a, 2009b).

In Fig. 5 the correlation between Sr and Zr is presented for the total of samples. These values are derived from the LA-ICP-MS analysis for the selected 20 samples since it is a more precise and accurate

Table 3

Major, minor and trace elements detected by SEM/EDX (values in wt%), XRF (values in ppm) and LA-ICP-MS (values in ppm) analysis. The LA-ICP-MS analysis was contacted on 20 selected samples. The mean values with their standard deviation (s.d.) and the max and min values are shown in the end of the table. n.d.: not detected.

Sample	Colour	SEM EDX analysis									mXRF analysis				
		Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	Fe_2O_3	Mn	Cu	Sr	Zr	Sb
R.1	Green	19.00	6.16	1.06	64.01	0.51	0.78	2.33	5.36	0.42	3797	n.d.	466	21	527
R.2	Amber	16.91	3.65	0.79	68.19	0.28	1.04	1.95	6.11	0.55	n.d.	n.d.	1945	93	n.d.
R.3	Turquoise	19.78	4.23	1.01	67.32	0.52	0.72	1.14	4.52	0.29	n.d.	5202	305	8	n.d.
R.4	Turquoise	17.26	4.00	1.52	67.46	0.82	0.78	1.88	5.52	0.75	n.d.	4322	280	18	n.d.
R.5	Turquoise	14.23	4.50	1.15	68.19	0.55	0.96	1.70	6.95	0.66	n.d.	11,450	700	28	n.d.
R.6	Green	20.12	4.36	1.03	64.71	0.37	0.97	2.46	4.71	0.42	8673	n.d.	492	24	n.d.
R.7	Green	18.71	4.07	1.20	66.85	0.59	0.96	1.59	5.59	0.43	n.d.	n.d.	422	38	574
R.9	Green yellow	18.71	4.41	1.43	66.58	0.59	0.78	2.09	4.90	0.55	1447	n.d.	281	17	1981
R.10	Yellow	17.40	3.94	1.06	71.27	0.63	0.57	0.94	4.02	0.20	n.d.	n.d.	253	12	1195
R.11	Green	21.05	4.64	0.93	66.54	0.40	0.75	1.71	3.71	0.29	n.d.	n.d.	653	35	2667
R.12	Green	18.77	3.36	1.31	65.60	0.82	0.94	2.24	5.19	0.68	8150	n.d.	655	51	n.d.
R.13	Green	13.42	0.55	3.04	71.13	0.36	0.89	1.22	9.02	0.55	n.d.	n.d.	424	29	n.d.
R.14	Turquoise	22.81	5.66	1.52	64.98	0.58	0.74	0.82	2.34	0.36	n.d.	5863	384	17	n.d.
R.15	Yellow	18.19	3.26	0.75	70.27	0.57	0.63	1.13	4.95	0.23	n.d.	n.d.	266	9	1195
R.16	Green	23.50	7.00	0.92	62.73	0.39	0.62	0.94	3.25	0.26	n.d.	n.d.	n.d.	n.d.	n.d.
R.17	Green	16.88	3.01	0.84	69.72	0.51	0.69	1.32	5.90	0.46	7311	n.d.	552	27	n.d.
R.18	Turquoise	20.36	4.86	1.21	65.24	0.48	0.83	1.70	4.28	0.45	n.d.	5709	290	15	n.d.
R.19	Green	15.33	2.63	1.06	72.89	0.71	0.91	1.09	5.32	0.43	n.d.	n.d.	425	11	n.d.
R.20	Green	17.19	3.63	1.15	70.49	0.52	0.76	1.10	4.79	0.38	n.d.	n.d.	335	18	2067
R.21	Green	19.09	4.72	0.76	67.83	0.45	0.83	1.38	4.63	0.31	n.d.	n.d.	333	12	1912
R.22	Green	18.39	2.89	0.96	68.63	0.88	0.90	1.85	4.92	0.58	n.d.	n.d.	360	16	3057
R.23	Green	16.89	2.62	0.79	70.60	0.39	1.15	1.48	5.98	0.49	n.d.	n.d.	382	21	477
R.24	Green	19.87	5.04	0.91	64.01	0.58	0.82	2.44	5.91	0.42	6191	n.d.	1358	31	n.d.
R.25	Yellow	18.81	3.88	1.24	68.37	0.43	0.72	1.83	4.30	0.42	n.d.	n.d.	242	21	2909
R.26	Green	16.28	2.43	1.04	69.63	0.48	0.96	1.89	6.67	0.62	n.d.	n.d.	711	38	n.d.
R.27	Green	10.42	6.65	1.65	75.09	0.44	0.69	1.06	3.51	0.49	n.d.	607	324	22	327
R.28	Green	21.32	6.76	1.26	61.29	0.89	0.85	2.11	4.82	0.31	3292	n.d.	403	17	408
R.29	Green	18.60	3.59	1.10	67.60	0.52	0.87	1.56	5.86	0.29	n.d.	n.d.	336	13	n.d.
R.30	Green	15.69	0.45	0.75	70.69	0.40	1.09	0.25	9.73	0.98	n.d.	n.d.	451	112	n.d.
R.31	Colourless	15.87	2.68	0.61	70.68	0.49	0.78	1.37	7.17	0.37	n.d.	n.d.	397	9	1495
R.32	Green	18.98	4.01	1.42	68.02	0.54	0.69	1.54	4.42	0.38	n.d.	n.d.	265	18	1939
R.33	Green	17.57	2.62	0.73	70.62	0.70	0.98	1.03	5.30	0.47	n.d.	n.d.	518	31	1986
R.34	Green	16.90	0.88	3.09	68.48	0.96	0.98	1.13	6.25	0.80	8408	n.d.	1142	52	2634
R.35	Green	21.37	6.18	0.67	64.91	0.52	0.56	1.60	3.89	0.29	n.d.	n.d.	348	13	677
R.36	Yellow	14.93	4.02	1.20	70.87	0.94	0.98	1.86	4.53	0.67	n.d.	n.d.	425	22	2523
R.37	Yellow	17.78	4.92	1.01	69.24	0.57	0.73	1.58	3.89	0.31	n.d.	n.d.	425	22	2523
R.38	Green	20.87	0.63	0.87	70.38	0.39	0.85	0.14	5.56	0.32	n.d.	n.d.	211	47	n.d.
R.39	Green	15.97	2.75	1.15	69.20	0.51	0.89	1.35	7.62	0.55	n.d.	n.d.	497	23	846
R.40	Colourless	16.37	4.80	1.12	68.93	0.91	0.83	1.81	4.47	0.76	n.d.	n.d.	496	24	2677
R.41	Green	19.07	4.87	1.08	57.68	0.92	1.92	4.52	8.92	1.04	544	n.d.	454	27	4910
R.42	Yellow	16.59	3.71	1.09	66.96	1.25	1.14	1.65	6.93	0.67	968	n.d.	484	19	1998
R.43	Colourless	18.71	0.85	0.67	71.54	0.62	0.25	0.84	6.24	0.27	128	n.d.	148	n.d.	6498
R.44	Colourless	16.52	3.86	1.00	69.86	0.57	1.01	1.75	4.79	0.47	n.d.	n.d.	524	26	1854
R.45	Green	17.32	4.47	0.88	67.23	0.50	0.72	2.51	5.94	0.42	n.d.	n.d.	364	14	1290
R.46	Green	20.80	4.43	1.39	66.60	0.45	0.63	1.37	3.88	0.34	n.d.	n.d.	270	22	2063
R.47	Colourless	19.64	3.38	0.66	68.55	0.55	0.71	1.10	5.19	0.22	n.d.	n.d.	363	11	1048
R.48	Colourless	19.43	2.50	0.51	70.84	0.52	0.86	0.82	4.15	0.37	n.d.	n.d.	473	20	1604
R.49	Colourless	21.26	3.26	0.77	66.55	0.46	0.94	0.89	5.59	0.28	n.d.	n.d.	414	18	1310
R.50	Green	20.70	4.35	1.31	66.41	0.55	0.67	1.48	4.16	0.37	n.d.	n.d.	296	26	1840
R.51	Green yellow	19.48	3.93	1.06	66.38	0.51	0.77	1.19	6.36	0.33	n.d.	n.d.	398	15	2262
R.52	Green yellow	20.19	5.84	1.19	68.14	0.34	0.66	0.68	2.74	0.17	156	n.d.	314	9	1298
R.53	Green	18.49	4.88	0.98	65.99	0.74	0.80	2.32	5.28	0.54	558	n.d.	358	12	1279
R.54	Green	23.24	6.10	1.37	63.82	0.57	0.52	1.23	2.92	0.23	396	n.d.	316	19	828
R.55	Green yellow	18.00	2.84	0.97	69.35	0.78	0.72	1.26	5.66	0.43	n.d.	n.d.	322	18	1550
R.56	Green yellow	19.09	4.71	0.90	66.78	0.56	0.65	1.52	5.19	0.32	985	n.d.	334	13	2364
R.57	Green	17.73	3.18	1.41	67.66	0.74	0.85	1.53	6.40	0.71	503	n.d.	443	19	966
R.58	Green yellow	19.43	3.36	1.10	68.27	0.50	0.89	0.97	5.14	0.34	n.d.	n.d.	290	15	2086
R.59	Green	19.36	3.97	1.30	67.16	0.49	0.75	1.67	4.79	0.49	n.d.	n.d.	242	16	2084
R.60	Green	18.46	1.00	1.20	72.59	0.67	0.85	0.25	4.56	0.42	n.d.	n.d.	354	103	n.d.
R.61	Green	20.19	2.88	1.15	67.82	0.35	0.44	1.02	5.79	0.36	n.d.	n.d.	177	12	2802
R.62	Green yellow	20.28	7.08	0.65	62.17	0.41	0.67	2.86	5.57	0.30	n.d.	n.d.	348	6	1118
R.63	Green	20.79	3.82	0.91	66.19	0.51	0.76	1.20	5.12	0.38	3648	n.d.	517	25	n.d.
R.64	Green	16.44	3.95	0.97	68.63	0.56	0.78	2.12	5.95	0.59	n.d.	n.d.	430	18	2422
R.65	Green	22.34	4.34	1.55	64.22	0.54	0.68	1.73	4.23	0.37	n.d.	n.d.	221	13	1802
R.66	Green	16.35	3.08	1.93	68.23	0.68	1.08	1.79	6.19	0.68	n.d.	n.d.	774	42	n.d.
R.67	Green	18.19	2.69	1.31	69.50	0.43	0.55	1.10	5.83	0.40	n.d.	n.d.	205	13	2992
R.68	Green	17.60	5.35	1.96	66.77	0.67	0.58	1.95	5.47	0.00	n.d.	n.d.	285	13	2460
R.69	Turquoise	20.60	6.01	0.91	62.11	0.75	0.90	2.67	5.71	0.34	n.d.	2595	426	8	n.d.
R.70	Turquoise	14.56	1.55	0.68	72.18	0.69	0.71	1.02	5.91	0.62	n.d.	19,784	913	59	n.d.
R.71	Amber	18.39	4.05	0.92	68.15	0.48	1.01	1.57	5.04	0.40	n.d.	n.d.	550	41	n.d.

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Table 3 (*continued*)

Sample	Colour	SEM EDX analysis									mXRF analysis				
		Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	Fe_2O_3	Mn	Cu	Sr	Zr	Sb
R.72	Green	13.55	2.41	1.12	71.60	0.49	1.23	1.79	6.94	0.90	n.d.	n.d.	482	23	3070
R.73	Green	17.73	3.91	1.53	68.20	0.62	0.82	1.74	4.99	0.45	n.d.	n.d.	279	15	2138
R.74	Green	18.87	1.90	0.84	71.24	0.51	1.06	0.65	4.65	0.29	n.d.	n.d.	488	15	n.d.
R.75	Green	21.05	2.84	0.72	67.84	0.42	1.26	0.66	4.97	0.25	550	n.d.	360	12	n.d.
R.76	Green yellow	20.36	6.92	0.93	63.94	0.44	0.75	1.45	4.92	0.29	n.d.	n.d.	293	7	1658
R.77	Green yellow	20.15	3.20	0.76	68.51	0.47	0.92	0.96	4.75	0.28	n.d.	n.d.	255	15	1028
R.78	Green	17.53	3.00	0.95	71.26	0.51	0.83	0.92	4.70	0.30	n.d.	n.d.	439	12	n.d.
R.79	Yellow	17.16	3.22	0.98	69.98	0.57	0.89	0.90	5.97	0.33	n.d.	n.d.	331	8	2646
R.80	Colourless	20.56	5.14	0.84	65.76	0.39	0.75	1.22	5.09	0.26	n.d.	n.d.	315	10	1830
R.81	Green	20.28	3.61	0.96	67.94	0.65	0.64	0.79	4.83	0.33	n.d.	n.d.	286	10	2238
R.82	Green	13.13	2.57	0.80	69.02	0.44	0.93	1.66	9.88	0.85	9878	n.d.	1711	40	3753
R.83	Green	19.57	0.86	0.52	72.40	0.73	0.66	0.29	4.82	0.15	n.d.	n.d.	397	17	n.d.
R.84	Green	20.03	2.30	0.89	69.35	0.64	0.61	0.77	4.76	0.41	2195	n.d.	419	24	n.d.
R.85	Green	20.08	3.93	0.88	67.35	0.49	0.84	1.39	4.78	0.26	n.d.	n.d.	403	12	n.d.
R.86	Colourless	20.22	0.85	1.16	70.26	0.58	0.93	0.15	4.16	0.33	11,951	2490	213	60	n.d.
Mean		18	4	1.1	68	0.6	0.8	1.4	5	0.4	3797	6447	446	24	1958
s.d.		2	2	0.4	3	0.2	0.2	0.7	1	0.2	3812	5857	288	19	1084
Max		24	7	3.1	75	1.3	1.9	4.5	10	1.0	11,951	19,784	1945	112	6498
Min		10	0.5	0.5	58	0.3	0.3	0.1	2	0.1	128	607	148	6	327

Sample	Colour	LA-ICP-MS analysis														
		P	Ti	Cr	Mn	Ni	Zn	Rb	Sr	Y	Zr	Sb	Ba	La	Nd	Pb
R.17	Green	741	243	12	5783	13	41	8	353	2	12	587	409	2	2	13
R.19	Green	745	256	14	193	8	24	7	443	2	12	11	75	3	3	1
R.28	Green	1077	387	12	3552	10	25	10	403	3	16	1616	61	4	4	7
R.33	Green	820	231	10	1287	9	30	7	325	2	12	1822	45	2	2	2
R.34	Green	485	304	8	4803	9	15	10	528	6	32	1529	207	5	6	7
R.38	Green	203	410	8	99	3	8	1	198	5	52	3	26	5	4	2
R.39	Green	681	381	14	522	10	27	6	447	3	18	814	104	3	3	7
R.42	Yellow	820	357	13	909	9	34	7	390	3	20	2216	88	4	3	4
R.50	Green	722	327	14	204	9	29	6	324	2	19	2804	67	3	4	6
R.51	Green yellow	900	356	14	217	9	32	8	422	3	20	3745	96	3	3	3
R.52	Green yellow	838	343	16	1386	12	36	6	347	3	16	3948	71	4	3	3
R.55	Green yellow	623	298	13	178	8	25	5	376	3	14	3003	66	4	4	2
R.57	Green	694	381	14	526	10	27	6	437	3	19	785	99	3	3	7
R.60	Green	191	509	12	95	5	12	2	213	5	78	2	47	5	4	3
R.61	Green	691	472	11	116	8	32	7	215	2	20	5435	31	3	3	3
R.76	Green yellow	945	335	13	164	10	30	7	428	2	15	2843	50	3	3	10
R.77	Green yellow	747	290	9	156	6	30	6	327	2	19	1274	70	2	2	3
R.81	Green	645	296	10	206	7	25	7	338	2	16	2610	64	2	2	10
R.84	Green	400	243	9	1617	7	21	5	237	2	14	–	41	3	3	1
R.85	Green	871	285	13	225	9	22	6	454	2	16	3	82	3	3	2
Mean		692	335	12	1112	8	26	6	360	3	22	1845	90	3	3	5
s.d.		227	74	2	1659	2	8	2	91	1	16	1540	84	1	1	3
Max		1077	509	16	5783	13	41	10	528	6	78	5435	409	5	6	13
Min		191	231	8	95	3	8	1	198	2	12	2	26	2	2	1

technique. Mean value of Sr for Rhodian samples is 360 ppm in accordance with Mesopotamian samples (406 ppm) and Pylos samples (413 ppm); while the samples from Egypt, Tiryns and Thessaly have elevated values of Sr with mean values of 641 ppm, 781 ppm and 500 ppm respectively. Additionally, average value of Zr in Rhodian samples is 22 ppm and for samples from Mesopotamia, Egypt, Pylos, Tiryns and Thessaly are 7, 41, 35, 34 and 51 ppm respectively. It seems that Rhodian samples have relatively elevated value when compared to the Mesopotamian samples. It is likely though that Zr might come either from the sand source or from the ashes used as alkali that might have been added to the samples from Rhodes. Analysis of wood ash has shown that the ash contains significant amount of Zr e.g. beech, oak and fern assigned the following values to Zr: 41, 34, 38 ppm, respectively (Jackson et al., 2005) which cannot exclude the fact that ash from halophytic plants might contain similar amounts of Zr. Additionally, one needs to take into consideration the possibility that differences in these values may reflect various obstacles during the analytical process, such as the application of different analytical techniques or the chronological span of the compared data, as well as the possibility that

some of the analyzed samples might have been recycled, a practice common in antiquity especially in case of glass beads (Degryse et al., 2006).

Nonetheless, Fig. 5 suggests that Rhodian archaic glass falls closely to the range of the Mesopotamian samples, the Pylos samples and 3 of the Mesopotamian samples from Tiryns (the other two have elevated values of Sr and are scattered throughout the plot, see table 3, p. 1500, in Walton et al., 2009). Therefore, the levels of Sr and Zr trace elements in Rhodian samples resemble Mesopotamian rather than Egyptian manufacture. Overall, the study of these trace elements, while it is not certain, it nonetheless provides an indication of some links to Mesopotamian glass production.

In the following graph (Fig. 6) the correlation between Zr and Ti is shown. In this graph, we used the data obtained from the LA-ICP-MS for consistency purposes. The Rhodian samples have lower Zr values than the Egyptian samples and belong to the same trendline of the Mesopotamian samples which were excavated in Nuzi and Tel Brak (Shortland et al., 2007) as indicated on the graph. In addition, part of the samples from Tiryns which according to Walton et al. (2009) have a
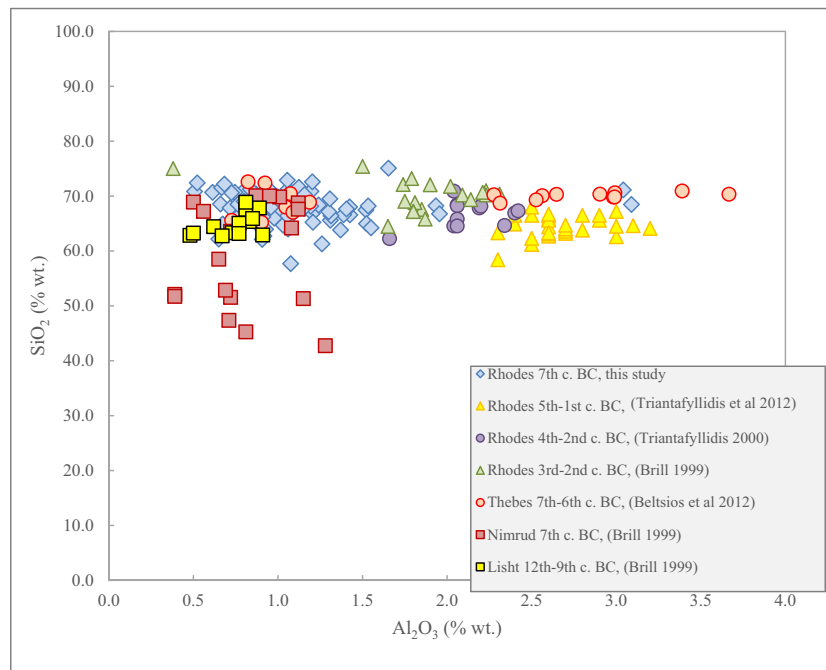
Fig. 3. SiO_2 vs Al_2O_3. There is no clustering between 7th c. BCE Rhodian samples (this study) and later Rhodian samples (Triantafyllidis et al., 2012; Triantafyllidis, 2000a, 2000b; Brill, 1999), while there is an overlap with few samples from Thebes (Beltsios et al., 2012), Nimrud and Lisht (Brill, 1999).
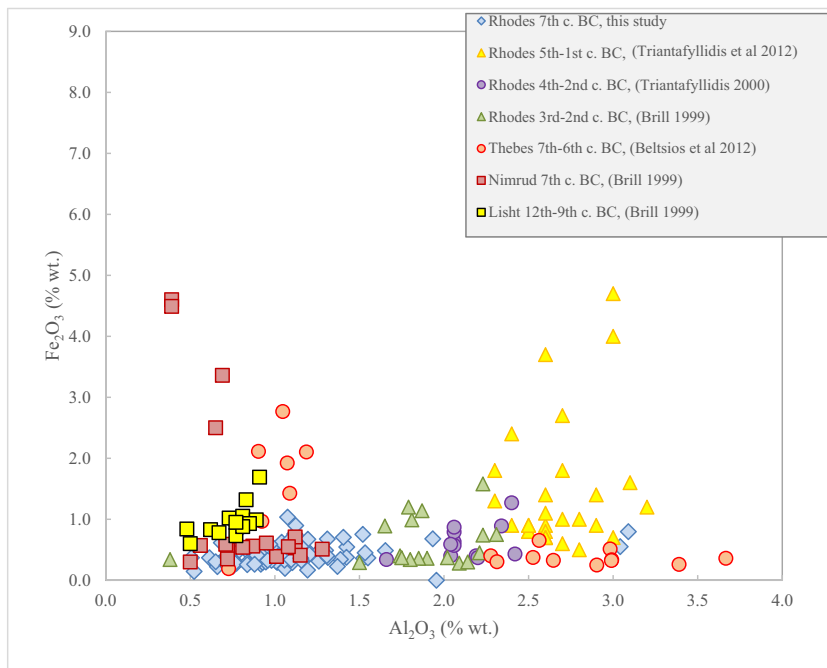

Fig. 4. Fe_2O_3 vs Al_2O_3. The 7th c. BCE Rhodian samples (this study) are not correlated with later Rhodian samples (Triantafyllidis et al., 2012; Triantafyllidis, 2000a, 2000b; Brill, 1999). In this plot Egyptian samples from Lisht (Brill, 1999) show slightly elevated values of Fe_2O_3 compared to Mesopotamian samples from Nimrud (Brill, 1999) which in turn overlap with the 7th c. BCE Rhodian samples.

Mesopotamian origin cluster together with the 7th c. BCE glass from Rhodes. On the other hand, the Egyptian samples, both from Amarna and Malkata (Shortland et al., 2007) and the ones from Thessaly and Tiryns which according to Smirniou et al. (2012) and Walton et al. (2009) have an Egyptian origin, show a rather scattered behavior and definitely distinct from the Mesopotamian samples. It is interesting to note on this graph again that the 3 Rhodian samples (indicated with arrows) that have an outlying behavior are natron glasses (see discussion below).

In Fig. 7 the correlation between Zr and Nd is presented. The samples are distinguished very clearly in two groups. The one group has Nd and Zr values lower than 4 and 20 ppm respectively and the other

one with values of Nd and Zr > 4 and 30 ppm respectively accordingly. The first group contains only the Rhodian samples and three samples from Tiryns which according to Walton et al. (2009) have a Mesopotamian origin. On the other hand, the second group contains the samples from Tiryns and Thessaly which were attributed an Egyptian origin by Walton et al. (2009) and Smirniou et al. (2012) respectively. Furthermore, as expected in the same area of the second group there are also the three natron glasses from Rhodes (indicated with arrows).

Finally, in Fig. 8 we demonstrate the correlation of the ratios of Zr/Ti and Cr/La. According to Shortland et al. (2007) these trace elements can provide differences in the original raw materials. Ti, Zr, La and Cr are four trace elements that except from their regional variability which
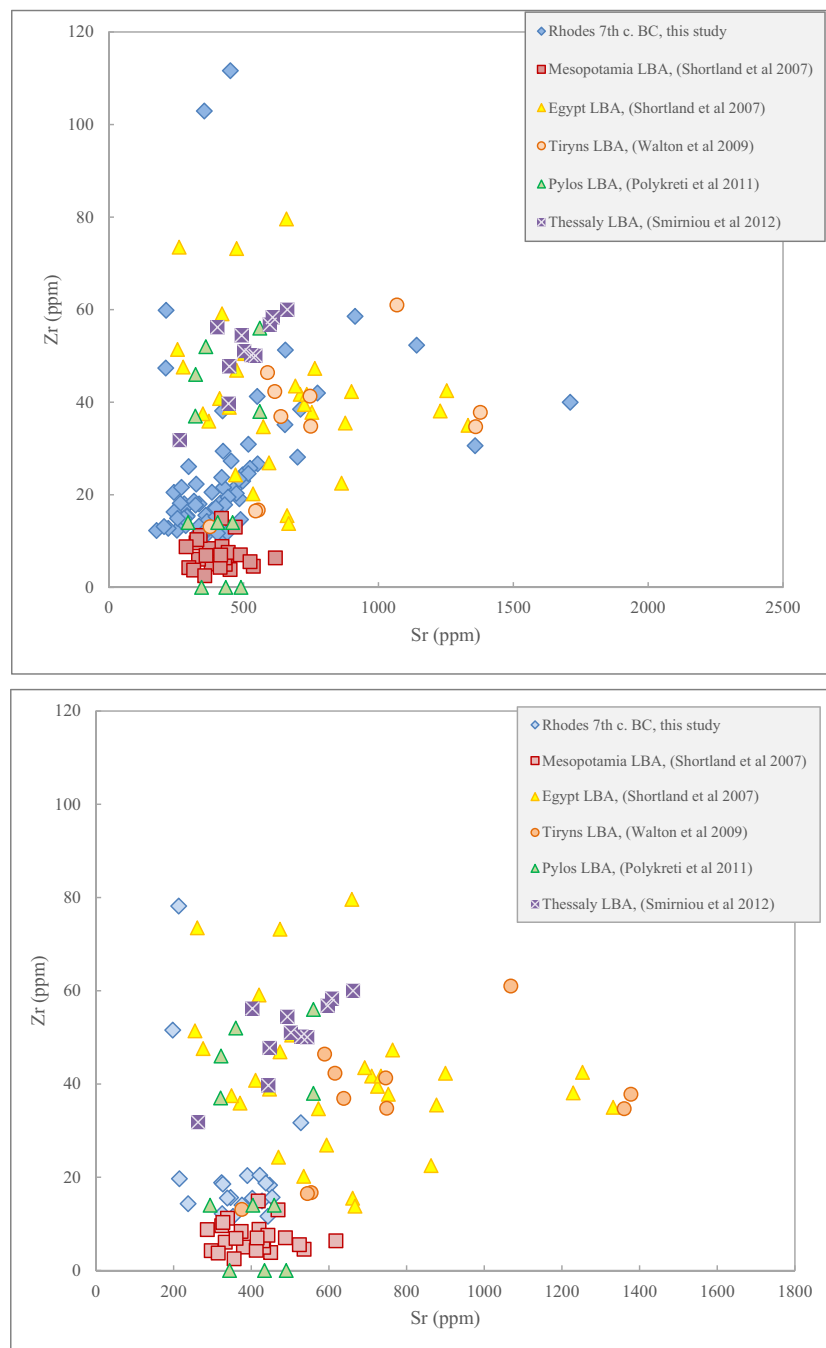
Fig. 5. Zr vs Sr. There is a slight overlap between the samples from Mesopotamia (Shortland et al., 2007) and the 7th c. BCE Rhodian samples (this study). The samples from Egypt (Shortland et al., 2007), Tiryns (Walton et al., 2009), Pylos (Polikreti et al., 2011) and Thessaly (Smirniou et al., 2012) are widely scattered in the graph with elevated amount of Zr.

can be reflected to the local geochemistry are also refractory and non-volatile and therefore not affected by the high temperature during the glass manufacture.

In Fig. 9 the majority of Rhodian samples fall closely and even overlaps with the Mesopotamian samples. They present lower Zr/Ti ratio compared to the Egyptian samples and also, they seem to have almost the double amount of Cr/La ratio which is a result of higher amounts of Cr in the glass. Chromite can be found in rocks which are abundant in the mountainous headwaters of the Mesopotamia and in particular of Tigris and Euphrates rivers. The erosion of such rocks could potentially produce chromite-bearing sands which may have had an important role in the Mesopotamian glasses (Shortland et al., 2007). Therefore, this could be a solid proof that the samples from Rhodes

have a Mesopotamian origin. It is also interesting to note that in Fig. 9 there are 3 samples (indicated with arrows) that exhibit high Zr/Ti ratio and low Cr/La ratio, and are part of the natron glass from Rhodes which has been discussed earlier.

Concluding, through the comparison of specific trace elements we can assume that the majority of the 7th c. BCE samples from Rhodes (this study) has similarities with Mesopotamian samples (Shortland et al., 2007) rather than Egyptian samples (Shortland et al., 2007). This can be extrapolated to the geochemistry of raw materials providing an indication regarding the provenance of the 7th c. BCE Rhodian samples. Furthermore, there are at least 3 samples (the natron samples) that show Egyptian similarities and might be connected to the foundation of Naukratis in Egypt (see discussion below).
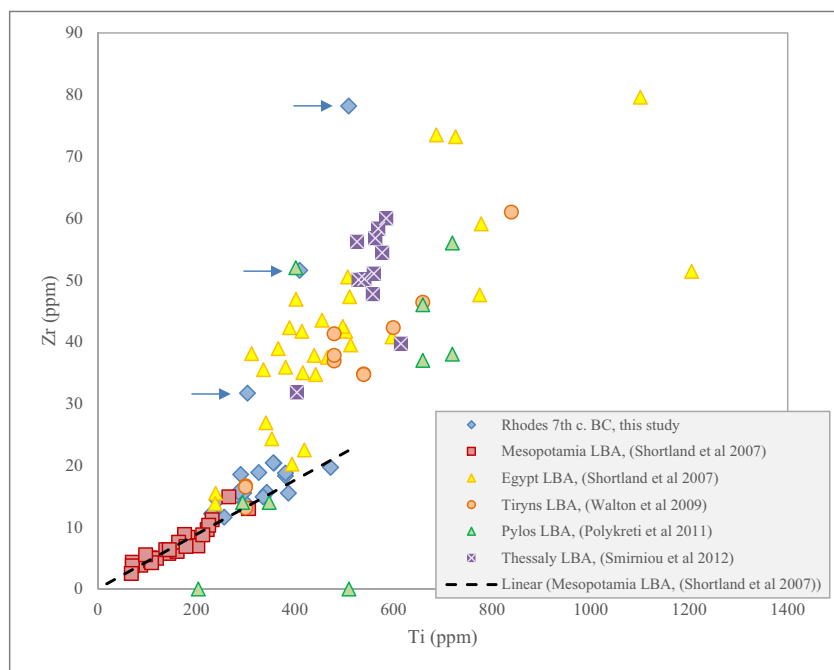
Fig. 6. Correlation of Zr and Ti for the 20 selected 7th c. BCE samples from Rhodes (this study) which fall in the same trend line of the Mesopotamian samples (Shortland et al., 2007). The samples from Egypt (Shortland et al., 2007), Tiryns (Walton et al., 2009), Pylos (Polikreti et al., 2011) and Thessaly (Smirniou et al., 2012) are scattered in the graph with elevated amount of Zr. The three natron glasses from Rhodes (this study) are indicated with the arrows.
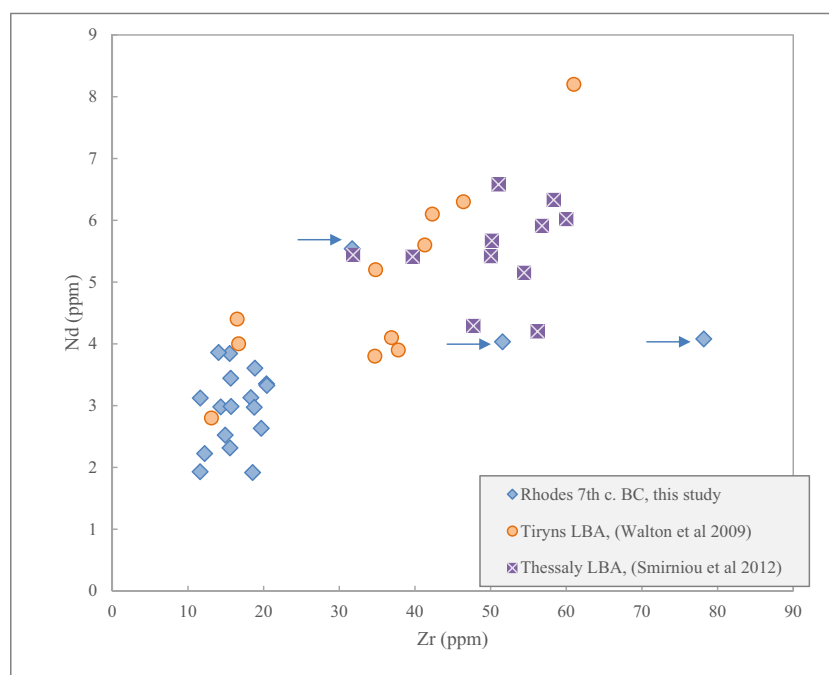
Fig. 7. Correlation of Zr and Nd for the 20 selected samples from Rhodes. The data are compared with LBA samples from Greece (Tiryns and Thessaly).

6. Alkalis

The second most important ingredient in ancient glassmaking is the alkali. The main function of alkali in glass is to lower the melting point of silica from 1783 °C to 1100–1200 °C depending on their concentration (Doremus, 1994; Nikita, 2004; Rehren and Pusch, 2005; Tanimoto and Rehren, 2008). During antiquity, there were two main sources of alkalis: ashes of certain plants (Barkoudah and Henderson, 2006; Henderson, 2013) and natron or/and trona minerals formed seasonally as water evaporates from the surface of alkali rich soils in specific lakes (Henderson, 2013).

The two alkali sources are easily distinguishable by comparing MgO to K_2O. Usually, the use of plant ash as an alkali in the basic glass reflects elevated values of both MgO and K_2O (> 1.5 wt%) (because of the high levels of these oxides in the plant ash composition which according to Barkoudah and Henderson (2006) average at 5.2 and 24.9 wt % respectively), while the use of natron (a purer source than plant ash) reflects lower values of the specific oxides (< 1 wt%) (Lilyquist and Brill, 1993).

In Fig. 9 K_2O against MgO are plotted for Archaic Rhodian samples. In the same figure values of the same samples used in Figs. 4 and 5 are incorporated for comparison purposes. The majority of Rhodian archaic samples fall in the region of "plant ash" glasses which have elevated values of both oxides (MgO ~2–7 wt% and K_2O ~1.5–3 wt%).

The rest of the glass from Greece, even the contemporary samples from Thebes, are manufactured using natron as a flux. They fall in the
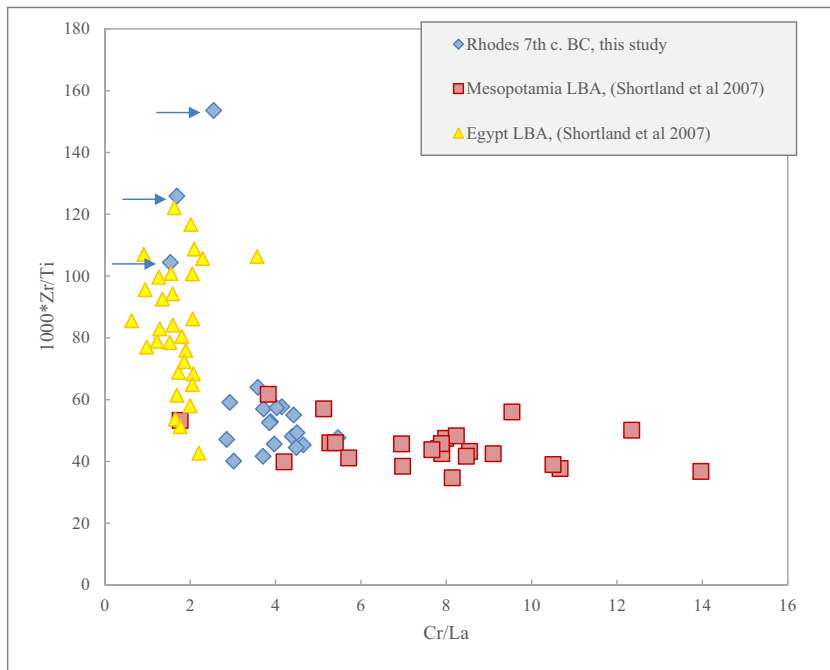
Fig. 8. Correlation of the 1000*Zr/Ti to Cr/La for the 20 7th c. BCE Rhodian samples (this study) compared with Mesopotamian and Egyptian samples (Shortland et al., 2007). The majority of Rhodian samples cluster and slightly overlap with the Mesopotamian samples. The three samples indicated with arrows are Rhodian natron glass.
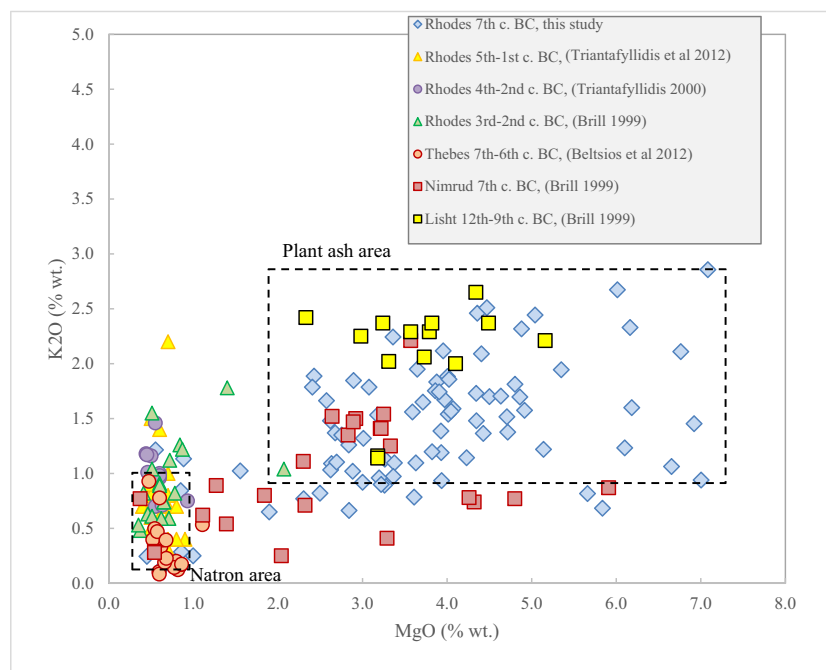
Fig. 9. K_2O vs MgO. The 'natron' and the 'plant ash' regions are presented with the small and big rectangular respectively.

low MgO and low K_2O region as it is presented in Fig. 9. The case of Mesopotamian (Nimrud) and Egyptian (Lisht) glass samples is different. Both assemblages use plant ash as a flux. As it is presented in Fig. 9, Egyptian samples have slightly elevated values of K_2O, while the Mesopotamian samples fall very close to the spread of Rhodian samples.

It is interesting to note that 8 samples from the 7th c. BCE Rhodian samples fall in the natron area, which might point to a transition between the two glassmaking traditions, from plant ash to natron based glass that possibly occurred on Rhodes during the Archaic period and may coincide with the foundation of Naukratis in north Egypt [detailed description of the glassmaking tradition in Rhodes during Archaic period can be found in Beltsios et al., 2012, p. 170]. The 6 out of these 8 samples show also a distinct behavior in the Fig. 6 (scattered Rhodian

samples with labels which are similar to the Egyptian samples). Furthermore, 3 (due to the lack of more analytical data) out of these 8 are distinguished in Figs. 7, 8, as showed above, having again an Egyptian behavior and thus indicating totally different manufacturing tradition. Whatever the case is i.e. either the glass was manufactured on Rhodes (less likely) or was imported as raw material or/and as final artefact (more likely), we believe we are witnessing a transition to the natron tradition on Rhodes island happening during this period (Archaic) and continuing to the following centuries (Classical and Hellenistic).

7. Lime

Lime (CaO), the third basic constituent of base glass composition,
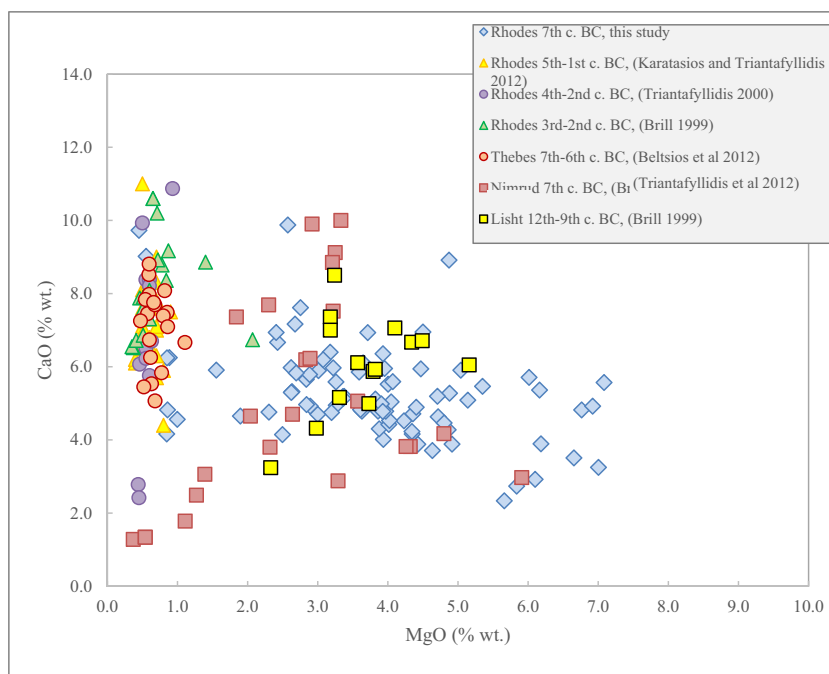
Fig. 10. CaO vs MgO. 7th c. BCE Rhodian samples (this study) are highly scattered due to MgO scattered values.

was added to glass either deliberately or as an impurity in the form of shells which exist in sand (Henderson, 2013). In plant ash glass, lime can also be introduced through the plant ash itself as CaO in plant ashes can be absorbed from the soil. Different geological environments can reflect different plant ash composition, which in turn has an effect on the final composition of glass (Barkoudah and Henderson, 2006).

The plot of CaO against MgO is shown in Fig. 10. The majority of Rhodian samples are plotted on the right side of the graph due to high MgO values while CaO content is more stable (for further discussion concerning the correlation between CaO and MgO for Rhodian samples see Beltsios et al., 2012, p. 172).

The observed scatter is likely resulting from impurities of the sand, as well as plant ashes present in the glass batch (Henderson, 2013, 64–65). One could expect to see a correlation between these two oxides on plant ash glass, since plant ash analyses show a positive correlation between CaO and MgO. This correlation though tends to diminish and disappear during the process of glassmaking (Henderson, 2013, 39). In Fig. 10, Mesopotamian (Nimrud) and Egyptian (Lisht) samples show a wide scatter and most of their values coincide with Rhodian samples. Most of the other samples from Rhodes and Thebes, however, have elevated values of CaO.

8. Conclusions discussion

Through the systematic archaeometrical study of Archaic glass from Rhodes island interesting conclusions derived. The glass in Rhodes most likely was imported from various regions since there are not any solid evidence for primary glass production yet (only few hypotheses). Nevertheless, the analytical data show that there is no continuity in the technology used for the Archaic glass and glass of the subsequent centuries in Rhodes in terms of the basic glass composition. It seems that during the Archaic period there is a stop in the supply of plant ash glass and the first signs of natron glass appear in Rhodes. The technology of glass found in Rhodes shifts both in terms of the silica raw materials towards other possible sources and in alkali raw material towards the use of a mineral source rather than plant ash. This transition to the new glassmaking tradition, especially in the alkali raw material, in Rhodes occurs already during the end of 7th c. BCE according to the analytical data we provided.

Furthermore, the chemical composition of the Archaic beads is not correlated with contemporary samples from the mainland Greece and more specifically from Thebes. Both assemblages have major differences in various major and minor elements as it has been also demonstrated elsewhere (Beltsios et al., 2012; Oikonomou, 2012) indicating possible different supplying centers of either glass objects of even raw glass.

Relating to the provenance of the Archaic beads, both major-minor and trace elements analysis show that there are strong indications for a Mesopotamian origin. As it was demonstrated in the corresponding plots (Figs. 5–8) there is higher correlation between Archaic samples from Rhodes with samples from Mesopotamia rather than samples from Egypt with the exception of few samples (at least 6) that show an Egyptian origin and is probably connected to the access of Rhodes in Egypt through the foundation of Naucratis.

This intriguing similarity between the majority of Archaic glass from Rhodes and the Late Bronze Age glass from Mesopotamia might have two possible explanations: 1. Either the production took place on the island of Rhodes and is connected with the older Mesopotamian tradition in terms of using similar or even the same raw materials, which is possible, but rather unlikely, since there are not yet any archaeological evidence suggesting primary glass production in the Archaic period on Rhodes island or 2. raw glass, or even finished objects, was imported from a glassmaking center located somewhere in Mesopotamia. In this case, secondary glassmaking can be suggested on Rhodes island; most of the beads are broken in half, very precisely (Fig. 2), which might suggest fault during the manufacturing process (e.g. subject to low annealing time) and not due to usage (breakage by accident after the full solidification of glass would cause irregular fracture due to the conchoidal property of glass) reinforcing the idea of secondary glassmaking on Rhodes island as early as the Archaic period.

Acknowledgments

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