Archaeological and Anthropological Sciences

DIFFERENT GLASSMAKING TECHNOLOGIES IN THE PRODUCTION OF IRON AGE BLACK GLASS FROM ITALY AND SLOVAKIA.

--Manuscript Draft--

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Abstract:	This study presents the results of an archaeometrical investigation performed on 75 black glass beads dated to the 9th-5th century BC coming from Bologna, Cumae and Pozzuoli (Italy), and Chotin (Slovakia). The analyses of the major, minor and trace elements - as well as that of Sr and Nd isotopes performed on a selection of samples coming from Bologna - provided evidence for two different production technologies in Iron Age black glass found in Italy (natron glass, probably produced in Egypt) and Slovakia (wood ash glass, probably produced in Europe). In both cases, the glasses derive their black colouration from the high presence of iron (around 12% FeO), introduced into the glass batches through the intentional choice of dark sands. The production model appears to be small-scale and experimental, characterised by the use of non-sorted raw materials and poorly defined formulae, producing glass with a high chemical variability. The wood ash technology appears to have dropped out of use in Europe until the Medieval period, while natron production spread quickly, becoming predominant throughout the Mediterranean.
Response to Reviewers:	Answers to referees' comments and list of revisions Reviewer #1: The authors took in consideration most of the comments raised by this reviewer. Few points remain to be clarified. - The experimental section has been improved. The authors added a comment regarding the experimental protocol used for EPMA being equal to the condition reported in Henderson 1988b. However, the LA-ICPMS section becomes more unclear than before. In the original version we read that NIST 612 and 614 were used for external calibration, and that two glass standards (not specified) were used as secondary standards to check for accuracy and precision. The new version states instead that NIST 610 and 614 were used for external calibration, and NIST 612 was used as secondary standard to check for accuracy and precision. What happened to

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UNIVERSITA' DEGLI STUDI DI TORINO

Dipartimento di Scienze della Terra

Torino, July the 8th, 2016

Manuscript Ms. No. AASC-D-16-00060_R1

Dr. Elisabetta Gliozzo
Main Editor
Archaeological and Anthropological Sciences

Dear Editor,

please find enclosed the revised version of the manuscript **"DIFFERENT GLASSMAKING TECHNOLOGIES IN THE PRODUCTION OF IRON AGE BLACK GLASS FROM ITALY AND SLOVAKIA.**" by Conte et al., modified according to reviewer's comments.

Below we have reported the answers to the referees' comments and the list of the revisions made.
We hope that now the manuscript is suitable for publication in AASC.

Best regards
On behalf of the co-authors

Sonia Conte

Answers to referees' comments and list of revisions

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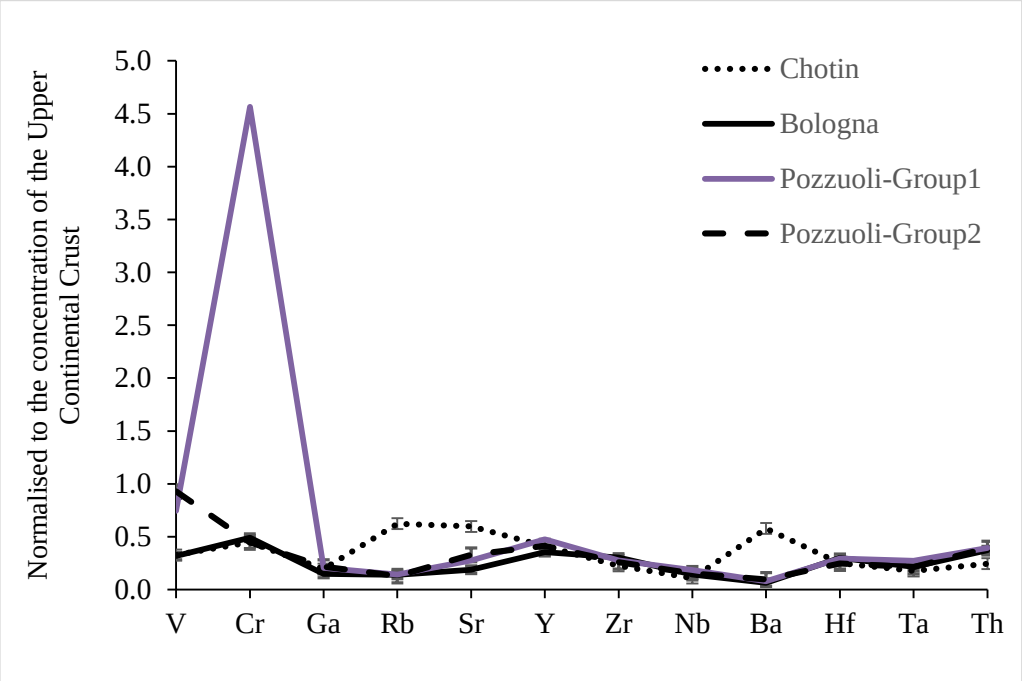

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DIFFERENT GLASSMAKING TECHNOLOGIES IN THE PRODUCTION OF IRON AGE BLACK GLASS FROM ITALY AND SLOVAKIA.

Sonia Conte[1]*, Rossella Arletti[1], Julian Henderson[2], Patrick Degryse[3], and Annelore Blomme[3]

Running title: Iron Age Black Glass from Italy and Slovakia.

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ABSTRACT

This study presents the results of an archaeometrical investigation performed on 75 black glass beads dated to the 9th-5th century BC coming from Bologna, Cumae and Pozzuoli (Italy), and Chotin (Slovakia). The analyses of the major, minor and trace elements - as well as that of Sr and Nd isotopes performed on a selection of samples coming from Bologna - provided evidence for two different production technologies in Iron Age black glass found in Italy (natron glass, probably produced in Egypt) and Slovakia (wood ash glass, probably produced in Europe). In both cases, the glasses derive their black colouration from the high presence of iron (around 12% FeO), introduced into the glass batches through the intentional choice of dark sands. The production model appears to be small-scale and experimental, characterised by the use of non-sorted raw materials and poorly defined formulae, producing glass with a high chemical variability. The wood ash technology appears to have dropped out of use in Europe until the Medieval period, while natron production spread quickly, becoming predominant throughout the Mediterranean.

Keywords: Black glass; Iron Age; archaeometry; trace elements; isotopes; LA-ICPMS.

Acknowledgements

The authors are indebted to Simona Bigi (Unimore) for the electron microprobe analyses and to Daniela Manzini (Centro Interdipartimentale Grandi Strumenti-Unimore) for help with the LA-ICPMS analyses. The Fondazione Cassa di Risparmio di Modena is acknowledged. JH is grateful to Dt Robert Brill, formerly of the Corning Museum of Glass, for giving him the Chotin beads and the associated file of information.

1. INTRODUCTION

Glass manufacturing derives from a background in metal and faience making, but unlike these, it represents the first production technology in which raw materials (i.e. crushed quartz or sand, plant ash, and colorants) were processed and transformed into a truly synthetic product, representing an important step change in ancient technology (Henderson 2013).

The first man-made glass was produced around 2300 BC in the area of modern Iraq and northern Syria (Mesopotamia) (Oppenheim 1973), but the mass-production of glass only started around 1500 BC in Mesopotamia, followed within 100 years by Egypt (Lilyquist and Brill 1993; Nicholson 1993; Shortland 2000; Shortland and Eremin 2006). Glass technology became fairly advanced in the Roman Empire and the introduction of glassblowing (halfway through the 1st century BC) helped to transform glass from a relatively exclusive material into an affordable common commodity (Cagno et al. 2014) which, because of its translucent quality, allowed traded liquids to be viewed.

Late Bronze Age (LBA) and Roman glass production have been investigated in depth (as reported in the next paragraph), but little is known about the glass produced during the Iron Age up to the time of Roman dominance. This is especially true for the European Iron Age, which has mainly been investigated by Arletti and co-workers (Arletti et al. 2009; 2011a, b; 2012), Gratuze and co-workers (Gratuze 2009; Gratuze and Billaud 2003; Gratuze and Lorenzi 2006; Gratuze and Picon 2006) and others (Henderson and Warren 1981; Henderson 1989; Wobrauschek et al. 2000; Karwowski 2004; Cecere et al. 2008; Angelini et al. 2011; Polla et al. 2011; Gallo et al. 2012; Panighello et al. 2012; Purowski et al. 2012). This period immediately follows the demise of the mixed alkali-LMHK technology in Europe (Henderson 1989) and that of the plant ash-HMG in the eastern Mediterranean (9th century BC), and represents the beginning of the spread of natron-LMG glass.

Studies on glass items dated to the first stage of the Iron Age reveal a complex situation characterised by the co-existence of different chemical types (HMG, LMHK, LMG), some being typical of this period (Alumina-cobalt blue and black natron glass with low lime, see Conte et al. 2016).

In this study a total of 75 glass samples from Italy (65 from Bologna, Cumae, Pozzuoli) and Slovakia (10 samples from Chotin) were investigated. They are all dated between the 9th and 5th century BC. The chemical investigation of this Italian and Slovakian Iron Age glass offers an excellent opportunity to shed light on this crucial period of technological transition, while also attempting to establish information about the glass production model. Moreover, all the glass here in exam are a 'black' (very deep translucent) colour. The black glass represents a category that has attracted great interest recently, as demonstrated not only by works on Roman glass (Van der Linden et al. 2009; Cholakova and Rehren 2012; Rehren et al. 2012; Cagno et al. 2014), but also by those on the early 1st millennium BC one (Gratuze and Picon 2006; Reade et al. 2009; Conte et al. 2016).

2. GLASSMAKING TECHNOLOGIES AND PRODUCTION MODELS BETWEEN THE LBA AND THE ROMAN PERIOD: THE STATE OF THE ART.

The first glass production technology (from the 2nd millennium BC until about the 10th-9th century BC) involved the use of two basic raw materials: ashes from salt-tolerant (halophytic) plants, and silica (Turner 1956; Forbes 1957; Henderson 1985; Henderson 2000; Barkoudah and Henderson 2006), resulting in characteristically high levels of magnesia (c. 2-6%) and potash (c. 0.5-4% K_2O) in the finished glass (High Magnesium Glass -HMG) (Sayre and Smith 1961; Henderson 1989, 2000, 2010; Towle et al. 2001; Gratuze and Billaud 2003; Nikita and Henderson 2006, Henderson 2013).

By the mid-2nd millennium BC, HMG glass was widespread among the strongly hierarchical Late Bronze Age societies in three principle areas: Mesopotamia, Egypt, and Greece (Nolte 1968; Barag 1970; Henderson 2013). It was also found in some Western Mediterranean sites dating from the Bronze Age through to the Early Iron Age (*e.g.* Hartmann et al. 1997; Santopadre and Verità 2000; Angelini et al. 2002; Gratuze and Billaud 2003; Conte et al. 2016).

The HMG glass production and trading model proposed by Rehren and co-workers (2001), and Pusch and Rehren (2007), postulates that only a few "primary" glass production sites existed in LBA Mesopotamia and Egypt. At these primary sites, glass was produced by mixing the silica source with the fluxing agents. This glass was traded in the form of ingots to "secondary" workshops scattered around the Mediterranean, where it was reheated and shaped into objects.

Although the evidence is thin on the ground this model is supported to some extent by some archaeological and chemical data. Chemical studies of finds including crucibles, ingot moulds, and glassy slag from the New Kingdom sites of Qantir – Pi-Ramesse (Rehren and Pusch 2005; Pusch and Rehren 2007) and possibly from Tell al-Amarna (Smirniou and Rehren 2011), demonstrated evidence for primary glass-making at these Egyptian centres. Likewise, the presence of independent primary workshops in Mesopotamia was established by studying glass trace elements (Shortland 2005; Shortland et al. 2007) and isotopic composition (Degryse et al. 2010, 2015; Henderson et al. 2010; Henderson 2013). The isotopic study by Degryse and co-workers (2010) and using a larger data set (Henderson et al. 2010; Henderson 2013) demonstrated that at least two centres of primary production existed in LBA Mesopotamia, possibly in the zones in which Nuzi, Iraq and Tell Brak, Syria are located.

Conversely, analyses of Mycenaean glass samples – which in stylistic analyses appeared to be of Greek manufacture – indicated that some were produced in Egypt and some in Mesopotamia (Panagiotaki 2008; Walton et al. 2009; Henderson et al. 2010).

Chemical analyses of LBA glass objects found in Europe revealed the presence, in addition to HMG glass, of a different chemical type, characterized by mixed alkalis (Na_2O and K_2O total around 14% to 18%, with sodium at 6-8%), low lime (ca. 2%), and low magnesia (<1%), which was named LMHK (low magnesium, high potassium) (Henderson 1988a, b; Santopadre and Verità 2000; Towle et al. 2001; Angelini et al. 2004; Venclová et al. 2011, Henderson 2013). The source and type of the alkali is still being debated, although the low levels of Cl and P_2O_5 may suggest the use of a leached tree ash material (Hartmann et al. 1997; Angelini et al. 2004; Henderson et al. 2015). Even if present in very low number, also High-K glass was found in LBA Europe (Towle

et al. 2001; Angelini et al. 2004, Angelini et al. 2010; Venclovà et al. 2011; Conte, unpublished data), representing the potash pole of the LMHK glass. This glass shows the same chemical features of the LMHK (MgO <1.5%, CaO <4%, P_2O_5 <1%), but different alkali contents, with the predominant presence of potash (12-18%) over soda (1-4%). As stated by Venclovà and co-workers (2011), this could indicate the use of a different source of K-ions or a different method of ash leaching. The LMHK composition was initially related to faience and glassy faience dated to the Early/Middle Bronze Age (24^{th}-15^{th} century BC) and mainly recovered in Italy (Angelini et al. 2005, 2006; Santopadre and Verità 2000), Slovakia (Angelini et al. 2006), and Ireland (Henderson 1988a). These items were probably produced locally on a small scale (Henderson 1988a; Angelini et al. 2006).

Starting from the 11^{th} century BC a massive transition from plant ash glass to mixed alkali glass occurred in the Western Mediterranean. Since this LMHK is completely different from the predominant coeval glass type, and does not have a chemical counterpart outside Europe, it is considered a typical European production. Specifically, chemical analyses of European glass provided evidence for glassmaking at the 11^{th}-9^{th} century BC site of Frattesina in Northern Italy (Henderson 1988a, b; Brill 1992; Towle et al. 2001; Angelini et al. 2004). Many studies revealed that the LMHK glass was widespread in Switzerland (Henderson 1988a, b), Germany (Hartmann et al. 1997), Bohemia-Czech Republic (Venclovà et al. 2011), France (Gratuze et al. 1998; Croutsch et al. 2011), England and Ireland (Henderson 1988a, b), and Greece (Nikita and Henderson 2006). The first isotopic study of LMHK glasses has provided evidence that it was fused in more than one place – one probably at Frattesina, the other possibly in southern Italy (Henderson et al. 2015).

The primary manufacture of LMHK glass in large quantities occurred in a period corresponding to the collapse of the great Bronze Age palatial economies of Mycenaean Greece, Egypt, Mesopotamia, and Hittite Turkey, along with a wide range of other socio-economic changes (including the breakdown of trade and exchange networks). LMHK glass thus filled a gap resulting from the disrupted supply of glass from the Aegean and Middle East to Europe (Henderson 1998b, 2013).

From the early first millennium BC, the use of natron as a glass flux spread through the Mediterranean and Levantine regions. Around the 10^{th} century BC, in Egypt, some glassmakers started to use this mineral (natron) as an alkali source (Schlick-Nolte and Werthmann 2003) producing the so-called LMG – low magnesium glass (K_2O and MgO $\leq$1.5%) (Sayre and Smith 1967). To date, literature records only few cases that evidence the use of natron in the early 1^{st} millennium BC, with examples coming from Nimdur (Reade et al. 2005), Hasanlu (Brill 1999), France (Gratuze and Picon 2006), Jordan (Pella – Reade et al. 2009) Italy – Sarno and Capua (Conte et al. 2016), Como (Angelini et al. 2011), Bologna (Arletti et al. 2011a; Polla et al. 2011), Sardinia (Angelini et al. 2012).

In Europe, natron-based glass replaced plant ash glass imported from the Near East and locally produced LMHK. Natron appears to have fed the prodigious growth of the Roman glass industry.

Theories regarding natron glass production during the Roman period are centred on

two models. The first is similar to the one proposed for LBA glass, with a system of a small number of primary and numerous secondary workshops (Henderson 1989; Freestone 2006). Primary glassmaking centres were active in Beirut in the Late Hellenistic- early Roman period (Kowatli et al. 2008), in Egypt in the 1st-3rd century AD, and Syro-Palestine in the 4th-8th century AD (Brill 1988, 1999; Freestone et al. 2000, 2002; Picon and Vichy 2003). The second (decentralised) model instead proposes the existence of many more glassmaking centres with associated glassworking centres. Archaeological, chemical and isotopic evidence also suggests that there were primary glassmaking centres also in the Roman western Mediterranean and Europe (Wedepohl et al. 2011a; Degryse and Schneider 2008; Degryse 2014). In the present state of knowledge, a combined occurrence of regional primary production in the west and large-scale distribution of raw glass from the south-eastern Mediterranean appears the most likely scenario – but this balance may change.

In any case, both the proposed models refer to natron glass production during the Roman period. For the centuries between the introduction of natron technology (10th-9th century BC) and the emergence of the Roman Empire (1st century BC), there is still no archaeological evidence of primary production sites (Henderson 2013) and glass production in this period is far from being fully understood.

3. ANALYSED SAMPLES

A total of 75 black glass samples were analysed from four different archaeological sites in Europe, dated from 9th to 5th century BC (Table 1).

3.1. Bologna Trade Fair Zone - Italy

These 11 samples come from an archaeological site discovered around 1960 in the area of the present day Bologna Trade Fair. The archaeological works recovered a large number of objects indicating the presence of a Villanovian village. The chronology of the site extends from Villanovian II (800-750 B.C.) to Villanovian III (750-680 BC) (Dore 2004). The village area was studied in 1979, but the archaeological excavations of the annexed necropolis were only conducted in 2006-2007 (Mengoli, unpublished data). These more recent excavations allowed the recovery and study of 1310 graves, providing a number of objects and artefacts of different typologies and materials (glass, bone, bronze, ceramic, and amber). The glass samples presented here are all annular black beads (Table 1) and derive from the necropolis excavations. Chemical data regarding glass beads of colours other than black and originating from this site have already been published (Arletti et al. 2011a).

3.2. Pozzuoli-Italy

These 43 samples originate from beads held in the Beck Collection in the Cambridge University Museum of Archaeology and Anthropology (Beck Collection 1997, 74-75). The beads may be from Pozzuoli, but there is also a strong possibility that they derived from the archaeological site of Cumae that is 6 kms away from Pozzuoli. Although not dated by an archaeological context these beads are characteristic of the 9th-8th century BC (Haevernick 1981; Spear 2001, 80; Spaer 2002, 55-57; Conte et al. 2016) and can be as late as the 7th century BC (Frey 1987). The beads are all black, their shapes include sub-

triangular, globular, cylindrical and are decorated with opaque white eyes and stripes; some have grooves from which the white glass has fallen out (Table 1).

3.3. Cumae-Italy

These 11 samples originate from beads held in the Beck Collection in the Cambridge University Museum of Archaeology and Anthropology (Beck Collection 1997, 75-76). All the beads are made of black glass and include sub-triangular, globular and cylindrical forms all decorated with opaque white glass including eye and spiral decoration (Table 1). A recent study of Iron Age glass from Sarno and Cumae (Conte et al. 2016), shows that eye beads and spherical black beads decorated with irregular blobs or bands, similar to those analysed here, were found. The published beads come from the *Fossakultur* necropoleis dated to the 9th-8th century BC, belonging to the pre-Hellenic phase. Moreover, Gratuze and Picon (2006) and Gratuze (2009) found more than 200 black annular and globular black beads, decorated or not with a white equatorial line or white blobs, in twelve French sites dated to the 9th-8th centuries BC.

3.4. Chotin-Slovakia

These 10 glass samples originate from excavations of cremation burials in cemeteries IA and IB at Chotin, Komarno district by Dr Mikuláš Dušek (Dušek 1966), given to Dr Robert Brill of the Corning Museum of Glass in 1967. The donut shaped beads date to the Hallstatt D period (Miroššayova and Olexa 2009) c. 650-475 BC (Table 1). Bead analyses were published by Brill (1999 vol. 1, 59; 1999b vol. 2, 49-50). Dr Brill kindly shared all this and other information with one of us (JH).

4. ANALYTICAL METHODS

Due to the good state of preservation, the removal of only small chips of a few hundred μm^3 was possible. Chemical analyses were carried out using electron microprobe (EMPA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS).

4.1. Electron microprobe analysis

The analyses on the Bologna glass samples were performed at the Department of Earth Sciences of the University of Modena and Reggio Emilia, using an ARL-SEMQ instrument equipped with four scanning wavelength-dispersive spectrometers (WDS). The chemical analyses of major and minor elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S, Cl) were carried out on glass chips embedded in epoxy resin and polished with diamond paste.

The following natural standards were employed as primary reference samples: albite (Na); olivine (Mg); microcline (K, Al); augite (Si, Ca); sodalite (Cl); apatite (P); ilmenite (Fe, Ti); spessartine (Mn). The analyses were performed operating at 15 kv accelerating voltage, 20 nA beam current, with counting times of 5-10-5 sec on background-peak-background, respectively. A 30 μm defocused electron beam was utilised in order to prevent the known migration phenomenon of alkalis. Several points were analysed on each sample to test homogeneity, and the mean value was calculated. The *probe* programme (Donovan and Rivers 1990) was used to process the results for matrix effects using phi (ρz) absorption correction, and to correct the interference between the Sb-*Lα*

and K-*K*β peaks and between the Ca-*K*β and P-*K*α peaks. The measured accuracy for the analysed elements was better than 3%, while precision (standard deviation) was between 1-2% and 2-3% for major and minor constituents, respectively. The detection limit for the minor elements was between 0.01 and 0.04 wt.%. The results are reported in Table 2, with values lower than detection limits removed.

The electron probe microanalyses of the balance of bead samples was performed using a Cambridge Microscan probe in the (then) Department of Earth Sciences, University of Oxford. Full analytical conditions, accuracy and precision of the technique are published in Henderson 1988b (the same experimental condition were used). For some samples (Pozz-54, 60, 81, 84, Cum-172) the closure is not good due to the low amount of material available and to the consequent difficulties in the sample preparation, leading to a not perfect polished surface.

4.2. Laser-ablation inductively coupled plasma mass spectrometry

LA-ICPMS was used to determine the concentration of 30 trace elements in 35 selected samples. Trace element analyses of the Cumae samples was not possible due to unavailability of the samples. All the analyses were carried out with a Thermo Fisher X-Series^{II} quadrupole based ICP-MS, coupled with a New Wave ablation system with a frequency quintupled (λ = 213 nm) Nd:YAG laser, at the Centro Grandi Strumenti of the University of Modena and Reggio Emilia. The laser repetition rate and the laser energy density on the sample surface were fixed at 20 Hz and ~18 J/cm^2, respectively. The analyses were carried out using a laser spot diameter of 100 µm on the same polished fragments used for EMPA. External calibration was performed using NIST SRM 610 and 614 glass as external standard, and ^{29}Si, previously determined by EMPA, as internal standard, following the method proposed by Longerich et al. (1996). Standard Reference Material NIST612 (Pearce et al. 1997) was used as a secondary reference sample to check precision and accuracy. The results, reported in supplementary material S1, indicate a very good precision of the measurement (SD< 7) and a rather good accuracy (<10% for most of the elements). Six points were analysed on each sample to test homogeneity and the mean value was calculated. The standard deviations among the points analysed on the same sample were below 10% for all the elements, with the exclusion of Sn and Pb with more variable SD.

4.3. Isotope analysis

Isotopic analyses of the Bologna black samples FiBo5, FiBo6, FiBo7, FiBo19, FiBo22, and FiBo23 were carried out at the University of Leuven (Belgium). Only these samples were selected for isotopic analyses due to the availability of materials, considering that this analysis requires at least 30 milligrams of glass. The glass samples were finely powdered and subjected to a digestion procedure. The samples were dissolved in a 3:1 mixture of 22M HF and 14M HNO_3 at 110°C overnight. These were dried and dissolved in aqua regia (3:1 mixture of 12M HCl and 14M HNO_3). The sequential extraction methods for the separation of Sr and Nd from the sample solutions were taken from Pin and co-workers (1994) but in a slightly modified version, as reported in Ganio and co-workers (2012). Sr was isolated via extraction chromatography using Sr spec resin (Eichrom). The acid 7M HNO_3 was used to rinse the columns and

0.05M HNO_3 to elute the Sr fraction from the resin. Nd was separated via a two-step extraction chromatography using (i) TRU spec (Eichrom) to separate the REE with 2M HNO_3; and (ii) Ln spec resin (Eichrom) to recover the Nd fraction from it with 0.25M HCl.

The elemental concentrations of both Sr and Nd were measured with a Xseries^{II} ICP-MS. The concentration results were used to calculate the dilutions for the isotope measurements. The Sr and Nd isotopic ratios were measured with a Thermo Scientific Neptune multi-collector ICP-MS. The adopted standards were NIST SRM 987 SrCO3 isotopic standard solution for the Sr measurements, and the La Jolla standard for Nd. All measurement values were corrected for HNO_3 blank and isobaric interferences. Finally, these were normalised to $^{86}Sr/^{88}Sr=0.1194$ and $^{146}Nd/^{144}Nd=0.7219$ to correct for instrumental mass discrimination. Repeated static measurements of the NBS 987 standard over the duration of the study yielded an average $^{87}Sr/^{86}Sr$ ratio of 0.71031 ± 0.00002. Repeated measurements of the La Jolla Nd standard yielded an average $^{143}Nd/^{144}Nd$ ratio of 0.512104 ± 0.000009.

5. RESULTS

5.1. Major, minor, and trace element compositions

The major and minor element data from the 75 analysed samples are reported in Table 2. Trace elements analysis was performed on a selection of 35 samples with the results reported in Table 3. The averaged trace element values were normalised to the concentration of the upper continental crust (Wedepohl 1995).

All the samples are silicate glasses, containing between 55.3% and 73.9% SiO_2. Figure 1 shows the relative levels of Na_2O and K_2O, the main fluxing oxides used. Two chemical groups can be observed: one including 9 Chotin specimens with high potash and low soda and the other including the 65 Bologna, Pozzuoli, and Cumae samples, with low potash and high soda. The sample CHO114,15 is a mixed-alkali glass. Associated with the high soda glasses, only a single sample, CUM-169, exhibits a low Na_2O content, which, along with its high SiO_2 level, could be a sign of weathering (Henderson 2013).

The Chotin samples appear very different chemically from all the other specimens, being characterised by low SiO_2 (56-61%) and Na_2O (0.1-1%), accompanied by high levels of K_2O (10.2-14.2%), Al_2O_3 (1.3-3.7%), MgO (2-5.3%), CaO (5.3-10.2%), and P_2O_5 (1.7-4.6%). The alkalis and phosphorus concentrations suggest the use of a potassium-rich plant ash flux in the glass. The only exception is sample CHO114,15, with K_2O and Na_2O levels around 5 and 8 wt. % respectively, which may indicate the use of different ashes, richer in soda, though the relationships between ash compositions, the origin of the plant and the glass produced are not simple.

On the basis of the K_2O and MgO levels, shown in Figure 2, it is possible to classify 44 samples (10 from Bologna, 4 from Cumae and 30 from Pozzuoli), as high soda natron based glasses, containing levels of potash and magnesia lower than 1.5%. The remaining 21 samples from the three localities fall outside the traditional ranges reported for natron glass, exhibiting higher MgO (0.5-4%), but compatible K_2O levels (0.8-1.8%) for natron glasses (excluding samples Cum-165, 170, 172 with K_2O 2-3%). Despite their MgO

levels, these samples exhibit a close chemical similarity to natron-based glass. They are all characterised, on average, by high Na_2O (16.2%), low K_2O (1.3%) and P_2O_5 (0.2%, excluded sample Pozz-50 with 0.5% P_2O_5), and very low CaO (2.8%).

All the analysed samples are very rich in iron, which is clearly related to their black colour. The FeO levels range from 5 to 20%, with the Pozzuoli samples exhibiting a wider range of variation (from 5% to 18%), and Chotin a narrower range (12% to 16%).

Manganese oxide is present in quantities below 0.1% or absent in the glass from Bologna, Cumae, and Pozzuoli, while in the Chotin samples it is present in percentages between 0.3% and 0.8%.

The distribution of the metallic elements is very heterogeneous, even among samples from the same site. Tin is lower than 5 ppm or absent in the majority of the glass samples, with the exception of the four Chotin samples CHOT114-3, 4, 5, 6, where it is present in quantities of around 145 ppm and positively correlated to high levels of Cu (1500 to 1850 ppm). Apparently, with the exclusion of these four Chotin samples, Cu is not correlated to any of the other elements.

The widest variation in metallic element concentrations was found in the Pozzuoli glasses, characterised by the most variable and highest levels of Cu, Sb, Zn, V, Cr, and Ni (Table 3). These samples can be divided into two sub-groups based on their Cr and Ni contents: Group 1 (samples Pozz-56, 57, 58, 59, 71, 73, 83) had high Cr (54-334 ppm) and Ni (40-350 ppm), but no Zn (12-31 ppm), while Group 2 had lower Cr (11.6-20.5 ppm) and Ni (6.3-20.8 ppm), but high Zn (123-722 ppm). Group 1 also exhibits higher Al_2O_3, TiO_2, and MgO compared to Group 2.

The trace element patterns reported in Figure 3 highlight that, despite their chemical variability, the Pozzuoli samples show a trend compatible with that of the Bologna glasses rich in Y, Zr, Hf, Ta, and Th, different from that of Chotin samples characterised by higher Rb, Sr and Ba, again reflecting the use of an ash alkali source in the latter.

The absolute concentrations of the Rare Earth Elements (REE) are relatively high in all the glasses. If normalised to the REE concentration of the upper continental crust (Wedepohl 1995), the Pozzuoli and Bologna samples show an Eu negative anomaly (confirming their compatibility), opposite to the positive anomaly of the Chotin glass samples.

5.2. Sr and Nd isotopic compositions of the Bologna black samples.

The Sr and Nd isotopic compositions of a selection of Bologna black samples are given in Table 4. The $^{87}Sr/^{86}Sr$ ratios for all the samples, with the exclusion of FiBo19, are higher (0.70919-0.71012) than that of modern seawater (0.70917) (Banner 2004). Sample FiBo19 is the only one with a $^{87}Sr/^{86}Sr$ ratio (0.70866) lower than present-day seawater, while also exhibiting the highest levels of CaO among the Bologna black samples (3.55% *vs*. 1.60% on average for samples FiBo5, FiBo6, FiBo7, FiBo22, FiBo23). The Nd isotopic data show a narrow range of εNd values between -10.63 and -11.74, with the exclusion of sample FiBo7 with an εNd of -8.63.

6. DISCUSSION

6.1. Major, minor, and trace elements compositions

6.1.1. Chotin glass

The Chotin specimens exhibit very different chemical features from all the other glass samples, being characterised by low soda, but high potash, lime and phosphorus oxides, which suggest that wood ash was used as a flux (Wedepohl 1997). To the authors' knowledge, this chemical type has no coeval counterpart. The previous technologies involving the use of salt-tolerant plant or leached wood ashes (HMG and LMHK/High-K, respectively) produced glass with a different chemistry, as reported in section 2. Specifically, the LBA High-K glass found in Europe (Towle et al. 2001; Angelini et al. 2004, Angelini et al. 2010; Venclovà et al. 2011; Conte, unpublished data) shows compatible K_2O levels with those recorded for the samples here discussed, but it is characterised by lower lime, magnesia and phosphorus oxides and higher soda contents than the Chotin glass, indicating a different alkali source and/or a different treatment of the ash. On the other hand, the early medieval glass found in Germany (Wedepohl 1997) and other parts of northwestern Europe (Henderson 1983) and labelled by Wedepohl (ibid.) as 'Early Wood Ash glass' includes chemical compositions that are very similar to the Chotin samples (excluding iron), with low soda, high potash, lime and phosphorus oxides.

'Early Wood Ash glass' was possibly produced with beech wood ashes in central Europe, between 800 and 1000 AD, and exhibits compositional similarities to most Chotin glass, even if lime is higher in the former (19% vs. 7% CaO). This difference could be due to the use of different plant genera/species and/or variable soil geochemistries (Barkoudah and Henderson 2006), the mixing of ashes or the proportion of trunk and/or bark used to the make the ashes. In the case of beech tree ashes, the K is apparently mainly concentrated in the trunk, while the Ca in the bark (Wedepohl 1997; Wedepohl and Simon 2010). The low CaO/K_2O ratio of the Chotin samples (0.6) might therefore indicate the use of high quality beech wood with a large proportion of trunk in the raw materials, although this must remain a tentative suggestion. Other plant ashes could have produced a similar ratio: ferns, for examples, sometimes exhibit CaO/K_2O values below 1 (Jackson et al. 2005; Wedepohl and Simon 2010). Jackson and co-workers (2005) have defined what they regard as ideal compositions for bracken, oak and beech. Regardless of which plant species was used, our glass compositional data suggest that they were probably tree ash. Wedepohl and co-workers (2011a) reported that, together with the major constituents of plants (MgO, K_2O, CaO, and P_2O_5), the elements Ba, Sr, and Rb are especially concentrated in wood ash glass, compared to plant ash and natron glass varieties. This appears to be true for Ba and Rb but not for Sr: some halophytic plants contain up to 2500 ppm (Barkoudah and Henderson 2006, Table 2), considerably higher levels than those detected by Wedepohl et al. (2011a, Table 2) who quote a mean value for 23 samples of 781 ppm. Tables 2 and 3, and Figure 3 underline the high concentrations of MgO, K_2O, CaO, P_2O_5, Ba, Sr, and Rb in the Chotin samples, representing the highest levels in the set. The presence of specific trace elements is due to their close chemical relationships to specific raw materials and impurities in the glass. Specifically, Sr is a crystal chemical companion of Ca, while Rb and Ba can be related to K (although Ba, for example, can also be introduced in baryte in sand). It can therefore

be assumed that a portion of these elements was introduced in the Chotin glass with the flux. Likewise, the MnO contents (0.3-0.8%) could derive from the wood ashes themselves (Wedepohl and Simon 2010; Wedepohl et al. 2011a).

The CaO/Sr ratio provides information on the source of lime, which in the case of glass produced with ashes, depends on the ashes themselves (Freestone et al. 2003). The ratio recorded for the Chotin samples (345) is closely compatible with that reported by Wedepohl and Simon (2010) for 'Early Wood Ash glass' (358).

It should be specified, however, that the Rb and Ba in the Chotin glass could be of mixed origin. Their high concentrations (265-466 Ba and 45-86 Rb ppm) and their positive correlation with alumina – present in relatively high levels (1.3-3.7%) and typically introduced with the vitrifying portion of the batch – suggest that they are partially derived from alkali feldspars, micas and possibly baryte present in the sand used to make the glass. The general chemical signature of the Chotin glass does in fact exhibit a high impurity pattern, indicating the use of an impure sand as the vitrifying source. The positive correlation between Al_2O_3 and TiO_2 (a common correlation in ancient glasses-e.g. Arletti et al. 2012) indicates the presence of specific minerals, such as feldspars, Ti oxides-rutile, ilmenite, and/or titanite, and clays (Brems and Degryse 2013; Shortland and Schroeder 2009). If compared with glasses made with very clean silica source, as the plant ash glass dated to the 8^{th}-7^{th} century BC analysed by Conte et al. (2016) showing 14 Zr, 0.3 Hf and 0.4 Th ppm, the levels of Zr (19-81 ppm), Hf (0.5-2 ppm), and Th (1.2-3.1) of the Chotin samples result very high. Moreover, the positive correlation between these elements indicate that they were introduced with zircon, the most abundant heavy mineral in quartz sand (Götze and Lewis 1994; Degryse and Shortland 2009; Brems and Degryse 2013). The high level of Y (7.5-9.5 ppm, compared to 2 ppm Y of the coeval plant ash glass-Conte et al. 2016) is also related to the heavy fraction of the sand, specifically to garnet (Wedepohl et al. 2011a). Zircon and garnet are also enriched in HREE. The presence of heavy minerals in the sand used is confirmed by the Nd (6.5-8 ppm), which can be introduced by clays and minerals other than quartz (Degryse and Shortland 2009). La is quite high (6.6-8.7 ppm), and could derive from monazite and/or allanite, enriched in LREE (Wedepohl et al. 2011a, b).

The positive Eu anomaly recorded in the Chotin glass depends on the possibility of Eu substituting for Sr in plagioclase. Enrichment in plagioclase during weathering, erosion, or sedimentary processes can cause positive Eu anomalies in sandy sediments, which in turn can be passed on to the glass (Vellmer and Wedepohl 1994; Gao and Wedepohl 1995). These data are in agreement with the abundant presence of feldspars, testified by the high levels of Al_2O_3, as discussed before.

The chemical features of the Chotin glass therefore strongly suggest that it was produced starting from wood ashes and an impure quartz sand rich in minerals other than quartz (such as zircon, feldspars, Ti-oxides, garnet, monazite, etc.).

6.1.2. Bologna, Pozzuoli, and Cumae glass

Among the 65 samples from Bologna, Pozzuoli, and Cumae, 44 were classified as natron glasses on the basis of their high contents of Na_2O in combination with low levels of MgO, K_2O, and P_2O_5 (samples Pozz-53, 54, 57 and 61 show slightly higher levels of

P_2O_5, 0.5-1.3%, probably related to the employ of a different sand containing apatite). The 21 remaining samples, despite their compatible levels of Na_2O, K_2O, and P_2O_5, show higher levels of magnesia (2.2%). In their work on Early Iron Age glass (9^{th}-8^{th} century BC) from Southern Italy, Conte and co-workers (2016) found black samples with the same chemical features as the latter and labelled them HMLK glass (high magnesium low potassium). These authors interpreted the high presence of magnesia as deriving from the use of a very impure sand (richer in Fe-Mg minerals, e.g. amphiboles and pyroxenes), rather than from the flux used in production. This hypothesis was supported by the lack of correlation between K and P oxides – typical of glass produced with plant ash – and by the higher contents of alumina – with respect to the natron samples (as found for the samples here studied (2.1% *vs*. 1.4% Al_2O_3, respectively)). Coeval glasses characterised by similar composition of that described (with K_2O around 2%) and, additionally, by high alumina (4-10%), were studied by Purowski et al. (2012) and Conte et al. (2016) and identified as natron samples, too. Also in these cases, the medium levels of potash have been interpreted as derived from the vitrifying portion of the glass, rather than from the flux (see also Henderson 2013). Therefore, all the Bologna, Pozzuoli, and Cumae samples of this study can be classified as natron glass.

These samples, dated to the 9^{th}-7^{th} century BC, are characterised by very low levels of lime (1.1-5.2% CaO) – uncommon for traditional natron glass in which levels typically range between 7 and 9% (Aerts 1998) – and very high contents of iron (5-20% FeO). These chemical features were found in other black natron glass samples dated to the Early Iron Age (10^{th}-8^{th} century BC) from Italy (Sarno and Cuma – Conte et al. 2016), France (Gratuze and Picon 2006), and Jordan (Pella – Reade et al. 2009). Such low levels of lime (always <5% CaO) indicate an inadequate understanding of glassmaking processes by the glassmakers. They changed from plant ashes to natron salt as a flux around the 10^{th} century BC but failed to recognize the need for particular types of sands (rich in lime) to stabilize the glass (Schlick-Nolte and Werthmann 2003). When producing plant ash glass, sufficient lime could be introduced with the flux but even this was not guaranteed and glassmakers may have tried several plant colonies before defining one that provided sufficient lime (Barkoudah and Henderson 2006). On the other hand, in natron glass the flux is lime-free and a different source of CaO was required, typically in the form of shell fragments in sand. In the case of glass varieties containing high levels of iron, like our 'black' samples, iron served both as a colouring agent and fortuitously also as a stabiliser (Reade et al. 2009), promoting their durability. Otherwise, most of the other glass produced in this period is likely to have been lost (Shortland et al. 2006).

All the Iron Age black samples found in Bologna, Pozzuoli, and Cumae here analysed can be classified as examples of early natron glass production, comparable with those found in Egypt (Schlick-Nolte and Werthmann 2003), Italy (Conte et al. 2016), France (Gratuze and Picon 2006), and Jordan (Reade et al. 2009).

It worth noting that the black natron glass samples in this study are characterised by high chemical variability. The wide variations in their chemical compositions could be related to the change in glassmaking technology. As observed by Henderson (2013), the transition from the previous plant-ash technology to the natron based system must have

involved experimentation with the new fluxing agent, perhaps producing glass varieties of unusual chemical compositions. This hypothesis is confirmed by studies on early natron glass found in France (Gratuze and Picon 2006) and Italy (Brill 1999; Towle and Henderson 2004; Arletti et al. 2011a; Conte et al. 2016), dated to the Early Iron Age (9th-7th century BC), in which the high chemical variability indicates the use of recipes and techniques that were not yet well defined and standardised. Another important consideration, especially as regards black glasses, is that they were made from very impure sands, as demonstrated by the trace and rare earth elements contents. This may also indicate that the glassmakers lacked a complete understanding of the effects of using different raw material sources.

The samples from Bologna and Pozzuoli have high Zr positively correlated with high Hf (54-90 and 43-96 ppm, 1.3-2.1 and 0.7-2.6 ppm, respectively), indicating, as observed for the Chotin glasses, the presence of zircon in the sands used, which also introduced HREE. The positive correlation between La (7.5-13.6 ppm Bologna, 5.5-18.8 ppm Pozzuoli) and Th is instead related to the heavy mineral monazite, which is rich in LREE. Y was introduced into the glass batch (5.2-10.6 ppm Bologna, 5.3-12.8 ppm Pozzuoli) mainly thought the heavy mineral garnet, along with HREE. In contrast to the Chotin glass, both the Bologna and Pozzuoli samples are characterised by a negative Eu anomaly, typical of the granitic rocks of the Earth's upper continental crust (Wedepohl and Simon 2010).

Also the sands employed for the production of the Bologna and Pozzuoli glasses are thus characterised by a high presence of heavy minerals other than quartz (zircon, garnet, monazite, etc.), as confirmed by the Nd contents (5.4-16 ppm, high if compared to those found in the plant ash glass made with quartz pebbles, analysed by Conte et al. (2016) with 0.8-5 ppm Nd). Likewise, Sr is related to Ca in the glass, but in the case of natron glasses this usually derives from shells or limestone introduced as a source of lime (Wedepohl and Baumann 2000; Freestone et al. 2003; Brems et al. 2013a). The CaO/Sr ratios found for these glass samples (Bologna 358, Pozzuoli 270) do not match either the use of fresh seashells (≤200) or limestone (≥600) (data from Freestone et al. 2003; Wedepohl et al. 2011a, b). This could indicate that the CaO/Sr ratio might have been influenced by minerals other than carbonates, present as impurities in the sands.

It can be deduced that the production of the Bologna and Pozzuoli glass involved the mixture of natron with very impure granitic sands, rich in heavy minerals other than quartz but poor in lime.

6.1.3. Relation between colour and colouring agents

All the glass samples examined here owe their black colour to high iron contents. In ancient times, a means for increasing iron content during glass production was the intentional choice of dark sand, rich in iron oxides, like black sand deposits (*e.g.* Eid et al. 1994). The data reported below suggest that different sources of impure sand were used as iron sources for the Chotin, Bologna, and Pozzuoli black glass. The variability in the measured concentrations of the metallic elements could be related to the presence of metallic or, more probably, mineral inclusions/remains in the glass, which give information on the mineralogical composition of the starting sands, as discussed below.

High levels of V and Cr in glass are generally related to the iron oxides present in quartz sand (Wedepohl et al. 2011a; b), potentially indicating the use of contaminated sands as iron source. The Chotin samples CHOT114-3, 4, 5, 6, along with high iron, vanadium and chromium levels, also exhibit high Cu (1500-1840 ppm) positively correlated with Sn (137-150 ppm), which could indicate that they were incorporated together in the glass batch in form of metallurgical scrap (Conte et al. 2015). The other Chotin glasses are characterised by lower levels of Sn and Cu. However, Cu is present, together with Zn and Pb, in considerable concentrations in all the glass samples (up to 500 ppm Cu, 100 ppm Zn, 100 ppm Pb). Wedepohl and co-workers (2011a) observed that among their Roman natron glass samples produced at Hambach (Germany), those with high iron (1.6% Fe_2O_3) were also characterised by higher Cu, Zn, and Pb than those with lower iron (0.7% Fe_2O_3). The authors suggested that detrital minerals from decomposed ore deposits such as galena (PbS), sphalerite (ZnS), and chalcosite (Cu_2S) were accumulated in the high-iron quartz sand of the River Rur used for the glass production, passing metals (Pb, Zn, Cu) into the glass. The hypothesis that these elements were introduced as impurities along with the impure sand is strengthened by the data reported by Foster and Jackson (2009). In their work on HIMT glass, the authors report that the levels of Cu, Pb, and Sb ≤90, 200, and 100 ppm respectively, are an indication of natural impurities present in the sands.

The samples from Bologna have homogeneous trace elements values with a narrow range of variation. They exhibit a positive correlation between FeO-TiO_2, suggesting the presence of Fe-Ti minerals (e.g. ilmenite) in the sand. At the same time, the FeO-TiO_2 and FeO-Al_2O_3 correlations could also indicate the presence of magnetite. Natural magnetite quite commonly contains quantities of alumina and titania (Rehren et al. 2012). The high Zn contents (213-405 ppm) again could be related to the presence of specific minerals, like sphalerite (ZnS).

Regarding the Pozzuoli specimens, as observed in the results section, the Group 1 shows higher Al_2O_3, TiO_2, MgO, Cr and Ni with respect to the Group 2, indicating a higher presence of heavy minerals in the sand, as also testified by the more elevated concentration of heavy rare earth elements (Table 3). The high contents of Cr indicate the presence of chromite (Brems and Degryse 2013), a heavy mineral that also introduces iron. Moreover, the Cr also correlated strongly with Ni and V, typically a sign of iron oxides in the sand.

It can be concluded that all the sands employed for the production of the Chotin, Bologna, and Pozzuoli samples were probably dark in colour and purposely selected. The use of such sands in fact, did ensure the black colouration of the finished glass.

6.1.4. $^{87}Sr/^{86}Sr$ and εNd of the Bologna black glass

An indication of where the glass was produced can be inferred from the isotopic results. The Bologna black samples exhibit $^{87}Sr/^{86}Sr$ ratios variable between 0.70919 and 0.71012 (higher than that of modern seawater (0.70917, Banner 2004)), and low CaO values (1.09-2% CaO), indicating low carbonate contents in the raw materials used. These high $^{87}Sr/^{86}Sr$ values reflect the influence of other minerals (like feldspar), with higher radiogenic Sr isotope signatures than that of present-day seawater. These samples

are clearly less influenced by shell materials, which are probably absent from the sand. This is consistent with the information obtained from the trace element data of the glass, indicating the use of sand with a CaO/Sr ratio derived from minerals other than carbonate, such as feldspar, mica, and clays (Degryse and Schneider 2008). The FiBo19 sample – the only one with an $^{87}Sr/^{86}Sr$ ratio (0.70866) lower than present-day seawater – also has a higher CaO content (3.5%), suggesting the presence of carbonates in the raw materials. Its $^{87}Sr/^{86}Sr$ ratio could indicate the presence of limestone (Freestone et al. 2003). The εNd values of the Bologna black samples vary between -10.63 and -11.74, with the exclusion of sample FiBo7, characterised by an εNd of -8.63.

Schaaf and Muller-Sohnius (2002) and Degryse and Schneider (2008) reported the $^{87}Sr/^{86}Sr$ and ƐNd values of five quartz-rich sandstones (with SiO_2 contents between 84.38% and 96.82%) from mid-western Egypt, and of quartz-rich sands from Belgium, Egypt (Wadi el Natrun), Mesopotamia (River Belus), and Italy (River Volturno). The plot in Figure 4 shows a comparison between these data and the Bologna black glass, which exhibits a strong similarity to the Egyptian materials (both sandstones and sands). The low values for εNd found by Schaaf and Muller-Sohnius (2002) and Degryse and Schneider (2008) in the quartz-rich sandstones and sands from inland Egypt are clearly influenced by the Saharan isotopic signature (typically between -12 and -13.5 ε Nd). The $^{87}Sr/^{86}Sr$ ratio, higher than that of modern seawater, coupled with low levels of CaO (1-3.3%), again suggests the influence of high radiogenic strontium minerals, other than carbonates, on the Sr isotopic ratio.

These results seem to suggest the use of an Egyptian vitrifying raw material, located inland, for the production of the black glass from Bologna. Considering that the black samples were identified as an early natron production, and natron probably came from Wadi el Natrun (Shortland et al. 2006), the hypothesis of an Egyptian origin for the black glass is very plausible, though other silica sources cannot be definitely excluded (*e.g.* Libyan sands, see the database reported in the Appendix of the book by Degryse 2014; or southern Italian sands with low Nd isotopic signatures, see Brems et al. 2013b).

7. CONCLUSIONS

The Iron Age black glass samples analysed in this work, dated between the 9th and the 5th century BC, can be subdivided principally on the basis of the fluxing agents employed for their production: probably wood ashes for the Chotin samples, and natron for the Bologna, Pozzuoli, and Cumae samples. All the glasses derive their black colouration from the high presence of iron (12% FeO, on average), which was introduced into the glass batches through the intentional choice of dark sands. Based on the minor, trace, and rare earth elements compositions it was possible to distinguish different, very impure sands used as vitrifying agents and iron sources, too.

The Chotin wood ash glass has no equivalent among its coeval glass chemical typologies, instead exhibiting a great affinity with the 'Early Wood Ash Glass' produced in central Europe during the Medieval period. This is the first evidence of the occurrence of this chemical type in such an early period. Purified tree ashes were probably used to make mixed alkali Final Bronze Age glasses, but they show different chemical composition and alkali ratio (Hartmann et al. 1997; Angelini et al. 2004; Venclovà et al.

2011; Henderson et al. 2015). It would seem that the glassmaking technology based upon the use of tree ashes was employed in Europe during periods of crisis. This may be the case for the mass-production of LMHK glass that occurred in Frattesina in the 11th-9th century BC, when the collapse of the LBA societies caused an interruption in the supply of HMG glass from the Near East (Henderson 1988a). Likewise, the definitive decline of the use of natron in the 9th century AD promoted the production of wood ash glass in Europe. The Chotin samples here analysed were produced with different flux and starting sands (richer in feldspar and Cu-Pb-Zn compounds), with respect to the Bologna, Pozzuoli and Cumae ones. Moreover, their affinity with the European glass productions based on the tree ashes could indicate that they were made in Europe, but certainly in a different place from the others. Their chemical variability suggests small-scale production characterised by the use of non-sorted materials and without well-established recipes. In the current state of knowledge, this glass could be classified as 'experimental', probably intended to temporarily fill the lacuna left by the decline of Frattesina glassmaking, at a moment of general technological transition, characterised in the Near East by the replacement of plant ashes with a new mineral flux (natron).

All the other samples in this study, from Bologna, Pozzuoli, and Cumae were dated to the 9th-7th century BC, and were classified as early natron products. They exhibit the same chemical features, including very low lime and high iron concentrations, as other black natron glass samples dated to the Early Iron Age (10th-8th century BC) and found in Egypt, Jordan, France, and Italy. Taking into account that they were among the earliest natron glass products and the technology employed (mixing of natron directly with impure sands as both vitrifying and iron source), it is possible to suggest that the natron black glasses of this study have an Egyptian origin. This hypothesis is further supported by the high isotopic compatibility of the Bologna samples with quartz sands and sandstones located in inland Egypt, also at Wadi el Natrun, where the natron was mainly extracted in antiquity (Shortland et al. 2006).

The use of different sands for the production of the Bologna (high presence of ilmenite and magnetite) and Pozzuoli glasses (Group 1 with chromite, Group 2 Zn minerals), could indicate that more than one raw glass production centre experimented with the new flux, or that different sands were tested to establish the best one in the same centre. The current lack of archaeological evidence of primary glassmaking sites is probably because this early production would have been on a smaller scale than subsequently required for Roman demands, and is likely to have been conducted using crucibles (Henderson 2013). The variations in major element compositions probably resulted, also in this case, from the use of non-selected raw materials and the adoption of formulae and melting conditions that were not yet standardised. Studies of black Roman samples revealed a very different production technology. Black Roman natron glass was made starting from typical natron-based glass, to which iron was added (possibly in secondary workshops) in the forms of iron ores (Group IIB, Van der Linden et al. 2009), hammer scale (Rehren et al. 2012; Cholakova and Rehren 2012), or pure magnetite (Group BG3, Cagno et al. 2014).

In conclusion, this study provides evidence for two different production technologies in Iron Age black glass found in Italy and Slovakia. While the wood ash technology

appears to have dropped out of use in Europe until the Medieval period, natron production spread quickly, becoming predominant throughout the Mediterranean.

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TABLE CAPTIONS

Table 1: Resume table of analysed samples.

(a) Museum number: Cambridge University Museum of Archaeology and Anthropology 1947.1937; **(b)** Museum number: Cambridge University Museum of Archaeology and Anthropology 1947.1971A (11): **Ref:** ***1***. Chotin I-A, Skelletgrab 266. Dušek 1966 pp. 67-68 and plate XXIX, no. *2;* also numbered 137/54, H 266/54. 2F; ***2.*** Chotin I-A, Skelletgrab 161. Dušek 1966 p. 56 and plate XV, no. 4. Orig. 1; ***3.*** Chotin I-A, Skelletgrab 108-A. Dušek 1966 p. 51 and plate VII, no. 39, also numbered 37/53, no. 108/53-1; ***4.*** Chotin I-A, Skelletgrab 175A. Dušek 1966 pp. 58-59 and plate XIX, no. 6; ***5.*** Spaer (2001, 80, Fig. 38) dates 'black' sub-triangular beads with 3 eyes formed from opaque white annulets to the end of the 9^{th}-8^{th} centuries BC with examples from the Levant and Sinai. Many examples of such beads have been excavated from secure 9^{th}-8^{th} century BC contexts from Kaman Kalehöyök, Anatolia and examined by one of us [JH] (pers. comm Dr. Omura). Such beads are also discussed by Spaer (2002, 55-57, 211 [no. 2926]) and Haevernick (1981). Gratuze and Picon (2006) and Gratuze (2009) analysed more than 200 'black' annular and globular black beads, decorated or not with a white equatorial line or white blobs, found in twelve French sites dated to the 9^{th}-8^{th} centuries BC. Conte et al. (2016) analysed 'black' triangular and spherical beads with white opaque eyes, annular beads, spherical beads with a white equatorial line or irregular blobs decorations, found in the *Fossakultur* necropoleis of Sarno and the site of Cumae dated to the 9^{th}-8^{th} centuries BC. ***6.*** Dore (2004) and Mengoli unpublished data.

Table 2: Major and minor element contents in wt.% of the glass samples, obtained by EMPA. (n.d. = not detected).

Table 3: Trace and minor element contents (in ppm) for selected glass samples, obtained by LA-ICPMS.

Table 4: $^{87}Sr/^{86}Sr$ and **Ɛ**Nd values of the analysed Bologna samples.

FIGURE CAPTIONS

Figure 1: Plot of K_2O vs. Na_2O for the analysed samples.

Figure 2: Plot of K_2O vs. MgO for the analysed samples.

Figure 3: Trace elements composition of all the analysed groups, normalised to the concentration of the Upper Continental Crust (Wedepohl 1995).

Figure 4: $^{87}Sr/^{86}Sr$ and ƐNd of the black Bologna samples compared to the values of quartz-rich sandstone from mid-western Egypt (Schaaf and Muller-Sohnius 2002), and quartz-rich sand from Belgium, Egypt (Wadi el Natrun), Mesopotamia (River Belus), and Italy (River Volturno) (Degryse and Schneider 2008).

SUPPLEMENTARY CAPTIONS

S1. Precision and accuracy calculated on the Standard Reference Material NIST612 at the Centro Interdipartimentale Grandi Strumenti of Modena and Reggio Emilia. The accuracy was reported as percentage of deviation average of own analysis compared to the standard. Standard deviations are

reported in absolute numbers. The standard deviation is the measure taken for precision on the one sigma level.

S2. Pictures of Bologna glass beads.

Figure 1

Click here to download Figure Fig.1-.tiff

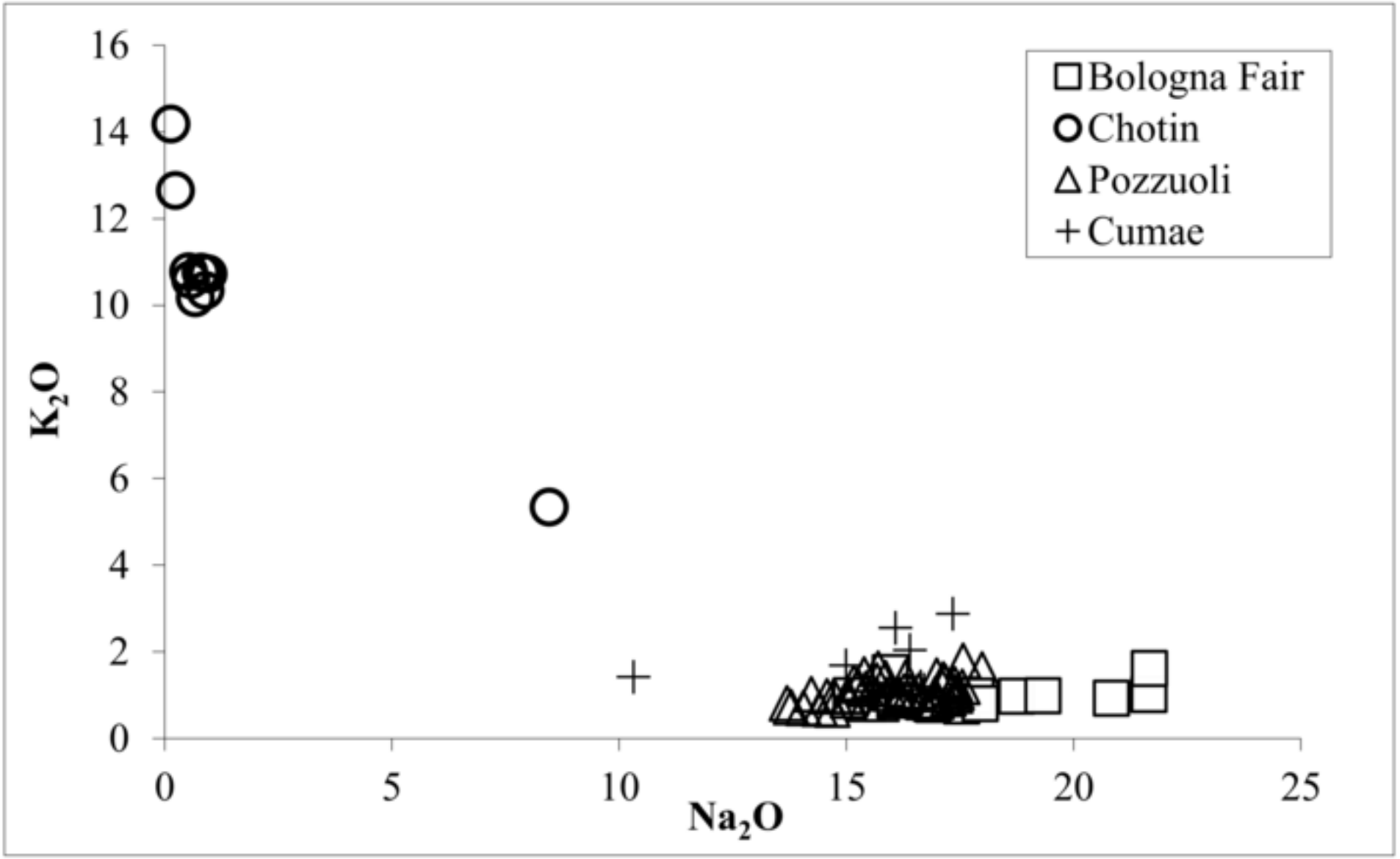

Figure 2

Click here to download Figure Fig.2-.tiff

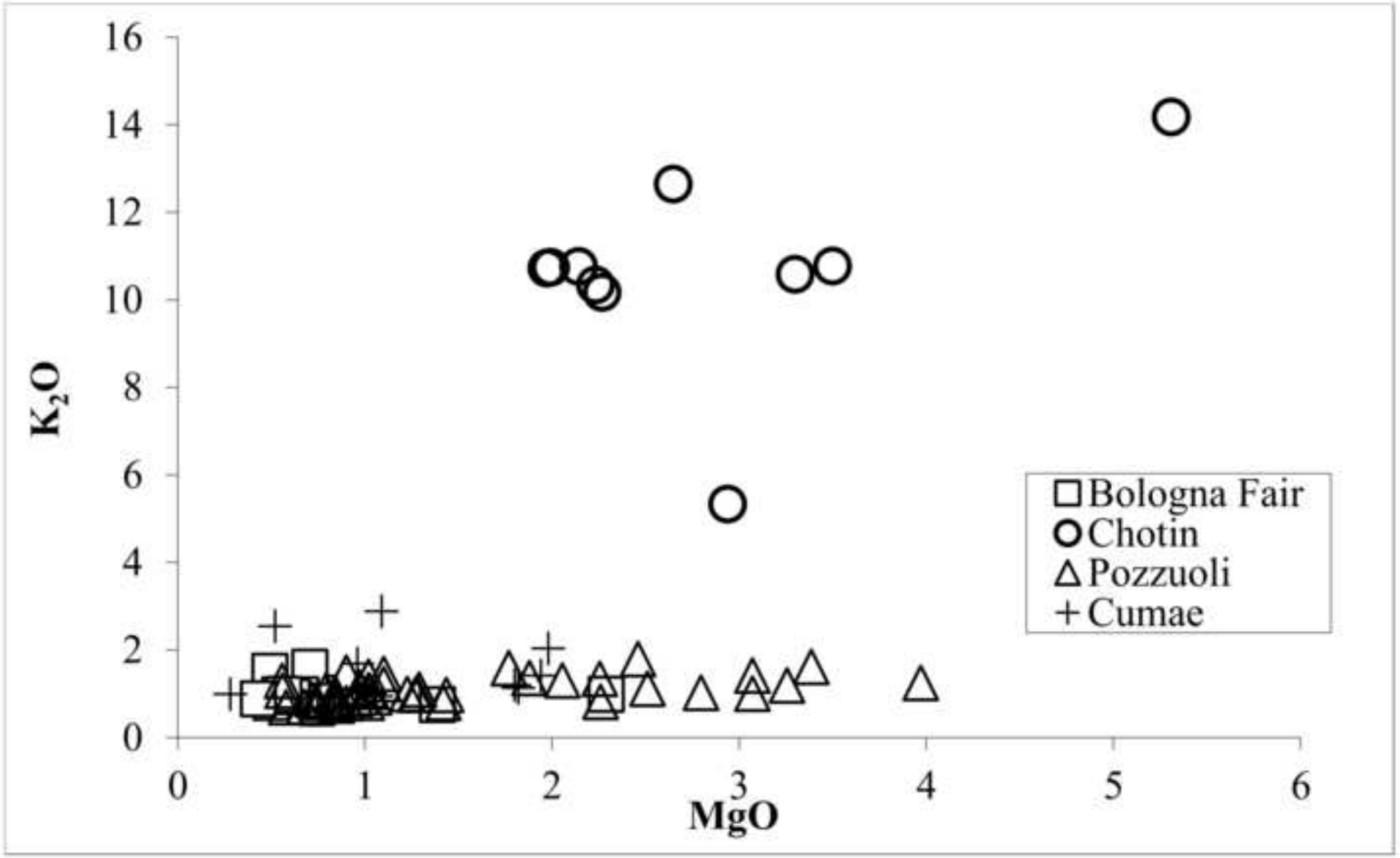

Figure 3

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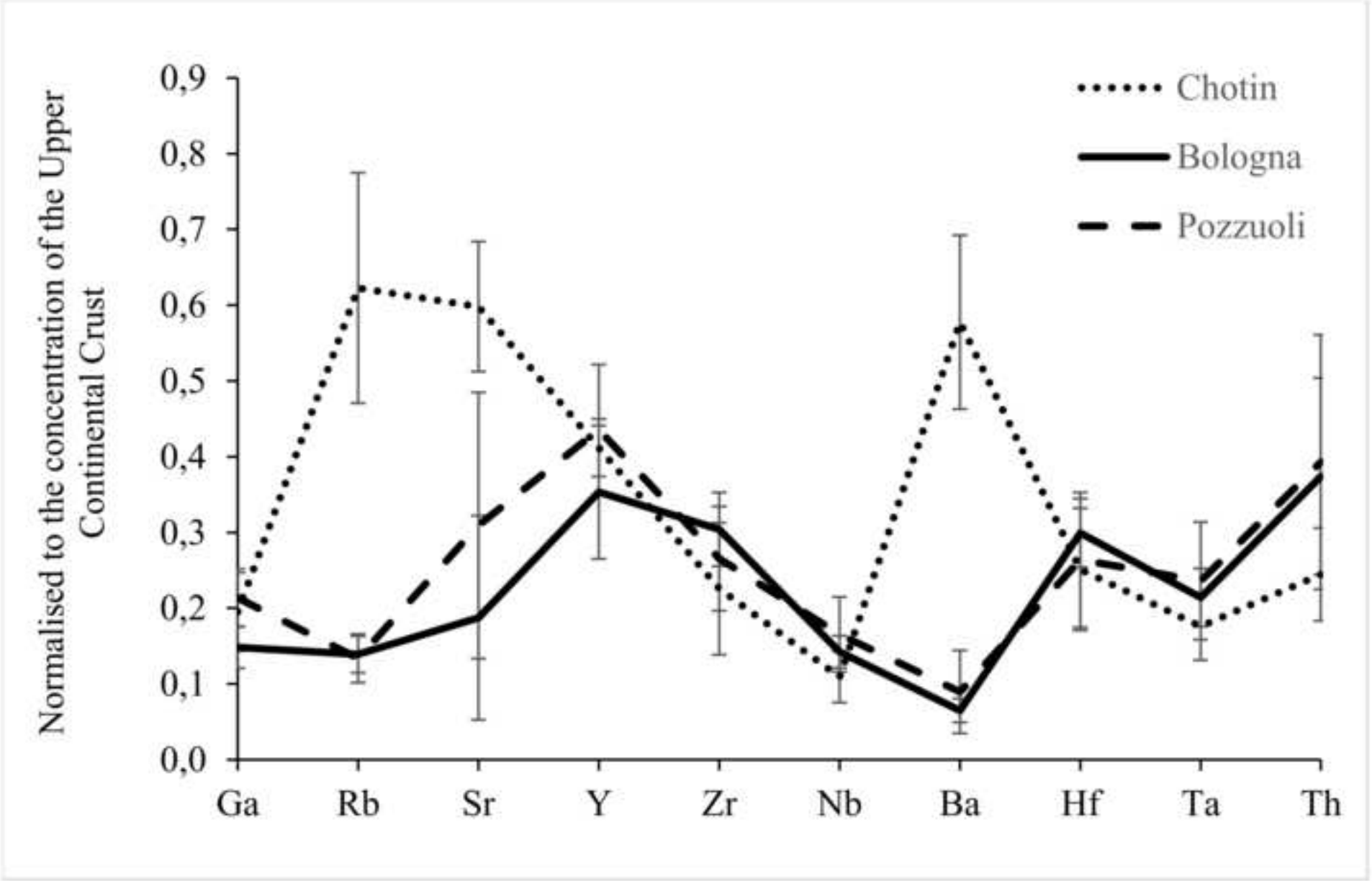

Figure 4

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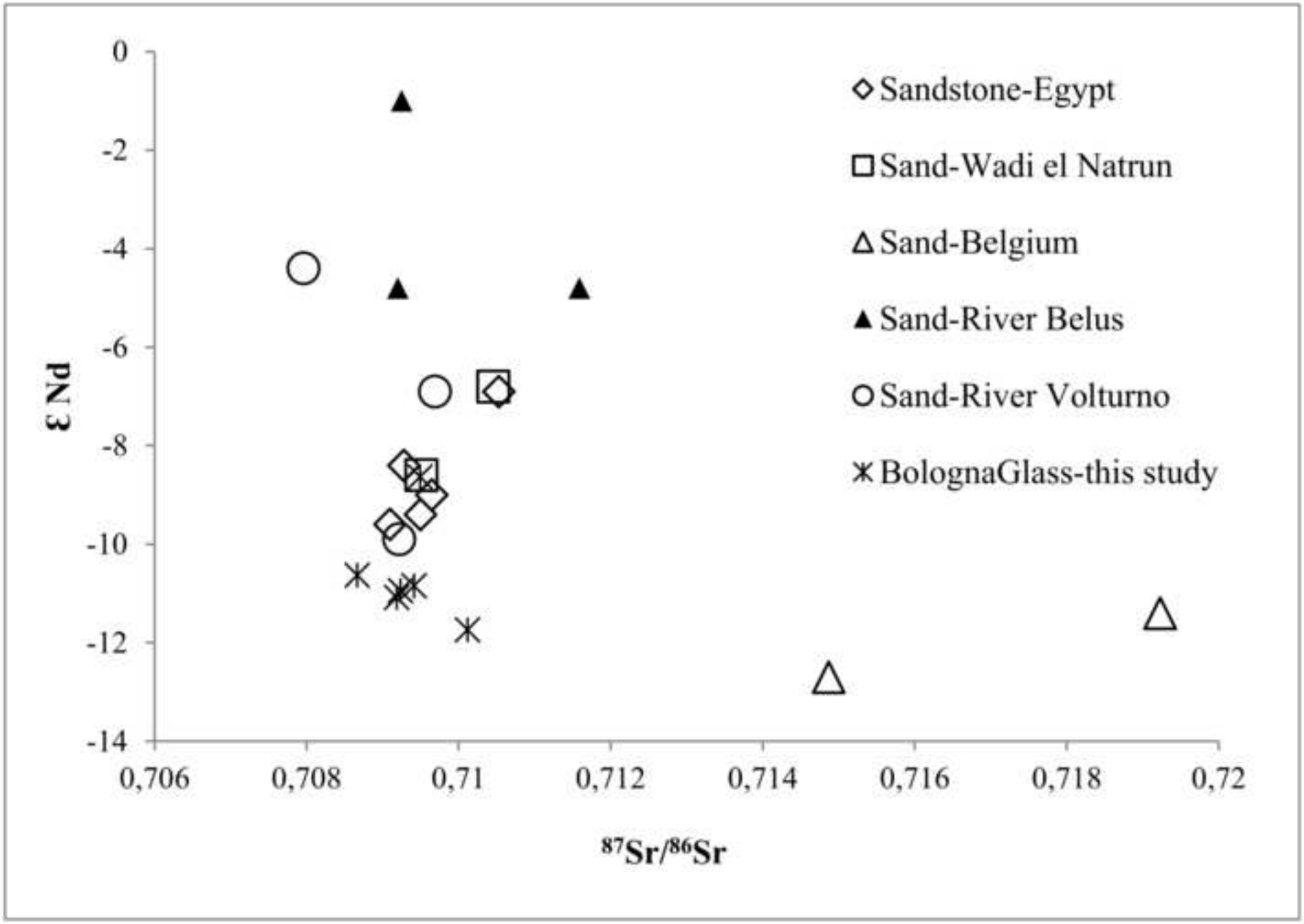

Table 1

	Sample	Typology	Chronology	Observations	References
Chotin	**Cho-114,3**	medium eye bead	7th-5th cen BC	four eyes (now lost). Deep translucent 'black' glass, now heavily weathered	1
	Cho-114,4	large extended biconical bead	7th-5th cen BC	deep translucent 'black' glass with weathered crust; feathered decoration lost, but weathered grooves remain	2
	Cho-114,5	medium donut shaped bead	7th-5th cen BC	dark translucent 'black' colours, bubbly with some weathering	3
	Cho-114,6	medium donut shaped bead	7th-5th cen BC	dark translucent 'black' colours, bubbly with some weathering	3
	Cho-114,9	medium donut shaped bead	7th-5th cen BC	dark translucent 'black' colours, bubbly with some weathering	3
	Cho-114,15	medium donut shaped bead	7th-5th cen BC	dark translucent 'black' colours, bubbly with some weathering	3
	Cho-115,7	medium donut shaped bead	7th-5th cen BC	dark translucent 'black' colours, bubbly with some weathering	3
	Cho-115,11	small donut-shaped bead	7th-5th cen BC	dark translucent 'black' colours with weathered crust	4
	Cho-115,15	small donut-shaped bead	7th-5th cen BC	dark translucent 'black' colours with weathered crust	4
	Cho-115,16	small donut-shaped bead	7th-5th cen BC	dark translucent 'black' colours with weathered crust	4
Bologna Fair	**FiBo5**	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 175 Bologna fiera excavations	6
	FiBo6	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 175 Bologna fiera excavations	6
	FiBo7	anular bead	8th-7th cen BC	deep translucent 'black' glass with weathered crust, from tomb 271 Bologna fiera excavations	6
	FiBo11	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 322 Bologna fiera excavations	6
	FiBo15	anular bead	8th-7th cen BC	dark translucent 'black' glass, bubbly with some weathering, from tomb 592 Bologna fiera excavations	6
	FiBo17	anular bead	8th-7th cen BC	dark translucent 'black' glass, bubbly with some weathering, from tomb 676 Bologna fiera excavations	6
	FiBo19	anular bead	8th-7th cen BC	translucent 'black' glass, bubbly with some weathering, from tomb 765 Bologna fiera excavations	6
	FiBo20	spherical bead	8th-7th cen BC	black colour glass, from tomb 712 Bologna fiera excavations	6
	FiBo22	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 755 Bologna fiera excavations	6
	FiBo23	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 918 Bologna fiera excavations	6
	FiBo25	anular bead	8th-7th cen BC	deep translucent 'black' glass, from tomb 1097 Bologna fiera excavations	6
Pozzuoli[(a)]	**Pozz-50**	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-51	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-52	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-53	globular bead	9th-8th cen BC	deep translucent 'black' with three eyes	5
	Pozz-54	globular bead	9th-8th cen BC	deep translucent 'black' with three eyes	5

	Sample	Typology	Chronology	Observations	References
Pozzuoli[a]	**Pozz-55**	globular bead	9th-8th cen BC	deep translucent 'black' with three eyes	5
	Pozz-56	globular bead	9th-8th cen BC	deep translucent 'black' with three eyes	5
	Pozz-57	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-58	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-59	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-60	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Pozz-61	sub-triangular bead	9th-8th cen BC	deep translucent 'black', broken, remaining eye an opaque white ring around a brown centre, weathered red opaque and iridescent	5
	Pozz-65	globular bead	9th-8th cen BC	deep translucent 'black', one eye: opaque white ring around a brown centre	5
	Pozz-66	globular bead	9th-8th cen BC	deep translucent 'black', one eye: opaque white ring around a brown centre	5
	Pozz-67	globular bead	9th-8th cen BC	deep translucent 'black', 3 eyes: only one opaque white ring around a brown centre remaining	5
	Pozz-68	cylindrical ellipsoidal bead	9th-8th cen BC	deep translucent 'black', slightly uneven white opaque stripes around perimeter, some uneven brown cubes attached	5
	Pozz-70	cylindrical ellipsoidal bead	9th-8th cen BC	deep translucent 'black', slightly uneven white opaque stripes around perimeter, some uneven brown cubes attached	5
	Pozz-71	cylindrical ellipsoidal bead	9th-8th cen BC	deep translucent 'black', slightly uneven white opaque stripes around perimeter, some uneven brown cubes attached	5
	Pozz-72	globular bead	9th-8th cen BC	deep translucent 'black', three white symmetrical stripes around perimeter	5
	Pozz-73	globular bead	9th-8th cen BC	deep translucent 'black' irregular shallow grooves around perimeter filled with possible white opaque glass, weathered, patchy opaque brown	5
	Pozz-74	globular bead	9th-8th cen BC	deep translucent 'black' irregular shallow grooves around perimeter filled with possible white opaque glass, weathered, patchy opaque brown	5
	Pozz-75	globular bead	9th-8th cen BC	deep translucent 'black' irregular shallow grooves around perimeter filled with possible white opaque glass, weathered, patchy opaque brown	5
	Pozz-76	cilindrical bead	9th-8th cen BC	deep translucent 'black' , opaque white spiral trailed around perimeter, opaque white chevrons	5
	Pozz-77	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-78	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-79	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-80	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-81	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-82	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-83	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-84	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-85	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-86	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5

	Sample	Typology	Chronology	Observations	References
Pozzuoli[a]	**Pozz-87**	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-88	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-89	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-90	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-92	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-93	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-94	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-95	globular bead	9th-8th cen BC	dark colours, deep translucent 'black', white and red opaque blobs, weathered, brown patches	5
	Pozz-96	globular bead	9th-8th cen BC	deep translucent 'black', opaque white blobs	5
	Pozz-97	globular bead	9th-8th cen BC	deep translucent 'black' weathered brown opaque surface	5
Cumae[b]	**Cum-164**	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Cum-165	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Cum-166	sub-triangular bead	9th-8th cen BC	deep translucent 'black' with three eyes: an opaque white ring around a brown centre	5
	Cum-167	sub-triangular bead	9th-8th cen BC	deep translucent 'black', opaque white rings around 'black' centres	5
	Cum-168	sub-triangular bead	9th-8th cen BC	deep translucent 'black', opaque white rings around 'black' centres	5
	Cum-169	sub-triangular bead	9th-8th cen BC	deep translucent 'black', opaque white rings around 'black' centres	5
	Cum-170	sub-cylindrical bead	9th-8th cen BC	deep translucent 'black', seven opaque white waves around the perimeters, brown surface	5
	Cum-171	globular bead	9th-8th cen BC	deep translucent 'black' globular, opaque white spiral around the perimeters, slightly uneven brown surface	5
	Cum-172	cilindrical bead	9th-8th cen BC	deep translucent 'black', uneven grooved around perimeter	5
	Cum-173	globular bead	9th-8th cen BC	deep translucent 'black', uneven grooved around perimeter	5
	Cum-174	globular bead	9th-8th cen BC	deep translucent 'black', one incomplete grooved around perimeter, brown opaque surface	5

Table 2

	Sample	SiO_2	Al_2O_3	TiO_2	MnO	MgO	FeO	CaO	Na_2O	K_2O	SO_3	Cl	P_2O_5	Totals
Chotin	**Cho-114,3**	60,76	3,31	0,14	0,34	2,00	14,72	5,26	0,88	10,74	0,11	0,16	1,83	100,56
	Cho-114,4	60,51	3,27	0,15	0,34	1,98	14,80	5,51	0,97	10,72	0,08	0,18	1,96	100,85
	Cho-114,5	59,98	3,70	0,15	0,36	2,15	14,32	5,87	0,81	10,75	0,13	0,16	2,13	100,82
	Cho-114,6	60,35	2,68	0,15	0,37	2,24	14,97	5,82	0,90	10,34	0,05	0,15	2,02	100,30
	Cho-114,9	57,56	1,70	0,05	0,55	3,30	14,77	10,23	0,58	10,58	0,09	0,07	1,76	101,24
	Cho-114,15	57,43	2,16	0,09	0,82	2,94	14,27	6,71	8,47	5,33	0,18	0,12	2,38	100,90
	Cho-115,7	58,96	2,09	0,10	0,33	2,65	12,72	6,39	0,24	12,64	0,08	n.d.	4,62	100,74
	Cho-115,11	55,95	1,89	0,09	0,39	3,50	15,86	8,04	0,53	10,76	0,17	n.d.	2,17	99,35
	Cho-115,15	55,74	1,32	0,05	0,65	5,31	12,69	7,24	0,14	14,17	0,20	n.d.	3,78	101,29
	Cho-115,16	61,32	2,50	0,07	0,34	2,27	12,61	7,71	0,68	10,16	0,03	0,04	2,31	100,04
Bologna Fair	**FiBo5**	62,52	1,27	0,16	0,04	0,75	11,69	1,47	21,66	1,01	0,21	0,52	0,12	101,61
	FiBo6	61,46	1,23	0,15	n.d.	0,71	11,40	1,75	21,67	1,61	0,20	0,62	0,12	101,14
	FiBo7	55,29	1,84	0,26	n.d.	1,39	19,89	1,09	17,55	0,75	0,20	0,42	0,09	98,96
	FiBo11	64,07	0,98	0,11	n.d.	0,66	12,22	1,68	17,86	0,97	0,10	0,48	0,11	99,46
	FiBo15	64,44	1,07	0,22	n.d.	0,49	13,72	1,35	15,97	1,51	0,16	0,59	0,09	99,78
	FiBo17	64,88	0,89	0,14	n.d.	0,50	10,36	1,48	17,95	0,80	0,18	0,31	0,19	97,91
	FiBo19	61,40	1,05	0,17	n.d.	2,29	12,22	3,55	15,11	0,98	0,19	0,50	0,23	98,01
	FiBo20	61,44	1,06	0,17	n.d.	0,61	10,29	1,69	20,84	0,92	0,09	0,56	0,11	98,00
	FiBo22	58,91	0,96	0,08	n.d.	0,55	15,50	1,72	18,75	0,97	0,12	0,40	0,16	98,38
	FiBo23	64,83	0,96	0,16	n.d.	0,57	11,24	1,98	19,33	0,98	0,18	0,45	0,18	101,01
	FiBo25	63,91	1,16	0,19	n.d.	0,43	13,89	1,51	16,07	0,88	0,11	0,24	0,09	98,72
Pozzuoli	**Pozz-50**	65,73	2,73	0,15	0,03	3,39	9,50	2,17	15,70	1,62	0,29	0,58	0,47	102,53
	Pozz-51	62,40	3,24	0,19	0,04	3,07	13,34	1,56	16,31	1,42	0,48	0,54	0,14	102,98
	Pozz-52	62,80	1,03	0,09	n.d.	0,56	14,54	1,60	16,40	1,07	0,15	0,44	0,07	98,88
	Pozz-53	66,19	1,01	0,08	0,03	0,56	14,40	1,73	15,16	1,29	0,14	0,41	0,60	101,81
	Pozz-54	67,16	1,48	0,11	0,07	0,84	14,20	2,05	14,23	1,02	0,39	0,75	1,31	103,81
	Pozz-55	63,82	2,21	0,09	0,06	1,44	11,45	2,70	14,57	0,98	0,20	0,52	0,29	98,64
	Pozz-56	63,60	1,20	0,08	0,03	0,90	12,16	2,28	16,92	0,79	0,20	0,46	0,21	99,08
	Pozz-57	64,23	1,83	0,14	0,03	1,42	10,20	1,29	15,77	0,80	0,24	0,38	0,51	97,11
	Pozz-58	66,97	3,37	0,22	n.d.	1,88	7,33	1,26	17,13	1,36	0,52	0,45	0,06	100,77
	Pozz-59	70,24	2,79	0,24	n.d.	1,10	5,44	1,55	16,99	1,45	0,49	0,49	0,17	101,32
	Pozz-60	70,75	1,07	0,11	n.d.	0,58	13,52	1,24	14,41	0,69	0,12	0,41	0,12	103,16
	Pozz-61	63,82	1,11	0,13	0,05	0,68	18,27	1,84	14,06	0,71	0,08	0,51	0,50	101,98
	Pozz-65	62,02	1,97	0,19	0,03	1,23	11,53	2,00	17,40	0,99	0,12	0,64	0,10	98,41
	Pozz-66	67,10	1,28	0,07	n.d.	2,26	12,61	3,58	13,69	0,81	0,21	0,59	0,17	102,85
	Pozz-67	63,97	1,12	0,07	0,04	0,85	17,93	2,52	13,78	0,73	0,12	0,49	0,12	102,09
	Pozz-68	62,90	1,12	0,09	0,04	2,80	12,21	3,37	16,96	1,03	0,11	0,76	0,18	101,72

	Sample	SiO_2	Al_2O_3	TiO_2	MnO	MgO	FeO	CaO	Na_2O	K_2O	SO_3	Cl	P_2O_5	Totals
Pozzuoli	**Pozz-70**	67,12	1,66	0,14	n.d.	1,10	12,81	1,81	15,25	1,22	0,15	0,80	0,15	102,39
	Pozz-71	68,29	1,14	0,15	0,03	3,07	6,68	4,03	16,18	1,01	0,43	0,63	0,26	102,10
	Pozz-72	65,46	1,21	0,15	n.d.	3,26	6,96	4,41	17,55	1,20	0,15	0,99	0,23	101,77
	Pozz-73	63,44	2,04	0,13	n.d.	3,97	9,99	3,11	17,39	1,25	0,30	0,94	0,12	102,89
	Pozz-74	70,43	1,25	0,09	0,03	0,85	9,21	1,86	16,98	0,85	0,12	0,53	0,10	102,54
	Pozz-75	69,07	1,93	0,13	0,05	1,02	7,81	2,78	15,86	1,39	0,40	0,49	0,10	102,79
	Pozz-76	62,42	1,05	0,09	n.d.	0,75	17,51	1,84	14,69	0,67	0,14	0,58	0,06	99,95
	Pozz-77	64,26	1,13	0,05	n.d.	0,95	10,75	4,65	15,04	0,88	0,09	0,51	0,10	98,65
	Pozz-78	67,52	1,49	0,13	0,05	0,79	11,70	1,59	17,42	1,07	0,09	0,50	0,07	102,75
	Pozz-79	66,28	1,53	0,09	0,09	0,97	12,99	2,93	15,43	1,14	0,15	0,48	0,10	102,89
	Pozz-80	66,56	1,39	0,21	n.d.	1,01	14,46	1,82	15,43	0,80	0,12	0,71	0,07	102,85
	Pozz-81	67,07	1,27	0,07	0,05	0,74	13,41	1,95	16,87	0,80	0,18	0,56	0,27	103,46
	Pozz-82	67,19	1,31	0,07	n.d.	0,74	12,76	1,96	16,70	0,84	0,18	0,53	0,20	102,72
	Pozz-83	68,45	2,74	0,11	n.d.	2,06	6,76	1,18	17,18	1,31	0,28	0,49	0,14	100,89
	Pozz-84	64,35	2,41	0,24	0,04	2,46	8,15	3,32	17,57	1,79	0,67	0,45	0,22	103,43
	Pozz-85	65,33	1,60	0,11	n.d.	2,26	9,55	5,23	15,67	1,34	0,20	0,78	0,19	102,54
	Pozz-86	65,32	2,01	0,27	0,04	0,90	12,71	2,31	15,39	1,48	0,09	0,59	0,24	101,53
	Pozz-87	63,75	1,88	0,16	n.d.	2,51	8,70	4,21	17,33	1,12	0,12	0,65	0,22	100,80
	Pozz-88	69,65	1,45	0,11	n.d.	0,85	9,30	1,78	16,15	0,94	0,18	0,47	0,10	101,23
	Pozz-89	68,06	1,34	0,11	n.d.	1,03	9,15	2,14	15,95	1,04	0,24	0,50	0,12	100,97
	Pozz-90	67,12	1,06	0,09	n.d.	0,72	12,26	1,19	16,66	0,87	0,03	0,52	0,07	100,81
	Pozz-92	68,08	1,29	0,13	n.d.	1,28	10,63	3,70	14,73	0,98	0,33	0,55	0,10	102,12
	Pozz-93	67,77	1,26	0,09	0,04	1,27	10,19	3,52	15,04	0,97	0,36	0,56	0,12	102,22
	Pozz-94	66,65	1,34	0,11	n.d.	1,29	10,54	2,21	16,59	1,10	0,91	0,84	0,12	102,07
	Pozz-95	65,30	3,01	0,16	n.d.	1,77	7,10	2,71	17,99	1,59	0,30	0,43	0,15	100,73
	Pozz-96	63,48	0,98	0,09	0,04	1,05	15,64	2,28	17,24	0,92	0,21	0,68	0,12	102,97
	Pozz-97	62,77	1,06	0,23	0,03	1,02	16,25	2,08	16,27	1,09	0,12	0,75	0,10	101,94
Cumae	**Cum-164**	66,43	2,00	0,16	0,07	1,06	10,55	2,94	15,93	0,95	0,18	0,92	0,10	101,62
	Cum-165	67,58	3,24	0,16	0,04	1,98	6,33	3,25	16,40	2,04	0,00	0,50	0,24	102,18
	Cum-166	68,08	2,23	0,13	n.d.	1,82	9,98	1,51	16,71	1,13	0,21	0,38	0,05	102,42
	Cum-167	67,97	2,00	0,11	n.d.	1,80	9,73	1,74	16,63	1,20	0,82	0,37	0,05	102,63
	Cum-168	64,40	1,45	0,14	0,04	0,87	13,42	3,80	15,84	0,76	0,00	0,41	0,05	101,42
	Cum-169	73,87	1,58	0,22	0,11	1,94	5,03	2,77	10,32	1,42	0,27	0,48	0,10	98,40
	Cum-170	67,98	1,79	0,09	0,05	1,09	8,76	1,38	17,34	2,88	0,49	0,48	0,20	102,82
	Cum-171	66,58	1,54	0,16	0,08	0,96	12,43	3,04	14,99	1,69	0,24	0,35	0,19	102,63
	Cum-172	63,85	1,86	0,32	0,08	0,52	16,30	1,17	16,08	2,55	0,18	0,44	0,22	103,93
	Cum-173	70,15	1,05	0,14	0,04	0,28	11,31	1,26	15,70	0,99	0,00	0,50	0,12	101,76
	Cum-174	67,79	1,22	0,11	0,07	0,99	12,28	1,59	15,87	1,04	0,00	0,61	0,07	101,85

Table 3

	Sample	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr	Nb	Sn	Sb	Ba	La	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Yb	Lu	Hf	Ta	Pb	Th	U
Chotin	Cho-114-3	19	18	11	20	1504	58	2,6	75	174	8,3	63	3,3	149	18	388	7,6	1,7	6,9	0,4	1,6	0,2	1,5	0,3	1,0	0,1	1,6	0,3	52	2,5	0,6
	Cho-114-4	22	16	11	18	1840	68	3,4	86	186	9,5	81	3,7	150	22	449	8,4	1,9	7,9	0,5	1,8	0,3	1,8	0,4	1,3	0,2	2,0	0,3	57	3,1	0,8
	Cho-114-5	21	15	11	21	1755	66	3,2	84	214	9,3	68	3,6	137	19	466	8,7	2,0	8,0	0,5	1,8	0,3	1,8	0,4	1,2	0,2	1,8	0,3	54	3,0	0,7
	Cho-114-6	21	16	12	25	1818	72	3,3	84	174	9,3	70	3,7	139	20	462	8,5	1,9	7,9	0,5	1,8	0,3	1,8	0,4	1,1	0,2	1,9	0,3	55	3,1	0,8
	Cho-114-15	13	18	466	12	653	253	9,2	26	364	8,0	56	2,1	1,9	656	289	8,1	1,8	7,9	0,5	1,5	0,2	1,4	0,3	0,8	0,1	1,5	0,2	551	1,7	1,8
	Cho-115-7	13	14	6,3	13	99	100	2,4	47	137	7,6	49	2,6	0,7	4,0	265	6,6	1,6	6,5	0,3	1,5	0,2	1,5	0,3	1,1	0,2	1,5	0,3	2,4	2,7	0,6
	Cho-115-11	19	20	6,5	15	408	58	2,2	45	217	8,6	36	2,0	2,9	16	393	6,8	1,6	7,1	0,5	1,9	0,3	2,0	0,4	1,1	0,2	1,2	0,2	23	2,2	0,5
	Cho-115-15	10	11	5,7	16	109	84	1,4	58	206	7,5	19	1,4	1,5	37	284	7,0	1,5	6,5	0,8	1,8	0,2	1,4	0,3	0,7	0,1	0,5	0,1	12	1,2	1,2
	Cho-115-16	15	16	12	20	508	54	3,4	70	206	8,1	42	2,4	11	7,9	380	8,3	1,9	8,1	0,6	1,9	0,3	1,6	0,3	0,8	0,1	1,2	0,2	109	2,3	0,9
Bologna Fair	FiBo6	20	18	2,4	7,9	229	268	2,2	16	59	5,3	71	3,7	0,9	30	42	7,6	1,6	6,4	0,2	1,1	0,2	1,0	0,2	0,6	0,1	1,7	0,3	7,4	2,7	1,9
	FiBo11	16	15	1,0	7,6	83	406	2,2	17	49	7,2	62	3,7	1,2	6,5	35	7,7	1,6	6,9	0,2	1,4	0,2	1,3	0,3	0,7	0,1	1,6	0,4	4,0	2,8	2,1
	FiBo15	16	18	1,8	7,4	94	312	2,7	20	43	7,5	90	4,0	1,1	2,1	65	14	3,1	13	0,3	1,5	0,2	1,3	0,3	0,8	0,1	2,1	0,3	5,2	5,1	2,1
	FiBo17	16	16	1,4	5,5	446	213	1,6	12	33	8,0	79	2,9	4,2	21	33	8,0	1,7	7,3	0,3	2,1	0,3	1,5	0,3	0,7	0,1	1,9	0,2	4,6	3,5	1,3
	FiBo19	15	16	2,1	8,9	110	228	2,2	15	153	7,4	54	3,2	0,6	679	43	9,0	2,1	9,3	0,3	1,7	0,2	1,3	0,3	0,6	0,1	1,3	0,3	21	3,2	1,9
	FiBo20	19	17	1,6	7,9	48	395	2,2	14	50	11	75	4,6	0,7	1,7	44	13	3,2	14	0,5	2,5	0,4	2,1	0,4	1,1	0,1	1,9	0,4	2,7	6,3	1,8
	FiBo25	16	21	1,6	7,3	96	293	1,6	12	28	5,2	74	3,9	0,6	48	41	7,5	1,6	6,8	0,2	1,1	0,1	0,9	0,2	0,6	0,1	1,8	0,3	5,5	3,3	1,7
Pozzuoli	Pozz-54	24	12	1,8	10,2	48	613	2,7	15	69	8,3	62	4,0	0,8	296	55	12,9	2,9	11,3	0,3	1,7	0,3	1,5	0,3	0,6	0,1	1,4	0,3	11,8	3,3	5,0
	Pozz-55	69	20	3,1	18	119	722	3,2	15	108	8,8	77	4,2	1,1	99	46	13	2,9	12	0,3	1,7	0,3	1,5	0,3	0,8	0,2	1,7	0,3	27	3,7	1,8
	Pozz-56	34	136	6,8	231	39	14	2,3	10	41	10	60	3,8	0,8	56	52	12	2,6	11	0,7	3,4	0,5	3,0	0,6	1,3	0,2	2,5	0,5	3,0	5,2	1,8
	Pozz-57	33	135	6,7	232	37	15	2,3	10	38	9,4	57	3,7	0,7	28	48	11	2,6	11	0,4	2,0	0,3	1,8	0,4	0,7	0,2	1,4	0,3	1,6	3,1	1,1
	Pozz-58	61	334	17	223	29	27	3,6	15	59	9,5	57	5,5	0,8	4,0	36	10	2,4	10	0,4	1,8	0,3	1,6	0,4	0,9	0,2	1,3	0,4	2,5	2,8	1,1
	Pozz-59	32	93	5,3	40	282	12	3,6	22	54	11	75	6,6	0,9	1654	80	19	4,0	16	0,4	2,1	0,3	1,9	0,4	0,9	0,2	1,7	0,5	11	5,2	1,0
	Pozz-60	74	18	1,8	13	347	460	3,0	13	82	8,2	47	4,6	1,3	25	58	14	3,1	15	0,2	1,3	0,2	1,1	0,2	0,4	0,1	0,7	0,2	15	2,3	1,5
	Pozz-65	41	21	3,1	15	517	343	3,3	16	78	10	80	6,1	3,1	27	74	17	3,7	14	0,3	1,9	0,3	1,7	0,4	0,8	0,2	1,8	0,5	5,7	7,7	1,8
	Pozz-66	37	14	2,5	9,3	12740	317	4,3	14	175	7,6	49	4,5	1,9	64	200	11	2,4	10	0,3	1,4	0,2	1,3	0,3	0,7	0,2	1,1	0,3	334	2,5	2,3
	Pozz-67	23	12	2,3	10	2496	290	2,7	12	92	9,2	59	2,9	1,2	109	54	12	2,9	12	0,4	2,2	0,3	1,7	0,3	0,6	0,1	1,3	0,2	2,6	4,8	2,0
	Pozz-71	29	54	4,8	55	55	15	2,1	15	206	13	81	4,9	0,9	392	66	14	3,2	13	0,4	2,4	0,4	2,1	0,5	0,9	0,2	1,8	0,4	3,9	4,2	1,6
	Pozz-72	23	14	1,7	7,9	31	123	3,2	16	210	10	96	6,0	0,9	48	43	16	3,5	14	0,3	2,2	0,4	2,0	0,4	1,1	0,2	2,6	0,6	18	8,1	2,8
	Pozz-73	40	113	5,0	82	41	15	3,2	23	161	11	83	6,0	1,1	308	66	13	2,9	12	0,2	1,9	0,3	2,0	0,4	1,2	0,2	2,0	0,5	5,3	5,5	1,6
	Pozz-74	26	13	3,6	12	833	209	2,6	12	102	6,9	44	3,1	0,9	306	58	10	2,5	10	0,3	1,8	0,3	1,5	0,3	0,6	0,1	1,1	0,3	1095	3,6	1,5
	Pozz-76	19	13	1,2	6,3	52	305	2,7	11	52	5,9	50	3,5	0,7	7,3	36	10	2,3	9,1	0,2	1,2	0,2	1,1	0,2	0,6	0,1	1,3	0,3	2,3	3,9	1,9
	Pozz-81	50	16	1,3	13	54	647	2,8	13	59	9,3	43	2,4	0,7	242	46	10	2,3	10	0,4	2,0	0,3	1,6	0,3	0,6	0,1	0,9	0,2	12	2,2	1,6
	Pozz-82	47	16	1,6	14	319	595	2,7	13	68	9,4	48	2,4	0,6	263	48	10	2,2	10	0,5	1,8	0,4	1,5	0,4	0,6	0,3	1,0	0,3	10	2,1	1,4
	Pozz-83	49	254	27	350	130	31	3,2	16	53	5,4	47	3,0	0,7	48	25	5,5	1,3	5,4	0,2	0,9	0,2	1,0	0,2	0,6	0,1	1,2	0,2	3,0	2,4	0,9
	Pozz-85	156	19	2,4	21	75	253	3,2	19	150	8,7	82	4,5	0,9	490	45	12	2,6	10	0,2	1,6	0,3	1,6	0,3	0,9	0,2	2,0	0,4	19	4,3	2,1

Table 4

Isotopic results					
Sample	**$^{87}Sr/^{86}Sr$**	**2σ**	**$^{143}Nd/^{144}Nd$**	**2σ**	**εNd**
FiBo5	0,70919	0,00007	0,512070	0,000097	-11,08
FiBo6	0,70923	0,00013	0,512077	0,000096	-10,94
FiBo7	0,70949	0,00015	0,512196	0,000056	-8,63
FiBo19	0,70866	0,00009	0,512093	0,000076	-10,63
FiBo22	0,70941	0,00010	0,512082	0,000051	-10,85
FiBo23	0,71012	0,00010	0,512036	0,000054	-11,74