A SCIENTIFIC AND ARCHAEOLOGICAL INVESTIGATION OF PREHISTORIC GLASSES FROM ITALY.

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CONTENTS

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ABSTRACT:

keywords: Ancient glass, Italy, Final Bronze Age, Proto-Villanovan, Early Iron Age, Etruscan, X-ray fluorescence, electron microprobe, scanning electron microscope

Ancient glasses are invariably complex materials, in which the specific chemical composition and microstructure capture aspects of their technologies. The chemical characterisation of glasses in specific archaeological contexts has given useful insight into the peculiarities of diverse glass-making technologies. In addition such studies generate more general information upon an important range of phenomenon, including the pyrotechnological milieu, empirical knowledge of sophisticated chemistry, organisation of production, access to significant raw materials and long-distance trade. This study examines a wide selection of glass artefacts recovered from archaeological contexts in Northern and Central Italy from approximately 1200 BC to 200 BC. The earliest material is from the Final Bronze Age, and extends the characterisation of an established glass type, which is unique to Europe and distinct from the contemporary technologies of the Eastern Mediterranean. Using a combination of X-ray fluorescence analysis, electron microprobe and scanning electron microscopy glass artefacts from a thousand-year period from the same region are investigated. The shifting technologies permit the discussion of localised production and importation of glass from elsewhere. The chemical analysis reveals a complex picture of glass production, which defies the expected pattern, and there is evidence for new compositional types, which may yet prove to be diagnostic of highly localised production. The changing compositions are discussed in relation to the broader archaeological context.

dedicated to Charles Drury

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CHAPTER 1: INTRODUCTION

This thesis is concerned with the chemical characterisation of glass from Prehistoric Northern and Central Italy, from approximately 1200 BC to 200 BC. The shifting compositions of glasses are identified and explained in terms of the technologies employed and the implications for understanding the archaeological context.

1.1 Project Origins

This project originated in a Nottingham University-funded Graduate Teaching Assistantship, initiated in October 1996. The project proposal drawn up by the Dept. of Archaeology was the investigation and characterisation of the Etruscan glass industry employing X-ray fluorescence (XRF) and Scanning Electron Microscope (SEM) analysis. The acquisition of samples is discussed in further detail in below (section 1.2), and the adoption of suitable analytical techniques is detailed in Chapter 4.

1.2 Sample Collection

The initial starting point of this study was a closer examination of evidence for the existence of an Etruscan or Iron Age North Italian glass industry independent of production in the Eastern Mediterranean region. The existence of such an industry, suggested by a number of authors (e.g. Haevernick 1959, Harden 1968) has been posited on the basis of typological studies, which identified several artefact types that were distinct in terms of form and distribution. These artefact types were: two kinds of core-formed glass vessels (the *stachelflaschen*, and trail-decorated aryballos) and brooch decoration.

The primary aim of the project was to investigate the chemical composition of these artefact types in order to test the hypothesis of a distinct technical tradition. Additional analyses of contemporary glass beads was regarded as a necessary adjunct to the distinct types: whilst bead forms are often less diagnostic, they would undoubtedly represent the wider glassmaking technology outside of the special forms.

Given that a number of the *stachelflaschen* are held in collections in England, the initial focus was upon this artefact type and soon widened to include the aryballos and brooch sliders. Institutions and individuals in the UK, Italy and the US were approached and visited in an attempt to establish the location and sampling access to as many of these artefacts as possible. Considerable effort and resources were expended in tracing suitable artefacts for sampling, with mixed results. Some of the artefacts are held in private collections, and the small number of each extant in museum collections ensures they are regarded as extremely precious. Unfortunately only a limited number were available for sampling from the *stachelflaschen* group and the brooch sliders and none of the trail decorated aryballos.

A comprehensive list of all the samples and the institutions holding the original artefacts can be found in in Appendix 1. Attempts to gain access to contemporary prehistoric beads were more successful than the other glass forms, largely due to the assistance of Dr Chris Chippendale and the Beck Collection from the Museum of Archaeology and Anthropology, University of Cambridge. However, some of the items amongst the collection were not well provenienced, and it was felt that additional material was needed. Finally, the intervention of Dr Armando De Guio, from the Dept of Archaeology, University of Padua proved critical. Dr De Guio, with longstanding research links with Nottingham University, negotiated access to several museum collections in the Veneto through the Superintendent of Archaeology for the region, Dott. Luigi Malnati. Within the framework of a joint research project, permission was granted to sample material selected with the assistance of Dott. Giovanna Gambacurta and Dott. Simonetta Bonomi. As a consequence two sampling trips were undertaken: in December 1998 and in January 2000.

Samples were taken from artefacts held by the following institutions:

- Museum of Archaeology and Anthropology, Cambridge University
- Bristol City Museum
- Lincoln City Museum
- National Museums and Galleries on Merseyside
- National Archaeological Museum of Adria
- Rovigo Museum
- Montagnana Museum
- National Archaeological Museum of Este

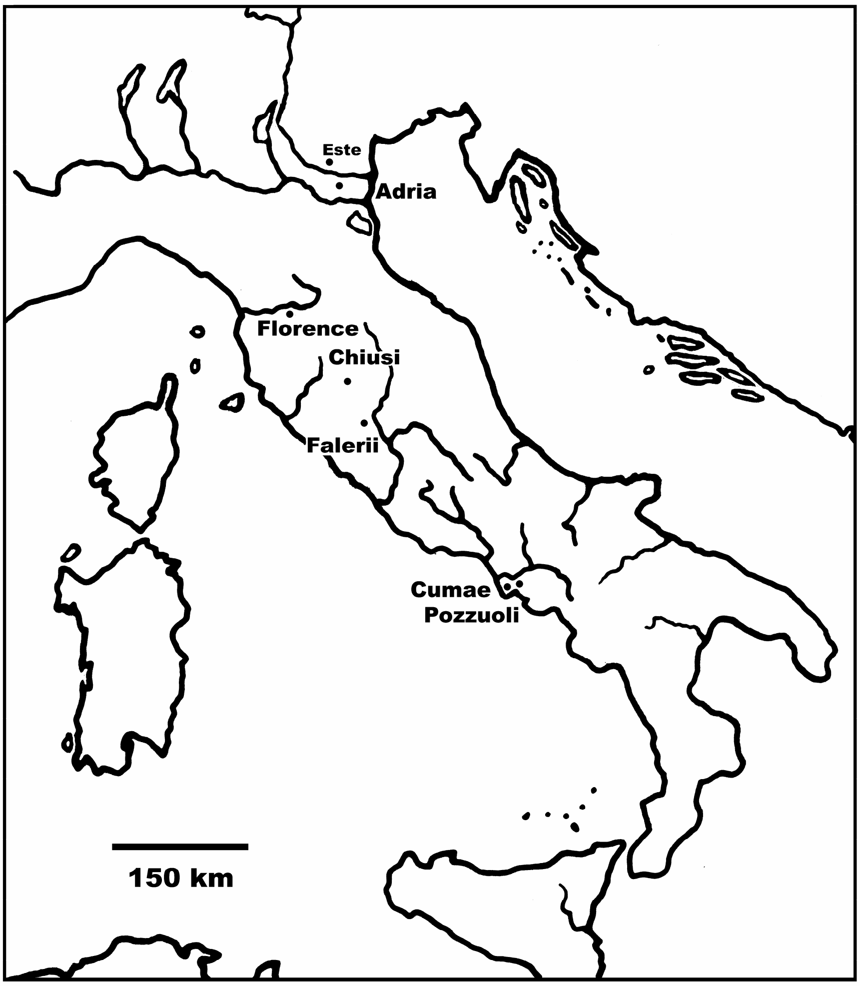
The samples originated from, or have been assigned the following provenance:

site	*date*
Frattesina	1200-900 BC
Mariconda di Malera	1200-900 BC
Montagnana (“Borgo San Zeno”)	1200-900 BC
“Etruscan”	800-500 BC
Pozzouli	700-600 BC
Cumae	700-600 BC
Co’Garizoni	300-200 BC
Canale Bianco	500-200 BC
Ca’Cima	600-500 BC
Casa di Muletti Prosdocimi	525-450 BC
Benvenuti	900-350 BC
Casa di Recovero.	900-600 BC
Casa di Alfonsi	525-450 BC
“Faliscan” Falerii	700-500 BC
Rebato	700-600 BC

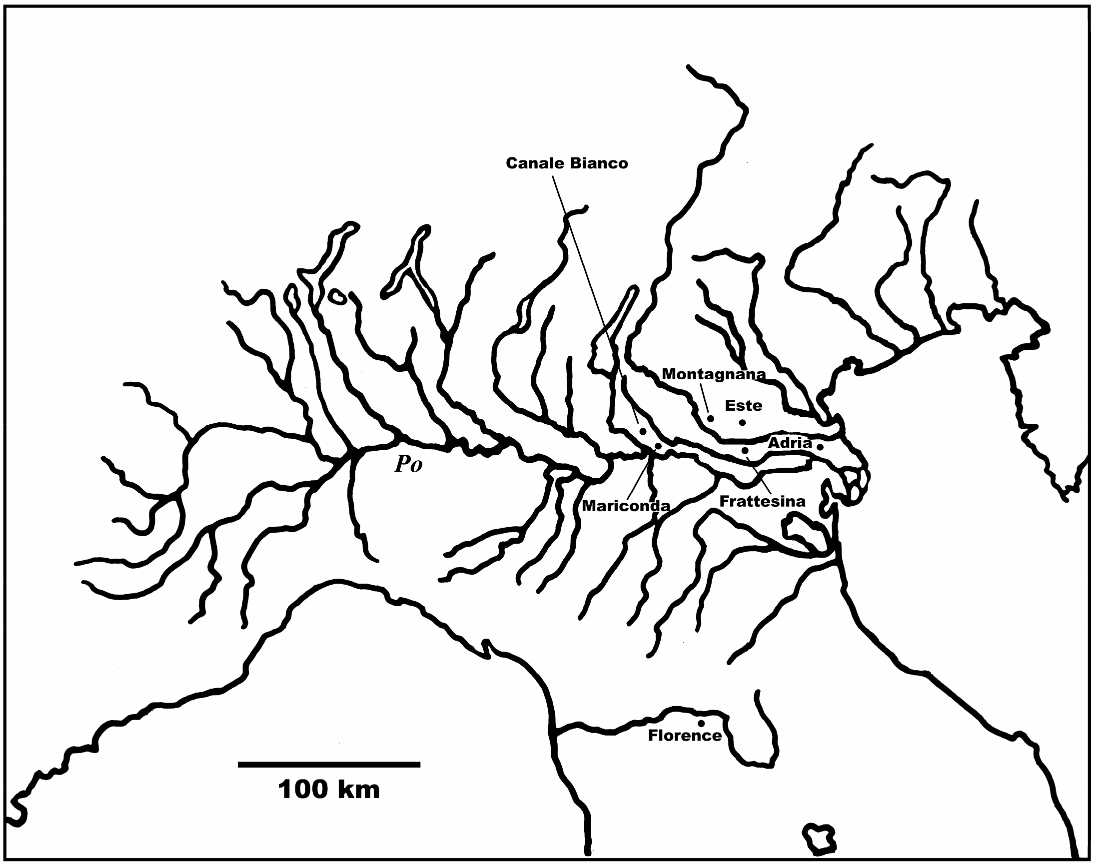
Table 1.1 Archaeological sites from which the sampled artefacts originate.

Individual samples and the original artefacts are described in greater detail in a Catalogue in Appendix 1. Further information on individual sites is given in Chapter 5.

The development of access to material inevitably led to a shift in the focus of the project. Since few samples were available for the distinctive core-formed glass vessels and brooch sliders, these products could no longer be entirely central to the thesis (although there is still sufficient analytical data from a handful of samples for some discussion on the issues surrounding these artefacts). Instead, the opportunity to sample Final Bronze Age through to Early Roman material from the Po Valley, alongside material from a slightly larger geographical area of



Figures 1.1 and 1.2 Location of key sites from which sampled artefacts originated



Central and Northern Italy from British-held collections meant that a broader range of issues could be addressed.

1.3 Selection of analytical techniques

Initially the principle analytical technique to be employed was X-ray fluorescence analysis, using a machine recently acquired by the Dept of Archaeology at Nottingham. A substantial effort was expended in defining ideal operating conditions for the analysis and quantification of ancient glasses using this piece of equipment. However, when samples were finally obtained, the demands of sample preparation meant that it was not the ideal technique for many of the artefacts examined. At that time SEM analysis was not available in Nottingham and access was arranged by Professor Julian Henderson and Dr Norman Charnley to an electron microprobe at the Dept of Earth Sciences, University of Oxford. Subsequent investigations using a SEM with semi-quantitative EDS analysis were undertaken using a machine at the Conservation Science and Research laboratory at the Conservation Centre in Liverpool, with the assistance of Dr Siobhan Watts. All analyses were undertaken by the author.

1.4 The investigation of glass technology.

The compositional analysis of ancient glass has been a cornerstone of archaeological science since the investigations of Klaproth in the late 18th Century (Caley 1949): indeed the first studies were the earliest materials science based research into any archaeological artefacts. Whilst such studies have never simply been empirical in nature, there is an increasing awareness amongst archaeological scientists that their investigations and explanation of patterning in their data should attempt to address wider questions than simple functionalist descriptions of ancient technologies (Sillar and Tite 2000).

The chemical characterisation of glasses, alongside an examination of microstructure and typology permits the reconstruction of the technologies involved in the primary manufacture. The existence of a large body of analytical data on glasses and the raw materials employed in glass manufacture enables archaeological scientists to define chronological and temporally specific technologies, and increasingly the culturally-determined technological choices involved in the industries.

This study represents an opportunity to discuss the kinds of theoretical assumptions, which underpin chemical characterisation studies, and these ideas are further explored in Chapter 2.

1.5 Technological aspects of glass beads.

Glass beads constitute the largest single form of artefact examined in this study, although a wide range of other artefacts are also sampled (including pendants, core-formed glass vessels, spindle whorls, brooch decorations, ingots, working waste and crucible residues). Beads represent a highly suitable type of object for analysis: in one material or another they are an almost ubiquitous artefact type in the archaeological record. Glass beads have a long history, the earliest having been recovered from the early third millennium BC onwards, initially in Syria (Tell Judeideh) and other sites in Mesopotamia, before their appearance along with amulets in Egypt during the Fifth Dynasty (2465-2323 BC) (Moorey 1985, p

194 – 200, Shortland and Tite, 2000, p 142, also see section 3.5). Glass (and faience) beads are found in West European contexts from the Late 3rd Millennium BC onwards (Azémar *et al*. 2000 p 75). Writers on the early development of glass technology (for example Peltenburg 1992) often regard the establishment of the core-formed glass vessel industries in Mesopotamia and Egypt in the Mid second Millennium BC as the most significant stage in the adoption of this material. However, this particular view ignores the widespread and sophisticated early use of glass technology represented by the manufacture and distribution of glass beads. Glass beads, with the infinite variety of forms, offer a sensitive and useful indicator of glassmaking technology. Clearly there are complicating factors, such as the well documented long distance trade in beads obscuring provenience (also see section 2.3), but nonetheless beads are an excellent resource for tracing change in ancient glass technology.

1.6 Objectives of the project.

This project seeks to address a number of clearly defined issues by chemically characterising glasses from archaeological contexts from Northern and Central Italy from circa 1200 to 200 BC.

The starting point is the further characterisation of the technology of glasses from Final Bronze Age Proto-Villanovan sites from the Po valley. Earlier studies have identified a mixed-alkali glass type unique to European Bronze age contexts. To date the Italian examples analysed are derived from a single site: Frattesina. With evidence for glassworking at several nearby contemporary sites, it will be useful to define the glass(es) worked there and be able to make a statement on the distribution and control of the technologies involved.

With the definition of the Final Bronze Age glass types, and the possibility of local production, this project aims to investigate the longevity of the technology in the region. To this end a range of glass artefacts, including regionally and temporally specific forms, from Early Iron Age Northern Italy were analysed to examine the evidence for localised production of the glass used in their manufacture.

The presence of glass forms unique to Etruscan contexts has been used to argue for a local glass industry. The analysis of these forms alongside contemporary beads is undertaken to test this hypothesis, in which the technology of “Etruscan” glasses is compared with earlier possibly local production and contemporary material from the Eastern Mediterranean.

By reconstructing the glass technology for this one region over a thousand year period, it is possible to construct a framework for changing technical choices, which is reviewed within the more general archaeological context.

CHAPTER 2: THE EVIDENCE FOR GLASS PRODUCTION IN PREHISTORIC NORTHERN ITALY, AND ASSUMPTIONS UNDERPINNING ITS STUDY.

2.1 Evidence for early glass production in prehistoric Italy: the Middle to Final Bronze Age.

Glass and faience have been fundamental to the study of Bronze and Iron Age Europe, initially for the purposes of contributing to the construction of chronologies before the advent of ^{14}C (Newton and Renfrew 1970, p 199). Studies discussing the possibility of independent faience production in Bronze Age Europe however, were undertaken before the development of ^{14}C (Beck and Stone 1936). Analytical work and the ensuing data analysis have been a key component in establishing the manufacture of faience in Bronze Age Europe (Beck and Stone 1936, Stone and Thomas 1956, Newton and Renfrew 1970, Harding 1971, Aspinall *et al.* 1972, McKerrell, H. 1972, Harding and Warren 1973).

Faience and glass beads have long been noted amongst material recovered from Bronze Age contexts from Central and Northern Italy: the earliest are segmented faience beads from the Early Bronze Age sites (Bergonzi and Cardarelli 1992, p 218), but both faience and glass are common finds from Middle Bronze Age excavations, and are frequently discovered in funerary contexts from then onwards (Bellintani and Biavati 1997, Bellintani *forthcoming*: Gastaldi 1876, Montelius 1895, Casi *et al.* 1993). The range of forms of glassy materials from Bronze Age contexts is quite varied, and includes forms common to the European and the Mediterranean regions (also see figure 2.1 for examples of these forms:

annular monochrome beads: A, eye-decorated beads: B), parallels to the Aegean (radial wheel: C), Alpine region (spirally decorated cylinder shaped beads: D) and a form apparently unique to Central and Northern Italy (cone-shaped beads: E) (Henderson 1988a, 1990, 1993b, Venclová 1990, Barfield 1978, Bellintani and Biavati 1997, Bellintani *et al.* 1998, Bellintani *forthcoming*, Santopadre and Verità 2000).

As acknowledged by a number of authors (for example Harding 1971) the independent production of an artefact may be indicated by a number of characteristics: typological difference marked by specific chronological and geographic distribution with chemically distinct composition. Despite the valuable contribution of chemical analysis to the definition of European faience production, there has been no systematic programme of analysis of the earliest glass objects from European contexts, even though distinct characterisation in terms of typology and distribution from Eastern Mediterranean material has taken place (Harding 1971). The limited chemical characterisation of a specific Middle and Late European Bronze Age glass has enabled archaeologists to trace the development of a distinct technology, with the possibility of locating its development out of faience technology: mixed-alkali glass (also known as low magnesia, high potash glass- LMHK (Henderson 1988a).

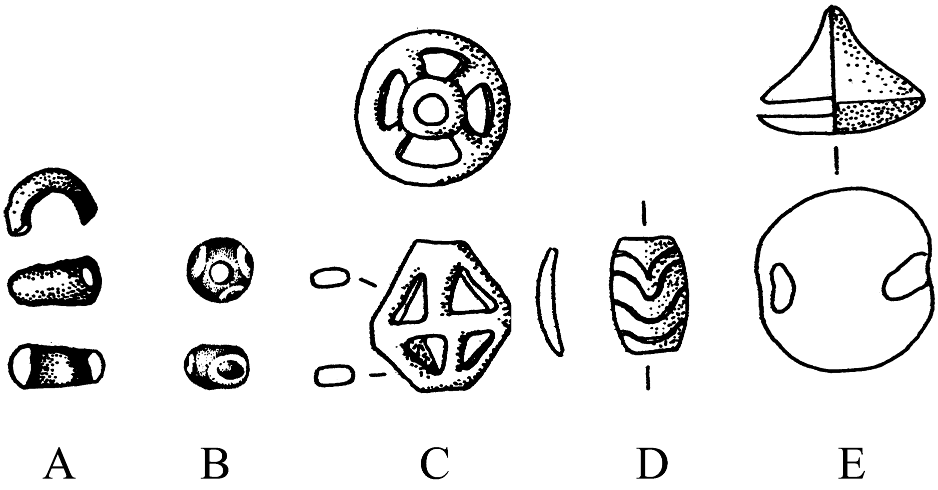


Fig 2.1 Examples of Bronze Age glass forms recovered from Central and Northern Italy, scale 1:1, after Henderson 1988a, 1990, 1993b, Venclová 1990, Barfield 1978, Bellintani and Biavati 1997, Bellintani *et al.* 1998, Bellintani *forthcoming*, Santopadre and Verità 2000.

The first qualitative and quantitative compositional analysis of a European Bronze Age mixed-alkali glass artefact was published by Biavati (1983), closely followed by Guido *et al.* (1984). The former paper examined material from Frattesina, Northern Italy, and the latter from Wilsford, Southern England. Both of these papers discussed the role of vegetable ashes as the source of the alkali components, and distinguished the respective compositions from contemporary glass production in the Eastern Mediterranean. However, it was not until a larger number of Bronze Age European glasses had been analysed that the mixed-alkali composition was identified as a specifically European Bronze Age phenomenon (Henderson 1988a, p 439). This hypothesis has been underpinned by additional analyses of Bronze Age glasses, and there is now a body of compositional data on mixed-alkali glasses from Britain and Ireland (Henderson 1988a), France (Guilaine *et al*. 1991, Gratuze *et al.*1998), Switzerland (Henderson 1988a, 1993b), Germany (Hartman *et al.* 1997), Greece (Henderson 1994) and Italy (Biavati 1983, Verità and Biavati 1989, Brill 1992, Santropadre and Verità 1993, 2000, Bellintani and Biavati 1997, Bellintani *et al*. 1998 and Bietti Sestieri, Henderson and Ponting *forthcoming* . Frattesina plays a pivotal role in the identification of this separate industry: not only was it amongst the first to be published, but the sheer quantity of material, the range of glassworking debris (and association with other manufacturing industries) have established it as a major glassworking site (if not glassmaking) in the Final Bronze Age (1200 – 900 BC). All of the other published Bronze Age compositional data is from completed artefacts and is not associated with evidence for glassworking or making.

Only a few authors have addressed the question of the Europe-wide chronology of the mixed-alkali glasses (Guilaine *et al.* 1991, Gratuze *et al.* 1998, Bellintani and Biavati 1997, and Bellintani *et al.* 1998). It is of interest to identify when this glass type was first developed, and to explore any antecedents. Guilaine *et al.* (1991) and Gratuze *et al.* (1998) have suggested that the mixed-alkali glass has been recovered from deposits in France as early as the Chalcolithic (2895 – 2420 BC, Guilaine *et al.* 1991, p 259). A faience bead from the Tumulus of Run-ar-Justicou (Gratuze *et al.* 1998, sample 73088), is dated from the Early Bronze Age to the beginning of the Middle Bronze Age on the basis of comparison to an assemblage from another cave site in Brittany (how this was dated is not specified) (Gratuze *et al.* 1998 p 11). The excavation was undertaken in 1881, and the possibility of artefact contamination cannot be excluded: other beads from this study were assigned later dates following compositional analysis (for example faceted bead 87391-52/7 from La Grotte de Rancogne). A similar bead to the faience bead 73088 from the Chalcolithic site of Le Peyere is cited as a parallel, unfortunately this too has had to be re-dated (see note on page 23 of Gratuze *et al.* 1998).

This faience bead does remain a very important artefact, since it offers a bridge between the faience and glassmaking technologies, with its mixed-alkali composition substantiating the hypothesis of the independent development of mixed-alkali glass in Europe. The separate trajectory of faience to glass, independent of the Eastern Mediterranean vitreous technologies is a significant contribution to the discussion of high temperature industries. The relationship between glass, faience and glassy faience are discussed at greater length in Chapter 3 (3.4). Clearly the dating of individual glass (and faience) artefacts is fundamental to any debate on this issue.

All of the other mixed-alkali glasses except two analysed in the Gratuze paper (Gratuze *et al.* 1998) date to the Final Bronze Age, with the two exceptions being from Le Fort-Harrouard, Sorel Moussel, which are given a Middle Bronze Age date (Gratuze *et al.* 1998, p 14). The authors of the paper recognise that the presence of glass beads in archaeological deposits peaks during the Final Bronze Age, but trace their presence in French deposits back to the Chalcolithic period. Although not referenced at this point, it seems likely that the earlier paper (Guilaine *et al.* 1991) is being considered here by Gratuze *et al.*(1998). Of the three examples assigned Chalcolithic dates: one, Le Peyere has been rejected as of such an early date (its high tin content suggesting it is coloured using a copper-tin alloy); and another, from Dolmen de Peirieres has a typical natron based composition which is not otherwise known before the 8th C. BC. This leaves a single bead dated to before the Middle Bronze Age: a fragment of a blue glass bead from Gord, Compeigne, Oise. A calibrated ^{14}C date has been assigned to the context of its discovery (2895 – 2420 BP) (Guilaine *et al.* 1991, p 259). This early date has since been rescinded by the original authors (Henderson *pers. comm.*). In their 1991 paper, however, other glass beads from Early Bronze Age deposits (Grotte au Collier) were discussed, but these are high magnesia, soda-lime-silica glasses typical of the Eastern Mediterranean region, and are likely to be imports. The next earliest identified mixed-alkali glasses from France are from the Middle Bronze Age site of Grotte de Bringairet, Armisson, Aude (Guilaine *et al.* 1991, p 259 and 263).

The recent discussion of cone-shaped beads from Central and Northern Italy (Bellintani *forthcoming*, Bellintani *et al.* 1998, Bellintani and Biavati 1997) integrate analysis of typology, chronology, distribution and chemical analysis. These studies locate the manufacture of the beads in the beginning of the Middle Bronze Age, with the possibility of localised variation in form out of a regionally distinct glass type (i.e. the mixed-alkali glass).

It would appear that a consensus is emerging for the existence of the mixed-alkali glass in the Middle Bronze Age (and therefore before the development of the site of Frattesina). The presence of mixed-alkali glass in French contexts from the

Middle Bronze Age would confirm the widespread adoption of the material at this point in time. It would seem most likely that Frattesina represents the continuity of this particular industrial tradition into the Final Bronze Age (as described in Bellintani *forthcoming*). The origins of this glass industry have not been established in 3rd Millenium BC France: two of the three examples from the Chalcolithic have been re-dated on the basis of their chemistry and the remaining mixed-alkali faience bead has recently had its early date revoked by Gratuze (Henderson *pers. comm*.). However, the existence of mixed-alkali faience suggests that it might be possible to trace the development of the mixed-alkali tradition between these two technologies.

A series of questions remain to be answered: since settlements contemporary to the Final Bronze Age site of Frattesina in the Po valley also have evidence for glassworking (i.e. Montagnana and Mariconda di Malera), it would be useful to identify the glass types being employed there. Is there a single tradition in the Po valley at this time, or a range of technologies? Recently published studies of glass and "glassy faience" from Middle Bronze Age sites in Italy (Prato di Frabulino, Poviglio and Trinitapoli) and an Iron Age site (Chiaromonte) suggest that the mixed-alkali technology might be more diverse and long-lived than previously thought (Santopadre and Verità 2000).

Given the strong evidence for regional glass manufacture from the beginning of the Middle Bronze Age to the Final Bronze Age, it would be useful to establish if there is any evidence for continuity for this glass making tradition into the Iron Age in Northern and Central Italy. The mixed-alkali glasses and glass-working debris, recovered from Rathgall in Ireland (Henderson 1988b) are dated to the 9th-7th Centuries BC, suggesting that elsewhere in Europe this glass type continues in use.

2.2 Characteristic glass forms from prehistoric Italy: The Early Iron Age and Etruscan periods.

Leech-shaped brooch decoration.

A series of brooch decorations made from glass have been noted as peculiar to Early Iron Age and Etruscan contexts in Central and Northern Italy (Montelius 1895: Serie A plate 7 and Serie B plates: 90, 94, 195, 219, 307, 318, 349, Grenier 1912 p 294-305, von Bissing 1942 144-168, Dohan 1942 Plate 19, Figure 40, Plate 22, Figure 61, Sundwall 1943, p 193, Figure 311, p 208, Figure 333, Harden 1968, p 59, Goldstein 1979, p 122-123, Grose 1989 p 70, 81-82, 87,Tatton-Brown 1995 p 321, Dobiat 1987, p 27-29, figure 17, plate 1). Their full distribution however, extends from Central Italy northwards as far as Poland, but is concentrated around the Northern Adriatic (Dobiat 1987, p 27-29, figure 17, plate 1, Map 13). These decorations take the form of a leech-shaped agglomeration of glass formed on a rod, which has then been decorated with the addition of trails of differently coloured glass wrapped around the glass matrix. These trails of glass are marvered flush with the surface of the main body of glass before being combed in alternate directions to create a feathered or chevron design. Often the combing action leaves a ribbed finish on the object, which has not been removed by further marvering. The colours used include blue, yellow, white and red opaque glasses, although they may often be difficult to discern because of surface degradation. Whilst the chevron design is a common decorative motif in glass vessels from the Eastern Mediterranean region from the 14th Century BC onwards (e.g. Stern and Schlick-Nolte 1994, p 150-151), its use on brooch decoration (sometimes referred to as brooch sliders) is more restricted. Beads with a similar decoration have been noted from Northern Italy to Greece (Tatton-Brown 1995, p 321, Grose 1989, p 81, Dobiat 1987 plate 3), and whilst these may originate in the same production as the brooch sliders, they may simply represent the noted widespread adoption of this decorative form. Rod-formed bracelets of similar design have also been recovered from Central and Northern Italy (Grose 1989, p 81).

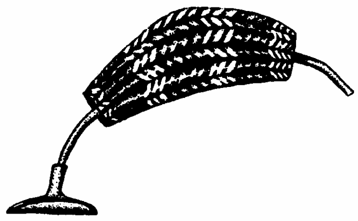


Figure 2.2 Leech-shaped brooch decoration from Rebato, grave 100, 675-575 BC. After Dobiat 1987, Figure 17, scale 1:2, also see sample 373 this study.

There has been no previous attempt to chemically characterise the glasses employed to make these artefacts. It has been assumed that they were produced in Central and Northern Italy on the basis of their distribution. It was considered useful to establish the nature of the glass technology employed, to discover if it can be correlated with the earlier mixed-alkali tradition in the region, and how it compares with contemporary Mediterranean glasses.

The stachelflaschen.

Previously, the earliest core-formed glass vessels found in Italy were certainly exotic imports: cups recovered from Etruscan contexts dated to the last quarter of the 8th Century BC and probably having a Phoenician or Assyrian origin (Giuntoli 1996, p 14, Tatton-Brown 1995, p 321-325) (n.b. see sample 236, this study). However, there is a series of vessels which appear to be a class of artefact limited to Etruscan contexts from c. 650-550 BC: the *stachelflaschen*. This category of artefacts was first defined by Haevernick in 1959, who recognised these core-formed glass vessels as a uniquely Etruscan phenomenon (Haevernick 1959, 1961). The vessels were produced using the conventional core-formed technique of applying hot glass to a friable core on a rod, which was subsequently removed after the finished vessel had been annealed and cooled (for a detailed description of the technique see Stern and Schlick-Nolte 1994, p 28-44, Gudenrath 1995, p 214-215). The decoration is what distinguishes these vessels from contemporary products from Egypt, Rhodes and Mesopotamia. The vessels have a raised scale decoration, consisting of either applied knops of glass, or drawn from the body of the object. Depending upon the underlying vessel form, a foot, base, neck, collar and handle may be added. Although a number of different coloured glasses have been used to make this form (amber, green and blue) all are monochrome (and mostly blue, both turquoise and dark blue opaque coloured). The decoration has been compared with that on a series of brooch decorations, which are contemporary, but are distributed outside the Etruscan zone from Este in Northern Italy to Yugoslavia and Slovenia (Haevenick 1959, p 62, Sternini 1995, p 22-23).

Since Haevernick's initial study identifying the type and listing 12 known examples, additional work by other authors have extended the number to over 100 (Haevernick 1959, 1961, Bizzarri, 1965, Harden 1968, p 46-72, 1981, p 138-141, Harden *et al*. 1968, Fremersdorf 1975, p 28, Goldstein 1979, p 122, Grose 1989, p 81-82, Capecchi 1993, p 129-134, Martelli 1994: the latter with the most comprehensive catelogue of 48 artefacts, Tatton-Brown 1995, p 321-322, Sternini 1995 p 22-23, Giuntoli 1996). 72 have known provenance's (see Capecchi 1993, p 131, Figure 2, after Giuntoli). The most common form is the oinochoe (see figure 2.3 below), but examples are also known in the forms of alabastron, pyx, lagynos and aryballos. These forms can be related to Greek and Eastern Mediterranean models in ceramic and metal, but given the widespread adoption of these shapes around the Mediterranean, the forms themselves do not indicate origin, although the slightly elongated oinochoe form has parallels in Etruscan-produced ceramics (Haevernick 1959, p 63). Haevernick initially suggested a 4th Century BC date on the basis on general form, which was soon amended, to the late 7th Century BC in the face of contextual data (Haevernick 1959, 1961). Harden (1981, p 139) argues for a long chronology for these vessels on the basis of art-historical discussion of the underlying form, and suggests a period from the late 7th Century to the early 3rd Century BC. Giuntoli, however rejects this, and after close examination of the few well- provenienced examples suggests a date of 650-550 for the entire group on the basis of archaeological context (Capecchi 1993, Giuntoli 1996 and Giuntoli *pers. comm.*). The decoration on the vessels may have parallels with early 7th Century BC Etruscan ceramic vases (Tatton-Brown 1995, p 321).

Figure 2.3 stachelflaschen: core formed glass vessel with decoration unique to Etruscan contexts. After Tatton-Brown and Andrews 1995, p 41, figure 43. Height = 6.5 cm, held by the British Museum: 1848.8-3.69, unknown provenance, full description in Harden 1981, p 139 and Figure 10.

As yet there is no direct evidence for glass working or making from Etruscan contexts (Giuntoli 1996, p 13), and these vessels have been assumed to be manufactured in Etruria on the basis of their distinct decoration and limited distribution. Many of the known examples are of unknown provenance, and are scattered amongst collections around the world.

No previous compositional analysis has been performed upon this group of artefacts, and it was therefore considered a matter of some interest to investigate whether or not the chemistry of these glasses reflects a distinct technological tradition. Since glassmaking has been strongly suggested for the Final Bronze Age in Northern Italy, it was therefore thought to be useful to determine if there is any evidence for technical continuity from the Protovillanovan *koine* of Frattesina to the Etruscan societies of 7th-6th Century BC Central Italy. An examination of glass beads from contemporary Etruscan contexts placed the glass chemistry of the *stachelflaschen* in their technological context. A survey of Etruscan glass objects was undertaken to illuminate the technologies involved, and address the question: is there a single tradition consistent with either well controlled domestic production or limited-source importation, or a diverse range of different traditions reflecting a fragmented and variable production?

2.3 Theoretical assumptions underpinning the research.

As a work of archaeological science, this study embodies a number of theoretical assumptions concerning the manner in which ancient materials are studied and interpreted. The theoretical understanding of X-ray techniques and their practical application to archaeological samples are discussed at some length in Chapter 4. Here the concepts underpinning the application of analytical techniques to the study of archaeological material are briefly considered. In this context the term “archaeological science” is simply used as a term to describe the application of methodologies developed by the physical sciences to ancient materials, rather than to lay claim to “scientific” status for the elaboration of wider inferences concerning the societies using the materials (Trigger 1988, p 1 and 1989, p 373-374).

The chemical analysis of ancient glass dates back to the late 18th and early 19th Centuries (Caley 1949, 1962, p 13 – 15, 1967, p 120), with the curiosity of early chemists driven, in part at least, to understand the technologies of the classical world to facilitate the production of contemporary materials. Amongst the justification for the investigation of “the nature and composition” of a range of pigments and vitreous materials from Pompeii, Humphrey Davy suggested to his audience

> “I shall be able to give some information not without interest to scientific men as well as to artists, and not wholly devoid of practical applications” (Davy 1815, p 99-100).

It is interesting to note Davy’s ethical approach to the sampling of the materials:

> “When preservation of a work of art was concerned, I made my researches upon mere atoms of the colour, taken from a place where the loss was imperceptible: and without having injured any of the precious remains of antiquity” (Davy 1815, p 100).

It wasn’t until later in the 19th Century that an explicit statement of the value of chemical analysis for the resolution of specifically archaeological questions was made. In the preface to the 1879 edition of his book (Manufacturing Arts in Ancient Times, with special reference to Bible History), James Napier discussed the origin of the dead and their grave goods from excavations at Mycenae:

> “I think it probable that if chemistry was called in as evidence in such enquiries, it would at least, yield much valuable circumstantial, if not positive evidence as to whether the articles found alongside the bodies

> were of Grecian or Scandinavian manufacture…and I think that nations so far apart as the north of Europe and Greece may, and in all probability had, different methods of compounding their alloys; so that, were this the case, strict analyses of the different articles found would approximately determine whether they were made in Greece or northern Europe. … With the knowledge which archaeologists have attained in respect to form and other characteristics of ancient works, I believe that, were analyses added to this knowledge, the archaeologist would soon come to determine not only the age, but the locality where the different articles were made."

Napier concluded his preface with a call to arms for archaeological scientists:

> "As yet I think archaeologists have not put that value upon chemical investigation that it deserves, and hope that this volume will help to stimulate to such an enquiry." (Napier 1879 p II-IV).

In the brief passage quoted above, Napier identifies a number of the key concerns of the chemical characterisation of ancient materials: identifying technological processes, technological traditions, the relationship to form, dating and provenance.

The application of natural sciences to archaeological research has expanded hugely since Napier's day, and extends to include such diverse areas as environmental reconstruction, paleopathology, biological evolution, dating, prospection and conservation science: nonetheless the compositional and structural analysis of artefacts remains at the heart of archaeological science (for a brief history of the development of archaeological science see Pollard and Heron 1996, p 1-19, and also: Caley 1951, 1962 and 1967, Brothwell and Higgs 1969, p 23-34, Harbottle 1982, Ciliberto 2000, and Brothwell and Pollard 2001b, p xvii-xx).

The value of an archaeological scientific investigation into any body of material is dependent on two key issues: the construction of a suitable archaeological question and the selection and application of the appropriate analytical technique(s) to the resolution of the question (the latter is considered in Chapter 4).

Clearly several assumptions are implicit in the chemical characterisation of a group of artefacts:

technological processes
technological tradition
grouping/association – difference
provenance

It is useful to consider the limitations of these concepts for the purpose of this study. The manner in which glass artefacts may be studied is examined in greater detail in Chapter 3, but it is important to question the usefulness of certain objectives to interpretation. The chemical and structural examination of glass artefacts permits the detailed reconstruction of an object's life history (or *chaine operatoire* –Tite 2000, xv-xvi, Tite 2001, p 443, Dobres and Hoffman 1994, p 237-239). Sufficient knowledge has been collectively accumulated by archaeological scientists to infer distinct raw materials, temperature regimes, oxidation states, forming activities, use, re-use and depositional environments for glass artefacts. Whilst an understanding of these processes is a worthy end in itself, and not a new objective for archaeologists, it is the interpretative value placed upon technology which varies between archaeologists.

The examination of a glass artefact (or group of artefacts) permits its relation to the larger body of compositional and structural data: a large number of regional and temporally specific traditions have already been defined. Clearly, the quantity (and quality) of data in existence for a region and period determines the capacity for defining new analyses. For any particular period the categorisation improves with additional data, as the groupings become better defined (or redefined), for example the five glass compositional groups defined by Sayre and Smith in 1961 for Europe, Western asia and Africa from 1500 BC until 1200 AD has been greatly extended (Sayre and Smith 1961, p 1824).

The grouping of artefacts, and differentiation on the basis of shared traits is also a long established archaeological practise, since Thomson's seriation in 1819 led to the definition of the Stone, Bronze and Iron Ages in European Prehistory (and their internal differentiation: Trigger 1988, p 1-2). The assumption that differences must exist between data sets from artefacts which are distinguished on other, archaeological grounds (such as form, association, context or date) is an eminently testable proposition in each case, using statistical techniques (e.g. Glascock 1992). The imposition of difference, using sophisticated statistical methodology is not difficult, but groupings still need to be explained in terms of their technology, and related to their archaeological significance.

Provenance studies based on chemical characterisation of some archaeological materials have been very successful, with unequivocal identification of the geological source for certain types of artefact (for example obsidian: Henderson 2000, p 305-314, Pollard and Heron 1996, p 81-103, Wilson and Pollard 2001). Similarly ceramics have been successfully characterised and related to specific geological sources of clay (Pollard and Heron 1996, p 104-148). Glass however, represents a more fundamental re-working of quite diverse raw components, which makes the establishment of a relationship between the finished product and specific geological sources difficult if not impossible. An individual glass artefact might contain components with separate and distant geological origins (for example exotic colourants in locally-produced glass, also see 3.7 below). Glass as a material does not readily lend itself to provenancing, in the manner of stone or ceramic. The well-documented and archaeologically attested phenomenon of geographically distinct manufacture, colouring, working, and recycling of glass renders the concept of provenance redundant (Wilson and Pollard 2001, p 512-513). However, the definition of technological tradition is in many ways more useful, for this can distinguish characteristics which might have a geologically specific aspect (such as a high-alumina cobalt colourant), alongside traits which are associated with raw component-selection which are less geographically dependant. The consideration of technical tradition also more readily permits the acknowledgement of culturally determined choice.

2.4 The relationship between technology and society

The elaboration of the technology represented in an artefact is not an isolated activity, in which the objective empirical truth of an object gives rise to useful knowledge. There are two fundamental areas of concern in this discussion.

The first is the recognition of technology and its components as a significant sphere of inquiry. The questions posed, and to a certain extent answers gained by any archaeologist are a consequence of his/her context: archaeology, like any other activity, past or present is socially embedded (for a discussion of the socially specific nature of scientific enquiry, see Gould 1981). This self-critical position has arisen with the rejection of a more general positivist approach in the "New Archaeology" of the late 1960's and early 1970's (e.g. Clarke 1968, 1973 and Binford 1962). The development of the "posties" (i.e. post-processualism, post-structuralism and more generally in academia, post-modernism), has in some cases led to the development of relativist perspectives upon archaeological interpretation (Miller and Tilley 1984, p 151, Shanks and Tilley 1992, Trigger 1986, p 11, 1990, p 379-382, Callinicos 1996). Without doubt, increasingly theory-literate archaeologists can make more confident inferences concerning past behaviours (Shanks and Tilley 1992, p 245): extreme relativism however reduces archaeological interpretations into competing stories about the past, which cannot be evaluated in terms other than their internal coherence. The recognition of the existence of a single, genuine past is a crucial starting point for effective archaeological enquiry ("the past is knowable" Bintliff 1988, p 2). The efficacy of interpretative schemes to approach that past is the arena in which ideas can be tested, this can only be achieved by drawing up paradigms that define "useful" data for collection and bridge the gap from data to the meta-narrative of particular world views. These paradigms constitute Binford’s “middle-range” theory, and are particularly useful for drawing up cross-cultural generalisations concerning the constraints on human behaviour placed by ecological or technological circumstances.

Having recognised that the selection of technology, its meaning and constituent threads of enquiry are choices reflecting contemporary concerns, the activity of employing these concepts to generate archaeological data should be undertaken with an awareness of what types of inferences may be drawn as a consequence. An understanding of technical processes permits inferences on: technical skills, tools, organisation of labour, procurement of raw materials, parallels between technological concepts and ideologies (for the latter see Trigger 1988, p 6, and for glass, the rituals associated with manufacture: Oppenheim *et al.* 1988, p 32-33).

The second important consideration for the discussion of ancient technology is how it is related to the wider society under consideration (i.e. on the basis of investigation of technologies, what forms of inference may be made). In his broad discussion of the role of artefacts in the reconstruction of technologies, Gordon (1993) suggests a useful (for historical periods,) series of principles for interpreting artefacts: beyond archaeometry, the components of the context are critical to realising the potential of an object. Gordon groups these as “backward-linkage” and “forward-linkage” components. The backward-linkage components consist of the boundaries established by the physical and chemical investigation of an object: the types of materials and processes involved in manufacture, which may be supplemented by experimental reconstruction work. The forward-linkage components are the observations of how objects have been used, and by whom, and how the form of an object relates to its function. Clearly these principles are well suited to functionalist interpretations concerning technology, but offers little assistance in the reconstruction of the associated social structures, which Gordon concedes are difficult to identify without the help of documents or oral histories (Gordon 1993, p 80-81). Fortunately archaeologists have long been developing intellectual tools which enable them to move from the analysis of material culture to social organisation (Wright 1993, p 243-244). Pfaffenburger (1992) illustrates the socially embedded nature of technology, and usefully challenges the functionalist framework of many studies of ancient technologies, suggesting the adoption (by anthropologists and archaeologists) of the concept of the “sociotechnical system” which links technology, material culture and the social coordination of labour. The question remains however, how far can observations made on technology be used to generate insights into the social formations, in which artefacts were conceived, used and deposited?

A session at the World Archaeology Congress in Cape Town in 1999 (Technological choices in ceramic production) addressed the problems of understanding ancient technologies in their wider contexts. The publication of these papers (Livingstone Smith 2000, Sillar 2000, Pool 2000) with a commentary (Sillar and Tite 2000) and subsequent reactions (Cumberpatch, Griffiths, Kolb, Neff, Roux, Stilborg, Sillar, Livingstone Smith, and Pool, 2001) constitute a significant discussion of a particular framework for studying ancient technology: “technological choices”. Whilst the particular focus of the papers is rooted in the examination of ceramic production, the authors acknowledge the wider application of this approach to materials science – based studies in archaeology. Despite some differences a number of key concepts are recognised as being useful.

- By undertaking material science based studies of ancient technological practices, it is possible to identify the junctures at which technological choices were being made in the past. To locate choices in technical activities (all actions impacting on material culture?), Sillar and Tite identify the important stages and relationships involved in pottery production. This kind of work is the principal strength of archaeological (and material) scientists. Sillar and Tite draw particular attention for the need (also recognised elsewhere) to integrate concepts from social sciences into the explanation of the choices made to avoid functional interpretations (Sillar and Tite 2000, p 2, p 15).

- The distinction between technology and cultural context is recognised as a false one, and that there is a reflexive relationship between the activities of ancient peoples and the structures of their societies. Technological activities are not simply a reflection of the mental templates possessed by people in the past.

- Technology can be fundamental to the social reproduction of societies- the act of doing and the transmission of knowledge and skills are powerful formative processes in the structuring of human relations.

None of these ideas are particularly new, but perhaps the significance of the papers (as noted by Cumberpatch, 2001, p 269) is the location of the discussion in Archaeometry, and therefore reaches an audience of archaeological scientists who might be less familiar with these concepts derived from the social sciences.

The deliberate structuring of processes and relationships influencing technical choices in pottery production (and use) is a useful and concrete example of how it is possible to begin to establish the manner in which culture (the sum of human relations) relates to technology.

Perhaps the weakness in the approach is the lack of an overall organisational principal: how should one delineate between the different identifiable relationships between the social context and technological choices? For example, in any given high-temperature industry it may be possible to identify technical selections which may have been based upon the constraints of access to raw materials, fuel, limitations of furnace technology, conservative craft tradition, ideology or technical knowledge. Structuring the competing influences cannot simply be subject to the specifics of a given situation, although choosing between the different influences might not be subject to a universal formulation (Sillar and Tite 2000, p 11). This was the territory over which several of the commentators battled, to appropriate the “technical choices” approach for their own specific theoretical position: “evolutionary archaeology” (Neff 2001) and “ceramic ecology” (Kolb 2001).

Interestingly, there was no mention in any of the original papers or commentaries of the significant body of social theory which explicitly addresses these issues, and attempts to structure the different social processes and their relationships with the material world. The single reference to Childe (Sillar and Tite 2000, p 9) is the closest any of the writers came to acknowledging the existence of Marxist Archaeology or Historical Materialism in general. Marxist analyses of history (and human evolution: see Engels 1876, Harman 1994) place human agency at the centre of understanding the development of human societies (e.g. Harman 1999, Callinicos 1995). Historical Materialism makes a claim for the primacy of certain kinds of social structures in the explanation of social systems (Callinicos 1995, p 41). The role of labour in the relationship between individual humans, groups of humans and the material world is central to this way of understanding the world. The dynamic relationship between the means of production (i.e. the technology) and the mode of production (i.e. the social organisation of labour) is seen as the motor behind human history (this is explained quite lucidly in Harman 1999 p 22-28). The concept of human consciousness is identified as a key factor in shaping human relations and includes the useful knowledge derived from performing tasks in the material world.

Marxist Archaeologists and historians have long discussed the role of technology in society, for example Childe 1936 p 20-36, 1942, p 7-24, 1957, Trigger 1980 p 136-143, 1986, Tringham 1983, Wailes 1996, Spriggs 1984. Indeed, there have even been specifically Marxist interpretations of pottery production, for example: Saunders 1996. The development of empirical knowledge whilst engaged in technology represents the increasing consciousness of individuals. A practical example of this would be the understanding of the role of different colourants in glassmaking: despite the obfuscation of ideology, such as the 7th Century BC documented rituals associated with glass furnace construction (Oppenheim *et al.* 1988, p 32-33), glassworkers were able to effect a wide range of colours in glass using colourants, sometimes constituting less than 1 % of the glass batch.

Marxist narratives have been accused of being reductive and mechanistic: a legacy of the Second International and Stalinism (Saunders 1996 p 125), in which simplistic readings of Marx by Plekanhov and Kautsky led to the inflexible orthodoxy of History as an inevitable sequence of developing modes of production. A crude critique of Historical Materialism has grown out of these readings in which Marxist analysis is written off as technologically deterministic and employing an evolutionary scheme. This superficial criticism of Marxism is at the heart of Post-modernist rejections of the Marxist intellectual tradition (Saunders 1996, p 126). It is important to note that many of the insights into social practise employed in the Archaeometry papers discussed above are derived from Marxist or Marxist-inspired sociology from the 1960's and 1970's which attempted to understand the influence of different forces, environmental, ideological, economic and social on human behaviour. The vulgar criticisms of Historical Materialism are ably answered elsewhere (e.g. Callinicos 1995 and 1996).

The elaboration of a methodology to examine the technological choices made in past activities, and a call for the use of sociological explanations ought to at least acknowledge the historic contribution of Marxist thought to the development of this position. The explicit use of Marxist theory may aid the integration of the processes influencing the technical choices. The construction of a universal model applicable to all situations is probably not possible given the particularist nature of the archaeological record, but the application of general principles probably is useful.

Nonetheless, the Archaeometry discussion is a welcome airing of the issues within the context of archaeological science. It is possible to construct a similar summary of factors effecting technical choices involved in glass production (see figure 2.4), which serves as a useful reminder when interpreting the results of analyses.

The chemical analysis of ancient glasses, comparative analyses of raw materials and experimental work have identified culturally specific variability in the manufacture of glass (see Chapter 3 for more details). The assembly of bodies of compositional data from the Eastern Mediterranean and Mesopotamian regions (e.g. Sayre and Smith 1961) enables the definition of groupings reflecting distinct technological traditions. The subsequent explanation of the compositional variation in terms of raw components leads directly to inferences concerning the selection and procurement of raw materials used in the primary manufacture:

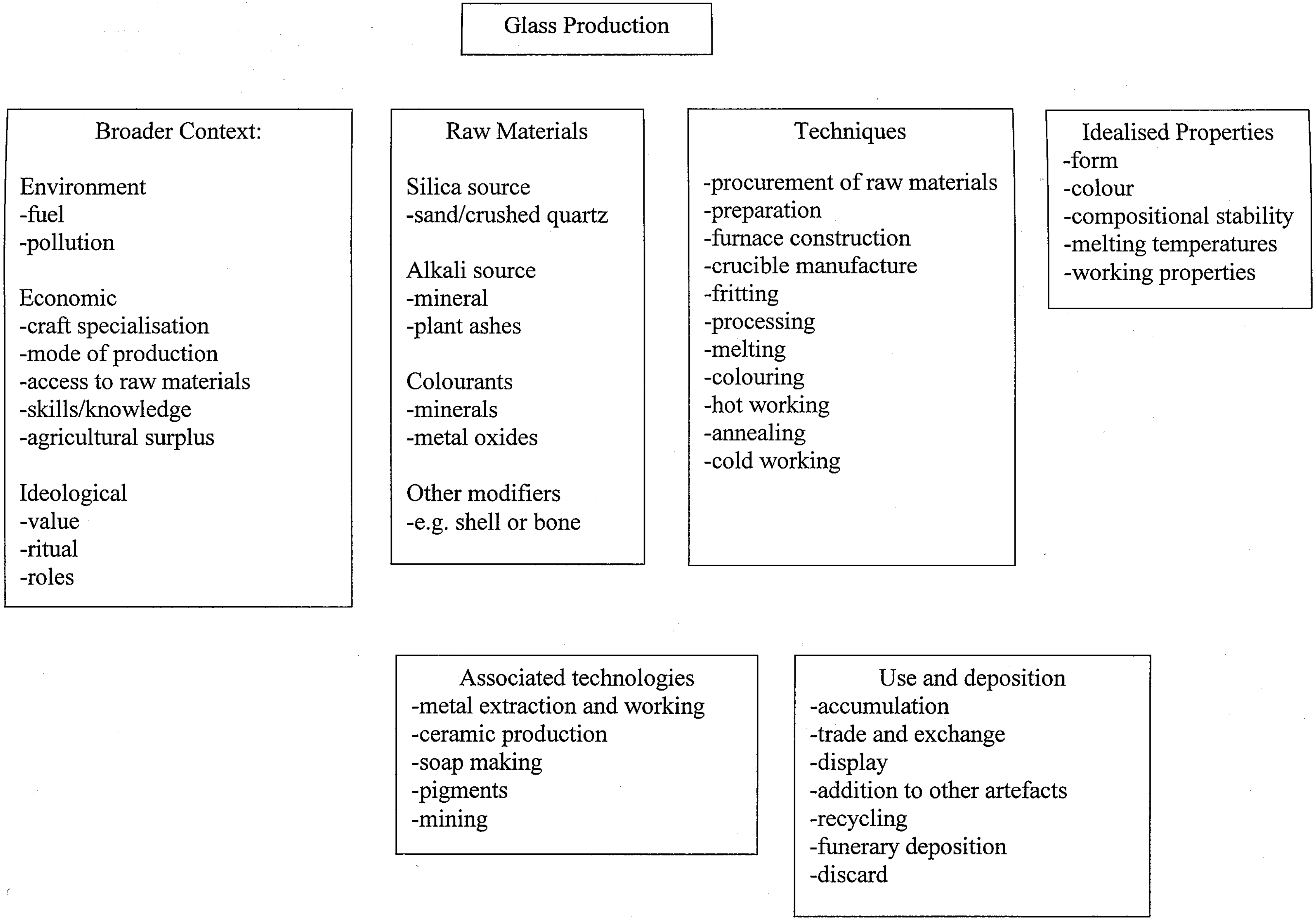


Figure 2.4 Key components in the *chaine operatoire* of glass artefacts

mineral or plant ash alkali sources, silica sources, colourants. The identification of regionally and chronologically distinct glass types, such as the Bronze Age mixed-alkali glass by Henderson (1988a) sheds new light on the technical capacity of a particular group. In this instance, where once before a group was assumed to be merely consumers of glass produced elsewhere, they are seen in a new light as sophisticated technologists producing their own glass. The homogeneity of glass compositions (or lack thereof) may suggest the degree of central control over production. The relationship of a glass object's chemistry to a specific tradition (such as the Ulu Burun ingots to Levantine production: Henderson 1989a, p 33-36, also see 3.7.20) can give rise to identification of long distance exchange in prestige items when they are found outside their homeland.

2.5 Summary

The glass samples analysed in this study are derived from Museum collections held in Italy and England, and originate in archaeological contexts from Northern and Central Italy from the Final Bronze Age to the early Roman period. The chemical analysis of these samples from does not simply represent an exercise in empiricism, in which an idealised Truth speaks out (Shanks and Tilley 1992, p 251): but the deliberate and self-conscious application of techniques drawn from the natural sciences to generate compositional data. It is considered useful to generate that data because it is assumed that:

1. ancient glass chemistry is variable (and verifiable)
2. the compositions and structure reflect the raw components and processes used in their manufacture
3. to some extent these components and practices may be reconstructed

4. the compositional variability reflect culturally specific practises (“technical choices”)
5. the reconstruction of glass technology for a region and period is inherently interesting
6. an understanding of glass technology permits inference upon a number of different issues, including: technical skills, tools, organisation of labour, procurement of raw materials, parallels between technological concepts and ideologies, exchange systems.

It is on the basis of these assumptions that useful statements on the technology and cultural context of the glasses can be made. The specific questions are laid out in Chapter 1 (1.6). Clearly, many of these assumptions have been verified by earlier workers studying ancient glass (although not explicitly): studies based upon the sorts of ideas laid out by Napier (see 2.3 above). The success of compositional analysis could easily lead to the routine application of analytical chemistry without the explicit elaboration of the underlying concepts, nonetheless this brief consideration suggests that the theoretical framework for this study is secure.

CHAPTER 3: THE ARCHAEOMETRY OF ANCIENT GLASS

3.1 Introduction.

This chapter considers ancient glass from the perspective of the archaeological scientist, and discusses the nature of glass and related materials as well as the various sources of information on glass chemistry. This is followed by a detailed description of the chemical components of glass in order to inform the interpretation of compositional analysis of ancient glasses.

3.2 Physical and Chemical Properties of Glass

It is useful to briefly outline the contemporary scientific concepts of the chemical structure of glass, since further discussion of components relies upon these models.

Glass can be considered as an additional state to solid, liquid and gas (e.g. Pollard and Heron 1996 p150). The glassy or vitreous state is achieved when a liquid is cooled, and transformed into a solid without the formation of a crystalline structure: glasses are sometimes referred to as non-crystalline solids.

This transformation, from liquid to non-crystalline solid is reliant upon the process taking place sufficiently quickly that the molecules in the liquid are unable to attain the long-range order necessary for the formation of crystal lattice structure. The transition can be seen in terms of the temperature and specific volume of the material.

When the liquid is cooled slowly and fails to achieve the long range order necessary to become crystalline, following the dashed line in Figure 3.1, then the material demonstrates no clear discontinuity between being a liquid and solid. If the liquid were to cool slowly and become crystalline, following the solid line in Figure 3.1, then a sharp drop in specific volume would be observed as the phase transition to crystalline solid took place. At temperatures below Tm the glass is metastable, it is too viscous to permit the rearrangement of its component molecules into crystals. TG on the diagram is known as the glass transition temperature, and is dependent on the composition of the melt and the cooling rate.

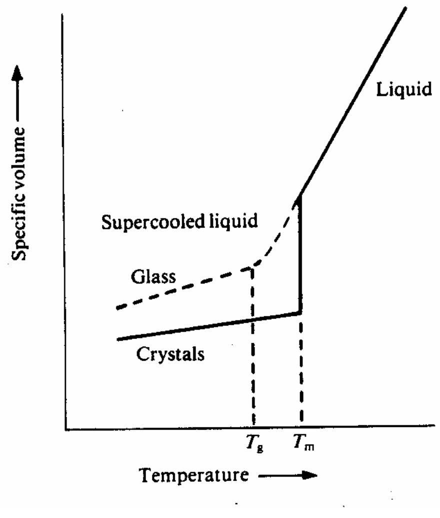


Figure 3.1 Specific volume against temperature for liquid, glassy and solid states (after Anderson *et al.* 1990, p 296, Figure 11.3)

Historically, there have been two competing models of the chemical structure of glasses, that of Zachariasen (1930) and Lebedev (dating to 1921). These models are described in detail elsewhere (Pollard and Heron 1996, p 152-163 discuss the models which are further detailed in Porai-Koshits, 1990). A number of features of both models are useful in this consideration of glass chemistry. In summary, the Zachariasen model (otherwise referred to as the continuous random network theory) has a number of features:

- Crystalline and glass forms of a material have similar mechanical properties, suggesting they have similar bonding
- Glasses do not have the long-range order which defines crystalline structures
- The structure of glasses is not entirely random because the intermolecular distances are consistent.

These observations lead to a number of inferences:

- The optical isotropy of glass is a consequence of the random atomic arrangement
- A random network gives rise to variability in bond energies which explains why thermal breakdown takes place over a long temperature range, rather than at a characteristic temperature as for crystals.
- Glass compositions are mixtures, not compounds.
- There are no crystal cleavage plains in glass, hence the concoidal fractures seen at breaks.
- On the basis of molecular geometry, that a glass-forming oxide must have a tetrahedral co-ordination with four oxygen atoms arranged around a metal atom.

In this model oxygen atoms are linked to not more than two other atoms, oxygen polyhedra share only corners, and to form a three dimensional structure at least three corners must be shared.

Further work by Warren (1937) and Warren and Biscoe (1938) have supported this model by establishing the average inter-atomic distances between silicon and oxygen, and oxygen and oxygen atoms in vitreous silica and soda-silica glass, suggesting a tetrahedral structure. In the case of the soda-silica glass, the sodium atoms were suggested as being located interstitially in the network. Discrete molecules of soda and sodium silicates could not exist within the glass structure on the basis of arguments concerning co-ordination numbers. Crucially, Warren calculated the maximum size of any crystalline structure within a soda-silica glass based on diffraction patterns as 7 Å ($1Å = 10^{-10}$m), which is approximately the size of a single silica crystal. This would therefore defy description as a crystalline structure, given the limited order involved.

The alternative model developed by Lebedev is the crystallite theory, in which glass is seen as being made up of small crystalline regions, which vary in size from 10 Å to 300 Å. This picture of a series of highly ordered crystallite domains clearly contradicts the random network theory, and yet the two models are currently seen as complementary. The two models can be integrated because the random network theory is based on an average perception of the structure, and assumes homogeneity. Structural inhomogeneity has been repeatedly observed in glasses: scanning electron microscopy and subsequent analysis have demonstrated phase-separation in many glasses. The combination of the two models has given rise to several useful insights:

- Single component glasses have homogenous structures, which are adequately understood using the random network theory.
- Multicomponent glasses whose overall composition is between two stable compounds exhibit phase separation.
- Additional components such as colorants are not distributed evenly throughout the structure, but are responsive to localised variation in ionic charge.

Glass-forming oxides have subsequently been classified as network formers, network modifiers and intermediates. Network formers are those oxides capable of forming glasses alone, without the addition of other material (such as SiO_2, B_2O_3 and P_2O_5). Network modifiers are those oxides whose cations disrupt the continuity of the network (for example Na_2O, K_2O, CaO and MgO). Intermediates are those oxides which can act as either network former or modifier, but cannot be a network former in the absence of other oxides (this group includes Al_2O_3, TiO_2 and ZrO_2).

Conventionally the random network theory structure is illustrated in two-dimensional form to contrast with a regular crystalline structure of similar composition (for example see Pollard and Heron 1996, Figure 5.4, p 157, Brill 1962, Figures 2 – 6 p 133-135, and Figure 3.2 below). In many ways it is an inaccurate expression of the random network structure, since it is difficult to demonstrate the tetrahedral arrangement of the oxygen atoms around silicon atoms in two-dimensions. However, such illustrations remain useful to show difference from crystalline structures and to suggest how modifiers and intermediates sit within the glass matrix.

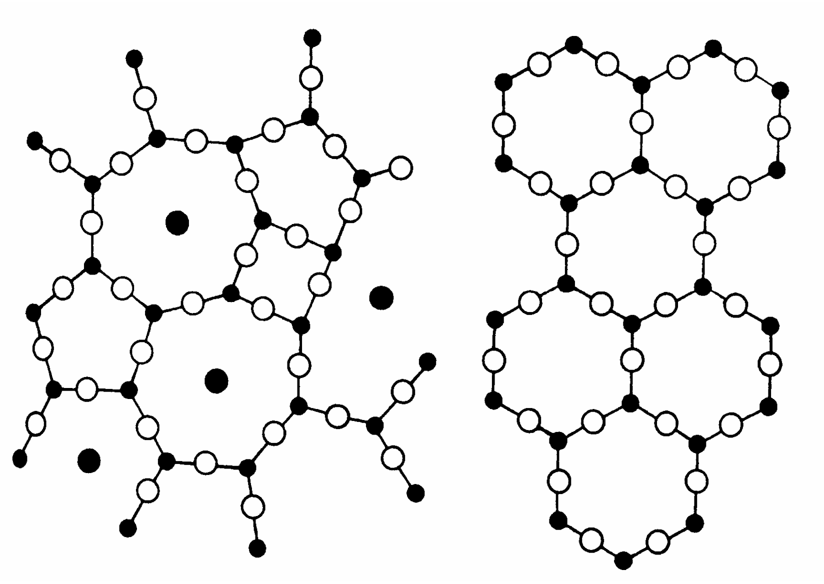


Figure 3.2 Illustration of the molecular structure of a glass (left) and (crystalline) quartz (right) according to the random network theory. Oxygen atoms are represented by empty circles, silicon by small black circles, and modifiers shown sitting interstitially by large black circles. After Hodges 1989, Figure 4, p 43.

3.3 Why are glasses complex materials?

Glasses, particularly ancient glasses are not produced from laboratory pure ingredients, but fashioned from a range of (often-) modified naturally occurring materials. As a consequence they are complex mixtures of both deliberate and accidental components arising from the raw materials, the tools used in their production and the environments in which they were produced. These conditions embedded in a glass artefact’s chemistry are further complicated by the impact of the environment in which the glass has been held since manufacture, whether mechanical alteration, the effect of pollution or the depositional environment, all of which can greatly alter a glass artefact’s chemistry. It is also important to note that glass technologists in the past have not been working within a post-enlightenment “scientific” intellectual framework, and although most studies of ancient glasses testify to a sophisticated understanding of the behaviour of different glass components, this knowledge will have been located in a different context. Inevitably such a different context may give rise to practices which introduce components for which modern glass technologists cannot readily identify functionalist explanations. We should not uncritically assume similar procedures in the past by analogy to modern practices, based upon scientific models of glass chemistry.

3.4 Related Materials.

Glass has similarities with other vitreous materials used in antiquity: faience, slag and glazes. These are briefly described.

3.4.1 Faience.

Faience is the term used for the material which has (or had) a glassy surface fused to a partially fused core. It was first used in Iran or Northern Mesopotamia during the Ubaid period (4500 BC) and was soon developed or diffused into Egypt and India, where it gradually replaced the glazing of stone (Moorey 1985, p 137, 141, 231). The core consists of finely ground quartz grains cemented together by having been sintered, i.e. having partially, but not entirely been fused by heating. The glassy surface is a layer of true glass adhering to the core. The creation of the surface layer can be achieved by several methods. Application of a glaze slurry containing the raw components (silica, calcium-rich material and alkali) to the porous core, which is allowed to dry before firing which forms the vitreous surface. Efflorescence is the process in which water-soluble alkaline salts are mixed in with the core material, after forming the desired shape, the object dries slowly and the alkaline salts migrate to the surface as the mixture dries. Upon firing a vitreous layer is formed on the surface. The cementation method involves the heating of a quartz-rich core in a powdered mixture of lime and alkali, which permits the formation of a vitreous layer on the surface of the core (Moorey, 1985 p 133, 159-162, Nicholson 1993, p 9-14, Wulff *et al.* 1968, Liu 2000, p 56). Faience production pre-dates the manufacture of true glasses, and has continued to the present day (Peltenburg 1992, p 10). Peltenburg’s useful examination of the relationship between the earlier use of faience and the development of glass production (Peltenburg 1992, 13-20) questions the widely held assumption that faience working led directly to the establishment of glass industries in North Syria/Mesopotamia in the sixteenth Century BC.

Some researchers have gone on to define an additional category of vitreous material, “glassy faience” in which a significant proportion of an artefact’s body consists of a glass phase in which is embedded crystalline material (Santopadre and Verità 2000, p 25, Lilyquist and Brill 1993, p 8, 18). This material has been suggested as an intermediate material between faience and glass. However the technology involved in its production is distinct from any of the documented faience techniques, and here is considered as a variation of “true” glass (which is frequently a mixed phase material).

3.4.2 Slag

Slag is the generic name given to waste products from a number of industrial processes. Typically it refers to the silica-rich material produced during the smelting of copper and iron ores. The slag formation is often encouraged by the addition of fluxes (i.e. potash, soda and calcium-rich material) in order that the metal be readily separated from the siliceous ore. Slags are typically poor-quality glasses- they contain unfused fragments of material and are full of gas bubbles from the evolution of CO_2 and CO during the smelting process. Whilst slags themselves are distinct from true glasses, they do represent a similar type of material in an appropriate technological milieu (hotworking), in which metalworkers probably contributed to the recognition of glass (Biek and Bayley 1979, p 3; Peltenburg 1992, p 20 – 23, Henderson 2000, p 53 - 54).

3.4.3 Glazes

The application of glazes to stone bodies also predate glass making and working. The earliest glazed material was the fusion of malachite to silica-rich stone steatite in the late 5th Millennium BC in Predynastic Egypt (Moorey 1985, p 136, Peltenburg 1971, p 7). This use of a glassy material was soon replaced by faience as the dominant technology (see above). The application of glazes to ceramic bodies coincides with the earliest core-formed glass vessels of the sixteenth Century BC in the Near East (Moorey, 1985, p 167). It seems unlikely that glazing led directly to the recognition of glass as a material, but is nonetheless a parallel technology reflecting a broad appreciation of high temperature materials.

3.5 Earliest glass.

The problem of identifying the earliest glass manufacture (in the Near East) has been addressed by a number of authors (for example: Beck 1934, Harden, 1968, p 46-53, Forbes 1966, p 115, Harding 1971, Oppenheim *et al.* 1988 p 105-128, Oppenheim 1973, Peltenburg 1992 and Moorey 1985 p 194-201). Isolated examples of glass beads have been recovered from archaeological contexts dating to the early third millennium BC onwards, initially in Syria (Tell Judeideh) and other sites in Mesopotamia, before their appearance along with amulets in Egypt during the Fifth Dynasty (2465-2323 BC) (Moorey 1985, p 194 – 200, Shortland and Tite, 2000, p 142).

Peltenburg's review of the available evidence classifies the development of glass production into two stages: the first as a series of isolated, infrequent and possibly accidental occurrence of glass items across Egypt, Syria, Mesopotamia, and Anatolya between 2500 and 1600 BC. The second stage is seen as the rapid development of a glass industry concerned with the production of core-formed glass vessels, a wide range of jewellery and architectural decorations, initially in Syria, but soon after in Egypt and Mesopotamia from 1600 BC (Peltenburg 1992, p 17). This system is useful for understanding the adoption of glass technology, and Peltenburg notes that the use of a technology is dependant upon the political and economic context as much as the nature of the innovation itself (Peltenburg 1992, p 18). However, Peltenburg underestimates the significance of glass bead manufacture: although relatively small scale in terms of volume of glass, nonetheless it is well established across the Near East before vessel production, and is a technology which demands a sophisticated appreciation of both glassmaking and glassworking. Although glass (like faience) appears first in the near East, before being adopted in Europe (either by diffusion or independent innovation), there is some evidence of very early glass use in Western Europe.

Recent analyses of prehistoric glass from France (Guilaine *et al*. 1991, Gratuze *et al.* 1998) have demonstrated not only the very early presence of glass in Chalcolithic contexts (at Gord, Compiegne, Oise, 2895 – 2420 BC calibrated C14: Guilaine *et al*. 1991, p 259), but also a strong likelihood of local production (on the basis of the glass chemistry). However, the early date assigned to these beads may now have been withdrawn by Gratuze (Julian Henderson, *pers. comm.*).

3.6 Sources of Information on glass technology

Our contemporary knowledge of glass, ancient and modern is derived from a range of sources. Whilst modern theoretical models of glass structure are outlined above, and are useful in modelling the properties of existing compositions and facilitate the development of new glasses, useful knowledge of glass has been extant for a much longer period of time. The glass researcher has several kinds of information concerning ancient glass technologies: textual (ancient and modern), analysis of artefacts and experimental reconstruction.

3.6.1 Texts

Textual descriptions of glass manufacture or alluding to its manufacture date back to the 15th Century BC, and the student of ancient glass has inherited a rich body of material. It is beyond the scope of this study to critically review each text here, but the principal contributions are listed in chronological order, along with references to discussion of their content.

The Annals of Tutmose (1479-1425 BC). It has been suggested that tribute demanded from Babylon during Tutmose's military campaigns included glass, referred to in the Annals as Babylonian lapis lazuli. This is considered by some as the origin of glassmaking and working in Egypt (Nicholson and Henderson 2000, p 195-196).

The Amarna Letters (1353-1335 BC). Letters from the city of Tell el-Amarna, the capital of the Pharaoh Akhenaten (1353-1335 BC), include reference to both the importation of glass as tribute and its export as a high status royal gift (Nicholson and Henderson 2000, p 196).

Cuniform texts. Four groups of Mesopotamian cuniform texts have been identified as instructions for the manufacture of glass. Their translation and interpretation have been progressing since 1909 (Oppenheim *et al*. 1988, p 22: Virolleaud 1909, Campbell Thompson 1925), but the most comprehensive treatment has been by Oppenheim *et al*. (1970, reprinted in 1988). The most significant group were recovered from the library of Asurbanipal at Ninevah, dating to the period 668 – 627 BC, but other fragments have been dated to the last third of the second millennium BC (Oppenheim *et al*. 1988, p 22 – 23). On philological grounds, it has been argued that some of the content of the descriptions may be dated to the mid second millennium BC (Oppenheim *et al*. 1988, p 81). For additional discussion of the rituals associated with the glassmaking processes, also see Henderson 2001 (p 471-472).

Biblical References. Although there are no direct biblical references to glass manufacture, the use of glass as a metaphor permits inference of the status of glass in the contemporary societies, for example:
Job 28.17, wisdom is compared with gold and glass, indicating the high status of each (7th Century BC, Forbes 1966 p 147).
I. Cor. 13.12, Paul's "through a glass darkly" could be a metal mirror (Forbes 1966, p 147).
II. Cor. 3.18 a "katoptron" in which we behold the glory of the Lord could also be a metal mirror (Forbes 1966, p 147).
Rev. 4.6, 15.2 John uses the term "hyalos" meaning sea of glass (Forbes 1966, p 147).

Talmud:
Babylonian Talmud, Shabbath, 154: a reference to the transport of raw glass for reworking into finished artefacts (Brill 1988, p 284) 5th Century AD
Palestinian Talmud, Sukkah IV, 59b and Niddah II, Halakhah 7 in which the fusion of glass is described and glass blowing is compared to God's blowing of life into a human body (Forbes 1966 p 151, Isings 1957, p 4).

Strabo <u>Geography</u> (written c. 10 AD) e.g. Book XVI, 2.25 cap 758 Chapter II, sec. 25). Strabo made a number of references to the production of glass, in Alexandria and on the Palestinian coast, including reference to the suitability of local sands for glassmaking (Forbes 1966, p 146, 156, Caley 1962, p 93, Tait 1995, p 51, 56, Isings 1957, p 4-5).

Pliny Natural History (written 77 AD) e.g. Book 36, chaps 65 and 66, Book 31, chap 46. Pliny made numerous references to raw materials, the production of glass and its working (hot and cold) into different forms, and locations of different glasshouses. Most famously he gives a mythological explanation of the accidental discovery of glass by natron merchants on the Phoenician coast (which is repeated by subsequent Classical authors) (Caley 1962, p 93 - 94, Forbes 1966 p 145 – 155, Tait 1995, p 20, 56, 57, 59, Stern and Schlick-Nolte 1994, p 20, 21, 72, 73, 108, Sayre and Smith 1967, p 301, Henderson 2000, p 66, also Henderson 2001, p 475).

Josephus De Bellio Iudaico (written late 1st Century AD). Josephus described the location of the famous glassmaking sands at the mouth of the River Belus on the Palestinian coast. (Josephus, p 132, Brill 1988, p 266, Forbes 1966, p 146)

Roman Epigraphic sources. A number of diverse epigraphic sources, such as names on bottle bases, mottos on vessels, text on stamped disc weights and stone inscriptions relating to glass have been recovered from Roman contexts. They permit identification of places of manufacture, individual producers, the social context of their use and prices (Barag 1987, Barag 1996).

9th Century Manuscript from Syria, held in British Museum. Describes the structure of the “Southern” furnace type used by glassmakers (Charleston 1978, p 10, Newton and Davison 1989, p 110 – 111, Henderson 2000, p 81)

Theophilus On Divers Arts c. 1122 (translated by Hawthorne and Smith, 1979). This technical treatise by a practitioner includes an entire book on glass technology and is a comprehensive source for the production of Northern European medieval glass, from construction of different furnaces and kilns to the fabrication of leaded windows. This work has informed all studies of European medieval glass.

Mappae Clavicula 12th Century. This is a compilation of writings drawing upon both historical and contemporary (12th Century) sources and includes descriptions of glassmaking (Biron *et al*. 1996, p 48).

Eraclius De coloribus et artibus Romanorum 12th Century (translated by Merrifield 1849, in a two volume collection of manuscripts : “Original Treatises dating from the 12th to the 18th Centuries on the arts of painting”). Eraclius’s text is also a compilation of sources by a non-practitioner, and includes description of both glassmaking and the production of glass gems, in a combination of poetry and prose (Merrifield 1849, Vol. I: p 166-259).

Abdallah al Qasani 1301. This author of a book on Medieval jewellery and faience manufacture from Tebriz in Iran includes useful information on glass colorants, including an intriguing reference to the importation of cobalt-manganese ore

(Ritter *et al*. 1935 p 35, Ganzenmuller 1939, p 136 – 7, Allen 1973). For a brief survey of Islamic Medieval sources on glass, see Irwin 1998.

15th C. Anonymous MS from Bologna (translated by Merrifield, 1849). This book of recipes includes instructions (Chapter VII) on the production of differently coloured glasses for making gems, enamel and colours for painting upon glass, as well as glazes (Merrifield 1849, Vol. II: p 325 –341 and 479 – 547).

Månsson, P. Glaskonst. 1524 (translated by R. Geste. Stockholm, 1915.) Gives a detailed description of a glass furnace used in Rome in the early 16th Century (Biek and Bayley 1979, Newton and Davison 1989, p 112 - 113)

Biringucci, V. Pirotechnia 1540 Venice (translated by Smith and Gnudi 1943). Biringuccio gives a detailed description of the preparation of the raw components and manufacture of glass, including the construction of the furnaces for fritting, glassmaking and annealing the final objects (McCray 1999).

Agricola, G. De Re Metallica, 1556 (translated by Hoover and Hoover 1912). This comprehensive treatise on Mining and allied industries includes a detailed description of the preparation of raw materials, construction of furnaces and production of glass articles, in addition to a series of four woodcuts illustrating the processes.

Neri, A. L'arte vetraria 1612, translated and added to by Merrett as The Art of Glass (1662, republished in 2001) (and also by Knuckel in the German edition) includes extensive descriptions on the preparation of raw materials, fusion of glass and its forming into finished items (Merret 1662, Turner 1962, McCray 1999).

In the post medieval period technical treatises and recipes proliferated as the basis of the European economy was transformed by the development of the capitalist mode of production (e.g. Diderot's encylopedia: "Encyclopédie ou Dictionaire Raisonée" vol. XVII, 1765). However, even relatively recent texts can be problematic for interpretation from specialist language into known raw components (for example see Moretti 1983).

3.6.2 Development of modern glass industries.

Since the early nineteenth Century there has been considerable interest in establishing the nature of ancient glasses as a means to improving the methodology of contemporary production (e.g. Davy, 1815, and Napier 1879). Leading technologists from the glass industry have often also been at the forefront of research into ancient glass technology (eg Turner, Rooksby and Cable). Archaeological science research has always benefited from the interest of physical scientists principally employed in other fields.

3.6.3 Direct study of ancient materials.

The study of glass artefacts in their own right constitutes the single most important source of information concerning ancient glasses. The direct study of ancient glass includes both typological and compositional analysis. Conventional typological work is well represented (for example Barag 1962, Beck and Stone 1936, Guido 1978), but from early on the study of glass has involved the analysis of its chemistry (such as Klaproth (1743-1817) Davy (1778-1829) and the contribution of John Percy to Layard 1853; Caley 1949,1962, p 13 – 15, Pollard and Heron 1996 p 3, Harbottle 1982).

Compositional analysis has always been a central strand of enquiry into ancient glasses, and a number of key works are mentioned below (section 3.7). Compositional analysis has increasingly been accompanied by examination of the microstructure, as its complexity has been recognised (e.g. Lilyquist and Brill 1993, p 18). Section 3.7 provides an extensive review of published compositional analyses and their interpretation.

Ancient glass technology has been widely investigated by conservation researchers, who have generated a large amount of compositional data on ancient glasses. Conservation research has been driven by a range of issues, from the preservation of artefacts, modelling degradation processes (and linking these to ancient technologies), developing treatments and protocols to investigating the possibilities of long-term nuclear waste storage in vitreous forms (Newton and Davison 1989, p 135, Freestone 2001, p 615).

3.6.4 Experimental work.

Experimental work has played an important role in defining some of the possibilities involved in ancient glass production, for example Nicholson’s attempts to reconstruct glass making at El Amarna, reconstruction of medieval glass furnaces and experimental work on raw ingredient chemistry (Nicholson 1995a, 1995b, Nicholson and Jackson 1998, Besberodov 1957, 1975, Brill 1999a, 1999b, Cable 1998, Sanderson and Hunter 1981a, 1981b, Smedley *et al.* 1998). The experimental work has been associated with specific texts (e.g. Brill in Oppenheim *et al.* 1988), excavated material and hypothetical reconstruction (Sanderson and Hunter1981a, Vandiver *et al.* 1991). Ethnographic observation has also been important in informing research into ancient glass technologies (Brill's film of operations at Herat, Wulff *et al.* 1968 and Peltenburg 1992, p 10). In addition to glassmaking, there has also been considerable interest in reconstructing ancient glassworking practices, integrating observation from the physical examination of artefacts (equipment and glassware) and the skills of modern glassworkers (e.g. Gudenrath 1995, Gam 1990,1991, Lierke 1991, 1993).

3.7 Interpreting compositional analyses of glass.

The various components of glass, as identified by compositional analyses, are discussed individually below. The aim of this approach is to organise the information in a way that permits an archaeologist to move from the compositional data towards inference concerning the glass technology. This is also a useful mechanism for structuring a review of published literature on ancient glass chemistry. A number of existing studies already thoroughly examine the history of compositional analysis either from a chronological perspective (e.g. Caley 1962) or from a consideration of the raw materials (e.g. Henderson 1985). It is hoped that the approach adopted here will function as a guide to understanding the analyses undertaken in this project and elsewhere.

As outlined above, our knowledge of ancient glass recipes is a combination of evidence from different sources. As a route to exploring the materials used in glass production, the chemical components routinely analysed are considered in light of their role in glass chemistry, their interpreted origin, and how they may be employed to characterise different productions.

The preparation and processing of raw materials in the manufacture of glass can greatly modify the chemistry of the resultant glass. Such processes are a necessary part of glass production since the process is a transformation of a number of unlikely looking ingredients into a composite material of radically different properties and appearance. Preparatory procedures are documented archaeologically and in the historical record. The grinding, washing, mixing, fritting and remelting operations are not shared by all glassmaking traditions: unfortunately these processes are not readily identified in the composition of the resultant glass. In large part the difficulties in back calculating the exact components are due to the variability in the chemistry of the raw materials which is then compounded by the alterations during the manufacture. Where these processes are relevant to the consideration of specific components and their precursors, they are mentioned in further detail. There is clearly a need for further experimental work to attempt to identify how specific components may be preferentially removed or enriched with different processes. Recent contributions to the study of ancient glassmaking process (Rehren 2000a and b), have challenged underlying assumptions concerning the calculation of compositions. Rehren has suggested that the two classic Mediterranean recipes for soda-lime-silica glasses (see 3.7.2 below) owe their consistency to buffered non-total batch melts rather than tightly controlled compositions. By plotting reduced compositions of glass analyses on ternary phase diagrams for soda-lime-silica systems, Rehren has shown that many ancient glasses lie on or close to eutectic troughs. This implies that glasses were formed (presumably alongside crystalline phases) out of variable compositional mixes of raw components, the specific composition relating to the maximum temperature reached which would determine the place a glass composition occupies along the eutectic trough. The resulting mixed phase material would have to be separated into glass and other phases, by an undefined process, before re-melting. This is an interesting departure, which as yet remains unresolved: the data reduction required in order to plot complex ancient glasses on laboratory-defined systems may not accurately reflect the melting behaviour of the original glass (or its host raw material mix). The extraction of a relatively homogenous glassy phase from the mixed glass-crystalline-unfused raw component mix represents a technological process as yet unimagined. The model is however, a powerful explanation of the impressively consistent compositions for many soda-lime-silica glasses. The model will only be fully evaluated by extensive experimental melts of glasses to construct appropriate phase diagrams for the complex compositions, alongside many “buffered” melts of diverse composition to establish if the reductive process occurs.

3.7.1 Silica.

SiO_2

Silica is the principal network former for all ancient and most modern glasses. Historically this has originated in sand (e.g. Boswell 1917) or ground up quartz pebbles from river beds, the sea shore or geological formations (e.g. Oppenheim *et al.* 1988, Henderson 1985, Brill 1999a).

The raw material employed, whether sand or pebbles is likely to have undergone a number of refining processes during the production of the glass. The sand or rocks are both likely to have been ground up, since this maximises the surface area of the silica for fusion with the other ingredients, facilitating the process leading to more rapid and lower temperature fusion (Smedley *et al*. 1998, p 151, Boswell 1917, p 5, West-Oram 1979, p 223). Since silica does not occur in a purely natural state in nature, other "contaminating" materials accompany it. These additional components are quite variable, both within and between geographic sources of the silica. Researchers of both modern and ancient glass technologies have undertaken analyses of sands and rock to identify their suitability for inclusion in glass manufacture. The most comprehensive survey of possible ancient silica source chemistry has been carried out by Brill (1999a, p 208-211, 1999b, p 474-480), but other significant analyses and surveys of other analyses include Turner (1956c, p 277-283), and Bezboradov (1975, p 57-60).

It is possible to point out the variability of sand compositions from a single source by comparing those published by Brill (1999a, p 474) and Turner (1956c, p 281 Table 2, after Heimann and Berl in 1935) taken from the mouth of the River Belus (modern site of River Na'aman, the location renowned for its glassmaking sand in the 1st C. AD):

	673	674	675	676	678	679	680	681	1	2	3
Li_2O	0.005	0.005	0.005	0.005	0.005		0.005	0.005			
B_2O3	0.005	0.005	0.005	0.005	0.005	0.005	0.01	0.005			
Na_2O	0.86	0.82	0.68	0.66	0.82	0.79	0.57	0.71			
MgO	0.33	0.33	0.56	0.78	0.46	0.39	1.69	0.41			
Al_2O_3	3.16	3	2.41	2.22	2.69	3	1.62	2.65	3.58	3.92	5.27
SiO_2	84.1	83.4	77	68.5	81.5	82.2	47.6	82.6	80.98	80.8	80.16
SO_3	0.005	0.005	0.02	0.005	0.005	0.005	0.24	0.005			
Cl	0.13	0.019	0.011	0.009	0.024	0.008	0.017	0.008			
K_2O	1.02	0.97	0.89	0.83	0.94	0.93	0.58	0.89			
CaO	5.92	6.37	9.98	14.6	8.49	7.91	25.1	7.98	9	8.82	8.6
TiO_2	0.05	0.03	0.03	0.05	0.05	0.05	0.07	0.05			
MnO	0.02	0.02	0.02	0.03	0.05	0.02	0.06	0.05			
Fe_2O_3	0.45	0.42	0.42	0.54	0.44	0.46	0.63	0.42	0.12	0.12	0.15
CuO	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001			
ZnO	0.0068	0.0068	0.0057	0.0078	0.0072	0.0057	0.0073	0.0058			
SrO	0.01	0.01	0.02	0.05	0.04	0.005	0.2	0.04			
ZrO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01			
Ag_2O	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001			
BaO	0.03	0.03	0.01	0.03	0.03	0.01	0.01	0.03			
PbO						0.001	0.001	0.001			
CO_2	4.08	4.69	7.72	11.46	4.63	3.38	10.82	3.15			
Loss									6.3	6.6	5.8
Total	100.19	100.14	99.799	99.794	100.2	99.182	89.242	99.022	99.98	100.26	99.98

Table 3.1 Chemical composition of sand from the mouth of the River Belus, values in weight %. Samples 1-3 from Turner 1956c, p 281, other samples from Brill 1999b, p 474.

The more detailed analyses of Brill clearly demonstrate the wide range of contaminants associated with sand, which can enter into the final glass composition. Individual materials other than silica are discussed further below.

The silica contents from this single source vary across the range 47.6 – 84.1 %. Whilst this particular source is significant as an example of a calcareous sand (see below), its silica content is not exceptionally low or variable when seen alongside other analyses.

The analyses of sands are not only subject to imprecision originating in the analytical procedure and the variation within a single deposit, but also from the treatment of the samples prior to analysis. Boswell (1917) and Peddle (1917) review the quality and location of British glassmaking sands and identify a number of critical factors relevant to all glass making sands.

The complementary papers are not concerned with ancient glass technology, but represent a thorough, empirical critique of glass making sands, their chemistry, and simple procedures that may be applied to the preparation of sand during glassmaking. Boswell and Peddle sought to establish the purest sand (i.e. as close to 100 % silica as possible), containing only quartz crystals in order that the glassmaker might exercise greatest control over the chemistry of the glassmaking process. In doing so they identify a number of activities that alter the final glass chemistry- procedures which could easily have been adopted in antiquity.

1. Grading. Both Boswell and Peddle stress the importance of using appropriately sized sand particles (Boswell 1917, p 5, Peddle 1917, p 36 –43). This is quoted as being important for the consistent fusion of the raw materials leading to a homogenous glass melt: too large particles (over 0.5 mm Boswell 1917 p 6) (over 0.3 mm Peddle, 1917, p 37) may not become fused and remain as unmelted stones in the glass. Too fine a particle size (less than 0.1 mm Boswell, 1917, p 5-6) (less than 0.12 mm Peddle, p 31), such as silt and clayey material lead to “blowing out” during melting, or cordiness by differential melting or the presence of gas bubbles in the melt which are difficult to

remove. If the sand is sorted by elutriation, rather than sieving, then the effects of washing are also introduced.

2. Washing. The washing of sands is recognised by Boswell as an iron-reducing activity (e.g. Boswell 1917 p 18), but it is Peddle who fully appreciates the value of washing sand in conjunction with grading it. Peddle identifies the principal source of the impurities in the sand originating from the finest fraction. This is identified by the analysis of the chemistry of the different particle size fractions of sand from a range of British, French, Dutch and Belgian glassmaking sands. The further washing of sand of particle size (0.12 – 0.3 mm) removes the fine material adhering to the surface of the larger particles, and results in a sand of greater purity. (Peddle 1917, p 35 - 50).

Whilst Boswell and Peddle's investigations are underpinned by analytical chemistry, they confirm the empirical knowledge possessed by glassmakers through practical experience: Theophilus's treatise of the 12th Century insists on the use of glassmaking sands which have been collected out of water (Theophilus, c1100, p 52).

Inclusions in sand and pebbles are listed by various authors (Henderson 1985, Boswell 1917, Peddle 1917, Henderson 2000, p 27):

Minerals:	titanite	$(CaO.\ TiO_2.SiO_2)$	titanium, calcium
	chromite	$(FeO.Cr_2O_3)$	chromium, +iron
	epidote	$(Ca_2(Al,Fe)3SiO_4.3OH)$	aluminium, calcium, iron
	feldspar (plagioclase)		aluminium, calcium, sodium
	feldspar (alkali)		aluminium, sodium, potassium
	illmenite	$(FeTiO_3)$	iron, titanium
	rutile	(TiO_2)	titanium
	sphene		
	magnetite		iron
	kaolin		aluminium
	zircon	$(ZrSiO_4)$	zirconium
	alumina	(Al_2O_3)	aluminium
	haemetite		iron
	garnet		iron
	tourmaline		
	staurolite		
	limonite		iron
	leucoxene		
	serpentine		
	pyroxenes		
Shell in sand:	calcium carbonate	$(CaCO_3)$	calcium

Since all ancient glasses employ silica as the network former, its presence or absence alone cannot be a useful indicator of any specific technological tradition. Similarly the overall percentage of silica in a glass analysis is a poor tool for characterisation, since glasses from a single source often have variable silica contents- although a general tendency might be a useful observation concerning a group of analyses. High silica contents (i.e. 90%+) indicates either a poor analysis, or a badly weathered glass in which the dissolution of network modifiers leaves an apparently silica-enriched glass behind. Such a high silica content may also be derived from the analysis of a faience object misidentified as glass.

Caley's observation that ancient glasses usually have a silica content within the range 60 – 80 % (Caley 1962, p 65) can now be extended: glasses from the 2nd and 1st Millenium BC tend to have higher silica contents than Medieval glass: 68-75 % compared with 51-58 % (Hartman *et al*. 1997, p 551). However, there is not a simple historical trajectory, contemporary glasses from different traditions may contain varying amounts of silica. For example, mixed-alkali glasses from the Final Bronze Age site of Billy Le Theil have an average silica content of 76.4 % (n = 11, stdev = 1.099, range = 75.5 – 78.9 %); whereas the contemporary soda-lime-silica glasses from La Colombine à Champlay have an average silica content of 61.7 % (n = 5, stdev = 0.619, range = 61 – 62.5). The contemporary site of Rancogne has soda-lime-silica glasses with silica content between 69 and 79.1 % (n = 5, stdev = 4.241, mean = 72.88 %) (figures taken from Gratuze *et al.* 1998, p 19 - 20). From this brief consideration of glasses from Late Bronze Age European contexts, it is clear that the silica content itself is not the principle discriminating component, but is nonetheless on occasion a characteristic of a tradition defined by other oxides.

3.7.2 Soda.

Na_2O

Soda is the principal fluxing agent in many (but not all) ancient glasses. Its role is to lower the melting point of the silica from 1710 °C to place it within the reach of ancient furnaces. The sources of soda for ancient glass production represent one of the key areas of discussion concerning glassmaking technology.

It was not until the late 18th/early 19th Century that soda was distinguished from potash (K_2O - see 3.7.3 below) (Turner, 1956, V p 285, Ashtor and Cevidalli 1983, p 492), which is the alternative fluxing agent for glass production. However, it is the diversity of possible sources of these materials, and their association with a range of oxides, which makes them interesting components of glass recipes. The earliest documentary records locate the soda-rich flux in the ashes of desert plants. This has been confirmed by the chemical analysis of desert plant ashes, based on both the translation of cuniform texts (Oppenheim *et al*. 1988, p 110-111, p 124), the observation of glassmaking in Herat during the 1960’s and 1970’s and the long documented tradition of soap-making from plant-ashes (Forbes 1965 p 186-188, Turner 1956c, p 285 - 287). Whilst the particular plant type specified in the cuniform texts (translated as “Naga”) is uncertain, it is assumed to be of the genera *salornica* or *salsola*. Desert plant ashes are not the only source of soda-rich ashes, coastal plants and seaweed will also yield high soda concentrations. There has been some discussion concerning the terminology for alkali ashes and their plant origins (e.g. Gasparetto 1975, Engle 1978) in an attempt to identify which species are the most likely to have been used in the past.

In their study of the substantial trade in alkali ashes from the Levant to Southern Europe from the 8th to the 18th Centuries AD, Ashtor and Cevidalli survey a range of possible plants from Italy, Southern France and the Levant used in the past for glass (and soap-) making (Ashtor and Cevidalli 1983). Whilst this study does consider the epistemology of the plant and alkali names, most usefully it locates the chemical analysis of different plant ashes at the heart of the discussion. Comparing the analysis of *salsola kali*, *salsola soda*, *hammada scoparia*, fern ash, “soda di Catania”(plants from Sicily), “Vareque ashes”(marine algae ashes), and beechwood ash, the authors demonstrated the wide range of values of soda and potash in these plant ashes. On the basis of these analyses Astor and Cevidalli suggest that *salsola* soda is the most likely principle soda source for export to Europe during the middle ages: it contains the highest proportion of soda of all the analyses. Over-exploitation of this specific species would also account for its relative scarcity today (Ashtor and Cevidalli 1983, p 500). Perhaps what is most useful to note from these analyses is the associated oxides which (if otherwise untreated) would accompany the soda into the final glass composition: potash (K_2O), lime (CaO) magnesia (MgO), alumina (Al_2O_3), manganese oxide (MnO), iron oxides (Fe_2O_3), phosphates (P_2O_5) and chlorine (Cl). It is the relationship between soda, potash and these other oxides and their relative concentrations, which are the principle means of discriminating between glass technologies.

Plant ashes have been extensively analysed by a number of authors in reference to their use for glass manufacture, including: Turner (1956c), Brill (1988, 1999a and b), Lehanier (1972) Besborodov (1975), Ashtor and Cevidalli (1983) Verità (1985). Sanderson and Hunter (1981a) highlight some of the problems of attempting to relate specific plant types to glass recipes, since the compositional variability can be extreme. For images of plants see Verità 1985, Ashtor and Cevidalli 1983, Engle 1978 and Henderson 2000, p 26.

In addition to plant ashes, the other principal source of soda for ancient glasses is known to have been the evaporate natron. The most famous source of natron is from Egypt, from Wadi-el-Natrun (Henderson 1985, p 273, Forbes 1966, p 127), but also from Barnugi and El Kab (Forbes 1965, p 182, Partington, 1935, p 145), and has also been noted from Tripoli in Syria (Moretti 1983, p 179). The possibility of a Syrian natron source is also mentioned by Partington: “Thothmes III also obtained natron from Syria” (1935, p 145, ref to Brugsch 1891, p 406, 426), but this has not been confirmed by any other sources. Other sources of natron are known from more recent exploitation for glass production, including: Magadi, East Africa, Wyoming, California, Utah, (Turner 1956c p 283, West-Oram 1979, p 229). This soda-rich mineral deposit had a long history in Egypt and the Middle East in the perfumery, mummification, food preservation, dye-making and soap making, prior to its use for the manufacture of glass. Natron is mostly the sesquicarbonate $Na_2\,CO_3.NaH\,CO_3.2H_2O$ (93.25 %), otherwise known as trona, with additional minor amounts of other salts (for detailed compositional analyses see Brill 1988, p 270, Table 9-9, Brill 1999a p 211 – 21 and Brill 1999b p 480 – 481, Turner 1956c p 284 Table 4, West-Oram 1979, p 230, Sayre and

Smith 1967, p 290). When heated it decomposes to soda with the loss of carbon dioxide (Kaczmarczyk and Hedges 1983, p 22).

Natron consists of (from Forbes 1965, p 181):

Sodium carbonate	22 – 75 %
Sodium bicarbonate	5 – 26 %
Sodium chloride	4 – 26 %
Sodium sulphate	0.8 – 39 %
Insolubles	0 – 16 %

Whilst the different forms of sodium compound in the alkali may be variable in their concentrations, all analyses of natron contain a very high proportion of sodium carbonates and commensurately low proportions of potash, lime, magnesia, alumina, manganese oxide, iron oxides and phosphates (typically less than 0.5 %: Brill 1999b p 480). (For an image of natron see Douglas and Frank 1972, p 58.)

The presence of soda as the principle alkali in a glass immediately identifies it as a specific glass type: soda-lime-silica (for it is invariably accompanied by lime). The next critical question is to review the magnesia and potash levels to identify the type of raw material used to provide the alkali.

It is the fundamental difference between the two soda sources which gave rise to the identification of glasses into distinct types in the seminal work of Sayre and

Smith in the 1960’s (Sayre and Smith 1961, Sayre and Smith 1967, Sayre and Smith 1974). They distinguished between two major groups of soda-lime-silica glasses found in the Near East and Europe from the 2nd Millennium BC to the end of the first Millennium AD on the basis of the magnesia content (this is discussed in further detail below). Sayre and Smith were able to demonstrate that the raised magnesia levels (and associated increase in potash) could be explained by the use of distinct alkali types: plant ash rather than natron (Sayre and Smith 1967, p 279 – 292). Analyses by other researchers have underpinned this insight (Henderson 1988b, p 77). The distinction also has temporal and geographic significance: the soda-lime-silica glasses of Mesopotamia, Mycenean Greece, Anatolia and Egypt of the 2nd Millennium BC are consistently high in magnesia indicating a plant-ash soda source, and from the 8th Century BC there is a shift in the Eastern Mediterranean to low magnesia, low potash soda-lime silica glasses as natron was adopted as the soda-source. There is now a suggestion that there may have been limited production of natron type glass prior to this (Henderson 2000, p 26). A recent review of 2nd Millennium BC Egyptian glass compositions suggests that cobalt-coloured high magnesia glasses may have been made from natron rather than a plant ash alkali source, with the magnesia entering the glass with the cobalt colourant (also see 3.7.20) (Shortland and Tite 2000). In the Levant, the natron type soda glass persisted until the ninth C AD, before the use again of soda-rich plant ash. A soda-rich plant ash glass employed in the early 9th C. (pre 808 AD) at Raqqa, Syria is one of the earliest examples (Henderson 1999, p 234). There is evidence to suggest that there was continuous use of plant-ash soda-lime-silica glass further east, which was then was readopted (Sayre and Smith 1967, p 283, Sayre and Smith 1974, p 61-62). It is important to note that the soda-ash type glass does occur during the Roman period in the Western Empire alongside the natron glass, but is a relatively small proportion of the overall production (Lemke 1998).

The picture of one “Mediterranean” soda-lime-silica glass tradition displacing another during the 8th C BC has also been supplemented by the identification of an apparently unique European compositional category in the Late Bronze Age (i.e. 1100 – 900 BC), defined as mixed-alkali glass (Henderson 1988a). The mixed-alkali technology is discussed in detail in section 3.7.3 below.

Variation in soda content can also be used to distinguish between glasses produced using similar raw ingredients, for example in the analysis of glass from Sepphoris, Fischer and McCray (1999, p 899) used the soda content to distinguish between two glass types used during the Roman period. Cast glass from the early Roman period had significantly more soda (19 wt%, average of 7 samples) than the contemporary blown glass (14.5 wt%, average of 14 samples). This is related to the different viscosities required for casting and blowing glass. The “casting” composition would be suitably viscous at 810 °C, with the “blowing” glass type only suitable for casting at a higher temperature of 910 °C.

In Europe, soda-rich glass continued in production after the Roman period: studies on the origins of the Venetian glass industry demonstrate a soda glass made with a flux of marine plant ash in the 8th C. AD (Biron *et al.* 1996, p 57, Verità 1985). Studies of the Limoges enamels show that until c 1200 they use a Roman-type soda glass (high soda, antimony opacifiers, low magnesium and low potassium), before changing to a plant ash soda glass (higher levels of potassium and magnesium, with a tin based opacifier). These analyses suggest either the continuation of Roman technology, or large-scale mining/reworking of Roman material.

A slight reduction over time in the soda content of soda-lime-silica glasses from Roman and post-Roman Northern European contexts has been attributed to the loss of sodium through volatization. This may have occurred during subsequent heating of the glass when recycled and would tend to confirm the hypothesis that much of the later material was the product of recycling (Velde 1990, 115 – 116). Studies of Late Roman and Islamic glasses has led to the recognition of differential groupings within the “Roman” tradition of soda-lime –silica glassmaking, which had previously been regarded as largely homogenous (Freestone *et al.*2000, 2001)

If soda is not the principle alkali, then it will be potash (K_2O). The dominant technology in N. Europe during the medieval period is the high-potash, high calcium glass in which the alkali was derived from the ashes of terrestrial plants such as ferns or beech wood (further discussion is given below). However, exceptions to this dominant technology have been noted, such as the 12th C AD blue glasses from York Minster which are soda-lime-silica glasses (Cox and Gillies 1986). It is worth commenting that these soda-lime-silica glasses are not compositionally homogenous, and includes examples of both plant ash and natron soda glasses. Both potash and soda glasses were produced during the Medieval period in France, but their distribution and dating locate each in separate traditions: a northern industry linked to the potash glass (similar to the German “waldglas”), and a gradually expanding southern industry using soda-rich plant ashes (Barrera and Velde 1989).

3.7.3 Potash

K_2O

Like soda, potash is a key fluxing agent in ancient (and some modern) glasses and was not distinguished chemically from soda until the late 18th/early 19th Century (Turner, 1956c p 285, Ashtor and Cevidalli 1983, p 492). Its presence in glass defines the glass type, and is directly related to the source of alkali. Potash can usually be associated with additional oxides, often permitting the identification of the alkali raw material

In natron potash is present in very small quantities (typically < 1 %, Brill 1999b p 480) and the resultant soda-lime-silica glasses have 1 % or less. Potash is present in slightly greater amounts in soda-rich plant-ashes, and these glasses have c 2.5 – 3.5 % potash accompanied by increased magnesia levels. In mixed-alkali glasses, the potash content is raised to 6.5 – 14 %, and as yet the precise techniques in producing this glass have not been defined, possibilities include the use of a soda/potash plant ash of equal proportions, and/or the processing of such a material (see discussion of mixed-alkali glasses below).

Soda and Potash are both present in significant proportions in the mixed-alkali type glass, as defined by Henderson (1988b, p 77). Examples of glasses with soda and potash contents of 6 – 14 % are known from the Bronze Age in Northern

Italy, Switzerland, France, Germany, Britain and Ireland. They have also been noted as an exception amongst glass from France in the 1st Century BC – 2nd Century AD contexts (Henderson 1988b, p 81), and as intermediate compositional types during the transition to potash glasses in 9-11th C AD, recovered from England, Ukraine, Russia and Denmark (Henderson 1988b, p 86).

Biavati (1983), closely followed by Guido *et al.* (1984) published the first qualitative and quantitative compositional analysis of a European Bronze Age mixed-alkali glass artefact. The former paper examined material from Frattesina, Northern Italy, and the latter from Wilsford, Southern England. Both of these papers discussed the role of vegetable ashes as the source of the alkali components, and distinguished the respective compositions from contemporary glass production in the Eastern Mediterranean. However, it was not until a larger number of Bronze Age European glasses had been analysed that the mixed-alkali composition was identified as a specifically European Bronze Age phenomenon (Henderson 1988a, p 439). This hypothesis has been underpinned by additional analyses of Bronze Age glasses, and there is now a body of compositional data on mixed-alkali glasses from Britain and Ireland (Henderson 1988a and b), France (Guilaine *et al.* 1991, Gratuze *et al.* 1998), Switzerland (Henderson 1988a and b), Germany (Hartmann *et al.* 1997) and Italy (Biavati 1983, Verità and Biavati 1989, Brill 1992, Santropadre and Verità 1993 and 1995, Bellintani and Biavati 1997, Bellintani *et al.* 1998 and Bietti Sestieri *et al., forthcoming*).

This glass is characterised by a high potassium oxide, low magnesium content (mixed-alkali glass). The composition is the subject of some discussion (see

Biavati 1983, Hartman *et al.* 1997 and Brill 1992, Henderson 1988b), and there is no clear consensus on the exact manufacturing process responsible for the distinct composition, except that it originates in the flux source which probably includes terrestrial plant ashes. Jackson *et al*. inadvertently made a mixed-alkali glass using seaweed ash (rather than desert plant ash) in experimental reproduction of a glass furnace at el Amarna (Jackson *et al*. 1997). The mixed-alkali material is accompanied by low lime and low magnesia levels (CaO mean = 1.85 %, MgO = 0.58 % (Brill 1992)), along with an associated reduction in phosphate, Brill suggests this is the consequence of a processed ash. Leaching of the ashes and recrystallisation would account for the resulting composition.

Previously it had been assumed that glass had been made in the Eastern Mediterranean region and traded in Europe as either finished artefacts or raw glass for working into local forms. The adoption of localised manufacture implies a very different structure for the organisation of production and exchange. The date of the first use of the mixed-alkali glass has not been clearly defined, and recent analyses undertaken in France suggest that it may have been in use as early as the Chalcolithic (late 3rd Millenium BC) (Guilaine *et al.* 1991 p 259, and also Gratuze *et al.* 1998). It is of great interest to identify when this glass type was first developed, and to explore any antecedents.

Whilst a number of glass beads have been recovered from Early Bronze Age European deposits (Grotte au Collier, Gratuze *et al.* 1998), these are high magnesia, soda-lime-silica glasses typical of the Eastern Mediterranean region, and are likely to be imports. The next earliest identified mixed-alkali glasses from

France are from the Middle Bronze Age site of Grotte de Bringairet, Armisson, Aude (Guilaine *et al.* 1991, p 259 and 263).

The suggested Chalcolothic origin of the mixed-alkali glasses currently hinges on the single example from Gord, which is followed by a hiatus until the beginning of the Middle Bronze Age. Clearly, additional well-dated glasses need to be analysed to be able to confidently assert the production of mixed-alkali glasses in Europe prior to the Middle Bronze Age.

The recent discussion of conic buttons from Central and Northern Italy (Bellintani *forthcoming*, Bellintani *et al.* 1998, Bellintani and Biavati 1997 and earlier: Barfield 1978) integrate analysis of typology, chronology, distribution and chemical analysis. These studies locate the manufacture of the conic buttons in the beginning of the Middle Bronze Age, with the possibility of localised variation in form out of a regionally distinct glass type (i.e. the mixed-alkali glass). A consensus is now emerging for the widespread use of the mixed-alkali glass in the Middle Bronze Age (and before the development of the site of Frattesina). It would seem most likely that Frattesina represents the continuity of this particular industrial tradition into the Final Bronze Age (Bellintani *forthcoming*).

The mixed-alkali glasses of Middle to Final Bronze Age Europe represent a distinct tradition, relatively well defined in terms of composition, location and duration. However, other examples of mixed-alkali glasses have been identified. Whilst they may be distinguished from each other in a number of ways, the existence of such glasses demonstrates that the mixed-alkali tradition is not representative of a unique practice (preparation of the raw materials). It has even been demonstrated that mixed-alkali glasses can be produced accidently from the burning of wheat chaff (Folk and Hoops 1982). Nonetheless, the mixed-alkali glasses from, for example La Négade (1st C BC – 2nd C AD, Henderson 1988b), Augusta Praetoria (2nd – 3rd C AD, Aosta, Mirti *et a.l* 1993), India (Brill 1987) and Ferghana (10th – 12th C AD Central Asia, Besborodov and Zadneprovsky 1967) suggest that there is a need for further research into the modification of plant ashes.

Glasses from the medieval period in Northern Europe have been characterised by very high levels of potash (12 – 18 %), which is consistent with the use of ashes from inland terrestrial plants, such as beechwood . However, potash glasses, with negligible soda contents, are also known from other contexts: high potash, low magnesia glasses have been found throughout China, India, Pakistan, and SE Asia during the 1st Millenium BC (Hall and Yablonsky 1998).

Raised potash levels in ancient glasses are usually accompanied by increased amounts of phosphorous pentoxide, magnesia and calcium oxide.

3.7.4 Magnesia

MgO

Magnesia acts as a stabilizer in glass chemistry, and inhibits devitrification by lowering the liquidus temperature (West-Oram 1979, p 234). The substitution of lime with magnesia, up to 5 % lowers the melting point of soda – lime – silica glasses by 100 °C (Rehren 2000b, p 15). Magnesia has not been a constant component of glasses and is therefore a useful characterising tool. It is found in the earliest glasses at levels of 2 – 6 %, but during the Roman period it was typically less than 1 %. Caley (1962, p 65) states that magnesia has been an almost universal component in ancient glasses, usually 2 – 5 %, sometimes < 1%. Early glass scientists saw the high magnesia content of 2nd Millenium BC Egyptian glasses as an indicator of its deliberate inclusion, in the form of Dolomitic (i.e. magnesium-rich) limestone, as the source of lime (rather than purer forms of limestone) (Forbes 1966, p 128, Caley 1962, p 79, Matson 1948, p 53 and 1951, p 84). It was Turner who was able to discern the likelihood of the magnesia in Egyptian glasses being derived from plant-ashes (Turner 1956c), based on compositional analyses of ashes. Limestone was not therefore required as a source of calcium oxide, since sands often contain a high proportion of calcium carbonate (Turner 1956b, p 176).

High magnesium soda lime silica glass (soda-rich plant ash)	High MgO	2.5-6 %
	Re. High K_2O	2.5-3.5%
	High Na_20	14-17%
Low magnesium, soda lime silica glass (natron)	Low K_2O	1%
	Low MgO	<1%
	High Na_2O	14-17%
Mixed-alkali glass	High K_2O	6.5-14%
	Low MgO	0.4-1%

Table 3.2. Key characteristics of 2nd and 1st Millenium BC glasses.

The compositional changes in glasses from the Eastern Mediterranean around the 8th C BC defined the adoption of natron as the principle source of soda, and was accompanied by a three-fivefold decrease in concentrations of magnesium and potassium oxide (Sayre and Smith 1967 p 281, Sayre 1963, p 269).

This picture of high-magnesia glass being replaced by low-magnesia glass in the 8th Century BC has been complicated by the investigation of 15th and 14th Century BC cobalt-coloured glasses from Egypt. Whilst this group of glasses are high in magnesia, it is suggested that this is derived from the cobalt-rich alum used as a colourant rather than a plant ash source, therefore indicating an earlier than anticipated use of natron in glass manufacture (Shortland and Tite 2000, also see 3.7.20 below).

There is evidence for continuity of production of high magnesia glass beyond the 8th Century BC around the Euphrates and Tigris valleys across to India, where it was used alongside low magnesia glasses (Sayre 1963, p 273, also Caley 1962, p 84)). During the Islamic period high-magnesia glasses becomes the dominant type used in the Levant, which may reflect the uninterrupted continuity of compositional type from the 2nd Millenium BC (Smith 1963 p 285).

Variation in the magnesia contents of glasses from Raqqa (Syria) into discreet groups suggests that there is some variation within the soda-rich plant ash tradition of 8th-9th Century AD Islamic glass production. It is difficult to establish for certain if this reflects either the selection of a different plant for the ash, or a distinct processing of the usual ash before use (Henderson 1996b).

During the 1st Millennia BC and AD, high magnesia glasses were also produced on the Indian subcontinent, however these can be distinguished from that produced in the Middle East, because the Indian material is associated with higher alumina and lower lime contents (Hall and Yablonsky, 1998, p 1242).

Raised levels of magnesia are also associated with potash–rich plant ashes, and the transition to potash glasses in Medieval Europe sees a corresponding increase in the magnesia contents of glasses over the preceding Roman natron soda-lime-silica glass. The analysis of Roman and medieval glasses from the Weald clearly illustrates the difference in magnesia content: 0.07 wt% in the Roman glasses from Colchester, and 4.26 wt% from the Wealden glasses (Green and Hart 1987)

Whilst Roman enamels and tesserae were basically the same composition as other Roman glasses, white enamels have been shown to have comparatively elevated magnesium levels suggesting a plant ash source for the base glass (Biron *et al*. 1996 p 58)

3.7.5 Alumina

Al_2O_3

Alumina acts as a stabiliser, inhibiting devitrification and lowering the melting point of soda-lime-silica glasses in small proportions (West-Oram 1979, p 227, Brill 1987). The presence of alumina as a major constituent improves the durability of the glass (Cole 1966, p 46). Above 7 % alumina, the glass viscosity begins to increase rapidly, making a glass more difficult to melt. It was first used as a deliberate component in glasses in the 19th Century. Study of the thermal history of glasses suggests that repeated re-melting of alumina containing glasses results in a relative enrichment in the alumina levels compared with other components (Jackson 1996, p 292-293). Alumina is a universal component of ancient glasses, usually in the range of 1 – 5 % (Caley 1962, p 65). Early reports of glass analyses before 1953 may tend to over-estimate the alumina content at the expense of the calcium oxide levels. Until Geilmann and Jeneman’s 1953 paper identifying phosphates in glass, the unidentified P_2O_5 would have been precipitated out as calcium phosphate, which would be counted as alumina, leading to underestimation of calcium oxide content and exaggeration of the alumina (Geilmann and Jeneman 1953, Caley 1962, p 54).

Analyses of sand have demonstrated that alumina in glasses may easily be derived from this silica source. For example, samples taken from the beach at Volturno in Italy have alumina contents as high as 12.5 %, although it is has not been clearly demonstrated if this particular sand was ever used in glassmaking (Brill 1999b, p 475). Analyses of Indian glassmaking sands have given values of 7.17 %, and a silica:alumina ratio of 11:9, which matches the high alumina compositions of many Indian glasses (Brill 1987 p 7 and p 22). Indian glasses from Kopia from 3rd C BC – 3rd C. AD have consistent compositions and are characterised by their high alumina content (mean = 6.67 %), low lime and magnesia (2.93 and 1.61 % respectively) (Caley 1962, p 86, Brill 1987).

The alumina contents of natron are very low, typically less than 0.5 %, and whilst plant ashes have variable compositions, ranging from 0.45 – 5.9 %, they are typically less than 2 % (Brill 1999b p 482 – 486). Roman glass invariably contains

2.5 % +/- 0.5% alumina (Henderson 1999), which is consistent with the use of sands such as that from the River Belus (Brill 1988). Modern glassmaking sands can contain up to 2 % alumina (Gould and Hampton 1930).

A number of studies have examined the contribution of the crucibles employed in glass-melting to the final glass composition (Forbes 1966, p 118), with alumina possibly originating in alumino-silicates in the refractory clays used for making crucibles. Recent work investigating the glass-ceramic interface of excavated refractory materials have identified that there is a slight enrichment in alumina in the glass immediately adjacent to the crucible (Velde 1990, p 112, Merchant *et al.* 1998). However, the contaminated zone is approximately 0.5 mm thick, and does not contribute a significant amount of alumina into the main body of glass melt. In a study of Roman glasses from France, Velde cannot identify any other component correlated to the alumina , and suggests a possible independent mineral source in the raw ingredients. However, this seems unlikely since the value of alumina to glass compositional stability was not known until the 19th Century: Brill's experimental work with Belus sand and natron to reproduce glass compositions from Jalame suggest that the alumina content in Roman glasses is most likely to be derived from the sand (Brill 1988).

Glass from late 8th- early 9th C Islamic contexts at Raqqa (, Syria) has been noted as a variation upon the "Roman" type natron glass: it has a high alumina content (range 1 – 4 %), but low magnesia levels suggesting the soda is from a mineral source (Henderson 1999). This range is still within the reported glass analyses for the Roman period in Northern Europe, which are identified as natron soda-lime-silica glasses (Velde 1990, p 114, table 5). The low alumina-high MgO characteristic of 12th C Islamic glasses, are present in Raqqa in late 8th-early 9th C material ahead of rest of Middle East's transition to this type (Henderson 1999). It has been suggested that the lower viscosity arising from the reduced alumina levels of the new recipe facilitated the manufacture of cast artefacts, leading to the widespread adoption of the low alumina glass type (McLoughlin *et al.* 2001). High levels of alumina noted in blue enamel on a "13th Century" Persian plate helped to inform the decision that this was faked in the 19th or early 20th Century (Carboni *et al*. 1998, p 90 - 91).

3.7.6 Calcium oxide

CaO

Lime is a glass stabiliser, and the most important modifier in glass-making, without which alkali-silica glasses would be water soluble (West-Oram 1979, p 233). High CaO content, although improving durability, increases the viscosity of a glass below 1000 °C, reducing its workability (Guido *et al*. 1984, and Matson 1951). Some writers have suggested that the lime content in ancient glasses was derived from the deliberate addition of limestone to the batch materials (Forbes 1966, p 117, Caley 1962, p 79, Matson 1948, p 53 and 1951, p 84). The CaO:MgO ratio is therefore supposed to indicate the type of limestone employed (also see magnesia above). This position has been modified, since the lime and magnesia contents, although useful discriminants for several ancient glass types, are not themselves correlated (Turner 1956b, p 176, Sayre and Smith 1967, p 287 - 288). Unfortunately this assumption occasionally persists in contemporary glass literature (Santopadre and Verità 2000, p 32).

Lime is frequently an incidental component in sands (from calcium carbonate in shell from beach sands, or eroded limestone in wind blown sands). Analyses of the Belus sands for example (see Table 3.1 above) show a lime content of 6 – 25 %. Experimental work to reconstruct compositions of glasses recovered from Jalame has produced sufficient levels of lime in the final glass without the need of additives to a sand-natron batch (Brill 1988). Sand from Amarna has been shown to contain up to 18.86 % lime (Nicholson and Henderson 2000, p 197, Turner 1956c, p 281).

Plant ashes are often very rich in calcium (9.6 – 34 %, Ashtor and Cevidalli 1983, 494 – 498, also see Brill 1999b p 482 - 486), as well as highly variable (Sanderson and Hunter 1981b), although the lime levels tend to be higher in the potash-rich ashes, rather than the soda-rich ashes. This means that it can be used as a discriminating component along with soda and potash as in Barrera and Velde's paper on French medieval glass compositions (Barrera and Velde 1989). Medieval potash glasses are often noted for their very high lime levels, thought to have originated in the wood ash used in their manufacture. This characteristic has been identified as a key discriminator for the analysis of Roman and post-Roman glasses (Sanderson and Hunter 1981a, Wedepohl 1997).

The earliest textual reference to the deliberate addition of lime-rich materials to a glass batch are in Pliny's Natural Histories, in which shell is named as a glassmaker's essential ingredient (Turner 1956a p 46, Henderson 1985 p 277, Henderson 2001 p 475). However, analyses of Roman glasses have demonstrated that they may have been made without the deliberate addition of a lime-rich material, but if a non calcerous sand was used, then additional lime would be essential if natron were the soda source. None of the medieval treatises describe a lime-rich raw material for glass manufacture, and it is not until the 17th Century that recipes begin to prescribe the use of chalk, and not until the late 19th Century that lime was appreciated as a critical stabiliser for soda glasses when using pure soda (Turner 1956 p 45 – 47). The earliest analytical evidence for the deliberate use of a lime-rich raw material has been identified in a sample of frit from early 9th Century Raqqa, in which a bone fragment was identified (Henderson 1999, 2000 p 89).

High-lime glasses (9.5 – 12.7 %) have been noted from post-Roman/Early Islamic contexts in Middle Egypt, in a glass composition, which would otherwise suggest a natron alkali source (Bimson and Freestone 1987, Matson 1948, p 52). In this case a calcium-rich sand or additional material has been employed.

Recent work on the glass slab found in-situ in a tank furnace at Bet She’rim, Israel, suggests that the high calcium content may be the reason that this was a failed glassmelt, leading to impartial fusing and devitrification. It has been suggested that the glassmakers used a calcareous sand in combination with a soda-rich plant ash (rather than natron), implying a 9th Century AD date, as the transition from natron to plant ash glass was taking place in the Levant (Freestone and Gorin-Rosen 1999, Freestone *et al.* 2000).

Calcerous sands might be distinguishable between in-land and sea shore sources on the basis of associated trace elements. The shell in sea shore sands has a greater capacity to absorb strontium than calcite, the typical component of limestone, and where in-land calcerous sands contain the latter the resulting glasses may be distinct (Freestone *et al.* 2000, p 73-74).

Calcium fluoride is known from the 16th Century AD onwards as a white opacifier in glasses, and was first used by the Chinese (Henderson 2000, p 38). Calcium phosphate may also act as an opacifier (Henderson 2000, p 38), and has been noted in white enamels decorating 13th and 14th Century AD Islamic glass vessels (Freestone and Stapleton 1998, p 125, figure 27.5).

Glasses analysed from Manching, from 260 – 50 BC contain lime in the range 8 – 9% and are “characteristic of all known celtic glasses” (Gebhard *et al*. 1989, p 209). As described above, there is possibility of undereporting of lime contents in some glasses prior to Geilmann and Jeneman’s paper (1953), because in earlier analyses, the unidentified P_2O_5 would have been precipitated out as calcium phosphate, which would be counted as alumina content leading to underestimation of calcium oxide content (Caley 1962, p 54).

3.7.7 Phosphorous pentoxide

P_2O_5

Geilmann first noted that phosphorus pentoxide is generally present in all ancient glasses, from a few hundreds of a percent up to 4% (Geilmann and Jeneman 1953). Whilst phosphorous pentoxide acts as a network former (like silica), and has been used in modern times for the small-scale production of scientific glasses, it is an accidental component of ancient glasses (West-Oram 1979, p 224 – 226).

Phosphorous pentoxide is not present in significant proportions in natron (<1 %, Brill 1999b p 480, Henderson 1988b p 87), but is present in all plant ashes (Biek and Bayley 1979, p 5). Soda-rich plant ashes contain 0.76 – 3.22 % phosphorous pentoxide, whilst potash rich plant ashes, such as beechwood contain up to 15.3 % (Besberodov 1975, p 50 table 5, Smedley *et al*. 1998, p 149 table 1).

The Phosphorous pentoxide content is 0.05% - 0.38 % in Egyptian glasses of the 2nd Millenium BC, and 0.04 – 0.24 % in Roman glasses, Medieval church window glass ranged from 2 – 4 %, reflecting the use of wood ashes in the batch (Caley 1962, p 54, Geilmann and Jeneman 1953).

3.7.8 Copper oxide

CuO, Cu_2O

Copper oxides are employed as colouring agents in glass compositions. The earliest documentary records of glass-making include the use of “fast copper”, in the Babylonian texts (Turner 1956c, Oppenheim *et al*. 1988). The earliest vitreous materials, glazed steatite of the late 5th Millenium BC (Moorey 1985, p 136) were bluish-green coloured due to the copper content: malachite had already a long history as a pigment. The earliest copper coloured red glass known to date is from Nuzi, circa 1500 BC (Henderson 1985, p 281 and Vandiver 1983). Egyptian blue glasses coloured by copper alone have been found to contain copper oxide in the range of 0.59 – 1.45 % (Kaczmarczyk and Hedges 1983, p 61). Humphrey Davy, one of the first to examine ancient glass chemistry, analysed and discussed copper- coloured “frit”, a combination of sand, carbonate of soda and copper filings for comparison with material from Pompeii, before concluding that the archaeological material was coloured using cobalt (Davy 1815, p 106-109, p 120).

The role of copper is complex, and a range of colours can be achieved in glass depending upon the oxidation state of the copper and the presence or absence of other materials. Oxidised glasses can contain high concentrations of copper dissolved into the matrix as cupric ions (Cu^{++}) producing a blue to green colour depending upon the concentration and glass type (Cable and Smedley 1998 p 153). More reducing conditions gives rise to an increasing proportion of cuprous ions (Cu^{+}), which will give a less intense colouration or even colourless glass. The capacity of a glass to contain dissolved cuprous ions is more limited than for cupric ions, which can lead to the precipitation of cuprous oxide or metallic copper when highly reduced copper containing glasses are cooled. The formation of dendrites of cuprous oxide gives rise to a red to brown colour range (Freestone 1987). Lambert and McLaughlin (1978) confirmed the oxidation state of copper in blue and red glasses from 18th Dynasty Egypt using X-ray photoelectron spectroscopy (XPS): red glasses: Cu^{+} or Cu^{0}, and the blue/green glasses: Cu^{2+}.

Experimental work to reproduce opaque red glasses from 6th Century BC Nimrud (Cable and Smedley 1992) elucidated the relationship between the copper oxide and other glass components. These red opaque glasses are also very high in lead (c. 25 % PbO, Freestone 1992). Simply retaining a reducing environment in the furnace was of itself insufficient to achieve the desired effect of maximum precipitation of cuprite. Highly reducing furnace conditions can lead to localised reduction of the copper oxide on the glass surface, even to the point of reducing it to metallic copper. However, frequently the experimental melts were highly segregated, and insufficiently reduced throughout the batch. The type of raw component proved essential for increasing homogeneity and creating reducing conditions within the melt: litharge (PbO) proved better than red lead (Pb_3O_4), and copper carbonate ($CuCo_3$- similar to the pigment/ore malachite, Cu CO_3.Cu(OH)2.H_2O) was more effective than cuprous oxide. The addition of tin and antimony to the melt facilitated the reduction of the cupric to cuprous oxide. The lead content of the glass, in proportions of the region of 25 wt%, increases the solubility of the cuprous oxide during the melt thereby increasing the potential for cuprite precipitation (Freestone 1992, p 186, also see Ahmed and Ashour 1981 for experimental work on cuprous oxide precipitation in high-lead glasses). An absence of lead leads to batch segregation and brown or less densely coloured red glasses.

The copper-containing red glasses are chronologically useful: those with low or lead-free tend to be dull liverish or dark red and are known from the mid 2nd Millenium BC in Egypt onwards (Bimson 1992, p 166). The high-lead copper containing red glasses (15-30 wt% PbO) are brilliant sealing wax-red, and all dated examples are from 850 BC and later (Brill, in Oppenheim *et al.* 1988, p 120, Bimson 1992, p 168). The two types are used contemporaneously thereafter up to at least the 7th Century AD (e.g. the Sutton Hoo material, Bimson 1992, p 169).

Henderson has suggested the development of regionally distinct red opaque glass production between western and eastern Britain after the 2nd Century BC, on the basis of varying copper and lead contents (Henderson 1989a, p 47-48, 2001, p 476).

Recent work on early medieval opaque red enamels has defined a type of material not related to a cuprite-coloured soda-lime-silica glass, but a copper oxide-lead oxide-silica material produced as a by product of metallurgical raffination process (Stapleton *et al*. 1999).

The raw materials employed to introduce copper into the glass melt have rarely been investigated to date, considering the central role it has played as a colourant.

Common copper bearing ores for metal extraction include cuprite (red oxide, Cu_2O), melaconite (black oxide CuO), malachite (green basic carbonate, $Cu\ CO_3.Cu(OH)_2.\ H_2O$) azurite (blue basic carbonate, $Cu_3(OH)_2(CO_3)_2$), the sulphate mineral chalcanthite (blue vitriol, $CuSO_4.5H_2O$), the chloride mineral atacamite ($Cu_2(OH)_3Cl$) and the silicate chrysocolla ($CuSiO_3.2\ H_2O$). More complex sulphide ores include chalcocite (copper glance, Cu_2S), covellite (CuS), the iron sulphide minerals chalcopyrites (copper pyrites, $Cu_2Fe_2S_4$) and bornite (peacock ore, Cu_5FeS_4). More rare, but significant in the development of copper alloys, are those ores which also contain arsenic and antimony: tetrahedrite, containing iron and antimony ($(Cu, Fe)_{12}Sb_4S_{13}$), bournonite containing lead and antimony ($CuPbSbS_3$), tennanite containing iron and arsenic and enargite containing ($Cu_3As.S_4$) (Hodges 1989, p 65).

The cuniform instructions for introducing the copper colourants to a glass (Oppenheim *et al.* 1988, p 121-123) conform to the manufacture of blue translucent and red opaque glasses respectively. Although there is some discussion concerning the nature of the copper-bearing materials, it seems most likely that in both cases, the “slow copper” and “fast bronze” are both copper-based metallic alloys (rather than mineral ores, Egyptian blue or metal slags) (Brill 1988, p 121). Furthermore, a large number of copper-containing ancient glasses have copper: tin ratios comparable to contemporary bronzes, suggesting that it is to metallurgy that glass scientists should look for the source of copper colourants in glass (Brill 1988, p 121, 123). Sayre and Smith (1967, p 307-9) compare the copper: tin: lead ratios of a number of glasses with contemporary bronzes, suggesting that oxidised bronzes have been used to colour the glasses. This is a line of enquiry, which deserves further exploration.

Recent excavations of 13th Century BC deposits at Pi-Ramasses in Egypt have located glass colouring activities at the heart of a bronze-casting factory (Rehren *et al.*, 1998). Some of the copper coloured blue glasses from Final Bronze Age Frattesina are accompanied by tin, in proportions indicating a bronze as the source of the colourant (Brill 1992, p 14). The appearance of traces of zinc and lead oxides in Egyptian copper coloured blue glasses, which were absent in contemporary copper metal artefacts may indicate the use of an ore rather than the refined metal (Kaczmarczyk and Hedges 1983, p 63). The absence of a correlation with alumina or iron elsewhere might suggest that a copper-containing metallurgical slag or copper mineral had not been used.

Copper and cobalt are correlated in cobalt-coloured blue glasses from Manching (260-50 BC), indicating the use of a colourant containing both components in these particular glasses (Gebhard *et al*. 1989, p 208).

3.7.9 Lead oxide

PbO

Lead compounds can act as network former, colourants and opacifiers in glass, as well as bringing sparkling brilliance to cut and polished translucent glasses. High lead opaque and translucent glasses have been identified from the mid- 2nd Millenium BC onwards, and are well represented in the surviving glass literature (Henderson 1985, p 276 – 277). The inclusion of lead oxide in a glass artefact over 1 % marks it out as being of particular interest.

The earliest high lead glass analysed to date is from 1400 BC from Nippur in Mesopotamia containing 15.83 % PbO, and are also known from the contemporary site at Nuzi, North Eastern Iraq (Henderson 1985, p 276, Vandiver 1983). High lead glazes are known from earlier contexts such as from 1700 BC Atchana in Turkey (Charleston, 1960, p 1, Caley 1962, p 85).

Increasing the lead content of a glass will also lower its melting point, and as a consequence enamels and glazes are often high in lead. Glasses containing 65 – 84 % lead oxide have melting points in the range of 740 – 760 °C (Wedepohl *et al*. 1995, p 65). The presence of substantial quantities of lead in glass facilitates the precipitation of cuprite to colour them red (see section 3.7.8). The lead content in red glasses changes through time: pre- 9th C BC it is c 1%, 9th - 6th C BC it is 3 %, 6th - 3rd C BC it is 15 - 30% (Henderson 1985, p 282, p 276, Turner 1954b, p 455).

Prehistoric yellow opaque glasses are often high in lead, since they are coloured and opacified with lead antimonate ($Pb_2Sb_2O_7$, see antimony section) (Brill 1988, p 116). A high lead content facilitates the formation of tin oxide crystals when they are included as opacifying agents (Smith and Sayre 1967, p 303).

There is an unexplained presence of raised lead levels in glasses from Vergina, Greece (from the 1st Millenia BC), with a mean of 1.42 % in uncoloured glasses (which have otherwise been decoloured using antimony). One might otherwise expect lead oxide levels of 0.1 % or less. This phenomenon may be associated with higher levels of silver in 2 of the 5 glasses. The lead is missing from the contemporary Greek material from Kakouli and the Phidias workshop (Brill 1994, p 17).

Lead oxide contents of up to 44 % were found in glass being worked at Meare Lake Village West in the Late Iron Age (Henderson and Warren 1981, 1985 p 276).

Very high lead glasses were used in Anglo-Scandinavian England (up to 70 wt%) which has been suggested as a uniquely English phenomenon (Bayley 1982, p 494), although this is now untenable in light of the widespread use of high lead glasses elsewhere.

High lead glasses were recognised by Sayre and Smith as a distinct compositional group when they noted the exceptionally high lead content of glass amongst a group of Islamic glasses from 8th –10th Century AD contexts (33-40 wt%, average 36%) (Sayre and Smith 1961).

The use of lead in a batch changes the refractive index of the resultant glass: Medieval and Renaissance texts specify its use for enamels or gemstones (Theophilus, Eraclius, 15th C. Merrifield 1849, p 216, 528, 530). Ravenscroft famously invented a high lead potash composition (30-35 % PbO) for the production of “crystal” glass in 1675/6; i.e. high quality tableware previously made using a soda-rich composition. The high refractive index lends itself to cutting and polishing. It is important to note that Ravenscroft was not the inventor of high lead glasses, but did combine a number of techniques to create a profligate and emulated business (for the establishment of similar industries around Europe see Charleston 1960). Similar high-lead colourless potash glass was already being produced in Russia in the 11th – 13th Centuries (Sayre and Smith 1961, p 1826, Besberodov 1957, p 179).

An unusual combination of lead compounds for opacification of late 13th C. AD Syrian glass has been noted by Bimson and Werner (1969): a solid solution of $PbSnO_3$ in $Pb_2Sb_2O_7$. This combination has been observed elsewhere in 11th Century AD glass from Novgorod and 14th Century AD Islamic glasses.

Whilst lead levels in medieval Islamic and Venetian enamels can be high, levels of lead over 30 % have been found for opaque white, yellow and green enamels, but not red or blue enamels of this period. This observation led to the suggestion that enamelling on a medieval plate was forged (Carboni *et al*. 1998).

High lead window glass of Ayyubid date from Qas'r al-Banât (Raqqa, Syria) is the earliest known example of high-lead window glass- 66.1 % PbO (Henderson 1999 p 233)

It is possible to distinguish between antimony-rich glass recovered from Persepolis and contemporary Eastern Mediterranean sites on the basis of lead contents (these are not high-lead glasses). This has been attributed to different antimony sources (higher lead here is also associated with greater titanium and zirconium) (Smith 1963, p 285-6).

Many Early Chinese glasses have very high lead contents (c 43.2 %). During the pre-Han and Han periods (Han period = 206 BC – AD 220), these high lead glasses were frequently lead-barium silicate glasses in which barium oxide accompanies the lead (also see 2.7.24 below) (Charleston, 1960, p 1, Caley 1962, p 66, Biek and Bayley, 1979, p 17). A high lead content without the associated barium indicates that a Chinese glass is from the Han period or later (Hall and Yablonsky 1998). Very high lead-content glasses (70% PbO) are also known from 8th Century AD Japan (Henderson 1985, p 277).

Lead isotope analysis has been undertaken in an attempt to relate the lead content of ancient glasses to geological sources mined in antiquity. This technique has not been widely adopted, and there remains the problems of mapping geological sources exploited in antiquity, and the confusion brought about by recycling of lead-containing materials may make it very difficult to identify specific sources (Henderson 2000, p 14). Relatively discrete groupings of archaeologically distinct material have been achieved (Brill 1969, 1970, Lilyquist and Brill 1993).

3.7.10 Chlorine

Cl

Chlorine exists in ionic form in glass (as Cl^- ions), and can only be dissolved into the glass matrix in very small quantities (typically less than 2 % in soda – lime – silica glasses). The presence of significant amounts of chlorine (up to about 1.2%) in ancient glasses is well known (Geilmann 1955, Velde and Gendron 1980, Bimson and Freestone 1983). In early glassmaking chlorine was inadvertently added via the plant ash or mineral salts used to supply the alkali, causing an immiscible scum to form on the surface of the molten glass (Turner 1956c). Removal of the scum left the glass virtually saturated in chlorine and the concentrations in ancient glass often approach the high temperature saturation concentration, measured at 1.42 wt % Cl for a soda-lime-silica glass (Bateson and Turner 1939, p 267). Since chlorine solubility in a glass decreases with an increasing temperature, the chlorine content may be used as an approximate indicator of a melting temperature for a glass. This phenomenon has been employed to substantiate the model of reduced glass compositions relating to eutectic troughs in the soda – lime – silica phase diagrams (Rehren 2000a and b, also see 3.7 above). The manner in which chlorine is lost by vaporisation during the melting of medieval potash glasses has been detailed by Gerth *et al.* (1998), explaining why relatively little chlorine may be available for inclusion in the final glass.

3.7.11 Chromium oxide

Cr_2O_3

Whilst the mineral chromite was used on some 16th and 17th century Islamic ceramics as a black underglaze, green coloured chromium compounds were not used as pigments or glass colourants until the 19th century. Medieval Venetian and Islamic opaque green enamels are produced using a combination of copper oxide and lead-tin yellow (Carboni *et al*. 1998).

3.7.12 Tin oxide

SnO

Occurs as an accidental ingredient when bronze is used as a source of copper colorant. However its principle role in glasses is as a colourant and opacifier in combination with other components. The highest level of SnO_2 reported in pre-Roman glasses is 0.6 % (Kaczmarczyk and Hedges 1983, p 82).

Tin oxide, uncombined with any other component gives a white opacification (Rooksby 1962, p 23-24). The earliest use as a white opacifier has been the subject of some discussion: for example Egyptian glasses from 14th C deposits from Tel el Amarna and Elephantine Island (Farnsworth and Ritchie 1938), 2nd BC glasses in Europe (Henderson 1985, p 286, 1989a) or during the Islamic period (Sayre and Smith 1967, p 296).

Neumann (1927) suggested that many Egyptian glasses were opacified with gas bubbles from incomplete fusion of the raw materials, but does claim that glasses were opacified using a tin oxide (Farnsworth and Ritchie 1938). Ritchie and Farnsworth disputed this, suggesting that with the exception of yellow opaque glasses (for which they couldn't identify the colourant, but asserted it couldn't be from the lead or antimony content), all the opaque glasses were opacified using gas bubbles. Henderson has recently restated that tin-based opacifiers were not employed in glasses before the 2nd Century BC in Europe (Henderson 2001, p 477).

Lead stannate has been identified as a yellow opacifier. $PbSnO_{3,}$ a lead tin oxide, is produced by adding tin to a lead-rich glass, and precipitating the lead tin oxide out (Sayre and Smith 1967, p 297). This colourant is unstable on heating, and above 900 ºC becomes tin oxide, which is white. The earliest example is from European Iron Age material from the 2nd Century BC (Henderson and Warren 1981, Henderson 1985, p 286, Henderson 1987d, p 20). The only known compound of lead oxide and tin oxide is Pb_2SnO_4 (which has an orthorhombic crystal structure); this can be made by heating lead monoxide and tin oxide in an oxidising environment. However this will not give the correct form necessary for the yellow opacifier. When heated in the presence of silica, in an oxidising environment in the temperature range 700-900 ºC, $PbSnO_3$ is formed, which has a cubic crystal structure (this structure is cubic like the other yellow opacifier lead antimonate). If the $PbSnO_3$ -containing glass is overheated, then the compound decomposes, and cannot be recovered by cooling or reheating (Rooksby 1964, p 20-25)

The use of lead-tin oxide as a yellow opacifier has chronological implications. Three groups of yellow opacifiers have been defined: the earliest from the 5th – 3rd C. BC was opacified with lead antimonate which is distinct from lead stannate yellow dating to the period 2nd – 1st C. BC. These glasses can in turn can be distinguished from a group of lead antimonate glasses of 1st C. BC – 2nd C. AD date (Henderson 1989a, p 49-51). Tin added to glaze compositions increases the refractive index (in a similar manner to lead), and has been noted as a frequent component of Egyptian glazes from the 18th Dynasty onwards (Kaczmarczyk and Hedges 1983, p 94).

3.7.13 Bismuth oxide

Bi_2O_3

Bismuth is only found in glasses as a trace element, and is usually present at 0.01% or less. Its interest to glass scientists lies in its relationship with specific copper and cobalt ores, and therefore as a potential identifier of the source of colourants. For example Bismuth is found in Aegean bronzes along with nickel, cobalt and silver. This correlation may be due to the association between bismuth and cobalt and nickel at Schneeberg, Saxony (Dayton 1981a, p 57: NB this source to be used with some circumspection given the number or erroneous statements within). A trace of bismuth in yellow opaque glass may indicate that the mineral Bindheimite ($Pb_2(Sb,Bi)_2O_6(O,OH)$) has been used as the source of lead antimonate, since it contains some Bismuth (Henderson 2000, p 35). For further discussion of this see the section on cobalt below.

3.7.14 Nickel oxide

NiO

Nickel in glasses is typically at very low levels, less than 0.01 %, but is occasionally associated with cobalt ores (Henderson 1985, p 284, and section 3.7.20 on cobalt below).

3.7.15 Manganese oxide

MnO

Manganese has been used as a deliberate colourant and decolourant, and has also probably also appeared as an accidental component in ancient glasses.

In many glasses it is barely present at all (i.e. less than 0.001 %). At levels of 0.1 – 0.4 % and above it is considered a deliberate component in ancient glasses (of soda-lime silica type) (Sayre 1963, p 265, Brill 1988, p 259 – 261, for further discussion also see Sanderson *et al*. 1984, p 54). Davy was the first glass analyst to identify manganese in ancient glasses: noting its presence as a colourant in Roman glasses (Davy 1815 p 117).

Manganese oxide acts as a decolourant by oxidising the divalent iron content, and as a decolouriser is present in many colourless glasses from the 1st Century BC to the 12th Century AD in the range 0.24 – 4.5 % (Sayre 1963, p 270). Larger amounts of manganese oxide (in the Mn^{+++} state) can give a violet colour to glass, for example 2.7 wt. % in a Late Roman piece from Sepphoris (Fischer and McCray 1999, p 901, Henderson 2000, p 34, Kaczmarczyk and Hedges 1983 p

30). If present in the more reduced state (Mn^{++}), then the manganese imparts a yellow colour to the glass (Theophilus c1100, p 56).

Manganese is not present in natron, and only appears in glassmaking sands at very low levels (< 0.1%, Brill 1999b, p 474 – 477, 480, Kaczmarczyk and Hedges 1983, p 30). Therefore its presence in a natron-type soda lime silica glass above 0.1 % indicates its deliberate addition. The presence of manganese in low concentrations (0.02 – 0.1 %) in Roman glasses from Jalame are regarded as accidental. In these glasses, manganese was correlated with iron, copper, vanadium, nickel and barium and probably originated in the mineral pyrolusite in the sand (Brill 1988, p 260). Manganese is similarly only present in soda-rich plant ashes in very low percentages (0.1%, Brill 1999b, p 482 – 484). Its concentration in potash – rich plant ashes is more variable: high concentrations have been found in wood ashes, with up to 13.7 % Mn_3O_4 in beechwood ash (Green and Hart 1987, p 278). Some cobalt ores are very rich in manganese, and cobalt- coloured glasses may subsequently become enriched in manganese by accident (Garner 1956, Young 1956, also see cobalt section 3.7.20 below for more discussion of this). The earliest documentary reference to the deliberate addition of manganese was by Pliny (Sayre and Smith 1967, p 301).

The use of manganese as a deliberate decolourant has chronological importance; antimony pentoxide was widely used as a decolourant in Europe and the Eastern Mediterranean area from the 15th Century BC until the second Century AD when it was gradually replaced by the use of manganese oxide. Further east in the area of the Euphrates valley, the tradition of antimony pentoxide as the principle decolourant persisted into the 5th – 7th Centuries AD (Sayre 1963, p 270 – 271). During the period of transition, some colourless glasses contain both components. Both antimony and manganese continued to be used as decolourants in the Middle East and Western Asia until the 14th Century AD, from when only manganese was used (Sayre and Smith 1967, p 301). The dual use of manganese and antimony in Roman glasses from the 1st to the 4th Century AD in the Western Empire has been explored (Velde and Hochuli-Gysel 1996). Whilst the addition of antimony could be correlated to the iron contents of the glasses, the use of manganese is less easily explained, and appears independent of other components. The use of both decolourants may be related to a desire to give different tints to the final glass.

The manganese level in a Bronze Age bead from Wilsford was higher than expected (0.31 and 1.05%), and may be related to the use of a plant ash alkali in this mixed-alkali glass. The general shift from antimony to manganese in opaque glasses happens in material found later in Britain (2nd-1st C. BC), and may have come in with a colourant (Guido *et al*. 1984, p 251): other contemporary mixed-alkali glasses from Frattesina are much lower (0.012 – 0.023, Brill 1999b, p 58).

The high levels of manganese found in Northern European Medieval glasses is thought to be an accidental introduction by the use of wood ashes high in manganese, to supply the (potash) alkali (Newton 1978). The final colour of the forest glasses with high manganese contents was determined as much by the furnace environment as variation in chemical composition (Sellner *et al*. 1979, Theophilus c1100 p 55 - 57).

With the adoption of purified alkalis by the glassworkers of Murano, manganese again had to be added as a separate component to their glasses; it is documented as an ingredient imported for use in the glasshouses of Murano (*lapis magnanensis*) from 1290 onwards (Jacoby 1993, p 77). The raw mineral is of uncertain origin, probably from France, Germany and Catalonia according to 14th Century sources, although during the 17th Century a Piedemontese source is recommended (Jacoby 1993, p 77).

3.7.16 Antimony compounds

Sb_2O_5, $Ca_2Sb_2O_7$, $Ca_2Sb_2O_6$, $Pb_2Sb_2O_7$

Antimony pentoxide Sb_2O_5, calcium antimonate $Ca_2Sb_2O_7$ or $Ca_2Sb_2O_6$, lead antimonate $Pb_2Sb_2O_7$.

Antimony and its compounds can act as a fining agent, colourant, opacifier and decolourant in glasses. The raw material for antimony in glasses is uncertain, but frequently thought to be the mineral stibnite (antimony sulphide) (Biek and Bayley 1979, p 9, Forbes 1966, Rooksby 1962, p 23), the mineral bindheimite, or the metallurgical byproduct antimonal litharge (Mass *et al*. 1998).

Lead antimonate ($Pb_2Sb_2O_7$) was the principle yellow opacifying colourant in ancient glasses and glazes from 1450 BC to 400 AD (Brill 1988, p116, Mass *et al*. 1998, p 139-140). A study of European yellow opaque glasses from the Iron Age has revealed that there was some diversity in the use of the colourant/opacifiers for yellow glass. From the 5th to the 3rd Centuries BC yellow glasses from across Europe were opacified/coloured yellow with lead antimonate, during the period from the 2nd to the 1st Centuries BC a different compound began to be used: lead stannate (Henderson 1987d, p 20). Whilst lead antimonate continued to be employed alongside the lead stannate, these glasses can be distinguished from the earlier yellow glasses on the basis of their lead to ferric oxide and antimony to manganese ratios (Henderson 1989a, p 49 – 52). Lead antimonate is also found in green opaque glasses, where it has been added to a glass which would otherwise be coloured blue (Brill 1988, p 116, 119). A recent study of Roman opaque glasses found a correlation between the lead and antimony in yellow and green glasses: whilst each sample had an excess of lead for the stoichiometric formation of $Pb_2Sb_2O_7$, the correlation of the two components suggests they originate in the same raw material, in this case an antimonal litharge from the cupellation of antimonal silver ores (Mass *et al.* 1998).

Calcium pyroantimonate ($CaSb_2O_6$) was used as a white opacifying agent from the 14th Century BC until the 5th Century AD when it was replaced by a tin-based white opacifier. This compound was also used to opacify glasses which have other colours (Sayre 1963, p 269, Rooksby 1962, p 22). It has been noted to have continued in use beyond the 5th Century: 9th Century AD white opaque glass from Ribe contain raised antimony levels (Henderson 1985, p 286).

Antimony oxide was first used to decolourise glass from the 7th Century BC, and is also associated with the adoption of a new alkali source (i.e. natron soda-lime-silica glass). It is present in the quantitiy of 0.5 – 3 %. It was supplemented by manganese, as a decolourant from the 1st Century BC before manganese became the principle decolouring agent after the 4th Century AD (Sayre 1963, p 263, Sayre and Smith 1961, p 1824, Brill 1988, p 116, Brill 1994, p 11). Both of these decolourants function by oxidising the divalent iron in glass (West-Oram 1979, p 235). Even after the adoption by the Romans of manganese as the primary decolourant, antimony may still have been retained by glassmakers for special pieces, such as cage cups (Sayre 1963, p 280). There is slight evidence for the later use of antimony as a decolourant at Sepphoris during the period 950-1516 AD (Fischer and McCray 1999, p 903).

Antimony has been used as a fining agent, not improving the flow of glass to permit the escape of gas bubbles from the melt (as claimed by Sayre 1963, p 266), but by enriching the oxygen content of the gas bubbles in glass, allowing them to be more readily absorbed (West-Oram 1979, p 239).

The levels of antimony have been employed to discriminate between Central European and British and Egyptian faience and glass beads from the Early Bronze Age: with a mean concentration of 190 ppm for the C. European beads and 5 ppm for beads from both contemporary British and Egyptian material (Harding and Warren 1973, p 64-66).

The presence of antimony in blue glasses may be associated with the use of antimony-rich bronzes used as the source of copper as a blue colourant.

3.7.17 Silver oxide

Ag_2O

Silver oxide is usually found in very low levels in ancient glasses (typically less than 0.005 %), and is only very rarely found as a deliberate component. Silver itself is present with gold and copper, in colloidal particles of metal in the Roman Lycurgus cup to give it its dichroic properties (present at levels in range 0.03 – 0.19 % Ag, Brill 1999b, p 146). X-ray diffraction studies of glassy material from a crucible from 10th Century AD Gloucester revealed that the glass was opacified and coloured yellow with silver arsenic sulphide ($Ag_2As_2S_4$) (Biek and Bayley 1979, p 13). Silver was also used for staining medieval window glass, a process not known before the 14th Century AD (Biek and Baley 1979, p 13, Newton and Davison 1989, p 99).

3.7.18 Gold

Au

Gold has only rarely been used in glassmaking. Its presence in metallic form in Roman dichroic glasses contributes to their colour (Newton and Davison 1989, p 10, Bimson and Freestone 1985, p 211). Since the 17th Century AD gold has been used to give ruby red colour to glasses when present as colloidal metal particles in the matrix (Barber and Freestone 1990, p 42, Newton and Davison 1989, p 10, Henderson 2000, p 33). Gold or a gold alloy may be the red colouring agent used in an enamel on a 13th-14th Century Islamic glass vessel (Henderson and Allen 1990, p 180-181).

Thin sheets of gold have also been used as decoration when “sandwiched” between sheets of glass in a variety of forms, typically bowls and beakers from the Hellenistic (3rd Century BC) through to Roman periods (Saldern 1991, p 120, Harden 1968, p 63)

3.7.19 Arsenic

As_2O_5

Traditionally, arsenic has been used as a fining agent, increasing oxygen and carbon dioxide loss in the temperature range 600 – 925 °C, by absorption of bubbles into the glass during manufacture. As a deliberate component in modern times its main role has been as a decolouriser, in soda-lime silica glasses, where its action has been to oxidise blueish-green FeO to the less highly coloured yellowish green Fe_2O_3 form (Cable 1969, West-Oram 1979, p 236). In many parts of the world minerals such as tennantite ($3Cu_2S.As_2S_3$) and energite ($3Cu_2S.As_2S_3$) are found in association with the copper ores chalcocite (Cu_2S) and covellite (CuS) and therefore arsenic is frequently found in metallic copper (Kaczmarczyk and Hedges 1983, p 70, 73).

Arsenic is also associated with some cobalt ores (see section 3.7.20), but is subject to boiling off during ore preparation (Sayre 1963, p 281), and it may be difficult to link ratios found in ores and metals with those in finished glasses. Elsewhere it appears as an impurity in bronzes (e.g. Rehren *et al.* 1998 p 232 - in 36 analyses of 13th Century BC bronze from Pi-Ramesses, average Arsenic content = 4,000 ppm).

Lead-ox-arsenate ($3Pb_3(AsO_4)_2.PbO$) is a white opacifying compound used in glasses made in 18th Century AD Venice (Rooksby 1962, p 25). Approximately 5 % arsenic oxide was added to a high lead glass, into which it would dissolve, and then precipitate out as lead-ox-arsenate.

3.7.20 Cobalt oxide

CoO

Cobalt oxide has a single function in glasses modern and ancient: it is a powerful colourant. In very low concentrations it will impart a strong blue colour to an otherwise colourless glass, however an excess of cobalt oxide will colour a glass so intensely it will appear black. Its use as a blue colourant indicates a sophisticated understanding and control over the raw components used in glassmaking.

Writers on the subject differ on how small a cobalt component is required to colour glasses: 10 ppm (0.001 %) to 100 ppm (0.01 %) (Bayley 1983, p 30), 0.005 % (Brill 1963, p 126), 0.05% (Henderson 2000, p 29). Levels in blue glasses from 14th Century BC Egypt ranged from 0.08 – 0.15 % (Farnsworth and Ritchie 1938, p 158 – 165), and levels as high as 0.2 % have been noted in dark blue enamels of the Roman period (Biek *et al.* 1980, p 73). In this study it is considered a deliberate colourant at 0.05 % and above.

Although it has been in use as a colourant for some 4500 years, cobalt was identified as a specific element in 1733 by Kennig Brandt (Taylor 1977, p 3; or 1742 according to Dayton 1981b, p 130). Cobalt was identified as a colourant in Roman glasses by Davy (1815), but this analysis was probably flawed, and the first published quantitative analysis to identify cobalt in glass was by Lepsius in 1877 (Caley 1962, p 20, Farnsworth and Ritchie 1938, p 162). However, the use of cobalt before the medieval period was not accepted by a number of glass scientists for a considerable period of time after this: Neumann continued to deny its use before 1540 (Neumann 1927, Henderson 1989a, p 34). The reluctance to recognise cobalt as a colourant was probably due to the low concentrations and analytical problems in quantifying such low concentrations faced by early 20th Century glass scientists (Geilmann 1961, p 55). Farnsworth and Ritchie published the definitive study establishing the widespread early use of cobalt, and summarised previous debate on the matter in 1938 in an examination of a series of 14th Century BC Egyptian glasses (Farnsworth and Ritchie 1938). The earliest documented use of cobalt in glass is from Egypt in the 5th Dynasty (i.e. from c. 2680 – 2530 BC) (Taylor 1977, p 4), and analyses by a number of glass scientists have verified its widespread use to the present day (Geilmann 1961, p 56). Cobalt has also been used as a pigment on pottery in Egypt during the 15th to the 13th Centuries BC (Bachmann *et al*. 1980).

Cobalt has been a widely discussed component of ancient glasses because of its strong association with other elements in the raw material. These relationships may be problematic, given the low levels of cobalt required to colour glasses, and the resulting dilution of associated minor constituents (Geilmann 1961, Henderson 1989a, p 33-36). Nonetheless clear distinctions can be made between glasses on the basis of elements correlated to the cobalt content.

Cobalt sources:

Cobalt ores can be classified into four types:

1. those with copper (such as black trianite: $2Co_2O.Cu.6H_2O$)
2. in ore rich in iron and manganese (absolites)

3. in arsenic and sulphur-rich ores (such as cobaltite/cobalt glance: $CoAsS$; smaltite : $CoAs_2$ and Linnaeite: Co_2S_4)
4. nickel and arsenic- rich ores (like skutterudite: $(Co,Ni,Fe)As_3$)

(after Henderson 1985, p 280 and Taylor 1977, p 3).

These are not the only associations which cobalt ores have been noted to possess: lead, zinc, alumina, magnesia, bismuth, antimony, silver and nickel have all been shown to be correlated to the cobalt contents of ancient glasses in order to distinguish between groups of material (Rehren *et al.* 1998, p 246, Sayre 1963, p 267, Dayton 1981a, p 57, Geilmann 1961, Henderson 1985, p 279, Henderson 1989, p 33 – 36, Garner 1956, Young 1956, Kaczmarczyk 1986, Shortland and Tite 2000, p 145).

Specific sources mined in the past 300 years are well characterised by modern chemists, widely distributed, and readily identified in the literature (for example Taylor 1977 p 4 – 10, Dayton 1981a, p 60): they are not however necessarily the same as those used in the past. The extraction and manufacture of cobalt colourants has historically been secondary to the mining of other materials (such as copper, silver or alum).

The first studies distinguishing between cobalt sources were the work of Young and Garner (Young 1956, Garner 1956), who were able to discern distinct cobalt types in Chinese blue and white decorated porcelain. The two groups were differentiated on the basis of their manganese:cobalt ratio, a shift in which proved to be chronologically significant. All pre-1400 AD samples contain MnO:CoO ratios of less than 0.5:1, whilst all post 1600 AD samples have ratios greater than 3:1 (with a range during the intervening period) (Young 1956, p 43). The difference between the ratios reflects the adoption of a manganese-rich ore (an absolite) during the later period. Since all known Chinese cobalt sources are manganese rich, then the cobalt for the earlier material must have been imported, probably from the Islamic world (since it was known as ‘Mohammedan Blue’ Garner 1956, p 48). The high iron and manganese contents of Chinese cobalt-coloured porcelain were first identified by Muspratt and Sheridan in 1853, who recognised their role as modifiers to the final colour (Taylor 1977, p 6).

The source of cobalt used in Egyptian glass and faience is also subject to a similar shift in associated oxides. Kaczmarczyk has noted that late 2nd Millennium Egyptian cobalt-coloured glasses and faience have elevated levels of alumina, magnesia, manganese, iron, nickel and zinc, whereas 1st Millenium BC cobalt – coloured glasses do not (Kaczmarczyk 1986, p 369 – 371). Further investigation of these glasses and possible sources of the cobalt, led to the analysis of alum from the Western desert at Dakhla Oasis, which contained the correlated transition metals in proportions suggesting its use as the cobalt source. This source had been considered but rejected by Farnsworth and Ritchie (1938). The analytical data for the alums is reproduced from Kaczmarczyk (1986) and also discussed by Shortland and Tite (2000). The additional magnesia associated with the cobalt source has led to a re-evaluation of the characterisation of many 2nd Millenium BC glasses from Egypt. The high-magnesia soda-lime glasses coloured with cobalt from Egypt, from the time of Tuthmosis III onwards (i.e. from the period 1504-

1450 BC), had previously been classified as a type made using a high-magnesia alkali source such as a plant ash. In light of the high magnesia content of the cobalt-bearing alums, and associated oxides (i.e. alumina, manganese, iron, nickel and zinc), it is possible to suggest that these glasses were made using a low-magneisa alkali source such as natron. This is significant since it suggests not only local production of glass in Egypt when previously glass had been considered an exotic import, but pushes back the beginning of the use of natron in glassmaking. Contemporary cobalt coloured glasses from the Mycenean world contain the same pattern of associated oxides, indicating a shared cobalt source (or glass production origin) (Sayre and Smith 1974, p 51-54). It seems likely that the 1st Millenium BC cobalt – coloured glass and faience from Egypt were coloured with the more pure cobalt bearing ores from Iran, which are not associated with raised levels of manganese, iron and zinc. The Iranian cobalt ores are known to be free of manganese, and associated with arsenic (Kaczmarczyk 1986, p 369 – 371). The latter, however is a poor identifier since it is subject to boiling off at high temperature (above 1250 °C), although its presence/absence may be helpful (Henderson 1985, p 279).

European Iron Age glasses coloured with cobalt shift from an antimony-rich source to a manganese-rich source c. 2nd Century BC (Henderson 2000, p 31, 2001, p 475).

Cobalt derives its name from the spirits thought by Medieval miners to have inhabited the copper and silver mines of the Erzgebirge (Saxony), and can be linked to the arsenic-rich cobalt ores accompanying the other metal ores (Taylor

1977, p 5 – 6). The mining of copper in the area has been continuous since the Bronze Age, and the extraction of cobalt for the colouring of glass documented since the 15th Century AD (Geilmann 1961, Taylor 1977, p 6). The possible role of waste materials from the extraction of silver for the source of cobalt in Mycenean glasses has been raised by Dayton, but has since been convincingly quashed (Dayton 1981a and b, Kaczmarczyk and Hedges, 1983, p 52-53, 301 – 302). The cobalt ores from the Erzebirge region are associated with silver, nickel and bismuth, however the widespread incidence of cobalt minerals in Germany, Austria, Switzerland, the Czech republic and Slovakia make it very difficult to relate cobalt colourants to specific sources in this area (Henderson 1985, p 279).

The mixed-alkali glass composition of the European Bronze Age (and possibly earlier) is predominantly blue-coloured. However, until c.1200 BC it is exclusively coloured by copper compounds, and only after this point is cobalt used alongside copper as a blue colourant (Guilaine *et al*. 1991). If this observation survives continued analysis of earlier mixed-alkali glasses, then it might indicate a shift in the mining of copper ores to include ones associated with cobalt – rich material (or simply the first recognition of cobalt rich material as a colourant). Cobalt blue mixed-alkali glass analysed by Brill from Frattesina contained substantial levels of nickel and arsenic which were considered characteristic of the cobalt source (Brill 1992, p 12 – 13).

The analysis of a number of Islamic blue glasses revealed associated impurities of lead and zinc. Those from the 12th –14th C. AD were comparable with contemporary cobalt blue glasses from Southern France (lead oxide range 0.01-5

%; zinc oxide range 0.05-0.9 %), suggesting a similar cobalt source. An Iranian source is suggested - Anorak, near Tabriz in Iran has a zinc-rich cobalt source (Henderson 1998, 2000, p 32). Interestingly, in a documentary source of 1301, a technical treatise by Abdallah al Qasani of Tabriz, both cobalt mineral and cobalt-manganese ore are discussed in relation to the faience industry (Ganzenmuller, 1939, 136-137). It is even suggested that cobalt – ores were exported from “Frankenlande” (probably modern Germany rather than France) to Persia. This is intriguing given that the cobalt colourant zaffre was referred to as “Damascus pigment” during the medieval period, and might therefore be considered an import from the Near East. Theophilus notes that the French were particularly adept at producing sheets of blue glass, although through recycling blue cullet from Roman deposits (Cox and Gillies 1986 p 62).

In a study of the Limoges enamels, there was a compositional division between early (1100 – 1200 AD) and late (1200 – 1350) materials. Although cobalt was employed as a blue colourant during both periods, it was found to be positively correlated with zinc in many of the later enamels. Whilst Biron *et al.* claim that no cobalt source is known in France (footnote no 94 in Biron *et al*. 1996), this is not strictly true, since deposits were worked during the 18th Century AD (Taylor 1977, p 6).

Cobalt blue Roman glasses from Jalame, Israel are associated with raised iron, alumina and zinc levels, however the basic glass is identical to other glasses in the main assemblage, demonstrating that the colourant had been added at the production site. The colourant must have been brought in as a highly concentrated glass or as the raw mineral (Brill 1988).

Bass has suggested that the cobalt-blue glass ingots from the Ulu Burun shipwreck were indicators of glass production in Palestine for Egypt, but the analyses (by Brill) are similar to the Egyptian and Mycenean glasses as defined by Kaczmarczyk (Henderson 1989, p 33-36).

3.7.21 Titanium oxide

TiO_2

Whilst titanium oxide is employed as an opacifying agent in modern glasses, there is no evidence to suggest its deliberate inclusion in ancient glasses (Rooksby 1962, p 20). It is often identified as a minor contaminant in glassmaking sands (Brill 1988, p 263). Titanium and strontium oxides were used to discriminate between sand sources for glasses from Pokrovka, Russia (400 BC – 200 AD): levels were between 0.11 and 0.542 % (Hall and Yablonsky 1998, p 1241 - 1242).

3.7.22 Sulfur

SO_3

Sulfur and its compounds are not regarded as deliberate additions to ancient glasses. Plant ashes are, however, often rich in sulphates (up to 31 % in kelp ash, Brill 1999b, p 486), and they are also present in natron (up to 7.37 % in Natron - Brill 1999b, p 480).

The amount of sulphur in a melt is limited to the saturation point in the particular glass type, so for example for the Roman glass from Jalame, this is 0.1 % (Brill 1988, p 274), and the melting temperature for a particular composition (Chopinet and Barton 1986).

Sulphur will act as a powerful colourant when in combination with iron as a ferri-sulphide formed in reducing conditions to give an amber colour (Schreurs, in Brill 1988, p 270). Research into the colouring effect of iron and sulphur have shown that when under reducing conditions, this ferri-sulphide complex (Fe^{3+}, S^{2-}) increasingly changes the colour of glass from bluish aqua (coloured by the already reduced Fe^{2+} ions) to amber (Schreurs and Brill 1984, p 200). Very reducing conditions within the melt are necessary to form the ferri-sulphide chromophore, and this might be achieved by the addition of powdered charcoal into the batch. To decolourise such a glass, it would be necessary to oxidise the iron and sulphur ions such as by the addition of a high manganese oxide (such as pyrolusite: MnO_2) (Schreurs and Brill 1984, p 208).

The sulphur content has not been widely used as a discriminating component of ancient glass, but it has been observed that 2nd Century AD tesserae from Salona, Dalmatia were found to have high sulphate contents (0.37 – 2.34 %, compared with 0.03 – 0.52 % for comparable material from Germany) (Caley 1962, p 96).

3.7.23 Iron oxide

FeO, Fe_2O_3

Iron is a universal component of ancient glasses, from trace to 10 %, only occasionally occurring at levels below 0.5 % (Caley 1962, p 65). It is mostly present as an unintentional (and undesired) component of sand – the levels are a fundamental point upon which to define a glassmaking sand, since it is a powerful colourant in its reduced forms. A very high content (10 % or greater) suggests that iron has been deliberately used to produce a dark glass (Caley 1962, p 33). A high iron content may suggest a metallurgical slag or obsidian have been used in its production (Brill 1987, p 5). It is possible to find very high iron contents in some sands: for example 31 % FeO was recorded by Brill (1999b, p 475) from sand recovered from the mouth of the River Volturno in Italy (an area in which Roman glassmaking is documented: Isings 1957, p 4-5). In some early Egyptian glazes, iron is associated with the use of manganese (Kaczmarczyk and Hedges, 1983, p 34).

The colouring effect of iron in glass is dependent upon the redox conditions of the glass during manufacture. It will appear blue in strongly reducing conditions due to the reduced ferrous ion Fe^{2+}, whereas the oxidised ferric ion Fe^{3+} gives a weaker yellow or brown colour. A combination of the two types of ion will give rise to varying shades of green. This is complicated by the presence of sulphur, which in strongly reducing conditions will form a ferri-sulphide complex, which will colour a glass amber (see section 3.7.22). Manganese and antimony are both effective decolourants for iron containing glasses, because they will oxidise the ferrous iron ions to the nearly colourless ferric state (Brill 1988, p 275). The addition of low levels of iron oxide (1.4 – 2.3 %) into a low lead glass will also facilitate the dissolution of copper into the melt and the subsequent precipitation of cuprite, which is useful in the production of red opaque glasses (Henderson 1985, p 282, Henderson 2000, p 33, Guido *et al*. 1984, p 251, Hughes 1972, p 99).

Iron oxide has also on occasion been noted as a red opaque colourant (e.g. Bimson and Werner 1969, p 263-264), although the manner in which this is achieved is unclear. The use of red iron oxide as a pigment is very well established in the archaeological record before the advent of glassmaking (i.e. ochre, haematite), but its use as a glass colourant is poorly documented. In their discussion of enamels on 13th and 14th Century Islamic glasses, Freestone and Stapleton (1998) describe two types of iron-containing red enamels. The first is where low-lead soda-lime silica glass has been finely ground and mixed with powdered iron oxide (c 3-5 % Fe_2O_3) and fired onto the surface of a glass vessel. The process is rapid to avoid collapse of the vessel, and the particles of glass and iron oxide are still well defined. In the second type, a high-lead glass is used with a higher iron content (c 10-25 % Fe_2O_3): with the lower melting point of a high-lead glass the enamel would flow more easily over a soda-lime-silica vessel without danger of it collapsing. The iron-oxide particles can still be discerned within the high-lead glass matrix. If ground glass and iron oxide powder were held at high temperature for sufficient time, the iron oxide would dissolve into the glass matrix with the colouring effects described above. For the iron oxide to have an opacifying and red-colouring effect it is necessary for the iron oxide to remain as distinct particles within the glass matrix (Verità 1998, p 131-132). In his brief discussion of red iron-containing glasses, Weyl does not mention the role of iron-oxide particles as an opacifying and colouring agent (Weyl 1999, p 94). The capacity for different base glasses to contain undissolved iron oxide particles has been underexplored, and is worthy of additional experimental research.

The iron oxide content of a glass has been used to discriminate an individual piece: the red enamel decoration of a supposed 13th Century AD glass plate was shown to be a later addition to an early plate. A level of 27% is three to six times the reported level for any previously analysed 13th Century red enamels (Carboni *et al*. 1998, p 90).

3.7.24 Barium oxide

BaO

Barium oxide levels in ancient glasses are typically less than 1 %, and most frequently lower than 0.1 % (although some Medieval glasses are occasionally found with higher quantities). Since the 19th Century it has been used to produce specialist technical glasses, but its use in ancient glasses is confined to a unique compositional type produced in China between the 6th Century BC until the 3rd Century AD. During this period high barium oxide glasses with 8 – 25 % BaO were produced (Brill 1987, p 16, Henderson 2000, p 51). The Chinese glasses are also high in lead (e.g. 19.2 % BaO, 24.5 % PbO, 41.9 % SiO_2 reported in Caley 1962, p 38, after Beck and Seligman 1934). It has been suggested that the inclusion of barium is accidental, given that barium ores are found alongside lead ores in China, and is of similar specific gravity (Caley 1962, p 89 - 91). Barium ores include the sulphate barite and the carbonates barytes ($Ba\ CO_3$) and witherite (West-Oram 1979, p 234).

3.7.25 Zinc oxide

ZnO

Whilst zinc was not isolated as an element until 1504 AD, it had been used for a much longer period in the manufacture of copper alloys (Dayton 1981b, p 130). Since the 19th C AD zinc compounds have been used as colourants in glasses, but prior to this its appearance was purely accidental (Kaczmarczyk and Hedges, 1983, p 63). Zinc oxide can modify the action of other colourants, such as cobalt blue to “Rinman’s green”, or nickel-brown into a blue/violet colour. Zinc is associated with some copper ores, lead ores and manganese/cobalt ores: up to 0.36 % ZnO has been recorded in cobalt blue glass, and 0.17 % in yellow glass of the New Kingdom period (Kaczmarczyk and Hedges, 1983, p 67). Sayre and Smith noted the high zinc content of New Kingdom cobalt-coloured blue Egyptian glasses were similar to Mycenean material, suggesting a shared colourant (and therefore possible origin) (Sayre and Smith 1974, p 51).

3.8 Conclusions.

Whilst the material presented here is not a complete record of all compositional analyses, it is sufficient to illustrate how the compositional analysis of ancient glasses and raw materials during the past 200 years have led to a broad understanding of glass technology and the often regional development of the manufacture of vitreous materials. The integration of historical and experimental data has established a sophisticated knowledge of the processes involved. Clearly the emphasis here has been on the technology alone of glass from Europe, the Near and Middle East. Significant work has also been undertaken upon glasses from South Asia, Central Asia, China and the Indian Ocean area.

The purpose of this chapter has been to establish the framework for the interpretation of the data from the compositional analysis of prehistoric Italian glasses. By addressing individual components and their role as reported in the technical and archaeological literature, the chapter acts as a guide to interpreting such data.

CHAPTER 4: ANALYTICAL PROCEDURES

4.1. Introduction

This chapter describes the selection and application of techniques applied to the compositional analysis of glass samples from Prehistoric Italy: X-ray Fluorescence Analysis (XRF), Energy Dispersive X-ray Micro Analysis (EDXMA) (the latter attached to a Scanning Electron Microscope- SEM), Electron Microprobe Analysis (EMP) and X-ray Diffraction (XRD). These forms of instrumental analysis share some basic principles and the discussion of certain aspects of their operation is relevant to each. In order to avoid repeated accounts of shared principles and phenomenon in the applications of these techniques, XRF analysis is described in some detail and the other methods are explained in so far as how they differ to XRF. The suite of techniques employed generates different but complimentary data concerning ancient glasses: qualitative and quantitative analysis of the oxides present in the glasses (XRF and EMP), imaging and selected qualitative analysis of discrete parts of a sample (EDXMA) and qualitative data on the crystalline phases of a sample (XRD).

In addition to the theoretical principles behind each technique, a consideration of their practical application to specimens of archaeological glass is included below. The emphasis is on understanding the techniques as applied to this project. The technical specifications for the equipment and procedures employed for the purposes of this project are also described alongside calculations of precision and accuracy for the quantitative data.

4.2 X-Ray Fluorescence Analysis.

The X-ray region of the electromagnetic spectrum lies between 0.1 and 200 Å (Å = 10^{-10} m), although the range used in X-ray spectrometry (the analytical region) is only between 0.1 - 25 Å. X-ray fluorescence spectrometry is only one of an number of routine techniques employing X-rays to investigate the structure or composition of materials, it is however:

> "one of the most widely used of all analytical methods for the qualitative identification of elements having atomic numbers greater than oxygen (>8); in addition it is often employed for semi quantitative or quantitative elemental analyses as well " (Skoog and Leary 1992).

The widespread adoption of this form of instrumental analysis, in both industry and universities has lead to the application of X-ray fluorescence, and closely related techniques (such as electron microprobe analysis and energy dispersive microanalysis), to the resolution of research questions in the fields of archaeology and conservation (see Hall *et al.* 1973 for an early account).

X-ray fluorescence analysis is concerned with the excitation of a samples' constituent atoms (regardless of their state of chemical combination), by the removal of inner shell electrons, and the identification of characteristic emitted X-rays as the atom returns to ground state. As with any tool, the practitioner must have some understanding of the theoretical and practical limitations of the technique, and to this end X-ray fluorescence analysis is explained below.

4.2.1. Principles of the Technique: X-ray generation

Although the atoms in a sample can be directly excited by electrons, as in electron microprobe analysis (see below), in XRF analysis the sample is exposed to a beam of primary X-rays generated in an X-ray tube.

An X-ray tube consists of an evacuated chamber in which electrons from a heated cathode are accelerated towards a metal anode by a potential (measured in keV). Upon impact part of the energy of the electrons become X-rays: this is continuous radiation known as *Bremstrahlung*, or breaking energy. The intensity of the resulting X-rays is controlled by the size of the heating current across the cathode, and the energy (or wavelength - because of wave/particle duality) is determined by the accelerating voltage. This relationship can be expressed as:

$$\lambda_o = 12{,}398/V$$

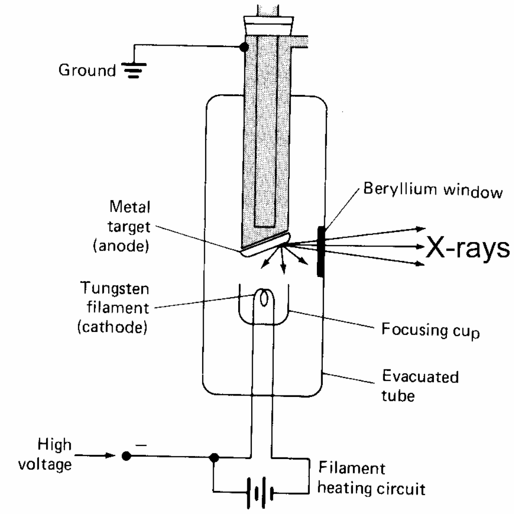
where: λ_o = short wavelength limit in Å

V = accelerating voltage in volts

(derived from the Duane-Hunt law, Skoog and Leary 1992, p 358).

Depending upon the metal target (anode) in the X-ray tube, one may get a line spectrum superimposed upon the continuum. X-ray line spectra are derived from energy transitions involving the innermost electron shells of an element: high energy electrons from the cathode eject electrons from the orbital closest to the nucleus of an atom forming excited ions. As electrons from the outer orbital undergo transitions to fill the vacancies in the inner orbitals, x-radiation is emitted.

The electronic transitions are directly related to the configuration of the atom, and are therefore characteristic of the element being excited. The spectral lines are termed K and L depending upon from which shell the transitions have taken place (elements with atomic numbers below 23 only produce a K series of lines). The minimum acceleration voltage required for the excitation of the lines of elements increases with the atomic number of the target material. The superimposition of spectral lines onto the continuum may need to be accounted for during the processing of detected spectra: it may also be a desired phenomena for excitation of a specific part of the spectrum.



Schematic of an X-ray tube.

Figure 4.1 schematic diagram of an X-ray tube, after Skoog and Leary 1992, figure 15-7, p 364)

The X-rays pass through a beryllium window towards the sample. Beryllium has good X-ray transmission properties because of its low atomic number. Depending upon the type of system in use (wavelength or energy dispersive, i.e. the detection method- see below), or the desired area of irradiation, the primary beam may have to be collimated between the X-ray tube and sample.

4.2.2 Interaction with the sample

When the primary X-ray beam impinges on the sample, a number of different phenomena take place.

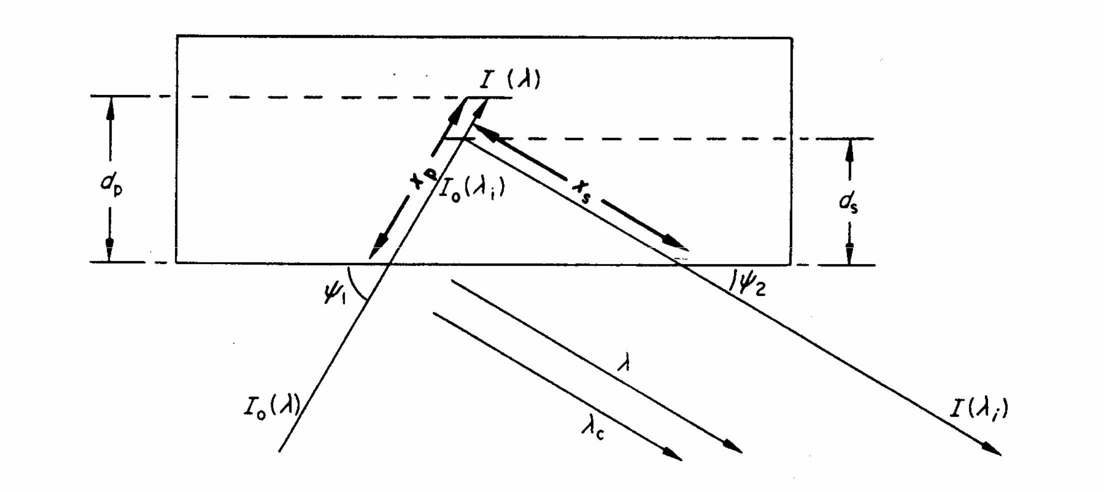


Figure 4.2 Primary beam interaction with the sample after Jenkins 1974 figure 3-3, p 40.

4.2.3 Scattering.

A proportion of the X-rays striking the sample become scattered, in one of two ways:

Coherent (Rayleigh) scattering is where the X-rays are elastically scattered, and the subsequently scattered ray retains the same wavelength and spectral lines characteristic of the primary beam (emergent beam λ in figure 4.2). This radiation will be detected.

Incoherent (Compton) scattering results in a ray of longer wavelength (lower energy) than the primary beam, giving rise to a broadened inelastic peak at the lower energy/higher wavelength side of the coherently scattered lines in the resulting spectra (emergent beam λ_C in figure 4.2).

4.2.4 Primary Absorption.

As an X-ray beam passes into a sample, its intensity is reduced as a consequence of absorption where an X-ray photon ejects an inner orbital electron to produce an excited ion. The greatest probability of absorption occurs when the energy of the photon is equal to the minimum energy required for the ejection of an electron from a particular atom. This optimum point is known as the Absorption edge, which is crucial in the excitation of the sample: the absorption edge is dependant on the electronic configuration of the stimulated atom; the actual energy required to reach the absorption edge of individual spectral lines increases with the atomic number the element concerned.

The attenuation of an X-ray beam as it passes through a material conforms to Beer's Law, which can be expressed as:

$$I(\lambda) = I_O \exp(-\mu\rho x)$$

where: $I(\lambda)$ = intensity of the beam

I_O = intensity of the primary beam

μ = mass absorption coefficient

ρ = density of the material

x = distance travelled

The mass absorption coefficient is a function of the wavelength of the incident beam and the atomic number of the material: in complex multi-element samples the mass absorption coefficient is the sum of the individual values weighted according to their relative concentrations.

4.2.5 Fluorescence.

The excited ion will return to its ground state by a series of electronic transitions like those involved in primary beam generation (see above). The transitions are dependent upon, and also characteristic of, the configuration of the excited ion, and result in the emission of secondary X-rays. The energy/wavelength of the emitted X-rays are related to the electron shells involved in the transitions: the principle shells K, L M etc. correspond to the energy levels in the Bohr model of the atom. The ejection of electrons from the inner shell result in two resolvable emission lines (K_α and K_β), of which the former is the most intense and of greater energy. Emission lines from the next shell (the second or L shell) are again of lower intensity and energy, resolvable into three spectral lines (L_α, L_β and L_γ) (Jenkins 1974).

4.2.6 Secondary absorption and escape depth.

The secondary X-ray beam is also subject to attenuation according to Beer's Law as it leaves its source. There comes a depth beyond the sample's surface when the incident beam no longer generates detectable fluorescence due to the combined affects of primary and secondary absorption, and this is known as the escape depth. For quantitative analysis it is important that the sample is thicker than the critical depth (Jenkins 1974), it can be calculated by:

$d_S = x_S \sin \psi_2$

where: d_S = escape depth

x_S = effective path length

ψ_2 = take off angle of secondary radiation

(also see figure 4.2)

4.2.7 Enhancement.

Whilst direct excitation of the sample is predominantly a consequence of radiation from the primary beam, additional fluorescence can be stimulated, known as secondary and tertiary fluorescence (Jenkins 1974, p 43). The enhancement effect occurs when the emitted radiation from an inner shell ionisation event excites other atoms within the sample (secondary fluorescence) which may in turn stimulate further fluorescence (tertiary fluorescence).

4.2.8 Auger Process and fluorescent yield.

In addition to the emission of x-radiation, an alternative de-excitation process can occur, in which the emitted photon of x-radiation ejects another electron instead of leaving the atom: an event known as auger emission. The fluorescent yield is the relative efficiency of the two de-excitation processes for a given energy level, and can be expressed:

$\omega_K = \sum (n)_K / N_K$

where: ω_K = fluorescent yield of an elements K shell

n = number of X-ray photons emitted

N = total number of vacancies

4.2.9 Detection of characteristic X-rays: energy dispersive systems

The detection of the secondary X-ray beam is essentially what defines the difference between the two XRF techniques in widespread use. Energy dispersive XRF is where the photons are identified according to their respective energies, the other technique is wavelength dispersive XRF, where the fluorescent x-radiation is characterised in terms of its wavelengths. The detection methods have implications for the geometry, detection, qualification and quantification of the results.

Energy dispersive systems use semi-conductor detectors, which are based upon either a lithium drifted silicon crystal or a lithium drifted germanium crystal (Skoog and Leary 1992). The former is constructed out of a wafer of crystalline silicon which consists of three zones: adjacent to the X-ray source a layer of p - type semi-conducting silicon coated with gold for electrical contact and protected by a beryllium window; a central intrinsic zone; and an n -type layer which is coated with aluminium (Skoog and Leary 1992). When an X-ray photon hits the detector, it is absorbed into the crystal with the creation of a cloud of electron pairs, each of which requires 3.8 eV to form. The number of these electron pairs is proportional to the energy of the incident photon:

$n = E / \varepsilon$**Error! Bookmark not defined.**

where: n = number of electron pairs

E = energy of the incident electron

ε**Error! Bookmark not defined.** = average energy required to generate one electron pair

(Jenkins 1974)

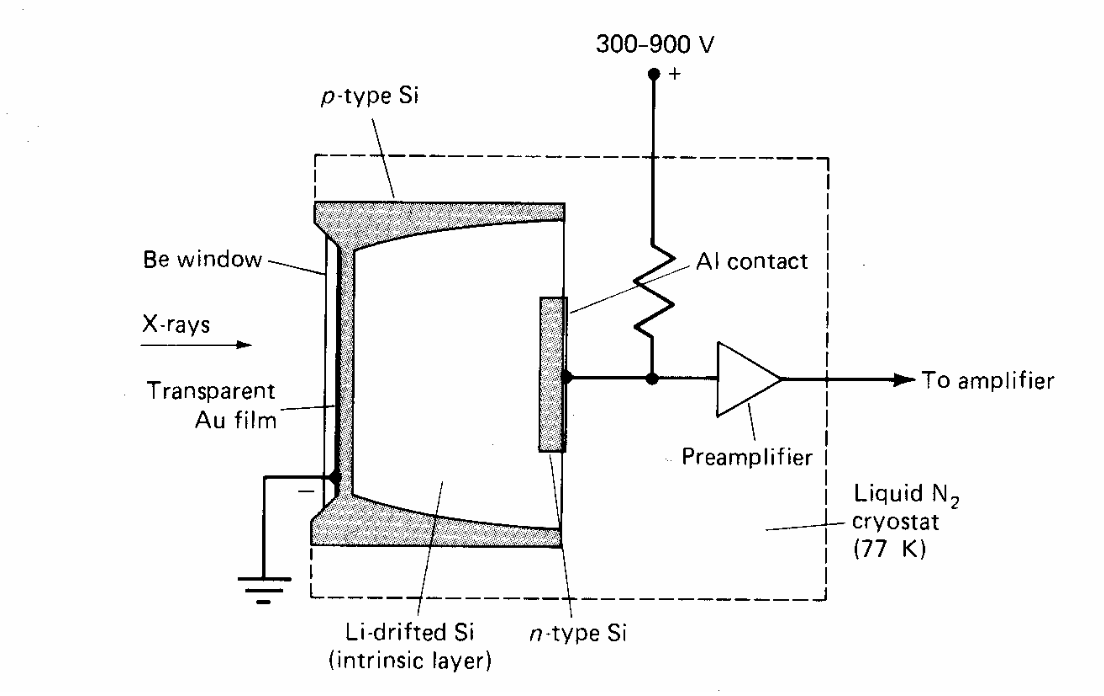


Figure 4.3 Schematic diagram of a lithium drifted silicon detector, after Skoog and Leary 1992, figure 15-12, p 371

A voltage is applied across the crystal, and the electrons produced by photon absorption are attracted towards the positive terminal forming a current pulse. The current passes through a preamplifier to an amplifier. The current pulse represents a single count defined by its magnitude which is proportional to the photon's energy. Each current pulse is sorted according to its size in a multichannel analyser. The data is displayed and stored as a spectra, in which the x-axis is the increasing energy values and the y-axis shows the relative intensity. The detector and preamplifier are maintained in a cryogenic state during use to limit the amount of electronic noise in the system and prevent the lithium diffusing out: this is effected using liquid nitrogen.

4.2.10 Qualification and Quantification of Results.

The various peaks on the spectra need to be associated with the specific spectral lines of individual elements in the sample. This is possible since the K_α, K_β etc. energies for each element are established and tabulated (for example see Jenkins 1974, Appendices I-III). The intensities of individual lines can be used to establish the amount of that element in the sample. The peak identification and processing associated with the calculation of concentrations are performed automatically by computer systems, which also control the detector and multichannel analyser. A number of factors are involved in these processes.

4.2.11 Resolution.

The resolution of the detector is defined as the width of an energy peak at half its maximum intensity (Jenkins 1974, p 72). The resolution is important in being able to distinguish and separate individual peaks: peak overlap can hinder quantification. Resolution in an energy dispersive system is related to energy of the incident photons and amount of electronic noise in the system: the resolution improves with decrease in wavelength. (Jenkins 1974, p 92).

4.2.12 Identification.

If the presence of an element is suspected in an analysed sample, because of a tentatively identified K_α, line, a corresponding, but less intense K_β line must also be present in the spectra.

4.2.13 Background.

Before the net intensities of individual peaks are calculated, the background of continuous radiation must be removed: this is achieved with the application of a computer "stripping" programme which creates a clean base line beneath the peaks by interpolating between a series of predetermined points selected to cut out as much of the background radiation as possible. Clearly, for the fluorescence of a particular spectral line to be detected, it must emerge sufficiently above the background in order to survive the stripping routine.

4.2.14 Intensity.

The intensity of a peak in energy dispersive systems is not represented by the peak height, but the area of the peak. However, because of differential primary and secondary absorption, the relative intensities do not simply correspond to elemental concentrations in the sample.

4.2.15 Calibration.

In order that one might sufficiently compensate for the matrix effects outlined above, and most accurately correlate intensity with concentration, then the spectra of known standards are employed. The accuracy of determining concentrations empirically, with the use of standards improves with the use of a standard that closely matches the unknown in terms of both components and their concentration. A similar composition will ensure that the absorption and enhancement effects are of a comparable nature and magnitude.

4.2.16 Wavelength Dispersive Systems.

Wavelength dispersive systems identify the characteristic radiation on the basis of the wavelength rather than energy of the fluorescent X-rays.

The x-radiation emitted by an excited sample is broken up into its constituent wavelengths by being diffracted through a crystal. This process is founded upon Braggs Law which states:

$$n\lambda = 2d \sin\theta$$

where:
n = an integer
λ = wavelength of the radiation
d = interplanar distance of the crystal
θ = angle of incidence

The angle of incidence and d – spacing of the crystal are controllable elements within the geometry of the spectrometer. The location of the detector in relation to the diffracting crystal determines which wavelength of energy is being detected. Clearly the properties of the crystal are crucial: a larger d – spacing equates to a greater range of wavelengths, but lower values of dispersion. Systems often include more than one crystal to enable a broader range of wavelengths to be detected (Skoog and Leary 1992, p 367).

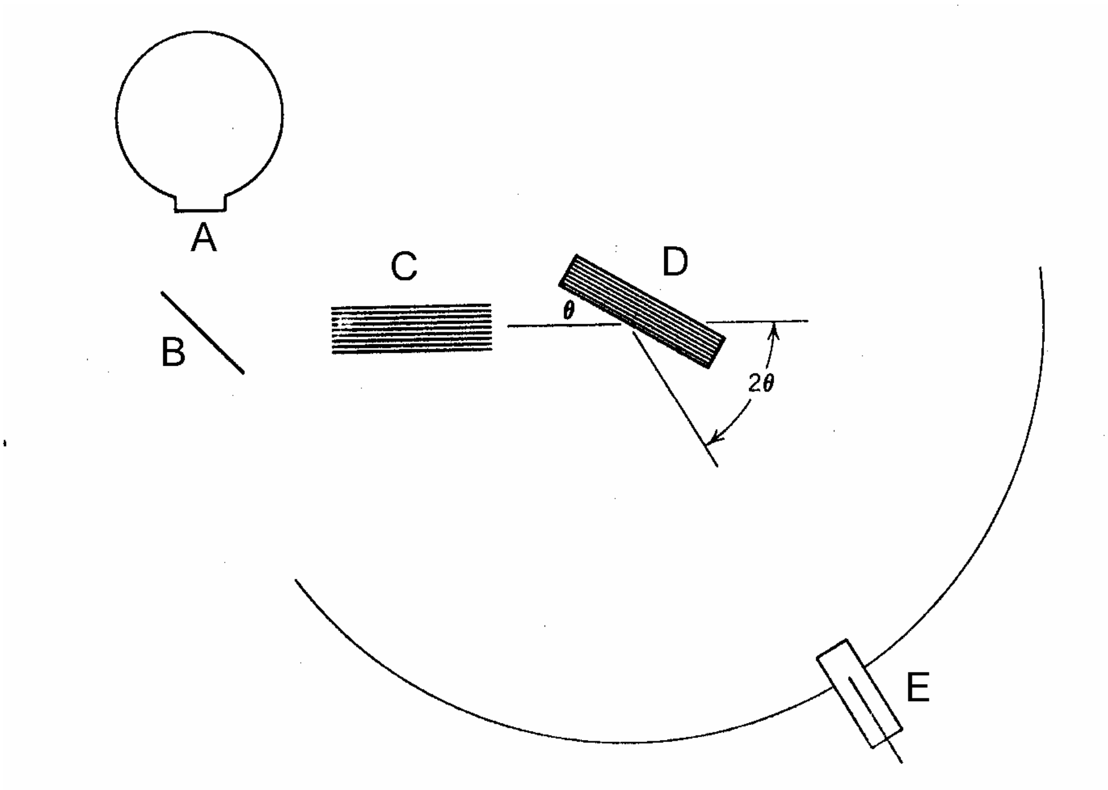


Figure 4.4. Schematic representation of wavelength dispersive XRF (after Birks 1963, Figure 2.2, p 8). A, X-ray source; B, specimen; C, collimator; D, diffracting crystal; E, detector.

4.2.17 Detection in wavelength dispersive systems.

The individual wavelengths are detected in a gas-filled proportional counter. X-rays pass through a window (of beryllium or Mylar) into an inert gas containing chamber. The X-ray photons ionise the gas, generating a large number of electrons and positive gaseous ions. The electrons are drawn towards a wire anode in the centre of the chamber, whilst the cations are attracted to the cathode detector body causing a measurable pulse. Each ion-pair (i.e. an electron and a positive gaseous ion) is generated per 25 –30 eV of photon energy. The amplitude of the pulse is therefore proportional to the X-ray energy. The signal is amplified by maintaining a high potential across the detector: the electrons are accelerated towards the anode causing secondary ionisation creating an avalanche of secondary electrons.

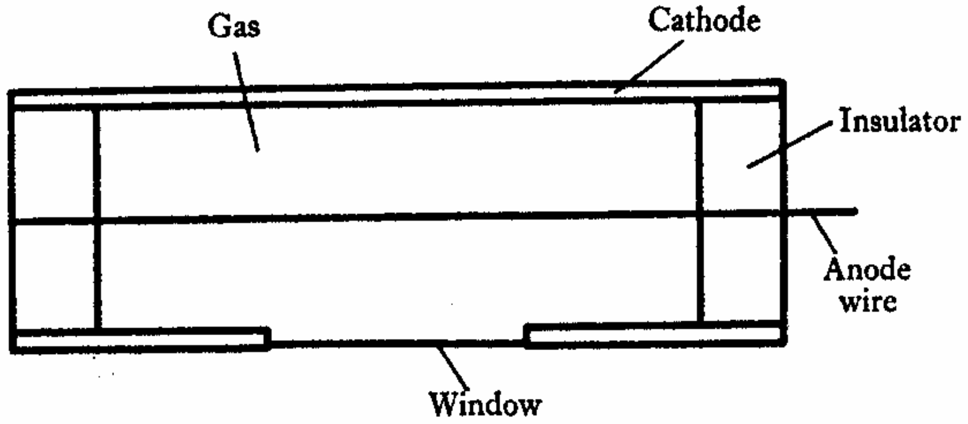


Figure 4.5 Schematic diagram of gas proportional counter (after Birks 1963, Figure 7.1, p 94).

4.2.18 Energy Dispersive and Wavelength Dispersive Systems.

The internal geometries of the systems are quite different, as are the demands placed upon the fluorescence efficiency by the respective detectors. In practice this means that the higher collection efficiency of energy dispersive systems means a lower beam current is required in electron beam systems (Reed 1996). Wavelength dispersive systems give better peak to background ratio and better resolution of closely spaced spectral lines, eliminating the peak-overlap problems experienced in energy dispersive systems. However, several recent studies (Verità *et al.* 1994, Potts *et al.* 1985 and Dunham and Wilkinson 1978) have demonstrated that although wavelength dispersive systems have lower detection limits, for the study of the components of ancient glasses and silicate rocks, the two techniques are of comparable sensitivity, precision and accuracy (ibid and Pollard and Heron 1996, p 47). Henderson (1988b, p 80) also contrasts the relative efficiencies of the two types of detector in their lower limits of detection, noting that EPMA is more efficient at detecting low atomic weight elements, whereas EDXRF is better for the heavier transition metals.

4.3 Energy Dispersive X-Ray MicroAnalysis (EDXMA).

The use of the electron beam within an scanning electron microscope (SEM) is sometimes referred to generically as electron microprobe analysis (e.g. Reed 1996), however this term is also used to specifically mean a system including a wavelength dispersive detector (see electron microprobe analysis below). The system described here employs an energy dispersive detector, and is therefore referred to as energy dispersive X-ray microanalysis. The use of an electron microscope as an analytical tool has many similarities with the X-ray fluorescence analysis described above, but also a number of important differences, which enable the researcher to recover different types of data.

4.3.1 Imaging.

A SEM was employed to examine the microstructure of the glasses and attempt to elucidate aspects of the various glasses' technologies by qualitative analysis of inclusions and inhomogeneities in the samples. An SEM employs electrons instead of visible light to construct an image of the sample's surface. An electron beam is generated, focussed and swept in a raster pattern over the surface of a sample. A number of signals are produced from the surface, including: secondary electrons, backscattered electrons, Auger eletrons and X-ray fluorescence. The secondary and backscattered electrons are detected and their intensity used to control a spot on a cathode ray tube display which construes the image. The magnification range is 10 x to 100,000x , depending upon the instrument (Skoog and Leary 1992, p 396).

In addition to greater powers of magnification and resolution over light microscopy, an SEM image can offer information in addition to surface topography. When in “backscatter” mode, the image is constructed using reflected or backscattered electrons, which shows the relative atomic weight of the area under examination. Discreet zones of differing chemical composition can be clearly identified, and thereafter analysed using the Energy Dispersive facility on the SEM. The analysis is similar to XRF analysis, and is described below. The small beam size (1 μm diameter (Reed 1996)) permits the selective analysis of a sample's surface such as unfused components or opacifying crystals within the glass matrix.

4.3.2 X-ray generation.

As described above, X-ray fluorescence can be achieved by exciting a sample's atoms using an incident beam of X-rays. In addition one can excite atoms using an electron beam, in a manner similar to that employed for generation of the incident X-ray beam in XRF analysis. Within the EDXRMA system the electron beam is generated by an electron gun positioned vertically above the sample stage.

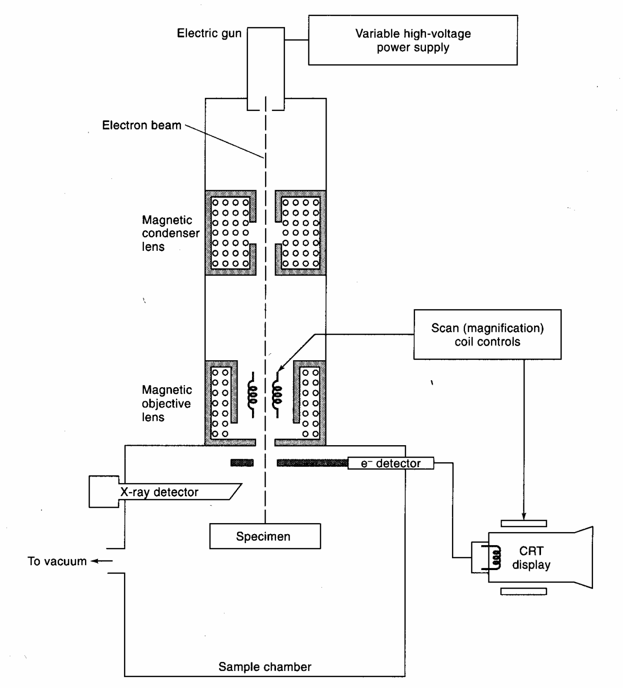


Figure 4.6 Schematic diagram of an SEM with an Energy Dispersive detector for analysis (after Skoog and Leary 1992, Figure 16-11, p 395).

Thermionically generated electrons are accelerated towards an anode plate with an aperture, through which they pass, towards the specimen. The beam of electrons is focused upon the sample using magnetic lenses. The electron gun and column is held under vacuum to prevent oxidation of the tungsten filament in the gun, and usually the sample chamber is also under vacuum to avoid absorption of fluorescent X-rays by air.

4.3.3 Interaction with the sample.

The electron beam strikes the surface of the sample and causes inner shell ionisation dependant upon the energy of the beam (determined by the accelerating voltage in the gun) and the absorption edges of elements in the sample. The beam of electrons and subsequent X-ray fluorescence are subject to the same attenuation processes from matrix effects as XRF analysis.

4.3.4 Detection.

The X-rays are detected using an energy dispersive detector, as described above.

4.3.5 Qualification and Quantification of results.

The peaks in the X-ray spectra are identified according to their energies, and may be quantified by comparison to known standards. In the application here, however, the analyses were standardless and semi-quantitative- performed for differentiation and identification of inhomogeneities in the samples. For the most part the analyses were reviewed by simply examining the resultant spectra and identifying distinguishing peaks on the spectra. Semi-quantitative overall results were calculated using the computer software within the operating system. Corrections for matrix effects are applied using the "ZAF" programme, which involves separate correction factors dependant upon atomic number, absorption and fluorescence of the identified components.

4.4 Electron Microprobe Analysis.

Electron microprobe analysis is the oldest technique of chemical analysis reliant upon the interaction of an electron beam with a sample and the identification of the resultant fluorescent radiation. Like an SEM, the electron microprobe uses the interaction between an electron beam and a sample’s surface. Although an electron microprobe may be an SEM (see above), typically it is dedicated to instrumental analysis, in which the location of the analysing beam of electrons is determined using visible light optics.

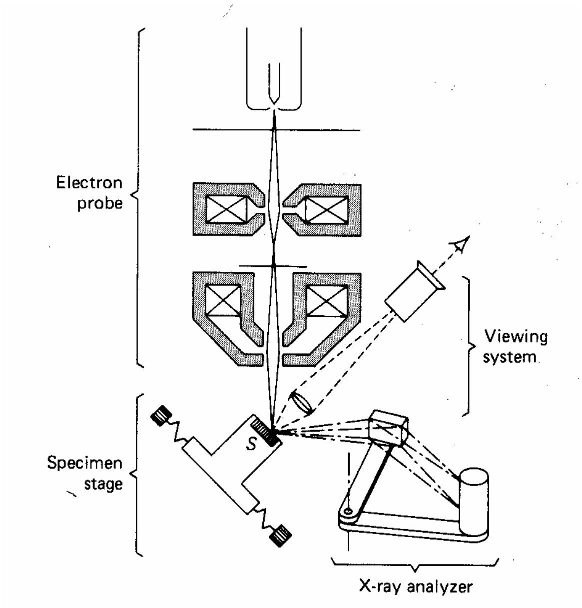


Figure 4.7 Schematic diagram of an electron microprobe: a wavelength dispersive detecting system and light optics viewing system (after Skoog and Leary 1992, Figure 15-19, p 381).

The interaction between the electron beam and the surface of the sample is subject to similar attenuation phenomenon due to matrix effects like EDXMA and XRF as described above.

Previous studies have identified particular problems experienced with the analysis of samples containing sodium and other volatile elements (Henderson 1988, p 78 and references). These problems are associated with either the localised heating of the sample surface, causing sodium migration away from the area being analysed, or conversely, the increase in measured sodium counts due to high temperatures and surface charging drawing sodium ions to the surface being analysed (particularly in mixed-alkali glasses). These phenomenon can be avoided by defocusing the electron beam in order that it is some 80 µm in diameter, and ensuring that the counting time does not exceed the critical temperature build up at the point being analysed. These corrective procedures were established by Henderson (ibid.), and were adopted here. For the specific operating conditions employed, see below.

4.5 X-ray Diffraction.

X-ray diffraction analysis is a long established procedure for investigating the crystalline structure of materials (Skoog and Leary 1992, p 378). This technique is not employed to study glasses, since they are non-crystalline solids, but is very useful for identifying crystalline inclusions in glassy matrices (such as opacifiers, colourants and weathering products).

The technique relies upon the reflective nature of surfaces within crystals, and the consistent order in lattice structure which crystals possess. The regular interplanar spacing in crystals is one of the defining characteristics of individual species. The technique employs an incident beam of X-rays upon the sample, and relies upon each lattice surface reflecting a proportion of the X-rays. At a certain angle of incidence, X-rays of a given wavelength scattered by parallel planes of atoms are in phase and a strong reflection takes place. When the reflected X-rays are in phase, the geometry of the system is conforming to Bragg’s law (see above), which generates a unique diffraction pattern, permitting the calculation of the d-spacing, or interplanar spacing of the crystal.

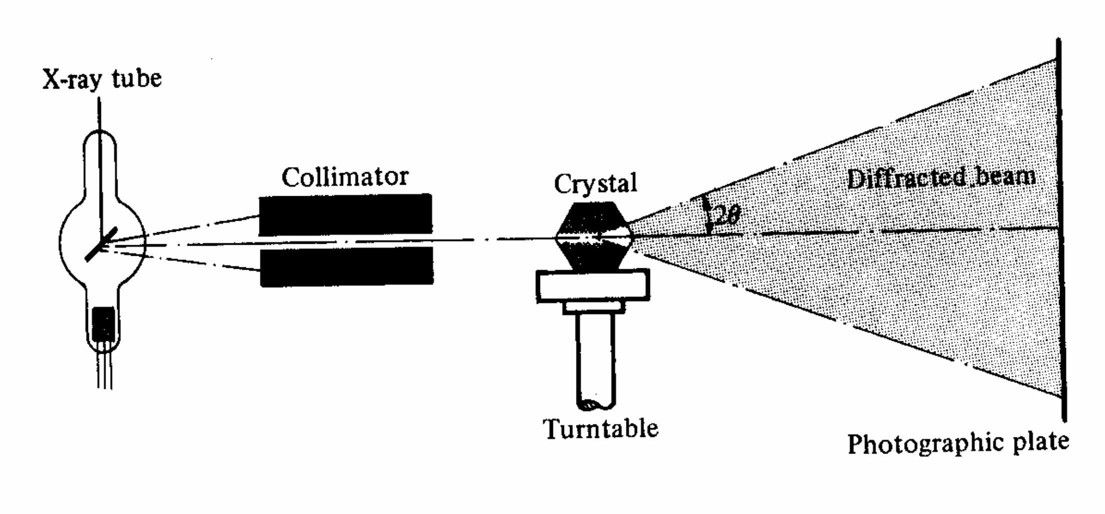


Figure 4.8 Schematic diagram of X-ray diffraction to determine crystal structure (after Anderson *et al.* 1991, Figure 6-15, p 105).

In practice, the sample is often ground up into a powder: of the huge number of crystals a number will be orientated such that they will conform to the Bragg condition for in-phase diffraction of the incident beam. The sample is typically mounted in a circular instrument, which records the location of the pattern either on photographic film arranged around the inside of the instrument (a Debye-Scherrer powder camera) or in an automatic system in which a detector scans for individual diffraction lines. Both the line location and relative intensities are characteristic of the crystal structure. With the traditional Debye-Scherrer camera system, the individual diffracted lines have to be measured from the photographic film in order to calculate the d- spacings, which are then compared to published data. Automated systems will perform the calculations and identify the crystalline components from computer-held libraries of data on crystalline structures. When standards are run alongside unknowns, then the automated system can be fully quantitative, but in the application to this project only the identification of crystal species was considered necessary.

4.6 Operating Conditions Employed

The sample preparation and operating conditions for each technique are specified below, alongside calculations of accuracy and precision for the quantitative methods (i.e. XRF and Electron Microprobe Analysis). Where necessary, a number of experiments were undertaken to ensure that the most appropriate procedures were adopted.

4.7 Experiments to establish ideal instrument and operating conditions for the analysis of ancient glasses I: XRF.

A number experiments were undertaken to identify the most suitable operating conditions for the XRF analyses. These experiments sought to ascertain the ideal:

accelerating voltage
beam current
primary X-ray beam diameter
counting time
background files

to establish the accuracy and precision of the technique when applied to suitable standards.

The quality of analyses are judged on the basis of several criteria, including: the peak:background ratio (a measure of the distinctiveness of a characteristic peak above the background x-radiation); the count rate recorded during the capture of a spectra (i.e. the number of X-ray photons entering the detector during any given period) and the capacity of the system to identify and detect the characteristic radiation of trace elements (measured in net intensity values).

The X-ray fluorescence system employed at Nottingham is a Philips PV 9500/70 which consists of a 9500 XRF subsystem and a 9100/70 analyser. This uses an energy-dispersive detector (a lithium-drifted silicon crystal) with a signal amplifier, multi-channel analyser (4K memory) and computer operating system. The 9500 subsystem operates in the ranges: 10 – 500 μA, 5 – 50 keV. The sample chamber is relatively large (130 mm diameter, 100 mm deep) which can be evacuated for the detection of low energy x-radiation. The X-rays were generated in a cathode ray tube with a rhodium target. The two principle spectral lines of rhodium ($K\alpha$ and $L\alpha$ at 20.165 and 2.69 keV respectively), make a dominant contribution to the low energy part of the spectrum making it suitable for use in the analysis of complex glasses (Henderson 1982, p 103).

A number of glass standards were employed, including Corning Standards A – D supplied by Dr Robert Brill of the Corning Museum of Glass, from batches produced for inter-laboratory tests (Brill 1972). The recommended compositions for these glasses are taken from Brill 1999 Vol II, p 544, except for SiO_2, which is taken from Brill 1972. The later recommended compositions do not give a value for SiO_2, which is calculated by difference from Optical Emission Spectroscopy and Inductively Coupled Plasma spectroscopy (Brill 1999b, Appendix A). The value by difference is rejected in favour of the directly measured value in the 1972 figures. The standards were mounted in epoxy resin blocks and polished with progressively finer carborundum papers and finished with 8 and 1 μm diamond paste polishing compound to ensure a flat unweathered surface for analysis. Jenkins (1977, p 105) recommends that surface roughness does not exceed 50 μm peak to peak for atomic number elements above Z = 25, and 10 μm for elements around Z = 12. For preparation of the archaeological samples, see below.

Calibration: the instrument was initially calibrated using an aluminium/copper standard, (with $K\alpha$ peaks at 1.486 and 8.040 keV respectively). This routine is performed automatically and is periodically repeated to identify instrumental shift. Essentially it ensures that the designation of specific photon energies is correct. Further calibration against complex glass standards was performed after collection of the spectra.

Since ancient glasses have complex compositions, and the operating system for the machine employed was relatively slow, it was decided to select a small number of elements to act as markers for the range of components being studied. These were sodium, potassium, iron and lead. Sodium is the lowest atomic weight element under examination, and its Kα energy line (1.041 keV) is the longest wavelength/lowest energy reliably detected using EDS systems. Potassium (Kα = 3.312 keV) is representative of an element from the 2 - 4 keV range, which is crowded with peaks of interest. Iron was chosen as an example of a mid-table transition metal (like manganese, cobalt or copper) with its Kα line at 6.398 keV. Lead is the highest atomic weight element under consideration and its Lα line is at 10.550 keV.

Figure 4.9 XRF Operating system.

Figure 4.10 XRF Machine

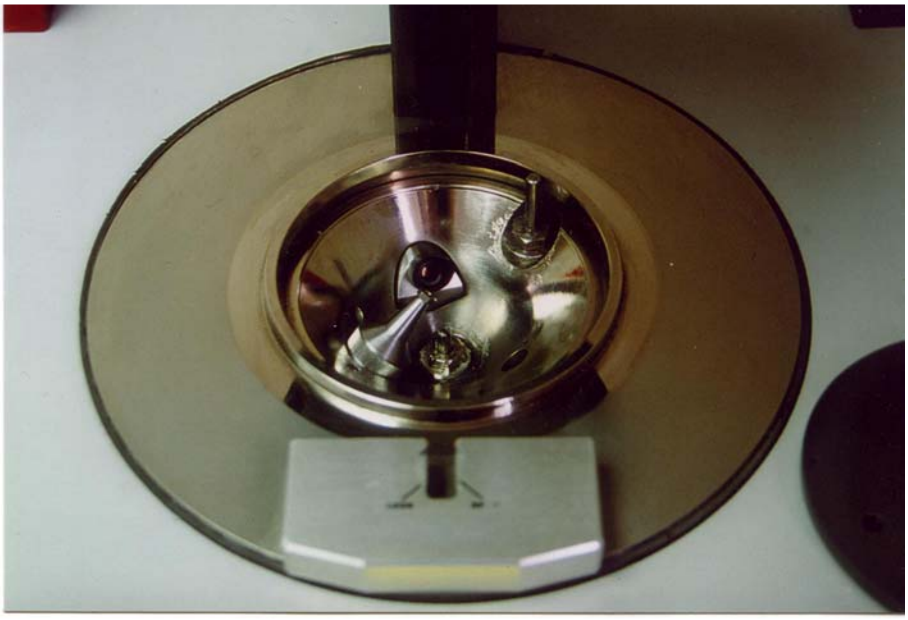


Figure 4.11 XRF sample chamber

4.7.1 X-ray tube potential.

To excite any single element, then an accelerating voltage should be greater than the absorption edge of the element. To do so most efficiently, then the voltage should be some 2.5 to 3 times the absorption edge. However, with a multi-element sample a compromise between the requirements for efficient excitation of a range of absorption edges is required. The manual accompanying the machine used (EDAX, 1983) recommends the following equation as a rule of thumb:

$$\text{keV} = 3/4.\text{El} + 3/2.\text{Eh}$$

where: keV is the accelerating voltage

El is the lowest energy absorption edge of any of the elements being detected

Eh is the highest energy absorption edge of any of the elements being detected

In the case of the ancient glasses being analysed, with reference to the Corning glasses A - D, sodium to lead represents a wide range of absorption edges for many of the components under consideration (i.e. an energy range of 1.041 - 10.55 keV).

therefore:

$$\text{keV} = (3/4 \times 1.041) + (3/2 \times 10.55)$$

$$\text{keV} = 16.60575$$

However, it is also noted that where one has variable concentrations of the different elements one should weight the accelerating voltage in favour of the minor component, in order to efficiently excite, and therefore detect its presence. When dealing with the complex multi-element glasses produced in antiquity it is not a simple matter to establish an ideal set of conditions suitable for all glass types. Several experiments were undertaken in an attempt to empirically establish appropriate accelerating voltages. Corning standards B and C were used since they represent complex glasses with soda-lime silica and lead-rich glasses respectively.

4.7.2 Relationship between peak:background ratio and accelerating voltage.

The peak:background ratio for sodium, potassium, iron and lead were recorded from analyses using 10 - 40 keV at 5 keV intervals, with a beam current of 500 μA , employing a 1 mm collimator for 1000 live seconds.

	10 keV	15 keV	20 keV	25 keV	30 keV	35 keV	40 keV
Na	8.16	8.75	10.2	6.65	4.08	2.5	1.72
K	5.07	5.53	6.47	6.73	5.89	5.45	4.02
Fe	2.33	4.58	5.1	5.24	5.61	5.44	5.88
Pb	0	1.06	2.46	3.8	4.85	5.17	5.9

Table 4.1 showing peak:background ratio in relation to accelerating voltage

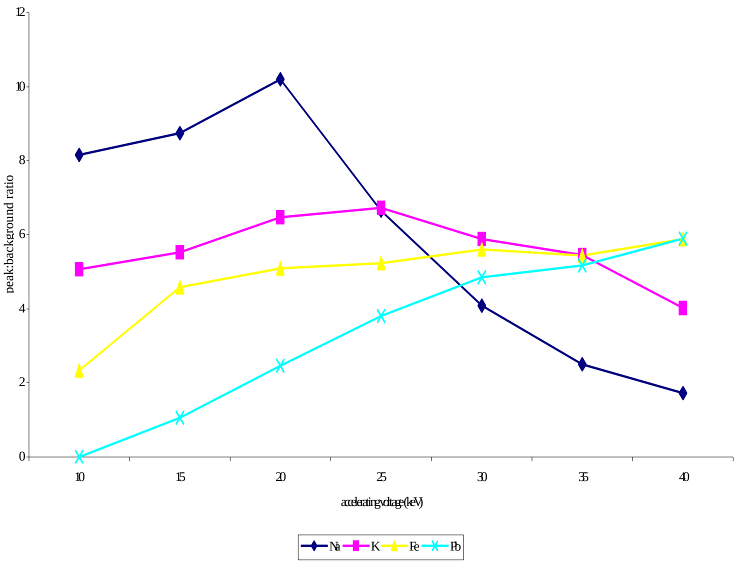


Figure 4.12 Chart showing peak:background ratio in relation to accelerating voltage.

Sodium clearly benefits from lower accelerating voltages than the other elements examined, with an optimum at a surprisingly high voltage of 20 keV, there is a rapid fall off in the ratio with increased rates. Potassium peaks at 25 keV, but does not undergo a rapid reduction in ratio at higher voltages. Iron has an optimum excitation voltage in this matrix at 30 keV and is stable at rates higher than this. Unsurprisingly lead is preferentially stimulated at the highest rates (in this case 40 keV), however its improvement in ratio becomes less rapid above 30 keV. Clearly no single accelerating voltage is ideal for all the elements, but a voltage in the region of 25 - 30 keV appears suitable.

4.7.3 Beam current: Relationship between peak:background ratio and beam current.

In order to explore the effect of varying the beam current upon the peak:background ratio, the beam current was gradually increased through the intervals 10, 50, 100 200, 300, 400 and 500 µA. A 3 mm collimator was fitted for all these analyses, with a counting time of 1000 seconds and accelerating voltage of 30 keV.

	10 µA	50 µA	100 µA	200 µA	300 µA	400 µA	500 µA
Na	3.46	3.47	3.24	3.64	3.62	3.69	3.73
K	5.71	5.29	5.79	5.67	5.54	5.65	5.57
Fe	5.75	5.65	5.73	5.55	5.6	5.6	5.54
Pb	5.67	5.13	5.19	5.35	5.05	4.88	4.82

Table 4.2 showing peak:background ratio in relation to beam current.

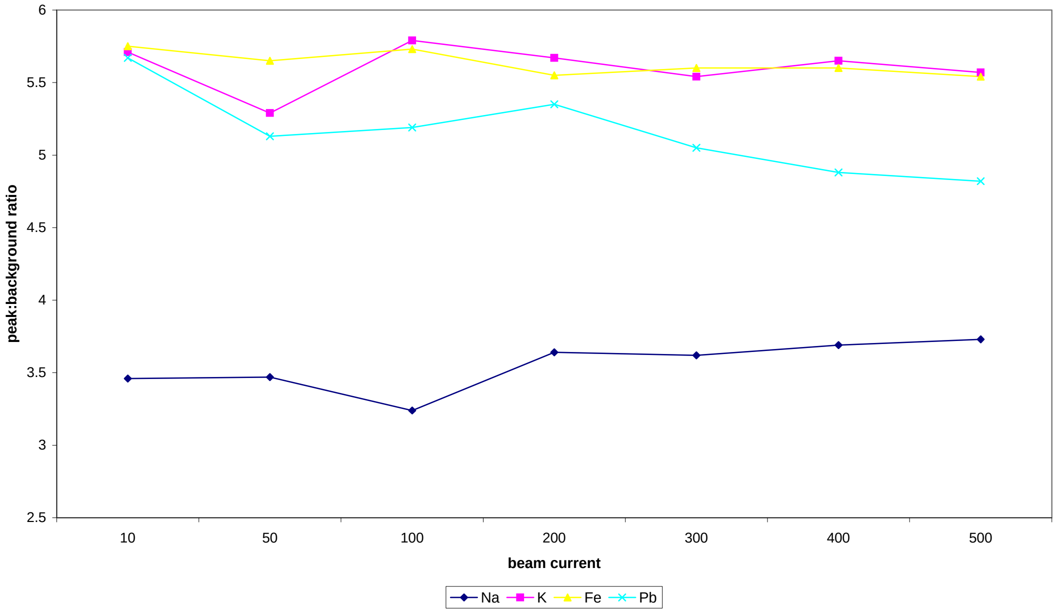


Figure 4.13 Chart showing variation in peak:background ratio in relation to beam current.

All the elements experience some instability over the 50 – 200 µA range. When the beam is above 200 µA, both potassium and iron are stable, but lead and sodium experience diverging trajectories with a gradual improvement in the ratio for sodium, and an overall decline for lead. Since sodium’s characteristic radiation is of low energy/long wavelength, and is therefore more readily absorbed and less easily detected, then the higher beam current should be selected.

4.7.4 Beam and the count rate.

Ideally the count rate should be as high as possible in order to give the best possible chance of achieving good peak shapes for quantification (i.e. a greater number of counts improves the statistics for quantification). With the system employed, the saturation point for the detector is a count rate of between 10 - 15,000 cps: this is the point at which the detector is experiencing a high proportion of dead time since it is being bombarded by more X-ray photons than it can deal with, giving rise to loss of resolution. In order to ensure that the selected conditions maximised the count rate without saturating the detector, then the count rate was noted through a range of beam current settings. The collimator size was also changed to demonstrate that this too can effect the count rate.

The primary beam of X-rays is directed towards the sample through a collimator body with an internal diameter of approximately 5 mm. The collimator body has an internal thread which was cut to fit variable collimators, permitting the reduction in size of the beam to diameters of 1, 1.5, 2, 2.5 and 3 mm. The collimators are stainless steel machine screws with a hole drilled down the centre, fabricated for the purpose of this project. The location of the beam and sample position are explained elsewhere (see below).

It is important to note that beam collimation is essential in order to analyse discrete portions of a sample's surface. Several experiments were undertaken to establish the impact of changing the primary beam diameter using collimators.

Analyses were undertaken using no collimator, the collimator body alone (i.e. 5 mm), and each of the collimators, in which the observed count rate was noted. The count rate fluctuates for any given set of conditions, but becomes relatively stable after a short period of time, the recorded count rate in the tables below reflect the approximate rate observed for those conditions. The experiment was repeated using Corning standards B and C, to illustrate the higher count rate for lead glasses (Corning C) compared with soda-lime-silica glasses (Corning B).

The count rate increases with both beam diameter and beam current. In terms of increased count rates, as large a collimated beam as possible should be employed: even with the 3 mm collimator in place, a lead – rich glass and a maximum beam current (i.e. 500 μA), then count rate does not approach the saturation point of 10 – 15,000+ cps.

Corning C	10 μA	50 μA	100 μA	200 μA	300 μA	400 μA	500 μA
No collimator body	2700	12500	24000	44000	60000	76000	90000
collimator body	350	1450	2800	5400	7500	10000	12000
3 mm collimator	150	750	1400	2750	3800	5100	6100
2.5 mm collimator	120	500	1000	1900	2600	3500	3900
2 mm collimator	80	300	600	1200	1750	2250	2700
1.5 mm collimator	40	200	350	700	950	1250	1450
1 mm collimator	25	80	150	300	400	500	650

Corning B	10 µA	50 µA	100 µA	200 µA	300 µA	400 µA	500 µA
No collimator body	2200	10000	19000	36000	48500	62500	70500
collimator body	200	1000	1900	3600	5000	6900	7800
3 mm collimator	120	450	1000	1900	2600	3400	3900
2.5 mm collimator	80	350	700	1300	1800	2400	2700
2 mm collimator	50	200	400	850	1150	1500	1800
1.5 mm collimator	30	120	250	450	650	850	1000
1 mm collimator	20	60	100	200	300	350	450

Tables 4.3 and 4.4 showing count rate in relation to beam current and primary beam diameter

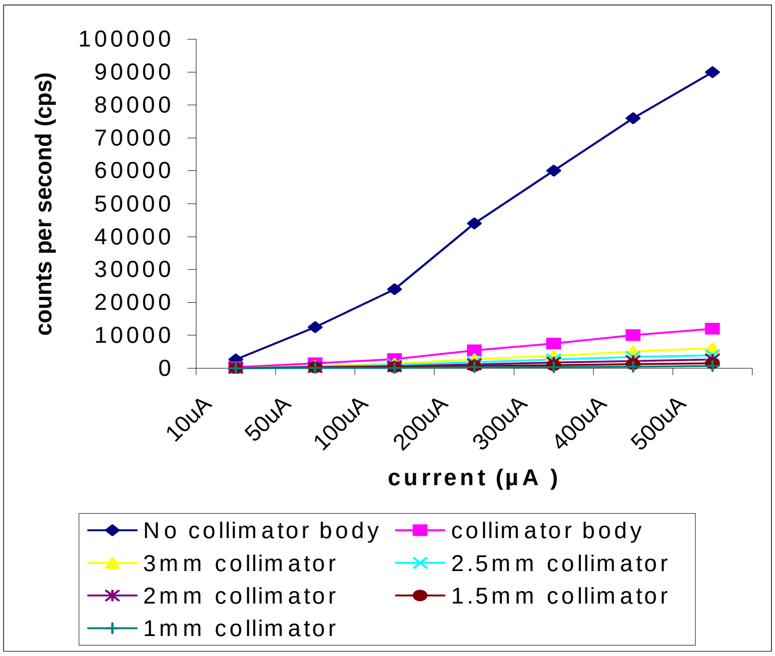


Figure 4.14 Chart showing impact of varying beam diameter and current: detector saturation is reached at 15,000 counts per second, using Corning standard C.

All analyses employed an accelerating voltage of 30 keV. Note the increased count rates for Corning C in comparison with Corning B for identical conditions: this is due to the high lead content of Corning C.

The saturation point is only achieved using an uncollimated beam, or with collimator body alone fitted. The graph below shows how the count rate increases with beam current for all beam diameters. Given that a collimated beam is to be applied for all analyses, then the maximum beam current of 500 μA can be safely used for all beam diameters up to 3 mm.

4.7.5 Primary X-ray beam diameter

Beam collimation and peak:background ratio

The peak to background ratio was noted during the analysis of Corning B, at 30 keV, 500 μA for 1000 seconds.

	1 mm	1.5 mm	2 mm	2.5 mm	3 mm	5 mm
Na	3.88	3.91	3.88	3.08	3.11	3.63
K	5.94	6.17	5.8	4.36	4.36	4.88
Fe	5.64	5.4	5.43	4.33	4.42	5.02
Pb	5.08	5.14	4.84	4.4	4.4	4.63

Table 4.5 showing peak:background ratio in relation to beam diameter.

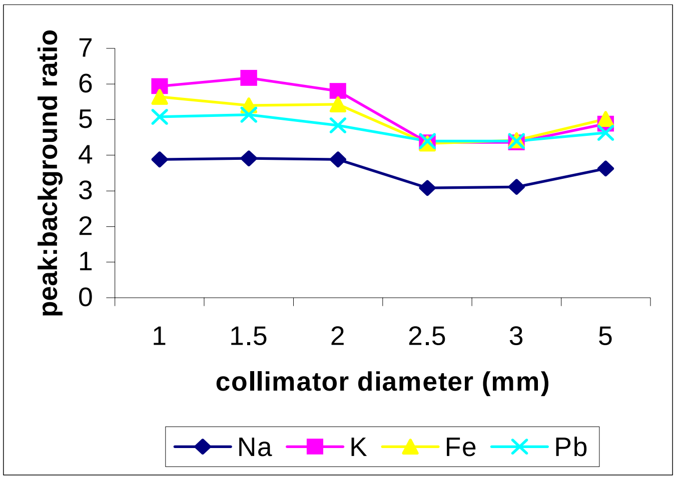


Figure 4.15 Chart showing peak:background ratio in relation to primary beam diameter.

All of the elements experience a similar variation in peak:background ratio, with a reduction in the ratio when the beam current is greater than 2 mm in diameter. For the purposes of this study, (the analyses include the examination of narrow decoration on beads and vessel bodies,) a small beam diameter is preferred. Although a larger diameter would give a greater count rate, and therefore lend itself to better statistics during quantification for any given analysis time, this experiment does demonstrate that there is no systematic deterioration in analytical quality as a consequence of reducing the primary beam diameter.

In order to ensure that the pattern observed above is not simply the product of random variation in the analysis, the measurement of the peak:background ratio for the 1 mm collimator was subsequently repeated five times under the same conditions. The results are tabulated below and displayed on the chart.

	1	2	3	4	5	range	average	stnd. dev.
Na	4.38	3.99	3.63	4.3	4.21	3.63-4.30	4.1	0.3
K	5.96	5.67	5.49	6.16	6.14	5.49-6.16	5.88	0.3
Fe	6	5.83	5.62	5.58	5.82	5.58-6.00	5.77	0.17
Pb	4.75	5.51	5.33	5.24	5.46	4.75-5.51	5.26	0.3

Table 4.6 showing variation of peak:background ratio when all the conditions are kept constant.

The range, average and standard deviation of the results can be compared between the repeat analysis and the collimation experiment, which are shown in the table below. The standard deviation of the results is greater for the collimator experiments, and when plotted (see chart below), one can see that the repeat results are random in their variation rather than systematic.

range	average	stnd. dev.
3.11-3.91	4.66	0.39
4.36-6.17	4.75	0.82
4.33-5.64	4.52	0.55
4.4-5.08	4.07	0.33

Table 4.7 showing range, average and standard deviation of results from table above.

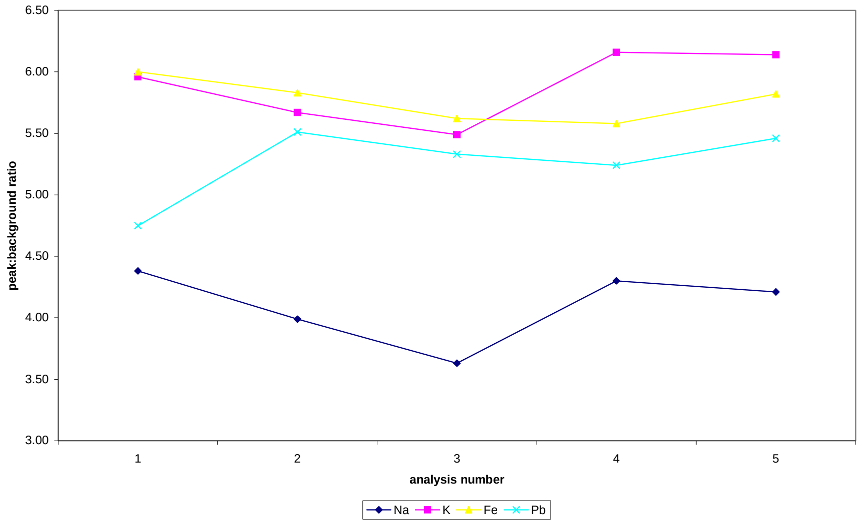


Figure 4.16 Chart showing random variation in peak:background ratio with conditions at: 500 µA, 30 keV for 1000 live seconds.

4.7.6 Counting time

The duration of each analysis is an important determinant in the quality of the results: ideally the quantification should be based on a maximum number of counts for the elements of interest, in order that the counting statistics are improved. To establish the effect of variable counting times, the peak:background ratio was recorded at 100 second intervals up to a maximum of 2000 seconds. The period is based on live seconds, which is typically longer than real time, since it is a measure of the time during which the detector is available to receive X-ray photons. The detector is momentarily closed during the absorption of photons, and the measurement of live time ensures that analyses with different count rates are of comparable duration.

	100	200	400	600	800	1000	1200	1400	1600	1800	2000
Na	4.16	5.12	4.42	3.68	3.85	4.2	3.9	3.98	3.97	3.78	3.92
K	7.02	5.75	6.55	7.36	6.39	5.73	6.4	5.72	5.81	5.56	6.24
Fe	5.49	7.11	5.58	5.58	6.03	6.08	6.11	5.78	5.86	5.51	5.89
Pb	5.48	6.09	5.12	5.01	5.38	5.06	5.37	5.2	5.11	5.35	5.21

Table 4.8 showing peak:background ratio in relation to analysis time.

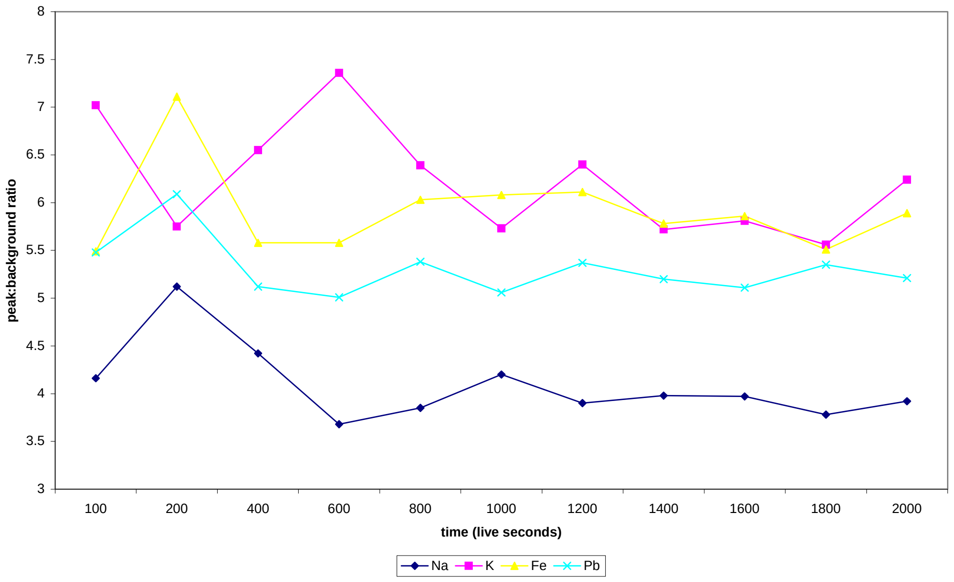


Figure 4.17 Chart showing peak:background ratio in relation to analysis time.

All of the elements experience random variation up to 800 seconds, thereafter they appear stable. Since there does not appear to be a significant improvement over 1000 seconds, this is selected as the most suitable time.

As a result of the above experiments, the conditions employed were: 30 keV, 500 µA for 1000 live seconds.

4.7.7 Background files

Net intensities and the background files.

Spectra for all of the corning standards (A - D) were recorded employing 30 (and 25) keV, 500 µA, and 1000 live seconds conditions. Net intensities were sought from all the spectra to ensure the conditions were appropriate for this range of glass types.

However, problems were encountered obtaining net intensities for a number of elements of interest. These were sodium, magnesium and nickel. Since these elements are known to be components of the standards, and all should be sufficiently excited by the above conditions to be detected, the “background file” was examined.

The background file consists of a series of points across the spectra, and is used to remove detected background radiation during the calculation of net intensity values for peaks of interest. The points should be carefully located around the peaks of interest. The position of these points is crucial to the identification of individual peaks, particularly those of low intensity owing to either small concentration and/or low energy (and therefore more susceptible to absorption). The background file initially used was designed for potassium-rich medieval glass compositions, and not fine-tuned for soda-lime-silica glasses.

The background file was easily amended to identify nickel, which was subsequently detected in all the standards. Manipulation of the background file was thought to be the solution to the detection of sodium and magnesium in all the glass standards. However, this proved not to be the case, because whilst it was possible to position points appropriate to the sodium and magnesium peaks of standards A and B, these were not ideally suited for C and D. Repeated changes to the background file enabled an optimum arrangement for standards A, B and D, but not C (background file STAN 1). It proved particularly difficult to obtain a net intensity value for sodium from Corning standard C. It contains the lowest concentration of soda of all the standards (1.2%), and is a high lead glass (36.91%). The characteristic x-radiation of sodium and magnesium is long wavelength/low energy (Kα at 1.041 and 1.253 keV respectively), and therefore more vulnerable to attenuation than higher energy radiation. The presence of such a high lead content in the glass matrix also means that the effective analytical depth for sodium and magnesium is less than it would otherwise be in a matrix of lower average atomic weight.

Net intensities were calculated for spectra recorded at both 25 and 30 keV (using background file STAN 1). It might be expected that the results from the lower accelerating voltage would yield higher net intensities for the low atomic weight elements (i.e. sodium and magnesium in this instance): this was not the case (see table below). With the exception of Corning C, all the values for sodium and magnesium showed a slight improvement at 30 keV.

		25 keV	30 keV
Corning A	Na	0.6879	0.8079
	Mg	0.328	0.404
Corning B	Na	0.8639	1.0139
	Mg	0.085	0.126
Corning C	Na	0	0
	Mg	0.263	0.255
Corning D	Na	0.064	0.085
	Mg	0.7939	0.8979

Table 4.9 of recorded net intensities from Corning standards A – D, using 500 μA, 1000 live seconds, 1 mm collimator and varying the accelerating voltage, background file STAN 1. Note the absence of any value for sodium in Corning C with this background file.

A background file was designed specifically to achieve a net intensity for all the elements of interest in Corning C under these operating conditions (background filename STAN 2).

To illustrate the impact of the high-lead matrix upon the measured net intensity for sodium in low-soda glasses, it is worth comparing the values for Corning standards C and D. Both of these standards have similarly low soda contents, but significantly different concentrations of lead (see below).

	Corning C	Corning D
Sodium	0.006	0.015
Magnesium	0.271	0.6389

Table 4.10 Net intensity values for sodium and magnesium in Corning Standards C and D.

	Corning C	Corning D
Soda	1.20%	1.32%
Magnesia	2.84%	4.09%

Table 4.11 Weight % content of soda and magnesia in Corning Standards C and D (Brill, 1972).

The low net intensity value recorded for sodium in Corning D is not due to the low soda content, but to the matrix absorption effects of a high lead glass: the similarly low-soda glass Corning C has a much higher net intensity value for sodium.

Summary of ideal conditions for use of XRF:

X-ray tube potential: 20-30 keV

beam current: 500 μA

beam diameter: 1 mm collimator acceptable, 3 mm better for statistics

counting time: 1000 live seconds

background files: STAN1 for glasses similar to Corning A, B and D, STAN2 for high lead glasses like Corning C.

4.7.8 Accuracy and Precision of XRF results.

The experiments above sought to optimise the operating and quantifying conditions, and based on these procedures, it is necessary to specify the degree of accuracy and precision of the results.

Accuracy describes the correctness of an experimental result, and is a relative term. Typically accuracy is described in terms of absolute or relative error. Precision is the reproducibility of results- the agreement between measurements made under identical conditions. The precision is usually expressed in terms of standard deviation (Skoog and Leary, 1992: p A-1)

The precision and accuracy were evaluated by performing repeat analyses of glass standards of known composition. Corning Standard A was treated as an unknown, and analysed repeatedly under the conditions 30 keV, 500 μA for 1000 live seconds. The spectra were quantified using Corning Standard B which was analysed at the same time. The background file STAN 1 was employed for calculating the net intensity values.

The values obtained from the repeat analyses are tabulated below:

	1	2	3	4	5	0	σ	σ as a % of 0
Na_2O	15.13	15.56	15.86	16.06	15.7	15.66	0.35	2.24
MgO	3.84	3.67	3.98	4.74	4.59	4.16	0.47	11.4
Al_2O_3	1.71	1.77	1.76	1.73	1.87	1.77	0.06	3.58
SiO_2	66.42	66.44	66.89	67.65	67.37	66.95	0.55	0.82
P_2O_5	0.1	0.15	0.12	0.09	0.12	0.12	0.02	20
K_2O	3.26	3.25	3.24	3.31	3.31	3.27	0.03	1.04
CaO	5.47	5.47	5.47	5.56	5.54	5.5	0.04	0.79
TiO	0.9	0.86	0.9	0.92	0.93	0.9	0.03	2.98
MnO	1.15	1.17	1.14	1.16	1.15	1.15	0.01	1.23
Fe_2O_3	1.03	1.05	1.02	1.04	1.04	1.03	0.01	1.14
CoO	0.13	0.12	0.12	0.13	0.12	0.13	0	2.43
NiO	0.01	0.01	0.01	0.02	0.01	0.01	0	33.17
CuO	1.08	1.08	1.06	1.07	1.08	1.07	0.01	0.77
ZnO	0.04	0.04	0.04	0.04	0.05	0.04	0	8.18
PbO	0.06	0.06	0.06	0.06	0.06	0.06	0	6.79
SrO	0.02	0.02	0.02	0.02	0.02	0.02	0	0
total	100.34	100.73	101.69	103.59	102.96	102.96		

Table 4.12 showing the results of repeat analyses of Corning A (wt. %), the mean value (0) and the standard deviation (σ). These results can be compared with the published values for Corning Standard A (see table below).

The accuracy of the repeat results can be expressed in terms of the absolute error of the mean (E_a).

$$E_a = 0 - x_1$$

where: 0 = average measurement

x_1 = true value

	0	Corning Standard A	Ea
Na_2O	15.66	14.52	1.14
MgO	4.16	2.81	1.35
Al_2O_3	1.77	1.01	0.76
SiO_2	66.95	66.56	0.39
P_2O_5	0.12	0.14	-0.02
K_2O	3.27	2.93	0.34
CaO	5.5	5.3	0.2
TiO	0.9	0.8	0.1
MnO	1.15	1.18	-0.03
Fe_2O_3	1.03	1.09	-0.06
CoO	0.13	0.15	-0.02
NiO	0.01	0.03	-0.02
CuO	1.07	1.22	-0.15
ZnO	0.04	0.04	0
PbO	0.06	0.08	-0.02
SrO	0.02	0.1	-0.08

Table 4.13 of absolute error of mean value from the true value (recommended composition from Brill 1999b, except SiO_2, which is from Brill 1972).

These gross errors are small, and appear insignificant, however, their impact on the data set should also be considered in relation to their proportion of the individual components' total. The individual errors may be expressed as percentages of the known value:

	1	2	3	4	5	average
Na_2O	5.8	8.81	10.91	12.31	9.79	9.52
MgO	44.36	37.97	49.62	78.2	72.56	56.54
Al_2O_3	71	77	76	73	87	76.8
SiO_2	0.21	0.18	0.5	1.64	1.22	0.75
P_2O_5	23.08	15.38	7.69	30.77	7.69	16.92
K_2O	13.59	13.24	12.89	15.33	15.33	14.08
CaO	8.75	8.75	8.75	10.54	10.14	9.38
TiO	12.5	7.5	12.5	15	16.25	12.75
MnO	15	17	14	16	15	15.4
Fe_2O_3	5.5	3.67	6.42	4.59	4.59	4.95
CoO	23.53	29.41	29.41	23.53	29.41	27.06
NiO	50	50	50	0	50	40
CuO	7.69	7.69	9.4	8.55	7.69	8.21
ZnO	9.09	9.09	9.09	9.09	13.64	10
PbO	50	50	50	50	50	50
SrO	80	80	80	80	80	80

Table 4.14 showing error of repeat analyses of Corning Standard A, error expressed as % of the published result (Brill 1972 and 1999).

It is necessary to review the errors: the mean Na_2O error is below 10%, a value which is remarkably good given the problems of detecting the low-energy x-radiation from sodium. The magnesia error is high, ranging from 30 – 69 % of the published value for Corning A, reflecting the problems of using a standard with low levels of magnesia (1.03 % in Corning B) to quantify an unknown containing twice that amount (2.66 % MgO in Corning A). This error should be less when analysing magnesia in archaeological samples if the most appropriate standard is chosen for quantification.

The errors associated with the detection of alumina are poor (mean = 76.8 %, range 71 – 87 %) illustrating the problem of resolving the aluminium Kα peak from the larger, adjacent silica Kα peak (at 1.486 and 1.739 keV respectively). Silica has an excellent mean error value (0.75 %) reflecting both its accurate measurement and benefiting from the improved statistics of being the largest single component (66.56 % in Corning A).

Phosphorus's apparent poor mean error (20.29 %) reflects its low concentration and difficulties resolving the Kα peak from that of silica (phosphorus Kα peak = 2.013 keV, concentration in Corning A = 0.14 wt. %): the absolute error of the mean result was still only 0.02 %.

Potash has a good mean error at 11.7 %, and the mean error for lime is an excellent 3.78 %. TiO (12.75 %), MnO (2.27 %) and iron oxide (5.16 %) are all acceptable. Cobalt is further adrift at 16.4 %, reflecting its relatively low concentration in Corning B in comparison with Corning A (0.035 and 0.15 wt. % respectively). Nickel oxide also has poor error values (mean error = 62 %)- the low concentrations and differential proportions in the two standards probably accounts for this. Both copper oxide and zinc oxide are acceptable at 11.92 and 7.5 % mean errors respectively. Lead oxide has a poor mean error of 24 %, due to the low concentration in Corning A (0.08 wt. %) in relation to Corning B (0.4 wt. %).

4.7.9 Problems encountered applying XRF to archaeological specimens.

The conditions defined by the above experimentation were employed in the analysis of an oinochoe from Lincoln Museum (M 1926.657, Haevernick, 1959, sample 11 in this project).

Figure 4.18 Sample 11: oinochoe from Etruscan context at Chiusi.

4.7.10 Surface preparation.

Previous work has emphasised the necessity of carefully preparing the sample prior to analysis (Cox and Pollard, 1977; Henderson, 1982, p 126). All archaeological glasses are likely to have weathered surfaces, which are chemically different from the original composition. This is the case even with examples which appear to be in good condition: the weathering may only be visible at microscopic level (Towle, 1995). This phenomenon is of great importance when one considers that XRF is essentially a surface technique. The analyst has to work with the assumption that below the surface there is an unaltered glass core available for analysis. The surface layers should be removed prior to the analysis.

In this case the surface area to be excited was polished using progressively finer carborundum papers (P 369, P 280 and P 1000) and finishing with a polishing pad coated in 8 micron diamond paste. The polished area was kept to a minimum by using a hand-held drill (a Dremel Multi-tool) with the carborundum papers mounted on polishing pads. To ensure that the polished area was as unobtrusive as possible, a small area on the base of the oinochoe was chosen

Figure 4.19 Sample preparation for XRF analysis- polishing archaeological artefact (sample 10).

Since the depth of the weathering layers is uncertain, the sample was polished, a spectrum collected, and the sample repolished before being re-analysed. After each polish the net intensity values for sodium, magnesium, aluminium, silica and phosphorus were obtained. By monitoring the varying net intensity values (see below), it is possible to see the increasing concentration of soda and decreasing concentration of silica. The lowered sodium value and consequential enrichment in silica are indicative of weathering layers where the alkali has leached from the glass (Douglas and El-Shamy, 1967). When the net intensity values for the sodium stabilised, then the weathering layers were considered to have been removed.

	ACT49	ACT50	ACT52	ACT53	Corning B
Na	0.225	0.396	0.5599	0.5009	0.9559
Mg	0.016	0.032	0.027	0.018	0.101
Al	2.5667	2.6967	2.0808	1.6848	2.3698
Si	24.9083	42.9352	46.3352	54.114	63.3566
P	0.178	0.135	0.096	0.072	0.9799

Table 4.15 showing net intensity values for select elements after successive polishes, and the values for Corning Standard B used for quantification.

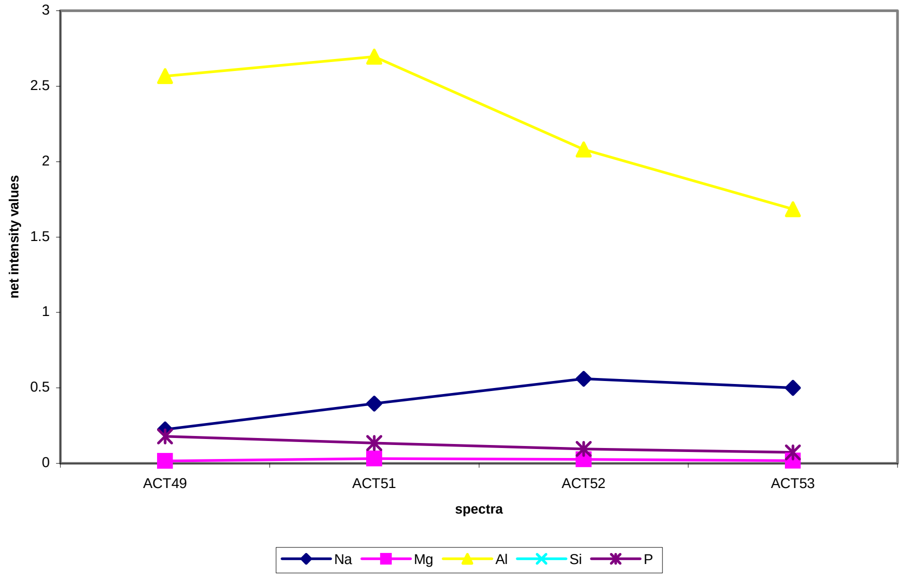


Figure 4.20 Chart showing detail of increasing sodium net intensity values as weathering layers were removed.

After selecting “ACT52” as a spectrum suitable for further processing, an initial quantification was performed using a spectrum collected from the contemporary analysis of Corning Standard B. The first quantification routine for spectrum ACT51 gave a poor result: the detected elements, when expressed as suitable oxides accounted for only 68 % of the total composition (see table below). In view of this, spectra ACT51 and ACT53 were also quantified to establish whether or not these were also of poor quality.

oxides	ACT51	ACT52	ACT53
Na	7.479	10.273	8.922
Mg	0.366	0.316	0.207
Al	4.651	3.662	2.907
Si	41.913	45.227	51.452
P	0.119	0.091	0.07
K	1.028	0.811	0.54
Ca	6.505	6.174	6.359
Ti	0.069	0.051	0.058
Cu	1.699	1.618	1.946
total:	63.829	68.223	72.461

Table 4.16 showing calculated wt. % composition for three spectra taken from base of Lincoln oinochoe.

The calculated compositions are clearly unreliable: not only is the overall total less than the 90% or so one would expect from this range of components, individually the measurements are inadequate: the silica content should be 60 % +, and the alkali content ought to be higher than the 9 – 11 % range in order for it to be an effective flux.

A visual examination of the individual spectra revealed that there were no significant peaks unaccounted for in the analyses. It was possible that the oinochoe was manufactured from an unusual glass type such as a boron-rich glass: since boron has a very low atomic number, its characteristic radiation (very low energy/long wavelength ($K\alpha = 0.138$ keV)), would not be detected by the system employed in the Archaeological Science Laboratory in Nottingham. A high boron content would indicate the vessel was a fake, since boron-rich glasses were not manufactured until the Nineteenth Century (J. Henderson, *pers. comm.*). To ensure that the glass was not a boro-silicate, a small chip was removed from the polished zone (< 2 mm long) and analysed using an environmental scanning electron microscope (ESEM) in the Dept of Materials at the University of Nottingham, with the assistance of Nicola Bock.

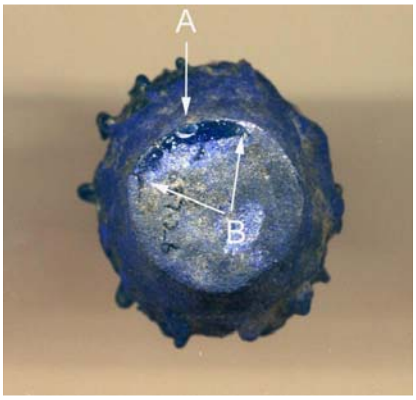


Figure 4.21 Base of oinochoe, sample 11 showing fragment removed for microanalysis (A) and zone polished for XRF (B). Scale 1:1. Note the crystalline weathering products removed by polishing.

The specifications of the instrument are not detailed here. The analysis was rapid and standardless, the flake was not mounted in epoxy resin, but stuck to an aluminium stub with an adhesive carbon pad. No further polishing was undertaken. The glass was analysed several times, at different points, which were selected visually by moving the sample around and examining the surface. Three of the results are included in the table below.

	1	2	3	average
Na_2O	26.21	24.44	21.62	24.09
MgO	0.52	0.69	0.51	0.57
Al_2O_3	0.86	1.17	1.02	1.02
SiO_2	66.64	67.39	66.21	66.75
SO_3	0.77	0.5	0.82	0.7
Cl	1.02	0.87	2.48	1.46
K_2O	0.37	0.29	1.58	0.75
CaO	3.62	3.58	4.52	3.91
Fe_2O_3		0.27	0.22	0.25
CuO		0.8	1.01	0.91
total:	100.01	100	99.99	

Table 4.17 showing results of rapid analyses of Lincoln oinochoe using ESEM.

Boron was not identified as a component of the glass. When performing standardless analyses with this system, then the results are automatically normalised to 100 %, which is far from ideal since errors become spread across the entire data set. Nonetheless, the results are useful for comparison with the more fully “quantified” analyses performed using XRF. The accelerating voltage was varied: the first analysis listed in the table above was at 20 keV, the other two at 30 keV- permitting the ready identification of iron and copper. All the analyses were for 100 live seconds. The peak identification was performed automatically by the operating system, as was the selection of background points for calculation of the net intensity values. Chlorine was readily identified in all the analyses, and would not have been present in an oxide state, but as chloride ions within the glass: a high chlorine content has been noted elsewhere as an indication of a heavily weathered glass (Towle, 1995). This is not readily identified using the XRF, since there is a spectral peak overlap between the chlorine Kα and the rhodium Lα peaks (2.621 and 2.696 keV respectively): the rhodium peak is derived from the generation of the primary x-radiation which involves a rhodium anode in the system employed in Nottingham.

4.7.11 Further archaeological samples: a Faliscan bead from the Ashmolean Museum.

In an attempt to understand why the XRF analysis of the Lincoln oinochoe was unsuccessful, an alternative archaeological sample was analysed. A blue and white glass eye-bead from the Ashmolean Museum was analysed. A small area of the blue glass matrix was polished using the procedure outlined above.

	ACT55	ACT56	ACT58	ACT60
Na	0.6899	0.6529	0.5919	0.7569
Mg	0.058	0.061	0	0.042
Al	1.5788	1.2809	1.3588	1.6538
Si	82.0978	71.949	69.7762	78.5663
P	0.138	0.144	0.062	0.092
K	2.0898	1.8248	1.8408	2.0938
Ca	27.7299	25.6782	26.3241	27.7369
Ti	0.383	0.28	0.279	0.255
Cu	6.4893	6.3563	6.2723	8.1881

Table 4.18 showing net intensity values for select elements after repeated polishing of glass bead.

The sodium net intensity value did not improve in a clear trajectory as can be observed with the oinochoe above. This suggests that the first polish removed the weathered layers, or that the variation is due to reasons other than the removal of alkali-depleted glass.

The latter two spectra were quantified with reference to Corning B:

	ACT58	ACT60
Na_2O	11.866	15.055
MgO	0	0.522
Al_2O_3	2.125	2.627
SiO_2	64.332	73.496
P_2O_5	0.059	0.087
K_2O	0.668	0.759
CaO	6.929	7.266
TiO	0.052	0.047
CuO	0.256	0.327
total:	86.287	100.186

Table 4.19 Quantified spectra from analysis of Faliscan bead

The results are cause for concern on several counts. Spectra ACT60 is clearly a reasonable result- the silica content is high, and alkali content relatively low, but within the bounds of possibility. The total composition is over 100 % - only nine oxides of interest are listed in this analysis and the total will increase if this spectrum is quantified for a wider range of components.

The net intensity values do not readily identify the most ideal spectrum for analysis: low magnesia count apart, ACT58 might otherwise be regarded as reasonable for quantification. Whilst the sodium count is lower than those preceding it, the sodium count does not follow an increasing trajectory, suggesting that the variation is due to random error. Similarly, the lack of a magnesium intensity for ACT58 would appear to reflect some other phenomenon.

4.7.12 Surface geometry.

Since there are no problems achieving successful analyses of the standard glasses, then the variable results from archaeological examples must be explained. The instrumentation employed cannot be responsible for the difficulties encountered. The principle problem is the quantification of the spectra to achieve a total, or near total compositional analysis.

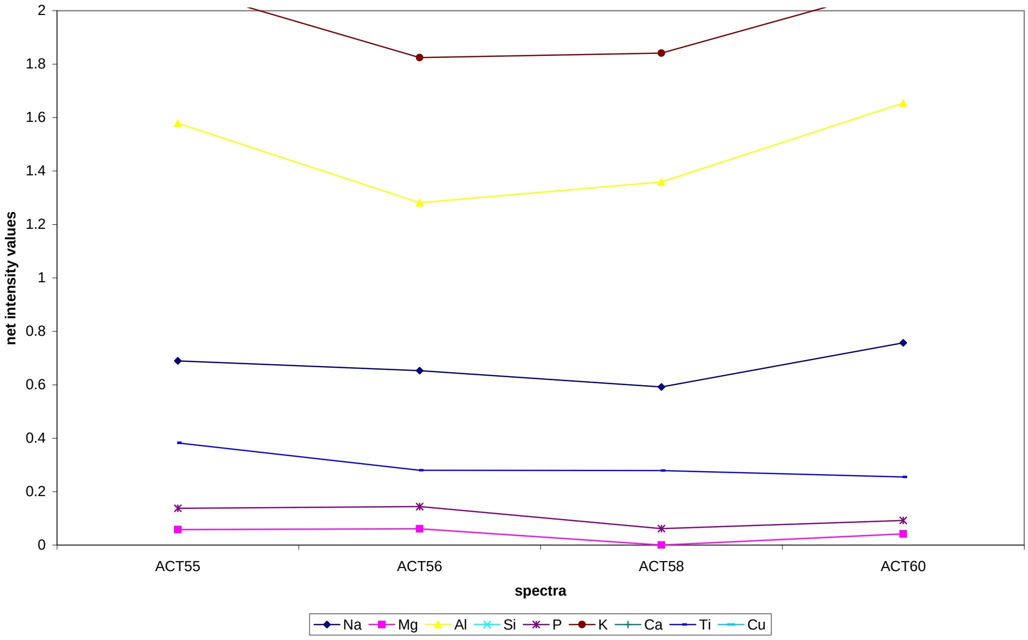


Figure 4.22 Chart detail showing net intensity values fluctuating after repeated polishing and analysis.

It might be argued that if a glass is severely weathered, even the exposed sub-surface is not of the original composition. However, were this the case, then one should still expect to be able effect a complete analysis, but achieve a result of skewed proportions (i.e. lower alkali, higher silica). However, this is not the case for the fragment of the oinochoe analysed by ESEM (see above)- the result, although normalised to 100 %, gives a quite different result to that of the XRF (even when the XRF results are also normalised).

It seems likely that the difficulties are the result of imperfect geometry during analysis, probably compounded by the difficulties of arranging the sample before the primary beam of X-rays. XRF analysis works on the assumption that the surface being analysed is perfectly flat: the Corning Standards are all mounted in epoxy resin, ground and polished to a 1 micron finish. As a result the count rate for the analysis of the standards (at 30 keV, 500 μA, 1 mm collimator) is typically in the region of 450 cps (for a non-lead standard).

In contrast, the archaeological samples are museum pieces, which require minimum intervention: they cannot be broken up and mounted up in epoxy resin for XRF analysis. The adopted procedure, of polishing a selected area as unobtrusively as possible, whilst using the smallest collimator (1 mm) means that the ensuing surface is not as flat as would be ideal. The location of the sample surface before the X-ray beam is reliable, using a window cut into an acetate sheet (as with the standards). Where the glass has a deeply weathered surface, as was the case with the Lincoln oinochoe (thick crystalline deposit over the body and foot), the act of polishing effectively creates a shallow depression in the sample's surface: this too distorts the geometry of the analysis. The count rates for the archaeological samples have been in the range 300 – 360 cps, reflecting the less than ideal detection of X-ray photons.

The problem of surface geometry also effects the analysis of the beads. Here the surface gradually becomes flattened with polishing- it is not acceptable, however, to grind a flat platform for analysis onto the side of each bead. As a result, a curved surface is arranged before the beam, which gives rise to a different excitation-detection.

The analysis of small archaeological artefacts which could not be either heavily sampled for mounting in epoxy resin blocks (like the standards), nor ground to a flat platform proved problematic. The XRF procedures developed here, whilst suitable for large glass pieces which could be suitably prepared or sampled were not appropriate for the minimal intervention required of small artefacts like glass beads.

In view of these observations, it was decided to pursue an alternative method of analysis for the principle quantitative analysis. Electron microprobe analysis was selected for a number of reasons: this technique is well established and an instrument is available at the Department of Earth Sciences in Oxford. Although the technique requires the sampling of the artefacts under study, in reality the removal of a small fragment for mounting in an epoxy resin block is less intrusive than the grinding and polishing of a flat platform on an artefact required to attempt high quality analysis using the XRF system. This can be readily observed by reference to Figure 4.21 above.

4.8 Experiments to establish ideal instrument and operating conditions for the analysis of ancient glasses II: Electron Microprobe Analysis.

4.8.1 Sample preparation.

The artefacts were sampled by pressure flaking a small fragment c. 1-2 mm^2 from an unobtrusive part of the archaeological artefacts (i.e. the base of vessels or adjacent to the perforation of beads). The samples were then mounted in epoxy resin blocks and polished down to 1 μm. The blocks were coated with carbon to make the surface conductive- a necessary preparation for non-conducting surfaces in electron microprobe analysis and SEM work.

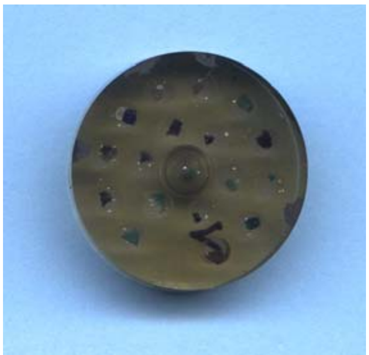


Figure 4.23 Archaeological Samples mounted in epoxy resin block, polished to 1 μm and carbon coated prior to EMP analysis and EDXMA work, scale 1:1.

Access to the machine itself was limited (due to costs), and therefore the opportunity to experiment with the operating conditions of the analyses were not an option as with XRF. Fortunately the machine has been used for the quantitative analysis of ancient glasses for at least a decade. Previous work has involved the definition of ideal conditions for analysing ancient glasses (Henderson 1988b). The instrument used for this project was a Cambridge Microscan 9 system, at the Dept. of Earth Sciences, University of Oxford. The operating parameters defined by Henderson (1988) were adopted. The machine was calibrated prior to use by Dr Norman Charnley (who maintains the laboratory in Oxford), using a range of pure element, geological and Corning Standards.

Prior to the analysis of the archaeological samples, Corning B, not used in the calibration procedure, was analysed as an unknown to check upon the system. The accumulated analyses of this standard can be used to ascertain the precision and accuracy of the data. The samples were analysed at 20 kV, with a beam current of 40 nA, and a defocused beam of 80 micron diameter.

	1	2	3	4	5	6	7	0	σ	σ as % of 0
Na_2O	16.26	16.76	16.28	16.62	15.44	16.71	16.62	16.38	0.43	2.61
MgO	1.18	1.09	1.12	1.07	1.1	1.1	1.16	1.12	0.04	3.27
Al_2O_3	4.35	4.41	4.38	4.37	4.85	5.36	4.44	4.59	0.35	7.65
SiO_2	60.95	61.87	60.98	60.36	62.96	62.86	61.98	61.71	0.92	1.49
P_2O_5	0.79	0.8	0.79	0.74	0.75	0.75	0.7	0.76	0.03	4.34
SO_3	0.51	0.57	0.51	0.45	0.54	0.48	0.69	0.54	0.07	13.53
Cl	0.2	0.22	0.18	0.17	0.16	0.17	0.16	0.18	0.02	11.5
K_2O	1.01	1.03	1.04	1.01	1.05	1.03	1.04	1.03	0.01	1.37
CaO	8.74	8.86	8.32	8.55	8.8	8.63	8.61	8.64	0.17	1.93
TiO_2	0.07	0.09	0.06	0.06	0.04	0	0.07	0.06	0.03	47.83
Cr_2O_3	0.03	0.02	0.02	0	0.02	0	0	0.01	0.01	90.27
MnO	0.27	0.26	0.24	0.23	0.29	0.26	0.23	0.25	0.02	8.1
FeO	0.3	0.35	0.35	0.38	0.33	0.38	0.35	0.35	0.03	7.42
CoO	0.05	0.06	0.05	0.08	0.05	0.05	0.08	0.06	0.01	21.82
NiO	0.05	0.06	0.05	0.13	0.06	0.12	0.09	0.08	0.03	38.96
CuO	2.87	2.78	2.76	2.6	2.68	2.77	2.71	2.74	0.08	2.89
ZnO	0.29	0.15	0.12	0.15	0.28	0.19	0.19	0.2	0.06	31.12
As_2O_5	0	0	0	0	0	0	0	0	0	0
SnO2	0	0.03	0.01	0.01	0.05	0.01	0.04	0.02	0.02	80.55
Sb_2O_5	0.41	0.42	0.3	0.46	0.48	0.52	0.44	0.43	0.06	14.86
BaO	0.12	0.12	0.1	0.12	0.12	0.12	0.12	0.12	0.01	5.97
PbO	0.43	0.48	0.54	0.48	0.49	0.47	0.35	0.46	0.05	11.87
Total	98.88	100.43	98.2	98.04	100.54	101.98	100.07			

Table 4.20 Repeat analyses of Corning Standard B using Electron Microprobe Analysis. In the table 0 indicates the mean value, σ is the standard deviation and final column shows the standard deviation as a percentage of the average.

	mean	Corning Standard B	Ea
Na_2O	16.38	17	0.62
MgO	1.12	1.03	0.09
Al_2O_3	4.59	4.36	0.23
SiO_2	61.71	61.55	0.16
P_2O_5	0.76	0.82	0.06
SO_3	0.54	0.5	0.04
Cl	0.18	0.2	0.02
K_2O	1.03	1	0.03
CaO	8.64	8.56	0.08
TiO_2	0.06	0.089	0.029
Cr_2O_3	0.01	0.005	0.005
MnO	0.25	0.25	0
FeO	0.35	0.34	0.01
CoO	0.06	0.046	0.014
NiO	0.08	0.099	0.019
CuO	2.74	2.66	0.08
ZnO	0.2	0.19	0.01
As_2O_5	0	0	0
SnO2	0.02	0.04	0.02
Sb_2O_5	0.43	0.46	0.03
BaO	0.12	0.12	0
PbO	0.46	0.61	0.15
Total		99.929	

Table 4.21 showing error expressed in terms of the absolute error of the mean (E_a).

$$E_a = 0 - x_1$$

where: 0 = average measurement

x_1 = true value

The errors may also be expressed as percentages of the known value:

	1	2	3	4	5	6	7	average error
Na_2O	5.79	2.9	5.68	3.71	10.54	3.19	3.71	5.07
MgO	0.84	8.4	5.88	10.08	7.56	7.56	2.52	6.12
Al_2O_3	3.08	4.5	3.79	3.55	14.93	27.01	5.21	8.87
SiO_2	0.97	0.52	0.93	1.93	2.29	2.13	0.7	1.35
P_2O_5	5.95	4.76	5.95	11.9	10.71	10.71	16.67	9.52
SO_3	5.56	5.56	5.56	16.67	0	11.11	27.78	10.32
Cl	0	10	10	15	20	15	20	12.86
K_2O	8.18	6.36	5.45	8.18	4.55	6.36	5.45	6.36
CaO	0.34	1.72	4.48	1.84	1.03	0.92	1.15	1.64
TiO_2	30	10	40	40	60	100	30	44.29
Cr_2O_3	500	300	300	100	300	100	100	242.86
MnO	3.57	7.14	14.29	17.86	3.57	7.14	17.86	10.2
FeO	14.29	0	0	8.57	5.71	8.57	0	5.31
CoO	42.86	71.43	42.86	128.57	42.86	42.86	128.57	71.43
NiO	44.44	33.33	44.44	44.44	33.33	33.33	0	33.33
CuO	6.3	2.96	2.22	3.7	0.74	2.59	0.37	2.7
ZnO	45	25	40	25	40	5	5	26.43
As_2O_5	0	0	0	0	0	0	0	0
SnO2	100	25	75	75	25	75	0	53.57
Sb_2O_5	10.87	8.7	34.78	0	4.35	13.04	4.35	10.87
BaO	14.29	14.29	28.57	14.29	14.29	14.29	14.29	16.33
PbO	7.5	20	35	20	22.5	17.5	12.5	19.29

Table 4.22 showing individual errors of analyses expressed as a percentage of the true value.

4.8.2 EMP of archaeological samples.

The data from the EMP analysis of archaeological samples have proven more consistent than that derived from XRF. Firstly, the analyses typically have totals of 100 % +/- 3%, without recourse to any normalisation procedures indicating a realistic analyses. On occasion, results would be very low (i.e. circa 60 %) with an unlikely composition (negligble SiO_2, very high Cl). These results are derived from analyses of the epoxy blocks rather than the glass sample due to misalignment of the electron beam during the setting up of the analyses. Such results are rejected. It is not possible to make a measurement of the accuracy of the analyses on unknown archaeological samples- this can only be done using well-analysed standards as unknowns (as above). It is possible to undertake repeated analyses of archaeological samples to achieve a measurement of the precision of the data. Sample 85 was analysed 8 times (at different locations on the mounted sample's surface).

	1	2	3	4	5	6	7	8	mean	stdev
Na_2O	15.5	15.86	15.84	15.55	15.71	15.58	15.54	15.78	15.67	0.14
MgO	2.29	2.25	2.23	2.16	2.28	2.28	2.18	2.37	2.26	0.07
Al_2O_3	1.52	1.66	1.51	1.5	1.76	1.48	1.44	1.96	1.6	0.18
SiO_2	65.15	65.7	64	65.4	65.31	65.76	65.5	65.83	65.33	0.59
P_2O_5	0.19	0.17	0.22	0.22	0.19	0.17	0.17	0.22	0.19	0.02
SO_3	0.18	0.18	0.21	0.21	0.18	0.21	0.21	0.21	0.2	0.02
Cl	0.73	0.73	0.78	0.82	0.76	0.84	0.82	0.77	0.78	0.04
K_2O	1.38	1.32	1.28	1.38	1.33	1.32	1.32	1.38	1.34	0.04
CaO	5.36	5.11	5.16	5.2	5.32	5.2	5.14	5.37	5.23	0.1
TiO_2	0.09	0.09	0.11	0.09	0.11	0.13	0.11	0.13	0.11	0.02
Cr_2O_3	0	0.03	0.02	0	0.02	0	0.02	0	0.01	0.01
MnO	0.03	0.01	0.04	0.01	0.01	0.03	0.01	0.03	0.02	0.01
FeO	9.86	9.45	9.87	9.62	8.85	10.06	9.83	8.85	9.55	0.47
CoO	0.06	0	0.02	0.03	0.03	0	0.02	0.08	0.03	0.03
NiO	0.02	0	0	0.01	0	0	0.02	0.02	0.01	0.01
CuO	0	0	0.04	0.08	0.01	0	0.04	0	0.02	0.03
ZnO	0.06	0.02	0.08	0.08	0.05	0.03	0	0	0.04	0.03
As_2O_5	0.02	0.03	0.02	0.02	0.02	0	0	0.05	0.02	0.02
SnO2	0.03	0	0.03	0.01	0.01	0	0	0	0.01	0.01
Sb_2O_5	0.02	0.09	0.02	0.04	0.15	0.09	0.06	0.09	0.07	0.04
BaO	0.02	0.04	0.04	0.02	0.05	0.04	0.01	0.01	0.03	0.02
PbO	0	0.01	0	0.04	0.01	0.06	0	0	0.02	0.02
Total	102.51	102.75	102.52	102.49	102.16	103.28	102.44	103.15		

Table 4.23 Repeat EMP analysis of sample 85 to establish Standard Deviation

4.8.3 Discussion of the errors.

The data from the EMP tests is more readily applicable to archaeological material than the XRF; since the sample preparation is identical (i.e. both standards and samples are mounted in epoxy resin and polished to 1 μm), whereas the XRF procedure was designed within the limitations of minimal intervention upon the artefact.

4.8.4 Comparison of the data quality between XRF and EMP.

It is possible to compare the evaluations of the quantitative data from XRF and EMP. The most obvious difference between the test results on Corning Standards A and B is the number of oxides for which data is available for comparison: some 22 oxides/elements for EMP and 16 oxides for XRF. This reflects the analysts' choice of key components for detection and quantification- the fewer number for XRF are because of the laboriously slow quantification procedure necessary with the system employed in Nottingham. There are still sufficient components for consideration. Whilst the tests consider data on different standards, they may still be compared. It is should also be noted that the XRF data was collected over the course of one day, whilst the EMP data at intervals over 12 months: errors due to instrumental drift should be minimised by the respective calibration procedures, but any persisting would be greater in the EMP data.

	EMP Ea Corn. B	XRF Ea Corn. A
Na_2O	0.62	1.36
MgO	0.09	1.5
Al_2O_3	0.23	0.77
SiO_2	0.16	0.39
P_2O_5	0.06	0.01
SO_3	0.04	
Cl	0.02	
K_2O	0.03	0.4
CaO	0.08	0.47
TiO_2	0.029	0.1
Cr_2O_3	0.005	
MnO	0	0.15
FeO	0.01	0.06
CoO	0.014	0.04
NiO	0.019	0.01
CuO	0.08	0.1
ZnO	0.01	0.004
As_2O_5	0	
SnO2	0.02	
Sb_2O_5	0.03	
BaO	0	
PbO	0.15	0.06
SrO		0.08

Table 4.24 Comparison of the average gross errors on Corning Standards A and B using XRF and EMP methods of analysis.

As with the discussion above, it is useful to convert these gross errors into measures of the percentage of the published value:

	EMP Ea as % of true value	XRF Ea as % of true value
Na_2O	3.81	9.51
MgO	8.04	56.39
Al_2O_3	5.25	77
SiO_2	0.26	0.59
P_2O_5	7.59	7.69
SO_3	7.84	
Cl	11.11	
K_2O	2.88	13.94
CaO	0.96	9.34
TiO_2	48.33	12.5
Cr_2O_3	25	
MnO	0	15
FeO	2.86	5.5
CoO	28	23.53
NiO	38	50
CuO	2.9	8.55
ZnO	8.33	9.09
As_2O_5	0	
SnO2	200	
Sb_2O_5	10	
BaO	0	
PbO	27.78	50
SrO		80

Table 4.25 Comparing percentage errors between XRF and EMP analyses.

The EMP data has much lower errors for all but two of the compared oxide components: CoO and TiO_2.The higher error encountered by EMP with these two oxides can be explained by two factors. Firstly they are both present in Corning Standard B at trace level (TiO_2 = 0.089 % and CoO = 0.046 %). They are also present in Corning Standard A at trace level (TiO_2 = 0.79 % and CoO = 0.17%), but of a different order of magnitude (9 x the TiO_2 and 4 x the CoO levels). Secondly, these are both oxides of transition metals with relatively high atomic weights (Ti = 22, Co = 27), and as described above, wavelength-dispersive systems tend to be less sensitive than energy dispersive systems for heavier elements.

The EMP data demonstrates the superior overall accuracy of the technique (using the described procedures) on glass standards. The precision is simularly impressive.

	EMP stdev	XRF stdev
Na_2O	0.43	0.35
MgO	0.04	0.47
Al_2O_3	0.35	0.06
SiO_2	0.92	0.55
P_2O_5	0.03	0.02
SO_3	0.07	
Cl	0.02	
K_2O	0.01	0.03
CaO	0.17	0.04
TiO_2	0.03	0.03
Cr_2O_3	0.01	
MnO	0.02	0.01
FeO	0.03	0.01
CoO	0.01	0
NiO	0.03	0
CuO	0.08	0.01
ZnO	0.06	0
As_2O_5	0	
SnO2	0.02	
Sb_2O_5	0.06	
BaO	0.01	
PbO	0.05	0
SrO		0

Table 4.26 Comparative standard deviations for EMP and XRF analyses

4.9 Non-Quantitative Methods.

In addition to the electron microprobe and limited XRF analyses, two other techniques were used: Energy Dispersive X-ray MicroAnalysis (using an SEM) and X-ray Diffraction. The principles behind both of these techniques are briefly described above. These techniques were employed to elucidate aspects of the glass technology not revealed through standard quantitative analysis.

4.9.1 Energy Dispersive X-ray Micro Analysis (EDXMA). The system used was a R. J. Lee Personal SEM at the Science and Research Department of the Conservation Centre, National Museums and Galleries on Mersyside. This system is a computer operated SEM with Energy Dispersive analysis capabilities. No additional sample preparation was required; the samples preperation for EMP analysis was appropiate for EDXMA work. The instrument was used for imaging and qualitative analysis of observed discrete inclusions in the glasses (e.g. see Figure below). The machine was operated at 20 keV and 5 μA.

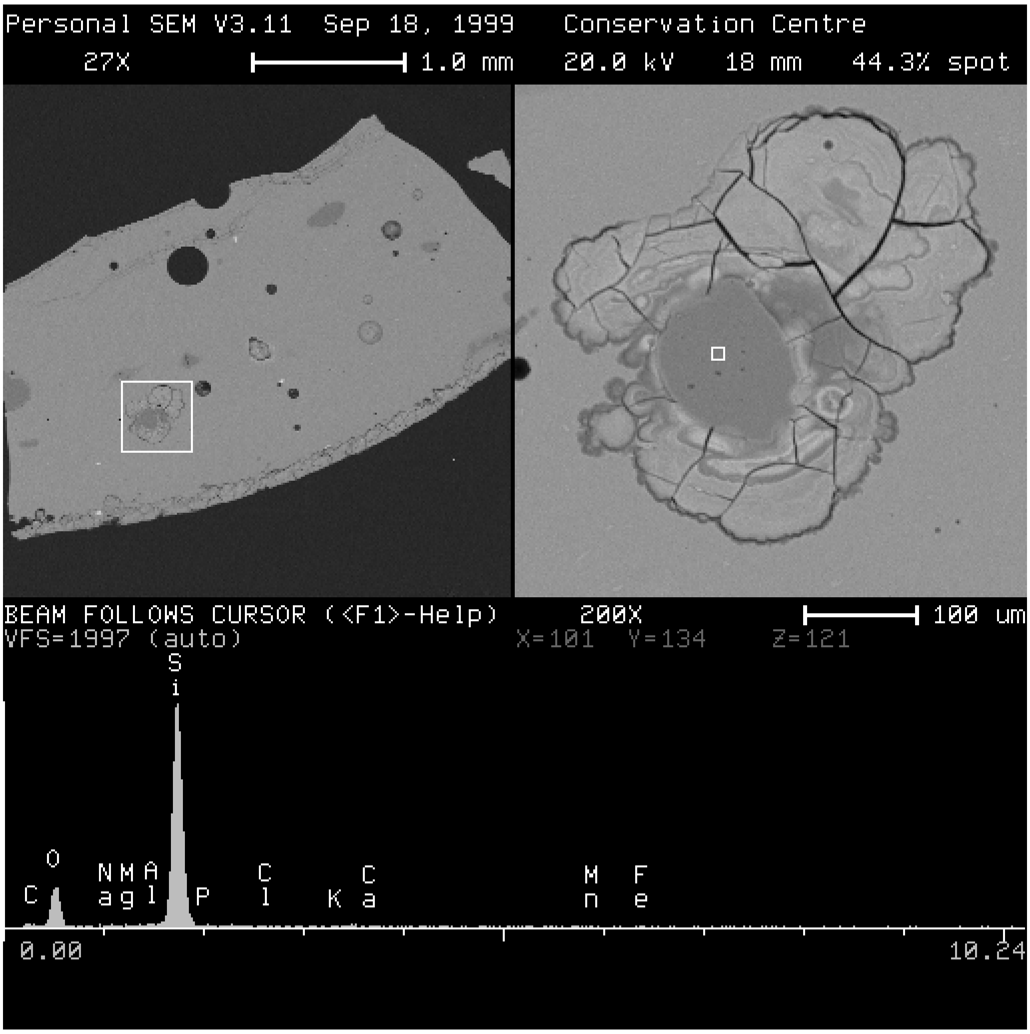


Figure 4.24 Micrograph and ED spectrum of silica-rich inclusion in Sample 51 (probably unfused raw ingredient or opacifier added at final stages of production).

4.9.2 X-Ray Diffraction

X-ray diffraction was selected to identify the crystalline phases in the glass matrix of a number of the samples. Quantitative analysis from the electron microprobe does not distinguish between the different phases under the beam during analysis. The EDXMA permits the analyst to distinguish between phases in the structure, and even give a compositional analysis, but does not tell how the elemental components are bonded. XRD will actually identify the crystal structures, permitting the reconstruction of their origin (such as what kind of mineral has been used).

Only a few samples were analysed using this method to identify inclusions in specific glasses. Material left from the preparation of EMP samples was used. This material was not available for more than a limited number of samples, and was in less than ideal quantities. The analysis was undertaken by Mr Dave Triff of the Dept of Materials, Nottingham University. The few mg used were ground in a ball mill, mixed into a paste with acetone, and placed on a glass plate in the sample holder of the XRD machine. Before the acetone had finally evaporated, the paste was agitated to ensure the crystalline component was not systematically aligned.

Unfortunately the samples tested were insufficient to give sufficient signal for reliable identification of the crystalline components of those glasses analysed.

Since the sampling procedure was constrained by the necessity to minimally damage the artefacts, XRD proved of little use here.

4.10 Conclusions.

This chapter has sought to explain the analytical techniques investigated and applied to the analyses of ancient glass for the purpose of this project. Rather than a single method, it has been found essential to integrate the data from a suite of techniques. The process of defining ideal operating conditions and the development of sampling and the preparation of material for analysis proved to be a useful exercise. Whilst XRF was initially considered to be the most appropriate technique for this project, the constraints of sample preparation meant that micro-techniques were adopted as the principle analytical tools.

CHAPTER 5: RESULTS AND DATA ANALYSIS.

5.1 Introduction

This chapter presents the results from the analysis of 248 samples of Italian glass beads, vessels, ingots and working debris. The samples are from sites ranging from the Final Bronze Age (c 1100 BC) to Iron Age and Roman material (up to the 2nd Century BC). The samples are mainly from sites from the Po valley in Northern Italy, and are supplemented by material from various British collections of Early Italian glass, which extend to Central Italy. The sample selection and strategy are discussed in greater detail in Chapter 2.

In this chapter, the characterisation of material from each individual site is outlined according to the basic analytical data, before discussing the analyses in light of the entire body of data and in comparison with appropriate published work. The complete results of the analyses are listed in Appendix 1. Tables of processed and on occasion raw data are used to substantiate arguments made in the text. Sample numbers can be used to cross reference to full artefact descriptions in the catalogue (Appendix 2) and pictures (Appendix 3).

The most significant question addressed by the analysis of this material is that of localised manufacture and continuity of technological traditions particularly between the Late Bronze Age and Iron Age. In addition the changes in glassmaking are traced through the first Millennium BC and related to the wider transitions noted from the Mediterranean region. The specific question of defining an Etruscan glassmaking tradition is addressed, and issues concerning the definition of production are raised. The broader archaeological inferences derived from the data are discussed in greater detail in Chapter 6.

5.2 Treatment of the data

All of the full compositions are not reproduced in this chapter, but may be found in Appendix 1. After analysis of samples, the data, which was stored on disc and on paper output, was transferred to Microsoft Excel files. The paper and computer records were double-checked with the layout of the individual stubs to ensure that analyses' location co-ordinates conformed to the mounted samples. The colour, site of origin and date for each sample was added to the compositional data. Initially the compositional data from each site was simply reviewed, and the individual examples identified according to their membership of the established glass categories: mixed-alkali, high - magnesia soda - lime - silica, low magnesia soda - lime - silica, potash, and high - lead glasses. Any other exceptional characteristics, such as exceptionally high or low values for alumina, lime or iron oxide were noted at this point. Oxides responsible for colouring individual samples were also identified. The data was then transferred to SPSS files for further processing.

In addition to the plotting of components in established bi-variate charts to examine variation within groups of glasses (which would tend simply to confirm the categorisation already performed using the classic groupings) several other statistical routines were employed. Principle Component Analysis (PCA), Correlation Matrices and Cluster Analysis were all used to identify variation within the data, establish which components were responsible for the variation and help select suitable oxides and factors for bi-variate plotting in order that the variation might be explained. PCA is a statistical technique for multivariate analysis, which is useful for looking at underlying trends across a large number of variables (Shennan 1988, p 261). The technique identifies the variables principally responsible for the observed variation in a complex dataset, and by the generation of factor matrices the relationships between variables can be observed. The allocation of scores for each variable in the principal components permits bi-variate plotting of the factors, more clearly identifying association and variation in the data (here the rotated matrices are generated using the Varimax method). The PCA matrices correlation matrices and dendrograms are not all reproduced here, since they are simply tools for identifying variation within datasets: bi-variate plots are more frequently included since they illustrate the explanation of such variation.

The mean values are given for glasses of a similar type from each site, alongside additional information where useful. In places this includes a reduced glass composition, on the model of Brill (1999b p 8-10), which seeks to characterise the glass on the basis of seven components. These figures have been normalised to 100 %. Some caution should be employed when using the reduced compositions, since they assume that the glass is manufactured in at least two stages: firstly as a colourless base to which colorants or opacifiers are added in a second, distinct activity. This division can be inferred from the cuniform texts (Oppenheim *et al.* 1988) and review of data on variously coloured glasses from single sources (see Brill 1988) as well as direct observation of archaeological specimens (Rehren 2000b, p 19), however it cannot be assumed to be the case for glass produced at all times. Additional caution should be exercised in light of the possibility of the colourant/opacifying materials supplementing the key components (for example, the introduction of additional magnesia, alumina and iron with cobalt colourants- see 3.7.20, and also Shortland and Tite 2000).

5.3 Characterisation of glasses from Final Bronze Age Sites

Samples were taken from material from three Final Bronze Age sites in the Po valley. One of these has been widely investigated by glass scientists before (Frattesina) on account of the extensive evidence for glassworking (and other industrial activities). The contemporary sites of Borgo San Zeno (Montagnana) and Mariconda have also yielded evidence of glassworking, and were considered useful indicators of the broader technology of glassmaking/working within which Frattesina was operating.

5.3.1 Montagnana

18 samples: 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 337, 338, 339, 340, 341and 342.

The Montagnana material was collected from Montagnana and Este Museums. All the material from the former was recovered from the Final Bronze Age site of Borgo San Zeno (samples 308- 319 inclusive), and the artefacts held by Este Museum are thought to be from the same site except 342 which was recovered from a nearby funerary context (“Corredo Ossuaria”). At the time of sample collection it was assumed that 342 was contemporary to the other samples. The material consisted of 14 samples from beads and their decoration, 3 samples from ingot fragments and one irregular glass fragment.

Glass types.

As expected, the glass is of the mixed-alkali type, a previously identified European Bronze Age compositional grouping (Henderson 1988a, also see section 3.7.3 above and 5.4.1 below). Sample 342 is an exception, and will be discussed separately below. The mean compositions, standard deviation, compositional ranges and reduced compositions are tabulated below.

The glasses contain between 4.15 and 8.16 wt % Na_2O, and between 7.02 and 12.88 wt % K_2O, with an average total alkali content of 15.88 %. These figures are well within the ranges of soda and potash compositions from previously published mixed-alkali glasses (see table 5.5).

	mean	stdev	min	max	Reduced comp.	sample 342
Na_2O	6.39	1.09	4.15	8.16	6.73	18.14
MgO	0.78	0.29	0.58	1.84	0.82	1.69
Al_2O_3	2.12	1.03	1.54	6.02	2.23	3.89
SiO_2	73.73	3.27	62.27	76.25	77.68	69.83
P_2O_5	0.13	0.03	0.07	0.19		0.02
SO_3	0.02	0.01	0.00	0.03		0.31
Cl	0.07	0.04	0.01	0.15		0.82
K_2O	9.53	1.75	7.02	12.88	10.04	0.20
CaO	1.65	0.50	1.28	3.35	1.74	4.21
TiO_2	0.06	0.03	0.02	0.18		0.07
Cr_2O_3	0.01	0.02	0.00	0.07		0.02
MnO	0.02	0.02	0.00	0.05		0.27
FeO	0.72	0.45	0.46	2.39	0.76	0.80
CoO	0.02	0.05	0.00	0.22		0.03
NiO	0.04	0.06	0.00	0.23		0.02
CuO	3.25	1.47	0.56	5.35		0.01
ZnO	0.02	0.02	0.00	0.06		0.02
As_2O_5	0.00	0.00	0.00	0.02		0.00
SnO_2	0.09	0.16	0.00	0.53		0.01
Sb_2O_5	0.02	0.03	0.00	0.11		0.06
BaO	0.04	0.01	0.02	0.06		0.02
PbO	0.03	0.04	0.00	0.11		0.03
Total					100	100.47

Table 5.1 Mean composition for mixed-alkali glasses from Montagnana, and sample 342.

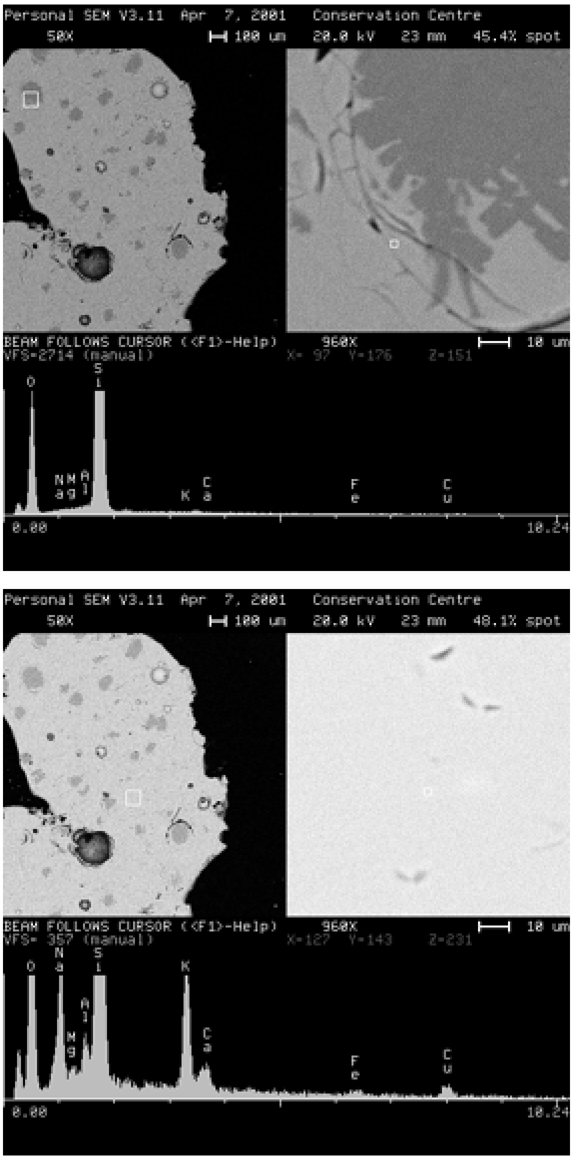


Figure 5.1 Backscattered electron SEM images of sample 311 showing silica-rich inclusions (dark grey) in a glassy matrix (light grey). Note the micro-cracks around the inclusion, and alkali depletion in the EDS spectrum. The EDS spectrum on the left is from the silica-rich zone, and of the glassy matrix to the right.

The glasses are also all mixed-phase, containing silica-rich components in a glassy matrix (see Figure 5.1). This phenomenon has been identified in previous studies (Biavati and Verità 1989, Santropadre and Verità 2000). The silica-rich phase has been identified in a small number of samples as tridymite, a crystalline form of silica formed at temperatures above 870 °C. It has been suggested that the silica-rich phase is the result of the addition of finely ground sand or quartz towards the end of the melt to opacify the glass, rather than remnant batch material. This has been asserted on the basis of observed irregular boundaries between the silica-rich phase and the glassy matrix (Biavati and Verità 1989, p 296). In addition to the well-defined silica-rich phase, there appears to be a network of cracks and alkaline-depleted zones within the glass, where weathering has preferentially removed the potash and soda contents of the glass. This porous structure is probably a consequence of the differential thermal expansion coefficients of the two phases and subsequent weathering. The observed sharp interface between two phases may therefore be due to the properties of the two phases, rather than the late introduction of additional silica to the melt. The silica-rich phase in part may be due to the formation of devitrification products crystallising out of the melt. Indeed, further comparison of examples from Frattesina with other mixed-phase glasses from prehistoric Italian contexts suggests that the Frattesina glasses contain more rounded crystalline "inclusions" than other glasses (Santropadre and Verità 2000, p 35), reflecting either higher temperatures or longer heating times. The consistent occurrence and distribution of the silica-rich phase in all the mixed-alkali glasses examined by SEM in this study would tend to suggest that this is a characteristic of the glassmaking technology, rather than a separate opacifying process. The incomplete fusion of the raw components, rather than complete dissolution into a single vitreous phase is a reflection of the technology involved. It has been suggested that the mixed phase glasses are the partial fusion of vitreous material recovered from the manufacture of cementation faience and silica-rich crystalline material (Santropadre and Verità 2000, p 40). However, examination of the artefact forms, from wound beads to shaped-ingots demonstrate that the mixed-alkali glass was worked whilst plastic, which could not be achieved with a barely adhering and semi-fused solid glass-sand mix. The material would have been maintained at the kind of temperatures from which glass could be made from raw components. The hot working characteristics of the artefacts identify the material as distinct from any faience technology, which involve baking and firing-type processes. On these grounds, the term “glass” is retained in preference to “glassy faience” for this mixed-phase material.

Colourants

All of the Montagnana samples are blue except 311 and 315, which are opaque reds. All of the 15 blue mixed-alkali glasses contain copper, but are not all simply coloured by copper oxide alone (mean copper oxide content = 3.25 %, range 0.56 - 5.35 %). Three of the blue glasses are principally coloured using cobalt oxide: samples 311, 312, and 337 contain 0.05, 0.06 and 0.22 % CoO respectively. Their copper oxide contents are commensurately lower: 1.41, 0.63 and 0.56 %. These cobalt-containing glasses also contains raised levels of both iron and nickel in comparison with the other blue mixed-alkali glasses. They do not contain raised levels of magnesia, alumina and zinc, which would be consistent with an Egyptian cobalt source, or the known zinc-rich sources in Iran (such as Tabriz: Henderson

1998, 2000, p 32). There is also no associated increase in arsenic, antimony, lead or manganese, which are elsewhere noted as companions of cobalt (see 3.7.20).

Amongst the other samples there is a group largely coloured by copper (2.08 - 5.35 % CuO), and several glasses with lower copper oxide contents with trace quantities of cobalt which may be intermediate glasses formed by the recycling of cullet (samples 310, 314, 318, 340: CuO content 1.72 - 3.88 %, CoO content 0.02 - 0.06 %). Interestingly, the highest cobalt coloured glass is an ingot fragment (sample 337), and has a concentration of cobalt four times the required quantity to colour the glass, raising the possibility of the use of concentrated coloured glass being produced with the intention of being used to colour other glasses (an early “zaffre”). Similarly, the highest copper - containing blue glass is also an ingot fragment (sample 308, CuO content = 5.35 %). Other writers have noted that the cobalt-coloured glasses from the contemporary site of Frattesina have raised levels of nickel (Brill 1992, p 14) this pattern can be observed in the Montagnana data, (see Figure 5.2,) which would tend to confirm that low levels of cobalt in some of the blue glasses is a consequence of recycling cobalt blue glasses. The cobalt ores from the Erzebirge region are associated with silver, nickel and bismuth, however the widespread incidence of cobalt minerals in Germany, Austria, Switzerland, the Czech republic and Slovakia make it very difficult to relate cobalt colourants to specific sources in this area (Henderson 1985, p 279).

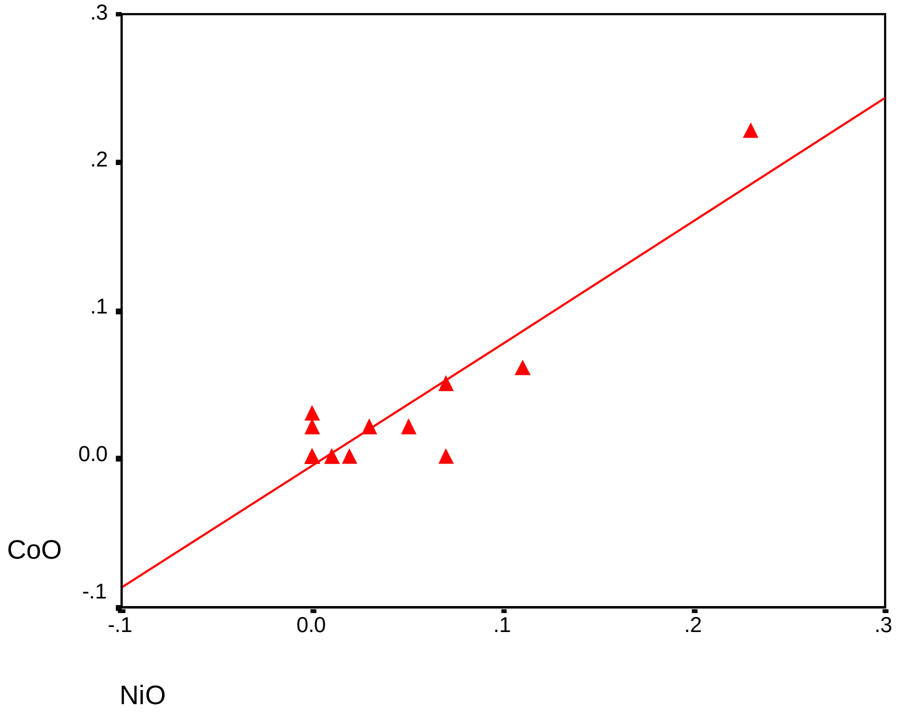


Chart 5.2 Showing correlation between cobalt and nickel oxides in blue mixed-alkali glasses from Montagnana.

The two opaque red glasses are both worthy of note (samples 311 and 315). Of the mixed-alkali glasses all but one have very low magnesia contents: average 0.77 %, range 0.58 - 1.84 %. Sample 311 has a magnesia content of 1.84 %, and if it is excluded from these figures, then the mean becomes 0.71 % with a reduced range of 0.58 - 0.88 %. Again these values are consistent with the previously published data. However, sample 311 cannot be readily dismissed as an intrusive find - it is a red opaque decorative band on a blue bead (sample 310) and has 5.8 % soda and 12.88 % potash (figure 5.5). It is distinct from the other mixed-alkali glasses on the basis of other variables: the alumina levels are very much higher (6.02 % compared with a mean of 1.88 %, range 1.54 - 2.45 % for the other glasses) and the iron content is elevated (2.39 %, compared with a mean of 0.61 %, range 0.46

- 1.09 for the other glasses). The lime levels are also slightly higher (3.35%) than the average for the rest of the mixed-alkali (mean = 1.54, range 1.28 - 2.09). Intriguingly, sample 311 has a relatively low copper content of 1.41 %. This amount is sufficient to be recognisable as a deliberate addition to the glass, and to impart colour, but it is lower than might be expected (in the region of 6- 10 %, Bimson 1992, p 167-168). The copper must be present as crystals of cuprous oxide (cuprite) and/or metallic copper (Hughes 1972, p 99). SEM imaging and qualitative EDS analysis of high atomic weight inclusions demonstrate the presence of copper-rich colourants (see figure 5.3).

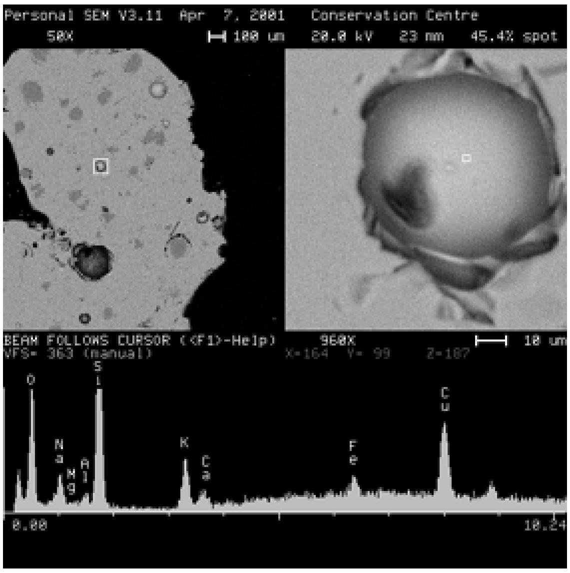


Figure 5.3 Backscattered electron SEM image of sample 311, also showing copper-rich inclusion using qualitative EDS analysis.

However, these inclusions are not common within the matrix of sample 311, and elemental mapping of the sample demonstrates that copper is present throughout the matrix, probably dissolved into the glass (see Figure 5.4).

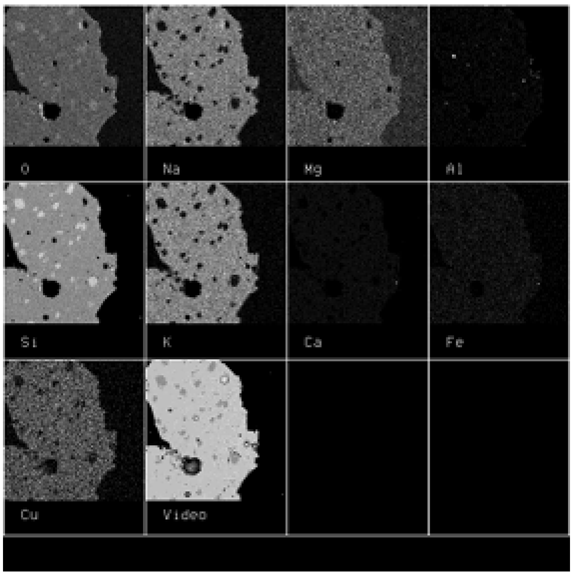


Figure 5.4 Elemental mapping of sample 311 using SEM. Note the silica-rich (and alkali-depleted) phases, and widely dispersed copper content.

Although these glasses predate the development of high-lead copper-coloured red glasses (Bimson 1992, p 168), it is possible that the high iron content facilitated the dissolution of copper oxide in the glass and the subsequent precipitation of cuprite/metallic copper (Henderson 1985, p 282, Guido *et al.* 1984, p 251, Hughes 1972, p 99). This bead’s decoration represents a significant technological feat, for the red-coloured glass has to be produced and maintained under reducing conditions, yet in this case it has been succesfully applied and marvered into to a glass core which has a much higher copper content (3.53 %), which has not been reduced itself. Could it have been applied, marvered flush and then polished to remove surface oxidation? Although sample 311 is from the mixed-alkali tradition, it is distinct from the other glasses from Montagnana, and perhaps should be regarded as a specialist composition developed to achieve and retain its red opaque colour when applied to a copper-rich blue coloured glass bead matrix.

Figure 5.5 sample 310 (bead matrix) and sample 311 (red opaque decoration). (Scale 2:1)

Another sample from this group (315) is also red opaque coloured. However, its composition is much more consistent with the main body of samples. Sample 315 is a broken annular bead, with rounded edges and a heat-distorted surface (see figure 5.6). The red colour does not extend over the entire surface and careful examination reveals that the bead is also dark blue in colour. The broken edges of the bead are rounded and coloured red. It seems most likely that this bead may never have been intended to appear red, but has undergone high temperatures and a reducing atmosphere after having been broken. This is significant in illustrating how the usual copper-coloured blue glass recovered from Montagnana can potentially be blue or red depending upon the final heat treatment, but is distinct from the glass composition employed as red decoration to the blue glasses. Work on similar material from Frattesina suggests that the red surface layer consists solely of copper oxide without the presence of glass (Santopadre and Verità 2000, p 38-39, and Figures 11-12). This has been interpreted as the deliberate application of a coating of finely powdered cuprite and metallic copper to the surface of the bead. However, this seems highly unlikely, given the frequent occurrence of red patches on a range of the artefacts discussed here (beads, bead decoration and ingot fragments), especially in the case of sample 315 where the broken edge of the bead is also red coloured. The separate application of a red coating was not necessary to achieve the required finish. The apparent surface enrichment of reduced copper oxide (c. 2 µm thick) observed by Santopadre and Verità is not likely to be an applied layer, but deserves experimental investigation to be more fully understood.

Figure 5.6 Images of sample 315, scale 2:1.

Sample 342.

During sampling it was assumed that sample 342 from Montagnana was from the excavation of the Bronze Age site of Borgo San Zeno. This was not a complete artefact, but a collection of small irregular fragments of translucent blue glass stored with an annular bead of translucent blue glass. The artefact is from a funerary context, but no other information is available. From the chemical analysis (see table 5.1 above) it is quite different to the mixed-alkali glasses recovered from Borgo San Zeno, and should not be considered alongside the other samples. It is a low magnesia, soda-lime-silica glass with a significant manganese content (0.27 %) typical of a Roman glass from the late 2nd Century BC onwards. Given the poorly recorded context, it seems most likely that this is a much later product and not contemporary to the other Montagnana material.

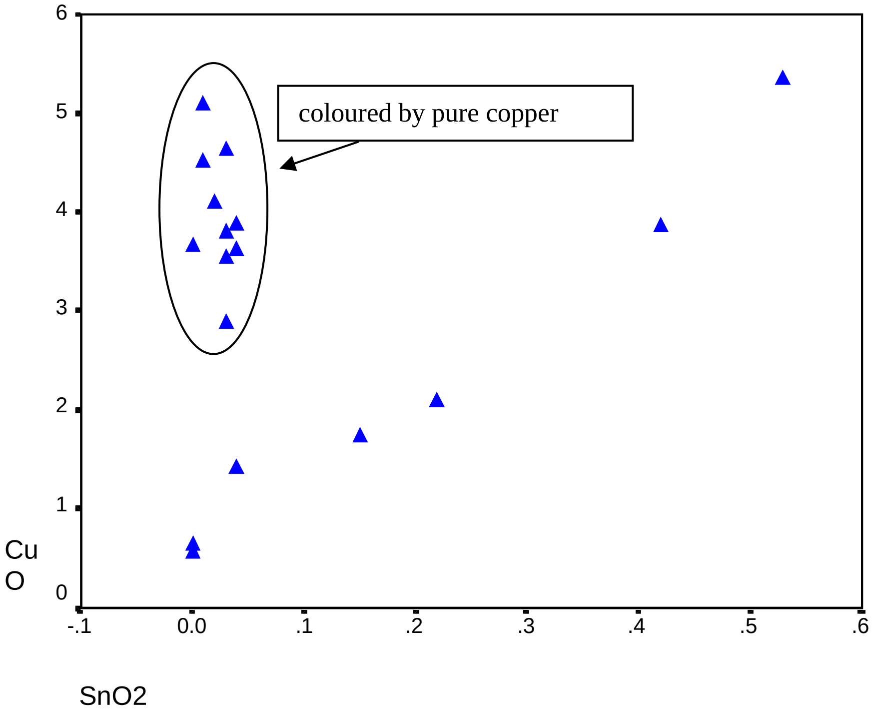


Figure 5.7 Copper and Tin contents of Bronze Age Glasses from Montagnana coloured by copper.

To investigate the use of copper and copper alloys in the colouring of the glasses, it is useful to examine the relationship between the copper and tin components in the copper coloured glasses (in this case the entire assemblage excluding samples 342 and 337). Simply running a correlation analysis between the two variables may not indicate the nature of the relationship: a bivariate correlation (Pearson) gives a correlation coefficient of 0.194. However, by displaying the data on a bivariate scatter plot is possible to discern two distinct types of copper colourant: one group containing almost pure copper, and the other containing a copper/tin tin alloy. A trend line on the latter group gives a gradient of y = (8.1949x) + 0.6492, which gives an approximate ratio of copper : tin of 1: 0.122 (i.e. 89 % copper/11% tin alloy). This indicates that the Montagnana assemblage represents the use of both copper - tin alloys and pure copper as colourants. The group designated as coloured using “pure” copper was examined to ensure that the copper is not associated with any other component, such as silica, alumina, lead oxide which might indicate that it is derived from some other material such as a copper-rich slag. A bivariate correlation matrix for these glasses demonstrated no positive corelates for copper oxide, and only a single strong negative correlation (-0.603) between cobalt oxide and copper oxide. This would tend to confirm that the copper raw material was almost pure.

A number of the Montagnana beads were decorated with white opaque glass trailed around a blue matrix, unfortunately this glass was badly weathered and friable, and none of the attempts to sample the white opaque glass were successful.

5.3.2 Frattesina

25 samples: 220, 222, 223, 224, 225, 226, 227, 228, 230, 233, 234, 235, 236, 289, 290, 291, 292, 293, 294, 295, 296, 298, 299, 300, and 301.

The Frattesina material was collected from the Museum of Adria (samples 220 - 236) and the Museum of Rovigo (samples 289 - 301): the latter holding the majority of glass collected from excavations and fieldwalking from Fratte Polesine.

The sampled Frattesina assemblage includes anthropomorphic figures, glass ingots, working waste, beads and applied bead decoration, crucible residue and a core-formed glass vessel.

Glass types

The dominant glassmaking tradition amongst the Frattesina material is the mixed-alkali glass type previously identified as a Bronze Age European phenomenon (Henderson 1988a, also see section 3.7.3 above and 5.4.1 below). 22 of the 25 samples are of this type, which have a mixed soda/potash composition. The soda values range from 3.3 - 8.83 % and the potash values range from 6.24 - 13.27 %, which are consistent with previously published analyses of this compositional type (both upper range values are less than 1 % above the other analyses, and the lower values are within previously published compositions). The average overall alkali content is 15.49 %.

Three analyses are not mixed-alkali glasses (samples 235, 236 and 294, a bead, a vessel and a crucible residue respectively), these are all potash glasses. In these glasses potash (16.53, 17.3 and 15.67 %) is the principle alkali, and there are commensurately low soda contents (0.96, 1.3 and 1.76 %). This technology is distinct from the mixed-alkali tradition, and suggests that a different plant ash has been employed in their manufacture. Potash-rich plant ashes are typically inland plants, such as wood or fern ash. The manufacture of potash glasses is well established in Northern Europe during the Medieval period, but has not been widely documented for earlier periods in the region. Potash glasses are known elsewhere during the 1st Millenium BC, such as China, India, Pakistan and SE Asia (Hall and Yablonsky 1998, p 1243).

The potash glasses are also characterised by slightly raised calcium oxide levels, which is consistent with observations of the later, medieval glasses. However, the lime levels of 2.05, 3.34 and 3.15 % are not comparable to the high lime potash glasses of Medieval Europe, which are typically much higher in the range of 10 - 22 % (for example see the analyses of Medieval Northern European window glasses in Brill 1999b, p 260 - 290). A low lime level is characteristic of the European mixed-alkali group. There are further aspects of these glasses, which distinguish them from other potash glasses. There is also no significant increase in magnesia levels when compared with the other mixed-alkali glasses, which is often a feature of potash glasses. Low magnesia content is one of the remarkable characteristics of the mixed-alkali glass type, and it is a feature shared by the potash glasses from Frattesina. The processes involved in the preparation of the raw materials for fusion into glass are therefore likely to be the same for both the mixed-alkali glass and the potash glass. This is likely to have been a refining of plant ashes which preferentially removed magnesia and calcium compounds.

Whilst there was no doubt that samples 235, 236 and 294 are from contemporary contexts to the other Frattesina material, the shared low-magnesia phenomenon is useful confirmation. The three artefacts involved, a miniature core-formed vessel, a finished bead and crucible residue demonstrate that this glass type is represented amongst both working debris and finished artefacts, meaning that potash glass is not an exotic import, but likely to have been worked alongside the mixed-alkali type. Its use for a bead (a ubiquitous artefact at Frattesina) and the miniature core-formed glass vessel indicate the potash glass is not a specialised recipe reserved for specific forms. However, it cannot be attributed to natural variation in the mixed-alkali recipe: there is no continuum of potash and soda values across the Frattesina data set between “mixed-alkali” and “potash” glasses. The difference between the two glass types is a distinct one, and although they are from the same technological tradition, they are not due to natural variation in plant ash chemistry.

	mean MA	min	max	stdev	reduced comp.	235	236	294	mean K2O
Na_2O	5.67	3.30	8.83	1.27	5.97	0.96	1.30	1.76	1.34
MgO	0.81	0.50	1.90	0.29	0.85	0.61	0.83	0.77	0.74
Al_2O_3	2.86	1.03	7.19	1.64	3.01	2.84	2.11	1.50	2.15
SiO_2	73.19	62.12	82.60	4.67	77.08	67.96	71.97	77.47	72.47
P_2O_5	0.14	0.05	0.24	0.05		0.21	0.25	0.14	0.20
SO_3	0.31	0.00	4.33	0.96		0.03	0.06	0.09	0.06
Cl	0.07	0.01	0.34	0.08		0.01	0.01	0.01	0.01
K_2O	9.82	6.24	13.27	2.05	10.34	16.53	17.30	15.67	16.50
CaO	1.96	1.02	3.94	0.81	2.06	2.05	3.34	3.15	2.85
TiO_2	0.06	0.00	0.19	0.04		0.06	0.13	0.07	0.09
Cr_2O_3	0.01	0.00	0.05	0.01		0	0.01	0.00	0.00
MnO	0.02	0.00	0.05	0.01		0.05	0.05	0.07	0.06
FeO	0.66	0.31	1.98	0.34	0.70	0.43	0.61	0.61	0.55
CoO	0.02	0.00	0.08	0.02		0.02	0.01	0.02	0.02
NiO	0.02	0.00	0.32	0.07		0	0.02	0.00	0.01
CuO	3.42	0.05	5.86	1.70		5.39	3.59	1.18	3.39
ZnO	0.01	0.00	0.03	0.01		0	0.02	0.02	0.01
As_2O_5	0.01	0.00	0.13	0.04		0	0.00	0.00	0.00
SnO_2	0.22	0.00	0.57	0.18		0	0.21	0.03	0.08
Sb_2O_5	0.02	0.00	0.09	0.02			0.01	0.02	0.02
BaO	0.05	0.02	0.06	0.01			0.05	0.05	0.05
PbO	0.03	0.00	0.18	0.04			0.03	0.04	0.04
Total					100	97.5	101.88	102.67	

Table 5.2 Summary of data for Frattesina glasses

Colourants

The Frattesina assemblage includes a range of colours, amongst those sampled here are 9 blue translucent glasses, 8 blue opaque glasses, 1 white opaque, 3 red opaque 2 green translucent and 2 aqua translucent. The “blue” category includes a range of shades including turquoise and azzure, and the distinction between opaque and translucent is not a clear one: all of the completed artefacts were densely coloured but often translucent when thin fragments were observed against a light source.

Samples 266 (aqua translucent ingot fragment) 294 (aqua translucent crucible residue) and 301 (pale green translucent pinched-off working waste) are all essentially uncoloured glasses, without the deliberate addition of colourants, and owe their respective tinges to a combination of their iron impurities and oxidation state during production.

There is no indication of the use of a decolourant in any of the Frattesina glasses: antimony pentoxide would be the most likely during this period. There is no accidental inclusion of manganese oxide in the glass compositions which is often a component of potash-rich plant ashes, and can have a decoloursing effect (see 3.7.15 and 3.7.16).

Copper is present in all of the blue and red glasses, and one dark green translucent glass (sample 300). The copper content is quite variable amongst this group (from 0.29 - 5.86 %), but the only sample with less than 1.3 % copper oxide content is sample 222, an opaque blue ingot fragment which is also coloured with cobalt (copper oxide = 0.29 %, cobalt oxide = 0.08%). This is the highest cobalt oxide content of any of the glasses from Frattesina. There are three samples with moderate cobalt oxide contents: samples 222, 234 and 290 containing 0.08, 0.06 and 0.06 % CoO respectively. 10 samples contain low cobalt oxide levels accompanied by significant proportions of copper oxide suggesting that the cobalt is an accidental component (i.e. 0.02 - 0.03 % CoO, with 1.36 - 5.46 % CuO). This would tend to be confirmed with similar levels of CoO in samples 294 and 301 which are essentially uncoloured glasses.

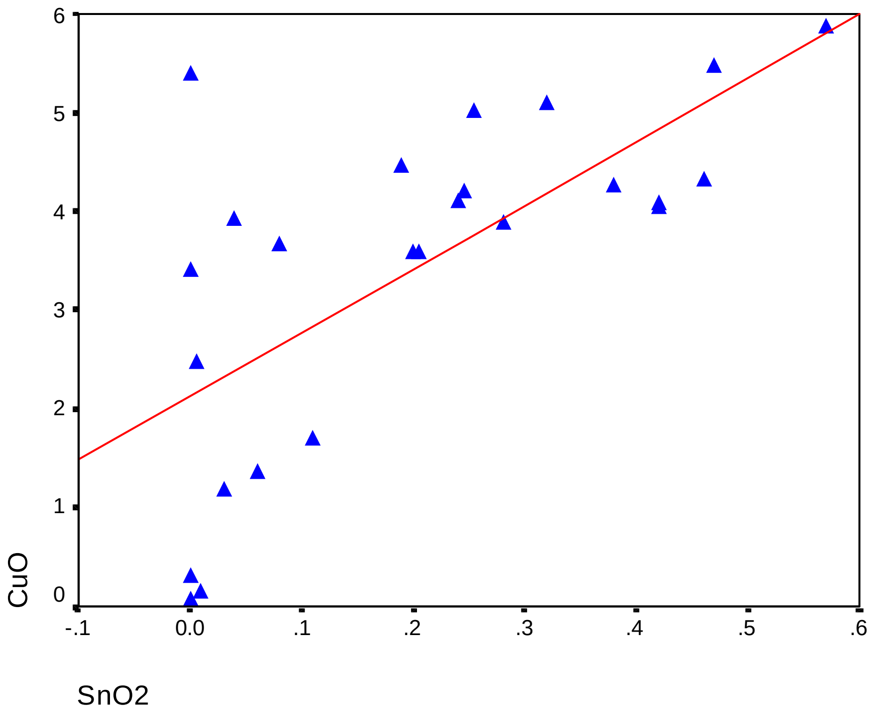


Figure 5.8 Scatter plot showing the relationship between tin and copper oxides in glasses from Frattesina.

The copper used as a colourant in the glasses is derived from two sources: a relatively pure copper, and a copper-tin alloy. A trendline across the correlated tin and copper -containing glasses has a gradient of y = 9.3641 x + 1.0442, which equates to a copper : tin ratio of approximately 1 : 0.107 (, or 90 % copper, 10 % tin).

5.3.3 Mariconda

19 samples: 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 219.

All the samples were collected from the Museum of Adria, and are derived from the Final Bronze Age site of Mariconda. The assemblage includes glass residue on “crucibles”, working waste, beads and a possible fragment of overheated frit.

Glass types

All of the Mariconda material is from the Bronze Age Europe mixed-alkali glass tradition (Henderson 1988a, also see section 3.7.3 and 5.4.1). The glasses contain significant quantities of both soda (4.79 - 6.79 %) and potash (7.34 - 12.03 %), and low levels of magnesia (0.46 - 1.76 %) and lime (1.51-3.19 %) characteristic of this glass type. Two of the samples are not from “true “ glasses, but are nonetheless worthy of note.

	Mean (excluding 205 and 206)	min	Max	stdev	Reduced comp.
Na_2O	5.99	4.79	6.79	0.53	6.03
MgO	0.87	0.46	1.76	0.34	0.88
Al_2O_3	2.81	1.86	4.26	0.77	2.83
SiO_2	76.99	70.91	81.88	3.39	77.48
P_2O_5	0.18	0.1	0.38	0.06	
SO_3	0.04	0	0.33	0.08	
Cl	0.08	0.03	0.21	0.05	
K_2O	9.63	7.34	12.03	1.18	9.69
CaO	2.20	1.51	3.19	0.48	2.22
TiO_2	0.07	0.04	0.13	0.02	
Cr_2O_3	0.02	0	0.12	0.03	
MnO	0.04	0	0.16	0.04	
FeO	0.86	0.49	1.37	0.25	0.87
CoO	0.11	0	0.36	0.12	
NiO	0.15	0	0.56	0.17	
CuO	1.39	0.08	3.33	1.30	
ZnO	0.01	0	0.06	0.02	
As_2O_5	0.04	0	0.18	0.06	
SnO_2	0.05	0	0.27	0.10	
Sb_2O_5	0.05	0	0.34	0.08	
BaO	0.03	0.01	0.05	0.02	
PbO	0.02	0	0.06	0.02	
Total					100

Table 5.3 Mean values for mixed-alkali glasses from Mariconda

Samples 204, 205 and 206

Samples 204, 205 and 206 are all derived from the same object (see figure 5.9), which was of uncertain nature during sampling. The artefact consists of a roughly triangular shaped fragment of material 15 mm long, 7 mm wide and 7 mm thick, consisting of three layers of material. The surface is a layer of blue (turquoise?) translucent glass 2.5 mm thick adhering to a band of friable white crystalline material 2.5 mm thick which in turn lies on a compact layer of grey granular material. All three layers were sampled and analysed.

Figure 5.9 Samples 204, 205 and 206 from fragment of “frit”. Scale 1:1.

	204	205	206
Na_2O	5.56	0.68	5.8
MgO	1.76	0.49	0.65
Al_2O_3	4.26	1.44	1.85
SiO_2	74.59	94.72	85.14
P_2O_5	0.17	0.1	0.17
SO_3	0.03	0	0.03
Cl	0.06	0.09	0.06
K_2O	7.34	1.34	6.99
CaO	1.68	1.15	1.66
TiO_2	0.13	0.04	0.06
Cr_2O_3	0.02	0.02	0.03
MnO	0.1	0.01	0.03
FeO	1.3	0.47	0.56
CoO	0	0	0
NiO	0.01	0	0
CuO	0.08	0.09	1.04
ZnO	0	0	0
As_2O_5	0	0	0
SnO_2	0	0.01	0.01
Sb_2O_5	0	0.02	0
BaO	0.04	0.02	0.05
PbO	0	0	0.04
Total	97.13	100.69	104.17

Table 5.4 Analytical data for samples 204, 205 and 206.

Sample 204 from the upper layer is a typical mixed-alkali glass, and is unremarkable, except perhaps for its low copper content (0.08 %) and absence of cobalt: its blue colour probably derived in part from the iron content (1.3 %). It also has slightly raised magnesia content in comparison with the rest of the assemblage (1.76 %), but is comparable with other contemporary mixed-alkali glasses. The crystalline material in the centre of the object proved to be almost entirely silica (94.72 %) supplemented with small quantities of alumina, lime and potash. This silica-rich composition might suggest that the object was a fragment of molten glass which has fused to a patch of sand, such as might happen during glassworking, or even be a fragment of poorly made faience with a vitreous layer adhering to a partially fused silica-rich core. The third layer, however proved to be of composition very similar to the glass. With raised silica levels and slightly lowered potash content, this material could be interpreted as a fragment of overfired frit. The upper surface of the artefact has become fully vitrified, the centre of the piece is a patch of silica-rich material, which has been incompletely mixed, and the third layer is of partially fused raw materials. Alternatively the material may be a fragment of faience-type material, formed by the efflorescence method (Nicholson 1993, p 10-14). In this process the surface of the object becomes enriched in alkaline salts during the drying of a paste object made from a mixture of silica and alkaline-rich materials. During subsequent firing the surface vitrifies, leaving a glassy surface fused to a sintered silica-rich core. This would explain the layered effect observed in the artefact, with a vitreous surface, an alkali-depleted zone and a core of composition similar to the surface. The appearance of this material would also be consistent with the suggested initial production technique for mixed-alkali glass described by Santopadre and Verità, in which the faience cementation method is outlined (Santopadre and Verità 2000, p 31-32). However, these authors fail to recognise that their suggested manufacturing process does not account for the indications of hotworking found on the Frattesina artefacts amongst their samples.

SEM images and EDS analysis of the different phases in each sample confirms the distinction between the three layers of the artefact suggested by the EMP results. Figures 5.10 and 5.11 demonstrate the two phases present in the upper glassy layer (sample 204), in which the darker zone is silica-rich. This can be contrasted with Figure 5.12 which shows a backscattered image of sample 205 which is principally silica-rich material, and figure 5.13 of sample 206, which is again a two-phase material.

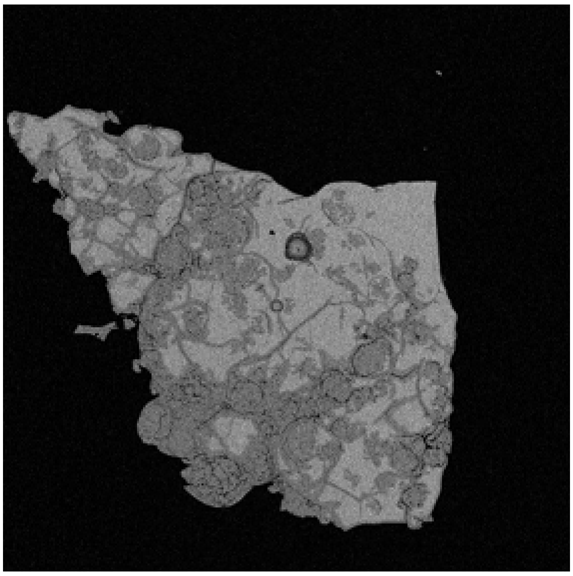


Figure 5.10 Backscattered SEM image of sample 204 showing the two-phase composition typical of the mixed-alkai glasses.

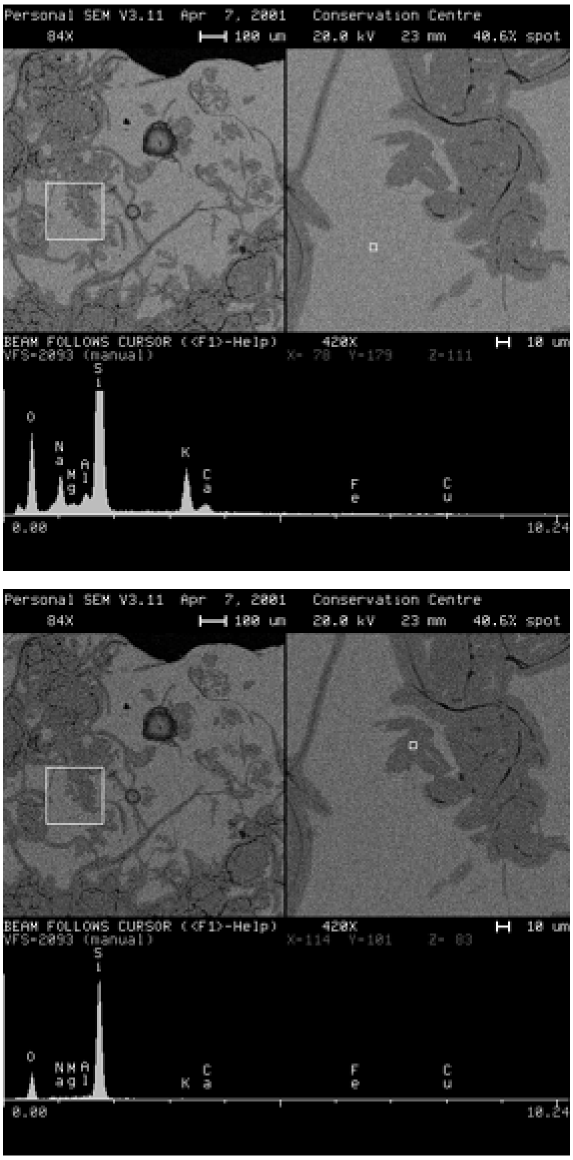


Figure 5.11 Backscattered SEM images of sample 204 with qualitative EDS analyses of the different phases.

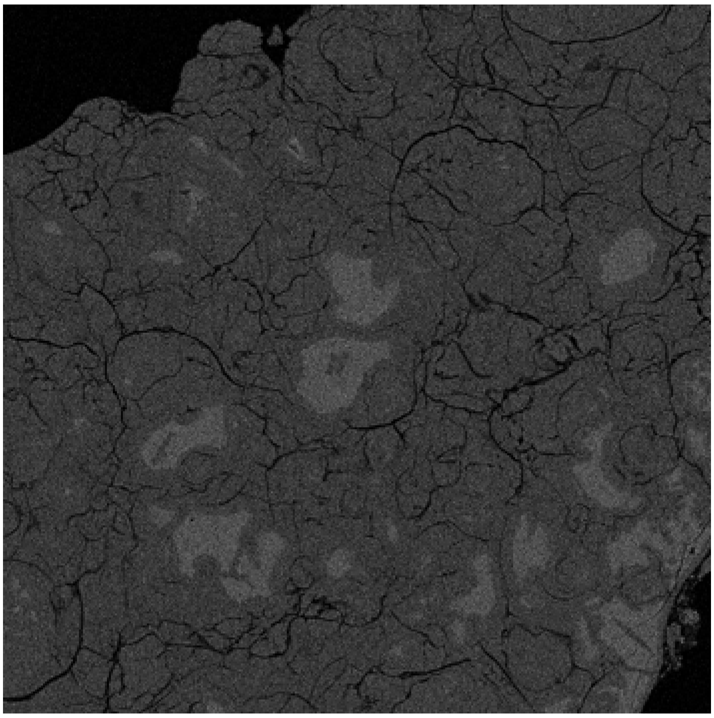


Figure 5.12 Backscattered SEM images of sample 205 showing two phases but dominated by the silica-rich phase

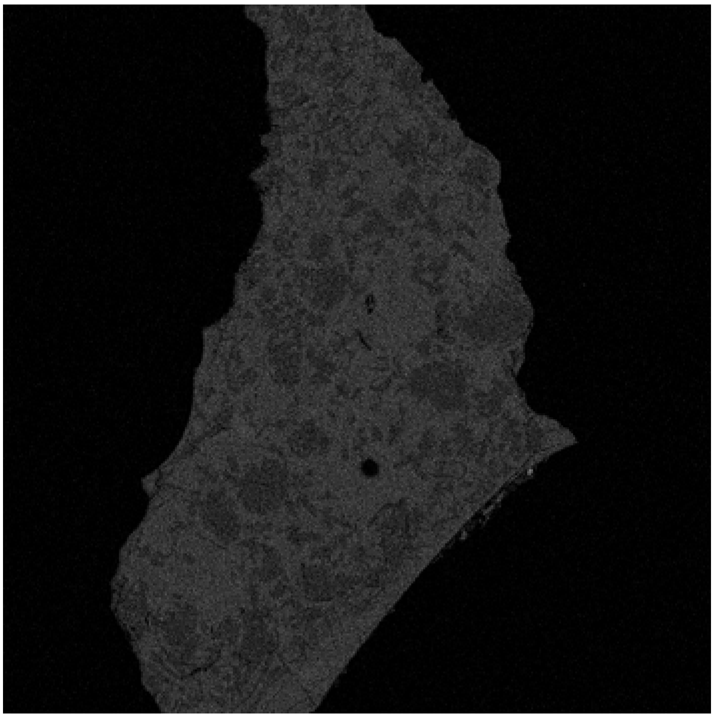


Figure 5.13 Backscattered SEM images of sample 206.

This interpretation is tentative, but does explain the lack of a deliberately added colourant in sample 204: all of the other Mariconda samples are coloured by copper, cobalt or both. This would suggest the addition of colourant is a secondary process to the primary fusion of the raw materials into glass. The absence of faience from the site would tend to suggest that this piece is not a fragment of faience production waste. If this object is a fragment of frit (or even faience waste), it is the only concrete evidence for the primary production of mixed-alkali glass. Whilst the sheer quantity of glassworking material from Frattesina in particular, and also Mariconda and Montagnana strongly suggest the production of mixed-alkali glass in the Po valley during the Final Bronze Age, there has been no definitive evidence of glassmaking. This piece might therefore be very significant.

Colourants

All of the sampled glasses were blue (translucent or opaque), attempts to sample the white spiral decoration on some of the beads were unsuccessful. Apart from sample 204 (see above) all of the glasses were coloured by copper or cobalt (11 samples of blue glasses contained 0.05+ % CoO). The oxides of these two elements are very strongly negatively correlated (-0.716, Pearson bivariate correlation), and demonstrate that the makers of these glasses knowingly selected cobalt or copper compounds as colourant, and were not tied into a craft tradition which demanded both to achieve the desired colour. Only one of the samples contained both oxides in quantities suitable for colouring (sample 218, 0.09 % Co O, and 3.29 % CuO), and one further sample coloured by copper oxide had a trace of cobalt oxide, suggesting that recycling was practised (sample 208, 3.33 % CuO, 0.02 % CoO).

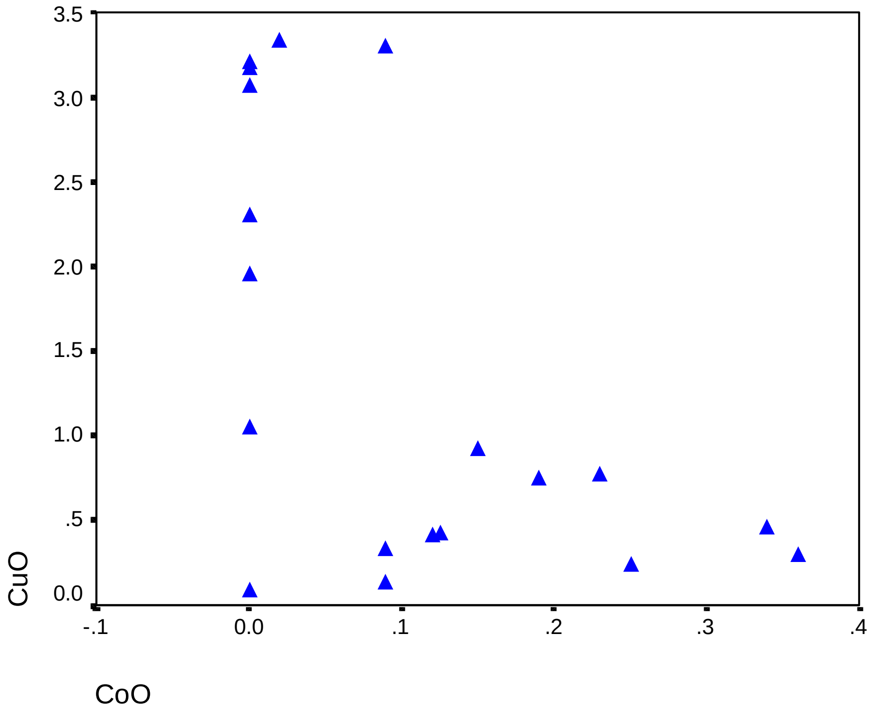


Table 5.14 Cobalt versus copper oxide content for glasses from Mariconda

An examination of those glasses coloured by copper compounds alone reveals that both pure copper and a copper-tin alloy were employed (see figure 5.15 below). A trend line across the copper-tin correlated data gives a gradient of y = 11.333 x + 0.4268, which equates with a copper : tin ratio of 1 : 0.08 (or a bronze composition of approximately 92 % copper 8 % tin).

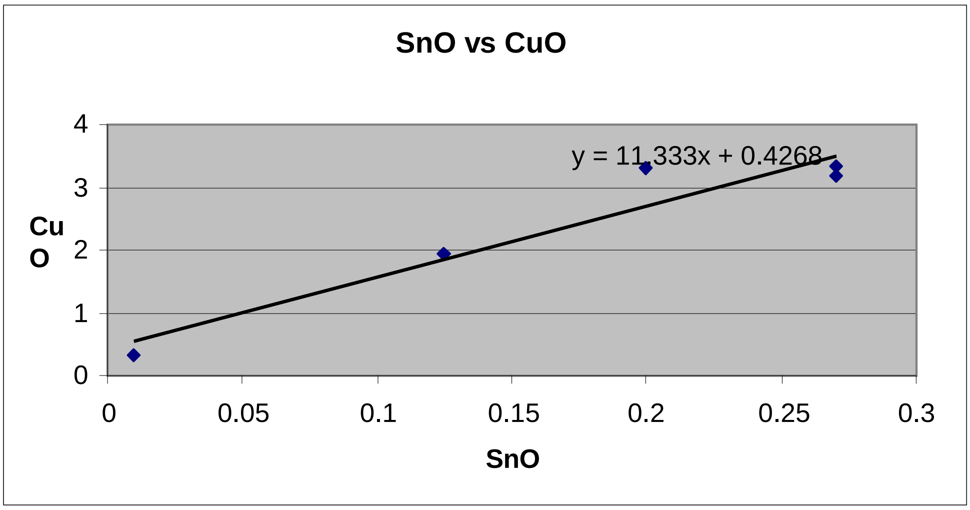


Figure 5.15 Scatter plot showing relationship between the copper and tin oxide contents of glasses from Mariconda coloured with copper alloy

5.3.4 Discussion of the Bronze Age material.

As described above this project involved the study of material from three Final Bronze Age sites, with 62 samples in total (one of which is excluded from this discussion, sample 342, see 5.3.1 above). The identification of mixed-alkali glasses and subsequent analysis of this particular glass technology is discussed in some detail above (section 3.7.3). The glasses from these three sites are remarkably consistent with the published material on mixed-alkali glasses from previous studies of European Bronze Age glasses, which are summarised in tables 5.5 - 5.8 below.

site	*date*		*Na_2O*	*K_2O*	*MgO*
Rathgall (n=16)	9th-7th C. BC	average	7.7	8.47	0.68
		range	3.3-8.8	7.3-10.3	0.6-0.80
Hauterive-Champréveyres	11th-10th C. BC	average	5.5	10.1	0.7
(n=31)		range	3.7-7.6	7.7-13.2	0.4-1.1
Kassell (n=4)	12th-8th C. BC	average	4.6	10.6	0.58
		range	3.07-5.6	8.97-13.9	0.54-0.63
Frattesina (Brill) (n=6)	12th-9th C. BC	average	5.63	9.91	0.58
		range	4.85-6.91	8.71-12.30	0.43-0.7
Frattesina (B+V) (n=3)	12th-9th C. BC	average	6.06	9.43	0.82
		range	5.0-7.4	8.5-9.9	0.7-0.9
Frattesina (Biavati) (n=3)	12th-9th C. BC	average	5.15	7.82	0.62
		range	3.79-6.12	6.77-8.96	0.59-0.64
Grotte de Bringairet (n=10)	16th-12th C. BC	average	6.72	8.78	0.75
		range	4.3-8.0	6.5-11.8	0.64-0.88
Grotte de Sindou (n=2)	12th-10th C. BC	average	6.5	8.35	0.6
		range	6.0-7.0	7.8-8.9	0.4-0.8
Billy le Theil (n=11)	12th-10th C. BC	average	4.4	10.8	0.6
		range	3.5-4.8	9.1-11.3	0.5-0.6
Le Fort-Harrouard (n=4)	1500-1100 BC	average	4.75	8.18	0.55
		range	3.4-6.3	5-10.2	0.4-0.7
Le Depot de Reallon (n=4)	1200-900 BC	average	4.98	9.48	0.65
		range	3.5-6	8.7-10.7	0.4-1.3
Rancogne (n=2)	1200-900 BC	average	4.65	8.6	0.7
		range	4.5-4.8	7.8-9.4	0.6-0.8
Gord (n=1)	2895-2420 BC(?)	1 sample	7.7	9.2	0.6
Vicofertile (n=1)	1500-1100 BC	1 sample	5	10.5	0.58
Quingento (n=1)	1500-1100 BC	1 sample	6.6	9.5	0.5
all mixed-alkali (n=99)	2895(?) - 600 BC	average	5.82	9.52	0.67
		range	3.07-8.8	5-13.2	0.4-1.3

Table 5.5 Values of soda, potash and magnesia from earlier studies of prehistoric mixed-alkali glasses. Values taken from: Rathgall (Henderson 1988b, 16 analyses), Hauterive-Champréveyres (Henderson 1993b, 31 analyses), Kassel (Hartman *et al.* 1997, 4 analyses), Frattesina (Brill 1992, 6 samples)(Biavatti and Verità 1989, 3 analyses) (Biavati 1983, 3 samples), Grotte de Brinairet, Grotte de Sindou, Gord (Guilaine *et al.* 1991), Billy le Theil, Rancogne, Le Fort-Harrouard, Le Depot de Reallon (Gratuze *et al.* 1998), Vicofertile and Quingento (Bellintani *et al.* 1998).

site	*date*		Na_2O	K_2O	MgO
Mariconda, Frattesina and	12th-9th C. BC	average	5.99	9.67	0.82
Montagnana (n=57)		range	3.3-8.83	6.24-13.27	0.3-0.46

Table 5.6 Values of soda, potash and magnesia contents from Bronze Age mixed-alkali glasses from Mariconda, Montagnana and Frattesina, analysed for this project.

The Frattesina assemblage included three distinct glasses, which may be characterised as potash rather than mixed-alkali glasses. These glasses share common features with the contemporary mixed-alkali glasses, such as low magnesia and lime contents which distinguish them from potash glasses from other periods and locations (see table 5.7 and section 5.3.2).

site	*date*		Na_2O	K_2O	MgO
Frattesina (n=3)	12th-9th C. BC	average	1.34	16.50	0.74
		range	0.96-1.76	15.67-17.30	0.61-0.83

Table 5.7 Values of soda, potash and magnesia contents from Bronze Age potash glasses from Frattesina.

It is important to note that these three contemporary sites from the Final Bronze Age not only have glass which is manufactured in the same tradition (perhaps even in the same place), but all of these sites have evidence of glassworking using the mixed-alkali glass. To date, examples of mixed-alkali glasses from other sites have been completed items only. Whilst it seems likely that this glass type was being manufactured at Frattesina, given the range and quantity of material recovered, there is no conclusive evidence that this was the case. It is also possible that glass was being manufactured from raw material at Mariconda (see 5.3.3 above). It is absolutely clear that the polity of Frattesina, for all its economic power and significance in inter-regional commerce (Bietti Sestieri 1997), it does not exercise monopolistic control over glass technology.

By comparing the standard deviations and mean values for the components for the glasses from these three sites, it is possible to see how similar they are:

	mean (this project)	stdev (this project)	stdev (other MA glasses)	mean (other MA glasses)
Na_2O	5.99	1.060	1.371	5.83
MgO	0.82	0.303	0.156	0.65
Al_2O_3	2.62	1.268	1.162	2.25
SiO_2	74.55	4.189	3.003	74.28
P_2O_5	0.15	0.054	0.712	0.26
SO_3	0.14	0.607	0.052	0.08
Cl	0.08	0.058	0.095	0.11
K_2O	9.67	1.702	1.488	9.52
CaO	1.94	0.657	2.061	2.64
TiO_2	0.06	0.031	0.023	0.08
Cr_2O_3	0.01	0.020	0.009	0.02
MnO	0.03	0.025	0.045	0.03
FeO	0.74	0.359	0.177	0.55
CoO	0.05	0.084	0.096	0.06
NiO	0.07	0.123	0.170	0.10
CuO	2.73	1.748	1.357	2.81
ZnO	0.01	0.018	0.026	0.03
As_2O_5	0.02	0.044	0.143	0.08
SnO_2	0.13	0.165	0.180	0.14
Sb_2O_5	0.03	0.053	0.202	0.17
BaO	0.04	0.014	0.003	0.01
PbO	0.02	0.035	0.085	0.05

Table 5.8 Standard deviations for mixed-alkali glasses from this study, and those previously published.

It is remarkable that the mixed-alkali glasses, from studies of material across Western Europe over a considerable timespan are so consistent: the 99 samples from previous studies demonstrate very little variation across the entire dataset, and when compared with the standard deviations for components from this study, they cannot be readily distinguished in terms of either mean values or degree of variance for the measured components.

In order to try and establish if the mixed-alkali glasses might be differentiated on compositional grounds, both PCA and Correlation analysis were performed on the merged data from the published analyses and this study. Since not all the published analyses have data on the same range of oxides, a reduced number of variables were examined in the PCA (i.e. 156 samples from 13 sites). For the maximum inclusion of samples, only 6 oxides could be included (Na2O, MgO, Al2O3, SiO2, K2O and CaO). Two components accounted for 61 % of the variation.

	Component 1	Component 2
Na_2O	-0.119	-0.883
MgO	0.701	-0.149
Al_2O_3	0.759	4.91E-02
SiO_2	-0.778	-1.36E-02
K_2O	-8.57E-02	0.82
CaO	0.603	0.352

Table 5.9 PCA analysis on combined Mixed-alkali glasses: Rotated Component Matrix. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 3 iterations.

A scatter plot of the 2 principal components labelled by site does not identify site-specific groups (figure 5.16). The tight clustering of samples from Billy Le Theil reflects their narrow compositional variation, rather than significant difference from the body of data as a whole.

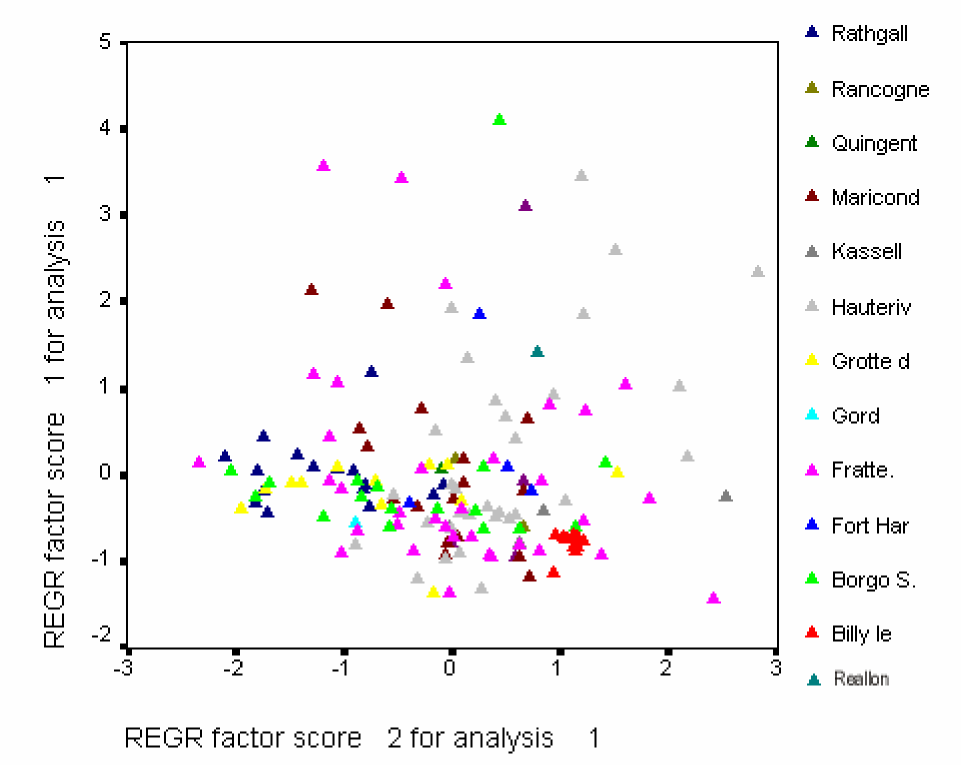


Figure 5.16 Scatter plot of 2 principal components of combined mixed-alkali glasses.

All the samples and all oxides sought were available for the generation of a correlation matrix, permitting the identification of components for bi-variate plotting, however no site-specific groups were identified using this method.

Colourants in the mixed-alkali glasses.

The majority of the mixed-alkali glasses are coloured blue, in a range including turquoise translucent to dark blue opaque, but also include opaque white, opaque red and uncoloured glasses (which often carry faint tints due to their iron content).

Guilaine has noted that mixed-alkali glasses were not coloured using cobalt prior to 1200 BC (Guilaine *et al.* 1991), and this observation remains true for those early glasses published in the meantime (i.e. Bellintani *et al.* 1998 and Gratuze *et al.* 1998). Both cobalt and copper oxides are used in glasses from Final Bronze Age contexts examined here.

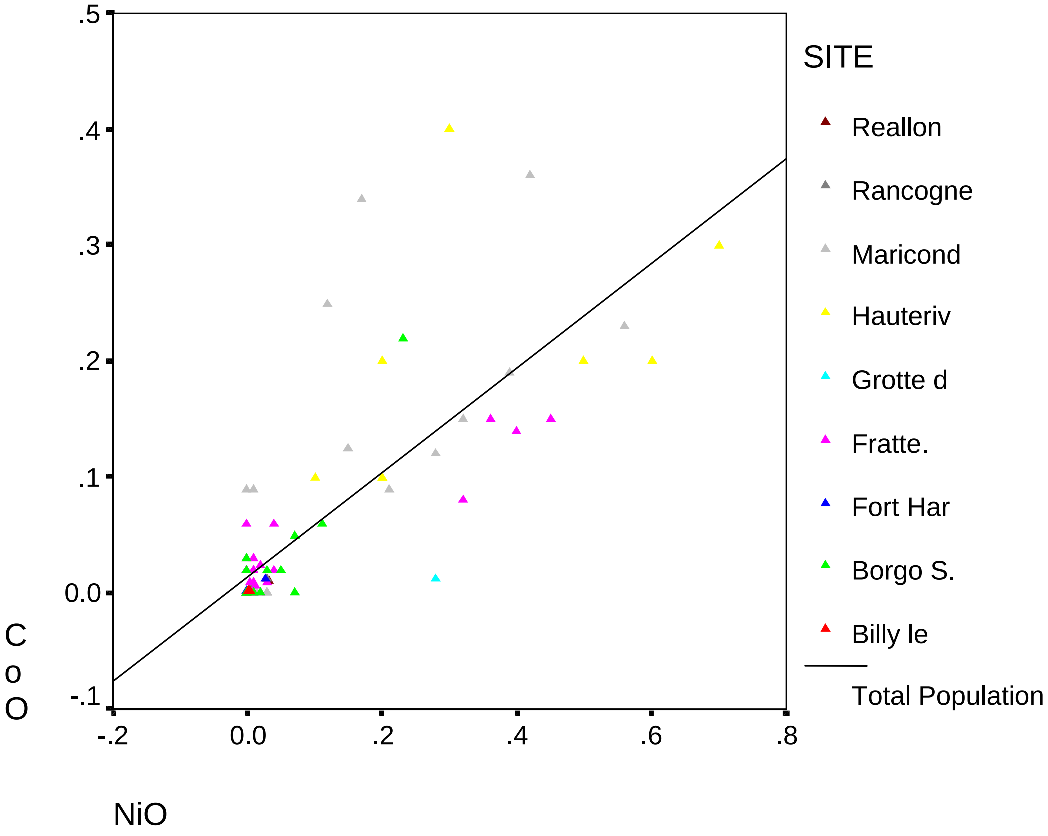


Figure 5.17 Cobalt oxide vs nickel oxide, all published mixed-alkali glasses and this study.

Figure 5.17 clearly shows the correlation between cobalt and nickel across all mixed-alkali glasses, where cobalt has been used as a colourant.

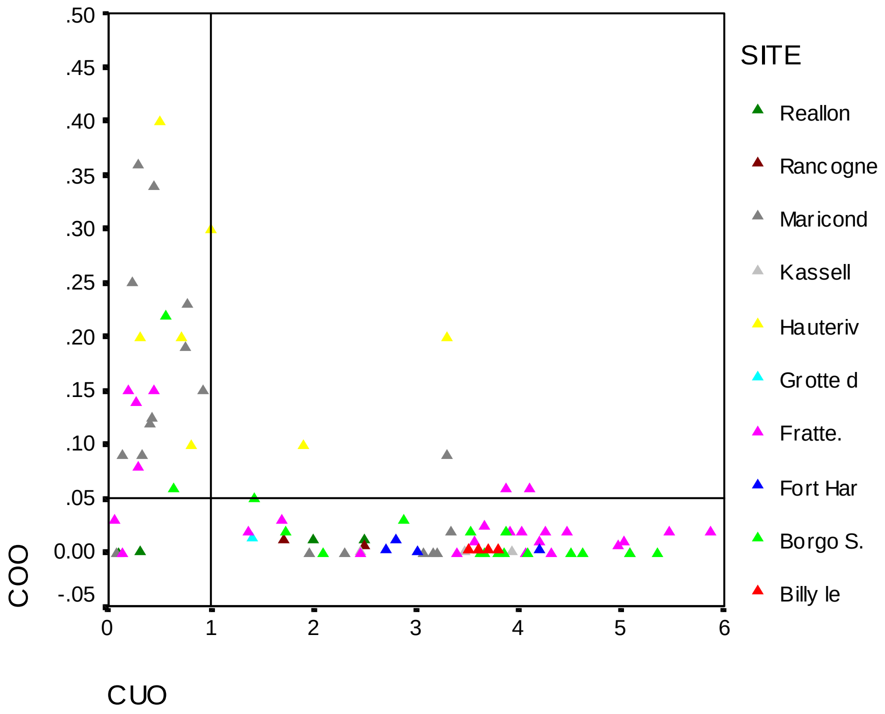


Figure 5.18 Scatter plot of copper and cobalt oxide contents of published mixed-alkali glasses and this study.

The use of copper and cobalt as colourants can be seen as alternate choices amongst the mixed-alkali glass making tradition: whilst a few glasses contain significant quantities of both colourants, the majority of glasses contain one or other in amounts sufficient to colour the glass (i.e. >0.05 % CoO and >1% CuO). Whilst those sites with glass employing cobalt oxide as a colourant (Hauterive-Champréveyres, Frattesina, Mariconda and Borgo San Zeno (Montagnana)) also used copper oxide, a number of sites had material exclusively coloured with copper oxide (Le Depot de Reallon, Le Fort-Harroud, Kassell, Rancogne, Billy le Theil and Grotte de Sindou). The few examples coloured with both oxides were derived from the first group, and seem likely to be the product of recyling of glass from both colouring traditions. Clearly there is not universal or continual access to the cobalt containing colourant. This is significant because it would suggest that despite the impressively consistent composition of the mixed-alkali glasses, there would appear to be distinct patterns of colourant use. This would imply numerous production (or glass colouring) centres. Where cobalt is used, it is alongside copper, but there would appear to be more limited access to the cobalt. The more limited use of cobalt in the French material may reflect a lack of access to the raw material (from the Erzebirge?).

Whilst the Bronze Age mixed-alkali glasses have been well characterised, there remains a number of technological issues which are unresolved. There is a clear need for experimental work to establish working properties, microstructure and temperatures employed in the manufacture of these glasses. It would be useful to establish how the red glasses remain red and workable in an oxidising environment in decoration such as with sample 310 (see 5.3.1). The retention of a significant silica-rich crystalline phase would define the limitations of the temperature regime used. Similar work has already been undertaken for other compositional types (for example Stern and Schlick-Nolte 1994, p 21-24 and McLoughlin *et al.*2001 for the working properties of soda-lime silica glasses): defining the technological boundaries for their production and working would be helpful. Experimental work could also contribute to a better understanding of the chemistry of the raw components- what kind of refining processes could give rise to the resultant, highly consistent glass chemistry (such as suggested by Santopadre and Verità 2000, p 29-31).

5.4 Etruscan Material.

The group of samples defined here as Etruscan are from artefacts of diverse provenance, some of which have been assigned an Etruscan origin on grounds of typology rather than secure archaeological context. Nonetheless, this collection of samples represents a diverse range of artefacts and permits useful observations on the relationship between Etruscan glasses and the Final Bronze Age mixed-alkali glassmaking tradition.

18 samples: 10, 11, 12, 150 - 161, 176 - 178 inclusive.

The Etruscan samples are all taken from material held in the UK, since approaches to Italian and US institutions for samples of Etruscan glass were unsuccessful. They are from several museum collections: Lincoln County Museum, National Museums and Galleries on Merseyside, Bristol City Museum and from Cambridge University Museum of Archaeology. The artefacts ranged from core-formed glass vessels to beads and complex brooch decorations, variously dated to the period 800-500 BC.

Glass types

This group of glasses contains: potash glasses (5 examples: 150, 151, 159, 160 and 161), high - magnesia soda - lime - silica glasses (1 example: sample 152) and low magnesia soda - lime - silica glasses (12 examples: 10, 11, 12, 153, 154, 155, 156, 157, 158, 159, 176, 177, 178). Clearly this assemblage cannot be considered as coming from a single glassmaking tradition. The variable provenance means that it is useful to discuss these glasses initially in terms of their general type, before consideration of form and association.

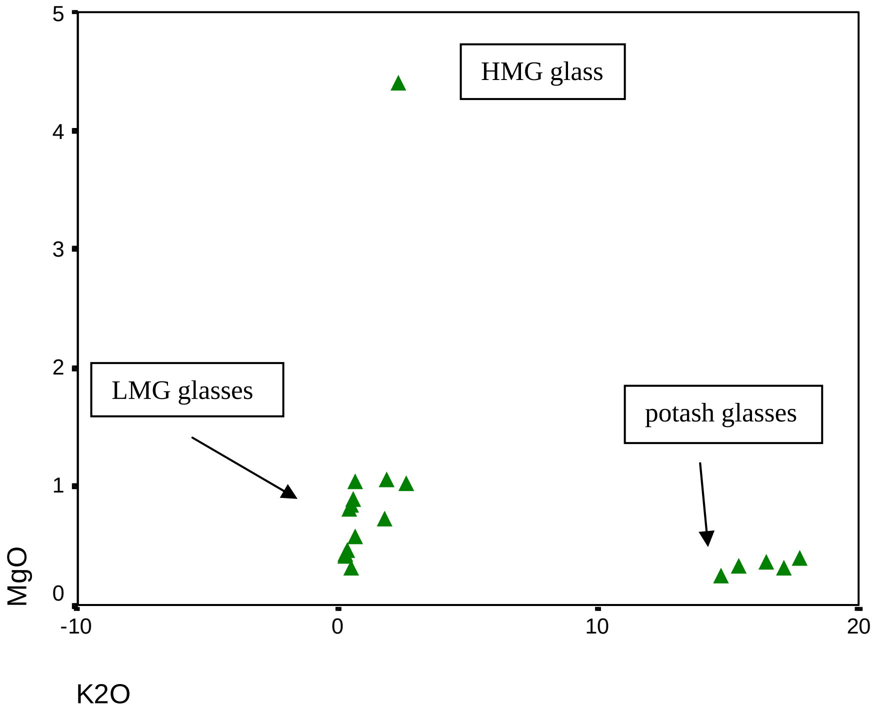


Figure 5.19 Glass types from the Etruscan group: magnesia against potassium oxide.

The potash glasses are a remarkable phenomenon: they are all very similar in composition, and each contains no identifiable soda. They are all undecorated blue translucent annular beads. These glasses are characterised by their high potash content (mean 16.29 %, range 14.73 - 17.70 %), and absence of soda (i.e. below the lower limit of detection for the machine used here: 0.01 % Na_2O, Henderson 1988b, p 80). The lack of soda is most unusual, and without parallel in the glass literature for all periods of production. There is however, no reason to doubt the analyses. They have no overall lack of alkali, which might indicate a weathered glass, all approach 100 % totals and were not analysed consecutively, suggesting that a temporary machine error is not responsible for the low soda values. The EMPA results were confirmed by repeat analysis of three samples (159, 160 and 161) using EDS analysis on an SEM specifically designed for the detection of low atomic weight elements. Spectra from these analyses demonstrate no characteristic sodium peak (Figure 5.20).

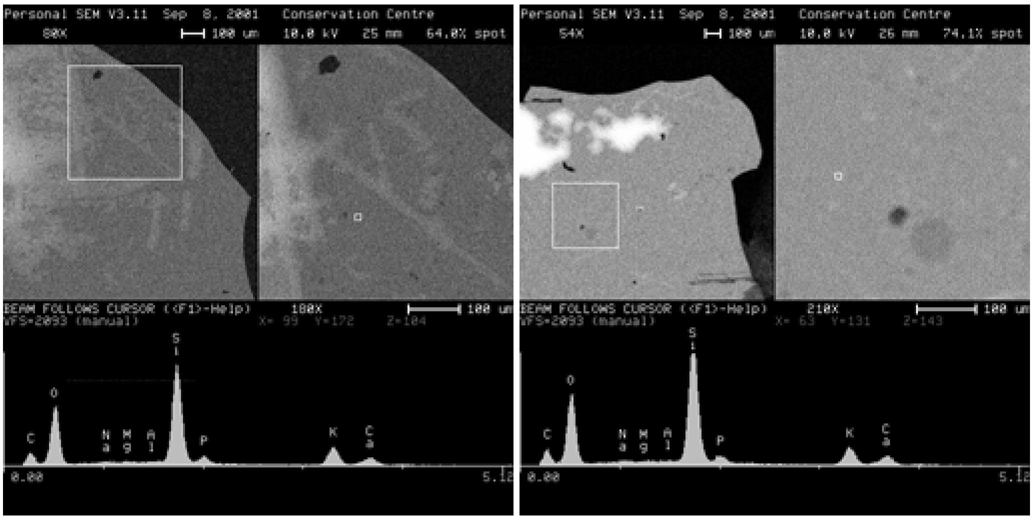


Figure 5.20 SEM images and EDS spectra for Etruscan potash glasses 159 and 160.

Several aspects of the glasses' chemistry are consistent with the use of a terrestrial plant ash as the alkali source. The high potassium oxide levels are accompanied by similarly high phosphate and lime levels: phosphorous pentoxide mean 6.19 %, range 5.44 - 7.34 compared to a mean of 0.12 %, range 0 - 0.5 % for the other "Etruscan" group, and a mean of 11.47 % lime, range 10.6 - 12.51 % compared with a mean value of 6.62 %, range 3.25 - 8.56 for the other glasses. However, the magnesia levels remain remarkably low for a glass made with a plant ash: mean

0.31, range 0.24 - 0.38 %. This would suggest some kind of preparatory process preferentially removing the magnesia, but not the phosphates and lime.

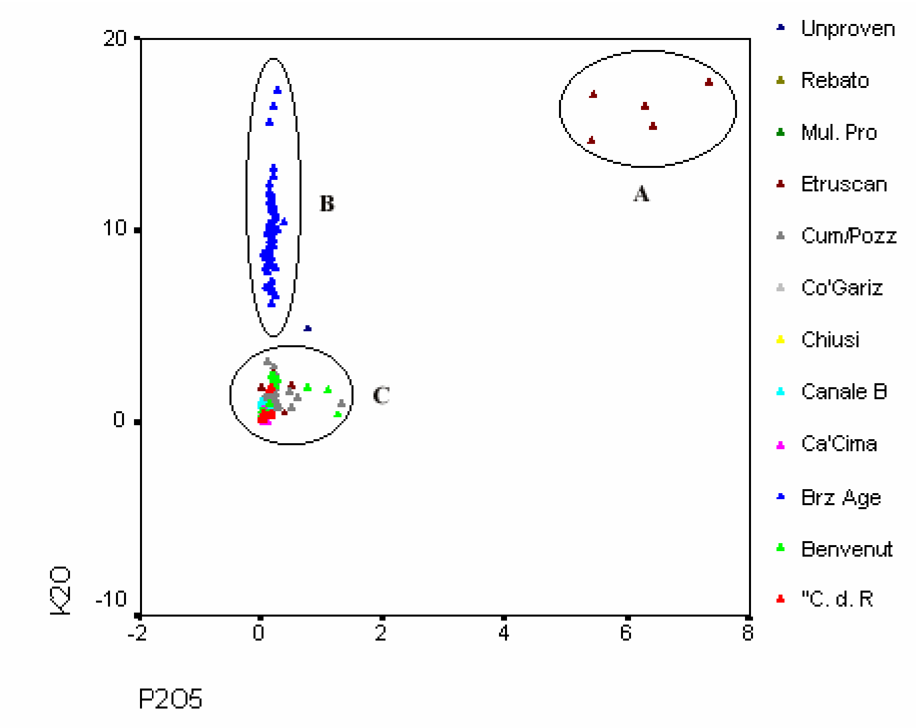


Figure 5.21 Scatter plot of potash against phosphorous pentoxide for all samples in this study. Group A is the Etruscan potash glasses, quite distinct from the Bronze Age mixed-alkali glasses (Group B) and the soda-lime-silica glasses (Group C).

When compared with all the other samples examined in this study, in terms of the phosphorous pentoxide and potassium oxide content, the Etruscan potash glasses are quite distinct. The strong association between these two components suggests a terrestrial plant ash as the alkali source for the glasses (also see 3.7.7).

These glasses are also characterised by their low alumina and iron levels, reflecting a pure silica source (mean values of 0.49 and 0.24 compared with 2.05 and 1.45% respectively).

sample	150	151	159	160	161	mean	stdev	min	max	reduced comp.
Na_2O	0.00	0.00	0.00	0.00	0.00	0.00	0	0	0.00	0
MgO	0.38	0.32	0.34	0.24	0.29	0.31	0.05	0.24	0.38	0.35
Al_2O_3	0.75	0.32	0.63	0.34	0.40	0.49	0.19	0.32	0.75	0.54
SiO_2	58.27	62.87	61.30	65.62	61.82	61.98	2.66	58.27	65.62	68.27
P_2O_5	7.34	6.43	6.31	5.44	5.45	6.19	0.79	5.44	7.34	
SO_3	0.52	0.58	0.52	0.00	0.47	0.42	0.24	0	0.58	
Cl	0.11	0.11	0.08	0.11	0.06	0.09	0.02	0.06	0.11	
K_2O	17.70	15.42	16.48	14.73	17.14	16.29	1.22	14.73	17.70	17.95
CaO	12.51	11.98	11.58	10.67	10.60	11.47	0.83	10.6	12.51	12.63
TiO_2	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.02	0.02	
Cr_2O_3	0.00	0.02	0.00	0.00	0.02	0.01	0.01	0	0.02	
MnO	0.01	0.03	0.03	0.08	0.07	0.04	0.03	0.01	0.08	
FeO	0.24	0.18	0.26	0.29	0.21	0.24	0.04	0.18	0.29	0.26
CoO	0.00	0.02	0.08	0.05	0.06	0.04	0.03	0	0.08	
NiO	0.06	0.10	0.01	0.08	0.01	0.05	0.04	0.01	0.10	
CuO	0.05	0.00	0.00	0.00	0.04	0.02	0.02	0	0.05	
ZnO	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0	0.02	
As_2O_5	0.85	0.21	0.07	0.32	1.91	0.67	0.75	0.07	1.91	
SnO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0	0.00	
Sb_2O_5	0.02	0.00	0.00	0.00	0.00	0.00	0.01	0	0.02	
BaO	0.04	0.04	0.04	0.04	0.05	0.04	0.00	0.04	0.05	
PbO	0.01	0.02	0.01	0.05	0.01	0.02	0.02	0.01	0.05	
Total	98.88	98.67	97.76	98.10	98.63					100

Table 5.10 Summary data for Etruscan Potash glasses

The potash glasses are all blue translucent and of similar form. Samples 159, 160 and 161 are coloured with the use of cobalt oxide, containing 0.08, 0.05 and 0.06 % CoO respectively. Sample 150 contains no cobalt oxide, and very low copper content (0.05 %): it is probably coloured by reduced iron oxide (0.24 %). Sample 151 contained very low cobalt oxide levels (0.02 %), which must be responsible for the glass’s colour, in the absence of any copper.

The potash glasses from Frattesina can be briefly compared with these from Etruscan contexts (see Tables 5.2 and 5.10). The Frattesina potash glasses contain low soda levels compared with none detected in the Etruscan examples, and both groups have similarly low magnesia contents. Both groups have low alumina contents, but the Etruscan glasses contain less than 0.8% Al2O3, compared with a range of 1.5 - 2.84 % for the Frattesina glasses. The silica contents of the Etruscan glasses are lower, and do not contain the silica-rich crystalline phase present in the Frattesina material. The very high phosphorous pentoxide content of the Etruscan glasses (5.44 - 7.34 %), consistant with a potash-rich terrestrial plant ash is not matched in the Frattesina glasses (0.14 - 0.25 %, also see Figure 5.21). The two groups are also markedly different in their lime levels, with much greater quantities present in the Etruscan group (10.6 - 12.51 % compared to 2.05 - 3.15 %).

The Etruscan potash glasses contain elevated arsenic levels. This may be associated with the use of arsenic-rich cobalt for blue colourant, but there is no simple correlation between these components, with sample 150 containing 0.85 % As_2O_5, but no detectable cobalt oxide. The two samples with the highest arsenic content also contain the greatest amount of copper oxide (samples 150 and 161), which may indicate the use of an arsenic-rich copper. Arsenic can easily boil off during the preparation of metal ores, which may account for the variation in the levels seen here: its presence remains significant, but at present not entirely explicable. The Etruscan potash glasses are distinct from the earlier Frattesina potash glasses (which could be readily identified with the mixed-alkali technology). The Etruscan material nonetheless is a significant discovery. The technology involved would appear to employ a terrestrial plant ash, rich in both potash and phosphates. The low magnesia content may indicate some refining process which has preferentially removed this component, but would be different to that used in the production of the Frattesina glasses, since phosphorous pentoxide remain to be included in the final glass composition.

Two of the potash glass beads are from a single artefact: threaded on a copper alloy "earing" (samples 150 and 151, Bead Study Trust 1997, p 84: see Figure 5.22 below), and are associated with a further anomalous composition: the only high magnesia soda - lime - silica glass in the "Etruscan" group. Samples 159 - 161 are from an uncatalogued group from the Beck Collection labelled "Etruscan, 800 - 600 BC, from Florence".

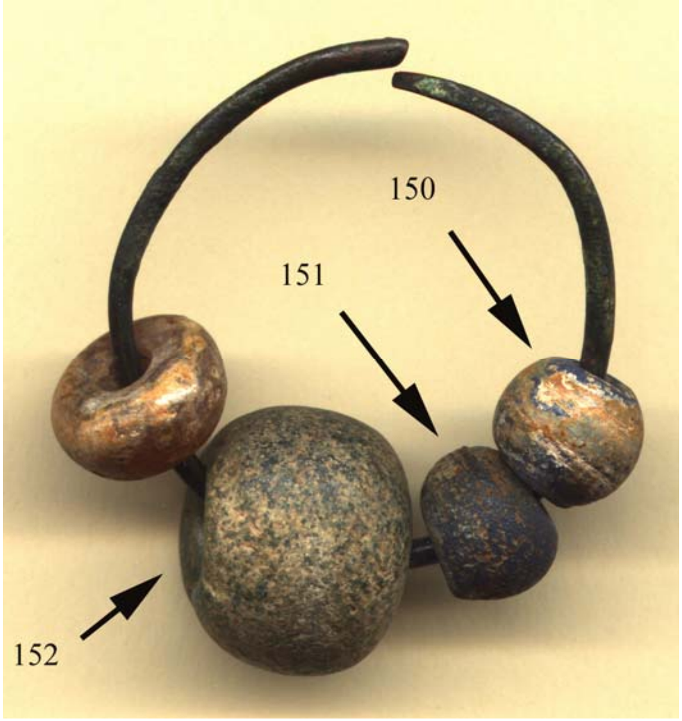


Figure 5.22 Etruscan earring with artefacts from which samples 150-152 were taken. The unlabelled bead is made of amber. Scale 2:1

There is only one high - magnesia soda - lime - silica glass (sample 152), which was associated with samples 150 and 151 (see above). With 4.38 % magnesia, this sample's composition is consistent with the use of a soda - rich plant ash for the alkali source, and also contains raised level of potash (2.33 %).

All of the other glasses are low - magnesia soda - lime - silica glasses consistent with the use of a natron type soda source.

	mean	stdev	min	max	reduced comp.
Na_2O	17.67	1.71	14.8	20.02	18.21
MgO	0.70	0.27	0.3	1.05	0.72
Al_2O_3	2.17	1.78	0.35	6.08	2.23
SiO_2	67.50	4.89	61.5	74.78	69.57
P_2O_5	0.11	0.16	0	0.50	
SO_3	0.29	0.14	0	0.48	
Cl	0.90	0.29	0.43	1.49	
K_2O	0.88	0.76	0.31	2.60	0.91
CaO	6.59	1.65	3.25	8.56	6.79
TiO_2	0.10	0.07	0.04	0.26	
Cr_2O_3	0.01	0.02	0	0.05	
MnO	0.53	0.67	0	2.02	
FeO	1.53	2.04	0.29	7.34	1.57
CoO	0.07	0.07	0	0.25	
NiO	0.05	0.06	0	0.16	
CuO	0.56	0.72	0	1.99	
ZnO	0.01	0.02	0	0.05	
As_2O_5	0.01	0.02	0	0.06	
SnO_2	0.26	0.67	0.01	2.37	
Sb_2O_5	0.42	0.63	0	1.69	
BaO	0.05	0.02	0.01	0.09	
PbO	1.67	3.54	0	12.33	
Total					100.00

Table 5.11 Summary data of low –magnesia –soda –lime silica glasses from "Etruscan" group.

The glasses making up this group are of variable provenance, and cannot therefore be considered of a single tradition. The diversity is well illustrated by the variation in glass types, and also the diversity of alumina contents of these glasses.

Samples were taken from two Etruscan core-formed glass vessels (samples 10-12). As described in Chapter 1 (1.3.2), these are representative of a glass vessel type unique to Etruscan contexts. No previous chemical analysis has been performed on this group, and this study is the first attempt to characterise the glass employed in their manufacture.

Figure 5.23 Etruscan core-formed glass vessel, from which samples 11 and 12 were taken.

Although the underlying form, whether oinochoe, alabastron or aryballos, may have an eastern origin, the decoration is known only from Etruscan material suggesting they were produced within the Etruscan world.

Whilst three samples from two artefacts do not represent a comprehensive survey of Etruscan glass vessels, the results are worth commenting upon. Firstly it is interesting to note that despite their separate provenance, the two vessels have a similar chemistry.

	Etruscan glass vessels 650-550 BC	
	average	Range
Na_2O	17.9	17.62-18.08
K_2O	0.33	0.31-0.36
MgO	0.42	0.4-0.42

Table 5.12 Key components of Etruscan core-formed glass vessels.

The Etruscan glass vessels are fabricated from low magnesia soda-lime-silica glass: they have a low phosphate content (avg. = 0.02 wt.%), and raised chlorine and sulphur oxide levels associated with the use of natron. They are distinguished by their colouring agents: both contain copper (1.04 and 1.99 wt.% respectively). The darker, more densely coloured vessel also contains 0.11 wt.% cobalt oxide, sufficient to give the piece its hue. Most importantly, these analyses demonstrate no link whatsoever between the North Italian mixed-alkali glassmaking tradition and the Etruscan core-formed glass vessels.

Colourants.

The colourants used for the potash glasses have been briefly discussed above. The “Etruscan” group of glasses includes 9 blue translucent glasses (samples 10, 11, 12, 150, 151, 158, 159, 160 and 161), 3 clear translucent glasses (samples 153, 154 and 155), 2 white opaque glasses (samples 157 and 178), 2 red opaque glasses (samples 156 and 177), 1 yellow opaque (sample 176) and 1 green translucent glass (sample 152).

Of the blue translucent glasses, samples 150 and 10 are coloured using copper oxide (containing 0.05 and 1.05 % copper oxide respectively). Samples 151 and 158 must have been coloured with very low cobalt content (0.02 % in each, and copper contents of none and 0.12 %), and samples 160, 161, 12, 159 and 11 were all definitely coloured with cobalt (with 0.05, 0.06, 0.08, 0.08 and 0.11 % CoO).

sample	150	10	151	158	160	161	12	159	11
Na2O	0.00	17.62	0.00	20.02	0.00	0.00	18.08	0.00	17.99
MgO	0.38	0.45	0.32	0.80	0.24	0.29	0.4	0.34	0.42
Al2O3	0.75	0.43	0.32	2.24	0.34	0.40	0.35	0.63	0.35
SiO2	58.27	74.78	62.87	68.18	65.62	61.82	74.37	61.30	74.06
P2O5	7.34	0.02	6.43	0.02	5.44	5.45	0.02	6.31	0.02
SO3	0.52	0.21	0.58	0.24	0.00	0.47	0.21	0.52	0.24
Cl	0.11	1.01	0.11	1.49	0.11	0.06	1	0.08	0.98
K2O	17.70	0.36	15.42	0.41	14.73	17.14	0.31	16.48	0.31
CaO	12.51	7.84	11.98	6.86	10.67	10.60	7.23	11.58	7.33
TiO2	0.02	0.06	0.02	0.09	0.02	0.02	0.04	0.02	0.04
Cr2O3	0.00	0.02	0.02	0.02	0.00	0.02	0	0.00	0
MnO	0.01	0.01	0.03	0.55	0.08	0.07	0.01	0.03	0
FeO	0.24	0.29	0.18	0.93	0.29	0.21	0.4	0.26	0.4
CoO	0.00	0.02	0.02	0.02	0.05	0.06	0.08	0.08	0.11
NiO	0.06	0.02	0.10	0.06	0.08	0.01	0	0.01	0
CuO	0.05	1.04	0.00	0.12	0.00	0.04	1.85	0.00	1.99
ZnO	0.00	0.00	0.00	0.00	0.02	0.00	0	0.00	0
As2O5	0.85	0.00	0.21	0.00	0.32	1.91	0	0.07	0
SnO2	0.00	0.01	0.00	0.03	0.00	0.00	0.01	0.00	0.04
Sb2O5	0.02	0.00	0.00	0.30	0.00	0.00	0.04	0.00	0.02
BaO	0.04	0.04	0.04	0.06	0.04	0.05	0.02	0.04	0.01
PbO	0.01	0.06	0.02	0.16	0.05	0.01	0	0.01	0.15
Total	98.88	104.29	98.67	102.60	98.10	98.63	104.42	97.76	104.46

Table 5.13 Blue glasses from Etruscan group.

The three clear translucent glass samples were taken from a fragmentary brooch decoration and two annular beads (samples 153 - 155). Intriguingly, all three contain CoO at levels of 0.05, 0.11 and 0.02 respectively. These levels might be expected to colour the glasses blue and remains a mystery. Samples 152 and 153 have both been decolourised using manganese oxide, containing 2.02 and 1.44 %

respectively, which would strongly suggest that these glasses are from later contexts, from the 2nd Century BC onwards (see section 3.7.15).

Sample 157 is a white opaque glass decoration on a red opaque bead, coloured using tin oxide (2.37 % SnO_2). The lead content of this glass (2.25 % PbO) suggests that the glass may originally have been intended to be coloured opaque yellow using lead stannate ($PbSnO_3$). When heated above 900 °C, lead stannate decomposes to tin oxide, a process that is irreversible (see 3.7.12). The use of tin oxide (and lead stannate) to colour and opacify glasses is currently dated to the 2nd Century BC onwards (Henderson 1985, p 286, Henderson and Warren 1981, Henderson 1989a, p 49 - 51). Given the relatively poor provenance, it seems most likely that this particular artefact has been misidentified as Etruscan (Bead Study Trust 1997 p 84), and was actually made later than the Etruscan era.

The other “white” opaque glass (sample 178) is from the combed decoration of a leech - shaped brooch slider. Initially considered an accidental inclusion, possibly of quartz, upon analysis it proved to be a fragment of glass. Backscattered SEM imaging and EDS analysis demonstrated that the EMPA analysis was not of the intended white inclusion, but of glass adhering to the edge of a silica-rich core. This highlights the potential for error when using a microprobe aligned using an optical system.

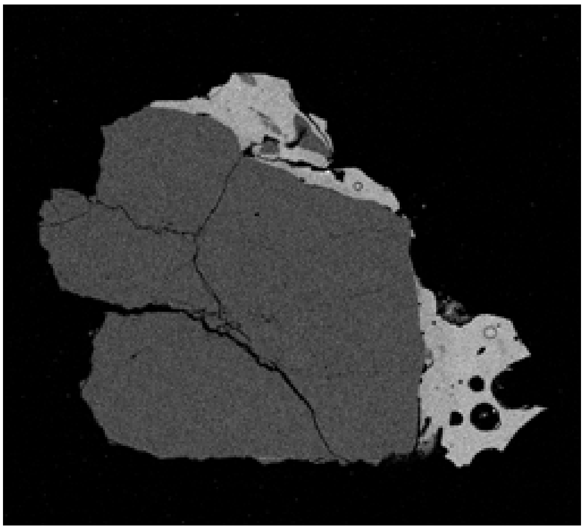


Figure 5.24 Backscattered SEM image of sample 178. The dark grey zone is almost pure silica.

Examination of the vitreous phase adhering to the silica-rich lump showed it to contain inclusions very high in copper, antimony and arsenic, suggesting that this was a glass coloured red with reduced copper oxide from an unusual bronze (Figure 5.25).

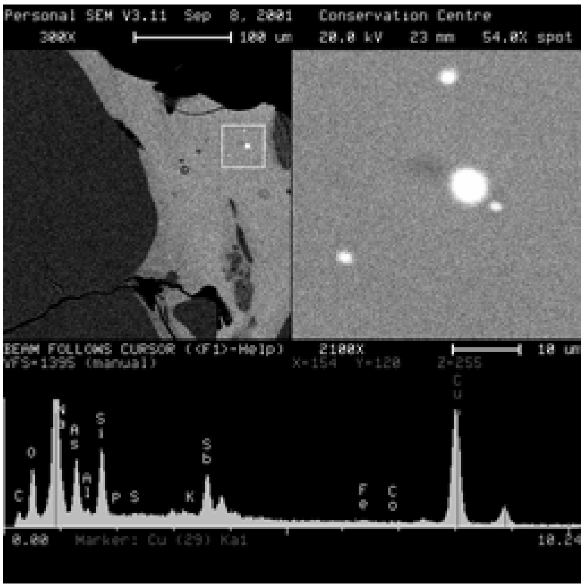


Figure 5.25 Backscattered Sem image and EDS analysis of inclusions in sample 178

The two red opaque glasses (156 and 177) are from the same composite artefacts as the white opaques (i.e. a bead and a brooch slider). Sample 156 has a low copper oxide content of 0.19 %, and a raised iron oxide level of 7.34. It was initially assumed that the colour is due to the copper being in the reduced cuprous state (see 3.7.8 for more details). Added iron has been noted as a method of facilitating the dissolution of copper oxide into a glass, and the subsequent precipitation of cuprite (see 3.7.23). Sample 177 has a similar low copper oxide content (0.67 %) and raised iron level (3.88 %), and may be coloured in the same way. SEM imaging of the samples failed to identify copper rich inclusions- either cuprite or metallic copper in the glass matrix. Since both of these glasses contain high iron levels additional consideration was given to the possibility of iron oxides as a colourant. A number of authors have noted the use of iron oxide as a colourant for red enamels (Bimson and Werner 1969, p 263-264, Freestone and Stapleton 1998, Verità 1998, p 131-132, Carboni *et al*. 1998, p 90, Biek *et al.* 1980, also see 3.7.23 above). In the examples discussed in previous studies, finely ground red iron oxide (haematite) and uncoloured glass are mixed and rapidly fused to another surface. Both high-lead and soda-lime-silica glasses have been employed, but in each case the process is regarded as rapid to avoid complete fusion and dissolution of the iron oxide into the glass matrix, and thereby losing its colouring properties (Verità 1998, p 131-132). The capacity of either high-lead or soda-lime silica glass to be sufficiently hot to be workable and simultaneously contain undissolved red iron oxide has yet to be determined, and might usefully be established by experimental work. However, even elemental dot mapping of sample 177 failed to identify discrete iron-rich inclusions in this glass. Occasional, small (15 µm diameter) copper-rich inclusions could be discerned, and these must be responsible for the colour (Figure 5.26).

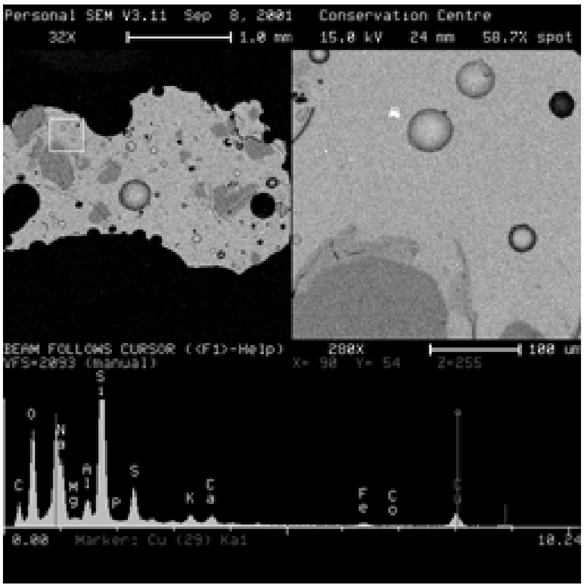


Figure 5.26 Backscattered SEM image and EDS analysis of copper-rich inclusions in sample 177.

The only yellow opaque glass amongst this group is sample 176, from the same brooch decoration as samples 177 and 178. It is opacified and coloured using lead antimonate (12.33 PbO, and 1.35 % Sb_2O_5).

The single green translucent sample (152) was also the only high - magnesia soda - lime - silica glass amongst this assemblage, and was associated with two potash glasses (sample 151 and 152). It has only a very low iron oxide content (0.48 %) and only small amounts of other modifiers to account for its colour (0.11% MnO, 0.22 % Sb2O5) which must be due to iron oxide.

5.4.1 Discussion of glasses from Etruscan Contexts

Although the sites of Cumae and Pozzouli are sometimes considered to be within the Etruscan cultural sphere, these cities are located South of the Etruscan heartland (see figure 1.1), and were both principally Greek settlements. For these reasons, and their distinct chemical composition, samples from these sites are considered separately below.

Given the poor provenance of several of the “Etruscan” items, and the likely inclusion of several later glasses (see above), a certain circumspection is required when discussing this collection of analyses. The principle observation to be made concerning the Etruscan glasses is that there is no evidence for continuity or shared technological tradition with the Final Bronze Age glasses from the Po valley. This is an important observation since it has been suggested that Frattesina may represent some form of early proto-Etruscan colony in the Po Valley (Bietti-Siesteri 1997). It can now be seen that the technological milieu of the Frattesina glass industry is more closely related to a longstanding and broader European tradition than that employed in the (later) Etruscan world.

Despite the presence of distinct typological forms (such as the stachelflaschen), the chemical composition of the Etruscan glasses considered above is neither sufficiently homogenous nor distinct to be classified as an individual production tradition. Whilst there can be no doubt about the technological sophistication of Etruscan high temperature industries (e.g. Spivey 1997, Martelli 1994) there is as yet no direct evidence for glassmaking or glassworking from Etruscan contexts:

however the unique forms would suggest that glassworking at least was taking place.

The presence of the potash glasses amongst this group is an intriguing suggestion of a distinct technological tradition, which might prove to be diagnostic of an Etruscan production. Unfortunately the forms and colour (blue translucent undecorated annular beads) are poor markers to aid selection of these artefacts for further analysis. There is a clear need for additional analyses of well provenanced glass objects from Etruscan contexts.

The variable compositions of the glass amongst the Etruscan material, like much contemporary glass, tends to suggest that glass production was both highly localised and uncontrolled. Whilst it is not at present possible to locate individual manufacturing traditions, nor may it ever be so, it seems likely that production of glass consumed in Etruscan contexts was a non-centralised affair without the consistency which marks so many other periods of glass production. Whereas from the Middle Bronze Age to Final Bronze Age (1400 - 900 BC) the glass consumed by communities in Central and Northern Italy (and elsewhere in Europe) tend to be compositionally consistent, whether mixed-alkali or soda-lime-silica glasses, the glasses deposited during the Early Iron Age to the Roman Period (900 - 300 BC) are far more variable. The glasses from Cumae and Pozzouli are an exception to this and are discussed below.

5.5 7th Century BC Beads from Pozzouli and Cumae

The material from Pozzouli (near Naples) and Cumae dates to the 7th Century BC, and is distinct from the rest of the assemblage analysed as part of this study in terms of both typology and chemical composition. Whilst the forms and colours are well known from Etruscan contexts across Prehistoric Italy (Bead Study Trust 1997, p 75, Hencken 1968b, Heurtley and Skeat 1933, p 38-39), these are treated as distinct from the other Iron Age glasses since they are from Southern Central Italy and have quite unusual compositions.

5.5.1 Pozzouli

46 samples: 50 - 68, 70 - 97 inclusive.

All of the Pozzuoli samples were taken from beads in the Beck collection held by Cambridge University Museum of Archaeology.

Glass types

The glass compositions from Pozzuoli are quite remarkable: although there is a limited range of typological forms and colours, the compositions include a number of characteristics which are consistent, indicating that the entire group is made in the same manufacturing tradition. The chemical composition of the glasses defies the ready categorisation adopted elsewhere for 1st Millennium BC glasses: they are all soda-lime silica glasses, but have magnesia contents across a continuum from 0.53 - 3.97 %. Whilst a group may be defined as containing less than 1.5 % magnesia (figure 5.27), the division is less credible since the magnesia is not correlated with the potash content, as in many other glasses. If there was a diverse range of artefact forms this might be taken to indicate glasses from both high and low magnesia soda-lime-silica glass making traditions, with intermediate compositions arising out of the mixture of both glass types. With this assemblage of material, the matrix of most of the artefacts appears black (or dark brown), there is a relatively limited range of forms, and a scatter plot containing magnesia (see figure 5.27) shows a continuum rather than grouping into the conventional high and low magnesia glass types.

	mean All	min	max	stdev
Na_2O	15.96	12.17	17.99	1.20
MgO	1.66	0.53	3.97	0.94
Al_2O_3	1.70	0.88	3.39	0.72
SiO_2	65.62	59.07	72.22	2.46
P_2O_5	0.22	0.05	1.67	0.25
SO_3	0.23	0.03	0.91	0.16
Cl	0.59	0.37	0.99	0.15
K_2O	1.12	0.62	1.79	0.27
CaO	2.68	1.16	5.37	1.28
TiO_2	0.13	0.05	0.27	0.05
Cr_2O_3	0.02	0	0.10	0.02
MnO	0.03	0	0.09	0.02
FeO	11.28	5.39	19.07	3.43
CoO	0.02	0	0.08	0.02
NiO	0.02	0	0.08	0.02
CuO	0.07	0	1.47	0.23
ZnO	0.04	0	0.17	0.04
As_2O_5	0.01	0	0.20	0.03
SnO_2	0.01	0	0.05	0.01
Sb_2O_5	0.05	0	0.24	0.05
BaO	0.03	0	0.05	0.01
PbO	0.02	0	0.12	0.03

Table 5.14 mean values and variation for all samples from Puzzuoli material

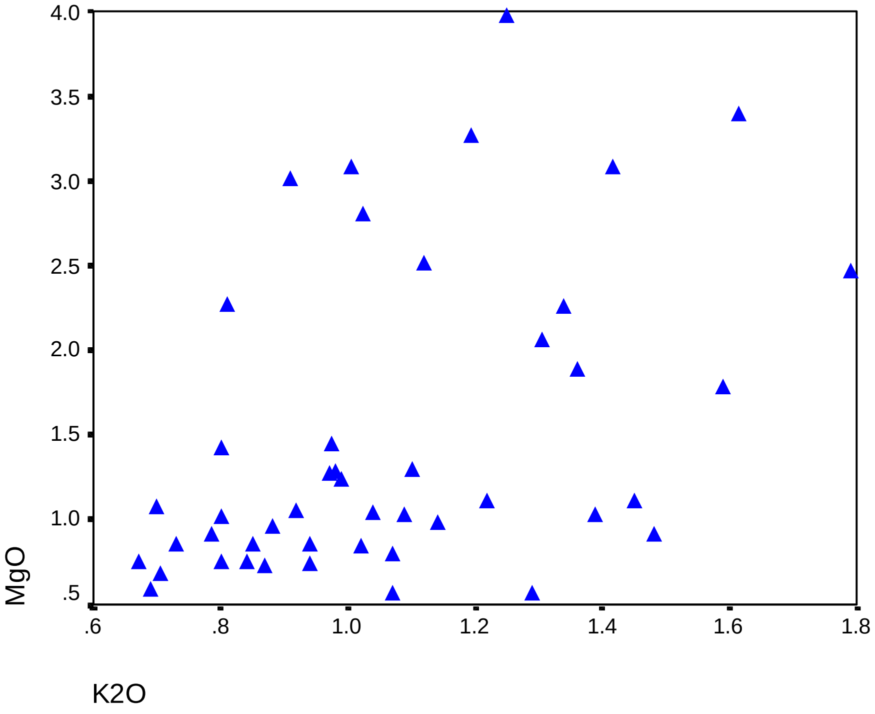


Figure 5.27 Glass types from the Pozzuoli group: magnesia against potash

A review of artefacts at either end of the magnesia spectrum reveals no discernible relationship between magnesia content and form or colour. It is suggested that these glasses are therefore from the same glassmaking tradition which employs a recipe with a highly variable magnesia-containing raw component. Whilst this might be a soda-rich plant ash, it cannot be definitively established. An alternative explanation might be the mixing of glasses from the low and high-magnesia soda-lime silica glass making traditions, and the addition of an iron-rich colouring agent.

In an attempt to identify which raw ingredient component accounts for the variable magnesia content, PCA analysis was undertaken. The different components should include correlated variables which account for difference within the dataset, for example if a plant ash contained correlated magnesia, potash, soda and phosphate components, they should appear in the same component in the rotated component matrix (see Table 5.15).

	1	2	3	4	5	6	7	8
Na_2O	-1.64E-02	0.248	0.444	-0.182	5.64E-02	**-0.528**	-0.145	-0.481
MgO	-1.14E-02	**0.571**	0.149	-4.21E-02	7.09E-01	-6.33E-02	3.71E-02	-7.73E-02
Al_2O_3	1.46E-01	**0.848**	0.28	-7.84E-02	-0.139	-1.02E-01	7.33E-02	-1.88E-02
SiO_2	0.307	-0.151	9.68E-02	-6.30E-01	-0.321	5.71E-02	8.58E-03	1.40E-02
P_2O_5	-0.126	2.34E-02	1.76E-01	-3.89E-02	9.72E-03	4.67E-02	-6.13E-02	8.01E-01
SO_3	0.309	3.18E-01	**0.625**	-2.14E-01	4.76E-02	7.94E-02	2.10E-01	0.12
Cl	-0.237	-0.15	0.242	-3.74E-02	7.07E-01	-2.74E-01	0.129	0.14
K_2O	0.333	**0.59**	0.451	-3.03E-02	9.97E-02	-0.357	0.14	1.57E-02
CaO	0.216	-5.12E-02	-0.1	5.00E-02	8.38E-01	0.203	-5.16E-02	-1.02E-01
TiO_2	8.76E-02	4.60E-01	0.124	1.50E-01	-2.21E-03	-0.292	6.02E-01	-1.20E-03
Cr_2O_3	-3.16E-01	**0.749**	1.68E-03	7.69E-02	6.72E-02	5.93E-02	-0.226	9.67E-03
MnO	0.274	-2.47E-02	1.21E-01	5.08E-01	-1.53E-01	-7.13E-02	-0.423	5.38E-01
FeO	-0.341	-4.13E-01	-0.349	**0.528**	-0.191	8.83E-02	2.21E-02	0.305
CoO	-6.00E-02	-2.38E-02	5.17E-02	-8.14E-02	1.48E-02	8.79E-01	-1.44E-02	2.62E-02
NiO	-5.49E-02	1.28E-01	8.44E-01	-8.31E-03	6.23E-02	2.10E-02	-1.19E-01	1.44E-01
CuO	8.33E-01	-4.33E-02	0.239	1.14E-01	-2.24E-02	-6.81E-02	2.17E-02	-6.88E-02
ZnO	-1.09E-03	-4.30E-01	9.29E-02	0.249	-3.37E-02	4.95E-01	-3.99E-01	6.76E-03
As_2O_5	8.67E-01	-5.59E-02	-1.30E-01	-1.47E-02	1.30E-01	-3.66E-02	2.19E-02	2.72E-02
SnO_2	0.179	-6.87E-02	-0.142	7.05E-01	-9.40E-02	3.82E-02	9.40E-02	6.54E-02
Sb_2O_5	**0.802**	1.31E-01	1.15E-02	-0.153	-9.93E-02	2.18E-02	2.25E-01	-5.20E-02
BaO	0.242	-0.199	-4.66E-02	0.147	3.70E-02	6.21E-02	**0.803**	-1.11E-01
PbO	0.148	1.06E-03	-3.63E-01	**-0.562**	-2.52E-02	1.53E-02	-0.248	0.333

Table 5.15 Rotated Component Matrix for glasses from Pozzuoli Extraction method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalisation. Rotation converged in 15 iterations.

However this is not the case in this matrix. The repeated plotting of individual components fail to reproduce the low-magnesia versus all other glasses differentiation seen in figure 5.27.

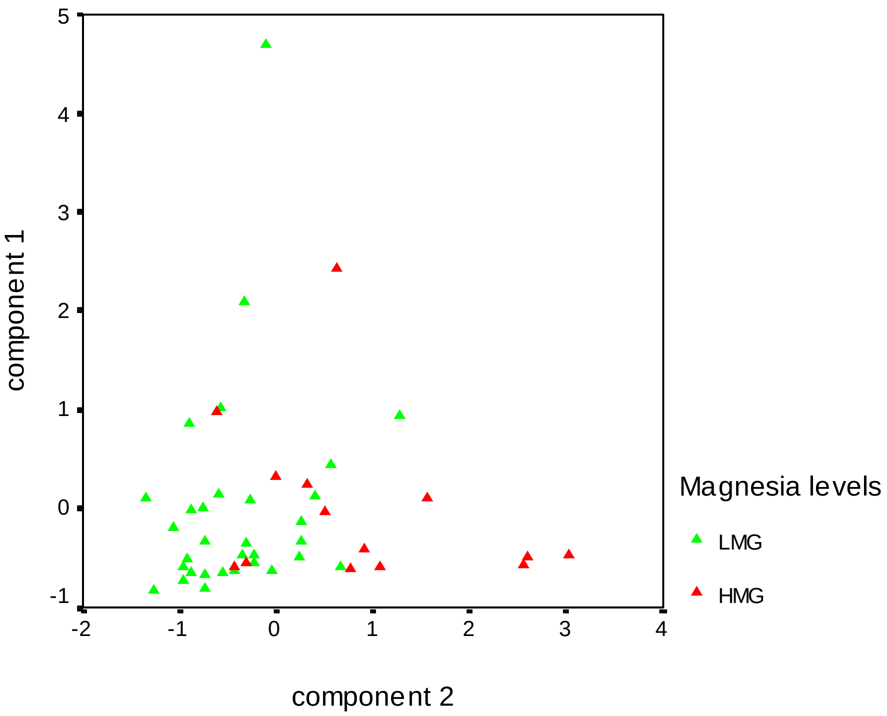


Figure 5.27 Scatter plot of first 2 principlal components for Pozzuoli glasses, showing how magnesia content is not a significant discriminant for these glasses (LMG = <1.5 % MgO, HMG = > 1.5 % MgO).

The most remarkable attribute of this group of glasses is their shared high iron content. A range of 5.39 - 19.07, mean 11.28 % iron oxide content is rare amongst prehistoric glasses from Europe and the Near East (4 exceptions: Brill 1999b: Hasanlu p 44, Chotin p 59, see Table 5.16). The few other glasses with comparable high iron contents are exceptions amongst their respective assemblages, and are distinct from these glasses and each other in terms of other components. The origin of the high iron content is difficult to establish. Whilst it is possible that an iron-rich metallurgical slag was added to the glass melt, this seems unlikely since one would also expect elevated and variable alumina and lime levels, which are not noted (Brill 1999b, p 510).

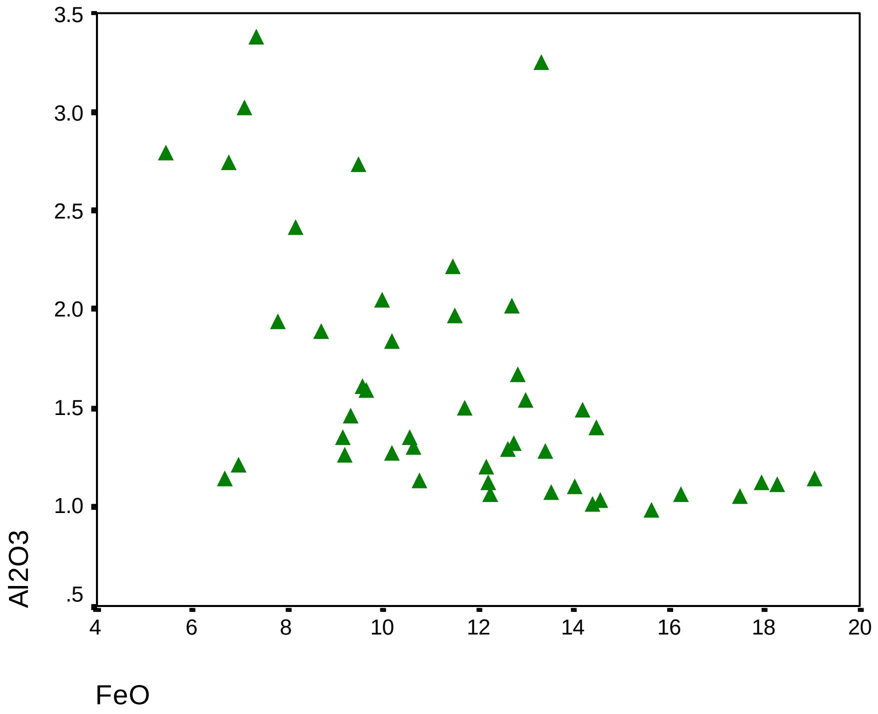


Figure 5.29 Alumina against Iron Oxide amongst the Pozzouli group.

Brill's sample no.	3462	3463	5431	5433
Li_2O	0.001	0.001	0.005	0.01
B_2O_3	0.02	0.02	0.3	0.3
Na_2O	2.16	1.99	17.1	18.4
MgO	2.01	3.4	0.9	3.82
Al_2O3	1.33	1.17	0.8	2.32
SiO_2 (a)				
SiO_2 (d)	57.12	61.68	63.82	59.71
P_2O_5	1.88	1.64		0.26
SO_3				
Cl				
K_2O	7.76	7.9	0.83	1.53
CaO	6.41	5.94	1.56	5.02
TiO_2	0.13	0.1	3.32	0.15
V_2O_5	0.005	0.005	0.02	
Cr_2O_3			0.008	0.005
MnO	0.24	0.5	0.011	0.04
Fe_2O_3	**20.2**	**14.9**	**11.2**	**7.9**
CoO				
NiO	0.01	0.005	0.01	0.005
CuO	0.44	0.55	0.005	0.12
ZnO	0.016	0.012		
As_2O_5			0.004	0.032
SrO	0.05	0.05	0.03	0.03
ZrO_2	0.01	0.01	0.02	
Ag_2O	0.001	0.001	0.05	
SnO_2	0.08	0.005	0.001	0.01
Sb_2O_5	0.01	0.01		
BaO	0.1	0.1		0.22
PbO	0.01	0.005	0.01	0.02
Bi_2O_3				0.1
total	99.993	99.994	100.004	100.002
site	Chotin	Chotin	Hasanlu	Hasanlu
date	700-400 BC	700-400 BC	1100-800 BC	1100-800 BC
colour	10	10	10	10
ref	Brill 99	Brill 99	Brill 99	Brill 99
method	ICP/OES	ICP/OES	ICP/OES	ICP/OES

Table 5.16 Comparable prehistoric high-iron glasses

It seems most likely that a high-iron sand has been employed in the production of these glasses. The deliberate selection of a black sand, such as that analysed by Brill from the mouth of the River Volturna, can yield an iron oxide content as high as 31.4 % (Brill 1999a p 209, 1999b, p 475).

Colourants

The high iron content is responsible for the colour of most of the beads, however it is important to note that without exception all of the Pozzuoli glasses have high iron contents. Thirty-one of the samples are from glass which appeared “black” i.e. they were very intensely coloured (for examples see figure 5.30), whilst six appeared green opaque, which was probably due to weathering layers rather than the colour of the original glass (see below), and may originally have been similar to the black glasses. The four brown opaque glasses are also heavily weathered, and the original colour is not readily apparent: it seems most likely that they would originally have appeared black. One of the samples is very dark blue (sample 85, figure 5.31), and has a low cobalt content (0.03 % CoO), the iron content (9.5 % FeO) should otherwise be dominant suggesting that the iron is present as the reduced form (Fe^{2+}) which is also blue. Whilst it is possible that the cobalt is an accidental component of the glass, perhaps arising by recycling other glass, this seems unlikely since 0.03 % CoO would be sufficient to colour most soda-lime-silica glasses blue, and is therefore unlikely to be the diluted cobalt from mixing different glasses. Only 10 of the glasses from Pozzouli had undetected levels of cobalt oxide, the remaining 36 glasses contained from 0.01 - 0.08 %, with 10 glasses containing 0.05 % or more cobalt oxide. Since only one of the cobalt-containing glasses could be clearly identified as appearing blue (i.e. sample 85, see above), the use of cobalt here is a curious phenomenon. It may be the consequence of recycling of glass from elsewhere, but this seems unlikely given the tight compositional grouping of many of these glasses (as low-magnesia soda-lime-silica glasses, see Figure 5.27). Alternative explanations might include the addition of a cobalt-containing raw material, which has become an established part of a craft tradition. This practise of continuing to use a component, which had once proved useful as a colourant, has been noted elsewhere (Gebhard *et al*. 1989, p 215). The glasses examined here may have originally been blue glasses, which have been re-melted and coloured "black" with the addition of an iron-rich material. The cobalt oxide content only correlates with zinc oxide (Pearson correlation coefficient = 0.293, significant at the 0.05 level), rather than the suite of elements often found (see 3.7.21 for additional discussion). Whilst it is difficult to assign a specific cobalt source, this would be consistent with that known from Tabriz in Iran, rather than those from the Erzebirge region of Europe or from Egypt during the second Millennium BC. The iron oxide is strongly negatively correlated with soda, magnesia, alumina, silica, sulphur oxides, potassium oxide and antimony (Correlation is significant at the 0.01 level (2-tailed)), suggesting that the iron source is independent of all of these key glassmaking components.

Figure 5.30 Examples of "black", green, and brown glasses (samples 57, 67 and 62 respectively). Scale 2:1

Figure 5.31 Blue glass bead, sample 85

Four of the samples are from red decorative glass which has been added to the dark matrix of various beads as small crumbs which have been marvered flush with the surface (for example see figure 5.33). These samples are also high in iron (see table 5.17 below), and contain small amounts of copper oxide. Backscattered imaging and semi-quantitative analysis has shown the presence of small copper-rich inclusions, which account for the colour (see figure 5.33). The associated presence of sulphur suggests that the copper originated in a sulphur-rich ore (see 3.7.8).

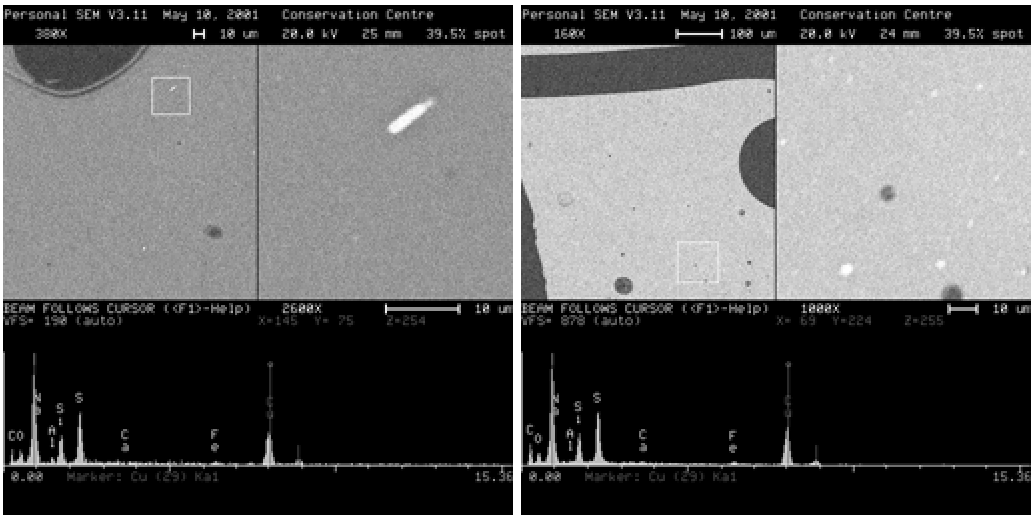


Figure 5.32 Backscattered SEM image of samples 75 and 84 showing copper (and sulphur)-rich inclusions.

Figure 5.33 Sample 74 taken from the red decoration of this bead.

sample	75	84	89	93	mean	stdev	min	max
Na_2O	15.86	17.57	15.95	15.04	16.11	1.06	15.04	17.57
MgO	1.02	2.46	1.03	1.27	1.45	0.69	1.02	2.46
Al_2O_3	1.93	2.41	1.34	1.26	1.74	0.54	1.26	2.41
SiO_2	69.07	64.35	68.06	67.77	67.31	2.05	64.35	69.07
P_2O_5	0.10	0.22	0.12	0.12	0.14	0.05	0.10	0.22
SO_3	0.40	0.67	0.24	0.36	0.42	0.18	0.24	0.67
Cl	0.49	0.45	0.50	0.56	0.50	0.05	0.45	0.56
K_2O	1.39	1.79	1.04	0.97	1.30	0.38	0.97	1.79
CaO	2.78	3.32	2.14	3.52	2.94	0.62	2.14	3.52
TiO_2	0.13	0.24	0.11	0.09	0.14	0.07	0.09	0.24
Cr_2O_3	0.00	0.00	0.00	0.02	0.01	0.01	0.00	0.02
MnO	0.05	0.04	0.01	0.04	0.04	0.02	0.01	0.05
FeO	7.81	8.15	9.15	10.19	8.83	1.07	7.81	10.19
CoO	0.00	0.00	0.08	0.02	0.03	0.04	0.00	0.08
NiO	0.00	0.06	0.00	0.01	0.02	0.03	0.00	0.06
CuO	**1.16**	**1.47**	**0.83**	**0.79**	**1.06**	**0.32**	**0.79**	**1.47**
ZnO	0.02	0.00	0.02	0.05	0.02	0.02	0.00	0.05
As_2O_5	0.20	0.05	0.08	0.00	0.08	0.09	0.00	0.20
SnO_2	0.01	0.01	0.01	0.03	0.02	0.01	0.01	0.03
Sb_2O_5	0.24	0.13	0.22	0.06	0.16	0.08	0.06	0.24
BaO	0.05	0.04	0.04	0.05	0.05	0.01	0.04	0.05
PbO	0.08	0.00	0.00	0.00	0.02	0.04	0.00	0.08
Total	102.79	103.43	100.97	102.22				

Table 5.17 Composition of red opaque glass decoration on Pozzouli beads.

5.5.2 Cumae

13 samples: 162 - 174 inclusive.

All of the Cumae samples were taken from beads in the Beck collection held by Cambridge University Museum of Archaeology. These beads date to the 8th - 7th Century BC and are very similar in the range of forms, colour and glass type as the Pozzouli material.

Glass Types

The glass types represented amongst the Cumae assemblage are comparable with those from Pozzouli: a number of them are very high in iron. All of the glasses are soda-lime silica glasses, two are high magnesia, soda-lime silica glasses (samples 162 and 163), and all the others are low magnesia soda-lime silica glasses (although with variable magnesia contents between 0.28 and 1.98 % MgO). This distinction is not arbitary, since samples 162 and 163 are also quite different in terms of form and colour from the beads from which the other samples are taken. The two high-magnesia soda - lime - silica glasses are distinct from the other Cumae glasses because of their relatively low iron oxide contents (see Table 5.18), and raised lime contents.

sample	mean high FeO	stdev	min	max	162	163
Na_2O	15.62	1.86	10.32	17.34	16.40	17.26
MgO	1.21	0.59	0.28	1.98	3.57	6.02
Al_2O_3	1.81	0.59	1.05	3.24	0.52	1.26
SiO_2	67.70	2.70	63.85	73.87	68.81	63.37

P_2O_5	0.13	0.07	0.05	0.24	0.17	0.10
SO_3	0.22	0.25	0	0.82	0.24	0.00
Cl	0.49	0.16	0.35	0.92	0.92	0.70
K_2O	1.51	0.70	0.76	2.88	1.62	3.26
CaO	2.22	0.94	1.17	3.80	7.04	6.79
TiO_2	0.16	0.06	0.09	0.32	0.04	0.02
Cr_2O_3	0.02	0.01	0	0.05	0.02	0.00
MnO	0.05	0.03	0.01	0.11	0.03	0.05
FeO	10.56	3.18	5.03	16.30	0.37	0.46
CoO	0.03	0.01	0	0.05	0.05	0.02
NiO	0.02	0.02	0	0.05	0.00	0.02
CuO	0.03	0.04	0	0.10	1.45	1.22
ZnO	0.03	0.05	0	0.15	0.00	0.02
As_2O_5	0.00	0.01	0	0.04	0.02	0.04
SnO_2	0.01	0.01	0	0.04	0.01	0.00
Sb_2O_5	0.06	0.07	0	0.20	0.09	0.00
BaO	0.04	0.01	0.01	0.06	0.01	0.02
PbO	0.04	0.03	0	0.09	0.03	0.00
Total					101.41	100.63

Table 5.18 Summary data for high iron and high magnesia glasses from Cumae

The high iron glasses have magnesia contents within the range 0.28 and 1.98 %, which place them all within the low - magnesia soda - lime - silica glass tradition, using a natron type soda source. However, the magnesia contents are probably not the most significant characteristic of these glasses. The Cumae high iron containing glasses are only 11 samples, with an average of 1.21 MgO %, the Pozzuoli high iron glasses have a range of 0.53 - 3.97 % MgO, but with a similar mean value of 1.66. Since all 46 of the Pozzuoli samples are high in iron, they are more likely to be more representative of this particular type of glass. The Cumae high iron samples are consistent with the Pozzuoli glasses: both groups of samples have similar means (i.e. within the low magnesia category), but the spread of magnesia values is greater for the larger number of samples from Pozzuoli. It seems most likely that the variable magnesia content is due to the use of a soda source with similarly variable magnesia content, such as a plant ash, the low, but variable potash content would tend to confirm this (0.76 - 2.88 %).

Colourants.

Sample 162 is difficult to describe in terms of colour: it is presently both green translucent and mottled brown (described as “buff” in the Beck catelogue (Bead Study Trust 1997 p 79), this colour variation is probably due to differential weathering, which may be due to variation in the burial environment rather than the bead’s composition. The area sampled was translucent green, and the colour can be attributed to the copper content (1.45 % CuO). Intriguingly, this glass contains 0.05 % Cobalt oxide, which might be expected to impart a blue colour: in this instance the copper oxide must be the dominant colourant. Sample 163 is dark blue translucent in colour also due to its copper content (1.22 %), probably deepened by the low cobalt oxide component (0.025 %). Like the Pozzouli material, many of the Cumae glasses contain significant cobalt oxide content: only one glass has undetected levels of cobalt oxide (sample 169), with the others ranging from 0.02 - 0.05 % CoO, and 2 glasses containing 0.05 % of this oxide.

All of the samples except 162 and 163 are from the same high iron tradition. Sample 167 is the only glass that does not appear black, and is from the white opaque decoration of a sub-triangular black bead (see figure 5.34).

Figure 5.34 Sub-triangular bead, sample 167 taken from white opaque glass decoration.

The compositional data for this white glass was unexpected, since it differed little from the high-iron “black” glasses from Cumae. Additional backscattered SEM imaging and semi-quantitative EDS analysis demonstrated why. The sample taken from the artefact consisted of both white glass, low in iron, but containing calcium antimonate crystals and black glass, high in iron (figure 5.35). The EMPA analysis was from the black glass rather than the opaque white fragment.

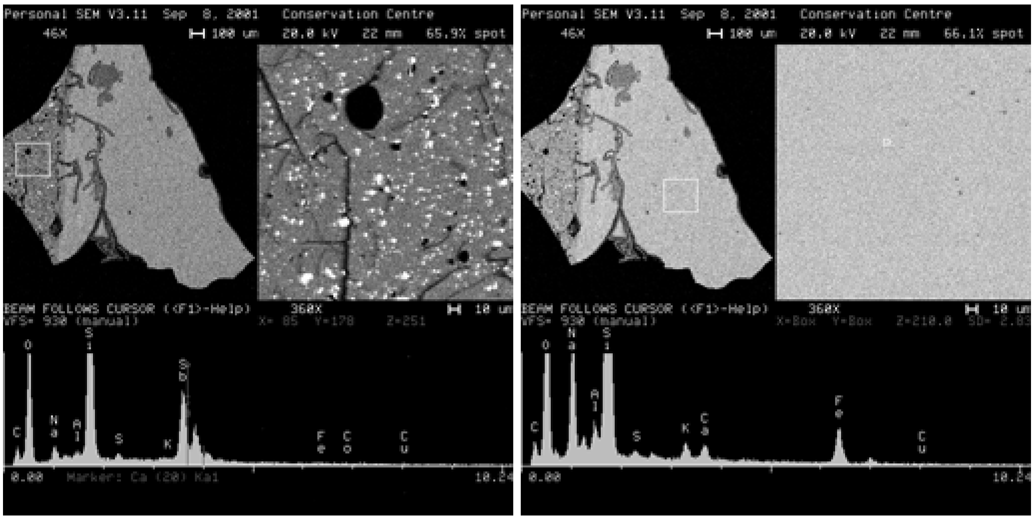


Figure 5.35 Backscatterred SEM image and EDS analysis of sample 167.

The black glasses, (samples 164, 165, 166, 168, 169, 170, 171, 172, 173 and 174) are coloured by their high iron contents, which makes then appear black.

5.5.3 Discussion of 7th Century BC glasses from Pozzuoli and Cumae

In the Bead Study Trust catalogue (Bead Study Trust 1997, p 23-24, 74-76) the black or brown beads decorated with white opaque eyes are described as typical of Etruscan necklaces, and might be a European product. This bead type is well-represented in Etruscan contexts to the North (Hencken 1968a and b), and further afield in Central Europe (Spaer 1987). Unfortunately they are not amongst those objects otherwise described as Etruscan studied as part of this project, and are therefore considered separately. It is possible that these glasses represent a genuinely distinct Etruscan glassmaking tradition, but in this case the artefacts sampled are from the periphery of the Etruscan sphere. The high iron containing glasses are therefore contenders for a uniquely Etruscan glass production in which large amounts of iron are added to a low-magnesia soda-lime-silica type glass composition. Statistical analysis of the combined datasets from the two sites fail to generate meaningful subdivision between the groups or within the combined data. It was not possible to generate a rotated component matrix and principle component variables scrutiny (the routine fails after 25 iterations). The inability to link the iron oxide to any of the key glassmaking oxides suggests that it was either added independently, or was associated with the silica source.

5.6 Glass from the Este Culture

A large number of samples were recovered from amongst the Iron Age material held by Este museum, derived from cemeteries beneath the modern city of Este (Chieco Bianchi and Capuis, 1985a Tavola I and 1985b). The assemblages sampled included Casa di Recovero, Casa Muletti Prosdocimi, Casa Alfonsi, Villa Benvenuti and Fondo Rebato. The material from the Este culture has been excavated since the early 1880s (Chieco Bianchi and Capuis, 1985a, p 19-34), and the meticulous retention of grave-group context for much of the material has ensured that these collections have been central to the construction of chronologies for Prehistoric Northern Italy (Randall-MacIver 1927a and b, Müller-Karpe 1959, Ridgeway 1979 p 422). This material dates from c 900 BC to c 350 BC (Ridgeway 1979 p 485).

5.6.1 Casa di Recovero

16 samples: 336, 344, 345, 347, 367, 368, 369, 370, 374, 375, 376, 393, 397, 398, 400, 401. All the samples were collected from the Museum of Este, and all are from finished artefacts derived from funerary contexts from the site of Casa di Recovero dating to the 9th to 7th Centuries BC. The excavations took place over a long period of time (1882-1964: Chieco Bianchi and Capuis, 1985a, p 19-32). The sampled assemblage principally consists of beads, but also includes spindle whorls and a brooch slider.

Glass types

All of the glasses successfully analysed from Casa di Recovero are soda-lime silica glasses, and none have sufficiently high potash contents to be described as mixed-alkali: all but two of the samples have less than 0.5 % potash (the two exceptions contain 1.68 and 1.84 %: samples 336 and 345 respectively). However, the assemblage as a whole is not compositionally homogenous and is remarkable in comparison with other groups of analyses by being compositionally variable. The date of the material coincides with the transition from high magnesia soda-lime silica glasses to low magnesia soda lime glasses as the dominant glassmaking tradition in the Mediterranean, and it is no surprise therefore that both types are represented amongst the assemblage.

Eight of the samples are low-magnesia, soda-lime silica glasses (with less than 1.2 % MgO), which would be consistent with a natron-type soda source for the glass (see 3.7.2 above and Lilyquist and Brill 1993, p 56, Fig 5.1). Seven of the samples are high-magnesia, soda-lime silica glasses (with more than 2.6 % MgO), typical of glasses made using soda-rich plant ashes (Lilyquist and Brill 1993, p 56, Fig 5.1). One of the samples has an intermediate magnesia content of 1.95 %, and may indicate a glass containing cullet from both traditions. However, despite being able to characterise the glasses into these basic groups, the individual analyses are still quite diverse within these categories, indeed several features are shared by glasses across this division.

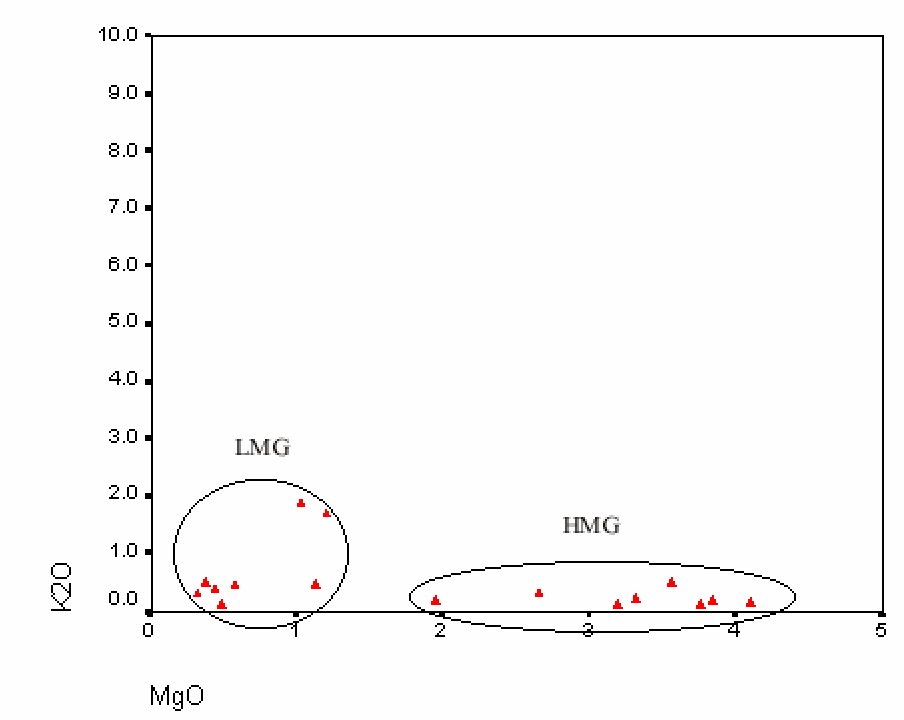


Figure 5.36 MgO vs K2O demonstrating glasses from Casa di Recovero are all either high or low magnesia soda-lime-silica glasses.

According to previous analyses of raw materials and glasses, natron and soda-rich plant-ash glasses can be distinguished by several components (Lilyquist and Brill 1993, p 56, Fig 5.1): plant ash soda rich glasses contain higher quantities of magnesia which may be accompanied by increased levels of potassium oxide, lime, alumina, manganese oxide, iron oxide, chlorine and phosphorous pentoxide. Reference to table 5.19 below will reveal that the Casa di Recovero glasses do not conform precisely to this convention. The high magnesia glasses also tend to contain increased levels of alumina, manganese oxide and chlorine, but not potash, lime, iron and phosphorous pentoxide. Whilst the fundamental division of the glasses into high and low magnesia glasses can be made, there remains considerable variability within the groups.

Many of the glasses have very high alumina contents, which may indicate a shared silica source for glasses from both groups, if for instance a sand rich in alumina has been employed. Six glasses contain less than 2 % alumina (367, 369, 370, 393, 400 and 401), all of which are low magnesia glasses, two of this group contain elevated alumina levels (336 and 345, with 7.09 and 6.24 % Al_2O_3 respectively). Across the entire data set, the alumina is strongly correlated with several components: FeO (0.506*), MgO (0.612*) TiO_2 (0.781**) and As_2O_5 (0.563**) (**Correlation is significant at the 0.01 level (2-tailed)*Correlation is significant at the 0.05 level (2-tailed). However, bivariate plotting of alumina against these other oxides does not reveal a consistent relationship. The high alumina content is not associated with only the high magnesia glasses for example, and cannot therefore be linked to either a plant ash or a particular silica source used in those glasses.

sample	mean LMG	min	max	reduced	mean HMG	min	max	reduced	intermediate? 344
Na_2O	17.06	14.53	20.2	17.49	18.35	13.79	22.17	18.64	17.05
MgO	0.70	0.33	1.2	0.71	3.45	2.66	4.1	3.50	1.95
Al_2O_3	2.57	0.45	7.09	2.63	8.34	5.065	16.35	8.47	4.35
SiO_2	67.54	59.75	72.885	69.22	60.27	40.61	68.965	61.20	71.74
P_2O_5	0.11	0.045	0.17		0.04	0	0.15		0
SO_3	0.24	0.12	0.39		0.33	0.03	0.48		0.25
Cl	0.95	0.34	1.31		0.48	0.3	0.615		0.62
K_2O	0.71	0.11	1.84	0.73	0.23	0.095	0.49	0.23	0.15
CaO	4.55	2.02	6.22	4.66	3.56	2.31	5.1	3.62	3.44
TiO_2	0.12	0.02	0.33		0.24	0.02	1.09		0.04
Cr_2O_3	0.01	0	0.02		0.01	0	0.02		0.02
MnO	0.12	0.005	0.34		0.38	0.16	1		0.33
FeO	4.45	0.21	10.76	4.56	4.27	0.625	21.3	4.34	0.74
CoO	0.11	0	0.29		0.06	0	0.17		0.05
NiO	0.07	0	0.27		0.06	0	0.15		0.08
CuO	0.21	0.005	0.71		0.02	0	0.09		0
ZnO	0.01	0	0.03		0.06	0	0.22		0.06
As_2O_5	0.03	0	0.12		0.04	0	0.22		0
SnO_2	0.03	0	0.08		0.01	0	0.03		0
Sb_2O_5	0.22	0	1.21		0.22	0	1.16		0
BaO	0.05	0.02	0.1		0.04	0.01	0.07		0.04
PbO	1.33	0	8.33		0.32	0	1.78		0
Total				100				100	100.91

Table 5.19 Summary data for Casa di Recovero.

	Component 1	Component 2	Component 3	Component 4	Component 5
Na_2O	-0.495	-0.129	0.593	0.107	0.16
MgO	8.35E-02	-0.129	0.473	-0.424	0.731
Al_2O_3	7.44E-01	-0.204	0.325	1.80E-02	4.96E-01
SiO_2	-9.14E-01	-2.67E-02	-0.261	-1.03E-01	-2.17E-01
P_2O_5	1.58E-01	0.431	0.255	5.78E-01	-0.481
SO_3	-0.405	0.239	5.71E-01	2.53E-01	0.527
Cl	-0.409	2.20E-02	-3.20E-01	-1.41E-01	-8.23E-01
K_2O	0.131	9.99E-02	-3.49E-02	9.53E-01	5.69E-02
CaO	-0.176	-9.44E-02	0.103	-3.06E-01	-8.87E-01
TiO_2	0.928	-8.07E-02	-0.199	1.10E-01	1.92E-01
Cr_2O_3	-0.116	-2.03E-01	0.336	7.61E-01	9.51E-02
MnO	6.12E-02	-6.85E-04	0.935	1.41E-01	2.91E-01
FeO	9.09E-01	-6.87E-02	-2.38E-01	1.27E-01	-1.33E-01
CoO	6.72E-02	5.26E-01	2.63E-01	7.61E-01	1.47E-01
NiO	-0.135	8.38E-01	0.375	0.172	0.144
CuO	3.90E-02	8.58E-01	-2.17E-01	4.03E-01	1.62E-02
ZnO	-2.87E-02	-1.04E-01	9.64E-01	8.98E-03	-4.56E-02
As_2O_5	8.53E-01	3.77E-01	-9.70E-02	1.54E-01	1.00E-01
SnO_2	-7.00E-02	8.51E-01	-2.91E-01	-8.00E-02	-1.02E-01
Sb_2O_5	1.58E-02	7.52E-01	5.85E-01	8.92E-02	-1.03E-01
BaO	0.384	1.00E-01	-0.116	8.32E-01	1.14E-01
PbO	0.161	9.39E-01	-1.52E-01	-5.68E-02	-3.88E-03

Table 5.20 Rotated Component Matrix for all compositional data from Casa di Recovero. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Rotation converged in 8 iterations.

By performing PCA on this data set it is possible to see that 5 components account for 90 % of the variance in the data set. The components in table 5.20 confirm the association between Al_2O_3, FeO, TiO_2 and As_2O_5 identified from the correlation analysis (see Component 1).

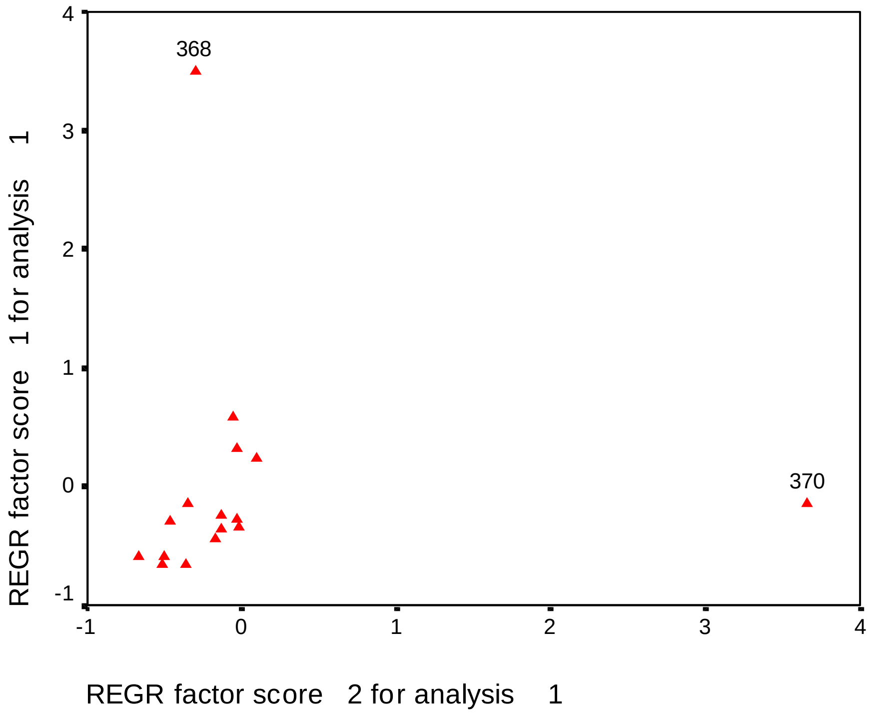


Figure 5.37 Scatter plot of first two Principal components for glasses from Casa di Recovero.

Two samples (368 and 370) are distinct from the other glasses. Sample 368 is a high-magnesia soda-lime-silica glass, but is distinguished by its very high alumina and iron contents (16.3 and 21.3 % respectively). Sample 370 is a low-magnesia soda-lime silica glass containing a significant proportion of lead (8.33 %). The components which mark these glasses out as different to the other s are those deliberately added as colourants.

Colourants

The majority of the glasses from Casa di Recovero are blue translucent and blue opaque (12 of 16), three are brown opaque or brown translucent- all dark glasses now badly weathered which may have appeared either black or amber in colour originally. One of the glasses is green opaque. A number of the artefacts sampled had yellow and white opaque glass decoration, unfortunately these were all badly weathered, and analyses were unsuccessful.

The low magnesia glasses (samples 336, 345, 367, 369, 370, 393, 400 and 401) and high magnesia glasses (samples 347, 368, 374, 375, 376, 397, 398) both contain glasses which have high iron contents. Samples 345, 367 and 393 are low magnesia glasses with 8.97, 10.76 and 7.89% FeO respectively, whilst sample 368 is high in magnesia and contains a massive 21.3 % iron oxide. The very high levels of iron oxide in glasses from both groups represent the deliberate addition of an iron-rich material, presumably as a colourant designed to make the resultant glass appear black. Iron working slag is a possible source of raw material for this component, and may contribute to the variable alumina levels observed amongst the glasses.

Cobalt is a colourant common to both glass types, and is highly correlated with nickel and copper, which may indicate a European source (as opposed to a Middle Eastern or Egyptian origin). It is not possible to discern a relationship between the cobalt and alumina contents, since the underlying alumina levels are variable. Egyptian glasses coloured with distinctive local cobalt have raised alumina levels of c. 2.4 % compared with 1% for contemporary glasses (Kaczmarczyk and Hedges 1983, p 136, Shortland and Tite 2000).

None of the glasses have been deliberately coloured with copper compounds. Two of the glasses have significant levels of antimony (samples 347 and 370, high and low magnesia glasses respectively with 1.16 and 1.21 % Sb_2O_5). Both are coloured with cobalt, and it seems likely that in part the antimony component is derived from the cobalt source rather than a deliberate attempt to decolour the blue glasses. Sample 370 also contains a significant lead oxide component (see above). The colour of this sample (pale green opaque) would therefore tend to suggest that this glass has a cobalt coloured glass matrix opacified with yellow lead antimonate crystals to give an opaque green glass. The green opaque glass is from a complex artefact a "leech" shaped brooch slider made of dark green opaque glass decorated with yellow opaque glass which had been trailed around the body of the artefact, marvered flush and then combed into chevrons (see figure 5.42).

5.6.2 Benvenuti

34 samples: 321, 322, 323, 325, 326, 327, 328, 331, 332, 333, 334, 335, 351, 352, 353, 354, 357, 358, 359, 360, 362, 364, 365, 377, 378, 379, 380, 382, 384, 385, 386, 390, 391, 395.

All of the samples from Benvenuti are from funerary contexts, and are therefore of completed artefacts rather than industrial waste. This assemblage largely consists of beads, but also includes a spindle whorl and irregular fragments of (clear) glass.

Glass Types

The glass recovered from Benvenuti represents a wide range of glassmaking technologies, suggesting the community using the cemetery had access to glass from different sources. Implicit in this observation is the suggestion that this community was not producing its own glass, since no single tradition dominates the assemblage. Unsurprisingly, the assemblage contains no examples of mixed-alkali glass, however there are examples of both high and low magnesia soda-lime silica glasses, with low magnesia glasses being the dominant tradition (27 out of 34 samples are low-magnesia soda-lime-silica glasses). There is also a high lead, low alkali glass of unusual composition (sample 359, see table 5.21 below).

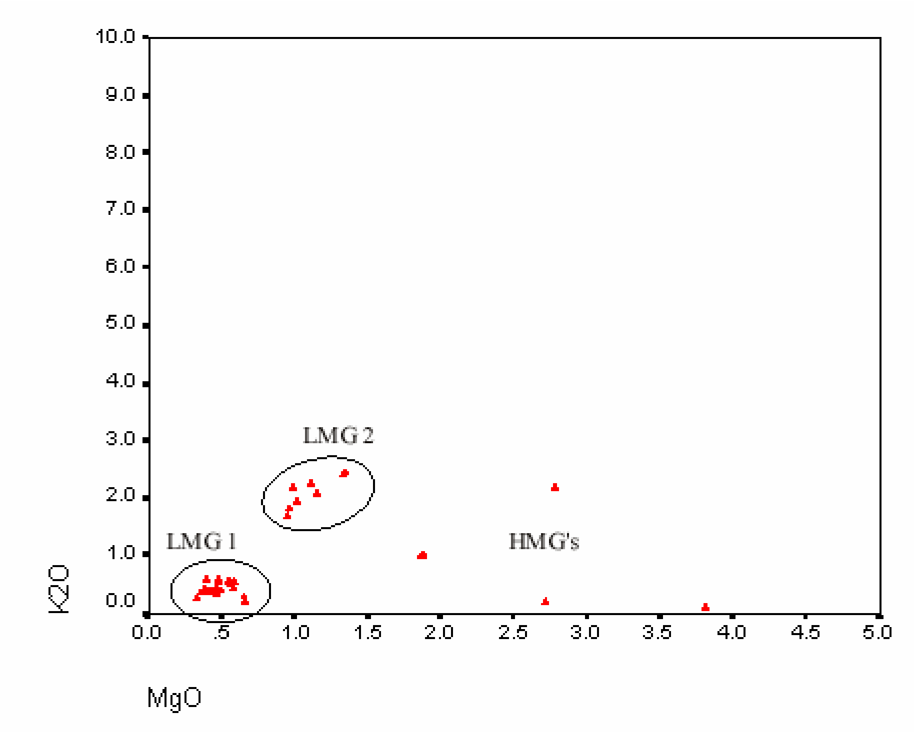


Figure 5.38 Glass types from Benvenuti: magnesia against potassium oxide.

The Benvenuti group contains six high-magnesia glasses, made using soda-rich plant ashes contain 1.86, 1.88, 1.89, 2.79, 2.72 and 3.81 % magnesia (samples 377, 378, 379, 322, 364 and 382 respectively), compared with a range of 0.34 - 1.35, mean 0.66 for the low-magnesia glasses. The high-magnesia glasses are all beads, but are not visibly distinct from the rest of the assemblage or even similar to each other in terms of colour, condition or form. Sample 322 has the raised potash, lime and phosphate levels, which classically define the plant-ash soda-lime silica glasses in comparison with those made with natron. Samples 364 and 382 are similar to each other, but different to sample 322: they do not have raised potash, lime and phosphate levels, but contain significantly higher alumina and manganese oxide. It seems most likely that the high-magnesia glasses were made according to two different recipes, both containing soda-rich plant ashes.

sample	mean LMG	reduced	mean HMG	reduced	359
Na_2O	17.43	18.06	18.09	18.48	2.92
MgO	0.66	0.69	2.49	2.54	0.57
Al_2O_3	3.34	3.46	2.22	2.27	2.67
SiO_2	67.63	70.07	68.31	69.77	41.26
P_2O_5	0.14		0.11		1.26
SO_3	0.27		0.41		0.24
Cl	0.94		0.72		0.42
K_2O	0.92	0.95	0.92	0.94	0.44
CaO	4.83	5.00	5.50	5.61	1.78
TiO_2	0.15		0.06		0.09
Cr_2O_3	0.01		0.01		0.00
MnO	0.14		0.26		2.26
FeO	1.71	1.77	0.38	0.39	6.36
CoO	0.13		0.02		0.06
NiO	0.07		0.02		0.00
CuO	0.31		0.18		0.16
ZnO	0.02		0.04		0.66
As_2O_5	0.01		0.00		3.02
SnO_2	0.06		0.02		0.01
Sb_2O_5	0.22		0.03		0.13
BaO	0.06		0.03		0.11
PbO	1.01		0.04		37.65
Total	100.08	100.00	99.83	100.00	102.07

Table 5.21 Summary data for glasses from Benvenuti

The low magnesia glasses can also be further broken down into two groups, since there is a discontinuous range of magnesia values 0.34 - 0.67 % MgO and 0.96 - 1.35 % MgO. These samples are characterised in table 5.22 and figure 5.38 as LMG 1 and LMG 2 respectively. LMG1 includes samples 334, 335, 325, 328, 333, 327, 321, 326, 323, 331, 332, 354, 385, 386, 360, 384, 362, 391, 390. LMG2 includes samples 358, 357, 351, 365, 380, 395, 352, 353. This subdivision is also evident across several other components, with higher soda contents in the latter group (12 - 18.2 % Na2O and 17.17 - 22.73 % Na2O) accompanied by higher alumina (0.63 - 2.46, mean 1.81 %, and 6.13 - 8.24, mean 6.99 %). LMG2 also contains lower lime and higher manganese oxide than LMG1.

sample	mean LMG 1	min	max	stdev	mean LMG 2	min	max	stdev
Na_2O	16.22	12	18.2	1.59	20.30	17.17	22.73	1.86
MgO	0.48	0.34	0.67	0.09	1.11	0.96	1.35	0.16
Al_2O_3	1.81	0.63	2.46	0.57	6.99	6.13	8.24	0.73
SiO_2	70.72	60.79	78.85	3.62	60.31	56.62	64.73	3.35
P_2O_5	0.05	0.01	0.12	0.03	0.38	0.17	1.09	0.35
SO_3	0.23	0.105	0.4	0.08	0.36	0.21	0.45	0.10
Cl	1.12	0.46	1.49	0.32	0.52	0.44	0.6	0.06
K_2O	0.42	0.19	0.61	0.12	2.11	1.69	2.46	0.28
CaO	5.67	3.13	8.99	1.38	2.85	2.36	3.77	0.56
TiO_2	0.07	0.02	0.13	0.03	0.33	0.27	0.4	0.05
Cr_2O_3	0.01	0	0.05	0.01	0.02	0	0.03	0.01
MnO	0.05	0	0.25	0.07	0.34	0.27	0.42	0.06
FeO	1.18	0.38	1.82	0.39	2.96	1.81	3.87	0.89
CoO	0.11	0	0.25	0.08	0.19	0	0.39	0.16
NiO	0.07	0	0.26	0.10	0.09	0	0.24	0.09
CuO	0.34	0.05	1.73	0.44	0.23	0.04	0.48	0.16
ZnO	0.02	0	0.12	0.03	0.01	0	0.05	0.02
As_2O_5	0.02	0	0.2	0.05	0.00	0	0.02	0.01
SnO_2	0.03	0	0.17	0.04	0.12	0	0.88	0.31
Sb_2O_5	0.27	0	1.57	0.36	0.11	0.02	0.26	0.10
BaO	0.04	0.02	0.07	0.01	0.09	0.07	0.1	0.01
PbO	1.27	0	14.69	3.30	0.37	0.03	1.79	0.59

Table 5.22 Summary data for LMG glasses from Benvenuti

The LMG2 group can be further subdivided: samples 377, 378 and 379 are all from irregular fragments of clear, translucent glass fragments, and are sufficiently similar analyses for them to have originally been from the same artefact or batch. They are distinct from the other LMG2 glasses by having a higher magnesia content and lower potash levels, in addition to much lower alumina and iron levels which would indicate a distinct silica source, not surprising in the production of uncoloured glass. The other LMG 2 glasses all contain impurities of lead oxide, copper oxide, nickel oxide and chromium oxide greater than the clear glasses, suggesting that the clear glasses have been deliberately produced with purified ingredients without the use of mixed glass cullet.

sample	358	357	351	365	380	395	352	353	377	378	379
Na_2O	17.17	18.08	20.46	19.97	21.5	20.9	22.73	21.55	18.68	18.59	18.63
MgO	0.96	0.97	0.99	1.02	1.11	1.15	1.33	1.35	1.86	1.88	1.89
Al_2O_3	6.28	6.45	7.04	6.13	7.16	6.81	8.24	7.77	0.32	0.32	0.32
SiO_2	64.73	63.95	60.15	63.8	57.82	57.76	56.62	57.64	69.08	69.48	69.72
P_2O_5	1.09	0.75	0.19	0.24	0.22	0.19	0.19	0.17	0.12	0.12	0.12
SO_3	0.24	0.21	0.3	0.45	0.39	0.45	0.42	0.45	0.51	0.52	0.45
Cl	0.48	0.49	0.5	0.6	0.56	0.58	0.5	0.44	0.73	0.79	0.69
K_2O	1.69	1.81	2.19	1.94	2.25	2.08	2.43	2.46	0.99	0.99	1.01
CaO	3.77	3.7	2.36	2.48	2.58	2.68	2.65	2.54	6.76	6.81	6.8
TiO_2	0.27	0.31	0.35	0.29	0.36	0.31	0.4	0.38	0.02	0.04	0.02
Cr_2O_3	0.02	0.03	0.03	0.02	0	0	0.02	0	0	0.02	0
MnO	0.27	0.38	0.42	0.31	0.41	0.33	0.35	0.27	0	0.03	0.04
FeO	1.81	1.92	3.87	1.99	3.84	3.34	3.53	3.38	0.1	0.21	0.18
CoO	0	0	0.39	0.02	0.31	0.28	0.25	0.28	0	0.02	0
NiO	0.02	0	0.15	0	0.04	0.18	0.05	0.24	0	0	0
CuO	0.12	0.04	0.34	0.09	0.36	0.48	0.13	0.3	0.01	0.04	0.01
ZnO	0.03	0	0.05	0.02	0	0	0	0	0	0.12	0
As_2O_5	0	0	0	0	0	0	0	0.02	0	0	0
SnO_2	0	0	0.01	0.01	0.04	0.88	0	0.03	0	0.01	0
Sb_2O_5	0.02	0.02	0.22	0.02	0.11	0.26	0.02	0.19	0.02	0.02	0
BaO	0.07	0.1	0.09	0.07	0.1	0.1	0.1	0.09	0.02	0.04	0.04
PbO	0.03	0.04	0.33	0.14	0.48	1.79	0.05	0.11	0	0	0
Total	99.07	99.25	100.43	99.61	99.64	100.56	100.01	99.66	99.22	100.05	99.92

Table 5.23 Low magnesia glasses LMG2 including samples 377 – 379 of clear translucent glass.

Despite being differently coloured, the LMG 2 group, excluding 377-379, all contain high titanium oxide levels which are strongly correlated with the iron and alumina contents, suggesting a shared silica source.

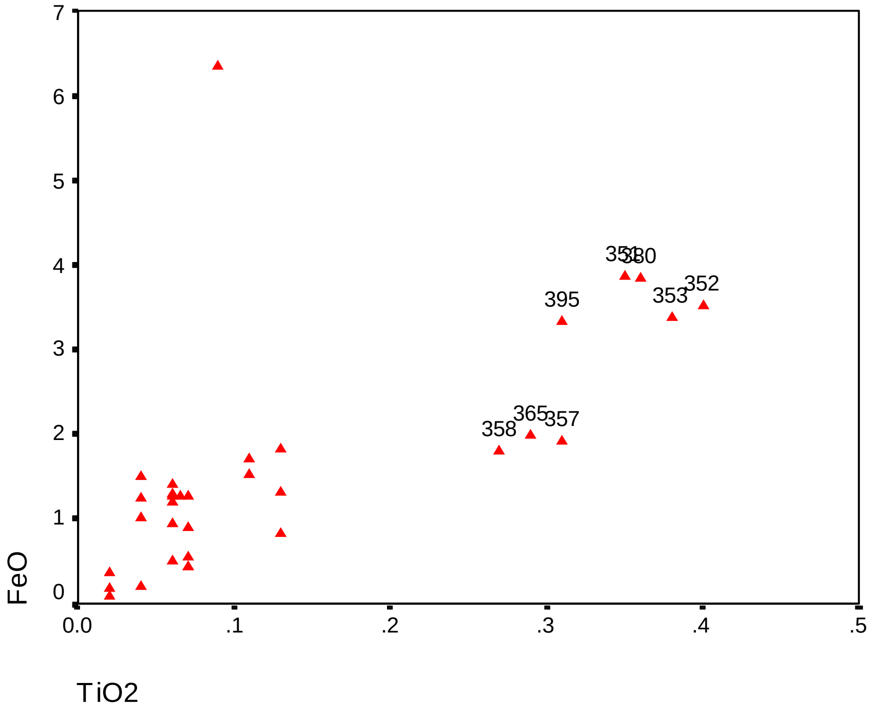


Figure 5.39 Scatter plot of titanium oxide and iron contents in glasses from Benvenuti.

Sample 359 is a glass unlike any other from this assemblage. It is a sample from a spindle whorl of composite structure. The spindle whorl has ceramic or ceramic/metal core (it is very dense) with a weathered green opaque glass "glaze" finish. The glassy surface is in turn decorated with both horizontal bands and zig-zag decoration of white opaque glass. The sample was taken from the green glass coating on the exterior. The resulting analysis is quite unusual (see table 5.21).

Figure 5.40 Sample 359 taken from glass coating of spindle whorl. Scale 2:1

Whilst this glass belongs nominally to the low magnesia soda-lime silica glass group LMG 1, it is a distinct glass composition with a high lead composition (37.65 % PbO). The high lead content alone is not exceptional, since high lead glasses are known from 1400 BC onwards (see 3.7.9). In this case there is a low overall alkali content (3.36 % total), which may reflect a weathered composition, although less alkali is necessary when fusing high lead glasses (high-lead glasses from Nimrud contained 3.46 and 3.68 % total alkali (Brill 1999b, p 48)). High levels of arsenic (3.02 % As_2O_5) also accompany the high lead. The high iron and manganese contents may have been added to to give a dark opaque glass sufficient to cover the core and give a contrasting background for the white decoration. This artefact is very dense, and may have a ceramic core, making the “glass” surface a glaze. The high lead composition would enhance the adhering properties of the glaze.

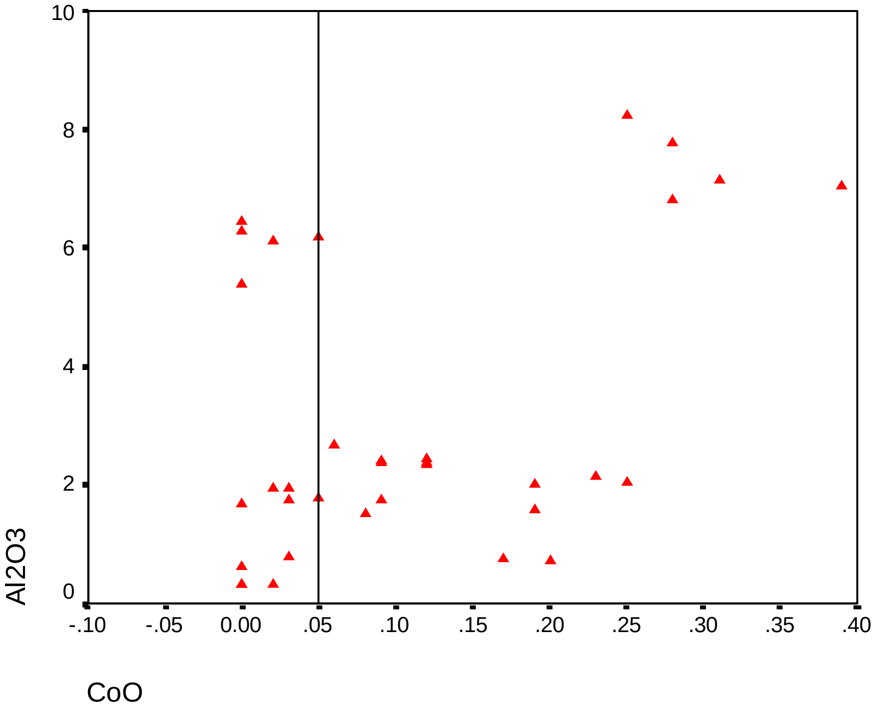


Figure 5.41 Alumina and cobalt oxide levels in cobalt-coloured blue glasses from Benvenuti

Colourants

The Benvenuti assemblage principally consists of blue (opaque and translucent) glasses (22 samples), but also includes 3 clear translucent, 2 yellow opaque, 2 green opaque, 3 white opaque, 1 aqua and 1 brown opaque glass (the white and brown opaques are heavily weathered.

A number of the cobalt-coloured blue glasses contain particularly high levels of alumina, suggesting that these beads from Benvenuti were manufactured using two distinct cobalt sources, with the high alumina glasses also tending to contain higher levels of cobalt oxide (see Figure 5.41). This raises the possibility of the cobalt colourant originating in the Egyptian source noted by Kaczmarczyk (1986), however the high-alumina cobalt containing glasses (samples 351, 352, 353, 380, 395) are all from the LMG 2 group, which contain high alumina and titanium oxide levels irrespective of the presence of cobalt.

5.6.3 Rebato

Only two samples were taken from material from this site: samples 343 and 373. The Rebato artefacts were recovered from excavations of a 7th Century BC cemetery, and are held at Este Museum (Chieco Bianchi and Capuis 1985a, p 10 Figure 1, Plates 1 and 2).

Figure 5.42 Brooch decoration from which sample 373 was taken (scale 1:1).

Glass types.

Both of the glasses are low - magnesia soda - lime- silica glasses. The glasses, in addition to being from quite different artefacts (a bead and a brooch decoration), are not very similar in terms of their chemical composition: 343 has lower alumina and iron levels, and higher lime than 373, suggesting quite distinct silica sources.

sample	343	373
Na_2O	13.07	19.42
MgO	0.41	1.03
Al_2O_3	2.27	5.70
SiO_2	63.12	63.53
P_2O_5	0.02	0.19
SO_3	0.23	0.24
Cl	0.79	0.43
K_2O	1.15	1.95
CaO	7.20	2.70
TiO_2	0.04	0.24
Cr_2O_3	0.00	0.02
MnO	0.03	0.23
FeO	0.87	2.49
CoO	0.02	0.31
NiO	0.00	0.29
CuO	0.06	0.47
ZnO	0.02	0.03
As_2O_5	0.00	0.00
SnO_2	0.00	0.04
Sb_2O_5	1.57	0.20
BaO	0.06	0.07
PbO	10.83	0.19
Total	101.76	99.77

Table 5.24 Compositional data for samples from Rebato.

Sample 343 is of a heavily weathered glass bead, in which the matrix is now opaque brown, but the decoration of blue and white stratified eyes and opaque yellow “knops” can be clearly discerned, despite a heavy layer of varnish having been used as a (modern) stabilising agent. The sample included both matrix and yellow glass, and the analysis is clearly of a glass coloured and opacified using lead antimonate.

Sample 373 is also from a heavily weathered (and varnished) glass now appearing brown and opaque. The analysis suggests that the original glass would have been dark blue (or black) since it contains 0.31 % cobalt oxide and 2.49 % iron oxide. It is possible that the cobalt source has contributed to the raised iron content in this glass, and also to the higher levels observed of copper, nickel, manganese and potash (see 3.7.20).

5.6.4 Alfonsi

A single sample from the cemetery site of Casa Alfonsi was taken from a brooch decoration held by Este Museum (sample 348). The tomb is dated to 525-450 BC (Este III D1, Ridgeway 1979, p 485). The material from Casa Alfonsi was recovered during excavations in 1906 and 1907 (Chieco Bianchi and Capuis 1985a p 10, 34, Figure 1 and Plates 1 and 2).

This sample is from a badly weathered blue translucent glass. It is a low - magnesia soda - lime - silica glass (0.43 % MgO) with a low alumina content (0.81 %). There is a low overall alkali content (11.89 %) and no significant amount of lead oxide suggesting that the analysis may be of a weathered glass. It is coloured with cobalt oxide (0.4 %) and has associated nickel, copper and arsenic (but no manganese). This is a very high cobalt oxide content, and the original glass may have appeared black.

sample	348
Na_2O	11.73
MgO	0.43
Al_2O_3	0.81
SiO_2	80.09
P_2O_5	0.02
SO_3	0.18
Cl	0.76
K_2O	0.16
CaO	5.14
TiO_2	0.04
Cr_2O_3	0.02
MnO	0.00
FeO	0.79
CoO	0.40
NiO	0.14
CuO	0.12
ZnO	0.09
As_2O_5	0.21
SnO_2	0.04
Sb_2O_5	0.06
BaO	0.02
PbO	0.04
Total	101.29

Table 5.25 Compositional data from sample 348 from Alfonsi

Figure 5.43 Sample 348

5.6.5 Muletti Prosdocimi

3 samples: 320, 349 and 350.

The three samples from Muletti Prosdocimi are from glass beads recovered during the excavation of a cemetery between 1886 and 1925, and are now currently held at Este Museum (Chieco Bianci and Capuis 1985a p 32-34). The tomb groups with which they are associated are dated to the period 525 – 450 BC.

Glass types

Sample 320 is a high - magnesia soda - lime - silica glass, containing 3.73 % MgO. It does not contain raised levels of potash and phosphorus pentoxide, which might be expected of a plant ash soda -source. It is badly weathered, but upon sampling the bead matrix appeared to be of blue translucent glass, probably coloured by the low copper oxide content (0.57 %), since no cobalt was detected.

Samples 349 and 350 are both low - magnesia. soda - lime silica glasses, but are not otherwise alike.

sample	320	349	350
Na_2O	16.62	17.81	17.51
MgO	3.73	0.56	0.83
Al_2O_3	2.74	0.39	2.27
SiO_2	63.18	69.36	65.84
P_2O_5	0.12	0.02	0.12
SO_3	0.48	0.18	0.33
Cl	0.61	1.33	0.85
K_2O	0.89	0.09	0.63
CaO	8.68	10.09	5.83
TiO_2	0.04	0.06	0.13
Cr_2O_3	0.02	0.00	0.02
MnO	0.11	0.04	0.29
FeO	0.58	0.23	6.23
CoO	0.00	0.00	0.00
NiO	0.06	0.00	0.00
CuO	0.57	0.00	0.58
ZnO	0.05	0.00	0.00
As_2O_5	0.00	0.00	0.00
SnO_2	0.01	0.03	0.01
Sb_2O_5	0.02	1.67	0.07
BaO	0.04	0.02	0.05
PbO	0.00	0.09	0.33
Total	98.55	101.97	101.92

Table 5.26 Compositional data from samples from Muletti Prosdocimi

Sample 349 is from a fragment of a badly weathered aqua translucent glass bead, which contains very low amounts of alumina (0.39 %) and iron oxide (0.23 %), a high lime content (10.09 %) and was decolourised with the addition of antimony pentoxide (1.67 %).

Sample 350 is from a heavily weathered brown opaque bead distinguished by its high iron content (6.23 %)

5.6.6. Discussion of the Este glasses.

Considered as a group, the glasses from Este Culture cemeteries do not constitute a singular technology, or readily identifiable type. There is no evidence for continuity of glass production from the industry associated with settlements in the Po Valley from Final Bronze Age. There is no sign even of recycling of the earlier glass, or occasional examples of the earlier material remaining in circulation to be deposited alongside beads from the Early Iron Age. Unsurprisingly, the variation seen within the Benvenuti material, is reflected across the data set as a whole: i.e. two groups of LMG glasses, a few HMG glasses, and no high potash or mixed-alkali type-glasses (figures 5.44 and 5.38). The subdivision of this material into sites is essentially an arbitrary act based upon 19th Century urban property boundaries rather than any archaeological characteristic (Chieco Bianchi and Capuis 1985a, p 10 Figure 1).

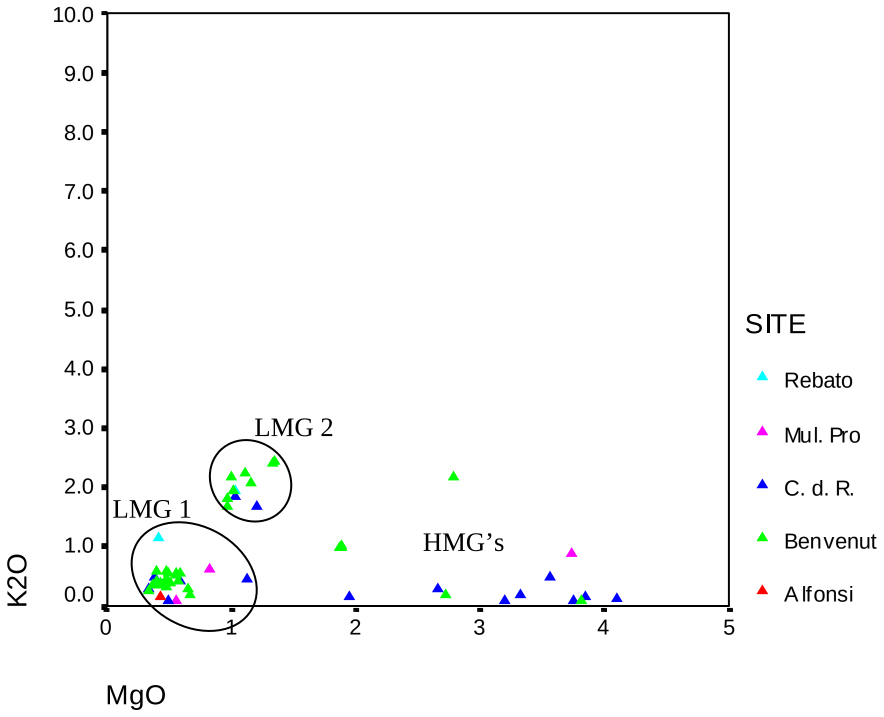


Figure 5.44 Glass types from Este Culture Cemeteries base on the magnesia and potassium oxide contents.

The Este glasses are also discussed as a single group in further detail below (see page 314).

5.7 Co Garizoni

16 samples: 272 - 274, and 276 - 288 inclusive.

All of the Co’Garizoni samples were taken from artefacts held at Adria Museum, and are derived from rescue excavations of a cemetery near Adria in 1966. The cemetary dates to the 3rd – 2nd Century BC (Simonetta Bonomi *pers. comm*, Fogolari and Scarfi 1970, p 14). The beads are all of identical form and there are three colours represented amongst the original assemblage (opaque white, blue and green).

Figure 5.55 samples 272, 285 and 288 illustrate the form and range of colours amongst the beads sampled from Co’Garizoni (scale 2:1)

Glass types

All of the Co’Garizoni glass samples are classic low-magnesia soda - lime - silica glasses, consistent with use of a natron -type soda source. The soda values range from 13.82 - 17.94 %, and the magnesia content is consistently low with a range of 0.35 - 0.56 %. The alumina content is unexceptional with a mean of 2.42 %, range 2.28 - 2.61 %. The potassium oxide and phosphorous pentoxide levels are also compatable with a natron type glass with means and ranges of 0.68, 0.53 - 0.82 % and 0.06, 0.02 - 0.09 % respectively. A low iron containing silica source has been used throughout (0.32 - 0.78 %), and coupled with concentrations of other metals (except deliberate colourants) suggests that either a very clean sand or ground quartz was employed.

sample	mean all	stdev	min	max	reduced comp.
Na_2O	16.22	1.38	13.82	17.94	17.48
MgO	0.44	0.08	0.35	0.56	0.48
Al_2O_3	2.42	0.09	2.28	2.61	2.61
SiO_2	66.08	2.06	59.43	67.82	71.24
P_2O_5	0.06	0.02	0.02	0.09	
SO_3	0.47	0.09	0.33	0.71	
Cl	0.86	0.11	0.59	1.03	
K_2O	0.68	0.09	0.53	0.82	0.73
CaO	6.47	0.72	5.64	8.23	6.97
TiO_2	0.05	0.01	0.04	0.06	
Cr_2O_3	0.01	0.01	0.00	0.02	
MnO	0.61	0.39	0.02	1.24	
FeO	0.46	0.16	0.32	0.78	0.50
CoO	0.03	0.04	0.00	0.11	
NiO	0.00	0.01	0.00	0.02	
CuO	0.10	0.23	0.00	0.91	
ZnO	0.01	0.02	0.00	0.06	
As_2O_5	0.03	0.04	0.00	0.14	
SnO_2	0.03	0.02	0.01	0.06	
Sb_2O_5	4.30	2.07	0.52	8.54	
BaO	0.05	0.01	0.04	0.06	
PbO	1.48	2.63	0.00	8.80	
Total					100

Table 5.27 summary data for all samples from Co'Garizoni

Colourants

The only way to distinguish compositionally between these glasses is on the basis of their colourants.

The white glasses are opacified by calcium antimonate, the most widely used white opacifier during the 2nd and 1st Millennia BC (Kaczmarczyk and Hedges 1983, p 145). The white glasses contain the highest antimony levels (measured as Sb_2O_5), ranging from 3.37 - 8.54, mean 5.42 %, compared with a range of 0.52 - 2.38, mean 1.83 for all of the other glasses.

	mean white	stdev	min	max
Na_2O	15.89	1.28	13.82	17.46
MgO	0.40	0.06	0.35	0.55
Al_2O_3	2.42	0.08	2.29	2.59
SiO_2	65.75	2.40	59.43	67.55
P_2O_5	0.05	0.02	0.02	0.09
SO_3	0.50	0.09	0.38	0.71
Cl	0.82	0.10	0.59	0.94
K_2O	0.64	0.07	0.53	0.73
CaO	6.36	0.85	5.64	8.23
TiO_2	0.05	0.01	0.04	0.06
Cr_2O_3	0.01	0.01	0.00	0.02
MnO	0.43	0.24	0.02	0.67
FeO	0.37	0.03	0.32	0.43
CoO	0.01	0.01	0.00	0.03
NiO	0.00	0.01	0.00	0.02
CuO	0.00	0.00	0.00	0.01
ZnO	0.01	0.02	0.00	0.05
As_2O_5	0.05	0.04	0.01	0.14
SnO_2	0.04	0.01	0.01	0.06
Sb_2O_5	5.42	1.34	3.37	8.54
BaO	0.04	0.01	0.04	0.06
PbO	1.71	3.00	0.01	8.80

Table 5.28 Summary data for all white opaque samples from Co’Garizoni

The blue glasses also contain a significant antimony content, also probably present as the white opacifier, calcium antimonate. These glasses have their colour modified by the addition of cobalt oxide, resulting in a blue opaque glass.

	mean blue	stdev	min	max
Na_2O	16.85	1.63	14.42	17.94
MgO	0.53	0.02	0.51	0.55
Al_2O_3	2.46	0.10	2.40	2.61
SiO_2	66.95	0.69	66.15	67.82
P_2O_5	0.07	0.00	0.07	0.07
SO_3	0.40	0.05	0.33	0.45
Cl	0.94	0.02	0.91	0.96
K_2O	0.79	0.03	0.76	0.82
CaO	6.80	0.12	6.72	6.98
TiO_2	0.05	0.01	0.04	0.06
Cr_2O_3	0.01	0.01	0.00	0.02
MnO	1.16	0.05	1.11	1.24
FeO	0.72	0.05	0.66	0.78
CoO	0.10	0.01	0.09	0.11
NiO	0.01	0.01	0.00	0.02
CuO	0.17	0.04	0.13	0.21
ZnO	0.02	0.03	0.00	0.06
As_2O_5	0.00	0.00	0.00	0.00
SnO_2	0.02	0.01	0.01	0.03
Sb_2O_5	2.15	0.16	2.05	2.38
BaO	0.06	0.00	0.06	0.06
PbO	0.18	0.24	0.00	0.53

Table 5.29 Summary data for all opaque blue glasses from Co’Garizoni.

The cobalt content is strongly associated with manganese oxide, iron oxide, and potash, all of which must therefore be diagnostic of the cobalt raw material. The cobalt content is not associated with alumina, nickel or arsenic. It seems most likely that the cobalt-containing absolite mineral has been used (see section 3.7.20).

	K_2O	MnO	FeO	CoO	BaO
K_2O	1	0.916*	0.69**	0.831**	0.388
MnO	0.916**	1	0.833**	0.871**	0.557**
FeO	0.690**	8.30E-01	1	0.887**	0.757**
CoO	0.831**	0.871*	0.887**	1	0.7**
BaO	0.388	5.57E-01	0.757**	0.700**	1.00E+00

Table 5.30 Correlation between cobalt and associated oxides amongst Co’Garizoni (** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed))

The single green glass sampled (sample 288) is coloured and opacified by a combination of lead antimonate (which is a yellow opacifier) in a blue matrix coloured by copper oxide.

	sample 288
Na_2O	17.32
MgO	0.56
Al_2O_3	2.28
SiO_2	66.22
P_2O_5	0.02
SO_3	0.39
Cl	1.03
K_2O	0.58
CaO	6.27
TiO_2	0.04
Cr_2O_3	0.00
MnO	0.35
FeO	0.49
CoO	0.00
NiO	0.00
CuO	0.91
ZnO	0.00
As_2O_5	0.00
SnO_2	0.05
Sb_2O_5	0.52
BaO	0.05
PbO	4.04
Total	101.12

Table 5.31 Compositional data for green glass from Co’Garizoni (sample 288).

This is attested by the raised lead oxide level, 4.04 % compared to an average of 1.83 % for all of the other glasses, and a raised copper content of 0.91 %. The trace of tin oxide present is probably associated with the use of a bronze for the source of the copper.

If the reduced compositions of the three colours are considered then it is possible to see how similar the underlying glass compositions are, with only slight variation contributed by increased potash and iron levels in the blue glasses originating in the cobalt source. These are so slight that they do not significantly alter the overall picture of a single glass type being employed.

	reduced comp. All	reduced comp. White	reduced comp. Blue	reduced comp. Green
Na_2O	17.48	17.30	17.72	18.48
MgO	0.48	0.43	0.56	0.60
Al_2O_3	2.61	2.63	2.59	2.43
SiO_2	71.24	71.60	70.40	70.66
K_2O	0.73	0.70	0.83	0.62
CaO	6.97	6.93	7.15	6.69
FeO	0.50	0.40	0.75	0.52
Total	100	100	100	100

Table 5.32 Reduced compositions for different coloured glasses from Co’Garizoni

5.8 Canale Bianco

18 samples, 239 - 244, 246 - 250, 254 - 257, 263, 302, 304.

All of the samples are derived from the collection held at Adria Museum, and are from the rescue excavations of a nearby necropolis, in this case associated with the canalisation of a tributary of the Po. The artefacts sampled date from the 5th to the 2nd Centuries BC. The assemblage largely consists of beads: complex stratified eye beads (e.g. samples 302 and 254), spirally decorated beads, ring beads and also includes spindle whorls.

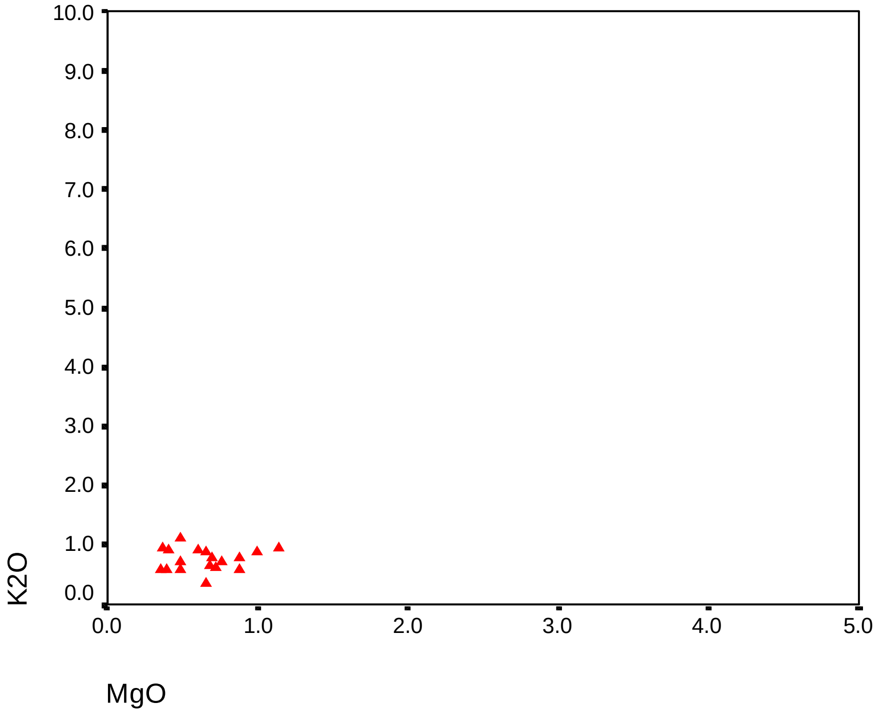


Figure 5.56 Scatter plot of potash against magnesia for glasses from Canale Bianco.

Glass types

All except one of the Canale Bianco glasses are low- magnesia, soda-lime silica glasses (see Figure 5.56), the exception being a single high lead glass containing 20.52 % lead oxide (sample 255), this glass is an opaque yellow, coloured and opacified with lead antimonate crystals. The assemblage is quite diverse in terms of artefact types, forms and colours making their collective composition unsuitable for reduction into a single “type” for tabulation, although a consideration of the compositional ranges may be useful.

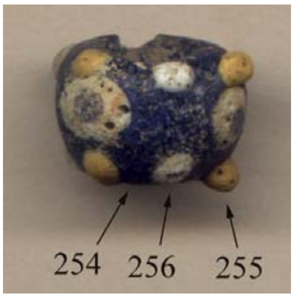


Figure 5.57 Bead from Canale Bianco, sample 255 from yellow opaque decoration.

sample	mean	stdev	min	max	255
Na_2O	16.42	1.21	14.15	18.09	12.96
MgO	0.66	0.22	0.36	1.14	0.35
Al_2O_3	2.30	0.46	1.14	3.38	1.91
SiO_2	66.91	3.04	61.97	73.89	54.52
P_2O_5	0.06	0.04	0	0.14	0.02
SO_3	0.29	0.10	0.12	0.52	0.26
Cl	0.92	0.17	0.57	1.35	0.82
K_2O	0.77	0.19	0.38	1.11	0.60
CaO	8.10	1.60	5.8	12.08	5.32
TiO_2	0.04	0.02	0	0.09	0.06
Cr_2O_3	0.01	0.01	0	0.03	0.00
MnO	0.88	1.19	0	3.72	0.04
FeO	1.14	1.95	0.24	8.63	1.99
CoO	0.05	0.06	0	0.20	0.04
NiO	0.01	0.02	0	0.08	0.00
CuO	0.21	0.35	0	1.15	0.00
ZnO	0.02	0.03	0	0.11	0.09
As_2O_5	0.00	0.01	0	0.02	0.00
SnO_2	0.02	0.02	0	0.06	0.01
Sb_2O_5	0.80	1.38	0	5.16	2.55
BaO	0.06	0.02	0.04	0.13	0.02
PbO	0.86	2.22	0	9.30	20.52
Total					102.08

Table 5.33 Summary data for glasses from Canale Bianco

Colourants

The Canale Bianco assemblage represents a wide range of glass colours: 5 blue translucent glasses, 2 blue opaques, 1 white opaque, 2 colourless translucent, 1 green translucent, 2 yellow opaques, 2 brown opaques (probably badly weathered), 1 “black” and 2 aqua translucent glasses.

The blue samples are mostly coloured by the addition of cobalt oxide (six samples: 241, 242, 254, 257, 263 and 302), with only one blue glass coloured by copper alone (sample 304).

sample	241	242	254	257	263	302	304
Na_2O	17.58	17.36	16.22	15.34	16.10	15.75	17.47
MgO	0.72	0.68	0.65	0.66	1.14	0.49	0.48
Al_2O_3	2.17	2.14	1.14	2.11	2.51	3.38	2.51
SiO_2	66.76	67.67	73.89	67.30	66.07	69.07	69.96
P_2O_5	0.05	0.00	0.07	0.02	0.12	0.05	0.02
SO_3	0.30	0.36	0.12	0.33	0.24	0.42	0.52
Cl	0.98	1.04	1.35	0.85	0.95	0.82	0.57
K_2O	0.63	0.66	0.38	0.91	0.97	0.61	1.11
CaO	7.30	7.27	6.74	8.98	9.84	9.35	7.55
TiO_2	0.06	0.02	0.09	0.04	0.04	0.00	0.04
Cr_2O_3	0.00	0.02	0.03	0.02	0.00	0.00	0.00
MnO	1.49	1.56	0.94	0.10	0.68	0.03	0.01
FeO	0.77	0.79	0.72	1.25	1.17	0.56	0.24
CoO	0.06	0.11	0.11	0.12	0.16	0.20	0.02
NiO	0.00	0.02	0.02	0.00	0.01	0.00	0.00
CuO	0.10	0.17	0.13	0.32	0.22	0.04	1.15
ZnO	0.00	0.02	0.11	0.00	0.03	0.00	0.00
As_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO_2	0.03	0.00	0.00	0.01	0.03	0.00	0.01
Sb_2O_5	0.06	0.02	0.00	0.20	0.07	0.02	0.09
BaO	0.06	0.06	0.05	0.04	0.06	0.05	0.05
PbO	0.08	0.09	0.01	1.53	0.18	0.04	0.00
Total	99.20	100.06	102.77	100.13	100.59	100.88	101.80

Table 5.34 blue samples from Canale Bianco

Statistical analysis of the data for these glasses reveals no significant correlation between cobalt and other components (such as alumina, copper oxide, manganese oxide, iron oxide, zinc oxide or arsenic oxide), suggesting that a pure or refined cobalt raw material was employed. Interestingly, the copper coloured blue glass sample (sample 304) is derived from an artefact which also includes cobalt-coloured glass (sample 302).

Figure 5.58 Artefact from which samples 302 and 304 were taken (scale 2:1).

Sample 302 was removed from the core of the bead (dark blue translucent glass containing 0.2 % CoO), and sample 304 was taken from a lighter blue opaque (turquoise?) decorative crumb attached to the surface of the bead. This is clearly a complex structured artefact, in which composite roundels of decorated glass have been inserted and marvered onto a blue core, and then the decoration augmented with the further addition of blue and yellow opaque crumbs. The craftsperson (or people) manufacturing the object had access to different shades of blue coloured glass, and distinguished between them both in their manufacture and use (this distinction is less clear in the Bronze age material).

The colourless translucent samples (243 and 250), green translucent (244) and aqua translucent (248 and 249) are treated as similar in terms of colour: they have not been manufactured with the intention of being strongly coloured. The samples come from beads (243 and 244) and spindle whorls (248, 249 and 250). These clear or lightly coloured translucent glasses were initially assumed to be "naturally" coloured by low iron containing sand, but examination of the analytical data (see Table 5.35 below) show that each of them is deliberately decoloured by the addition of modifying agents. Samples 248, 243, 249 and 250 are all decoloured with the addition of antimony pentoxide, with 1.2, 3.29, 0.93 and 0.84 % respectively. The first use of use of this decolourant is associated with the shift to natron-type soda-lime silica glasses in the 8th Century BC, and is the sole known decolourant until supplemented and finally replaced by manganese after the 1st Century BC (see 3.7.16 above). Sample 244 surprisingly contains 1.25 % manganese oxide. Since this is a low-magnesia soda-lime-silica glass, the manganese is not an accidental component originating in a plant ash, and must therefore be considered a deliberate addition. The use of manganese oxide as a decolourant is not documented before the 2nd Century BC (Sayre 1963). This would suggest that sample 244 is from an artefact incorrectly dated to the period 3rd - 2nd Century BC. Review of its form would tend to confirm this, since it is a ring bead (or *ringperlen*) common across Central and Southern Europe from the 2nd Century BC onwards (Zepezauer 1993, p 30-63, 95)

Figure 5.59 Bead from which sample 244 was taken (scale 1:1).

sample	243	244	248	249	250
Na_2O	17.67	16.36	16.34	17.07	17.19
MgO	0.70	0.88	0.88	0.36	0.41
Al_2O_3	2.32	2.20	2.65	2.61	2.63
SiO_2	67.93	63.42	66.12	69.13	70.47
P_2O_5	0.05	0.12	0.07	0.05	0.02
SO_3	0.21	0.27	0.24	0.30	0.27
Cl	0.86	0.61	0.91	0.91	0.93
K_2O	0.78	0.80	0.58	0.95	0.94
CaO	9.11	12.08	8.73	5.80	5.87
TiO_2	0.04	0.04	0.06	0.06	0.04
Cr_2O_3	0.00	0.00	0.02	0.02	0.00
MnO	0.00	1.25	0.01	0.01	0.03
FeO	0.35	0.31	0.66	0.29	0.42
CoO	0.00	0.02	0.00	0.00	0.00
NiO	0.02	0.00	0.00	0.00	0.02
CuO	0.04	0.01	0.00	1.09	0.00
ZnO	0.02	0.00	0.00	0.00	0.00
As_2O_5	0.00	0.00	0.02	0.00	0.00
SnO_2	0.03	0.00	0.05	0.03	0.01
Sb_2O_5	1.20	0.41	3.29	0.93	0.84
BaO	0.05	0.06	0.04	0.06	0.05
PbO	0.00	0.02	0.01	0.47	0.56
Total	101.38	98.86	100.68	100.14	100.70

Table 5.35 clear and pale coloured translucent glasses from Canale Bianco

Both yellow opaque glasses (samples 247 and 255) are coloured with lead antimonate. Sample 255 has a sufficiently high lead content (20.52 %) to be considered a high lead glass.

The white opaque glass (sample 256) was one of the few analyses of this type to be successful: many of the white opaque glasses were badly weathered and the samples too friable to survive polishing during preparation for analysis. Its raised antimony content (5.16 %) suggests that calcium pyroantimonate is the opacifier and colouring agent.

The only “black” glass from the Canale Bianco assemblage (sample 246 see Figure 5.61) was not coloured by iron oxide or an excess of cobalt as elsewhere, but with a high manganese content of 3.62 %. Interestingly this high manganese content is also present in one of the brown opaque glasses (sample 240). Sample 240 therefore probably appeared black after manufacture, and has weathered to its current condition. However, sample 239, which is very similar to 240 in terms of form, decoration and colour, does not have such elevated manganese content, but a high iron content of 8.63 %, showing the choices of colourant available to the manufacturer. Ten of the Canale Bianco glasses contain manganese oxide at 0.1 % and above, suggesting that these samples should be placed towards the later phase of the site’s use (samples 239, 240, 241, 242, 244, 246, 247, 254, 257, 263).

Figure 5.60 sample 246 taken from the “black” matrix of this bead

Figure 5.61 Samples 339 and 340, coloured using different oxides

5.9 Ca’Cima

7 samples: 264 - 270 inclusive

All of the Ca’Cima samples were taken from the assemblage held by the Museum of Adria. The material is from recent rescue excavations of a necropolis dating to the 6th C BC. All the glassy material recovered from this site were completed artefacts from funerary contexts. There was no evidence for associated glass production or working. It includes stratified and simple eye beads (e.g sample 266) from different coloured glass, zig-zag decorated beads, rod-formed pin heads and pendants such as the goat’s-head pendant (e.g. sample 267).

Glass types

The Ca’Cima glasses are all low - magnesium soda-lime -silica glasses, consistent with the use of a mineral soda raw material. It seems unlikely that the diverse artefact types and styles are from the same source, but their similar glassmaking tradition reflects the widespread adoption of this type during the middle Iron Age.

sample	mean	stdev	min	max
Na_2O	16.82	1.61	14.73	19.37
MgO	0.53	0.11	0.42	0.68
Al_2O_3	1.51	0.88	0.52	2.44
SiO_2	65.77	2.10	61.57	67.51
P_2O_5	0.05	0.03	0.02	0.10
SO_3	0.25	0.13	0.15	0.54
Cl	1.31	0.22	1.02	1.56
K_2O	0.31	0.24	0.06	0.77
CaO	9.16	0.96	8.2	10.72
TiO_2	0.07	0.03	0.04	0.13
Cr_2O_3	0.02	0.01	0	0.04
MnO	0.04	0.02	0.01	0.08
FeO	2.24	2.92	0.32	7.16
CoO	0.03	0.04	0	0.11
NiO	0.00	0.00	0	0.01
CuO	0.54	1.29	0	3.45
ZnO	0.02	0.03	0	0.09
As_2O_5	0.01	0.01	0	0.03
SnO_2	0.03	0.02	0	0.06
Sb_2O_5	2.23	1.66	0	3.75
BaO	0.04	0.02	0.01	0.06
PbO	0.31	0.71	0	1.91

Table 5.36 Summary data for glasses from Ca'Cima

Colourants

There are three white opaque glasses amongst those sampled, each of which is opacified and coloured using calcium antimonate (samples 267, 269 and 270). The compositions of these three glasses are very close, despite coming from quite distinct artefacts (a goat's head pendant, bead and pin head respectively). The goat's head pendant is almost certainly an exotic import, probably Phoenician (also see 5.12.5).

sample	267	269	270	mean	stdev	min	max
Na_2O	18.30	17.08	16.81	17.40	0.79	16.81	18.30
MgO	0.53	0.42	0.42	0.46	0.06	0.42	0.53
Al_2O_3	1.61	2.41	2.44	2.15	0.47	1.61	2.44
SiO_2	67.51	66.34	67.32	67.06	0.63	66.34	67.51
P_2O_5	0.05	0.05	0.02	0.04	0.02	0.02	0.05
SO_3	0.24	0.18	0.18	0.20	0.03	0.18	0.24
Cl	1.53	1.45	1.56	1.51	0.06	1.45	1.56
K_2O	0.35	0.36	0.36	0.36	0.01	0.35	0.36
CaO	8.88	8.20	8.31	8.46	0.37	8.2	8.88
TiO_2	0.06	0.06	0.04	0.05	0.01	0.04	0.06
Cr_2O_3	0.04	0.00	0.02	0.02	0.02	0	0.04
MnO	0.05	0.01	0.01	0.02	0.02	0.01	0.05
FeO	0.34	0.34	0.32	0.33	0.01	0.32	0.34
CoO	0.00	0.03	0.05	0.03	0.03	0	0.05
NiO	0.00	0.00	0.01	0.00	0.01	0	0.01
CuO	0.00	0.05	0.00	0.02	0.03	0	0.05
ZnO	0.02	0.09	0.00	0.04	0.05	0	0.09
As_2O_5	0.03	0.02	0.02	0.02	0.01	0.02	0.03
SnO_2	0.04	0.00	0.01	0.02	0.02	0	0.04
Sb_2O_5	3.73	3.18	3.75	3.55	0.32	3.18	3.75
BaO	0.04	0.05	0.05	0.05	0.01	0.04	0.05
PbO	0.06	0.00	0.01	0.02	0.03	0	0.06
Total	103.41	100.32	101.71				

Table 5.37 Compositional data for white opaque glasses from Ca’Cima

The green translucent (sample 264) and “black” (sample 266) glasses owe their colour to their iron oxide contents (7.16 and 5.73 % respectively). The two blue samples (265 and 268) are coloured quite differently. Sample 265 was taken from the blue opaque eye decoration of a bead, and is opacified with calcium antimonate and coloured blue with copper oxide (3.24 % Sb2O5, 3.45 % CuO). Sample 268, which is translucent blue glass is coloured by cobalt oxide alone (0.11 %). None of the Ca’ Cima samples contain sufficient manganese to be considered a deliberate addition.

5.10 Faliscan

The only sample successfully analysed from a group of Faliscan beads from the Ashmolean Museum was sample 16. This sample is of the blue translucent matrix of a stratified eye - decorated annular bead. Sample 16 is a high - magnesia soda - lime silica glass, with 2.66 % MgO. It is however, not a classic example of this type of glass, since it has very low potash (0.24 %) and low phosphorus pentoxide (0.05 %) which are typically associated with the raised magnesia levels in glasses made with a plant ash alkali source. It is possible that the magnesia is therefore associated with another raw material in the original recipe (such as the silica source if this was a sand containing degraded dolomitic limestone for example). It is also possible that a soda - rich plant ash has been processed prior to use which has preferentially removed the “missing” components.

sample	16
Na_2O	16.12
MgO	2.66
Al_2O_3	4.61
SiO_2	70.86
P_2O_5	0.05
SO_3	0.34
Cl	0.67
K_2O	0.24
CaO	3.00
TiO_2	0.04
Cr_2O_3	0.00
MnO	0.18
FeO	1.04
CoO	0.02
NiO	0.05
CuO	0.00
ZnO	0.16
As_2O_5	0.00
SnO_2	0.01
Sb_2O_5	0.02
BaO	0.04
PbO	0.01
Total	100.12

Table 5.38 data from Faliscan sample 16

The colourant employed in the manufacture of sample 16 must have been reduced iron oxide (1.04 %) perhaps supplemented with a small amount of cobalt oxide (0.02 %). The manganese and iron contents may be associated with the cobalt - rich raw material.

5.11 Unprovenanced items.

11 samples: 237, 238, 245, 251, 252, 253, 261, 305, 307a, 307b and 307c.

A number of artefacts were sampled from Adria Museum despite having uncertain provenance. All of these artefacts were recognised by their various forms as being of Iron Age date, and originated in archaeological contexts in the vicinity of Adria.

The chemical composition of each individual bead is not considered in detail here, but the data considered alongside comparative material when specific forms are discussed across site boundaries below. Four of the samples can be considered together from the unprovenanced group since they are similar in terms of colour and form (see below). All but one of the unprovenanced samples are low - magnesia soda - lime - silica glasses, and whilst they should not be considered as representative of a single production tradition or even the consumption range of a single community, it is still useful to illustrate the compositional variability of this diverse group of artefacts.

sample	mean (LMGs)	stdev	min	max	238
Na_2O	16.43	1.79	12.96	18.73	10.10
MgO	0.54	0.16	0.38	0.84	1.80
Al_2O_3	1.84	0.84	0.90	3.19	1.87
SiO_2	70.16	3.52	64.90	75.80	61.87
P_2O_5	0.04	0.03	0.02	0.10	0.75
SO_3	0.24	0.12	0.09	0.46	0.30
Cl	1.17	0.20	0.86	1.40	1.33
K_2O	0.55	0.19	0.29	0.82	4.88
CaO	7.32	1.82	4.77	10.61	11.97
TiO_2	0.05	0.02	0.02	0.07	0.07
Cr_2O_3	0.02	0.01	0.00	0.04	0.01
MnO	0.22	0.41	0.01	1.04	0.24
FeO	1.44	2.31	0.29	7.84	0.60
CoO	0.10	0.15	0.01	0.41	0.02
NiO	0.00	0.01	0.00	0.02	0.02
CuO	0.60	0.68	0.00	1.97	0.01
ZnO	0.01	0.02	0.00	0.05	0.03
As_2O_5	0.01	0.03	0.00	0.08	0.07
SnO_2	0.05	0.04	0.01	0.13	0.03
Sb_2O_5	0.83	1.26	0.02	3.53	5.22
BaO	0.04	0.02	0.01	0.07	0.04
PbO	0.12	0.12	0.00	0.30	0.12
Total					101.29

Table 5.39 Summary of data for unprovenanced prehistoric glasses from Adria

The only non low - magnesia soda - lime - silica glass amongst the group is a single mixed-alkali glass of unusual composition, sample 238 (see table 5.39). This glass is unlike the mixed-alkali glasses of late Bronze Age Europe, such as those from Frattesina and Mariconda. Sample 238 has soda as the principle alkali (10.01 %), with potash as a secondary, but still major contributor (4.88 %), with the raised phosphorus pentoxide and high lime levels consistent with the use of a plant ash. The artefact is probably from a much later context (possibly 17th Century AD: Julian Henderson *pers. comm.*)

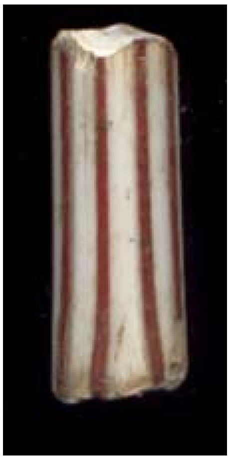


Figure 5.62 Sample 238 (scale 2:1).

Samples 251, 252, 253 and 305 are all taken from pale blue opaque beads decorated with stratified eyes constructed of alternate bands of blue and white opaque glass. In each case the sample is of the pale blue opaque glass bead matrix.

Figure 5.63 Samples 251, 252, 253 and 305 (scale 1:1).

sample	251	252	253	305	mean	stdev	min	max	reduced comp.
Na_2O	15.73	14.64	15.70	15.96	15.51	0.59	14.64	15.96	15.93
MgO	0.47	0.46	0.39	0.79	0.53	0.18	0.39	0.79	0.54
Al_2O_3	1.32	2.12	1.88	3.19	2.13	0.78	1.32	3.19	2.19
SiO_2	69.46	70.21	71.63	69.46	70.19	1.02	69.46	71.63	72.10
P_2O_5	0.05	0.05	0.02	0.02	0.04	0.02	0.02	0.05	
SO_3	0.15	0.18	0.24	0.35	0.23	0.09	0.15	0.35	
Cl	1.40	1.02	0.95	1.08	1.11	0.20	0.95	1.40	
K_2O	0.29	0.70	0.64	0.54	0.54	0.18	0.29	0.70	0.56
CaO	8.14	7.59	7.02	9.03	7.95	0.86	7.02	9.03	8.16
TiO_2	0.04	0.04	0.06	0.07	0.05	0.01	0.04	0.07	
Cr_2O_3	0.02	0.00	0.02	0.00	0.01	0.01	0.00	0.02	
MnO	0.03	0.01	0.04	0.04	0.03	0.01	0.01	0.04	
FeO	0.80	0.48	0.34	0.42	0.51	0.20	0.34	0.80	0.52
CoO	0.03	0.05	0.03	0.01	0.03	0.02	0.01	0.05	
NiO	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.01	
CuO	1.97	1.01	0.84	1.33	1.29	0.50	0.84	1.97	
ZnO	0.05	0.05	0.00	0.03	0.03	0.02	0.00	0.05	
As_2O_5	0.00	0.00	0.00	0.03	0.01	0.01	0.00	0.03	
SnO_2	0.13	0.06	0.05	0.10	0.08	0.04	0.05	0.13	
Sb_2O_5	0.06	0.63	0.06	1.09	0.46	0.50	0.06	1.09	
BaO	0.07	0.05	0.04	0.06	0.05	0.01	0.04	0.07	
PbO	0.19	0.23	0.00	0.30	0.18	0.13	0.00	0.30	
Total	100.4	99.58	99.95	103.85					100

Table 5.40 Unprovenanaced blue opaque glasses from Adria.

These glasses are very similar in composition, as well as colour and form, sharing similar soda, magnesia, phosphorous pentoxide, potash and lime levels. They all contain low levels of cobalt oxide (0.01 - 0.05 %) and copper (0.84 - 1.97 %), and are coloured by the combination of both. Only one of the samples contains significant level of “antimony pentoxide” to suggest that it may have been opacified by the addition of calcium antimonate (sample 305, 1.09 % Sb2O5, also see 3.7.16 above)

5.12 Integration of data across sites: Global perspectives of the data.

5.12.1 Statistical analysis of the entire data set.

In addition to the detailed examination of compositional data from individual sites and periods, the entire data set was combined in order that trends within the whole body of data might be identified.

Principal component analysis was performed to identify trends across the combined data. Since the SPSS programme can only display up to 12 labels for variables in bi-variate plots, the site designations were changed to accommodate this. The samples from Mariconda, Montagnana and Frattesina were all labelled as “Brz Age” (excluding sample 342, see above), the Cumae and Pozzouli material labelled Cum/Pozz, and the Alfonsi and Faliscan samples labelled as unprovenanced since there was only 1 sample from each site. The change in site name does not effect in any way the outcome of the statistical routine.

8 components account for 76.7 % of the total variance in the merged dataset. The matrix was rotated on these 8 components to maximise the relationships between the variables (the Varimax method). Table 5.41 is the rotated principal components matrix for the measured oxide components in the samples. The loadings of the variables on these factors can provide information on the relationships between the variables (these relationships can also be identified using a bi-variate correlation analysis).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8
Na_2O	**0.89967**	-1.06E-01	1.30E-01	-3.26E-02	-1.35E-02	-2.10E-01	1.58E-01	0.03275
MgO	0.08051	-2.34E-02	-0.0709	-1.30E-01	-3.88E-02	-5.79E-02	**0.88407**	-0.00285
Al_2O_3	-0.03879	-4.77E-02	**0.68377**	-7.51E-02	2.55E-01	-0.06869	**0.51677**	4.03E-02
SiO_2	-0.47176	-3.58E-01	-0.48939	1.38E-01	2.11E-01	-0.3625	-2.70E-01	-1.02E-01
P_2O_5	-2.38E-01	8.63E-02	-0.03309	2.83E-02	-5.50E-04	**0.91906**	-5.57E-02	1.03E-02
SO_3	1.04E-01	2.35E-02	2.74E-01	4.18E-01	-1.25E-01	1.24E-01	0.30946	**5.30E-01**
Cl	**8.53E-01**	-1.83E-02	-5.61E-02	2.81E-01	-8.65E-02	-4.42E-02	-0.17583	-3.29E-02
K_2O	**-0.91294**	-8.99E-02	-0.04348	0.03309	0.08138	2.70E-01	-8.21E-02	-0.06106
CaO	4.76E-01	-6.51E-02	-2.64E-02	**5.74E-01**	-1.11E-01	4.92E-01	-1.31E-01	-1.28E-01
TiO_2	1.28E-01	-8.39E-02	**6.31E-01**	**-5.88E-01**	1.07E-01	5.64E-02	2.41E-01	6.10E-02
Cr_2O_3	9.80E-03	-5.65E-02	-5.93E-02	-1.43E-01	1.75E-01	-5.20E-02	-6.23E-02	**7.99E-01**
MnO	2.48E-01	2.98E-01	3.79E-01	3.09E-01	7.86E-02	-3.32E-02	-1.85E-02	-3.25E-01
FeO	2.83E-01	9.58E-02	-4.24E-03	**-8.26E-01**	-2.25E-01	3.97E-02	2.92E-02	1.82E-01
CoO	0.11494	2.29E-03	0.19348	-1.67E-02	**8.54E-01**	-2.81E-02	-1.02E-01	4.50E-02
NiO	-0.13426	8.80E-04	-1.08E-02	1.29E-02	**8.65E-01**	1.27E-02	8.57E-02	8.17E-02
CuO	**-0.77883**	-0.09808	8.22E-02	0.15531	-2.19E-01	-2.89E-01	-0.09273	4.32E-02
ZnO	0.06651	**8.66E-01**	-4.46E-02	-0.15286	5.68E-03	-7.69E-02	0.08572	-0.0194
As_2O_5	-0.13538	**0.79783**	0.05373	0.02604	0.0557	0.39538	-0.04355	0.00437
SnO_2	-0.29145	-0.06204	0.40655	0.19595	-0.21647	-0.203	-0.18792	0.15728
Sb_2O_5	0.31713	0.03492	0.0552	0.49935	-0.15562	0.0357	-0.12934	0.1056
BaO	0.00171	0.15143	**0.8136**	0.07917	0.11444	0.00611	-0.24959	-0.0778
PbO	0.056764	**0.838016**	0.111629	0.099001	-0.04155	-0.03891	-0.09202	-0.0599

Table 5.41 Rotated Principal Components Matrix for all samples. Rotation Method: Varimax with Kaiser Normalization. All values greater than +/- 0.5 are highlighted.

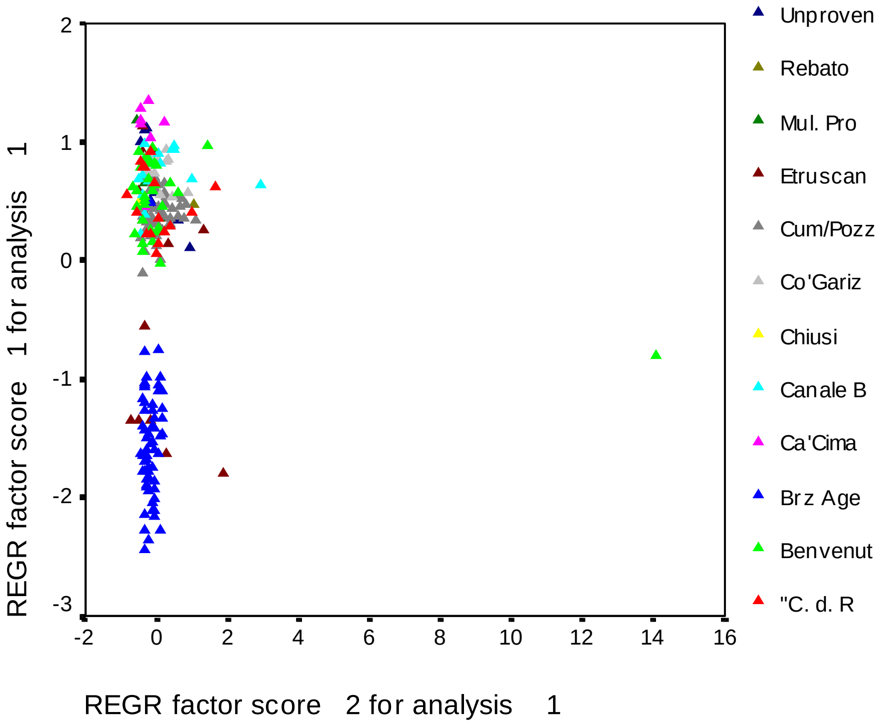


Figure 5.64 Scatter diagram of samples scores on the first two factors extracted by PCA (all samples).

The samples can be readily distinguished into two groups by plotting factor 1 against factor 2 from the PCA. The difference is also essentially a chronological feature, with one group almost entirely of Final Bronze Age glasses. The position of 5 Etruscan samples amongst the Bronze Age glasses is initially an exciting prospect, suggesting a shared technology. However a brief survey of the Rotated PCA matrix (see Table 5.41 above) reveals that potash and soda are key variables in the first factor, and are negatively correlated. The separation of the glasses into two groups is largely based on the high-potash and relatively low soda contents of the mixed-alkali glasses in comparison with the other glasses, which are soda-lime-silica compositions. Since the 5 Etruscan glasses contain no soda and commensurately high levels of potash, they are associated with the mixed-alkali glasses. A similar grouping can be achieved using the raw data, in which potash is plotted against any other component (for example figure 5.65). The single outlier from the site of Benvenuti is sample 359, a high lead glass containing 37.65 % PbO).

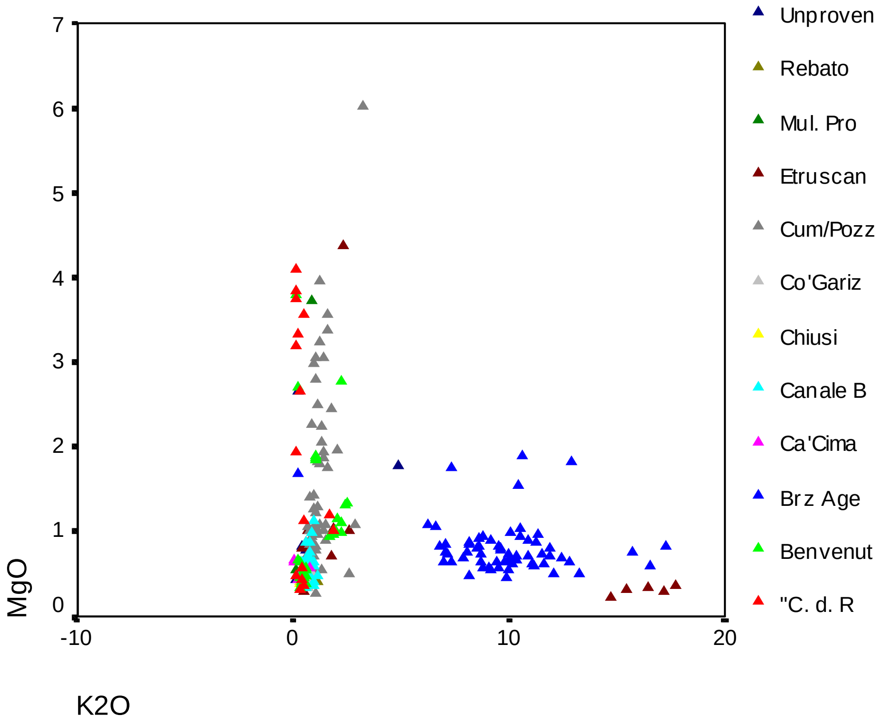


Figure 5.65 potash against magnesia for all samples.

If the Bronze Age mixed-alkali and Etruscan potash glasses are removed from the dataset, PCA can be performed again to try and discern patterning within the later glasses alone. 7 components account for 69.3 % of the variance.

	factor 1	factor 2	factor 3	factor 4	factor 5	factor 6	factor 7
Na_2O	**-0.6665**	0.22756	0.13246	0.20435	0.08269	-0.03749	0.2937
MgO	-0.04788	-0.05289	-0.09854	-0.05557	-0.05373	0.10258	**0.90369**
Al_2O_3	-0.10313	**0.6632**	-0.27978	0.28755	0.11418	-0.06897	0.39078
SiO_2	-0.38475	**-0.65943**	0.30695	0.17783	-0.10525	-0.06243	-0.25059
P_2O_5	**0.56011**	0.17521	-0.12215	-0.06933	-0.00935	0.46898	0.10159
SO_3	-0.06063	0.06536	0.07327	0.17619	**0.78959**	0.10277	0.20539
Cl	-0.15585	-0.05903	**0.63984**	-0.15381	0.02109	-0.31012	-0.35693
K_2O	-0.00552	0.26124	-0.10454	0.0445	0.12865	**0.71651**	0.2404
CaO	-0.10559	0.06586	**0.73444**	-0.24504	0.27537	-0.27052	-0.14214
TiO_2	-0.08664	**0.61416**	-0.48428	0.14879	-0.21168	0.26629	0.13883
Cr_2O_3	-0.12345	-0.08887	-0.04152	0.026	-0.04016	**0.58767**	-0.05502
MnO	0.24988	0.43394	0.19104	0.05465	0.15436	-0.36121	0.02966
FeO	0.09673	-0.02939	**-0.69179**	-0.2404	-0.45896	0.3091	-0.04536
CoO	-0.03137	0.18432	0.03661	**0.85185**	-0.06823	0.02508	-0.13974
NiO	-0.00902	0.03774	-0.07397	**0.8646**	0.06872	0.02667	0.1185
CuO	0.00398	-0.01682	**0.6517**	0.13339	-0.21215	0.28607	0.09125
ZnO	**0.8393**	-0.01958	-0.08991	0.06131	-0.11943	-0.06899	0.11675
As_2O_5	0.9075	0.12782	0.02	0.04859	0.01252	-0.0573	0.02899
SnO_2	-0.06269	0.41512	0.22038	-0.04413	-0.07428	0.06606	-0.16611
Sb_2O_5	0.0152	0.00164	0.04772	-0.2153	**0.79067**	-0.06886	-0.30851
BaO	0.14991	**0.78157**	0.09317	0.28105	0.10009	0.01529	-0.21414
PbO	**0.81302**	0.13221	0.0164	-0.00366	0.09042	-0.18035	-0.1007

Table 5.42 Rotated Principal Components Matrix for all samples except Bronze Age mixed-alkali and Etruscan potash glasses. Rotation Method: Varimax with Kaiser Normalization. All values greater than +/- 0.5 are highlighted.

However, the removal of the high potash glasses makes the data less easy to subdivide using multivariate statistics:

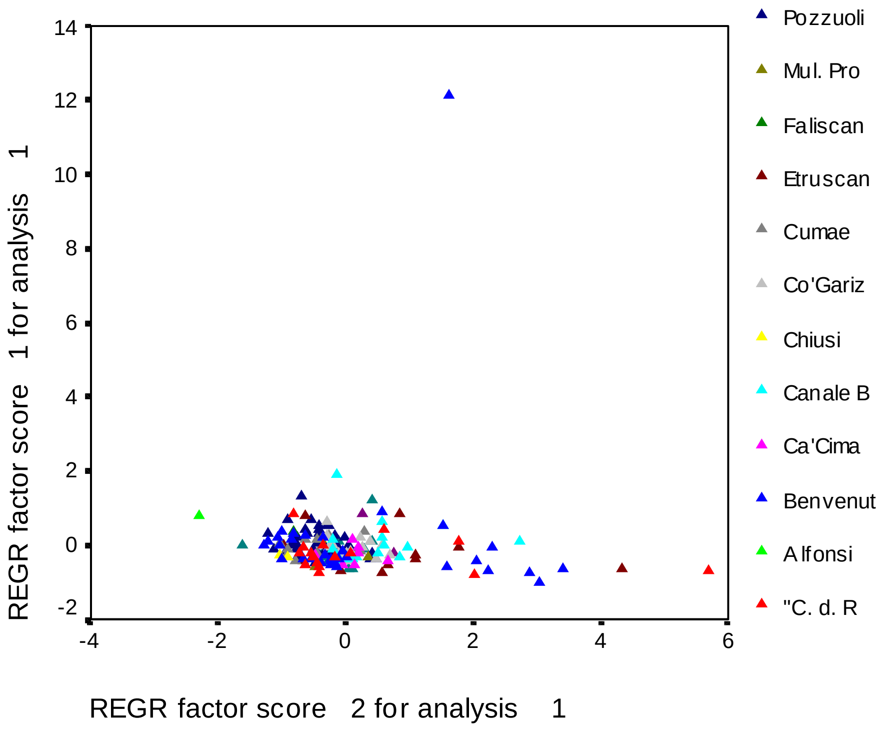


Figure 5.66 Scatter diagram of samples' scores on the first two factors extracted by PCA, Iron Age glasses only (excluding high potash glasses).

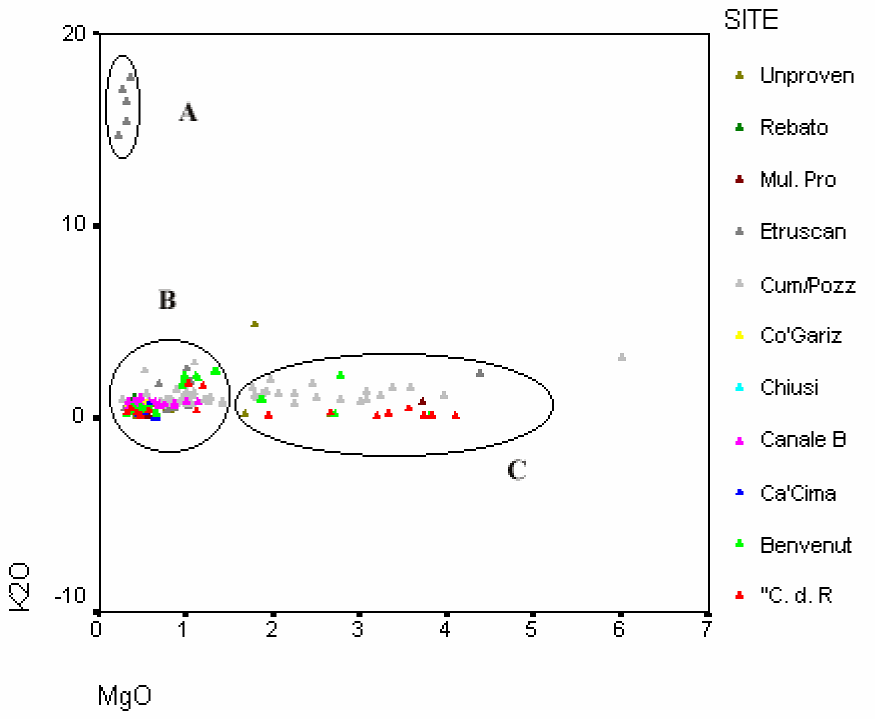


Figure 5.67 Magnesia against potash for Iron Age glasses only. Group A are the high potash Etruscan glasses, and groups B and C are low and high-magnesia soda-lime silica glasses respectively.

The sharp differentiation between high and low magnesia soda-lime silica glasses observed elsewhere (for example Henderson 1988a, p 447, Figure 3 and Lilyquist and Brill 1993, p 56, Figure 51) is not so readily apparent here. Whilst it is possible to delineate between the glasses, there is almost a continuum in terms of magnesia values. In part this might be through the recycling of glasses from both traditions. Nonetheless, the low-magnesia glasses are very tightly clustered.

It is possible to consider the Este glasses as a single group (i.e. those samples from material recovered from Villa Benvenuti, Casa di Revovero, Fondo Rebato, Casa Alfonsi and Casa Muletti Prosdocimi) and compare them with published analyses from elsewhere. This is a useful way to consider how distinct the Este glasses are, and whether or not one can posit a production distinct to the Eastern Mediterranean region.

There are relatively few published analyses of glasses from contemporary archaeological contexts anywhere, and a selection of analyses from a wide date range have been selected here for comparative purposes (all are from Brill 1999a and b). The sites are: Nimrud (700-600 BC), Mycenean (1400-1250 BC), Lisht (1200-900 BC), Hasanlu (1100-800 BC), Chotin (700-400 BC) and Amarna (1348-1335 BC).

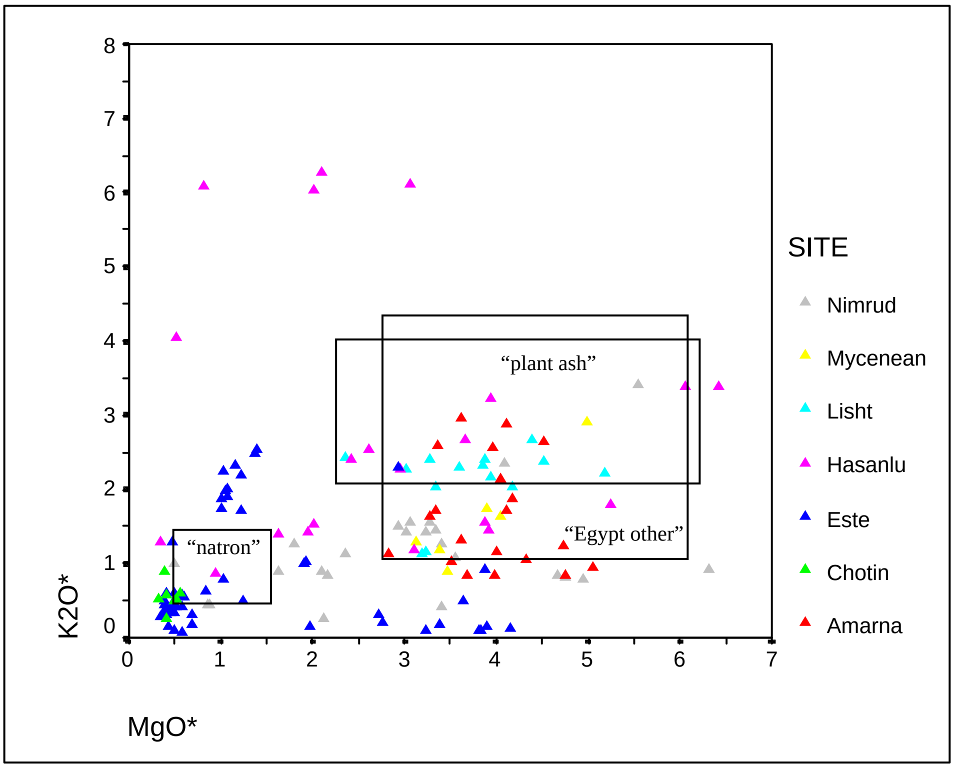


Figure 5.68 Magnesia against potash for Este glasses and comparative published material. Values normalised to six key components as described in Lilyquist and Brill 1993, p 40 in order that the defined zones for "natron", "plant ash" and "Egypt other" from ibid p 56 can be used.

As described elsewhere (section 5.6.6, Figure 5.44), the Este glasses can be subdivided into two low-magnesia groups, and a range of high magnesia glasses. Neither of the low-magnesia groups map directly onto Brill's definition of a "natron" type glass, and the high magnesia Este glasses are quite distinct from those recorded from Egypt and the Near East. The high-magnesia glasses from Este contain much lower levels of potash than all other glasses except those from Nimrud.

A further observation is how closely grouped the Este low-magnesia glasses and analyses of Chotin glasses are. The Chotin glasses are the closest in terms of both geography and chronology (coming from a site in former Jugoslavia), and would tend to further substantiate the idea that glass is being produced in the Northern Adriatic area during the 9th to 5th Centuries BC.

5.12.2. Discussion of artefacts types across site boundaries: Brooch Slider decorations

A number of brooch decorations were sampled for this project, of a form not found in the Eastern Mediterranean, but well known from an area stretching from Central Italy to Poland (also see 1.3.2). These consist of a large leech-shaped mass of opaque glass decorated with bands of different coloured opaque glass wrapped around the mass which is marvered flush and then combed in alternate directions into a feathered decoration. The combing action often leaves behind an uneven ridged surface.

Figure 5.69 Leech-shaped brooch decoration from which samples 175-178 were taken. Scale 1:1

These artefacts are well known from both Etruscan and non-Etruscan contexts from the 8th to the 7th Centuries BC (Montelius 1895 Serie A plate 7 and Serie B plates: 90, 94, 195, 219, 307, 318, 349, Harden 1968, p 59 and references, Tatton-Brown 1995 p 321 and references, Dobiat 1987, p 27-29, figure 17, plate 1).

Whilst the distribution of these artefacts is extensive, they are concentrated in the Northern Adriatic and in Tuscany (see Map 13 in Haevernick 1987). Previous writers have posited an Italian origin for these artefacts on the basis of the distribution (Dobiat 1987, p 28, Harden 1968, p 59, von Bissing 1942 144-168), but there is currently no evidence to establish this in preference to any other N. Adriatic location. It does seem most likely that they are fabricated within the region, rather than being exotic imports from the Eastern Mediterranean.

Although a total of 8 samples were recovered from 4 artefacts, only 5 analyses from 3 artefacts were successful, giving fully quantitative results (samples: 175-178, 370-371, 372, 373 of which 176, 177, 178, 370, and 373 were successful).

sample	176	177	178	370	373
Na_2O	14.87	18.44	14.8	16.14	19.42
MgO	0.3	1.01	1.05	1.13	1.03
Al_2O_3	0.43	6.08	4.78	1.16	5.7
SiO_2	69.16	61.91	62.6	66.51	63.53
P_2O_5	0.05	0.19	0.5	0.14	0.19
SO_3	0	0.24	0.42	0.36	0.24
Cl	0.59	0.43	0.52	0.81	0.43
K_2O	0.5	2.6	1.89	0.46	1.95
CaO	3.57	3.25	5.46	3.47	2.7
TiO_2	0.04	0.26	0.24	0.06	0.24
Cr_2O_3	0	0.05	0	0	0.02
MnO	0	0.23	0.18	0.16	0.23
FeO	0.61	3.38	2.24	1.83	2.49
CoO	0	0.25	0.14	0.23	0.31
NiO	0.01	0.14	0.16	0.27	0.29
CuO	0.08	0.67	0.74	0.71	0.47
ZnO	0.02	0	0.05	0	0.03
As_2O_5	0	0	0.06	0.12	0
SnO_2	0.03	0.01	0.13	0.08	0.04
Sb_2O_5	1.35	0.11	1.26	1.21	0.2
BaO	0.04	0.06	0.06	0.05	0.07
PbO	12.33	0.24	3.43	8.33	0.19
Total	103.98	99.55	100.71	103.23	99.77
site	Etruscan	Etruscan	Etruscan	C. d. R.	Rebato
date	800-600 BC	800-600 BC	800-600 BC	650-625 BC	650-625 BC
colour	yellow opaque	red opaque	white opaque	green opaque	brown opaque

Table 5.43 Compositions of brooch sliders

A brief examination of the compositions of the samples from the brooch decoration reveals them all to be unusual glasses.

Samples 176, 177 and 178 are from the same artefact, and yet are quite different, regardless of colourants: 176 is a high lead glass, opacified and coloured yellow with lead antimonate, it contains low magnesia, low alumina and low potash levels typical of natron-type glasses. Sample 177 has a high iron content, which may contribute to the red colour and a high alumina content, its potash content is high, and has raised magnesia levels suggesting a soda-rich ash as the alkali source. Sample 178 was supposed to be of a white opaque inclusion in the glass body of the artefact, but the analysis turned out to be of adhering red opaque glass (see section 5.4, and figures 5.24 and 5.25). The composition includes high iron levels, some lead, antimony and slightly raised but intermediate magnesia and potash.

Samples 370 and 373 are from different artefacts, but are similarly distinct compositions. 370 has low alumina, intermediate magnesia and a low potash content, the high cobalt (accompanied by nickel) in combination with lead and antimony suggests the green colourant is generated with yellow lead antimonate crystals in a cobalt-blue matrix. 373 was also coloured by cobalt (although it has since weathered to a brown opaque colour), and also has intermediate magnesia and potash levels for a soda-lime-silica glass.

The highly variable compositions for this small number of samples are unlike those for published contemporary glasses from the Eastern Mediterranean and Mesopotamia (for example from Hasanlu, Nimrud and Persepolis: Brill 1999a, p 43-47, 1999b, p 43-50), which tend to conform to the established categories.

The glasses from the brooch decorations may be more closely related to that from the Iron Age cemetery site of Chotin in Yugoslavia (8 - 5th Century BC, Brill 1999a, p 49-50, 1999b, p 59). Beads from this site have been analysed by Brill, and the compositions demonstrate significant variability across several key components (potash, soda, iron oxide). There would appear to be emerging evidence for a highly variable glass production industry located in either Northern Italy or elsewhere in the Northern Adriatic during the Iron Age and Etruscan periods. The distribution crosses the established "ethnic" borders of the region, making it difficult to assign a specific cultural milieu for its origin.

5.12.3 Discussion of artefacts types across site boundaries: Spindle Whorls

Perhaps less typologically homogenous, but longer-lived as a form are the glass and glass-composite spindle whorls, which appear throughout the assemblages examined here (i.e. from the Final Bronze Age to the Roman period). This group of artefacts share a common form, hence their grouping for discussion, but have period-specific decoration.

Figure 5.70 examples of spindle whorls, sample 313 from a (Montagnana), sample 359 from b (Benvenuti) and sample 247 and 248 from c (Canale Bianco). Scale 1:1.

The form is most frequently found in ceramic (for example from Rebato, Tomb 100, illustrated in Haevernick 1987, drawing no. 17, and Ridgeway 1979, p 430, figure 5), but is well established in glass (for example Montelius 1895 Serie B plate 84, Fogolari and Scarfi 1970, p 76-77 and plate 49). For this project 10 samples were taken from 8 artefacts (samples 247, 248, 249, 250, 313, 336, 359, 369, 393 and 396), of which 9 were successfully analysed (396 failed).

sample	313	359	336	369	393	247	248	249	250
Na_2O	7.12	2.92	19.94	17.53	14.53	15.02	16.34	17.07	17.19
MgO	0.7	0.57	1.2	0.44	0.38	0.48	0.88	0.36	0.41
Al_2O_3	1.67	2.67	7.09	1.96	0.69	2.14	2.65	2.61	2.63
SiO_2	75.75	41.26	62.53	72.47	69.52	63.17	66.12	69.13	70.47
P_2O_5	0.1	1.26	0.12	0.15	0.05	0.05	0.07	0.05	0.02
SO_3	0.03	0.24	0.39	0.15	0.21	0.24	0.24	0.3	0.27
Cl	0.05	0.42	0.59	1.31	0.98	1.04	0.91	0.91	0.93
K_2O	7.88	0.44	1.68	0.38	0.49	0.72	0.58	0.95	0.94
CaO	1.28	1.78	2.02	6.22	4.55	6.9	8.73	5.8	5.87
TiO_2	0.04	0.09	0.33	0.04	0.07	0.04	0.06	0.06	0.04
Cr_2O_3	0	0	0.02	0	0.01	0	0.02	0.02	0
MnO	0.01	2.26	0.26	0.01	0.05	0.61	0.01	0.01	0.03
FeO	0.54	6.36	3.64	1.09	7.89	0.71	0.66	0.29	0.42
CoO	0	0.06	0.2	0.03	0.02	0	0	0	0
NiO	0.07	0	0.06	0.08	0.02	0.01	0	0	0.02
CuO	5.08	0.16	0.38	0.12	0.01	0.1	0	1.09	0
ZnO	0	0.66	0	0.02	0.01	0.02	0	0	0
As_2O_5	0	3.02	0	0	0.00	0	0.02	0	0
SnO_2	0.01	0.01	0.03	0.01	0.01	0.01	0.05	0.03	0.01
Sb_2O_5	0	0.13	0.17	0.04	0.19	0.71	3.29	0.93	0.84
BaO	0.05	0.11	0.09	0.04	0.04	0.06	0.04	0.06	0.05
PbO	0	37.65	0.14	0.11	1.44	9.3	0.01	0.47	0.56
Total	100.38	102.07	100.88	102.2	101.11	101.33	100.68	100.14	100.7
site	Borgo S. Zeno	Benvenuti	C. d. R.	C. d. R.	C. d. R.	Canale Bi.	Canale Bi.	Canale Bi.	Canale Bi.
date	1100-900 BC	625-575 BC	625-575 BC	625-575 BC	625-575 BC	300-200 BC	300-200 BC	400-100 BC	400-100 BC
colour	blue opaque	green opaque	blue trans.	blue trans.	brown opaque	yellow opaque	aqua	aqua	clear

Table 5.44 Compositional data for spindle whorls.

Perhaps unsurprisingly, the glass compositions reflect the broad changes taking place throughout the entire dataset: the Final Bronze Age example from Montagnana is a classic mixed-alkali glass (sample 313) coloured blue with the addition of copper oxide. Sample 359, from the Iron Age site of Benvenuti is an exceptional composition, and is discussed in more detail elsewhere (see 5.6.2). Samples 336, 369 and 393 have compositions which defy the conventional HMG/LMG classification, and are therefore characteristic of many Iron Age glasses from the N. Adriatic. Samples 247 and 248 are both low-magnesia-soda-lime silica glasses, typical of the natron-type glasses known throughout the

Mediterranean world from the 8th Century BC onwards, both have been decolourised using low levels of antimony, with 249 further modified with the addition of copper.

5.12.4 Discussion of artefacts types across site boundaries: Eye-decorated beads

Many of the beads examined here belong to the broad category “eye beads”: a total of 65 individual artefacts (including an eye bead in a fused mass of glass waste: sample 297). The eye beads include all of those decorated with a single or multiple rings of glass marvered flush into the bead matrix, individual crumbs of glass, inserted canes and stratified layers of differently coloured glass.

A number of studies have discussed eye-decorated beads, their definition, origins and history in Europe and the Eastern Mediterranean (Eisen 1916a, Beck 1928, Venclová 1983 and 1990, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996).

The earliest eye-beads were made in Egypt of fired clay, and have been dated to period 1570-1293(i.e. the 18th Dynasty): glass eye-beads in Egypt were first produced during the reign of Ramases II (i.e. 1279-1212) (Eisen 1916a, p 6-8, Nicholson 1993, p 6-7,). The decoration of glass beads with eyes was also common in the Levant and Mesopotamia during the 15th-13th Centuries BC (Spaer 1987, p 1). Eye-decoration of beads predate the small core-formed figurines and mask pendants of the 8th-7th Centuries BC, which are suggested as predecessors in the Mediterranean region for all eye-beads by Venclová (1983, p 12).

Eye-beads are represented throughout the assemblage examined here and are not specific to any one period or site. They are less frequent amongst the Final Bronze Age material (only 2 examples samples here: samples 297 and 316), and are most common from the 8th Century BC onwards (although they are well known from Final Bronze Age contexts, for example see Salzani 1989 and 1992). The earlier studies suggest both Eastern Mediterranean and Central European production centres for different variations in eye-decoration technique on the basis of distribution (Spaer 1987, p 3-5, Venclová 1983, p 12-16, Haevernick 1987). Amongst those beads analysed here, the eye-beads have been analysed statistically in an attempt to establish discrete compositional groupings, which differentiate them from contemporary samples from other artefacts (using hierarchical cluster analysis). It has not been possible to generate compositional groupings for eye-beads independent of other material, suggesting that eye-beads are not manufactured at specialist centres separate to other bead manufacture. When the eye beads alone are examined using cluster analysis, the sites of Pozzouli and Cumae (and one sample, 345, from Casa di Recovero) are repeatedly shown as distinct from the other glasses. This difference is principally due to the high-iron contents of these glasses (as discussed in 5.5 above), a characteristic shared by sample 345, which may share a common origin. Much of the Pozzouli and Cumae material is typologically distinct from the rest of the assemblage and is worth additional discussion.

This study represents the first series of chemical analysis upon the black beads of Pozzouli and Cumae: they are not all eye-beads, but also include beads which have trails of white glass wrapped around the matrix, either as single bands or spirals. Most of these beads have eye-decoration: several have single or multiple spots marvered into the bead surface, but most are sub-triangular, decorated with stratified eyes constructed from layers of alternately coloured black and white glass fused to a black core (see figure 5.71).

Figure 5.71 Sub triangular stratified eye-bead from Pozzouli from which sample 59 was taken. Scale 1:1

Typological study of the dominant form (i.e. the sub-triangular eye-bead) reveals a distribution stretching from the Orkney Islands to the Levant, and dating to the 8th to the 6th Century BC (Haevernick 1987 p 23-26, 112-117, Map 12). Without comparable compositional analysis of this broader group it is not possible to ascertain whether or they were all fabricated from this unusual glass compositional type. The distribution of the sub-triangular eye-beads is concentrated upon the Aegean, and the provenance of the examples analysed here (close to the Greek settlement of Pithecussae: Bead Study Trust 1997, p 23-24) suggest that if this form has a single manufacturing centre it might be elsewhere than the Italian peninsular (also see Morel 1984 for discussion of early Greek settlements). Other beads from the Pozzuoli/Cumae assemblage, such as sample 73, also have a wide circulation including the Aegean (see figure 5.72 and Heurtley and Skeat 1933, p 38-39).

Figure 5.72 Sample 73 from Cumae

Until additional analyses are performed it remains possible that these glasses were from a highly localised and possibly Etruscan manufacture of a form adapted across a large geographical area. Clearly typological study alone gives only a limited understanding of the use and distribution of the sub-triangular eye-beads: chemical analysis would underpin (or challenge) the assumptions held on the basis of distribution maps alone. Given the non-association between specific forms and chemical composition noted amongst some of the glasses (see above), there is a case for more routine chemical analysis of glass alongside typological work.

5.12.5 Discussion of artefact types across site boundaries: Punic head bead

Many of the glass artefacts recovered from Italian first Millennium BC contexts have been identified as products of the Levant, Mesopotamia and Egypt (see

Chapter 1, and for example glass bowls (Rathje 1979, p 167, Tatton-Brown 1995, p 322) and many of the core-formed glass vessels recovered from Etruscan tombs (Bissing 1930, 1938 and 1942, Harden 1968, 1981, Bonomi 1996)). It has been the principle objective of this study to examine those artefacts which might demonstrate the existence of localised glass production, and has therefore concentrated upon beads. One of the well-established “exotic” imports is the category of rod-formed glass pendants, in the form of human and animal heads. This group of artefacts has been the subject of a number of studies (for example: Seefried 1986 and 1979, Haevernick 1977 and Tatton-Brown 1981 p 143-163, Stern and Schlick-Nolte 1994, p 180-191), and all conclude that they are of Phoenician origin dating to the 6th-3rd Centuries BC. One example was examined here (sample 267) to see how it compared with forms which are less easily related to “exotic” origins in terms of form (see 5.9, and figure 5.73).

Figure 5.73 Sample 267 taken from this rod-formed pendant. Scale 1:1.

Unsurprisingly the glass type proved to be low-magnesia soda-lime-silica glass, consistent with the classic category defined from the Eastern Mediterranean region, probably produced from a lime-rich sand and a natron-type soda source (opacified and coloured with calcium antimonate). Perhaps what is most significant is how similar the composition is to many of the other glasses sampled: for example from the site of Ca’Cima the other two white opaque glasses are almost identical to 267 in terms of composition (see 5.9). The forms of the other glasses are less distinct as “exotic” imports: 269 is a white bead with a single zig-zag decorative band of dark glass around the circumference, and 270 is a decorative pin-head. The significance of the rod-formed goat’s head is to suggest how frequently imported glass is employed in undiagnostic forms.

5.13 Summary

This chapter has provided a detailed discussion of the compositional analyses of the glasses and their interpretation in terms of glass technology. Several observations should be highlighted.

The mixed-alkali glasses analysed from Final Bronze Age contexts in the Po valley are very similar to those published from across Europe dating from 1500 - 600 BC. This group of glasses is remarkably compositionally consistent, reflecting either a deeply conservative technological tradition, a shared refining process, or possibly an accidental reducing process during melting. Further experimental work will be fundamental to understanding this phenomenon.

There is no evidence of technological continuity in glassmaking from the Final Bronze Age into the Iron Age from the mixed-alkali glasses of Mariconda, Montagnana and Fratessina to later Iron Age communities in the North of Italy or Etruscan societies to the South.

Superficially the Early Iron Age glass compositions reflect the predominant technologies established in the Eastern Mediterranean, and the transition from high-magnesia to low-magnesia soda - lime - silica glasses around the 8th Century BC is also manifested amongst the assemblages analysed here. However the high-magnesia glasses form Este have significantly lower potash levels, and a number of the low-magnesia samples are more similar to other glasses from the Northern Adriatic area than Eastern Mediterranean glasses. It is possible to tentatively advance a case for a regional production in the Early Iron Age, which is distinct from the preceding Bronze Age tradition.

The glasses analysed here from Etruscan or associated contexts demonstrate a diverse range of compositions, suggesting that there is no single Etruscan glassmaking tradition. The presence of uniquely Etruscan forms does suggest that glassworking at least was being undertaken, and the broad compositional variation may indicate localised production in addition to importation from the Eastern Mediterranaean. A number of sub-groups of the Etruscan glasses are quite distinct from the established types, particularly the potash glasses and high-iron glasses from Cumae and Pozzuoli: these compositional groupings may prove to be specifically Etruscan, or in the case of the high iron glasses, Italian or Greek technologies. The potash Etruscan glasses are without parallel amongst contemporary or later glasses, and at present represent a distinct if limited technology.

CHAPTER 6: GLASS PRODUCTION AND EXCHANGE IN PREHISTORIC NORTHERN ITALY

6.1 Introduction

The analysed material is from sites in Italy from the Final Bronze Age to the Early Roman Period, from the Po Valley in the North of Italy and as far South as modern Naples. The central focus has been upon the further characterisation of the earlier glasses and an evaluation of the evidence for continued production of glass by subsequent communities in the Po Valley and further afield. Examination of the chemical composition of the later material has permitted extensive discussion of the glassmaking technologies involved.

It is beyond the remit of this study to comprehensively review the existing archaeological narratives for Italy during the period 1200 – 200 BC. It is the intention, therefore in this chapter to outline the chronological and cultural framework from whence the glass came, and extend the discussion of a number of the artefacts.

This study has principally been concerned with glass from many different sites in Northern and Central Italy, over a long time period. The sampling strategy is discussed elsewhere (see Chapter 2), for a number of reasons it is not possible to claim that the artefacts examined are fully representative of the full range of types, forms and colours originating in Italy, extant in museum collections around the world. Surviving glass objects should not necessarily be considered as a reflection of all glasses used during this period, since glass more than many materials is particularly vulnerable to the vagaries of survival in the archaeological record and the excavation process (for post-depositional deterioration of glasses see Freestone 2001). Given this proviso, the samples still offer information concerning the glasses in use, and in some instances are the first analyses of any vitreous materials for a number of the locations and periods. Furthermore the chronological spread of the samples provides an opportunity to investigate long term changes in glass technology.

6.2 Traditional perspectives of Italian prehistory.

Historically the Pre- and proto-history of the Italian peninsular has been constructed by antiquarians and archaeologists into a number of cultural historical mosaics, assembled principally to form chronological schemes in the absence of either independent dating techniques or substantial quantities of material correlated to external chronologies. Individual cultures have been defined, largely on the basis of funerary material in addition to limited settlement data (for example: Montelius 1895, Randall-McIver 1924, 1927a and b). The advent of ^{14}C and subsequent calibration using dendrochronology inevitably brought about a re-evaluation of the dating of individual sites and a refinement of the chronologies. The necessary re-evaluation of the culture-historical approach, which was no longer so essential for the construction of chronology was slower to happen, and it was not until relatively recently that the traditional explanatory models for change in Italian pre- and proto-history were challenged (Ridgeway and Ridgeway 1979, p 3-5).

It is impossible to discuss material without reference to the cultural-historical model which has arisen over a long period of time, but the names still retain some use as chronological markers if not explanations of historical change (i.e. a group of invaders bringing change in material culture or burial behaviour). Therefore the discussions below use some of these terms in a chronological sense only.

Peroni's paper on the broad historical changes from the Final Bronze Age to the Iron Age in Italy outlines the general shifts in demography, agricultural base, metallurgy, settlement pattern, social structure, "markets" and wealth accumulation taking place between 1200 and 700 BC (Peroni 1969). Whilst it is possible to disagree with the detail and explanatory power of some of the ideas employed in structuring the information (such as shifting markets driving changes in metallurgy), it is nonetheless an admirable attempt to summarise the qualitative changes taking place during this period. The clearest assertion is that the Final Bronze Age and Early Iron Age period marks a distinct departure from the preceding period (Peroni 1969, p 20).

However, it is very difficult to construct a single narrative, which encompasses the highly localised trajectories of societies in prehistoric Central and Northern Italy. Although the Proto-Villanovan has been used as an umbrella term to describe the societies of Final Bronze Age Central and Northern Italy, in which a shared funerary ritual places them within a broader "urnfeld" context, regional diversity can be identified (Peroni 1969, p 22-23). The localised developments clearly manifested themselves in the different "cultures" of the Early Iron Age, such as the Villanovan of Central Italy and as far North as the Bologna area, contemporary with the neighbouring Golasecca and Este cultures, and the Picene, Latial and Iapygian Cultures further south. The settlement (and therefore population) density of 9th Century BC Po valley is very meagre compared with the Villanovan heartlands (Peroni 1969, p 26).

It is therefore not possible to talk about a single historical trajectory in the sense of an inevitable development of larger and ever more complex social formations, from kin-based groups through proto-urban settlements to city-states. A reductive social-evolutionary system cannot be used as a backdrop for glass-use or manufacture. The glasses analysed in this study are considered here in more general terms, and their value for wider inference in the study of Pre- and Proto-historic Italy. The key themes examined are localised production, regional trade and exotic imports.

6.3 The final Bronze Age: the evidence for localised production at Frattesina, Mariconda and Montagnana.

To firmly establish the primary manufacture of glass is extremely difficult for all periods. An unambiguous assertion for glass manufacture requires an identification of material unique to the processes involved, namely frit, the partially reacted raw components which by its very nature is compositionally unstable, and unlikely to survive in the archaeological record. To date this has only been unambiguously identified at 8th-9th Century AD Raqqa where an overheated portion of frit survived to be recognised during excavations (Henderson 2000, p 38-39). Furnaces can be very difficult to interpret, since their use in connection with glass may be related to the reheating of glass manufactured elsewhere. Only rarely have furnaces been discovered with the remains of primary glassmaking in situ: for example the “great glass slab” from Bet She’Arim dating to the 9th Century AD (Freestone and Gorin-Rosen 1999), although remains of tank furnaces in fragmentary form have also been found elsewhere (Freestone and Gorin-Rosen 1999, p 106-109, Henderson 1999). Where glass has been prepared in crucibles or fritting trays, the actual furnace structure itself is unlikely to be diagnostic of primary glass manufacture (Henderson 2000, p 40). Other associated material, such as crucibles, glass trails, ingot or “chunk” glass fragments and moulds, which may well be present at glassmaking sites, only testify to the working of glass and cannot therefore be considered definitive of primary production itself.

In the absence of direct evidence for primary glass manufacture at a specific location, it may be inferred more or less confidently by the collection of other evidence. A site, which has produced any quantity of glass, could have evidence for high-temperature structures, crucibles, trails of glass, ingot or “chunk” glass, finished objects and wasters of malformed objects from failed manufacture. Clearly these may also be found at sites involved in glassworking alone, but are also often recovered from glassmaking centres. It should be noted that glassmaking has been identified as an activity carried out separately from glassworking, and therefore many associated glassworking objects might not necessarily be found (Freestone and Gorin-Rosen 1999). The complete separation of the activities is only likely to take place under circumstances where there is a strong single state such as during the Roman period. The identification of a unique glass compositional type in completed artefacts, wasters, ingots and crucible residues might suggest that glass was being manufactured at a particular site. However, this would be a classic example of archaeological negative evidence: the absence of additional sites producing the same glass type does not preclude the possibility of it being present elsewhere.

Despite recent comments suggesting Frattesina was the only European glassworking centre of the period (Santopadre and Verità 2000, p 25), the Final Bronze Age sites of Frattesina, Mariconda and Montagnana (Borgo San Zeno) have all produced a range of material associated with glassworking, and this is worth further discussion. Both Frattesina and Mariconda have whole or fragmentary ceramic plates, in addition to conventional crucible forms with glass adhering to them (for the crucibles see figure 6.1 and also Bellintani 1997, p 125, fig 8, and Biavati and Verità 1989, p 296, fig. 2). The ceramic plates are not simply shallow crucibles, but represent a tool type associated with bead forming. This artefact type consists of purpose-made ceramic plates and re-used pottery (see figure 6.2). Their common characteristic is that the flat plates have had molten glass on one surface. Their presence at both Frattesina and Mariconda permits inferences concerning the glass technology at both sites.

Figure 6.1 crucible containing glass from Frattesina. Scale 1:2

Figure 6.2 Re-used oinochoe lid, sample 200 removed from glass on upper surface. Note retaining rim of clay added to lid prior to application of glass. Scale 1:3

The nearest parallel in the glass literature is a flat iron plate recovered with beadmaking material from 8th Century AD contexts at Ribe in Denmark (Gam 1990). Copies of the Ribe plates have been employed in experimental beadmaking at Lejre for preheating, as a working surface and finally annealing after bead fabrication. However, these functional analogies are inappropriate for understanding the role of the flat ceramic plates recovered from Mariconda and Frattesina. The ceramic plates from Mariconda and Frattesina have been used in a different manner, since they have been designed for use with molten glass.

The re-used oinochoe lid from Mariconda (figure 6.2) has had a retaining rim of clay added prior to the glass being deposited. Clearly this was fabricated with the knowledge that the glass on its upper surface would be molten. This observation has implications for not only the manner in which the beads were manufactured, but also the nature of the pyrotechnology employed at Mariconda. The form is curious: if the glassworker intended the object to simply act as a reservoir for molten glass, then the under side of the lid would have been more appropriate, since it already has a projecting lip for locating the lid in an oinochoe jar (see Figure 6.2). It is suggested that the selection of the flat side was to avoid the deep recess (10.5 mm), since an essentially flat surface was required: perhaps for the gathering of hot glass on a mandrel/pontil at a very low angle.

There is limited direct evidence of glass making at Mariconda (also see 5.3.3 above), and it has been assumed that the glass has simply been heated and worked. Glassworking as opposed to glassmaking, can be a much lower temperature activity: beads and similar artefacts can be formed from softened glass rather than from “liquid” glass. The implication of this is that whilst glassworking is an activity requiring a high degree of skill and technical ability, it is distinct from the more specialised activity of glassmaking, which requires higher temperatures and empirical “knowledge” of glass chemistry. However, the presence of the oinochoe lid with its lip designed to retain the molten glass, demonstrate the technical capacity of the Mariconda workers to achieve temperatures appropriate for glassmaking. The deliberately high temperatures used at Mariconda demonstrate the possibility of sophisticated high temperature processes like glassmaking and colouring.

The assemblages from Frattesina, Mariconda and Montagnana also included a large number of fragments of flat glass disks. From the edge fragments, it is possible to suggest that these have a consistent diameter, approx. 8-10 cm, and are between 0.6 and 1.5 cm thick. These disks appear to have been poured onto a flat surface, and on occasion manipulated (there are tool marks on the upper surface) whilst soft. It is suggested that the disks represent a convenient form for the storage of unworked glass and are therefore ingots.

Several of these ingots are coloured red on the surface, one almost completely (figure 6.3) others in places (figure 6.4). The cores of these glass ingots are all blue, and the red surface is due to the copper content having been locally reduced to cuprous oxide (i.e. Cu_2O -see 3.7.8 above). The surface of these ingots have clearly been held in a strongly reducing environment for sufficient time for the change in colour to take place. Given that the main body of glass for each ingot is still blue coloured, several interpretations are possible.

- the colour change was brought about accidentally after the manufacture of the ingots, such as by accidental conflagration

- the colour change happened as an accidental result of annealing of the ingots in a reducing environment, such as buried in ashes at the edge of a hearth (as described in experimental work by Gam 1990). If so, this would suggest that annealed ingots were valued over and above those that fractured, since the volume of glass would be the same irrespective of the ingot breaking. This value might be significant as an indicator of a quality of glass composition
- the ingots were held in a reducing environment to deliberately bring about the colour change, and thus demonstrate the possibility of achieving opaque red from a particular body of glass. This would be a visible marker of a glass suggesting trade in the item extending beyond the immediate area of its initial production.

Figure 6.3 Glass ingot fragment from Frattesina. Sample 292 taken from this artefact. Scale 1:2

Figure 6.4 Glass ingot fragment from Frattesina, surface partially reduced. Sample 293 taken from this artefact. Scale 1:2.

In addition to the disc-shaped ingots, several irregularly-shaped fragments had dimensions exceeding those from discs, for example sample 208 (figure 6.5). This irregular piece of glass has broken edges, none of which are deformed by heat and was clearly broken out of a larger mass of glass. Elsewhere such material has been described as “chunk” glass, although this has typically been in the context of the discussion of glass manufactured in large volumes in tank furnaces (Freestone and Gorin-Rosen 1999, p 108). This would suggest that the disc-shaped ingots are not the only form in which fully-formed glass was stored for remelting.

Figure 6.5 Fragment of “chunk” glass from Mariconda. Sample 208 removed from this artefact. Scale 1:1.

Whilst it is not possible to definitely assert the production of glass at Frattesina, there is limited evidence for glass colouring, a technology requiring similar levels of technology (i.e. knowledge of components and capacity to reach and maintain high temperatures and have access to suitable ceramics). Amongst the working debris were trails of colourless or faintly coloured translucent glasses (e.g. see figure 6.6 below), and residues of colourless glass were also found attached to crucible fragments, for example sample 221 (see figure 6.1 above). None of the finished artefacts from the Final Bronze Age sites were from uncoloured glass. The presence therefore of uncoloured glass as waste material suggests that the addition of colourants was a separate process to primary fusion, and this activity at least was taking place at Frattesina. None of the ingot or “raw” glass fragments was uncoloured glass, suggesting that the colouring process took place before the manufacture of portable items (i.e finished objects or ingots for trade), implying primary manufacture at Frattesina.

Figure 6.6 Trail of uncoloured glass working waste from Frattesina, sample 301. Scale 1:1.

The discussion of glass colourants in the Final Bronze Age glasses links the glass technology into a broader debate concerning the role of Frattesina and contemporary sites into the circulation of metals and long term change in the region. In a recent article, Pearce has placed Frattesina at the heart of the debate concerning the shifting patterns of settlement and bronze supply in the Late Bronze Age (Pearce 2000). Frattesina, the Protovillanovan settlement in the Po valley, dates to the Final Bronze Age (c 1200-900 BC), and along with neighbouring sites such as Mariconda and Montagnana represent a change in settlement pattern in the Po valley from the Terramare and Palafitte settlements of the Middle and Recent Bronze Ages. The Protovillanovan cultural milieu (or koinè) extended from the southern Po valley and parts of Emilia-Romagna into Etruria, Marche and Campania, although it has been used as a generic term for a wider description of Final Bronze Age cultures (see Fugazzola Delpino 1979, p 46-47). The decline of the Terramare/Palafitte settlements and development the Protovillanovan coincides with a fundamental shift in the extraction and trade of metals in the region. The decline of the long established southern Trentino Alpine copper industry based around the Valsugana River (Pearce 2000, p 108) can be seen to take place at the same time as the expansion of the Tuscan industry after the 13th C BC (Pearce 2000, p 112, also see Sperber 1999). There is a possibility of some chronological overlap between the Terramare and the Protovillanovan: for example Late Helladic (LH C III) pottery is found at both Frattesina and the nearby sites of Fondo Paviani, Castello del Tartaro and Fabrica (Pearce 2000 p 111). Nonethless the historical trajectory remains one of decline for the Terramare in the face of the development of Protovillanovan settlements. Interestingly, the Terramare polity of Grandi Veronese (consisting of the Terramare Fondo Paviani, Castello del Tartaro and Fabrica) can be seen as a functional precurser to that of Frattesina, with bronze-working, amber-working and glass-working at some or all of the sites.

It is the wide-range of craft/industrial activities discovered at Frattesina that have marked it out as an exceptional site: ceramic production, bronze melting and casting, the working of African ivory, Baltic amber, horn, bone, antler and ostrich shell (Pearce 2000, p 109, Bietti Sestieri 1981, p 146-148). Glass working is only one of many industrial activities taking place at Frattesina. It is worth noting that with the identification of glassworking, ceramic production, antler, bone and bronze working at Montagnana (Pearce 2000, p 110), and glass working at least at Mariconda, the unique role assigned to Frattesina may require review: clearly the

Protovillanovan settlements in the Po valley were engaging in production and trading systems extending far beyond their immediate region. The polity of Frattesina did not possess exclusive control over these activities.

Equally, the development of Frattesina as a polity engaged in both regional and long-distance exchange systems was not simply an overnight innovation, since the Terramare precursers have evidence for similar if not so extensive activities. Bietti Sestieri's claim of Eastern Mediterranean traders appearing "at the head of the Adriatic in the last centuries of the Final Bronze Age" being responsible for the development no longer seems tenable (Bietti Sestieri 1981, p 147). The traditional reliance of external eastern Mediterranean intervention to explain culture change unfortunately fails to explain the transition from Terramare to Protovillanovan in the Po valley after the fall of the palace cultures (Pearce 2000, p 111).

An alternative interpretation for the changes in settlement pattern and eclipse of the Grand Veronese polity has been proffered by Pearce, in which the Tuscan bronze is posited as a higher value material. The presence of tin ores adjacent to copper ores in the Colline Metallifere of Tuscany gave the metallurgists a productive advantage over those working the south Alpine ores from the Trentino, who did not have such ready access to tin for alloying. The reconstitution of settlements in the Po valley may well be rooted in this development in access and control over Tuscan bronze.

As yet, this explanation is predicated on a limited number of bronze analyses (Pearce 2000, p 113), and awaits further comparison of Early Tuscan and Trentino bronzes. In the meantime it is worth briefly examining the copper and tin contents of those glasses from Frattesina, Mariconda and Montagnana coloured with copper alloy.

From Figure 6.7 it is possible to observe two distinct types of copper alloy material as a source of colourant: one in which there is a negligible tin content, despite the copper oxide value ranging from 2 to 6 %, and the other in which the tin and copper oxide contents are closely related. There is no evidence for preferential use of bronze over more pure copper between the sites examined. If the analysis is restricted to those samples containing correlated tin and copper contents (figure 6.8), then an average trendline suggests a copper alloy containing approximately 12% tin.

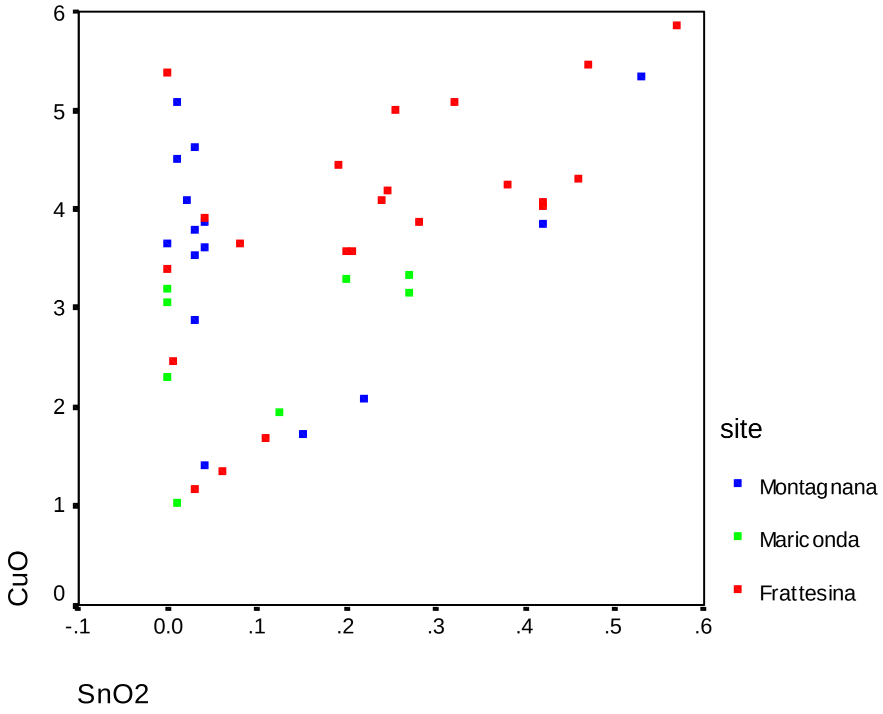


Figure 6.7 Copper and tin oxide contents for copper-containing glasses from Frattesina, Mariconda and Montagnana.

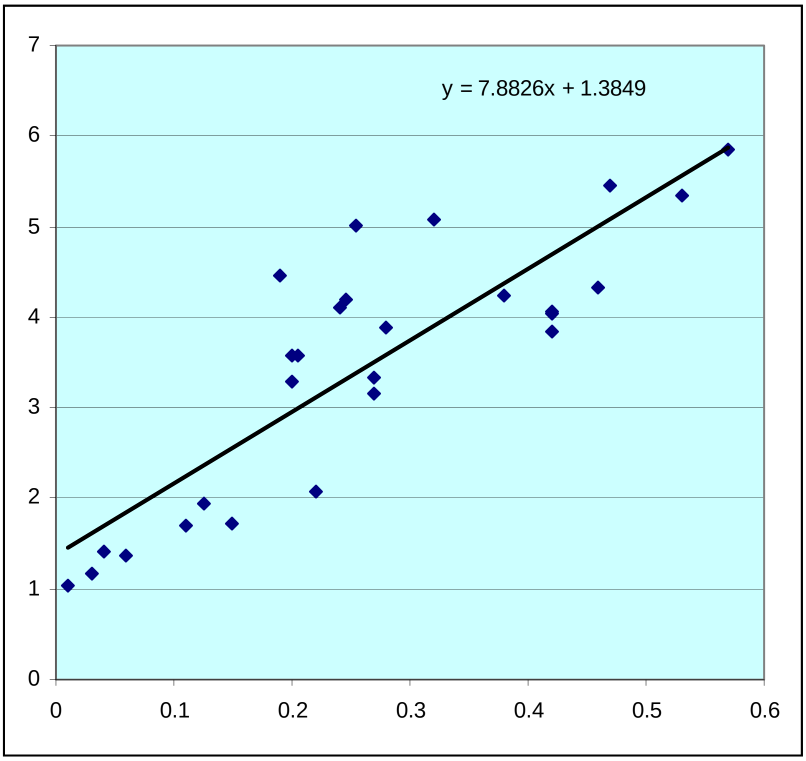


Figure 6.8 copper and tin oxide contents in glasses coloured using high-tin bronze

Bronze workers are known to have a sophisticated understanding of the use and technical value of tin in bronzes (Craddock 1978, 1995, Pearce 1999, Henderson 2000), and would therefore have been able to distinguish between high-tin bronze and relatively pure copper. During the excavations at Frattesina it was noted that there was no distinction between domestic and industrial areas within the site, or even between industrial activities (Bietti Sestieri 1981, p 146). The lack of separation of activities into distinct zones suggests the glassworkers were probably equally familiar with the role of tin in bronze as the use of copper as a colourant in glass. The same people may have undertaken both metalworking and glassworking. It remains something of a mystery as to why both pure copper and tin-bronzes were used. It does however further demonstrate the access of the glassmakers/colourers to both pure copper and bronze, and if this was the craftspeople of Frattesina, suggests that alloying of metals was also within their technical capacity (indeed, a lead ingot is amongst the material recovered from Frattesina: Bietti Sestieri 1981).

The mixed-alkali glass from the Final Bronze Age sites is from a broader European tradition, which on the evidence currently available, probably began in the Middle Bronze Age (see 2.1 and 3.7.3 above). It is known from other analyses that the mixed-alkali composition continues in production elsewhere in Europe (examples are known from Rathgall in Ireland from contexts dating to 9th – 7th Century BC (Henderson 1988b). On the basis of the work here there is no evidence for later production or use of the mixed-alkali glass. There appears to be a sharp dislocation in the manufacture of this glass type, which coincides with the abandonment of the many of the Protovillanovan settlements in the Po valley (Peroni 1969, p 26), including Frattesina, Mariconda and Montagnana, a phenomenon which tends to imply that this material was being produced at least one of these sites.

Of the mixed-alkali glasses from outside of Italy analysed by previous workers (see 5.3.4), they are frequently recovered alongside glasses of different types (for example Raftery and Henderson 1987, p 50). All of the samples analysed here from the Final Bronze Age sites of Mariconda, Montagnana and Frattesina are from the same glassmaking tradition. This is additional circumstantial evidence for local manufacture of the type, since it is the dominant (overwhelming) tradition of glass being worked and consumed in a context of extensive long distance trade in prestige goods. Elsewhere the mixed-alkali glass may simply be one of several types being exchanged and consumed. The Po valley is located at the heart of a long distance trade system, and critically at the juncture of several cultural spheres: part of an intense trans-Alpine network (Endrizzi and Marzatico 1997), on the periphery of the Alpine Bronze industry, but also between the worlds of urnfield culture of Central Europe and the wider Mediterranean cultures.

The study of vitreous materials from Italy by Santopadre and Verità (2000) includes samples from the Iron Age site of Chiaromonte in Southern Italy. The paper compares material from the Middle and Late Bronze Ages and Iron Ages, and includes quite different materials under the umbrella term “glassy faience”. However, the analyses of the later material from Chiaromonte shows that it is not directly related to the mixed-alkali tradition of Frattesina/Mariconda/Montagnana. The proportions of potash to soda, key defining components of the Bronze Age type, are reversed (Santopadre and Verità 2000, p 31). The microstructure of the Chiaromonte material is quite different from the Bronze Age glasses considered here, which would tend to suggest quite different manufacturing processes were employed. However, the low magnesia and lime contents may indicate similar plant-ash processing in the preparation of the flux. It is difficult on current evidence to regard the Chiaromonte material as a continuation of the tradition seen in the Po Valley during the Bronze Age.

6.4 The evidence for regional production and exotic imports from the Early Iron Age to the Etruscans.

An examination of the chemical composition of the glasses analysed for this project reveals that an argument cannot be made for continuous production from the Final Bronze Age into the Iron Age and beyond. The sharp dislocation of settlement in the Po Valley is matched by the demise of the mixed-alkali glass composition in Italy. Despite the recovery of glass artefacts from contexts dating from the 9th Century onwards, the consistent compositional grouping evident in the Final Bronze Age material is no longer in evidence for the glass being consumed by the different communities in Northern Italy. The glass samples taken from early Iron Age contexts in the Po valley are relatively few in number, reflecting the relative paucity of material available. The dating of individual artefacts can sometimes be problematic, given that some of the material is derived from long-lived cemeteries, and some artefact-forms are almost universal. The reworking of the chronologies of the Este and Golasecca cultures permits accurate dating for many of the glasses sampled which are from tomb groups (Ridgeway 1979, p 419 – 487, and Peroni *et al.* 1975, Chieco Bianchi and Capuis 1985a and b). What is generally clear is the distinctly regional trajectory of development in Central and Northern Italy with the development of the Villanovan societies from Bologna southwards into Etruria and beyond to Campania (Torrelli 1986, p 50), and the distinct Este and Golaseccan cultures in the North of Italy (Ridgeway 1979).

None of the material sampled from the Iron Age onwards can be directly associated with either glass working or glassmaking activities. Without exception the later samples are all from funerary contexts. This inevitably means that it is more difficult to understand the pathway of an artefact from primary production to its burial environment, and thereby reconstruct its biography. Nonetheless, a discussion of the glass chemistry alongside typology, distribution and comparable technologies permits inference on the organisation of glass technology.

The range of glass compositional types from Benvenuti and Casa di Ricovero (see 5.6 and 5.7) demonstrates the diversity in use during the lifetime of these cemeteries alone (from approximately 900 BC to 350 BC). The transition from high - magnesia to low – magnesia soda – lime – silica glass which has been noted during earlier studies of material from the Eastern Mediterranean region is present amongst the material here, but neither glass group is sufficiently internally homogenous to suggest dominant production technologies. This transition is not easy to date: the latest well dated high magnesia glass is sample 382 from Benvenuti, originating in tomb 122, dated to 675-575 BC (Este III B1 - III B6, Ridgeway 1979, p 485), and is from the same phase as low – magnesia glasses from this site. This is relatively late for the transition to be taking place, since other authors have noted the shift during the 8th Century BC (see 3.7.2). It is possible that this sample, a yellow opaque glass is an example of an exceptional composition being employed in the manufacture of a particular colour (yellow opaque).

The overall pattern would seem to indicate the consumption of glass produced in many different places, or a limited number of places using a highly variable glassmaking technology. It may be easy to re-adopt the conventional picture of glass being manufactured in the Eastern Mediterranean and entering into Northern Italy through well established exchange systems (such are known to have existed for other materials such as ceramics, metalwork, ivory and faience: Rathje 1979, Turfa 1986). However, whilst undoubtedly many glass artefacts found in Central and Northern Italy dating to the Iron Age and Etruscan periods originated in the Levant (such as Phoenician glass bowls and Egyptian core-formed vessels: e.g. Rathje 1979, p 167), there is evidence for regional production of some of the material.

6.5 Further considerations of Trade and Exchange

The study of production and use of glass in prehistoric Italy generates several intriguing patterns, which remain to be addressed. How is it that the ProtoVillanovan settlements in the Po valley, with their extensive long distance trading connections, and evidence for significant craft production (such as Frattesina, Mariconda and Montagnana) were abandoned and eclipsed by the growth of the Villanovan and later Etruscan settlements in the region? How was it that the subsequent societies in Northern and Central Italy were unable to sustain a comparable glass industry, particularly in light of the impressive productive capacity of the Villanovan and Etruscan societies?

Whilst there are no easy answers to these questions, a number of concepts borrowed from debates concerning technological change in other contexts may help. The “Brenner debate”, concerning the transition from Feudalism to Capitalism in Western Europe during the Medieval period includes a number of important characterisations of pre-capitalist societies.

The terms of the discussion are detailed elsewhere (for example Saunders 1996, p 127-134), but what is of use here is the specific identification of key components shared by pre-Capitalist agrarian societies. Those societies which are based on subsistence farming, in which the producers remain tied to the land, support hierarchies which can only appropriate surplus’s through extra-economic forms of coercion (i.e. physically coerced labour). The relations of the producers and élites in such circumstances constrain the capacity to intensify production, since the producers can meet their own subsistence needs, and the élites would find it difficult to reinvest surplus in the development of production. In the face of such limititations, there is a tendency to invest surplus into political rather than economic accumulation such as military expenditure and conspicuous consumption. In the long term this would create a development towards economic stagnation. Most significant for the discussion here is the impact of the growth of trade and “urban” markets on pre-Capitalist societies. Since producers and élites would be receiving sufficient from the existing arrangement to reproduce themselves independently of the market, the potential for trade itself would not lead to intensification of production. Production for trade and exchange therefore exists separately to production for use within a “commercial-specialised sector” of the economy. Whilst Brenner has been criticised for privileging the relations of production over the forces of production, and ignoring the capacity of agrarian societies to innovate and adopt technological changes, he provides an effective refutation of “trade” as the principal or only dynamic in culture change (Saunders 1996 p 127-134).

Whilst the ideas outlined here are derived from a specific debate concerning changes in Early Medieval society, they have implications for the way in which technology and trade are conceptualised in Prehistoric Italy. By removing the emphasis on regional and long-distance trade as the most fundamental dynamic in the explanation of the societies, then it becomes possible to consider alternative mechanisms for change. Therefore, the importance placed upon the evidence for craft production, using materials from the Baltic to Africa, recovered from the Po Valley Proto-Villanovan sites may well be exaggerated. The settlements themselves may well have functioned as nodal points for the articulation of rural surplus for larger rural areas and the production of goods for commercial trade. The recovery of glassworking debris from three of the Po valley sites suggests that Frattesina should not necessarily be privileged over others in its role as a manufacturing and redistribution centre.

Futhermore, the abandonment of the Po valley sites suggests a fundamental shift in the nature of the societies in the North of Italy, the distinctly different trajectories of the North East (e.g. the Este and Golasecca cultures) compared with the Villanovan and Etruscan societies suggest that a reconstitution of the social structures had taken place (Peroni 1969, p 26-27). That these changes coincided with the adoption of iron use is surely no coincidence.

6.6 Conclusions for this Chapter

The role of glass in the economies of Final Bronze Age and Iron Age economies of Northern and Central Italy should be seen within a larger context of production and exchange. Glass itself cannot be seen as a fundamental cornerstone of the economic base of a prehistoric society in the same way as bronze production was. Bronze, once smelted and cast into ingots becomes a form of wealth unlike any other, since it could not only be traded or accumulated as a prestige commodity alongside other materials (such as glass, amber, or ivory): its use for tools ensured it had a capacity to also unlock productive capacity in the agricultural base upon which all the contemporary societies relied. Its use in weaponry only extended this role, in its use in primitive accumulation. Glass on the other hand can only have been used in non-utilitarian artefacts, and its role in any prehistoric economy has to be seen as secondary to other aspects of production. The ubiquity of glass artefacts in burial contexts from the Bronze Age onwards nonetheless demonstrates the importance placed on this material. The location of glassworking (and possibly making) alongside bronze casting and the working of African ivory, Baltic amber, horn, bone, antler and ostrich shell at Frattesina certainly suggests a status for glass alongside the most valuable materials of the day (Bergonzi and Cardarelli 1992).

The general trend across the period and place of study includes the development from a non-state levels society to highly stratified city states (Service 1971). Although it is important to note that the societies in Central and Northern Italy during this period are not homogenous, and contemporary cultures display different degrees of complexity. The chemical composition of glass in the Final

Bronze Age is impressively consistent, and is produced in a context without the trappings of state level society, suggesting either strong central control to the glassmaking technology (i.e. a single or very few sources), a tightly defined and controlled technology widely used (suggesting a strong knowledge/ideological constraints), or an unknown shared physico-chemical reducing mechanism which homogenises the composition. The compositions become much more variable in the Early Iron Age, and despite the long development of state-level society in the Proto-Villanovan to Etruscan settlements, this is not reflected in standardised glass manufacture or consumption. Whilst the general adoption of low-magnesia soda-lime-silica glass can be noted, hugely variable glass compositions suggests multiple manufacture or import from multiple sources for consumption in Etruscan contexts. In this instance, the craft specialisation which has taken place elsewhere in Etruscan society with the adoption and manufacture of new forms in ceramics, metals and stone, is not matched in the inferred structure of the organisation of glass making/working. As noted elsewhere (Wailes 1996) craft specialisation may reflect other changes in society rather than simply be the driving force behind the changes in societal formations.

It is tempting to see glass beads and other artefacts functioning in a manner analogous to “trade” beads from the 17th to the Late 19th Centuries: where the mass-produced glass beads of Western Europe were used in exchange for slaves and raw materials from Africa and North America. In this case the dominant economies of the Aegean and Eastern Mediterranean being the source of the glass artefacts as they plunder the resources of Central and Northern Italy, specifically the metals of the Colline Metalifere. However, the analogy is weak, putting aside the problems of correlating the exchange mechanisms of a capitalist world economy with the pre-industrial economies of the 1st Millenium BC Mediterranean world, there is strong evidence for independent production of glass, and certainly the working up of local forms in a cultural context which has distinct regional and local identities. Ultimately the Villanovan and Etruscan cultural zones, whilst participating in many aspects of a wider “Greek” culture, remained free of the colonies established elsewhere in the Italian peninsular and Mediterranean.

In disentangling the overlap of local, regional and long distance manufacture and distribution of glass, the archaeologist is examining the consequences, rather than the agent of change in economy and society. The long-lived and widespread distribution of glass beads makes them suitable for the study of shifting exchange patterns. It is interesting to note that communities simultaneously participate in quite different systems: depositing both locally made and imported glass in graves.

It is possible to suggest an outline for the development of glass production and use during the 1st Millenium BC in Central and Northern Italy. The Final Bronze Age sites in the Po valley reveal the existence of a distinctly European glass type (i.e. mixed-alkali glass) which is either manufactured in a single place, or made within a tightly controlled technical tradition. A growing body of analytical data suggests that this glassmaking tradition started in the Middle Bronze Age, but in Italy at least, does not continue beyond the Final Bronze Age. During the Early Iron Age, there is both typological and compositional evidence for regional production of glass: the highly variable chemical composition of both beads and brooch sliders would suggest that although glass is likely to have been made in the Northern Adriatic region, it is a far less sophisticated technology, using raw components of inconsistent composition. Whilst glass was imported into the region from the Middle Bronze Age onwards (Harding 1971), the proportion increased from the 8th Century onwards: a development frequently attributed to “Phoenician” trade (Turfa 1986, p 66-68). The transition from high-magnesia soda-lime-silica-glass to low-magnesia soda-lime-silica glass noted elsewhere in the Mediterranean can be identified amongst the material examined here, demonstrating the inclusion of material from outside the immediate region. However, the presence of local forms alongside core-formed vessels from the Levant during the 6th and 5th Centuries BC suggests a strong local tradition of glassworking. The continuity of variable glass chemistry for beads, such as the high-potash examples from Etruscan contexts also suggest localised glassmaking. The later material does tend to become more compositionally homogenous, with the dominance of the classic “Roman” composition from the 4th Century BC onwards. At present it is difficult to establish for certain what this indicates: production in a restricted geographical area, the export of the suitable raw ingredients, or a homogenising process either intentional in the preparation of the components or as an accident of the melting process. Recent work on Late and post-Roman glass in the Levant (Freestone *et al.* 2001) has demonstrated internal differentiation for Late Roman glass, between the North Western European material and that from the Levant, which had previously been regarded as homogenous. With additional analysis of contemporary material from elsewhere in the Mediterranean from the latter part of the 1st Millennium BC, it should be possible to resolve this question.

CHAPTER 7: CONCLUSIONS

This chapter draws together the conclusions reached during the course this research and contains tentative suggestions for further research in light of the study.

7.1 Analytical Techniques

Electron probe microanalysis proved a highly effective technique for the generation of compositional data, providing a chemical characterisation of the glasses studied here.

Despite extensive work with XRF equipment, this method proved less suitable in this case: the need for minimal intervention upon small archaeological artefacts constrained the capacity to create ideal circumstances for generating accurate data. The XRF equipment employed at Nottingham was accurate when using glasses which could be prepared in an appropriate manner, for example large fragments of glass (i.e. 6 mm^2 and larger) which could be mounted, polished and presented to the X-ray beam.

The EMP system used here included an optical arrangement for aligning the electron beam for analysis. Whilst this was effective with both transmitted and reflected light for ensuring the area analysed was away from large gas holes or inhomogeneities in the sample, it was not possible to discern which phase(s) were being excited during the analysis of mixed phase glasses. Inevitably a certain amount of averaging across phase boundaries must have taken place for some samples. This analyses of groups of mixed-phase glasses were remarkably consistent.

SEM imaging with semi-quantitative EDS analysis was useful for examining and defining micro-structure within the glasses, including opacifying and colouring agents and different phases. Ideally a microprobe with SEM imaging capacity would be used in future studies (i.e. an SEM with Wavelength Dispersive X-ray analysis capability).

XRD was only used for a small number of samples, with inconclusive results. This technique could not be more widely applied during the course of the study due to the limitations of sample size, but ideally would be employed more widely in future work to resolve questions concerning the microstructure of multi-phase glasses.

7.2 Experimental work

This study has focused attention upon glass technologies and has highlighted several areas in which experimental work would aid the interpretation of some of the data. The mixed-alkali glasses which contain a silica-rich crystalline phase are the subject of some debate- is the silica-rich phase the late addition of finely ground sand to act as an opacifying agent, or is it unreacted remnant raw material? Only through experimental work could this be fully resolved. The working properties and temperature ranges required to maintain the observed structural integrity would give greater insight into how this glass type was formed and treated. In the absence of remains of contemporary furnaces, the definition of temperature parameters necessary for the processes involved would generate information about their capacities, which might usefully be compared with parallel research in early bronze technology.

The use of iron and copper in such glasses as a red colouring agent also requires direct experimental work to inform the interpretation of the composition of these glasses. The capacity to use a red opaque glass opacified and coloured with cuprous oxide to decorate a blue opaque glass of similar composition clearly demands further investigation of the properties of such glasses. How long and at which temperatures could such a red glass retain its working and colour properties in an oxidising environment? As always, the results of experimental work carry the qualifying condition of demonstrating the possible, rather than identifying the definite processes involved.

The processing of different plant ashes and experimental melting might profitably be undertaken as means of reconstructing the mixed-alkali composition. Given its longevity from the beginning of the Middle Bronze Age to the Final Bronze Age (in Italy), and the impressive consistency of the compositions, it seems likely that refining processes rather than specific plant selection account for this. The existence of a few glasses clearly made in the same tradition with exceptionally low soda levels seems likely to be due to plant ash compositional variability, the compositional similarity on other counts suggests a shared process. It is always possible that a physico-chemical reducing process generates a limited compositional result from variable raw materials, again this can only be investigated through experimental work in the laboratory, and the construction of appropriate phase diagrams.

Similarly, the “Etruscan” potash composition would appear to contain a processed ash, in which the magnesia, soda and lime have been preferentially removed. The solution and evaporation of a range of plant ashes would help to define the processes and possible ash-types employed.

7.3 Final Bronze Age

The analysis of glass from the Final Bronze Age sites of Frattesina, Mariconda and Montagnana has significantly extended the characterisation of the mixed-alkali glassmaking tradition. Whilst the majority of the glasses sampled from the three sites are consistent with the established definition of this uniquely European glass type, a small number are subtly distinct as potash glasses but are nonetheless clearly manufactured within the same tradition on the basis of other components. Whilst it is not possible to definitely assert the primary manufacture of glass at Frattesina, this does seem to have been very likely, and there is now some tentative evidence for glassmaking at Mariconda. Clearly Frattesina did not control the supply of this glass type in the region, with extensive evidence for glassworking at the other two sites. The idea of Frattesina as a settlement of singular importance in the Po valley needs to be modified.

Whilst the end of mixed-alkali glass use in Italy is sharply defined, the wider adoption/use of this glass type in Middle and Late Bronze Age Europe is less well defined. This is principally due to the limited compositional analysis of glasses from such contexts. It seems likely, given the established nature of exchange in other materials, that the mixed-alkali glass was more widely used in Central Europe. There remains the need for additional characterisation studies on other European Bronze Age glasses to more fully delineate the use of this material.

7.4 Iron Age and Etruscan

There is no evidence for continuity of glass production from the Final Bronze Age into the Iron Age, either within or without the Villanovan/Etruscan *koine* of Central and Northern Italy. Instead, the chemical composition of glasses from these contexts represent a more complex picture of production and consumption. The transition from high to low magnesia-soda-lime-silica glasses can be recognised within the data set, suggesting that a significant proportion of the glass originated in the Eastern Mediterranean region. However, the Este glasses, along with material analysed by others from former Yugoslavia can be distinguished from material from the Eastern Mediterranean.

However, there are glasses that do not conform to the conventional classification of either high/low magnesia-soda-lime-silica, with a continuum of soda, potash or magnesia contents. The highly variable nature of their compositions is what characterises them and suggests that they represent a glass technology that does not employ consistent raw materials or a homogenising process. Given the limited distribution of some of the glass forms, it seems likely that the glass production of this type is localised to Italy and the N. Adriatic. A group of high-iron glasses recovered from Greek settlements in Southern Central Italy may represent a new, highly localised glass type used for forms found across a large area (from the

Aegean to Central Europe). The absence of data on further examples from elsewhere makes this an intriguing proposition.

The few examples of potash glasses from “Etruscan” contexts are an exciting discovery: they are without parallel in the glass literature from any period. It is possible these glasses are indicators of *an* Etruscan technology, rather than *the* Etruscan glassmaking technology in a localised and fragmented industry.

Further investigation of glass from Etruscan contexts, preferably from recently excavated secure deposits would help clarify this picture of glassmaking in Iron Age and Etruscan Italy. Rather than single or even regionally specific traditions, it would appear that glass production is highly variable affair lacking the strong conformity which marks other contemporary productions in ceramics or metalwork.

7.5 The scientific analysis of glass and technological choices.

The recent discussion within the pages of Archaeometry has highlighted a range of issues facing archaeological scientists, at the centre of which is the necessity to locate the study of technology within a broader archaeological context in order to avoid functionalist explanations (see 2.4 and 6.5). Whilst the published discussion has centred on ceramic production, the principle arguments apply equally to ancient glass industries. In this case, the shifting compositions of glass noted in this study do not simply indicate variation between domestic production/importation, but illustrate a more complex situation suggesting highly variable (localised?) production alongside importation. Indeed the dislocation in glass composition which coincides with the abandonment of Proto-Villanovan settlements in the Po valley speaks of a more fundamental economic re-alignment which can also be traced in Copper alloy metal production (6.3). The manufacture of glass in Prehistoric Italy is not independent of the economic and political context, but nonetheless exhibits surprising variation from the expected pattern, especially within the Etruscan sphere.

7.6 In conclusion.

This study constitutes the first general survey of the chemistry of glasses from Central and Northern Italy from the 1st Millennium BC, and as such the data (and conclusions) should inform future studies of ancient glass technology for both the Italian peninsular and the N. Adriatic for this period. The successful characterisation of these glasses enables detailed technological understanding of individual glasses, the definition of discrete groups and the generation of wider inference concerning the organisation of glass production for specific periods.

This study has highlighted the extent to which the Protovillanovan settlements of the Final Bronze Age Po valley were engaged in glassworking. It is interesting to note the widespread adoption of a single technological tradition. There is tentative evidence for actual glass production at Mariconda and the definition of the glassmaking tradition has been extended to include potash as well as mixed-alkali glasses. The tools and associated glassworking debris offer new insight into the bead making processes in use.

There is evidence for localised glass production in the highly variable compositions recovered from Early Iron Age contexts in Northern Italy. However, the transition from high-magnesia to low magnesia glasses noted in the Eastern Mediterranean region during this period can be observed amongst the Italian material, demonstrating an imported component amongst the assemblages sampled.

The compositional diversity continues within the Etruscan world: as yet it remains difficult to talk of an Etruscan glass industry as a single entity. The presence of forms unique to Etruscan contexts has been used to argue for a distinct industry. Unfortunately the chemistry of the *stachelflaschen* does not substantiate the hypothesis of a distinct glassmaking tradition. This does not mean that the primary glass was not produced in Italy, but that the tradition employed is closely associated with that in the Eastern Mediterranean, and therefore the Etruscan vessels may have been made from imported glass. However, the presence of potash glasses of unique type suggest that glassmaking and working may have been taking place alongside the importation of raw glass and finished exotic items from the Eastern Mediterranean.

Whilst the presence of high-iron glasses from Cumae and Pozzouli may indicate another “Etruscan” glass type in a highly fragmented glassmaking industry, their origin in Greek contexts in South Central Italy ensures that this glass type should be treated with some caution before being welcomed into the Etruscan fold.

This study has generated highly specific insights into the technology of a number of glasses used from 1200 to 200 BC in Northern and Central Italy. The technological choices made in their manufacture reflect culturally specific contexts. However, the relatively few analyses also permit the construction of a framework for glass production (and consumption) for the region over the course of a thousand years. The long-term changes can be traced, and the glass compositions demonstrate a surprising degree of both diversity and conformity when considered in their archaeological context. Further targeted analytical work can only help elaborate the picture, and resolve a number of specific questions raised by this study.

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APPENDIX 1.

Compositional Data

sample	10	11	12	16	50	51	52	53	54	55	56	57	58
Na_2O	17.62	17.99	18.08	16.12	15.70	16.31	16.40	15.16	14.23	14.57	16.92	15.77	17.13
MgO	0.45	0.42	0.40	2.66	3.39	3.07	0.56	0.56	0.84	1.44	0.90	1.42	1.88
Al_2O_3	0.43	0.35	0.35	4.61	2.73	3.24	1.03	1.01	1.48	2.21	1.20	1.83	3.37
SiO_2	74.78	74.06	74.37	70.86	65.73	62.40	62.80	66.19	67.16	63.82	63.60	64.23	66.97
P_2O_5	0.02	0.02	0.02	0.05	0.47	0.14	0.07	0.60	1.31	0.29	0.21	0.51	0.06
SO_3	0.21	0.24	0.21	0.34	0.29	0.48	0.15	0.14	0.39	0.20	0.20	0.24	0.52
Cl	1.01	0.98	1.00	0.67	0.58	0.54	0.44	0.41	0.75	0.52	0.46	0.38	0.45
K_2O	0.36	0.31	0.31	0.24	1.62	1.42	1.07	1.29	1.02	0.98	0.79	0.80	1.36
CaO	7.84	7.33	7.23	3.00	2.17	1.56	1.60	1.73	2.05	2.70	2.28	1.29	1.26
TiO_2	0.06	0.04	0.04	0.04	0.15	0.19	0.09	0.08	0.11	0.09	0.08	0.14	0.22
Cr_2O_3	0.02	0.00	0.00	0.00	0.07	0.08	0.00	0.02	0.00	0.01	0.01	0.02	0.06
MnO	0.01	0.00	0.01	0.18	0.03	0.04	0.01	0.03	0.07	0.06	0.03	0.03	0.02
FeO	0.29	0.40	0.40	1.04	9.50	13.34	14.54	14.40	14.20	11.45	12.16	10.20	7.33
CoO	0.02	0.11	0.08	0.02	0.02	0.02	0.00	0.02	0.03	0.04	0.01	0.08	0.03
NiO	0.02	0.00	0.00	0.05	0.04	0.04	0.01	0.01	0.04	0.01	0.01	0.00	0.03
CuO	1.04	1.99	1.85	0.00	0.01	0.01	0.01	0.08	0.00	0.03	0.06	0.01	0.01
ZnO	0.00	0.00	0.00	0.16	0.01	0.01	0.03	0.02	0.05	0.08	0.11	0.08	0.01
As_2O_5	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO_2	0.01	0.04	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.01	0.01
Sb_2O_5	0.00	0.02	0.04	0.02	0.03	0.06	0.02	0.02	0.02	0.08	0.04	0.02	0.03
BaO	0.04	0.01	0.02	0.04	0.02	0.03	0.04	0.04	0.02	0.03	0.03	0.04	0.03
PbO_2	0.06	0.15	0.00	0.01	0.03	0.02	0.01	0.02	0.03	0.07	0.02	0.01	0.00
Total	104.29	104.46	104.42	100.12	102.53	102.98	98.88	101.81	103.81	98.64	99.08	97.11	100.77
site	Etruscan	Chiusi	Chiusi	Faliscan	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli

sample	59	60	61	62	63	65	66	67	68	70	71	72	73
Na2O	16.99	14.41	14.06	12.17	15.09	17.40	13.69	13.78	16.96	15.25	16.18	17.55	17.39
MgO	1.10	0.58	0.68	1.07	3.00	1.23	2.26	0.85	2.80	1.10	3.07	3.26	3.97
Al2O3	2.79	1.07	1.11	1.14	1.58	1.97	1.28	1.12	1.12	1.66	1.14	1.21	2.04
SiO2	70.24	70.75	63.82	63.61	66.30	62.02	67.10	63.97	62.90	67.12	68.29	65.46	63.44
P2O5	0.17	0.12	0.50	0.10	0.12	0.10	0.17	0.12	0.18	0.15	0.26	0.23	0.12
SO3	0.49	0.12	0.08	0.12	0.12	0.12	0.21	0.12	0.11	0.15	0.43	0.15	0.30
Cl	0.49	0.41	0.51	0.44	0.45	0.64	0.59	0.49	0.76	0.80	0.63	0.99	0.94
K2O	1.45	0.69	0.71	0.70	0.91	0.99	0.81	0.73	1.03	1.22	1.01	1.20	1.25
CaO	1.55	1.24	1.84	3.31	4.65	2.00	3.58	2.52	3.37	1.81	4.03	4.41	3.11
TiO2	0.24	0.11	0.13	0.14	0.24	0.19	0.07	0.07	0.09	0.14	0.15	0.15	0.13
Cr2O3	0.02	0.00	0.03	0.00	0.00	0.01	0.00	0.05	0.02	0.00	0.03	0.02	0.05
MnO	0.02	0.01	0.05	0.04	0.01	0.03	0.00	0.04	0.04	0.01	0.03	0.02	0.01
FeO	5.44	13.52	18.27	19.07	9.64	11.53	12.61	17.93	12.21	12.81	6.68	6.96	9.99
CoO	0.01	0.03	0.05	0.02	0.03	0.03	0.05	0.05	0.01	0.02	0.02	0.03	0.00
NiO	0.02	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.03	0.03	0.01	0.04	0.02
CuO	0.01	0.00	0.01	0.00	0.00	0.03	0.00	0.00	0.01	0.00	0.04	0.02	0.00
ZnO	0.00	0.00	0.06	0.08	0.00	0.02	0.12	0.08	0.02	0.00	0.02	0.03	0.00
As2O5	0.00	0.00	0.00	0.04	0.02	0.00	0.05	0.00	0.00	0.00	0.01	0.01	0.02
SnO2	0.01	0.00	0.01	0.03	0.00	0.01	0.03	0.03	0.01	0.00	0.02	0.01	0.01
Sb2O5	0.23	0.00	0.04	0.00	0.00	0.03	0.15	0.04	0.03	0.04	0.07	0.02	0.02
BaO	0.04	0.05	0.03	0.04	0.05	0.05	0.05	0.05	0.04	0.04	0.03	0.03	0.04
PbO2	0.04	0.05	0.04	0.01	0.05	0.05	0.03	0.04	0.03	0.04	0.01	0.00	0.04
Total	101.32	103.16	101.98	102.13	102.26	98.41	102.85	102.09	101.72	102.39	102.10	101.77	102.89
site	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli

sample	74	75	76	77	78	79	80	81	82	83	84	85	86
Na2O	16.98	15.86	14.69	15.04	17.42	15.43	15.43	16.87	16.70	17.18	17.57	15.67	15.39
MgO	0.85	1.02	0.75	0.95	0.79	0.97	1.01	0.74	0.74	2.06	2.46	2.26	0.90
Al2O3	1.25	1.93	1.05	1.13	1.49	1.53	1.39	1.27	1.31	2.74	2.41	1.60	2.01
SiO2	70.43	69.07	62.42	64.26	67.52	66.28	66.56	67.07	67.19	68.45	64.35	65.33	65.32
P2O5	0.10	0.10	0.06	0.10	0.07	0.10	0.07	0.27	0.20	0.14	0.22	0.19	0.24
SO3	0.12	0.40	0.14	0.09	0.09	0.15	0.12	0.18	0.18	0.28	0.67	0.20	0.09
Cl	0.53	0.49	0.58	0.51	0.50	0.48	0.71	0.56	0.53	0.49	0.45	0.78	0.59
K2O	0.85	1.39	0.67	0.88	1.07	1.14	0.80	0.80	0.84	1.31	1.79	1.34	1.48
CaO	1.86	2.78	1.84	4.65	1.59	2.93	1.82	1.95	1.96	1.18	3.32	5.23	2.31
TiO2	0.09	0.13	0.09	0.05	0.13	0.09	0.21	0.07	0.07	0.11	0.24	0.11	0.27
Cr2O3	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.03	0.02	0.02	0.00	0.01	0.00
MnO	0.03	0.05	0.02	0.01	0.05	0.09	0.00	0.05	0.00	0.02	0.04	0.02	0.04
FeO	9.21	7.81	17.51	10.75	11.70	12.99	14.46	13.41	12.76	6.76	8.15	9.55	12.71
CoO	0.00	0.00	0.00	0.06	0.02	0.05	0.02	0.02	0.02	0.02	0.00	0.03	0.00
NiO	0.00	0.00	0.01	0.02	0.04	0.07	0.01	0.00	0.00	0.07	0.06	0.01	0.01
CuO	0.00	1.16	0.00	0.01	0.13	0.32	0.04	0.00	0.08	0.00	1.47	0.02	0.01
ZnO	0.06	0.02	0.04	0.06	0.06	0.17	0.12	0.11	0.05	0.01	0.00	0.04	0.00
As2O5	0.00	0.20	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.05	0.02	0.00
SnO2	0.01	0.01	0.01	0.00	0.01	0.03	0.01	0.01	0.00	0.01	0.01	0.01	0.03
Sb2O5	0.02	0.24	0.02	0.00	0.02	0.02	0.02	0.02	0.04	0.02	0.13	0.07	0.09
BaO	0.01	0.05	0.03	0.02	0.05	0.02	0.05	0.00	0.02	0.02	0.04	0.03	0.04
PbO2	0.12	0.08	0.03	0.04	0.00	0.01	0.00	0.03	0.01	0.05	0.00	0.02	0.00
Total	102.54	102.79	99.95	98.65	102.75	102.89	102.85	103.46	102.72	100.89	103.43	102.54	101.53
site	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli

sample	87	88	89	90	91	92	93	94	95	96	97	150	151
Na2O	17.33	16.15	15.95	16.66	14.02	14.73	15.04	16.59	17.99	17.24	16.27	0.00	0.00
MgO	2.51	0.85	1.03	0.72	0.73	1.28	1.27	1.29	1.77	1.05	1.02	0.38	0.32
Al2O3	1.88	1.45	1.34	1.06	1.10	1.29	1.26	1.34	3.01	0.98	1.06	0.75	0.32
SiO2	63.75	69.65	68.06	67.12	67.29	68.08	67.77	66.65	65.30	63.48	62.77	58.27	62.87
P2O5	0.22	0.10	0.12	0.07	0.07	0.10	0.12	0.12	0.15	0.12	0.10	7.34	6.43
SO3	0.12	0.18	0.24	0.03	0.03	0.33	0.36	0.91	0.30	0.21	0.12	0.52	0.58
Cl	0.65	0.47	0.50	0.52	0.48	0.55	0.56	0.84	0.43	0.68	0.75	0.11	0.11
K2O	1.12	0.94	1.04	0.87	0.94	0.98	0.97	1.10	1.59	0.92	1.09	17.70	15.42
CaO	4.21	1.78	2.14	1.19	2.44	3.70	3.52	2.21	2.71	2.28	2.08	12.51	11.98
TiO2	0.16	0.11	0.11	0.09	0.11	0.13	0.09	0.11	0.16	0.09	0.23	0.02	0.02
Cr2O3	0.02	0.00	0.00	0.02	0.02	0.00	0.02	0.02	0.02	0.00	0.02	0.00	0.02
MnO	0.01	0.01	0.01	0.01	0.03	0.01	0.04	0.00	0.00	0.04	0.03	0.01	0.03
FeO	8.70	9.30	9.15	12.26	14.00	10.63	10.19	10.54	7.10	15.64	16.25	0.24	0.18
CoO	0.05	0.00	0.08	0.03	0.06	0.03	0.02	0.06	0.02	0.00	0.00	0.00	0.02
NiO	0.00	0.00	0.00	0.03	0.00	0.02	0.01	0.08	0.00	0.00	0.00	0.06	0.10
CuO	0.01	0.09	0.83	0.04	0.00	0.01	0.79	0.00	0.01	0.03	0.03	0.05	0.00
ZnO	0.02	0.02	0.02	0.00	0.00	0.12	0.05	0.05	0.02	0.05	0.00	0.00	0.00
As2O5	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.85	0.21
SnO2	0.00	0.01	0.01	0.03	0.01	0.00	0.03	0.00	0.01	0.01	0.05	0.00	0.00
Sb2O5	0.02	0.07	0.22	0.04	0.07	0.04	0.06	0.06	0.09	0.07	0.02	0.02	0.00
BaO	0.02	0.04	0.04	0.02	0.02	0.04	0.05	0.05	0.04	0.04	0.05	0.04	0.04
PbO2	0.00	0.01	0.00	0.00	0.05	0.05	0.00	0.05	0.01	0.00	0.00	0.01	0.02
Total	100.80	101.23	100.97	100.81	101.47	102.12	102.22	102.07	100.73	102.97	101.94	98.88	98.67
site	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Pozzuoli	Etruscan	Etruscan

sample	**152**	**153**	**154**	**155**	**156**	**157**	**158**	**159**	**160**	**161**	**162**	**163**	**164**
Na2O	16.79	18.70	18.58	19.61	17.65	15.63	20.02	0.00	0.00	0.00	16.40	17.26	15.93
MgO	4.38	0.56	0.88	0.71	0.83	1.03	0.80	0.34	0.24	0.29	3.57	6.02	1.06
Al2O3	0.68	2.33	2.19	2.06	2.24	2.53	2.24	0.63	0.34	0.40	0.52	1.26	2.00
SiO2	66.67	68.08	63.13	67.10	61.50	65.16	68.18	61.30	65.62	61.82	68.81	63.37	66.43
P2O5	0.24	0.02	0.05	0.00	0.38	0.07	0.02	6.31	5.44	5.45	0.17	0.10	0.10
SO3	0.45	0.48	0.48	0.39	0.21	0.36	0.24	0.52	0.00	0.47	0.24	0.00	0.18
Cl	0.70	1.02	0.88	0.92	1.15	0.82	1.49	0.08	0.11	0.06	0.92	0.70	0.92
K2O	2.33	0.66	0.57	1.78	0.52	0.66	0.41	16.48	14.73	17.14	1.62	3.26	0.95
CaO	7.44	7.67	7.15	7.18	6.93	8.56	6.86	11.58	10.67	10.60	7.04	6.79	2.94
TiO2	0.04	0.07	0.07	0.07	0.09	0.13	0.09	0.02	0.02	0.02	0.04	0.02	0.16
Cr2O3	0.00	0.04	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.02	0.02	0.00	0.03
MnO	0.11	0.04	2.02	1.44	0.96	0.90	0.55	0.03	0.08	0.07	0.03	0.05	0.07
FeO	0.48	0.42	0.72	0.64	7.34	0.96	0.93	0.26	0.29	0.21	0.37	0.46	10.55
CoO	0.00	0.05	0.11	0.02	0.02	0.03	0.02	0.08	0.05	0.06	0.05	0.02	0.03
NiO	0.00	0.02	0.09	0.05	0.00	0.00	0.06	0.01	0.08	0.01	0.00	0.02	0.02
CuO	0.00	0.00	0.00	0.01	0.19	0.01	0.12	0.00	0.00	0.04	1.45	1.22	0.03
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.05
As2O5	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.32	1.91	0.02	0.04	0.00
SnO2	0.00	0.03	0.13	0.01	0.33	2.37	0.03	0.00	0.00	0.00	0.01	0.00	0.04
Sb2O5	0.22	1.69	0.17	0.00	0.09	0.00	0.30	0.00	0.00	0.00	0.09	0.00	0.06
BaO	0.01	0.05	0.06	0.05	0.07	0.09	0.06	0.04	0.04	0.05	0.01	0.02	0.06
PbO2	0.00	0.01	0.00	0.00	1.38	2.25	0.16	0.01	0.05	0.01	0.03	0.00	0.01
Total	100.56	101.94	97.28	102.04	101.88	101.58	102.60	97.76	98.10	98.63	101.41	100.63	101.62
site	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Etruscan	Cumae	Cumae	Cumae

sample	165	166	167	168	169	170	171	172	173	174	176	177	178
Na2O	16.40	16.71	16.63	15.84	10.32	17.34	14.99	16.08	15.70	15.87	14.87	18.44	14.80
MgO	1.98	1.82	1.80	0.87	1.94	1.09	0.96	0.52	0.28	0.99	0.30	1.01	1.05
Al2O3	3.24	2.23	2.00	1.45	1.58	1.79	1.54	1.86	1.05	1.22	0.43	6.08	4.78
SiO2	67.58	68.08	67.97	64.40	73.87	67.98	66.58	63.85	70.15	67.79	69.16	61.91	62.60
P2O5	0.24	0.05	0.05	0.05	0.10	0.20	0.19	0.22	0.12	0.07	0.05	0.19	0.50
SO3	0.00	0.21	0.82	0.00	0.27	0.49	0.24	0.18	0.00	0.00	0.00	0.24	0.42
Cl	0.50	0.38	0.37	0.41	0.48	0.48	0.35	0.44	0.50	0.61	0.59	0.43	0.52
K2O	2.04	1.13	1.20	0.76	1.42	2.88	1.69	2.55	0.99	1.04	0.50	2.60	1.89
CaO	3.25	1.51	1.74	3.80	2.77	1.38	3.04	1.17	1.26	1.59	3.57	3.25	5.46
TiO2	0.16	0.13	0.11	0.14	0.22	0.09	0.16	0.32	0.14	0.11	0.04	0.26	0.24
Cr2O3	0.02	0.03	0.03	0.00	0.00	0.03	0.02	0.05	0.03	0.03	0.00	0.05	0.00
MnO	0.04	0.01	0.01	0.04	0.11	0.05	0.08	0.08	0.04	0.07	0.00	0.23	0.18
FeO	6.33	9.98	9.73	13.42	5.03	8.76	12.43	16.30	11.31	12.28	0.61	3.38	2.24
CoO	0.03	0.03	0.03	0.03	0.00	0.03	0.02	0.05	0.02	0.03	0.00	0.25	0.14
NiO	0.05	0.02	0.05	0.01	0.02	0.02	0.00	0.00	0.00	0.00	0.01	0.14	0.16
CuO	0.01	0.04	0.00	0.04	0.01	0.10	0.10	0.01	0.03	0.01	0.08	0.67	0.74
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.15	0.02	0.05	0.02	0.00	0.05
As2O5	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06
SnO2	0.01	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.00	0.03	0.01	0.13
Sb2O5	0.20	0.00	0.04	0.02	0.20	0.04	0.06	0.00	0.02	0.00	1.35	0.11	1.26
BaO	0.05	0.02	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.01	0.04	0.06	0.06
PbO2	0.01	0.04	0.00	0.09	0.01	0.03	0.05	0.05	0.05	0.08	12.33	0.24	3.43
Total	102.18	102.42	102.63	101.42	98.40	102.82	102.63	103.93	101.76	101.85	103.98	99.55	100.71
site	Cumae	Cumae	Cumae	Cumae	Cumae	Cumae	Cumae	Cumae	Cumae	Cumae	Etruscan	Etruscan	Etruscan

sample	200	201	202	203	204	206	207	208	209	210	211	212	213
Na2O	5.50	5.11	5.88	6.26	5.56	5.80	5.77	6.21	4.79	6.79	6.29	5.57	6.29
MgO	0.73	0.95	0.55	0.83	1.76	0.65	0.79	0.91	1.04	1.55	0.65	0.83	0.52
Al2O3	1.86	2.48	3.58	2.35	4.26	1.85	2.19	1.99	2.77	3.80	2.07	3.89	2.41
SiO2	80.33	80.07	81.88	74.94	74.59	85.14	80.94	79.47	74.70	71.51	79.97	73.87	79.97
P2O5	0.20	0.20	0.12	0.19	0.17	0.17	0.15	0.20	0.19	0.38	0.17	0.15	0.12
SO3	0.00	0.02	0.03	0.00	0.03	0.03	0.03	0.03	0.00	0.12	0.00	0.33	0.03
Cl	0.04	0.03	0.06	0.11	0.06	0.06	0.07	0.05	0.04	0.16	0.05	0.21	0.07
K2O	10.92	10.54	9.17	9.48	7.34	6.99	9.58	9.19	10.53	10.46	9.82	8.57	12.03
CaO	1.94	3.03	1.78	2.18	1.68	1.66	2.09	2.42	3.19	2.58	1.80	2.42	1.51
TiO2	0.06	0.08	0.04	0.07	0.13	0.06	0.07	0.06	0.09	0.13	0.06	0.07	0.06
Cr2O3	0.00	0.03	0.00	0.00	0.02	0.03	0.02	0.00	0.00	0.02	0.02	0.02	0.00
MnO	0.03	0.03	0.01	0.04	0.10	0.03	0.04	0.03	0.03	0.02	0.04	0.01	0.01
FeO	0.49	0.90	0.79	1.01	1.30	0.56	0.88	0.63	0.98	1.37	0.67	0.90	0.66
CoO	0.00	0.13	0.09	0.23	0.00	0.00	0.19	0.02	0.09	0.00	0.00	0.00	0.12
NiO	0.03	0.15	0.01	0.56	0.01	0.00	0.39	0.01	0.21	0.02	0.03	0.03	0.28
CuO	2.30	0.42	0.13	0.76	0.08	1.04	0.74	3.33	0.32	1.95	3.06	3.20	0.40
ZnO	0.00	0.03	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.05	0.05
As2O5	0.00	0.04	0.00	0.15	0.00	0.00	0.18	0.00	0.02	0.00	0.00	0.00	0.07
SnO2	0.00	0.00	0.00	0.03	0.00	0.01	0.00	0.27	0.01	0.13	0.00	0.00	0.00
Sb2O5	0.02	0.02	0.00	0.15	0.00	0.00	0.11	0.00	0.02	0.00	0.08	0.06	0.04
BaO	0.05	0.04	0.01	0.01	0.04	0.05	0.05	0.04	0.04	0.04	0.05	0.02	0.02
PbO2	0.00	0.01	0.01	0.01	0.00	0.04	0.01	0.03	0.06	0.00	0.01	0.03	0.00
Total	104.50	104.27	104.14	99.36	97.13	104.17	104.31	104.89	99.12	101.01	104.84	100.23	104.66
site	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda

sample	214	215	216	217	218	219	220	222	223	224	225	226	227
Na2O	6.46	6.25	5.83	6.63	6.42	6.25	4.25	6.54	4.73	5.51	7.13	8.83	5.40
MgO	0.90	0.46	1.00	0.92	0.86	0.48	0.75	0.66	0.94	1.07	0.59	0.84	0.56
Al2O3	2.94	3.49	2.94	2.03	2.00	3.59	3.66	4.19	5.22	7.19	1.41	1.88	1.03
SiO2	78.50	75.37	78.42	73.52	70.91	76.80	69.91	74.48	65.25	62.12	74.20	74.05	75.33
P2O5	0.22	0.10	0.25	0.17	0.24	0.10	0.14	0.15	0.14	0.22	0.05	0.15	0.12
SO3	0.03	0.03	0.03	0.03	0.03	0.03	0.05	0.27	1.67	4.33	0.03	0.03	0.09
Cl	0.07	0.10	0.09	0.06	0.07	0.16	0.03	0.06	0.15	0.01	0.10	0.20	0.04
K2O	10.86	9.87	10.07	8.58	8.11	8.19	11.51	7.29	8.76	6.62	8.78	6.78	10.01
CaO	2.29	1.70	2.79	2.29	2.21	1.74	1.93	1.41	2.05	2.66	1.02	1.96	1.35
TiO2	0.07	0.06	0.07	0.07	0.04	0.06	0.06	0.06	0.07	0.09	0.06	0.06	0.04
Cr2O3	0.02	0.00	0.00	0.00	0.00	0.12	0.02	0.05	0.03	0.03	0.00	0.00	0.02
MnO	0.03	0.05	0.03	0.01	0.16	0.00	0.01	0.00	0.04	0.01	0.01	0.01	0.03
FeO	1.02	0.69	1.12	0.68	0.51	0.93	0.65	0.61	0.66	0.83	0.55	0.69	0.31
CoO	0.34	0.25	0.15	0.00	0.09	0.36	0.01	0.08	0.00	0.02	0.02	0.00	0.02
NiO	0.17	0.12	0.32	0.03	0.00	0.42	0.01	0.32	0.00	0.04	0.00	0.02	0.01
CuO	0.45	0.23	0.92	3.16	3.29	0.29	3.57	0.29	5.08	5.46	4.25	0.14	5.86
ZnO	0.00	0.06	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
As2O5	0.03	0.00	0.17	0.00	0.00	0.04	0.00	0.13	0.00	0.00	0.00	0.00	0.00
SnO2	0.00	0.00	0.00	0.27	0.20	0.00	0.20	0.00	0.32	0.47	0.38	0.01	0.57
Sb2O5	0.02	0.00	0.34	0.02	0.02	0.02	0.00	0.06	0.00	0.00	0.04	0.00	0.00
BaO	0.04	0.01	0.05	0.02	0.01	0.05	0.05	0.04	0.05	0.06	0.04	0.05	0.04
PbO2	0.00	0.01	0.03	0.06	0.00	0.01	0.04	0.01	0.01	0.07	0.00	0.01	0.00
Total	104.46	98.85	104.62	98.60	95.17	99.64	96.82	96.70	95.17	96.81	98.66	95.71	100.83
site	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Mariconda	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.

sample	228	230	233	234	235	236	237	238	239	240	241	242	243
Na2O	6.52	4.08	6.54	7.46	0.96	1.30	18.73	10.10	14.15	14.18	17.58	17.36	17.67
MgO	0.65	0.66	0.75	0.80	0.61	0.83	0.46	1.80	0.76	1.00	0.72	0.68	0.70
Al2O3	1.61	2.41	2.50	4.57	2.84	2.11	3.13	1.87	2.25	2.28	2.17	2.14	2.32
SiO2	74.58	73.66	73.17	69.87	67.96	71.97	65.92	61.87	61.97	64.51	66.76	67.67	67.93
P2O5	0.15	0.19	0.11	0.07	0.21	0.25	0.05	0.75	0.12	0.14	0.05	0.00	0.05
SO3	0.06	0.02	0.03	0.00	0.03	0.06	0.38	0.30	0.21	0.18	0.30	0.36	0.21
Cl	0.34	0.03	0.07	0.11	0.01	0.01	1.20	1.33	0.85	1.00	0.98	1.04	0.86
K2O	10.03	12.80	9.96	8.54	16.53	17.30	0.82	4.88	0.73	0.88	0.63	0.66	0.78
CaO	1.68	1.79	1.61	1.26	2.05	3.34	7.14	11.97	8.31	9.27	7.30	7.27	9.11
TiO2	0.04	0.04	0.07	0.07	0.06	0.13	0.03	0.07	0.05	0.04	0.06	0.02	0.04
Cr2O3	0.00	0.02	0.01	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.02	0.00
MnO	0.01	0.04	0.01	0.03	0.05	0.05	0.04	0.24	0.83	3.72	1.49	1.56	0.00
FeO	0.43	0.51	0.58	0.70	0.43	0.61	0.36	0.60	8.63	1.23	0.77	0.79	0.35
CoO	0.02	0.00	0.03	0.06	0.02	0.01	0.05	0.02	0.03	0.02	0.06	0.11	0.00
NiO	0.01	0.01	0.02	0.00	0.00	0.02	0.01	0.02	0.00	0.01	0.00	0.02	0.02
CuO	4.03	2.46	3.67	3.88	5.39	3.59	0.02	0.01	0.06	0.05	0.10	0.17	0.04
ZnO	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.03	0.02	0.02	0.00	0.02	0.02
As2O5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00
SnO2	0.42	0.01	0.08	0.28	0.00	0.21	0.04	0.03	0.05	0.03	0.03	0.00	0.03
Sb2O5	0.00	0.03	0.01	0.00		0.01	2.69	5.22	0.11	0.02	0.06	0.02	1.20
BaO	0.02	0.04	0.05	0.06		0.05	0.04	0.04	0.05	0.05	0.06	0.06	0.05
PbO2	0.03	0.03	0.02	0.01		0.03	0.04	0.12	1.11	0.89	0.08	0.09	0.00
Total	100.63	98.82	99.25	97.77	97.50	101.88	101.11	101.29	100.31	99.52	99.20	100.06	101.38
site	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Unprovena	Unprovena	Canale Bi.	Canale Bi.	Canale Bi.	Canale Bi.	Canale Bi.

sample	244	245	246	247	248	249	250	251	252	253	254	255	256
Na2O	16.36	18.48	18.09	15.02	16.34	17.07	17.19	15.73	14.64	15.70	16.22	12.96	17.24
MgO	0.88	0.63	0.60	0.48	0.88	0.36	0.41	0.47	0.46	0.39	0.65	0.35	0.39
Al2O3	2.20	2.35	2.35	2.14	2.65	2.61	2.63	1.32	2.12	1.88	1.14	1.91	1.66
SiO2	63.42	67.54	64.16	63.17	66.12	69.13	70.47	69.46	70.21	71.63	73.89	54.52	65.92
P2O5	0.12	0.07	0.07	0.05	0.07	0.05	0.02	0.05	0.05	0.02	0.07	0.02	0.07
SO3	0.27	0.18	0.33	0.24	0.24	0.30	0.27	0.15	0.18	0.24	0.12	0.26	0.42
Cl	0.61	1.36	0.96	1.04	0.91	0.91	0.93	1.40	1.02	0.95	1.35	0.82	0.97
K2O	0.80	0.80	0.94	0.72	0.58	0.95	0.94	0.29	0.70	0.64	0.38	0.60	0.58
CaO	12.08	8.11	6.94	6.90	8.73	5.80	5.87	8.14	7.59	7.02	6.74	5.32	7.70
TiO2	0.04	0.02	0.04	0.04	0.06	0.06	0.04	0.04	0.04	0.06	0.09	0.06	0.06
Cr2O3	0.00	0.04	0.00	0.00	0.02	0.02	0.00	0.02	0.00	0.02	0.03	0.00	0.02
MnO	1.25	0.04	3.62	0.61	0.01	0.01	0.03	0.03	0.01	0.04	0.94	0.04	0.03
FeO	0.31	0.29	0.61	0.71	0.66	0.29	0.42	0.80	0.48	0.34	0.72	1.99	0.75
CoO	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.03	0.05	0.03	0.11	0.04	0.00
NiO	0.00	0.00	0.08	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.03
CuO	0.01	0.00	0.03	0.10	0.00	1.09	0.00	1.97	1.01	0.84	0.13	0.00	0.00
ZnO	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.05	0.05	0.00	0.11	0.09	0.00
As2O5	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
SnO2	0.00	0.04	0.03	0.01	0.05	0.03	0.01	0.13	0.06	0.05	0.00	0.01	0.06
Sb2O5	0.41	0.02	0.39	0.71	3.29	0.93	0.84	0.06	0.63	0.06	0.00	2.55	5.16
BaO	0.06	0.04	0.13	0.06	0.04	0.06	0.05	0.07	0.05	0.04	0.05	0.02	0.04
PbO2	0.02	0.05	0.25	9.30	0.01	0.47	0.56	0.19	0.23	0.00	0.01	20.52	0.07
Total	98.86	100.08	99.64	101.33	100.68	100.14	100.70	100.40	99.58	99.95	102.77	102.08	101.19
site	Canale Bi.	Unprovena	Canale Bi.	Canale Bi.	Canale Bi.	Canale Bi.	Canale Bi.	Unprovena	Unprovena	Unprovena	Canale Bi.	Canale Bi.	Canale Bi.

sample	257	261	263	264	265	266	267	268	269	270	272	273	274
Na2O	15.34	17.10	16.10	14.73	15.59	15.85	18.30	19.37	17.08	16.81	15.37	14.51	13.88
MgO	0.66	0.84	1.14	0.64	0.45	0.68	0.53	0.57	0.42	0.42	0.42	0.39	0.55
Al2O3	2.11	1.15	2.51	0.70	0.65	0.52	1.61	2.27	2.41	2.44	2.49	2.41	2.42
SiO2	67.30	64.90	66.07	66.04	67.00	64.58	67.51	61.57	66.34	67.32	59.43	66.55	67.06
P2O5	0.02	0.10	0.12	0.05	0.02	0.10	0.05	0.05	0.05	0.02	0.09	0.02	0.07
SO3	0.33	0.18	0.24	0.27	0.15	0.18	0.24	0.54	0.18	0.18	0.71	0.38	0.51
Cl	0.85	1.03	0.95	1.37	1.05	1.18	1.53	1.02	1.45	1.56	0.66	0.79	0.94
K2O	0.91	0.39	0.97	0.06	0.20	0.07	0.35	0.77	0.36	0.36	0.53	0.56	0.68
CaO	8.98	10.61	9.84	10.17	9.26	10.72	8.88	8.56	8.20	8.31	8.23	5.64	7.40
TiO2	0.04	0.04	0.04	0.13	0.07	0.06	0.06	0.06	0.06	0.04	0.05	0.04	0.06
Cr2O3	0.02	0.00	0.00	0.00	0.03	0.02	0.04	0.02	0.00	0.02	0.01	0.00	0.02
MnO	0.10	0.01	0.68	0.03	0.03	0.04	0.05	0.08	0.01	0.01	0.28	0.02	0.47
FeO	1.25	7.84	1.17	7.16	0.60	5.73	0.34	1.20	0.34	0.32	0.36	0.33	0.35
CoO	0.12	0.02	0.16	0.00	0.00	0.05	0.00	0.11	0.03	0.05	0.00	0.01	0.00
NiO	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.00
CuO	0.32	0.01	0.22	0.00	3.45	0.00	0.00	0.26	0.05	0.00	0.01	0.01	0.00
ZnO	0.00	0.02	0.03	0.02	0.00	0.00	0.02	0.00	0.09	0.00	0.00	0.00	0.00
As2O5	0.00	0.00	0.00	0.00	0.03	0.00	0.03	0.00	0.02	0.02	0.14	0.01	0.02
SnO2	0.01	0.03	0.03	0.01	0.05	0.04	0.04	0.06	0.00	0.01	0.06	0.02	0.01
Sb2O5	0.20	0.18	0.07	0.00	3.24	0.02	3.73	1.70	3.18	3.75	8.54	3.37	3.91
BaO	0.04	0.01	0.06	0.05	0.05	0.01	0.04	0.06	0.05	0.05	0.06	0.05	0.04
PbO2	1.53	0.00	0.18	0.00	0.11	0.09	0.06	1.91	0.00	0.01	2.39	6.21	0.05
Total	100.13	104.46	100.59	101.44	102.03	99.94	103.41	100.18	100.32	101.71	99.82	101.28	98.44
site	Canale Bi.	Unprovena	Canale Bi.	Ca'Cima	Ca'Cima	Ca'Cima	Ca'Cima	Ca'Cima	Ca'Cima	Ca'Cima	Co'Garizon	Co'Garizon	Co'Garizon

sample	276	277	278	279	280	281	282	283	284	285	286	287	288
Na2O	16.63	16.67	16.81	17.46	16.29	13.82	16.42	16.89	14.42	17.94	17.48	17.56	17.32
MgO	0.35	0.38	0.40	0.46	0.38	0.36	0.35	0.35	0.55	0.51	0.55	0.51	0.56
Al2O3	2.37	2.40	2.29	2.47	2.59	2.40	2.36	2.37	2.44	2.40	2.61	2.40	2.28
SiO2	66.29	67.13	66.11	66.19	67.08	63.12	67.55	66.70	67.82	67.01	66.83	66.15	66.22
P2O5	0.05	0.05	0.05	0.05	0.05	0.05	0.07	0.05	0.07	0.07	0.07	0.07	0.02
SO3	0.54	0.48	0.57	0.54	0.45	0.41	0.45	0.48	0.33	0.45	0.39	0.42	0.39
Cl	0.86	0.89	0.84	0.88	0.82	0.59	0.86	0.86	0.95	0.95	0.96	0.91	1.03
K2O	0.67	0.73	0.67	0.61	0.73	0.54	0.69	0.67	0.76	0.80	0.78	0.82	0.58
CaO	5.89	6.01	6.04	7.24	5.97	5.78	5.82	5.99	6.98	6.72	6.76	6.75	6.27
TiO2	0.04	0.06	0.04	0.04	0.06	0.04	0.04	0.04	0.04	0.04	0.04	0.06	0.04
Cr2O3	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02	0.00	0.02	0.00	0.00	0.00
MnO	0.59	0.67	0.61	0.25	0.57	0.05	0.57	0.63	1.15	1.11	1.24	1.15	0.35
FeO	0.32	0.38	0.37	0.43	0.37	0.38	0.37	0.38	0.72	0.66	0.78	0.70	0.49
CoO	0.02	0.03	0.02	0.02	0.03	0.00	0.03	0.00	0.09	0.11	0.09	0.09	0.00
NiO	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00
CuO	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.19	0.14	0.21	0.13	0.91
ZnO	0.00	0.03	0.00	0.00	0.05	0.00	0.00	0.00	0.02	0.00	0.00	0.06	0.00
As2O5	0.04	0.02	0.08	0.02	0.06	0.06	0.04	0.02	0.00	0.00	0.00	0.00	0.00
SnO2	0.05	0.04	0.04	0.05	0.05	0.03	0.04	0.03	0.01	0.03	0.03	0.01	0.05
Sb2O5	5.53	5.11	5.53	4.61	6.02	6.14	5.46	5.42	2.38	2.05	2.05	2.13	0.52
BaO	0.04	0.05	0.04	0.05	0.04	0.04	0.05	0.04	0.06	0.06	0.06	0.06	0.05
PbO2	0.26	0.19	0.20	0.01	0.23	8.80	0.24	0.26	0.05	0.00	0.15	0.53	4.04
Total	100.55	101.33	100.72	101.38	101.86	102.61	101.41	101.21	99.04	101.09	101.08	100.51	101.12
site	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon	Co'Garizon

sample	**289**	**290**	**291**	**292**	**293**	**294**	**295**	**296**	**298**	**299**	**300**	**301**	**302**
Na_2O	6.78	4.57	4.73	5.76	3.30	1.76	5.32	4.96	4.74	5.61	5.64	6.29	15.75
MgO	0.76	0.70	0.73	0.68	0.50	0.77	0.65	0.98	0.87	0.63	1.10	1.90	0.49
Al_2O_3	2.03	2.91	1.17	1.64	1.52	1.50	1.57	3.21	3.82	1.25	2.66	5.41	3.38
SiO_2	74.61	66.58	73.93	76.99	78.43	77.47	82.60	79.14	71.93	75.71	74.69	68.97	69.07
P_2O_5	0.07	0.14	0.15	0.19	0.20	0.14	0.07	0.15	0.18	0.15	0.15	0.24	0.05
SO_3	0.03	0.06	0.03	0.03	0.03	0.09	0.03	0.03	0.03	0.03	0.00	0.03	0.42
Cl	0.05	0.01	0.01	0.05	0.02	0.01	0.06	0.07	0.08	0.02	0.11	0.01	0.82
K_2O	8.09	12.47	11.90	9.96	13.27	15.67	8.68	11.36	11.23	11.07	6.24	10.63	0.61
CaO	1.36	3.67	1.79	1.71	1.16	3.15	1.37	1.82	2.18	1.76	3.94	3.56	9.35
TiO_2	0.04	0.00	0.04	0.04	0.04	0.07	0.04	0.09	0.08	0.04	0.07	0.19	0.00
Cr_2O_3	0.00	0.02	0.03	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.03	0.00
MnO	0.03	0.04	0.05	0.03	0.01	0.07	0.04	0.03	0.03	0.01	0.01	0.04	0.03
FeO	0.68	0.44	0.47	0.47	0.41	0.61	0.43	0.99	0.88	0.47	0.87	1.98	0.56
CoO	0.02	0.06	0.00	0.01	0.00	0.02	0.02	0.03	0.01	0.02	0.00	0.03	0.20
NiO	0.00	0.04	0.01	0.03	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
CuO	3.91	4.10	4.07	4.19	4.32	1.18	1.36	1.69	5.02	4.46	3.40	0.05	0.04
ZnO	0.00	0.00	0.02	0.01	0.00	0.02	0.00	0.00	0.00	0.03	0.03	0.02	0.00
As_2O_5	0.00	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO_2	0.04	0.24	0.42	0.25	0.46	0.03	0.06	0.11	0.26	0.19	0.00	0.00	0.00
Sb_2O_5	0.00	0.00	0.02	0.00	0.00	0.02	0.02	0.04	0.03	0.00	0.09	0.00	0.02
BaO	0.05	0.06	0.04	0.05	0.05	0.05	0.04	0.04	0.06	0.05	0.06	0.06	0.05
PbO_2	0.00	0.00	0.00	0.00	0.08	0.04	0.01	0.04	0.03	0.03	0.18	0.02	0.04
Total	98.55	96.22	99.61	102.07	103.80	102.67	102.37	104.79	101.43	101.53	99.24	99.46	100.88
site	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Fratte.	Canale Bi.

sample	**304**	**305**	**308**	**309**	**310**	**311**	**312**	**313**	**314**	**315**	**316**	**317**	**318**
Na_2O	17.47	15.96	6.05	5.63	8.16	5.80	7.17	7.12	5.84	7.04	4.15	5.65	6.81
MgO	0.48	0.79	0.58	0.61	0.86	1.84	0.82	0.70	0.67	0.64	0.81	0.63	0.58
Al_2O_3	2.51	3.19	1.56	1.64	1.99	6.02	1.84	1.67	2.02	1.67	2.45	2.00	2.03
SiO_2	69.96	69.46	72.49	74.51	74.48	62.27	74.25	75.75	74.87	73.99	73.07	76.25	75.89
P_2O_5	0.02	0.02	0.12	0.17	0.10	0.19	0.15	0.10	0.15	0.17	0.12	0.15	0.12
SO_3	0.52	0.35	0.03	0.00	0.03	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.03
Cl	0.57	1.08	0.05	0.06	0.09	0.08	0.09	0.05	0.04	0.09	0.01	0.06	0.09
K_2O	1.11	0.54	9.47	11.16	7.02	12.88	9.62	7.88	10.36	9.46	11.84	10.19	9.02
CaO	7.55	9.03	1.45	1.50	1.37	3.35	1.56	1.28	1.51	1.76	2.09	1.47	1.50
TiO_2	0.04	0.07	0.06	0.06	0.06	0.18	0.06	0.04	0.06	0.06	0.06	0.06	0.06
Cr_2O_3	0.00	0.00	0.03	0.02	0.02	0.00	0.00	0.00	0.02	0.07	0.00	0.02	0.02
MnO	0.01	0.04	0.03	0.00	0.04	0.05	0.04	0.01	0.00	0.01	0.04	0.01	0.01
FeO	0.24	0.42	0.49	0.54	0.71	2.39	0.66	0.54	0.48	0.51	0.62	0.49	0.65
CoO	0.02	0.01	0.00	0.00	0.02	0.05	0.06	0.00	0.02	0.00	0.00	0.00	0.03
NiO	0.00	0.01	0.00	0.01	0.00	0.07	0.11	0.07	0.05	0.01	0.00	0.00	0.00
CuO	1.15	1.33	5.35	3.62	3.53	1.41	0.63	5.08	1.72	3.79	3.66	2.08	2.88
ZnO	0.00	0.03	0.02	0.00	0.02	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.06
As_2O_5	0.00	0.03	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
SnO_2	0.01	0.10	0.53	0.04	0.03	0.04	0.00	0.01	0.15	0.03	0.00	0.22	0.03
Sb_2O_5	0.09	1.09	0.02	0.09	0.02	0.02	0.11	0.00	0.00	0.00	0.02	0.00	0.00
BaO	0.05	0.06	0.05	0.02	0.04	0.05	0.02	0.05	0.04	0.05	0.06	0.04	0.02
PbO_2	0.00	0.30	0.00	0.10	0.05	0.11	0.00	0.00	0.00	0.03	0.00	0.00	0.01
Total	101.80	103.85	98.38	99.78	98.64	96.88	97.29	100.38	98.03	99.38	99.03	99.35	99.84
site	Canale Bi.	Unprovena	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z

sample	319	320	321	322	323	325	326	327	328	331	332	333	334
Na2O	7.59	16.62	17.27	17.70	18.20	15.69	17.07	17.19	16.66	17.88	17.60	17.66	16.00
MgO	0.77	3.73	0.43	2.79	0.47	0.37	0.43	0.41	0.39	0.47	0.47	0.39	0.56
Al2O3	1.79	2.74	2.35	0.78	1.79	2.46	2.41	2.39	2.40	1.74	1.51	1.95	1.69
SiO2	74.31	63.18	69.07	65.04	69.04	71.87	71.17	72.08	72.52	64.97	70.09	70.54	68.96
P2O5	0.12	0.12	0.05	0.27	0.05	0.01	0.02	0.02	0.02	0.05	0.05	0.07	0.05
SO3	0.03	0.48	0.21	0.36	0.27	0.11	0.18	0.18	0.15	0.24	0.24	0.15	0.36
Cl	0.11	0.61	1.28	0.94	1.33	1.39	1.27	1.34	1.32	1.30	1.25	1.38	1.08
K2O	7.09	0.89	0.41	2.19	0.45	0.37	0.35	0.35	0.44	0.40	0.33	0.36	0.53
CaO	1.50	8.68	5.14	6.16	5.91	5.21	5.20	5.12	5.33	5.85	5.71	6.79	8.99
TiO2	0.06	0.04	0.06	0.06	0.04	0.07	0.06	0.07	0.06	0.06	0.06	0.06	0.02
Cr2O3	0.02	0.02	0.02	0.02	0.00	0.01	0.00	0.02	0.02	0.00	0.02	0.02	0.05
MnO	0.01	0.11	0.04	0.04	0.01	0.01	0.01	0.04	0.03	0.03	0.03	0.00	0.01
FeO	0.63	0.58	1.41	0.51	1.25	1.28	1.30	1.28	1.27	1.20	1.30	0.95	0.38
CoO	0.00	0.00	0.12	0.03	0.05	0.12	0.09	0.12	0.09	0.09	0.08	0.02	0.00
NiO	0.00	0.06	0.00	0.03	0.05	0.00	0.00	0.03	0.02	0.02	0.00	0.00	0.01
CuO	4.62	0.57	0.21	0.83	0.21	0.11	0.16	0.08	0.06	0.10	0.18	0.10	1.73
ZnO	0.02	0.05	0.02	0.06	0.00	0.04	0.00	0.05	0.06	0.02	0.00	0.00	0.00
As2O5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO2	0.03	0.01	0.00	0.01	0.05	0.03	0.01	0.06	0.01	0.01	0.00	0.03	0.17
Sb2O5	0.04	0.02	0.19	0.06	0.06	0.29	0.24	0.24	0.30	0.13	0.11	0.00	0.80
BaO	0.05	0.04	0.04	0.02	0.04	0.03	0.04	0.05	0.05	0.04	0.05	0.04	0.05
PbO2	0.01	0.00	0.05	0.01	1.16	0.09	0.17	0.13	0.14	1.13	0.85	0.03	0.33
Total	98.80	98.55	98.37	97.91	100.43	99.52	100.18	101.25	101.34	95.73	99.93	100.54	101.77
site	Borgo S. Z	Mul. Pros.	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti

sample	335	336	337	338	339	340	341	342	343	344	345	347	348
Na2O	14.06	19.94	6.57	5.50	7.92	6.87	4.79	18.14	13.07	17.05	16.20	22.17	11.73
MgO	0.34	1.20	0.88	0.71	0.74	0.74	0.63	1.69	0.41	1.95	1.03	3.56	0.43
Al2O3	1.76	7.09	1.85	2.02	1.83	2.14	1.54	3.89	2.27	4.35	6.24	9.30	0.81
SiO2	60.79	62.53	76.00	70.62	75.24	75.25	74.13	69.83	63.12	71.74	59.75	56.33	80.09
P2O5	0.05	0.12	0.17	0.12	0.07	0.12	0.15	0.02	0.02	0.00	0.17	0.15	0.02
SO3	0.15	0.39	0.03	0.03	0.02	0.00	0.00	0.31	0.23	0.25	0.36	0.48	0.18
Cl	1.49	0.59	0.02	0.05	0.15	0.12	0.04	0.82	0.79	0.62	0.34	0.50	0.76
K2O	0.28	1.68	8.16	10.36	7.12	8.72	11.65	0.20	1.15	0.15	1.84	0.49	0.16
CaO	6.41	2.02	2.09	1.38	1.37	1.35	1.54	4.21	7.20	3.44	2.55	5.10	5.14
TiO2	0.04	0.33	0.06	0.06	0.05	0.04	0.02	0.07	0.04	0.04	0.29	0.02	0.04
Cr2O3	0.00	0.02	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.02	0.02	0.02	0.02
MnO	0.03	0.26	0.01	0.01	0.01	0.01	0.01	0.27	0.03	0.33	0.34	1.00	0.00
FeO	1.50	3.64	1.09	0.66	0.65	0.62	0.46	0.80	0.87	0.74	8.97	0.98	0.79
CoO	0.03	0.20	0.22	0.00	0.00	0.02	0.00	0.03	0.02	0.05	0.29	0.17	0.40
NiO	0.00	0.06	0.23	0.00	0.02	0.03	0.00	0.02	0.00	0.08	0.12	0.15	0.14
CuO	0.05	0.38	0.56	4.50	4.09	3.88	3.85	0.01	0.06	0.00	0.24	0.00	0.12
ZnO	0.01	0.00	0.00	0.02	0.02	0.00	0.02	0.02	0.02	0.06	0.03	0.22	0.09
As2O5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.02	0.21
SnO2	0.03	0.03	0.00	0.01	0.02	0.04	0.42	0.01	0.00	0.00	0.00	0.00	0.04
Sb2O5	1.57	0.17	0.02	0.00	0.02	0.00	0.02	0.06	1.57	0.00	0.11	1.16	0.06
BaO	0.06	0.09	0.04	0.06	0.06	0.05	0.05	0.02	0.06	0.04	0.10	0.04	0.02
PbO2	14.69	0.14	0.01	0.10	0.03	0.00	0.07	0.03	10.83	0.00	0.39	0.03	0.04
Total	103.34	100.88	98.01	96.21	99.40	100.00	99.39	100.47	101.76	100.91	99.50	101.89	101.29
site	Benvenuti	"C. d. R."	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Borgo S. Z	Rebato	"C. d. R."	"C. d. R."	"C. d. R."	Alfonsi

sample	349	350	351	352	353	354	357	358	359	360	362	364	365
Na_2O	17.81	17.51	20.46	22.73	21.55	15.21	18.08	17.17	2.92	17.53	17.34	18.22	19.97
MgO	0.56	0.83	0.99	1.33	1.35	0.48	0.97	0.96	0.57	0.50	0.59	2.72	1.02
Al_2O_3	0.39	2.27	7.04	8.24	7.77	2.04	6.45	6.28	2.67	1.96	0.63	5.41	6.13
SiO_2	69.36	65.84	60.15	56.62	57.64	71.94	63.95	64.73	41.26	71.84	70.12	68.05	63.80
P_2O_5	0.02	0.12	0.19	0.19	0.17	0.02	0.75	1.09	1.26	0.02	0.05	0.00	0.24
SO_3	0.18	0.33	0.30	0.42	0.45	0.40	0.21	0.24	0.24	0.18	0.21	0.34	0.45
Cl	1.33	0.85	0.50	0.50	0.44	0.46	0.49	0.48	0.42	1.28	1.25	0.58	0.60
K_2O	0.09	0.63	2.19	2.43	2.46	0.58	1.81	1.69	0.44	0.41	0.55	0.21	1.94
CaO	10.09	5.83	2.36	2.65	2.54	4.47	3.70	3.77	1.78	6.31	7.64	3.38	2.48
TiO_2	0.06	0.13	0.35	0.40	0.38	0.13	0.31	0.27	0.09	0.04	0.07	0.07	0.29
Cr_2O_3	0.00	0.02	0.03	0.02	0.00	0.00	0.03	0.02	0.00	0.02	0.00	0.00	0.02
MnO	0.04	0.29	0.42	0.35	0.27	0.07	0.38	0.27	2.26	0.01	0.01	1.11	0.31
FeO	0.23	6.23	3.87	3.53	3.38	1.31	1.92	1.81	6.36	1.01	0.45	0.43	1.99
CoO	0.00	0.00	0.39	0.25	0.28	0.25	0.00	0.00	0.06	0.03	0.00	0.00	0.02
NiO	0.00	0.00	0.15	0.05	0.24	0.21	0.00	0.02	0.00	0.00	0.00	0.02	0.00
CuO	0.00	0.58	0.34	0.13	0.30	0.31	0.04	0.12	0.16	0.10	1.31	0.17	0.09
ZnO	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.03	0.66	0.02	0.12	0.02	0.02
As_2O_5	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	3.02	0.00	0.00	0.00	0.00
SnO_2	0.03	0.01	0.01	0.00	0.03	0.05	0.00	0.00	0.01	0.01	0.00	0.03	0.01
Sb_2O_5	1.67	0.07	0.22	0.02	0.19	0.35	0.02	0.02	0.13	0.04	0.00	0.02	0.02
BaO	0.02	0.05	0.09	0.10	0.09	0.04	0.10	0.07	0.11	0.04	0.04	0.02	0.07
PbO_2	0.09	0.33	0.33	0.05	0.11	1.84	0.04	0.03	37.65	0.00	0.00	0.19	0.14
Total	101.97	101.92	100.43	100.01	99.66	100.16	99.25	99.07	102.07	101.35	100.38	100.99	99.61
site	Mul. Pros.	Mul. Pros.	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti

sample	367	368	369	370	373	374	375	376	377	378	379	380	382
Na2O	14.78	13.79	17.53	16.14	19.42	17.57	18.46	19.41	18.68	18.59	18.63	21.50	16.71
MgO	0.58	2.66	0.44	1.13	1.03	3.84	4.10	3.33	1.86	1.88	1.89	1.11	3.81
Al2O3	1.47	16.35	1.96	1.16	5.70	6.34	6.58	6.39	0.32	0.32	0.32	7.16	6.19
SiO2	64.76	40.61	72.47	66.51	63.53	66.34	64.79	64.57	69.08	69.48	69.72	57.82	68.51
P2O5	0.14	0.05	0.15	0.14	0.19	0.02	0.00	0.02	0.12	0.12	0.12	0.22	0.02
SO3	0.18	0.03	0.15	0.36	0.24	0.31	0.43	0.40	0.51	0.52	0.45	0.39	0.25
Cl	1.15	0.30	1.31	0.81	0.43	0.45	0.49	0.54	0.73	0.79	0.69	0.56	0.61
K2O	0.43	0.31	0.38	0.46	1.95	0.16	0.14	0.19	0.99	0.99	1.01	2.25	0.11
CaO	5.98	3.05	6.22	3.47	2.70	3.48	3.91	3.53	6.76	6.81	6.80	2.58	3.06
TiO2	0.09	1.09	0.04	0.06	0.24	0.07	0.11	0.09	0.02	0.04	0.02	0.36	0.13
Cr2O3	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.02
MnO	0.09	0.16	0.01	0.16	0.23	0.30	0.26	0.37	0.00	0.03	0.04	0.41	0.33
FeO	10.76	21.30	1.09	1.83	2.49	0.80	0.96	0.98	0.10	0.21	0.18	3.84	0.84
CoO	0.05	0.03	0.03	0.23	0.31	0.00	0.05	0.05	0.00	0.02	0.00	0.31	0.05
NiO	0.03	0.00	0.08	0.27	0.29	0.08	0.06	0.05	0.00	0.00	0.00	0.04	0.09
CuO	0.09	0.09	0.12	0.71	0.47	0.00	0.03	0.01	0.01	0.04	0.01	0.36	0.00
ZnO	0.02	0.00	0.02	0.00	0.03	0.03	0.00	0.09	0.00	0.12	0.00	0.00	0.02
As2O5	0.00	0.22	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO2	0.03	0.01	0.01	0.08	0.04	0.03	0.01	0.00	0.00	0.01	0.00	0.04	0.04
Sb2O5	0.05	0.02	0.04	1.21	0.20	0.06	0.02	0.00	0.02	0.02	0.00	0.11	0.04
BaO	0.02	0.07	0.04	0.05	0.07	0.04	0.01	0.04	0.02	0.04	0.04	0.10	0.02
PbO2	0.14	1.78	0.11	8.33	0.19	0.03	0.00	0.05	0.00	0.00	0.00	0.48	0.01
Total	100.84	101.92	102.20	103.23	99.77	99.95	100.41	100.11	99.22	100.05	99.92	99.64	100.86
site	"C. d. R."	"C. d. R."	"C. d. R."	"C. d. R."	Rebato	"C. d. R."	"C. d. R."	"C. d. R."	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti

sample	384	385	386	390	391	393	395	397	398	400	401	307a	307b
Na2O	14.83	12.00	14.59	15.84	15.62	14.53	20.90	16.81	18.72	17.15	20.20	17.44	17.57
MgO	0.55	0.40	0.49	0.67	0.65	0.38	1.15	3.75	3.20	0.33	0.49	0.51	0.50
Al2O3	2.02	1.58	2.15	0.72	0.76	0.69	6.81	6.28	5.07	1.47	0.45	1.24	1.15
SiO2	73.28	78.85	74.00	72.08	70.43	69.52	57.76	67.89	68.97	72.89	71.86	72.02	74.67
P2O5	0.12	0.05	0.10	0.02	0.05	0.05	0.19	0.05	0.02	0.05	0.05	0.04	0.02
SO3	0.31	0.25	0.31	0.27	0.27	0.21	0.45	0.28	0.33	0.18	0.12	0.09	0.15
Cl	0.67	0.52	0.64	1.00	1.03	0.98	0.58	0.60	0.62	1.27	1.17	1.38	1.39
K2O	0.57	0.61	0.55	0.19	0.30	0.49	2.08	0.11	0.10	0.29	0.11	0.52	0.30
CaO	3.80	3.13	3.78	6.30	6.58	4.55	2.68	3.04	2.31	6.04	5.58	4.82	4.77
TiO2	0.13	0.11	0.11	0.07	0.07	0.07	0.31	0.11	0.04	0.04	0.02	0.07	0.07
Cr2O3	0.00	0.02	0.02	0.02	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.03
MnO	0.25	0.15	0.19	0.04	0.01	0.05	0.33	0.31	0.19	0.01	0.01	1.04	0.94
FeO	1.82	1.52	1.71	0.91	0.56	7.89	3.34	0.80	0.63	1.18	0.21	1.72	1.70
CoO	0.19	0.19	0.23	0.20	0.17	0.02	0.28	0.06	0.04	0.05	0.00	0.41	0.37
NiO	0.26	0.12	0.21	0.23	0.18	0.02	0.18	0.08	0.05	0.02	0.00	0.02	0.00
CuO	0.40	0.38	0.43	0.29	0.21	0.01	0.48	0.04	0.00	0.13	0.01	0.49	0.29
ZnO	0.05	0.05	0.03	0.00	0.00	0.01	0.00	0.05	0.01	0.01	0.00	0.00	0.00
As2O5	0.00	0.00	0.00	0.20	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnO2	0.04	0.04	0.01	0.03	0.00	0.01	0.88	0.01	0.00	0.01	0.03	0.05	0.03
Sb2O5	0.22	0.17	0.20	0.17	0.04	0.19	0.26	0.02	0.06	0.02	0.00	0.03	0.02
BaO	0.06	0.07	0.05	0.04	0.02	0.04	0.10	0.02	0.03	0.05	0.04	0.04	0.04
PbO2	1.33	0.85	1.22	0.11	0.10	1.44	1.79	0.01	0.00	0.00	0.05	0.03	0.06
Total	100.90	101.06	101.02	99.40	97.15	101.11	100.56	100.32	100.35	101.16	100.40	101.93	104.07
site	Benvenuti	Benvenuti	Benvenuti	Benvenuti	Benvenuti	"C. d. R."	Benvenuti	"C. d. R."	"C. d. R."	"C. d. R."	"C. d. R."	Unprovena	Unprovena

sample	307c	
Na2O	12.96	
MgO	0.38	
Al2O3	0.90	
SiO2	75.80	
P2O5	0.02	
SO3	0.46	
Cl	0.86	
K2O	0.47	
CaO	6.01	
TiO2	0.04	
Cr2O3	0.02	
MnO	0.01	
FeO	0.43	
CoO	0.02	
NiO	0.01	
CuO	0.00	
ZnO	0.00	
As2O5	0.08	
SnO2	0.01	
Sb2O5	3.53	
BaO	0.02	
PbO2	0.27	
Total	102.30	
site	Unprovenanced	

APPENDIX 2: SAMPLE CATALOGUE

Sample 10

Location: Liverpool Site: unknown invent.: 10159M

650-550 BC

Core formed glass vessel of blue opaque glass. Oinochoe form decorated with "scales" ("stachelflaschen"). 85 mm high, base diameter 22 mm, body max diameter 38 mm. Heavily restored and gap-filled. Also see Haevernick 1959, 1961, Harden 1968, Martelli 1994 and Giuntoli 1996.

Samples 11 and 12

Location: Lincoln Site: Chiusi invent.: M1926.657

650-550 BC

Core formed glass vessel of blue opaque glass. Oinochoe form decorated with "scales" ("stachelflaschen"). 67 mm high, base diameter 23 mm, body max diameter 32 mm. Sample 11 from a decorative scale on the body, sample 12 from the base. Also see Haevernick 1959, 1961, Harden 1968, Martelli 1994 and Giuntoli 1996.

Sample 16

Location: Ashmolean Site: Civita Castellana (Falerii Veteres) invent.: Pr 284-320

800-700 BC

Annular bead of translucent blue glass decorated with 2 stratified eyes of white opaque glass @ matrix. Width 8 mm, length 4mm. Sample from matrix. Also see Brown 1980, p 43, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 50

Location: Cambridge Site: Pozzouli invent.: 1947.1937 A

700-600 BC

Sub triangular bead of "black" opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Width 24 mm, length 19 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 51

Location: Cambridge Site: Pozzouli invent.: 1947.1937 B

700-600 BC

Sub triangular bead of "black" opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Width 22 mm, length 15 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 52

Location: Cambridge Site: Pozzouli invent.: 1947.1937 C

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Width 23 mm, length 17 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 53

Location: Cambridge Site: Pozzouli invent.: 1947.1937 D

700-600 BC

Globular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Width 22 mm, length 15 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 54

Location: Cambridge Site: Pozzouli invent.: 1947.1937 E

700-600 BC

Globular bead of dark green (weathered?) opaque glass decorated with 3 stratified eyes. Eye decoration has completely weathered away. Eyes placed irregularly on bead. Width 14 mm, length 15 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 55

Location: Cambridge Site: Pozzouli invent.: 1947.1937 F

700-600 BC

Globular bead of “black” opaque glass decorated with 3 stratified eyes. Eye decoration has completely weathered away. Eyes placed irregularly on bead. Wound bead- can see break-off point for trail at neck. Width 12.5 mm, length 11 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 56

Location: Cambridge Site: Pozzouli invent.: 1947.1937 G

700-600 BC

Globular bead of “black” opaque glass decorated with 2 stratified eyes of white opaque glass @ black matrix. Eye decoration has almost completely weathered away. Width 12 mm, length 8 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 57

Location: Cambridge Site: Pozzouli invent.: 1947.1937 H

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Wound bead- can see break-off point for trail at neck. Width 24 mm, length 18 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 58

Location: Cambridge Site: Pozzouli invent.: 1947.1937 I

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Width 24 mm, length 19 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 59

Location: Cambridge Site: Pozzouli invent.: 1947.1937 J

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. Width 20 mm, length 17 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 60

Location: Cambridge Site: Pozzouli invent.: 1947.1937 K

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. Wound bead- can see break-off point for trail at neck. Width 23 mm, length 17 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 61

Location: Cambridge Site: Pozzouli invent.: 1947.1937 L

700-600 BC

Sub triangular bead of “black” opaque glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. One corner of bead is missing. White opaque decoration has largely weathered away. Width 25 mm, length 21 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 62

Location: Cambridge Site: Pozzouli invent.: 1947.1937 M

700-600 BC

Globular bead of dark brown (weathered?) opaque glass decorated with 1 stratified eye of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has largely weathered away. Impressed ring decoration around the perforation may originally have held glass of another colour. Width 17 mm, length 14 mm. Bead Study Trust 1997 p 74, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Samples 63 and 64

Location: Cambridge Site: Pozzouli invent.: 1947.1937 N

700-600 BC

Globular bead of brown opaque (weathered) glass decorated with 3 stratified eyes of white opaque glass @ dark opaque glass @ white opaque glass @ dark opaque glass. White opaque decoration has partially weathered away. Width 19 mm, length 14 mm. Sample 63 is of the matrix, sample 64 of the white opaque decoration: the analysis of the latter was unsuccessful. Bead Study Trust 1997 p 74-75, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 65

Location: Cambridge Site: Pozzouli invent.: 1947.1937 O

700-600 BC

Fragment of ellipsoidal bead of “black” opaque glass decorated with a single trail of white opaque glass wrapped 3 times around the body of the bead. White opaque decoration has partially weathered away. Width 19 mm, length 14 mm. Bead Study Trust 1997 p 74.

Sample 66

Location: Cambridge Site: Pozzouli invent.: 1947.1937 P

700-600 BC

Cylinder bead of “black” opaque glass decorated with 3 bands of white opaque glass wrapped around the body of the bead. White opaque decoration has largely weathered away. Width 17 mm, length 18 mm. Bead Study Trust 1997 p 74.

Sample 67

Location: Cambridge Site: Pozzouli invent.: 1947.1937 Q

700-600 BC

Ellipsoidal bead of “black” opaque glass, flattened on one side, decorated with a band of white opaque glass wrapped 5 times around the body of the bead. White opaque decoration has largely weathered away. Width 18 mm, length 15 mm. Bead Study Trust 1997 p 74.

Samples 68 and 69

Location: Cambridge Site: Pozzouli invent.: 1947.1937 R

700-600 BC

Globular bead of “black” opaque glass decorated with 3 horizontal bands of white opaque glass wrapped around the body of the bead. White opaque decoration has partially weathered away. Sample 68 is from the dark matrix, and sample 69 is of the white opaque glass: the analysis of the latter was unsuccessful. Width 17 mm, length 14 mm. Bead Study Trust 1997 p 74.

Sample 70

Location: Cambridge Site: Pozzouli invent.: 1947.1937 S

700-600 BC

Globular bead of “black” opaque glass decorated with a horizontal groove around the body of the bead, which probably originally contained white opaque glass. Width 9 mm, length 9 mm. Bead Study Trust 1997 p 74.

Sample 71

Location: Cambridge Site: Pozzouli invent.: 1947.1937 T

700-600 BC

Globular bead of “black” opaque glass decorated with a horizontal groove around the body of the bead, which probably originally contained white opaque glass. Ring depression around one of the perforations may also have contained a differently coloured glass which has subsequently weathered away. Width 14 mm, length 11 mm. Bead Study Trust 1997 p 74.

Sample 72

Location: Cambridge Site: Pozzouli invent.: 1947.1937 U

700-600 BC

Globular bead of “black” opaque glass decorated with a horizontal band of white opaque glass. White opaque decoration has largely weathered away. Width 14 mm, length 11 mm. Bead Study Trust 1997 p 74.

Sample 73

Location: Cambridge Site: Pozzouli invent.: 1947.1937 V

700-600 BC

Broken cylinder bead of “black” opaque glass decorated with a trail of white opaque glass wrapped at least 6 times around the body of the bead and combed into a chevron design. Width 10 mm, length 13 mm. Bead Study Trust 1997 p 74 (also see first illustration on this page).

Samples 74 and 75

Location: Cambridge Site: Pozzouli invent.: 1947.1937 W

700-600 BC

Irregular shaped bead of “black” opaque glass decorated with crumbs of red opaque, white opaque and yellow glass marvered into the surface. Sample 74 is from the matrix, and sample 75 is from the red opaque glass. Width 10 mm, length 13 mm. Bead Study Trust 1997 p 74.

Sample 76

Location: Cambridge Site: Pozzouli invent.: 1947.1937 X

700-600 BC

Globular bead of “black” opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque has largely weathered away leaving behind irregular craters in the surface. Wound bead: can see the break-off point adjacent to one of the perforations. Width 11 mm, length 9 mm. Bead Study Trust 1997 p 74.

Sample 77

Location: Cambridge Site: Pozzouli invent.: 1947.1937 Y

700-600 BC

Globular bead of "black" opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque has largely weathered away leaving behind irregular craters in the surface. It is possible that one of the crumbs was a stratified eye with white opaque arranged around red opaque decoration. Width 11 mm, length 9 mm. Bead Study Trust 1997 p 74.

Sample 78

Location: Cambridge Site: Pozzouli invent.: 1947.1937 Z

700-600 BC

Annular bead of "black" opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque has largely weathered away leaving behind irregular craters in the surface. Width 10.5 mm, length 7 mm. Bead Study Trust 1997 p 74.

Sample 79

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AA

700-600 BC

Annular bead of “black” opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. Width 11.5 mm, length 10.5 mm. Bead Study Trust 1997 p 74.

Sample 80

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AB

700-600 BC

Annular bead of “black” opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. Matrix includes many small gas holes, and the white opaque decoration has largely weathered away leaving irregular craters. Width 10 mm, length 8 mm. Bead Study Trust 1997 p 74.

Sample 81

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AC

700-600 BC

Globular bead of “black” opaque glass decorated with crumbs of red, yellow and white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 10.5 mm, length 9 mm. Bead Study Trust 1997 p 74.

Sample 82

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AD

700-600 BC

Globular bead of “black” opaque glass decorated with crumbs of white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 10.5 mm, length 9 mm. Bead Study Trust 1997 p 74.

Samples 83 and 84

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AE

700-600 BC

Globular bead of “black” opaque glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Sample 83 is of the matrix and sample 84 is of the red opaque glass. Width 10 mm, length 9 mm. Bead Study Trust 1997 p 74.

Samples 85

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AF

700-600 BC

Globular bead of dark blue translucent glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 13.5 mm, length 10.5 mm. Bead Study Trust 1997 p 74.

Samples 86

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AG

700-600 BC

Globular bead of “black” glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 10 mm, length 8 mm. Bead Study Trust 1997 p 74.

Sample 87

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AH

700-600 BC

Globular bead of “black” glass decorated with crumbs of white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 10 mm, length 7.5 mm. Bead Study Trust 1997 p 74.

Samples 88 and 89

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AI

700-600 BC

Annular bead of “black” glass decorated with crumbs of red and white opaque glass marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Wound bead- can see break-off point next to perforation. Sample 88 is of the matrix, sample 89 from red decoration. Width 7.5 mm, length 10 mm. Bead Study Trust 1997 p 74.

Samples 90

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AJ

700-600 BC

Annular bead of “black” glass decorated with 1 red and 3 white opaque glass crumbs marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 10 mm, length 7 mm. Bead Study Trust 1997 p 74.

Sample 91

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AK

700-600 BC

Annular bead of weathered green opaque glass decorated with 1 red and numerous white opaque glass crumbs marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Width 13.5 mm, length 8.5 mm. Bead Study Trust 1997 p 74.

Samples 92 and 93

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AK

700-600 BC

Globular bead of “black” glass decorated with red and white opaque glass crumbs marvered into the surface. The white opaque decoration has largely weathered away leaving irregular craters. Wound bead. Sample 92 is of the matrix, sample 93 is from the red decoration. Width 10 mm, length 8.5 mm. Bead Study Trust 1997 p 74.

Sample 94

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AM

700-600 BC

Globular bead of “black” glass decorated with red and white opaque glass crumbs marvered into the surface. The white opaque decoration has partially weathered away. Abortive hole adjacent to one of the perforations demonstrates that this is not a wound bead, but a pierced ball of glass. Width 14.5 mm, length 13.5 mm. Bead Study Trust 1997 p 74, illustrated on page 75.

Sample 95

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AN

700-600 BC

Globular bead of “black” glass decorated with red and white opaque crumbs of glass marvered into the surface. White glass is powdery and largely weathered away. Width 19 mm, length 10 mm. Bead Study Trust 1997 p 75.

Sample 96

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AO

700-600 BC

Globular bead of “black” glass decorated with three “eyes” of weathered glass which are only partially marvered into the matrix. Colour of “eyes” indistinguishable from the matrix, both of which are heavily weathered. Width 13 mm, length 10 mm. Bead Study Trust 1997 p 75.

Sample 97

Location: Cambridge Site: Pozzouli invent.: 1947.1937 AP

700-600 BC

Globular bead of “black” glass, undecorated. Wound bead. Width 10 mm, length 8 mm. Bead Study Trust 1997 p 75.

Sample 150

Location: Cambridge Site: Etruscan invent.: 1947.1946 A

800-500 BC

Globular bead of blue translucent glass, undecorated. 1 of three sampled beads from this artefact: a copper alloy hoop, probably an earring. Has a brown weathering layer. Wound bead. Also see samples 151 and 152. Width 10 mm, length 9 mm. Bead Study Trust 1997 p 84.

Sample 151

Location: Cambridge Site: Etruscan invent.: 1947.1946 A

800-500 BC

Globular bead of blue translucent glass, undecorated. 2 of three sampled beads from this artefact: a copper alloy hoop, probably an earring. Heavily pitted and has a brown weathering layer. Wound bead. Also see samples 150 and 152. Width 10 mm, length 8 mm. Bead Study Trust 1997 p 84.

Sample 152

Location: Cambridge Site: Etruscan invent.: 1947.1946 A

800-500 BC

Globular bead of pale green translucent glass, undecorated. 3 of three sampled beads from this artefact: a copper alloy hoop, probably an earring. Heavily pitted and has a brown weathering layer. Wound bead. Also see samples 150 and 151. Width 18 mm, length 15 mm. Bead Study Trust 1997 p 84.

Sample 153

Location: Cambridge Site: Etruscan invent.: 1947.1946 B

700 BC

Irregular fragment of clear translucent glass, undecorated. Suspended upon a copper alloy brooch fragment, probably originally a bead. Has an iridescent weathering layer. Max dimension 28 mm. Bead Study Trust 1997 p 84.

Sample 154

Location: Cambridge Site: “Etruscan” invent.: 1947.1946 C

“700 BC” (probably 2nd Century BC onwards)

Annular bead of clear translucent glass, undecorated. Form is that of a ring bead (or *ringperlen*) common across Central and Southern Europe from the 2nd Century BC onwards (Zepezauer 1993, p 30-63, 95). Contains significant levels of manganese: the use of manganese as a decolourant in is not documented before the 2nd Century BC (Sayre 1963). 1 of a group of 3 beads, described as “Etruscan (?) 600 BC (?)” in the Bead Study Trust catalogue. The others may also be assigned a later date: see samples 155 and 156. Width 18.5 mm, length 10 mm. Bead Study Trust 1997 p 84.

Sample 155

Location: Cambridge Site: “Etruscan” invent.: 1947.1946 C

“700 BC” (probably 2nd Century BC onwards)

Fragment of annular bead of clear translucent glass, undecorated. Form is that of a ring bead (or *ringperlen*) common across Central and Southern Europe from the 2nd Century BC onwards (Zepezauer 1993, p 30-63, 95). 2 of a group of 3 beads, described as “Etruscan (?) 600 BC (?)” in the Bead Study Trust catalogue. The others may also be assigned a later date: see samples 154 and 156. Width 18.5 mm, length 12 mm. Bead Study Trust 1997 p 84.

Samples 156, 157 and 158

Location: Cambridge Site: “Etruscan” invent.: 1947.1946 C

“700 BC” (probably 2nd Century BC onwards)

Annular bead of red opaque glass decorated with crumbs of opaque white, opaque yellow, blue translucent and clear translucent glass crumbs marvered into the surface. 3 of a group of 3 beads, described as “Etruscan (?) 600 BC (?)” in the Bead Study Trust catalogue. Sample 156 is of the red opaque matrix, sample 157 is from the white opaque decoration and 158 from blue translucent decoration. The white decoration is opacified with tin oxide, which means it is more likely to be 2nd – 1st Century BC (see 3.7.12). The others may also be assigned a later date: see samples 154 and 155. Width 27 mm, length 17 mm. Bead Study Trust 1997 p 84.

Sample 159

Location: Cambridge Site: “Florence Etruscan” invent.: 1947.1947 III

800-500 BC

Globular bead of blue translucent glass, undecorated. Yellow weathering layer, horizontal striations suggesting it is a wound bead. Width 10 mm, length 7.5 mm. Not in Bead Study Trust catalogue, but stored and labelled within the other Italian material.

Sample 160

Location: Cambridge Site: “Florence Etruscan” invent.: 1947.1947 III B

800-500 BC

Globular bead of blue translucent glass, undecorated. Yellow weathering layer, horizontal striations suggesting it is a wound bead. Width 10 mm, length 8.5 mm. Not in Bead Study Trust catalogue, but stored and labelled within the other Italian material.

Sample 161

Location: Cambridge Site: “Florence Etruscan” invent.: 1947.1947 III C

800-500 BC

Globular bead of blue translucent glass, undecorated. Yellow weathering layer, flat platform on one side, probably original since there are weathering product on it: from polishing during the finishing processes of manufacture. Width 9 mm, length 8 mm. Not in Bead Study Trust catalogue, but stored and labelled within the other Italian material.

Sample 162

Location: Cambridge Site: Cumae invent.: 1947.1960

800-600 BC

Annular bead of green translucent glass, undecorated. Brown opaque weathering layer. Wound bead: can see the breaking-off point. Width 12 mm, length 8 mm. Bead Study Trust 1997 p 78.

Sample 163

Location: Cambridge Site: Cumae invent.: 1947.1960

800-600 BC

Globular bead of blue translucent glass, undecorated. Lots of gas bubbles. Width 21 mm, length 15.5 mm. Bead Study Trust 1997 p 78.

Sample 164

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Sub-triangular bead of “black” glass, decorated with 3 stratified eyes of white opaque @ matrix @ white opaque around matrix. White decoration is very powdery and has partially weathered away. Width 17 mm, length 13.5 mm. Bead Study Trust 1997 p 75, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 165

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Sub-triangular bead of “black” glass, decorated with 3 stratified eyes of white opaque @ matrix @ white opaque around matrix. White decoration is very powdery and has partially weathered away. Width 18 mm, length 14 mm. Bead Study Trust 1997 p 75, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Samples 166 and 167

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Sub-triangular bead of “black” glass, decorated with 3 stratified eyes of white opaque @ matrix @ white opaque around matrix. White decoration is very powdery and has partially weathered away. Sample 166 is of the matrix, sample 167 is of the white opaque decoration. EMP analysis of 167 is probably of matrix adhering to white decoration. Width 19 mm, length 14 mm. Bead Study Trust 1997 p 75, and for eye beads in general: Eisen 1916a, Beck 1928, Venclová 1983, Hencken 1968b, Spaer 1987, Haevernick 1987 and Francis 1996, Nicholson 1993, p 6-7.

Sample 168

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Plano-convex bead of “black” glass, decorated with a band of white opaque glass wrapped 4 times @ matrix and drawn into chevron. White decoration is very powdery and has partially weathered away. Brown weathering layer on matrix. Width 14 mm, length 15 mm. Bead Study Trust 1997 p 76, and Heurtley and Skeat 1933 p 38.

Sample 169

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Cylinder-shaped bead with convex ends, of “black” glass, decorated with a band of white opaque glass wrapped 4 times @ matrix. White decoration is very powdery and has largely weathered away leaving a channel behind. Width 12.5 mm, length 12.5 mm. Bead Study Trust 1997 p 76.

Sample 170

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Plano-convex bead of “black” glass, decorated with a band of white opaque glass wrapped 5 times @ matrix. White decoration is very powdery and has partially weathered away. Brown weathering layer on matrix. Width 12 mm, length 11 mm. Bead Study Trust 1997 p 76, and Heurtley and Skeat 1933 p 38.

Sample 171

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Large fragment of plano-convex bead of “black” glass, decorated with a band of white opaque glass wrapped 5 times @ matrix. White decoration is very powdery and has largely weathered away leaving behind a channel. Width 11.5 mm, length 12 mm. Bead Study Trust 1997 p 76, and Heurtley and Skeat 1933 p 38.

Sample 172

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Globular bead of “black” glass. Groove around the middle of the bead probably held white decoration which has since weathered away. Wound bead. Width 12 mm, length 11 mm. Bead Study Trust 1997 p 76.

Sample 173

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Globular bead of “black” glass. Groove around the middle of the bead probably held white decoration which has since weathered away. Wound bead. Width 12 mm, length 10 mm. Bead Study Trust 1997 p 76.

Sample 174

Location: Cambridge Site: Cumae invent.: 1947.1971 A

800-600 BC

Irregular shaped bead of “black” glass. Decorated with crumbs of red opaque, white opaque and green opaque glass marvered into the surface. Large craters in the surface suggest some of the decoration has weathered away. Width 14.5 mm, length 12 mm. Bead Study Trust 1997 p 76.

Sample 175, 176, 177 and 178

Location: Bristol Site: "Etruscan" invent.: Fa 332

800-600 BC

Packaging also labelled with: " 286", "2132" and "SW88055". From the Bomford Collection.

Brooch slider. Leech-shaped gather of blue opaque glass decorated with bands of yellow opaque, and red opaque glass wrapped around the blue matrix and combed into chevrons. The combing action has left a ridged surface. Appears to be lots of small quartz (?) inclusions 1-2 mm diameter embedded in the object. Sample 175 (failed) is from the blue matrix, sample 176 is of the yellow opaque decoration, sample 177 is from the red opaque decoration, sample 178 is of the white opaque inclusion. Length 49.5 mm, width 28.5 mm. References: Montelius 1895: Serie A plate 7 and Serie B plates: 90, 94, 195, 219, 307, 318, 349, Grenier 1912 p 294-305, von Bissing 1942 144-168, Dohan 1942 Plate 19, Figure 40, Plate 22, Figure 61, Sundwall 1943, p 193, Figure 311, p 208, Figure 333, Harden 1968, p 59, Goldstein 1979, p 122-123, Grose 1989 p 70, 81-82, 87,Tatton-Brown 1995 p 321, Dobiat 1987, p 27-29, figure 17, plate 1. Also see samples 370-373.

Sample 200

Location: Adria Site: Mariconda di Malera invent.: IG 147000

1100-900 BC

Ceramic lid to oinochoe jar, with translucent blue glass adhering to upper (slightly concave side. Lid has a lip of additional clay added to retain molten glass one one side (applied before glass). Used as working platform in beadmaking. Lid is 130 mm in diameter, and up to 25 mm thick (including ridge to locate in top of oinochoe jar). Glass is an irregular spread 95 x 75 mm, up to 5 mm thick. Also see Salzani 1986, p 109 and 115, and sample 201 below.

Sample 201

Location: Adria Site: Mariconda di Malera invent.: IG 147001

1100-900 BC

Twisted ceramic plate, with translucent blue glass on upper surface. Irregular broken edges except for a short (50 mm) curved edge, suggesting the plate was originally circular. Possibly used as a working platform in beadmaking. Overall dimensions of ceramic plate: length l00 mm, width 75 mm, thickness 9 mm. Glass is an irregular spread 55 x 45 mm up to 6.5 mm thick. Also see Salzani 1986, p 109 and 114, and sample 200 above.

Sample 202

Location: Adria Site: Mariconda di Malera invent.: IG 147011

1100-900 BC

Incomplete annular bead of translucent blue glass. Possibly a waster- the bead is twisted which must have taken place whilst hot and plastic. Width 4 mm, length 2.5 mm. Also see Salzoni 1986, p 109 and 115.

Sample 203

Location: Adria Site: Mariconda di Malera invent.: IG 147014

1100-900 BC

Irregular fragment of opaque blue glass. Rounded heat-deformed edges, heavily weathered with iridescent surface. Possible working waste. 16 mm x 10 mm x 10 mm. Also see Salzani 1986, p 109 and 115.

Sample 204-206

Location: Adria Site: Mariconda di Malera invent.: IG 147016

1100-900 BC

Irregular fragment of glassy material, consisting of three layers: blue glass (sample 204, white opaque glassy material (sample 205), grey opaque crystalline material (sample 206). Possibly a fragment of faience. Length 15 mm, width 7 mm, thickness 7mm.

Sample 207

Location: Adria Site: Mariconda di Malera invent.: IG 147007

1100-900 BC

Fragment of annular bead of translucent blue glass. Width 12 mm, length 4 mm. Also see Salzani 1986, p 109 and 115.

Sample 208

Location: Adria Site: Mariconda di Malera invent.: IG 147015

1100-900 BC

Irregular fragment of opaque blue glass broken from a much larger piece (“raw glass”). None of the edges deformed by heat. Dimensions 19 x 23.5 x 15 mm. Also see Salzani 1986, p 109 and 115.

Sample 209

Location: Adria Site: Mariconda di Malera invent.: IG 147017

1100-900 BC

Irregular fragment of translucent blue glass. Working waste. Appears “black”, but actually intensely coloured blue. Length 19 mm, width 8.5 mm.

Sample 210

Location: Adria Site: Mariconda di Malera invent.: IG 147002

1100-900 BC

Half of a globular bead from opaque blue glass. Width 15 mm, length 15.5 mm. Wound bead? - horizontal striations, matrix heavily seeded.

Sample 211

Location: Adria Site: Mariconda di Malera invent.: IG 147018

1100-900 BC

Irregular fragment of translucent blue glass. Working waste. Appears “black”, but actually intensely coloured blue. Matrix heavily seeded. Width 8.5 mm, length 10 mm. Also see Salzani 1986, p 109 and 115.

Sample 212

Location: Adria Site: Mariconda di Malera invent.: IG 147005

1100-900 BC

Half a barrel shaped bead of translucent blue glass decorated with 4 horizontal bands of opaque white glass. Width 8 mm, length 11 mm. Also see Salzani 1986, p 109 and 115.

Sample 213

Location: Adria Site: Mariconda di Malera invent.: IG 147006

1100-900 BC

Half a barrel shaped bead of translucent blue glass decorated with a band of opaque white glass wrapped around the bead. Width 8 mm, length 11 mm. Also see Salzani 1986, p 109 and 115.

Sample 214

Location: Adria Site: Mariconda di Malera invent.: IG 147004

1100-900 BC

Barrel shaped bead of translucent blue glass decorated with a single trail of opaque white glass wrapped 4 x @ the bead. Asymmetrical pinched and deformed whilst hot and plastic- possible waster. Width 9 mm, length 12 mm. Also see Salzani 1986, p 109 and 115.

Sample 215

Location: Adria Site: Mariconda di Malera invent.: IG 147009

1100-900 BC

Barrel shaped bead of translucent blue glass decorated with a single trail of opaque white glass wrapped 5 x @ the bead. Width 6.5 mm, length 11 mm. Also see Salzani 1986, p 109 and 115.

Sample 216

Location: Adria Site: Mariconda di Malera invent.: IG 147008

1100-900 BC

Half a globular bead of translucent blue glass decorated with a single trail of white opaque glass wrapped 3 x @ the bead. Width 8.5 mm, length 8 mm. Also see Salzani 1986, p 109 and 115.

Sample 217

Location: Adria Site: Mariconda di Malera invent.: IG 147013

1100-900 BC

Annular bead of translucent blue glass. Clearly made by trailing glass around a rod. Not marvered or smoothed by heating. Width, 5.5 mm, length, 2 mm. . Also see Salzani 1986, p 109 and 115.

Sample 218

Location: Adria Site: Mariconda di Malera invent.: IG 147009

1100-900 BC

Wound annular bead from blue translucent glass. Width 10 mm, length 2 mm. Also see Salzani 1986, p 109 and 115.

Sample 219

Location: Adria Site: Mariconda di Malera invent.: IG 147010

1100-900 BC

Annular bead of dark blue opaque glass. Smooth finished surface. Width 6.5 mm, length 3.5 mm. Also see Salzani 1986, p 109 and 115.

Sample 220

Location: Adria Site: Frattesine - surface find invent.: none

1100-900 BC

Fragment of rod-formed anthropomorphic (?) figure of opaque blue glass, torso only. Glass matrix heavily seeded. Note with object: “Perla framm Antropomorea (?). Da Fratta Polesine raccolta di superficie, sequestro carabineri 1995”. Width, 18 mm, length 17.5 mm.

Sample 221

Location: Adria Site: Fratte Abitato invent.: IG 32893

1100-900 BC

Fragment of crucible with irregular spread of translucent aqua glass adhering to upper surface. Marked as IG 31893, but published as IG 32893. Crucible form is of a shallow bowl with straight-sided sloping sides. Fabric is grey and coarse with large crystalline inclusions. Base of crucible 14 mm thick, sides taper from base to 6 mm at undecorated rim. Glass an irregular spread 50 mm x 35 mm up to 4 mm thick. Also see De Min 1986, p 126 and 138.

Sample 222

Location: Adria Site: Fratte Abitato invent.: IG 32893

1100-900 BC

Fragment of a disk ingot of dark blue opaque glass. Fragment includes a rounded edge and is twisted from being manipulated whilst hot and plastic. Upper surface has the indications of trails of hot glass which have incompletely fused with the main body of glass. These trails are from either the drawing off of glass from the ingot, or the formation of the disk. Matrix is heavily seeded. Width 58 mm, length 75 mm, thickness up to 16 mm. Also see De Min 1986, p 126 and 138.

Sample 223

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Fragment of a disk ingot of dark blue opaque glass with large area of red coloured surface. Fragment includes a rounded edge and is twisted from being manipulated whilst hot and plastic. The red surface is on the underside, and is probably due to the localised reduction of the copper content, which otherwise colours the glass blue. Possibly from the annealing of the disk in hot ashes. Width 43 mm, length 58 mm, thickness up to 11 mm. Also see De Min 1986, p 126 and 138.

Sample 224

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Irregular fragment of a disk ingot of dark blue opaque glass. Twisted, and showing signs of having been pinched by a tool whilst hot and plastic. Matrix is heavily seeded. Width 44 mm, length 65 mm, thickness up to 13 mm. Also see De Min 1986, p 126 and 138.

Sample 225

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Irregular fragment of a disk ingot of dark blue translucent glass. Fragment includes a rounded edge and is twisted from being manipulated whilst hot and plastic. Matrix is heavily seeded. Width 36 mm, length 50 mm, thickness up to 12 mm. Also see De Min 1986, p 126 and 138.

Sample 226

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Irregular fragment of working wasre, possibly the edge of a disk ingot, of translucent aqua glass. Upper surface has signs of trails which are not fused fully into the body of the glass after working formation of the piece. Width 30 mm, length 42 mm. Also see De Min 1986, p 126 and 138.

Sample 227

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Irregular fragment of working waste, possibly the edge of a disk ingot, of opaque blue glass with large area of red coloured surface. The red surface is probably due to the localised reduction of the copper content, which otherwise colours the glass blue. Width 21 mm, length 30 mm, thickness 12mm. Also see De Min 1986, p 126 and 138.

Sample 228

Location: Adria Site: Fratte Abitato invent.: IG 80883

1100-900 BC

Irregular fragment of working waste, possibly the edge of a disk ingot, of opaque blue glass with small area of red coloured surface. The red surface is probably due to the localised reduction of the copper content, which otherwise colours the glass blue. Upper surface very uneven from being manipulated whilst hot and plastic. Width 27 mm, length 38 mm, thickness up to 4 mm. Also see De Min 1986, p 126 and 138.

Sample 229

Location: Adria Site: Fratte Abitato invent.: IG 32888/32890

1100-900 BC

Fragment of annular bead of translucent blue glass. Width 16 mm. Length 5 mm. Also see De Min 1986, p 126 and 138.

Sample 230

Location: Adria Site: Fratte Abitato invent.: IG 32888/32890

1100-900 BC

Fragment of annular bead from blue translucent glass. Width approx. 15 mm, length 5 mm. Also see De Min 1986, p 126 and 138.

Sample 231

Location: Adria Site: Fratte Abitato invent.: IG 32890

1100-900 BC

Fragment of annular bead from blue translucent glass. Width approx. 16 mm, length 4 mm. Also see De Min 1986, p 126 and 138.

Sample 232

Location: Adria Site: Fratte Abitato invent.: IG 80881d

1100-900 BC

Fragment of elliptical bead of translucent blue glass. Horizontal striations in otherwise smmoth surface suggest it was formed by winding a glass trail around a rod. Matrix heavily seeded. Width 14.5 mm, length 17 mm. Also see De Min 1986, p 126 and 138.

Sample 233.

Location: Adria Site: Fratte Abitato invent.: IG 80881c

1100-900 BC

Half an ellipsoidal bead from translucent blue glass decorated with a single band of red opaque glass (<1 mm wide) wound 6 times around the bead. 10.5 mm wide, 16 mm long. Also see Salzani 1986, p 109 and 115.

Sample 234

Location: Adria Site: Fratte Abitato invent.: IG 32870

1100-900 BC

Tapered, cylinder shaped bead from opaque blue glass, decorated with a single band of opaque white glass wrapped 12x around the bead. Band dragged into chevrons. Width 6-9.5 mm, length 25 mm. Also see De Min 1986, p 126 and 138. Gambacurta 1987, p 199 fig. 9, p 211 fig. 24 and p 212. Type “M”: Perle cilindriche con decorazione a piuma d’uccello e a zig-zag incrociato.

Sample 235

Location: Adria Site: Fratte Necropoli invent.: IG 80919

1100-900 BC

Annular bead of translucent blue glass. Formed by winding around a rod- not smoothed. Width 6.5 mm, length 4 mm. Also see De Min and Gerhardingher 1986, p156 and 168.

Sample 236

Location: Adria Site: Fratte Necropoli invent.: IG 80914

1100-900 BC

Core-formed glass vessel, in Alabastron form, from opaque blue glass, with collar below rim. Miniature. This is the earliest core-formed glass vessel recovered from Italy, and predates imported examples known from Etruscan contexts of the 8th Century BC (Giuntoli 1996, p 14, Tatton-Brown 1995, p 321-325). Diameter 8-15 mm, height 30 mm. Also see De Min and Gerhardingher 1986, p 156 and 168.

Sample 237

Location: Adria Site: unknown invent.: IG 9167

400-200 BC

Anthropomorphic pendant of clear glass (slight yellowish tinge). Width 4 – 11.5 mm, length 20 mm. Also see sample 258.

Sample 238

Location: Adria Site: unknown invent.: IG 21970

Cylinder bead of white opaque glass decorated with virtical stripes of red opaque glass. Width 6.5 mm, length 18.5 mm. This artefact is probably a much later product (17th Century AD: Henderson *pers. comm*. 2002).

Sample 239

Location: Adria Site: Canale Bianco Necropoli invent.: IG 4919/9168

tomb 363

500-300 BC

Barrel shaped bead of brown (weathered) glass decorated with a single band of white opaque glass wrapped 6 x @ the bead and combed into chevrons. A band of red and white opaque glass wrapped around the perforations. All decoration marvered flush. Width 14 mm, length 19.5mm.

Sample 240

Tomb 363

Location: Adria Site: Canale Bianco Necropoli invent.: IG 4919/9168

500-300 BC

Barrel shaped bead of brown (weathered) glass decorated with a single band of white opaque glass wrapped 6 x @ the bead and combed into chevrons. A band of red and white opaque glass wrapped around the perforations. All decoration marvered flush. Width 14 .5 mm, length 17.5mm.

Sample 241

Tomb 25

Location: Adria Site: Canale Bianco Necropoli invent.: IG 9169

300-100 BC

Globular bead of blue translucent glass decorated with 8 stratified eyes (white opaque around blue around white opaque around blue). Eyes are inserted canes. Width 13.5 mm, length 12 mm.

Sample 242

Tomb 25

300-100 BC

Location: Adria Site: Canale Bianco Necropoli invent.: IG 9169

Globular bead of blue translucent glass decorated with 7 stratified eyes (white opaque around blue around white opaque around blue). Eyes are inserted canes. Width 13.5 mm, length 9.5 mm.

Sample 243

Location: Adria Site: Canale Bianco Necropoli invent.: IG 9170

500-300 BC

Globular bead of clear glass. Width 20 mm, length 14 mm.

Sample 244

Tomb 27

Location: Adria Site: Canale Bianco Necropoli invent.: IG 358

300-100 BC

Annular bead of pale green translucent glass. Width 30.5 mm, length 10.5 mm.

Sample 245

Location: Adria Site: unknown invent.: IG ? Bocchi collection 2907

Incomplete annular bead of amber coloured translucent glass decorated with alternate bands of yellow opaque and white opaque glass. Width 28 mm, length 12 mm. Ringperlen ? . Also see Gambacurta 1987, Type “I”, p 198, 200, p 210 fig. 22, p 212.

Sample 246

Location: Adria Site: Canale Bianco Necropoli invent.: none

Tomb 36

300-200 BC

Tapered cylinder bead of “black” glass decorated with two horizontal bands of white opaque glass. Matrix heavily seeded. Width 70.5 mm, length 4.5 mm.

Samples 247 and 248

Location: Adria Site: Canale Bianco Necropoli invent.: none

Tomb 157

300-200 BC

Rod-formed spindle whorl of pale green opaque glass decorated with: yellow opaque glass horns around the base, yellow opaque glass trail around the body, yellow opaque glass zig-zag decoration around the head on the base. Cold worked around the perforations. Also see Fogolari and Scarfi 1970, p 76,77 and plate 49. Sample 247 = yellow opaque decoration. Sample 248 = matrix. Width at base 28 mm, length 26 mm.

Samples 249 and 250

Location: Adria Site: Canale Bianco Necropoli invent.: 9113

Rod-formed spindle whorl of clear glass decorated around the waist with 7 bosses of translucent aqua glass. Sample 249 = aqua glass decoration. Sample 250 = matrix. Width at base of 28 mm, length 22 mm.

Sample 251

Location: Adria Site: unknown invent.: 21971

Globular bead of opaque blue glass decorated with 8 stratified eyes (white opaque around blue translucent around white opaque around blue translucent). Matrix heavily pitted. Width 17.5 mm, length 16 mm.

Sample 252

Location: Adria Site: unknown invent.: 9114

600-400 BC

Annular bead of blue opaque glass decorated with 8 stratified eyes arranged in vertical pairs (white opaque around blue translucent and white opaque around blue translucent around white opaque around blue translucent). Width 10 mm, length 5.5 mm.

Sample 253

Location: Adria Site: unknown invent.: 9114

600-400 BC

Globular bead of opaque blue glass decorated with seven stratified eyes (opaque white around blue translucent around opaque white around blue translucent around opaque white around blue translucent).Width 10 mm, length 7 mm.

Sample 254, 255 and 256

Location: Adria Site: Canale Bianco Necropoli invent.: none

300 BC

Annular bead of blue translucent glass decorated with 3 stratified eyes (white opaque @ blue translucent), 6 horns of white opaque glass and 6 horns of yellow opaque glass. Sample 254 = sample of blue matrix, sample 255 = opaque yellow decoration, sample 256 = white opaque decoration. Width 13 mm, length 9 mm.

Sample 257

Location: Adria Site: Canale Bianco Necropoli invent.: none

Tomb 391

300 BC

Annular bead of translucent blue glass decorated with six stratified eyes (opaque white around blue translucent glass). Width 11.5 mm, length 7 mm.

Sample 258

Location: Adria Site: Canale Bianco Necropoli invent.: none

Tomb 391

Anthropomorphic pendant of clear glass (slight yellowish tinge). Width 5.5 – 12.5 mm, length 17 mm. Also see sample 237.

Sample 259

Location: Adria Site: unknown invent.: IG 22034

Fragment of globular bead of yellow opaque glass decorated with two stratified eyes: white opaque around blue opaque around white opaque around blue opaque. Width 24 mm, length 25 mm.

Sample 260

Location: Adria Site: Pavanello invent.: K013

Fragment of cylinder (?) bead of opaque turquoise glass decorated with 6 stratified eyes: white opaque around blue opaque around white opaque around blue opaque. Deformed whilst hot and plastic- two of the eyes merge and a deep incision dragged through both the decoration and the matrix. The eyes not marvered flush with the matrix. Possible waster. Width 13 mm, length 12 mm.

Sample 261

Location: Adria Site: unknown invent.: none

Fragmentary annular bead of heavily weathered brown (?) glass decorated with three stratified eyes (white opaque around brown opaque around turquoise opaque, and three unstratified eyes of white opaque or turquoise opaque glass. None of the decoration has been marvered flush with the surface of the glass. Width 16 mm, length 11 mm.

Sample 262

Location: Adria Site: unknown invent.: none

Globular bead of yellow opaque glass. Squeezed into two lobes. Width 13 mm and 8 mm, length 9 mm.

Sample 263

Location: Adria Site: Canale Bianco Necropoli invent.: K037

Tomb 240

500-300 BC

Fragment of a globular bead of blue translucent glass decorated with two stratified eyes constructed from white opaque and blue translucent glass. Width 22 mm, length 20.5 mm.

Sample 264

Location: Adria Site: Necropolis di Ca' Cima invent.: none

Tomb 16/95

600-500 BC

Globular bead of heavily weathered green translucent glass decorated with three stratified eyes : white opaque around green translucent. Width 10 mm, length 8 mm.

Sample 265

Location: Adria Site: Necropolis di Ca' Cima invent.: none

Tomb 16/95

600-500 BC

Annular bead of blue opaque glass decorated with three stratified eyes: turquoise opaque around blue opaque and one unstratified eye of turquoise opaque glass. All decoration marvered flush with the surface of the bead. Width 12 mm, length 11.5 mm.

Sample 266.

Location: Adria Site: Necropoli di Ca’Cima invent.: IG ?

tomb16/95

Tomb 16/95

600-500 BC

Annular bead of badly weathered green glass decorated with 4 stratified eyes which have eroded away leaving the matrix behind. Width 18.5 mm length 10 mm.

Sample 267.

Location: Adria Site: Necropoli di Ca’Cima invent.: IG 9578

Tomb 13/95

500 BC

Rod –formed animal head pendant (goat’s head) of opaque white glass decorated with eyes of opaque yellow around green glass and nostrils and mouth of green translucent glass. Width 16.5 mm, length 31 mm, height 17 mm. Also see Stern and Schlick-Nolte, 1994, p190-191 and references. Also see Tatton-Brown in Lerje book.

Sample 268

Location: Adria Site: Necropoli di Ca’Cima invent.: none

Tomb 13/95

500 BC

Annular bead of blue translucent glass, heavily pitted weathering on the surface. Decoration has weathered away leaving behind a depression in the surface: a zig-zag horizontal band and a single eye. Width 13.5 mm, length 10 mm

Sample 269

Location: Adria Site: Necropoli di Ca'Cima invent.: 9599

Tomb 12/95

600-500 BC

Annular bead of white opaque glass decorated with a zig-zag horizontal band of bark brown translucent glass. Width 13 mm, length 9 mm.

Samples 270 and 271

Location: Adria Site: Necropoli di Ca'Cima invent.: 9202

Tomb 12/95

600-500 BC

Dome – shaped pin or brooch head of white opaque glass formed on an iron rod-the remains of which can be seen embedded in the base. The glass has been grozed around the rod to finish it. Decorated with nine horns of blue translucent glass. Width 13.5 mm, length 9.5 mm. Sample 270 = white opaque glass matrix, sample 271 = blue translucent glass decoration.

Sample 272

Location: Adria Site: Co' Garizoni 1966 invent.: IG 11.305

Tomb 47

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm. Also see Beck1926, p 26-27.

Sample 273

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.305

Tomb 47

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm.

Sample 274

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.305

Tomb 47

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 5 mm, length 6 mm.

Sample 275

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.305

Tomb 47

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 18 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 7 mm, length 6 mm.

Sample 276

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 18 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6.5 mm, length 6 mm.

Sample 277

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm.

Sample 278

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm.

Sample 279

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 5.5 mm, length 5.5 mm.

Sample 280

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm.

Sample 281

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 7 mm, length 6 mm.

Sample 282

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 6 mm.

Sample 283

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of white opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Indistinct zone on this bead may indicate that it was made using a two-piece mould. Width 6 mm, length 6 mm.

Sample 284

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.041

Tomb 29

Cylinder shaped bead of weathered blue opaque glass with moulded or drawn surface to give a decoration of six or more “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 5.5 mm.

Sample 285

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.042

Tomb 29

Cylinder shaped bead of blue opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 6 mm, length 5.5 mm.

Sample 286

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.042

Tomb 29

Cylinder shaped bead of blue opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 7 mm, length 6 mm.

Sample 287

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.042

Tomb 29

Cylinder shaped bead of blue opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 7 mm, length 6 mm.

Sample 288

Location: Adria Site: Co’ Garizoni 1966 invent.: IG 11.043

Tomb 29

Cylinder shaped bead of green opaque glass with moulded or drawn surface to give a decoration of 15 “knops” arranged alternately singly and in vertical pairs. Gives a granulated appearance. Width 7 mm, length 6 mm.

Sample 289

Location: Rovigo Site: Fratte Abitato invent.: IG 17319

1100-900 BC

Anthropomorphic figure, head and neck only, formed on a rod from translucent blue glass. max width 11.5 mm, max length 19 mm. Also see Verita and Biavati 1989.

Sample 290

Location: Rovigo Site: Fratte Abitato invent.: IG 32865

1100-900 BC

Annular bead of blue translucent glass with red patches on the surface. From a group of 240 similar beads. Width 4 mm, length 2 mm. Also see De Min 1986, p 126 and 138.

Sample 291

Location: Rovigo Site: Fratte Abitato invent.: IG 32865

1100-900 BC

Annular bead of blue translucent glass with red patches on the surface. From a group of 240 similar beads. Width 4 mm, length 2 mm. Also see De Min 1986, p 126 and 138.

Sample 292

Location: Rovigo Site: Fratte Abitato invent.: IG 17319

1100-900 BC

Irregular fragment of disk of blue translucent glass, covered with a red (reduced) surface. Ingot fragment. Thickness varies from 6.5 to 11.5 mm. Width 46 mm, length 74 mm.

Sample 293

Location: Rovigo Site: Fratte Abitato invent.: none

1100-900 BC

Fragment of flat disc of blue translucent glass with red patches on the (reduced) surface. Smooth rounded outer edge. Ingot fragment. Width 29.5 mm, length 44.5. Thickness 10-14.5 mm. Estimated original diameter of disc: 100 mm.

Sample 294

Location: Rovigo Site: Fratte Abitato invent.: none

1100-900 BC

Fragment of crucible with translucent blue glass adhering to the inner surface. The crucible fabric has been overheated on the outside and begun to melt, and has two distinct zones: a dark reddish brown exterior and a yellowish, reduced interior. The crucible fragment is 30 mm wide and 50 mm long and up to 15 mm thick. The glass is an irregular spread up to 1 mm thick.

Samples 295 and 296

Location: Rovigo Site: Fratte Abitato invent.: 272079

1100-900 BC

Irregular fragment of a crucible/ceramic platform with translucent blue glass adhering to one, slightly convex surface. Glass includes swirls of opaque red glass. Ceramic plate width 34 mm x 48 mm, 8 mm thick, red fabric. Used as working platform in beadmaking. Glass covers an area of approx. 25 x 28 mm and is 1.5 mm thick. Sample 295 = translucent blus glass, sample 296 = red swirl within blue glass.

Sample 297-299

Location: Rovigo Site: Fratte Abitato invent.: 272059

1100-900 BC

Irregular fragment of waste glass - a fused lump including fragments of stratified eye beads (white eyes on green matrix), blue translucent glass and green translucent glass.

Sample 297 = green translucent glass, sample 298 = white opaque glass, sample 299 = blue translucent glass.

Sample 300

Location: Rovigo Site: Fratte Abitato invent.: 272059

1100-900 BC

Fragment of flat disc of green translucent glass. Heavily seeded. Smooth rounded outer edge. Ingot fragment. Width 15 mm, length 19 mm.

Sample 301

Location: Rovigo Site: Fratte Abitato invent.: IG 272059

1100-900 BC

Pinched trail of pale green translucent glass, from the working of hot glass. Width 6 mm, length 20 mm. For experimental parallels see Gamm 1990.

Sample 302-304

Location: Adria Site: Canale Bianco invent.: none

Tomb 333

500 BC

Globular bead of dark opaque glass, decorated with 3 compound eyes and 9 opaque yellow horns. The compound eyes are made up of white opaque glass around a dark opaque matrix into which are set two types of eye decoration: a single yellow opaque glass around translucent blue eye surrounded by 6 white opaque around translucent blue eyes. Width 14.5 mm, length 13.5 mm. Also see Gambacurta 1987, Type “G”, Perle ad occhi composito, p 212, p207 fig. 21.

Sample 305

Location: Adria Site: unknown invent.: none

Globular bead of blue opaque glass decorated with four compound eyes of blue and white opaque glass. Width 21.5 mm, length 23 mm.

Sample 306

Location: Adria Site: unknown invent.: K041

Annular bead of blue opaque glass decorated with four swirled eyes of white opaque glass trailed onto and marvered into the surface of the bead. Width 29 mm, length 19 mm.

Sample 307 (brown, white and blue)

Location: Adria Site: unknown invent.: K043

Globular bead of translucent blue glass decorated with seven stratified eyes: white opaque glass around dark brown translucent glass around white opaque glass around blue translucent glass. Width 27 mm, length 23 mm. Analysed as “307(brown)”, “307(white)” and “307(blue)”.

Sample 308

Location: Montagnana Site: Borgo San Zeno invent.: 214964

1100-900 BC

Irregular fragment of blue translucent glass possibly part of a disc ingot. No decoration, but patches of surface are red opaque indicating localised reduction of the copper oxide component of the glass. Width 26 mm, length 26 mm, thickness, 14.5 mm. Citton and De Min 1990.

Sample 309

Location: Montagnana Site: Borgo San Zeno invent.: 214965

1100-900 BC

Irregular fragment of an opaque blue glass bead, possibly sub-triangular in form. The fracture surfaces are a red opaque colour, indicating exposure to heat in a reducing environment. Width 12.5 mm, length 9 mm. Citton and De Min 1990.

Samples 310 and 311

Location: Montagnana Site: Borgo San Zeno invent.: 61166

1100-900 BC

Cylindrical bead of blue opaque glass decorated with a single trail of red opaque glass wrapped 12x around the body of the bead and partially drawn into a chevron pattern. The decorative trail has been marvered flush with the surface of the body of the bead. The technology required to retain the reduced red opaque decoration workable without reducing the surface of the bead body is interesting. Sample 310 is of the blue matrix, and sample 311 is from the red decoration. Width 11 mm, length 38 mm. Citton and De Min 1990, pictured on page 18.

Sample 312

Location: Montagnana Site: Borgo San Zeno invent.: 61164

1100-900 BC

Fragment of ellipsoidal bead of blue opaque glass decorated with a trail of white opaque glass wrapped at least 6x around the body and drawn into a chevron pattern. Decoration marvered flush with the surface of the bead. Width 16 mm, length 22 mm. Citton and De Min 1990, pictured on page 18.

Sample 313

Location: Montagnana Site: Borgo San Zeno invent.: 61168

1100-900 BC

Fragment of blue opaque glass spindle whorl decorated with crumbs (or eyes) of white opaque glass which have not been marvered into the surface of the artefact. Width 23 mm, length 12.5 mm. Citton and De Min 1990.

Sample 314

Location: Montagnana Site: Borgo San Zeno invent.: 154129

1100-900 BC

Fragment of rounded blue opaque glass, undecorated. Horizontal striations, frequent gas bubbles in matrix. Width 15.5, length 14 mm. Citton and De Min 1990 pictured on page 18.

Sample 315

Location: Montagnana Site: Borgo San Zeno invent.: 214465

1100-900 BC

Fragment of an annular bead of red opaque glass. The fracture surfaces are also red, suggesting it was exposed to high temperatures in a reducing environment after being broken. Width 10 mm, length 7.5 mm. Citton and De Min 1990.

Sample 316

Location: Montagnana Site: Borgo San Zeno invent.: 154116

1100-900 BC

Fragment of rounded bead of opaque blue glass decorated with two unstratified eyes (single crumbs of white opaque glass marvered flush). Width 11.5 mm, length 10.5 mm. Citton and De Min 1990.

Sample 317

Location: Montagnana Site: Borgo San Zeno invent.: 154129

1100-900 BC

Fragment of irregular shaped bead of blue opaque glass. Width 14 mm, length 16 mm. Citton and De Min 1990.

Sample 318

Location: Montagnana Site: Borgo San Zeno invent.: 154129

1100-900 BC

Fragment of ellipsoidal bead of blue opaque glass, undecorated. Width 10 mm, length 14 mm. Citton and De Min 1990.

Sample 319

Location: Montagnana Site: Borgo San Zeno invent.: 61165

1100-900 BC

Fragment of ellipsoidal bead of blue opaque glass decorated with a trail of white opaque glass wrapped 3x around the body of the bead. Decorative band is marvered flush with surface of bead. Width 8 mm, length 10 mm. Citton and De Min 1990.

Sample 320

Location: Este Site: Casa Muletti Prosdocimi invent.: IG 6410

450 BC

Tomb 258

Fragment of annular bead of blue translucent glass (heavily weathered), decorated with 2 stratified eyes of white opaque glass around the matrix. Width 21 mm, length 16 mm. Chieco Bianchi, and Capuis, 1985a p 32-34, Figure 1, page 10, plates 1 and 2, drawing 248 number 15.

Sample 321

Location: Este Site: Villa Benvenuti invent.: IG 3950

Tomb 115

Rounded bead of blue opaque glass in two fragments, undecorated. Width 13 mm, length 10.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 322

Location: Este Site: Villa Benvenuti invent.: IG 3950

Tomb 115

Annular bead of aqua translucent glass, undecorated. Badly weathered with iridescent surface. Width 13.5 mm, length 7 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 323

Location: Este Site: Villa Benvenuti invent.: IG 3950

Tomb 115

Annular bead of blue opaque glass, undecorated. Badly weathered surface. Width 7 mm, length 4 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Samples 324-328

Location: Este Site: Villa Benvenuti invent.: IG 3950

Tomb 115

Annular beads of blue opaque glass, undecorated. Weathered surface. From a group of 37. Width 11.5 - 15 mm, length 7 - 10 mm. Analysis of sample 324 unsuccessful. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 330 - 333

Location: Este Site: Villa Benvenuti invent.: IG 3949

Tomb 115

Annular beads of blue opaque glass, undecorated. Weathered surface. From a group of 16. Width 6.5 - 8.5 mm, length 3.5 – 5 mm. Analysis of sample 330 unsuccessful. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 334

Location: Este Site: Villa Benvenuti invent.: IG 3949

Tomb 115

Annular bead of aqua translucent glass, decorated with 4 pairs of stratified eyes. Eyes constructed of inserted canes of white opaque @ blue translucent @ white opaque @ blue translucent @ white opaque @ blue translucent. Width 14 mm, length 9 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 335

Location: Este Site: Villa Benvenuti invent.: IG 3949

Tomb 115

Annular bead of yellow opaque glass, decorated with 4 pairs of stratified eyes and 1 additional eye. Eyes constructed of inserted canes of white opaque @ blue translucent @ white opaque @ blue translucent. Width 15.5 mm, length 12.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 336

Location: Este Site: Casa di Recovero invent.: IG 13717

Tomb 1 (1962)

625-575 BC

Spindle whorl of blue translucent glass, decorated with crumbs and zig-zag trails of yellow opaque glass in zones defined by horizontal bands of opaque yellow glass. Width 26.5 mm, length 25 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2, p 312-314, drawing 220.

Sample 337

Location: Este Site: Borgo San Zeno (Montagnana) invent.: IG 60845

1100-900 BC

Irregular fragment of blue opaque glass, part of a disc ingot. No decoration, but patches of surface are red opaque indicating localised reduction of the copper oxide component of the glass. Width 34 mm, length 74 mm, thickness, 15 mm. Citton and De Min 1990.

Sample 338

Location: Este Site: Borgo San Zeno (Montagnana) invent.: IG 60845

1100-900 BC

Irregular fragment of blue opaque glass, part of a disc ingot. No decoration. Contains large cavity, possibly a gas bubble but most likely to be result of folding during manufacture. Upper surface pinched from where it has been manipulated whilst hot. Width 30 mm, length 51 mm, thickness, 13 mm. Citton and De Min 1990.

Sample 339

Location: Este Site: Borgo San Zeno (Montagnana) invent.: IG 60854

1100-900 BC

Fragment of barrel shaped bead of blue opaque glass decorated with a trail of white opaque glass wrapped 4x around the body of the bead. White decoration has almost entirely weathered away. Width 10 mm, length 11.5 mm. Citton and De Min 1990, also Bellintani et al. 1998 p 16, figure 5 number 16.

Sample 340

Location: Este Site: Borgo San Zeno (Montagnana) invent.: IG 60857

1100-900 BC

Fragment of tapered bead of blue opaque glass decorated with a trail of red opaque glass wrapped 5x around the body of the bead. Sample included both red opaque and blue glass. Width 5 – 10.5 mm, length 14 mm. Citton and De Min 1990.

Sample 341

Location: Este Site: Borgo San Zeno (Montagnana) invent.: IG 60847

1100-900 BC

Irregular fused mass of small annular blue glass beads of blue opaque glass, all undecorated. max dimension 22 mm. Citton and De Min 1990.

Sample 342

Location: Este Site: Montagnana via Prateria invent.: IG 60969

2nd Century BC or later.

Tomb 1.

Irregular fragment of blue translucent glass (possibly a bead fragment). Initially considered as contemporary to the material from Borgo San Zeno, Montagnana (i.e. 1200-900 BC). The chemistry of the glass suggests it dates from the Roman period.

Sample 343

Location: Este Site: Rebato invent.: IG 8955

Tomb 149

700-500 BC

Rounded bead of blue opaque glass decorated with knops of yellow opaque glass and stratified eyes of white opaque glass @ blue translucent glass. Sample is of a yellow knop. Bead has been "conserved" with a thick layer of varnish. Width 12 mm, length 12 mm.

Sample 344

Location: Este Site: Casa di Recovero invent.: IG 7114

Tomb 177

625 – 575 BC

Annular bead of blue opaque glass decorated with three stratified eyes of white opaque glass around matrix. White decorative glass has largely weathered away. Width 10 mm, length 7 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2, p 150-152, drawing 88.

Sample 345

Location: Este Site: Casa di Recovero invent.: IG 7114

Tomb 177

625 – 575 BC

Annular bead of “black” glass, heavily weathered, decorated with three stratified eyes in which the eyes are swirls of white opaque glass around the matrix. Decoration marvered flush with the surface of the bead. Width 9.5 mm, length 6 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2, p 150-152, drawing 88.

Sample 347

Location: Este Site: Casa di Recovero invent.: IG 13668

Tomb 234

c 625 BC

Annular bead of blue translucent glass, decorated with three stratified eyes in which the eyes have weathered away. Width 9 mm, length 7 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2, p 281-294, drawing 195.

Sample 348

Location: Este Site: Casa Alfonsi invent.: IG 8229

Tomb 22

525 – 450 BC

Brooch decoration of “black” weathered glass (originally blue translucent), zoomorphic form with applied knops and incised decoration. Still contains corroded remains of copper-alloy brooch pin. Width 7 – 11 mm, length 43 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 34 and plates 1 and 2, p 405-406, drawing 273.

Sample 349

Location: Este Site: Casa Muletti Prosdocimi invent.: IG 9326

Tomb 254

525 – 450 BC

Fragment of an annular bead of aqua translucent glass, undecorated. Has iridescent weathering layer. Width 19 mm, length 12 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 32-34 and plates 1 and 2, p 358 - 360, drawing 243.

Sample 350

Location: Este Site: Casa Muletti Prosdocimi invent.: IG 9326

Tomb 254

525 – 450 BC

Annular bead of (weathered) brown opaque glass decorated with 4 stratified eyes of white opaque glass @ matrix @ white opaque glass @ matrix @ white opaque glass @ matrix. The decoration has mostly weathered away. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 32-34 and plates 1 and 2, p 358 - 360, drawing 243 (no. 22).

Samples 351 – 354

Location: Este Site: Benvenuti invent.: IG 4496

Tomb 78

Annular beads of blue translucent glass, undecorated, from a large group from this context. Width 6.5 – 8.5 mm, length 3.5 – 5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Samples 357 – 358

Location: Este Site: Benvenuti invent.: IG 4496

Tomb 78

Annular beads of white opaque glass, undecorated, from a large group from this context. Width 6.5 and 7 mm, length 4 and 4.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 359

Location: Este Site: Benvenuti invent.: unknown

Tomb 101

Spindle whorl of various materials: core is ceramic possibly with a metal weight (artefact is very dense), with a thick glass surface (“glaze”) of dark green opaque glass, decorated with white opaque bands defining zones filled with zig-zag patterns. Sample 359 is of the green glaze. Width 28 mm, length 19 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 360

Location: Este Site: Benvenuti invent.: unknown

Tomb 105

Rounded bead of blue opaque glass, undecorated. Width 13.5 mm, length 10.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 362

Location: Este Site: Benvenuti invent.: IG 5409

Tomb 104

Fragment of annular bead of aqua translucent glass decorated with a zig-zag trail which has weathered away leaving a depression around the middle of the bead. Width 17 mm, length 12 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 364

Location: Este Site: Benvenuti invent.: IG 4495

Tomb 78

Annular bead of blue translucent glass, undecorated. Width 14 mm, length 8.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 365

Location: Este Site: Benvenuti invent.: IG 4495

Tomb 78

Globular bead of weathered pale green opaque glass decorated with 3 stratified eyes of yellow opaque glass @ matrix @ yellow opaque glass @ matrix @ yellow opaque glass @ matrix. width 20.5 mm, length 16 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 367

Location: Este Site: Casa di Recovero invent.: IG 7427

Tomb 205

525 – 450 BC

Tubular shaped bead of weathered brown opaque glass decorated with 4 knops and collars around each perforation. Similar in style to sample 348. Width 8 mm, length 14 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 197 - 202, plates 1 and 2, drawing 122 (no 10).

Sample 368

Location: Este Site: Casa di Recovero invent.: IG 7427

Tomb 205

525 – 450 BC

Globular bead of weathered brown opaque glass, undecorated. Width 4 mm, length 4 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 197 - 202, plates 1 and 2, drawing 122.

Sample 369

Location: Este Site: Casa di Recovero invent.: IG 12164

Unstratified find.

Spindle whorl of blue translucent glass decorated with a trailed-on zig-zag pattern of white opaque glass (i.e. decoration has not been drawn after application). Width

17 mm, length 16.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 442, plates 1 and 2, drawing 298 (no 241).

Samples 370 and 371

Location: Este Site: Casa di Recovero invent.: IG 7880

Tomb 235

700 – 675 BC

Leech-shaped brooch slider of weathered pale green opaque glass decorated with yellow opaque glass trailed around the matrix and combed into a feathered pattern. Sample 370 is of the matrix, sample 371 is of the yellow opaque decoration (analysis of the latter failed). Matrix is very badly weathered, and the object has been “conserved” with a thick layer of varnish. Width 23.5 mm, length 52 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 294 - 300, plates 1 and 2, drawing 197 (no 14), also see: Montelius 1895: Serie A plate 7 and Serie B plates: 90, 94, 195, 219, 307, 318, 349, Grenier 1912 p 294-305, von Bissing 1942 144-168, Dohan 1942 Plate 19, Figure 40, Plate 22, Figure 61, Sundwall 1943, p 193, Figure 311, p 208, Figure 333, Harden 1968, p 59, Goldstein 1979, p 122-123, Grose 1989 p 70, 81-82, 87,Tatton-Brown 1995 p 321, Dobiat 1987, p 27-29, figure 17, plate 1.

Sample 373

Location: Este Site: Rebato invent.: IG 8415

Tomb 100

650 – 625 BC

Leech-shaped brooch slider of weathered brown opaque glass decorated with alternate trails of white opaque and yellow opaque glass combed into a feather pattern. Copper alloy brooch still in place. Brooch slider is heavily restored, and has a coat of varnish. Width 26.5 mm, length 60 mm. For parallels see: Montelius 1895: Serie A plate 7 and Serie B plates: 90, 94, 195, 219, 307, 318, 349, Grenier 1912 p 294-305, von Bissing 1942 144-168, Dohan 1942 Plate 19, Figure 40, Plate 22, Figure 61, Sundwall 1943, p 193, Figure 311, p 208, Figure 333, Harden 1968, p 59, Goldstein 1979, p 122-123, Grose 1989 p 70, 81-82, 87,Tatton-Brown 1995 p 321, Dobiat 1987, p 27-29, figure 17, plate 1.

Sample 374

Location: Este Site: Casa di Recovero invent.: IG 13557

Tomb 143

775-750 BC

Annular bead of blue opaque glass decorated with three stratified eyes of yellow opaque glass @ matrix. Decoration has largely weathered away. Width 10.5 mm, length 6.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 61 - 68, plates 1 and 2, drawing 16 (no 15).

Sample 375

Location: Este Site: Casa di Recovero invent.: IG 13557

Tomb 143

775-750 BC

Annular bead of blue opaque glass decorated with three stratified eyes of yellow opaque glass @ matrix. Decoration has largely weathered away. Width 11.5 mm, length 8 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 61 - 68, plates 1 and 2, drawing 16 (no 15).

Sample 376

Location: Este Site: Casa di Recovero invent.: IG 13557

Tomb 143

775-750 BC

Annular bead of blue opaque glass decorated with three stratified eyes of yellow opaque glass @ matrix. Decoration has largely weathered away. Width 12 mm, length 8 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 61 - 68, plates 1 and 2, drawing 16 (no 15).

Samples 377 – 379

Location: Este Site: Benvenuti invent.: unknown

Tomb 122

Irregular fragments of clear translucent glass associated with a large group of glass, faience, amber and bone beads and pendants. Maximum dimension of clear glass 16 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 380

Location: Este Site: Benvenuti invent.: unknown

Tomb 122

Cylinder shaped bead of blue opaque glass, undecorated. Width 8 mm, length 10 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 382

Location: Este Site: Benvenuti invent.: unknown

Tomb 122

Annular bead of yellow opaque glass, undecorated, heavily weathered. Width 7 mm, length 4 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 384 – 386

Location: Este Site: Benvenuti invent.: unknown

Tomb 79

Annular beads of blue opaque glass, undecorated. Width 5.5 – 6.5 mm, length 1.3 – 3.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Samples 390 and 391

Location: Este Site: Benvenuti invent.: 5312

Tomb 98

Tubular bead of plae blue opaque glass decorated with a collar, a trailed decoration and 6 knops, all of white opaque glass. Sample 390 is of the matrix, and sample 391 is from the white opaque decoration. Width 11.5 mm, length 24.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 393

Location: Este Site: Casa di Recovero invent.: IG 4835

Tomb 233

c 575 BC

Spindle whorl of weathered brown opaque glass decorated with zig-zag trails of yellow opaque glass. In poor condition and heavily varnished. Width 24.5 mm, length 20.5 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 276 - 281, plates 1 and 2, drawing 183 (no 11).

Sample 395

Location: Este Site: Benvenuti invent.: 4700

Tomb 126

Annular bead of weathered brown opaque glass decorated with 4 stratified eyes of yellow opaque glass @ matrix @ yellow opaque @ matrix @ yellow opaque @ matrix. Heavily varnished and in poor condition. Width 26.5 mm, length 20 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, and plates 1 and 2.

Sample 397

Location: Este Site: Casa di Recovero invent.: IG 13518

Tomb 236

750 BC

Annular bead of blue translucent glass decorated with 3 stratified eyes of yellow opaque glass @ matrix. Decoration has largely weathered away leaving behind a depression. Width 11 mm, length 7 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 300-312, plates 1 and 2, drawing 205 (no 12).

Sample 398

Location: Este Site: Casa di Recovero invent.: IG 13518

Tomb 236

750 BC

Annular bead of blue translucent glass decorated with 3 stratified eyes of yellow opaque glass @ matrix. Decoration has largely weathered away leaving behind a depression. Width 10.5 mm, length 7 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 300-312, plates 1 and 2, drawing 205 (no 12).

Sample 400

Location: Este Site: Casa di Recovero invent.: IG 7965

Tomb 236

750 BC

Annular bead of blue translucent glass decorated with alternate single and pairs of stratified eyes of white opaque glass @ blue translucent glass. Width 33 mm, length 23 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 300-312, plates 1 and 2, drawing 210 (no 81).

Sample 401

Location: Este Site: Casa di Recovero invent.: IG 7965

Tomb 236

750 BC

Irregular fragment (barrel - shaped?) bead of brown translucent, undecorated. Width c 25 mm, length c 26 mm. Chieco Bianchi, and Capuis, 1985a Figure 1, p 10, 19 – 32, 300-312, entry 86, plates 1 and 2.

APPENDIX 3: PLATES

Unless otherwise specified, all images are 100 % of the original (i.e. scale 1:1), sample number is indicated in lower left-hand corner of each image.


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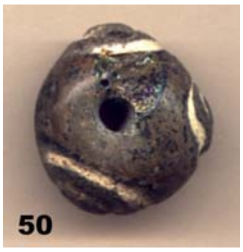
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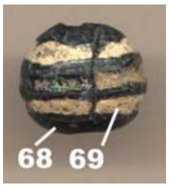
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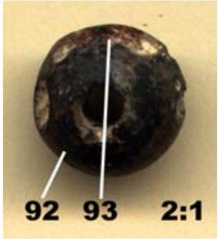
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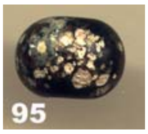
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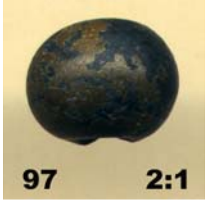
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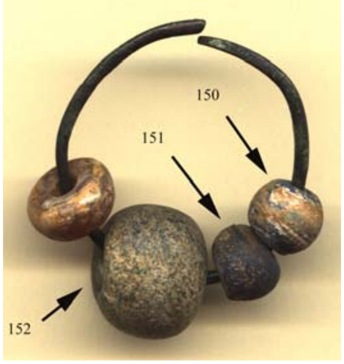
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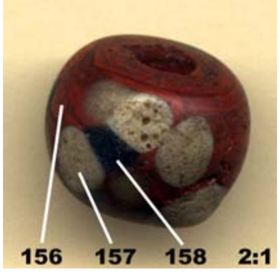
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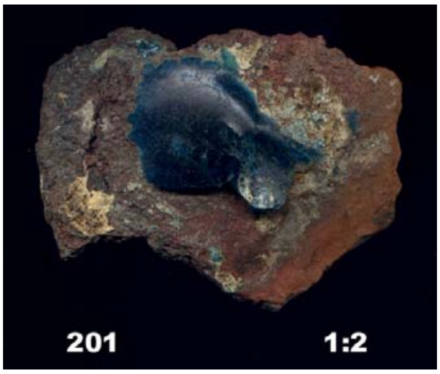
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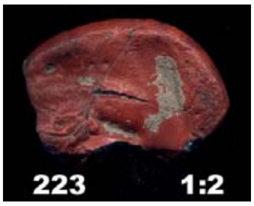
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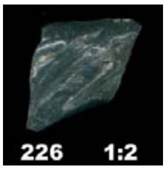
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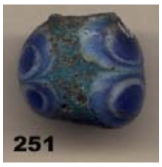
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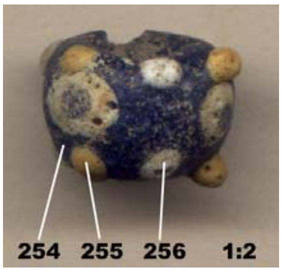
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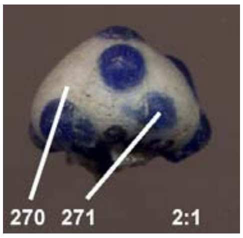
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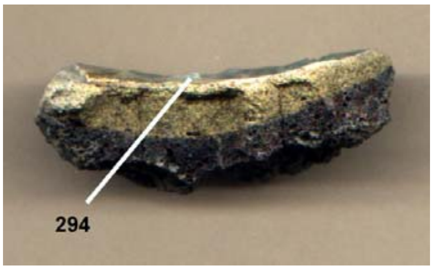
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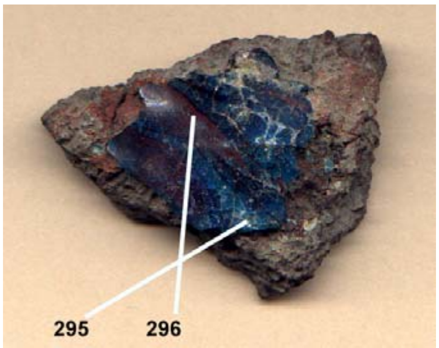
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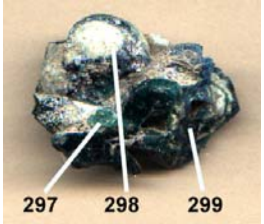
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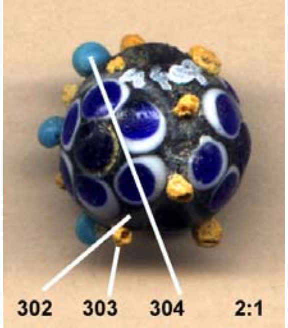
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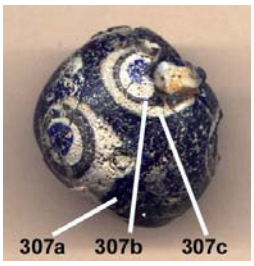
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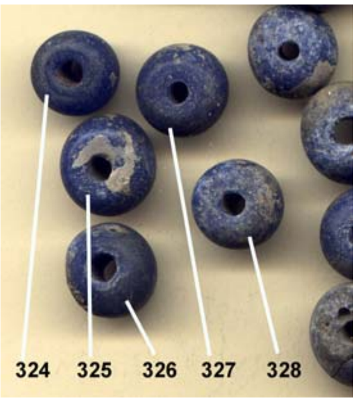
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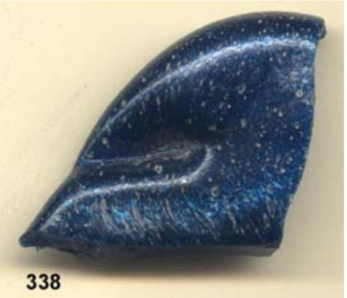
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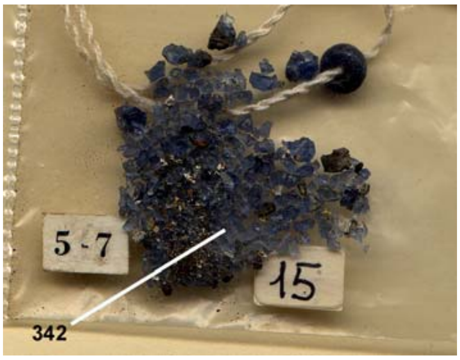

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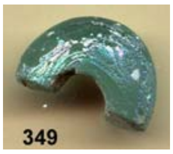
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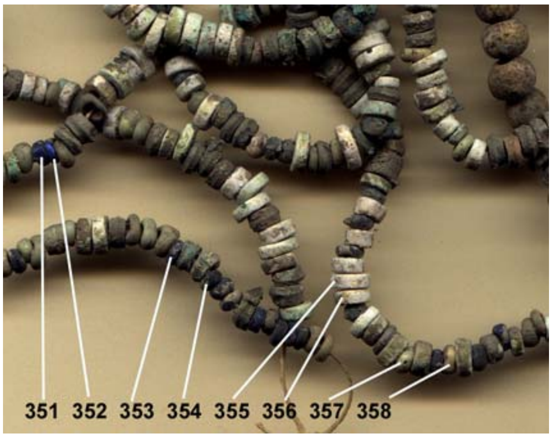
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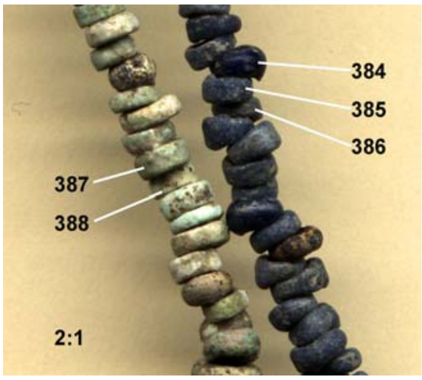
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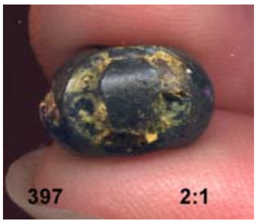
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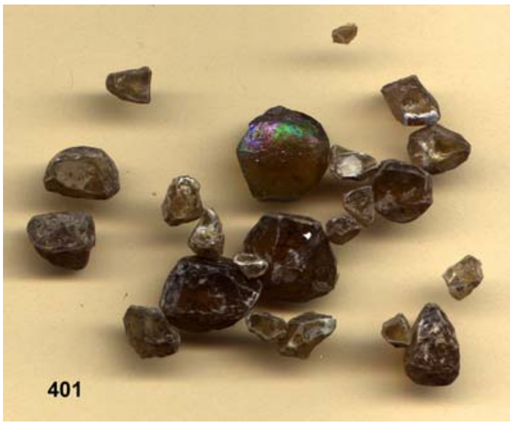
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