The Compositional Homogeneity of Potash-Lime-Silica Glasses in Northern Europe from 12^{th}-17^{th} Centuries.

Katharine Mary Anne Welham

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Department of Archaeology and Prehistory,
University of Sheffield

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To all the Friends of Fern and Bracken

ABSTRACT

This research investigates the compositional homogeneity of potash-lime-silica glasses from the 12th-17th centuries in Northern Europe, and the significance of this with respect to compositional studies of archaeological glasses. The variables in the glass making process that influence the formation of a homogeneous glass are discussed, and investigated using laboratory replication of beech and bracken ash glasses. The experimental results are compared to archaeological material from glass production sites at Blunden's Wood, Knightons, Sidney Wood, and Little Birches in England, and Hils in Germany.

Backscattered scanning electron microscope (SEM) imaging is used to qualify the extent of inhomogeneity in both the experimental and archaeological samples. It is confirmed that visually homogeneous glasses can contain inhomogeneities that are only visible under backscattered SEM imaging. It is seen that the size and orientation of inhomogeneities is varied, and specific glass artefact types (such as crucible and waste glass) are more prone to inhomogeneity than fully formed glass (such as window and vessel glass). Electron microprobe analysis (EPMA) is used to quantify the extent of elemental variations present in the inhomogeneous archaeological glasses. The results show that a number of elements are significantly influenced by inhomogeneity, including those (such as calcium, magnesium and sodium) which are commonly used to form compositional groupings of medieval glass.

It is concluded that although a number of variables in the glass making process influence the formation of a homogeneous glass, specific variables, such as increased furnace temperature and a high alkali concentration in the ash, appear to be the dominating factors. The presence of large elemental variations in a number of the archaeological glasses analysed confirms that inhomogeneity is a vital consideration in compositional studies of this material, and that particular care must be exercised when using analytical techniques that require only a small sample size.

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AHIV	Association Internationale pour l'Histoire du Verre
BAR	British Archaeological Reports
Be	Beech Ash Glass
BP	Bagot's Park Glass Site
Br	Bracken Ash Glass
BW	Blunden's Wood Glass Site
CB	Tall Form Crucible
CBA	Council for British Archaeology
CON	Conical Crucible
CYL	Cylindrical Crucible
EDS	Electron Dispersive Spectroscopy
EMPA	Electron Microprobe Analysis
EPMA	Electron Probe Microanalysis
FBe	Beech Ash Frit
FBr	Bracken Ash Frit
G	Hils Glass Sites
H	High
HMG	High Magnesium Glass
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
K	Knightons Glass Site
L	Low
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectroscopy
LBN	Little Birches (North Glass Site)
LBS	Little Birches (South Glass Site)
LLiF	Large Lithium Fluoride
LMG	Low Magnesium Glass
LOI	Loss on Ignition
LPET	Large Pentaerythitrol
M	Medium
n.a.	Not Analysed
NAA	Neutron Activation Analysis
n.d.	Not Detected
NERC	Natural and Environmental Research Council
NV	Not Visible
OES	Optical Emission Spectroscopy
PET	Pentaerythitrol
PIXE	Particle Induced X-Ray Emission
SEM	Scanning Electron Microscopy
SW	Sidney Wood Glasshouse
T	Temperature
t	Time
TAP	Thallium Acid Pthalate
WDS	Wave Dispersive Spectroscopy
XRF	X-ray Fluorescence Spectroscopy

CONTENTS

VOLUME I

VOLUME II

LIST OF FIGURES

VOLUME I

VOLUME II

LIST OF PLATES

VOLUME I

LIST OF TABLES

VOLUME I and II

CHAPTER 1

Introduction

1.1 Introduction

The aim of this research is to investigate the presence or absence of inhomogeneity in archaeological glasses, and determine what impact this has on compositional studies of the material. The archaeological questions frequently asked of glass assemblages are mainly focused on provenance, trade, and technology. Typological and compositional studies of glasses are both used to answer these types of questions. This research focuses on compositional analysis, which has become an increasingly common technique in the study of archaeological glass. Compositional data is used to group glasses based on similarities in elemental concentrations. These groupings are then used to infer meaning on a number of archaeological questions, which will be expanded upon in Section 1.4.

The fundamental assumption behind compositional studies of archaeological glass is that the glass analysed is **compositionally homogeneous** (see Section 1.3). However, if inhomogeneities are present in a glass, they will influence its chemical characteristics (see Section 1.2). This will affect the reliability of any analysis, and therefore significantly influence any interpretations made from the data. Homogeneity should therefore be of **primary importance** to the archaeologist, but it is an issue that has received little consideration within the archaeological literature. It is for this reason that it is the subject of this research. The main focus of this thesis will be on translucent, potash (potassium based) glasses from northern Europe dating from the 12th-17th centuries. The reasons for the choice of this specific glass type, period, and location of material will be covered in Section 1.6. However, initially it is important to understand what is meant by compositional homogeneity, and this will be discussed in Section 1.2.

1.2 What is Meant by Homogeneity in Glass?

All glasses can contain defects that are visible to the eye. Glass technologists refer to these as **visual defects**. Definitions of a few of the most common are listed below (Shelby 1997: 45):

- **Bubbles** (large gas filled inclusions >0.4mm in diameter)
- **Seed** (gas filled inclusions <0.4mm in diameter)
- **Stones** (particles of undissolved materials)

In addition to this a glass may also exhibit **phase separation**. This occurs when areas of less than 0.1µm in diameter exist, which differ in composition from the rest of the glass (Goodman 1987, Uhlmann and Kolbeck 1976). This would make the glass inhomogeneous on a **sub-micron** level but may not be significant when examining glass on a larger scale. The presence of phase separation can be viewed as a type of inhomogeneity but will not be considered here.

The focus of this research is **compositional homogeneity**. To explain what this means it is necessary to look at glass on a microscopic level. Glasses are either **opaque** or **translucent**. The difference between them can be identified using their microstructure. Opaque glasses are generally composed of crystals (which produce the colour and opacity) suspended in a glassy matrix (Plate 1:1).

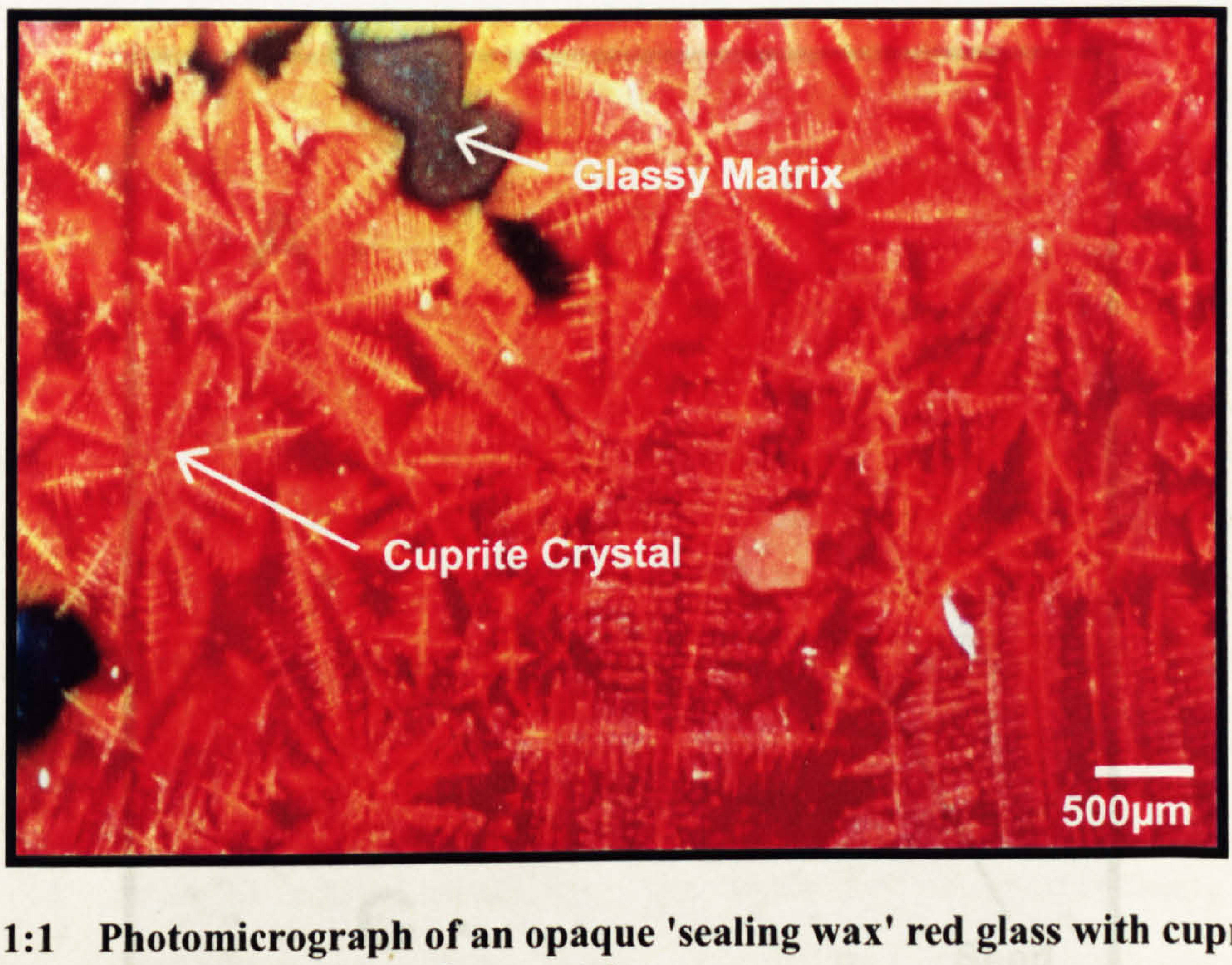


Plate 1:1 Photomicrograph of an opaque 'sealing wax' red glass with cuprite crystals in a clear glass matrix

Opaque glasses have been widely discussed in studies such as Bimson and Freestone (1985), Freestone (1987, 1993), Freestone and Bimson (1995), Mass *et al.* (1998), Welham *et al.* (2000). An example of an opaque 'sealing wax' red glass is illustrated in Plate 1:1. The red cuprite crystals have a different composition to the surrounding glass and therefore the material is known to be **inhomogeneous**. It is for this reason that opaque glasses will **not** be considered in this study. Opacity can also be produced by the presence of many bubbles in a translucent glass but this will not affect microstructure and therefore compositional homogeneity.

In comparison to opaque glasses, **translucent** glasses (Plate 1:2) contain **no crystals** and therefore have **no structure**. If the seed and bubbles were avoided, it could be assumed that an analysis taken at point '**A**' would have the same composition as one taken at '**B**' or '**C**'. If this were true the material would be homogeneous, a definition of this can be given as:

> '*A homogeneous body is one for which small samples taken from numerous different positions have exactly the same chemical composition or value of some other property. To describe this quantitatively the values and accuracy of measurements of the property chosen and also the size of the samples taken must be stated.*'
>
> (Cable and Bower 1965: 197)

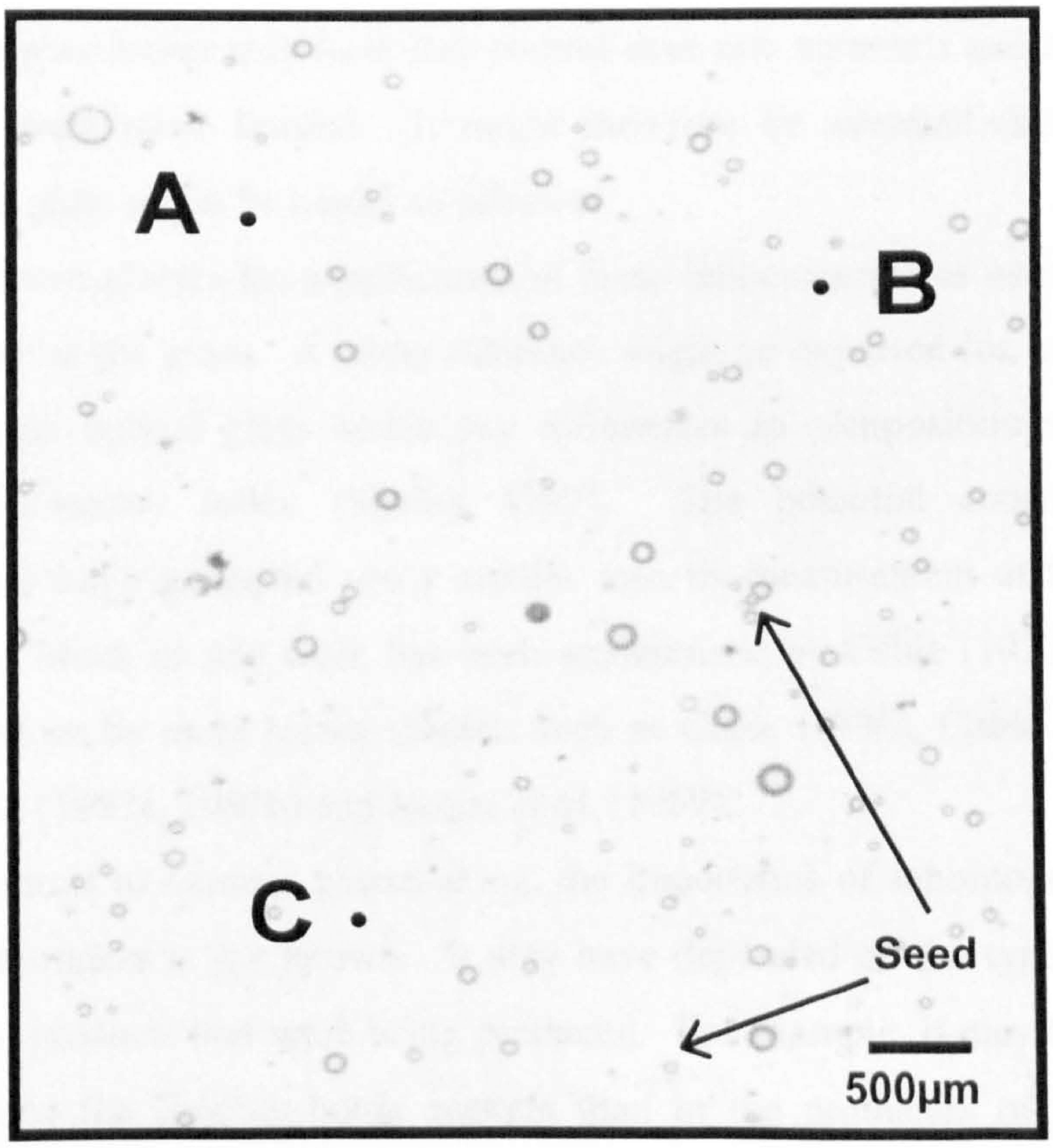


Plate 1:2 Photomicrograph of a translucent glass with seed

What is fundamental to this study is that the glass in Plate 1:1 may contain regions of differing composition that are not visible to the eye. For example, further investigation might reveal that points 'A', 'B' and 'C' have different compositions and therefore the material would be **inhomogeneous.**

Glass technologists refer to regions of inhomogeneity by a number of terms including *striae, ream, cord* and *vein* (Anon 1961: 192). The presence of inhomogeneity in modern industrial glasses can usually be seen as 'wavy' lines or as differences in colour intensity. These variations are generally relatively easy to detect visually on large items such as plate glass (Shelby 1997: 45), but in archaeological glasses, regions of inhomogeneity may not be so easy to see. This may be due to the small size of the artefact, fragmentation and/or the existence of weathering products that obscure the glass surface.

Inhomogeneity will influence the aesthetics and working properties of a glass, influencing such characteristics as refractive index and viscosity (Shelby 1997). It is for these reasons that it has been a vital consideration to the modern glassmaker. Glass production is a complex and high temperature process, and even using modern techniques, inhomogeneity is hard to avoid (Cable 1998). It is possible that in antiquity, the glassmaker may have less control over raw materials and the available technologies were more limited. It might therefore be assumed that forming a homogeneous glass might be harder to achieve.

In modern glasses the significance of these inhomogeneities usually depends on the end use of the glass. A wider tolerance might be expected for window glass compared to an optical glass where any differences in composition will cause a change in refractory index (Shelby 1997). The potential consequences of inhomogeneity have prompted many studies into its measurement and controlling mechanisms. Much of this work has been summarised by Cable (1970, 1998) and has been built on by more recent studies, such as Cable (1996), Cable and Walters (1980), Hense (1987a, 1987b) and Joanni *et al.* (1989).

In contrast to modern glassmaking, the importance of inhomogeneity to the medieval glassmaker is not known. It may have depended on the type, use and/or quality of the products that were being produced. For example, it may have been of less concern to the English bottle makers than to the producers of high quality drinking wares. What is also very probable is that in some cases it will not be possible to tell if the glass was intentionally or accidentally homogenous.

The reasons why homogeneity is an important issue to the archaeologist will now be discussed.

1.3 The Importance of Homogeneity to the Archaeologist

It was noted in Section 1.1 that the scientific study of archaeological glasses has predominantly focused on compositional analysis. The fundamental principles behind **all** studies that group glasses using similarities in their elemental concentrations are:

1. **Inter group homogeneity**
   This is homogeneity within groups of glasses made at the same site or using the same raw materials and technology. This assumes a consistency between raw materials and production technologies. Any differences arising can therefore be ascribed to the use of different raw materials.
2. **Intra sample homogeneity (compositional homogeneity)**
   This is homogeneity within a particular artefact or fragment to be analysed as described in Section 1.1.

In order to answer archaeological questions using (1), the fundamental assumption is that (2) exists. What is important to remember is that if a glass is not homogeneous, and the samples are not representative of the whole glass (see Section 1.1), then the compositional groups obtained may not be meaningful and any interpretations made using the data may be flawed (see Sections 1.4 and 9.3). Early compositional studies such as Turner (1956d: 165T, 1963) and Smith (1969) do mention the importance of careful sample selection. They note that weathering and corrosion products should be removed or avoided and only **homogeneous** samples should be selected. Whilst obtaining a clean surface for analysis is now a standard procedure, homogeneity is given little consideration. This may be because translucent glasses have generally been assumed by archaeologists to be homogeneous, as demonstrated in the following quote:

> *'Glass is usually a very homogeneous material and small flakes are generally representative of the chemical composition of the glass artefact.'*
>
> (Verità *et al.* 1994: 243)

However, a small number of studies have noted the presence of inhomogeneity. Brill and Moll (1963) discussed the applications of electron beam microprobe analysis (EPMA, see Section 1.5) to archaeological glass. They noted that this technique was well suited to investigate the presence of concentration gradients across cord and straie in ancient glasses. Cox and Ford (1989) documented the presence of inhomogeneities in their investigation of the weathering of medieval, potash based window glass. The main focus of their work was on how the inhomogeneities influenced the formation of corrosion products on the glass surface. However, they also carried out spot analyses using electron probe microanalysis (EPMA) but determined that there was no significant compositional difference between different localised areas of the uncorroded glass. Giannichedda *et al.* (2000) found that many of the glasses from a medieval glasshouse in the Gargassa Valley, northern Italy contained inhomogeneous phases. These were **not** visible to the eye and could **only** be detected under the scanning electron microscope (SEM). They therefore noted that care should be taken when analysing this type of material to avoid compositional bias in the results. The size and degree of compositional difference of the inhomogeneities compared to the bulk glass is therefore critical, as this will affect the choice of analytical technique. This will be discussed in Section 1.5, but before this, the effect of inhomogeneity on compositional studies of archaeological glass will be discussed in Section 1.4.

1.4 The Effect of Inhomogeneity on Compositional Studies of Glass

Early compositional studies, such as those by Geilmann and Bruckbaueer (1954), Geilmann *et al.* (1955) and Turner (1956b, 1956c), determined that glasses from different periods and geographical areas fell into broad compositional groups. A number of these variations could also be ascribed to the use of specific raw materials. Major compositional trends were noted, such as the presence of potassium based glasses in western medieval Europe, compared to the predominance of sodium based glasses elsewhere (Turner 1956b, 1956c).

Sayre and Smith (1961) carried out a major study of glass representing material produced in the Middle East, Africa and Europe from approximately 15th century BC through to the 10th century AD. They formed groups primarily based on relatively large scale differences in the magnesium, potassium, manganese, antimony and lead concentrations in their samples (Table 1:1). These results were then correlated with period and location, and the use of different raw materials (Sayre and Smith 1967, Smith 1969). For example, in soda-lime-silica glasses, they associated low levels of magnesium and potassium with the use of a mineral alkali source, whilst increased magnesium and potassium levels indicated the use of marine or terrestrial plant ashes (Sayre and Smith 1961). These two classifications are now commonly referred to as HMG (high magnesium glass) and LMG (low magnesium glass) (Henderson 1985: 275).

It can be seen from Table 1:1 that although many of the groups formed by Sayre and Smith (1961) have elemental concentrations that overlap, they all contain at least one element that is significantly different. For example, the ranges of the oxide weight percent values of the 'Second millennium BC' and 'Early Islamic' groups overlap for magnesium, potassium, antimony and lead, but they can be differentiated using manganese, which is significantly different for the two groups (see Table 1:1).

Group	No. of samples analysed	Mean percent concentrations and standard deviation ranges (in brackets)				
		MgO	K_2O	MnO	Sb_2O_3	PbO
Second millennium BC	15	3.6 (4.6-2.9)	1.13 (1.89-0.69)	0.032 (0.046-0.021)	0.058 (0.32-0.011)	0.0068 (0.048-0.0010)
Roman	34	0.86 (1.24-0.60)	0.29 (0.47-0.17)	0.022 (0.035-0.014)	1.01 (1.93-0.53)	0.019 (0.077-0.0047)
Antimony rich	73	1.04 (1.47-0.73)	0.38 (0.63-0.22)	0.41 (1.60-0.10)	0.040 (0.089-0.018)	0.014 (0.057-0.0033)
Early Islamic	66	4.9 (6.5-3.6)	1.45 (2.2-0.94)	0.47 (1.07-0.21)	0.021 (0.035-0.012)	0.0088 (0.047-0.0016)
Islamic lead	6	0.33 (0.47-0.24)	0.026 (0.051-0.016)	0.022 (0.031-0.016)	0.081 (0.19-0.035)	36 (40-33)

Table 1:1 Compositional groupings for ancient glass characterised by Sayre and Smith (1961: Table 1)

In recent years Sayre and Smith's (1961) classifications have been built and expanded upon, and the use of compositional analysis as a tool to investigate archaeological glass has become increasingly common. As the number of analysed glasses has increased and the sensitivity of analytical techniques has improved (see Section 1.5) the compositional differences used to distinguish between groups of glasses have reduced. Therefore the presence of inhomogeneity may have an even greater affect on any compositional groupings formed. A selection of published compositional studies of archaeological glasses from a range of different periods will now be discussed in Sections 1.4.1 and 1.4.2.

1.4.1 Compositional Analyses of Sodium Rich Glasses

The majority of published compositional data sets of archaeological glasses are of samples with a sodium rich composition. It will be seen that a wide range of elements and compositional differences are commonly used as grouping tools. However, in general the elemental differences used to discriminate between groups of glasses with sodium based compositions are significantly smaller than those used for potash based glasses (see Section 1.4.2). A number of compositional studies illustrating these points will be discussed below.

The composition of second millennium BC glass from Egypt and the Middle East has been investigated by a number of authors (Henderson 2000). Elemental data has been used to infer possible sources of raw materials (Sayre and Smith 1974, Shortland and Tite 2000) and production centres (Nicholson *et al.* 1997, Vandiver, 1983, and Vandiver, *et al.* 1991). A large compositional study of Egyptian and Mesopotamian glass was carried out by Lilyquist *et al.* (1993) using energy dispersive X-ray spectroscopy (EDS, see Section 1.5). Lilyquist *et al.* (1993) analysed a selection of Egyptian, pre-Malkata glasses and compared the data with analyses of glass from Malkata and Amarna, in Egypt, and Nuzi in Mesopotamia. Graphs of the normalised data for the weight percents of Na_2O versus CaO, K_2O versus MgO, Al_2O_3 and versus SiO_2 were used to determine differences in the four glass types. The difference in composition between cobalt blue and non-cobalt containing glasses throughout the total assemblage was also examined.

Lilyquist *et al.* (1993: 41) noted that the Nuzi and Egyptian glasses had a similar HMG soda-lime-silica composition, consistent with the use of plant ash as an alkali source. The mean concentrations of CaO, K_2O, MgO and Fe_2O_3 for the Nuzi glasses (which were all non-cobalt glasses) were also similar in composition to the pre-Malkata non-cobalt glasses. They noted that all the cobalt containing glasses contained greater than 1.2% Al_2O_3, and less than 2% K_2O, and the majority of the Egyptian and Mesopotamian non-cobalt glasses that were analysed contained higher levels of both of these elements. Lilyquist *et al.* (1993: 41) suggested that the difference in composition between the cobalt and non-cobalt containing glasses may be due to the use of two different recipes. They suggested that these glasses would therefore have been produced separately from each other, either within the same workshop or from a different production area. However, there are a number of cobalt and non-cobalt glasses that have aluminium and potassium concentrations that lie close to these cut of points (for example, less than ±0.2%) (Lilyquist *et al.* 1993: 57-8). Therefore if inhomogeneity was present that influenced the concentrations of these elements even in small amounts, this might account for the apparent differences in composition rather than this being the result of a different production area or workshop.

Another relatively large scale compositional investigation of archaeological glass has been carried out by Henderson (1979, 1982, 1987a, 1987b, 1991), and Henderson and Warren (1981) on British, Irish and European Iron Age beads. In these studies, compositional data was used to establish chemical groupings from which it could be inferred whether specific bead classes were made from different materials and therefore in specific locations.

Henderson (1991) investigated beads containing blue soda-lime-silica glass from Early Iron Age contexts at Wetwang Slack, North Humberside, and found that the cobalt and iron concentrations did correlate with different bead classes (Guido 1978). He suggested that these elemental differences were related to the original cobalt mineral used as a colourant. Therefore different bead types could be attributed to different workshops or the use of specific recipes for each bead class if made within the same workshop. Henderson (1991) then widened his study to include beads from later Iron Age contexts and wider geographical areas including Wales, Scotland and the Continent. He concluded that the type of cobalt colourant used changed between the third and second centuries BC and correlated with the rise in oppida in Europe during same period. The difference between these groups of glasses is based on small differences in the levels of cobalt (less than 0.1Wt.% CoO) and iron (less than 1Wt.% Fe_2O_3).

It can be seen that in this case the elemental differences used to distinguish between groups of glasses are small and based on elements linked to colourants in the glass. Although it is not known whether inhomogeneity particularly influences specific elements (see Section 8.4), the use of small elemental variations between groupings is important to note as these may be significantly influenced by the presence of inhomogeneity.

The evolution of glass technology over the 1st millennium AD has been also been investigated using compositional studies, such as those by Hunter and Heyworth (1998), Sanderson and Hunter (1980), and Sanderson *et al.* (1984). These studies covered a large number of different vessel types, from different sites and periods. Analyses of funnel beaker fragments excavated from Helgö, Sweden; Dorestadt, Holland, and Hamwic (Southampton), England, by Hunter and Heyworth (1998), and Sanderson *et al.* (1984) determined that there was a relationship between composition and the origin of the samples. The main elements used to distinguish between the groups were sodium: (Wt.% Na_2O: H13.2±2.1, D14.9±1.7, He16.9±2.2); magnesium (Wt.% MgO: H0.7±0.3, D0.9±0.4, He1.2±0.4); calcium (Wt.% CaO: H7.91±1.07, D10.23±2.22, He8.25±0.16); and manganese (Wt.% MnO: H0.49±0.2, D0.74±0.17, H 0.93±0.18) (H=Hamwic, D=Dorestadt, He=Helgö) (Hunter and Heyworth 1998: Table 6). It can be seen that if the elemental ranges are considered, in a number of these elements there is a continuum in the compositions of the different groups of glasses. Therefore it is again possible to see that if inhomogeneity were present in the glass samples analysed, it would not have to cause a large difference in composition before effecting an apparent difference in the sample groupings.

Compositional analysis has also been used to group sodium based glasses from later dated sites. Henkes and Henderson (1998) investigated the distribution of a variety of spun-stem *roemers* dating to the 16th-19th centuries excavated from sites in the Low Countries. They noted that no fragments of this type of vessel had ever been excavated from the major traditional *Waldglas roemer* production sites in Germany. It was noted that the spun-stem *roemers* were different in colour and stem design to the more common *Waldglas roemers.* EPMA analysis (see Section 1.5) was used to determine whether a difference could be observed between the three types of spun-stem *roemer*, and *Waldglas roemers.* The results showed that the spun-stem *roemers* did contain significantly more sodium (greater than 10Wt.% Na_2O) than the *Waldglas roemers* (less than 5Wt.% Na_2O). The spun-stem *roemer* composition was therefore characteristic of glass produced in the Low Countries at this time (Henkes and Henderson 1998: 103). In comparison to the analyses of earlier dated glass discussed at the beginning of this section, it can be seen that the compositional differences used to form these groupings are significantly larger. Therefore even if inhomogeneity were present in these samples, it might be less likely to cause a significant bias in the results.

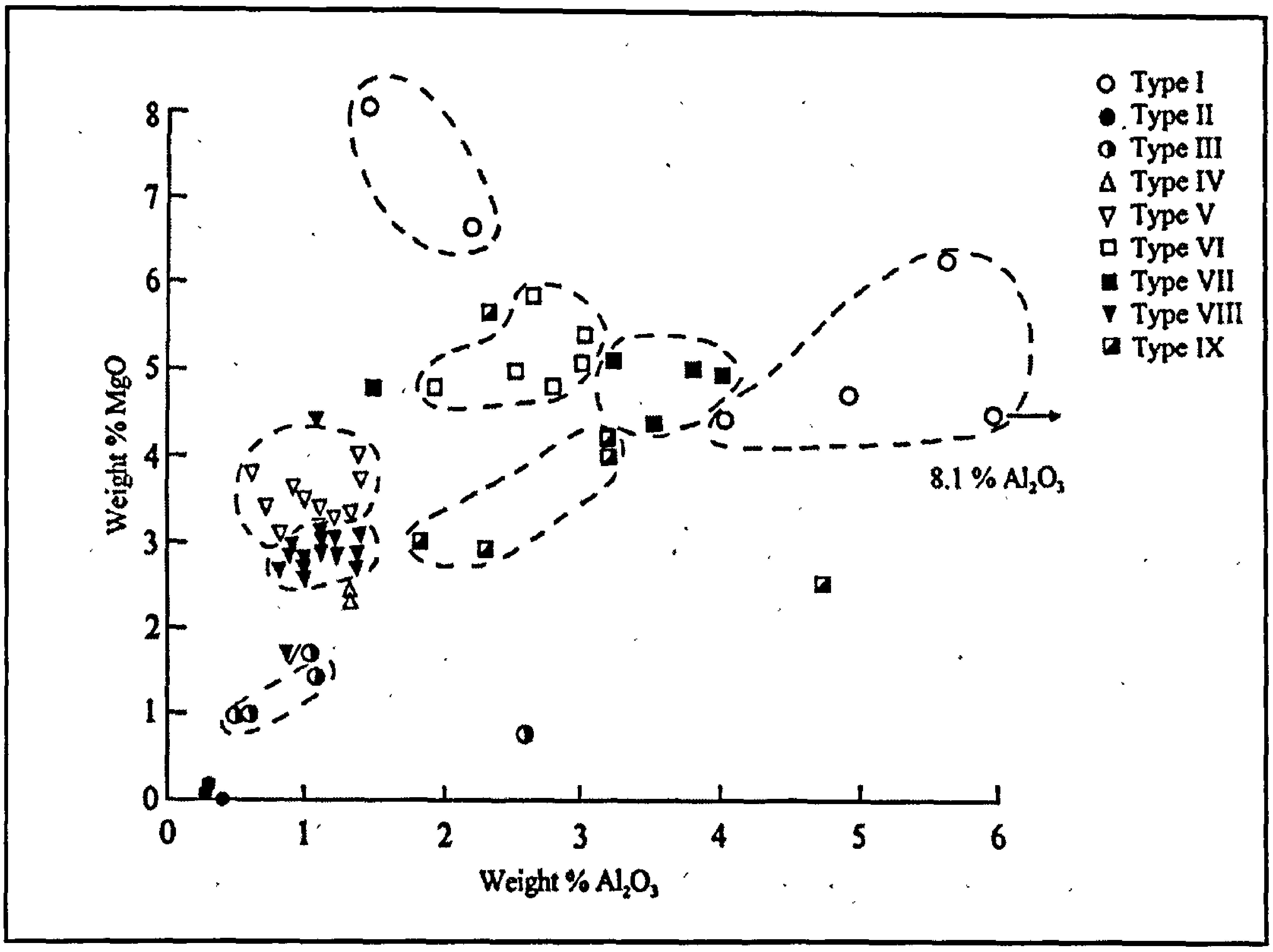
A number of compositional studies of later dated sodium based glasses have examined the difference between the composition of Venetian glasses and those made in the '*façon de Venise*' (Bronk *et al.* 2000, De Raedt *et al.* 2000, Pause 2000, Verità 1985). Bronk *et al.* (2000) used chemical analysis (EPMA and XRF, see Section 1.5) to distinguish between the two types produced during the 16th and 17th centuries. Bronk *et al.* (2000) compared the compositions of glass from the Lido di Venezia, the Rijksmuseum, Amsterdam, and published analyses of comparative material. The Lido di Venezia material was well documented as being of Venetian provenance. The analyses were compared to published data by plotting a graph of $CaO/(Na_2O+K_2O+CaO+MgO+P_2O_5)$ against $Na_2O/(Na_2O+K_2O+CaO+MgO+P_2O_5)$.

Bronk *et al.* (2000) placed the Lido glasses into two main groups based on analyses of '*vitrum blanchum*' glass (approximately 0.275-0.4 on the CaO axis and 0.375-0.5 on the Na_2O axis) or '*cristallo*' (approximately 0.125-0.25 on the CaO axis and 0.55-0.7 on the Na_2O axis) soda ash as a raw material. *Cristallo* glass was so called as it resembled rock crystal and was made from leached soda ash, whilst *vitrum blanchum* glass was not of such high quality and was made with unleached soda ash (Verità 1985). Bronk *et al.* (2000) suggested that the analyses of two glasses that fell in between these two groupings were made from a mixture of the two alkali sources. It can again be seen that the elemental differences between these different groupings are small, and therefore if inhomogeneity were present it might also account for these differences (see Section 9.2).

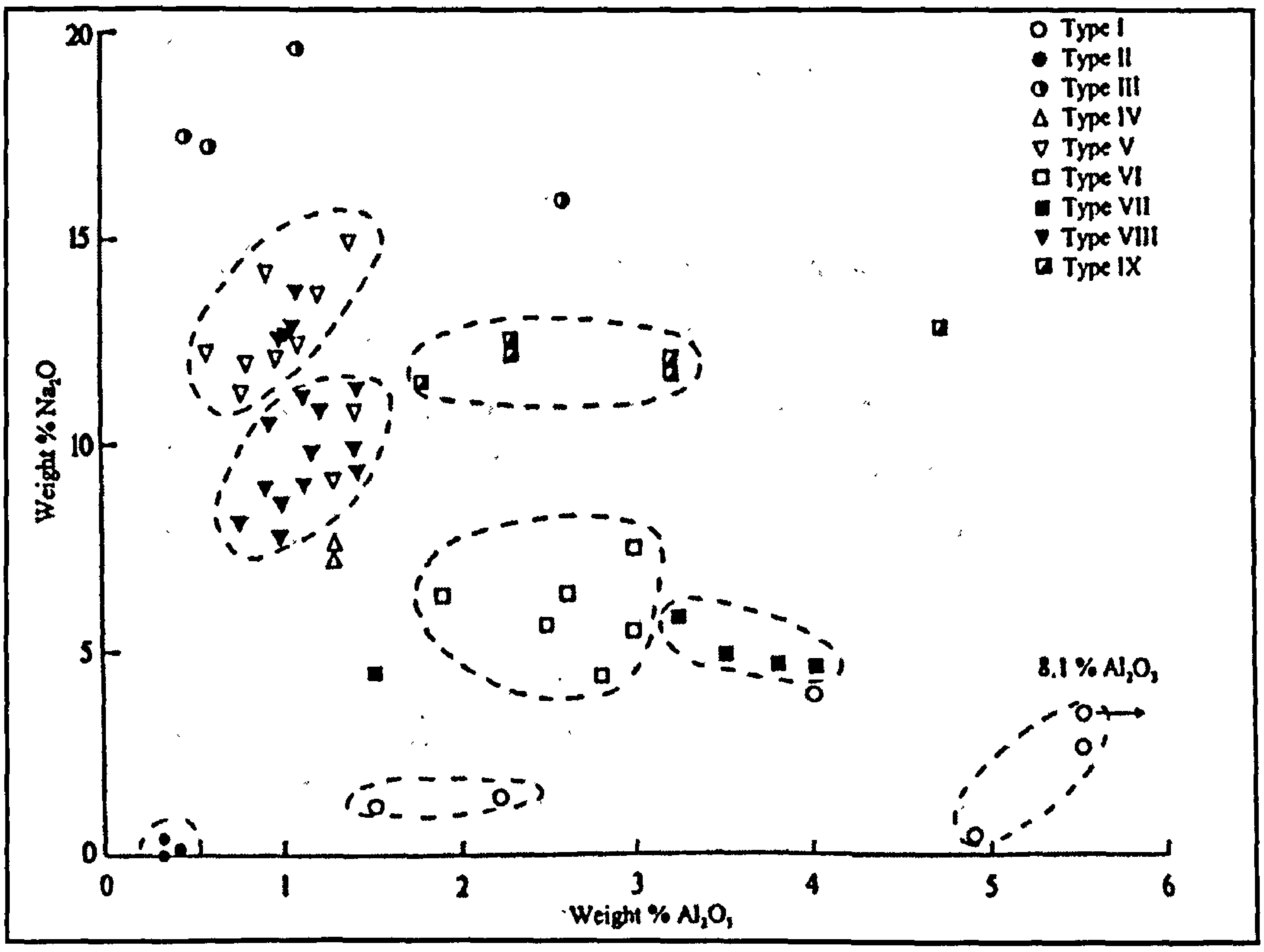
Henderson (1998, 2000) compared the analyses of 16th and 17th century beaker and goblet fragments from Lincoln. The origins of the vessels had been suggested using typology to be Italy, the Low Countries, northern and southern England. The aim of the analyses was therefore to determine whether a link could be established between composition and the suggested vessel sources, and also to infer the possible raw materials used in production of these glasses. Henderson (1998: 44) formed six main glass groups based on the sodium, potassium, calcium and lead contents of the samples analysed. The main soda-lime-silica group also contained four sub groupings (Type III, V, VIII and IX, see Figure 1:1). He used graphs of magnesia against alumina, and soda against alumina to illustrate differences between the four different glass types, and these are illustrated in Figure 1:1 (Henderson 1998: Figure 7, Henderson 2000: Figure 3.52).

Henderson (2000) noted that the difference in composition between the four types was related to the impurities contained in the raw materials. Elevated alumina levels from the sand source, and increased magnesia from a soda based plant ash. Combining the results of the compositional analysis with the typology study of the vessel fragments Henderson (1998, 2000) suggested that Type III were Venetian *cristallo* glasses made from high purity sands and raw materials. He suggested that the Type V glass was made in the *'façon de Venise'* style in the Low Countries, Type VIII glass were English drinking glasses, and Type IX was Flemish. This was confirmed by the similarity in composition to the spun-stem *roemers* discussed by Henkes and Henderson (1998) (see above). It can be seen in Figure 1:1, that although there are distinct compositional differences between a number of the different groupings, there is a continuum between some groups. Therefore the presence of inhomogeneity may cause samples to fall into different groupings (see Section 9.2).

The examples illustrated in this section have shown that a variety of different elements are used as grouping tools in sodium based glasses, and that in the majority of cases, the differences in elemental concentration used to distinguish between glass groupings are relatively small. Therefore the presence of inhomogeneity may be more likely to cause a significant bias in the results obtained (see Section 9.4). Compositional studies of potash rich 'medieval' type glasses will be discussed in Section 1.4.2.



Wt.% MgO against Wt.% Al_2O_3 (Henderson 2000: Figure 3.52)



Wt.% Na_2O against Wt.% Al_2O_3 (Henderson 1998: Figure 7)

Figure 1:1 Elemental groupings for Late 16th-17th century Lincoln Glass (Henderson 1998: Figure 7, Henderson 2000: Figure 3.52)

1.4.2 Compositional Analyses of Potash Rich Glasses

In comparison to the large number of published analyses of sodium based archaeological glasses (see Section 1.4.1), the available information on potash rich 'medieval' type glasses is small. Many studies of potash rich glasses use ratios of elemental concentrations (in particular, sodium, potassium, calcium and magnesium) to form groupings that discriminate between different sites and/or time periods. The groupings are based on the assumption that raw materials vary with production location and time period, and therefore different glass compositions can be linked to specific manufacturing locations and dates. For example, Kuisma-Kursula and Räisänen (1999), and Kuisma-Kursula *et al.* (1997) have carried this out on a broad scale in their analyses of European medieval glass. Foy (1977), Barrera and Velde (1989), Mortimer in Welch (1997), and Marquis *et al.* (2000) have examined glass over smaller geographical areas. These studies used compositional groupings to determine whether glasses were made locally or imported, and to ascertain how raw materials and technologies in localised areas have evolved over time.

A number of studies of medieval glasses have also used compositional analyses to infer information on possible raw material sources. These include studies of German glass by Gerth *et al.* (1998), Hartmann (1994), and Wedepohl (1997) where elemental concentrations and ratios have been related to the use of specific plant ashes as alkali sources. As with the sodium based glasses discussed in Section 1.4.1, the influence of inhomogeneity on the compositional study of medieval glass will depend on the compositional tolerances and the specific elements used to form groups. A number of published compositional studies of medieval glasses that illustrate these points will now be discussed.

The composition and typology of French glass was investigated by Barrera and Velde (1989), who studied over 500 fragments of French blown glass with known dates (10^{th}-18^{th} centuries AD) and geographical locations. They formed compositional groupings based on variations in potassium, calcium and sodium concentrations. The 'sodic' group contained glasses with greater than 6Wt.% Na_2O. The 'calcic' group was based on a $CaO+K_2O$ value of 30±1Wt.% with a $CaO/(CaO+K_2O)$ ratio of equal to 0.7 or above and a sodium content of less than 1Wt.%. In contrast the 'calco-potassic' group contained glasses that contained greater than 22 Wt.% $CaO+K_2O$, a $CaO/(CaO+K_2O)$ ratio of 0.4-0.6, and a sodium content of greater than 1Wt.% and less than 4Wt.%. These groupings were then used to correlate glasses from different time periods with different regions of production. It can again be seen that the compositional differences used to differentiate between these groups of glasses are larger than those frequently used in studies of sodium based glasses (see Section 1.4.1). However, the extent to which inhomogeneity may influence glass composition is not yet known, and the influence of inhomogeneity on this type of study will be discussed further in Section 9.3.1.

Marquis *et al.* (2000) investigated the transition in medieval stemmed glass tableware from northern and central France during 15th and 16th centuries. They analysed approximately 50 samples using EPMA (see Section 1.5), and categorised glasses using the compositional groupings developed by Barrera and Velde (1989) described above. However, in addition to the 'calcic' and 'calco-potassic' groups they had two sodium based groups, a 'low sodium' group (less than 10Wt.% Na_2O) and a 'high sodium' group (greater than 10Wt.% Na_2O). The potential influence of inhomogeneity on these groupings will therefore be similar to those seen in Barrera and Velde (1989) discussed above.

Mortimer in Welch (1997) examined glass from the glassmaking site at Little Birches, Staffordshire (see Section 7.3.1). The results of SEM-EDX analysis (see Section 1.5) determined that the majority of the Little Birches samples exhibited a similar chemical composition, with an approximate standard deviation for the group of less than ±0.5% for Na_2O, MgO, Al_2O_3, and P_2O_5, and ±1.5 for K_2O and CaO. She distinguished between glasses from this group and imported cullet by the increased levels of lime and lower total alkali (Na_2O+K_2O) concentrations found in the latter. Mortimer in Welch (1997: Figure 18) also used a plot of $CaO/(CaO+K_2O)$ against Na_2O (as used by (Barrera and Velde 1989), see above) to demonstrate the differences in alkali and lime ratios between the Little Birches glass and glass from other comparative English medieval glass production sites. Again these groupings are broader than those seen in the compositional studies of sodium glasses in Section 1.4.1. Therefore the influence of inhomogeneity on these types of groupings may not be so significant. However, the extent to which inhomogeneity influences glass composition is not yet known and this study will be discussed further in Section 9.3.2.

Medieval glass production in Germany has been investigated by Gerth *et al.* (1998), Hartmann (1994), and Wedepohl (1993, 1997: 247, 2000). Wedepohl (1993, 1997: 247, 2000) analysed a large number of fragments of German glass from a wide range of contexts. He has suggested that the transition of German medieval glass manufacture can be split into three main stages based on the levels of calcium, potassium and sodium in the glass:

1. Replacement of soda based glass by early woodash (potash based) glass at the start of the Carolingian period.
2. A major period of wood ash glass from 1000-1400AD.
3. The introduction of woodash-lime glass beginning at approximately 1300AD. In comparison to wood ash glass, this glass type contains reduced potassium and increased calcium levels.

Although the groups listed above are defined by differences in composition, they are based on relatively large compositional differences of several percent or more. It may therefore be possible that the presence of inhomogeneity may be less likely to have a significant influence on these types of groupings.

The studies discussed this Section and Section 1.4.1, have only covered a small sample of the large number of published compositional studies of archaeological glasses. It can be seen that the combination of elements used to form groupings is varied and depends on the nature of the glass being investigated and the archaeological question being asked. However, compositional studies of medieval potash based glasses are predominantly concentrated on the values of potassium, calcium, sodium and magnesium. Differences in the concentrations of these elements and elemental ratios (particularly for potassium and calcium) are commonly used as grouping tools.

What is important to remember, is that the elemental tolerances used to differentiate between groups of archaeological glasses have become progressively smaller (see Section 1.4.1). Therefore the presence of inhomogeneities (see Section 1.2) even on a small scale may have a significant influence on the compositional results and therefore introduce bias into any groupings formed. The degree to which inhomogeneity will affect the results of compositional analysis will also be influenced by the analytical method used to collect the data. This will therefore be discussed in Section 1.5.

1.5 The Choice of Analytical Technique and the Effects of Inhomogeneity

The impact of inhomogeneity on compositional analysis will alter depending on the technique used to acquire the data. Different analytical methods require specific sample sizes and analysis areas, and therefore with respect to homogeneity the following issues must be considered:

1. The possible orientation of inhomogeneities within the sample.
2. The size of inhomogeneities within the sample.
3. The size of the sample used for analysis.
4. The area of the sample selected in (3) that is actually analysed.
5. The resolution, accuracy and precision of the analytical technique.

Inhomogeneities tend to form in specific orientations, and are frequently found to run in parallel lines that align with the glass surface (Cable 1970: 95, Cable and Bower 1965, Cox and Ford 1989).

Figure 1:2 is a schematic representation of an inhomogeneous glass where the dark and light bands represent regions of different compositions. Lines ‘A’ and ‘B’ represent two different directions in which the glass could be sampled. If a section of the glass is removed along line ‘A’, this is in the same direction as the inhomogeneities run. The surface of the glass sample (Sample A) is therefore less likely to contain as many inhomogeneities as Sample B removed along line ‘B’ perpendicular to the direction in which the inhomogeneities are aligned.

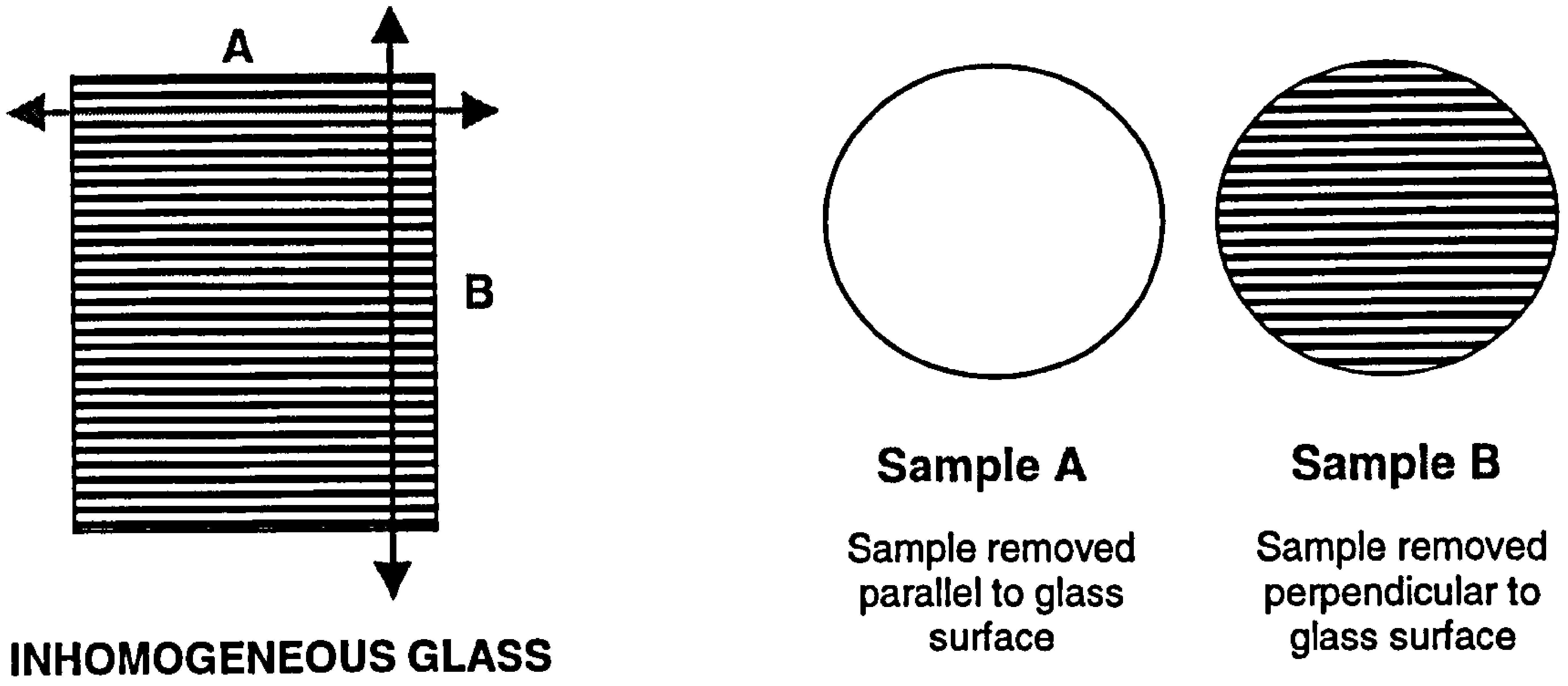
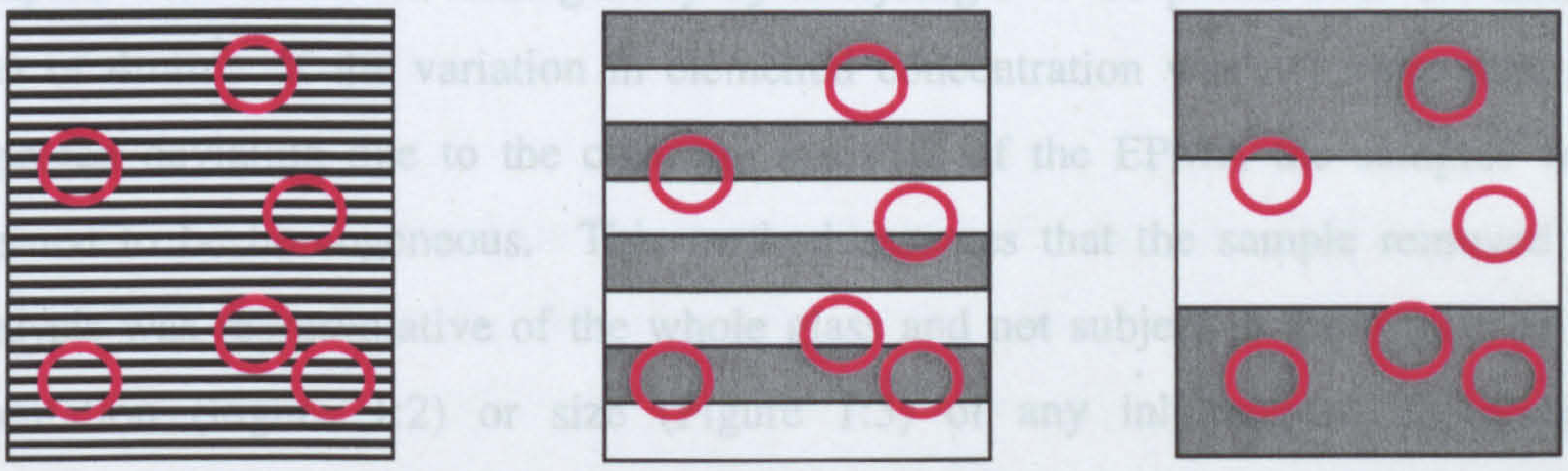


Figure 1:2 A schematic representation of an inhomogeneous glass illustrating how the orientation of the inhomogeneities and of the sample will affect the number of inhomogeneities present on the sample surface

Sample orientation is only a consideration for analytical methods that evaluate the surface of the glass. Techniques that obtain a bulk chemical composition using the sample in solution or powdered form will be less affected by inhomogeneity orientation if the sample size is greater than the pattern of inhomogeneities.

The effect of altering the sample size removed from an inhomogeneous glass is illustrated in Figure 1:3 (adapted from (Cable and Hakim 1973: Figure 1)). This schematic representation shows three inhomogeneous glasses each with different sized inhomogeneities (represented by dark and light bands). The red circles correspond to the sample area to be removed.



GLASS A	GLASS B	GLASS C
Sample size much larger than thickness of inhomogeneities	Sample size approximately equal to thickness of inhomogeneities	Sample size smaller than thickness of Inhomogeneities

Figure 1:3 A schematic representation of the effect of sample size in an inhomogeneous glass (adapted from (Cable and Hakim 1973: Figure 1))

It can be seen from Figure 1:3 that to obtain a sample that is representative of the bulk glass composition, the sample area should be **significantly larger** than any inhomogeneities present (Glass A). A reduction in sample size will mean that the glass is likely not to be representative of the whole material (Glass B), the chances of this occurring are increased as the sample size is decreased further (Glass C). What is also important to remember is that the area sampled is not necessarily the same size as the area analysed. Although the sample size in Glass A is most likely to remove material that is representative of the whole glass, if the area analysed is much smaller than the inhomogeneities present then the data obtained will **not** be representative of the mean composition of the glass (e.g. Glass C). Therefore it is the ratio of the size of the sample area analysed to the size of the inhomogeneities that is significant.

In addition, the presence of inhomogeneities in a sample becomes significant only when their compositional variability is larger than the inherent statistical deviation in the measured data. The resolution, precision and accuracy of the analytical technique must therefore also be considered, as more sensitive methods may be more significantly influenced by inhomogeneity. In their compositional study of medieval French glasses Barrera and Velde (1989: 102) state that the samples were tested for homogeneity by analysing 5 to 10 points over the sample area of $4mm^2$. If the variation in elemental concentration was not more than the expected deviation due to the counting statistics of the EPMA the samples were deemed to be homogeneous. This method assumes that the sample removed for analysis was representative of the whole glass and not subject to the effects of the orientation (Figure 1:2) or size (Figure 1:3) of any inhomogeneities present. However, it should be noted that this would be difficult to quantify.

In view of the issues discussed above it would appear that to avoid problems of inhomogeneity and obtain a mean calculation of composition, analytical techniques that use as large a sample as possible and require the sample to be in solution or in powder form would be best. However, to the archaeologist, techniques that use **smaller** samples that require **less** destruction of the artefact are frequently necessary. The considerations that are usually made when choosing a method for analysis of archaeological glass are, but not necessarily in this order:

- Sample size.
- Destruction of the artefact.
- Accuracy and precision of results.
- Limits of detection.
- The elemental suite required.
- Cost, speed and availability of analysis.

Analytical methods used in compositional studies of archaeological glass predominantly fall into two main categories:

a) Techniques that use the visible (or near visible) region of the spectrum, such as optical or atomic emission spectroscopy (OES/AES), atomic absorption spectroscopy (AAS) and inductively coupled plasma emission spectroscopy (ICP-AES).

b) Techniques that use X-rays, such as energy dispersive X-ray fluorescence analysis (XRF), analytical scanning electron microscopy (SEM-EDS/WDS), electron probe microanalysis (EPMA) (sometimes referred to as 'electron microprobe analysis' (EMPA) or a 'probe'), and particle induced X-ray emission (PIXE) (Henderson 2000: 20, Pollard and Heron 1996: 20).

Early compositional studies such as those by Bezborodov (1957), Geilmann *et al.* (1955), Turner (1956a, 1956c) (see Section 1.3) were predominantly carried out using OES or AES. OES provided multi-element analysis but was gradually replaced by AAS, which improved accuracy and precision but increased analysis times, as only single element analysis was possible and complex sample dissolution was required (Hughes *et al.* 1976). Typical sample sizes required for AAS range from 2-10mg (Hughes *et al.* 1976: 19), whilst Hatcher *et al.* (1995: 85) suggest approximately 25mg of glass. Examples of AAS analyses from a broad range of different glass types can be found in Brill (1999a, 1999b).

More recently AAS has been superseded by ICP-AES and examples of studies on Roman glasses using this method can be seen in Baxter *et al.* (1995), Jackson *et al.* (1991a, 1991b), and Mirti *et al.* (1993). Although sample dissolution is still required, ICP-AES has the advantage of multi-element analysis combined with increased accuracy, precision and a larger elemental suite that includes major, minor and trace elements (Hatcher *et al.* 1995, Heyworth *et al.* 1988). Typical sample sizes required for ICP-AES are 100-150mg (Jackson *et al.* 1991a: 77, Mirti *et al.* 2000: 361). Further developments have led to the introduction of inductively coupled plasma mass spectroscopy (ICP-MS) which enables both the chemical composition and isotopic ratios of a sample to be obtained. Laser ablation has also recently been added to this system (LA-ICP-MS). This highly sensitive method does not require sample dissolution and uses a laser to volatilise a small section (approximately 50µm in diameter and depth) from the surface of the sample (Gratuze *et al.* 1993, Gratuze *et al.* 1997). However, this therefore means that the same point cannot be reanalysed (Henderson 2000: 10).

X-ray based analytical techniques are also widely used in the compositional study of archaeological glasses. The major advantages to the archaeologist is that, in comparison to the emission/absorption methods described above, X-ray techniques can be used for non-destructive testing, whilst enabling analysis to be carried out at the micron or sub-micron level (Reed 1996, Verità and Toninato 1990). Where a sample has to be removed for analysis (for example, if the specimen is too large to fit in the sample chamber) only millimetre (or less) sized fragments are required, but the area required for analysis can be significantly smaller than this (Henderson 1988: 78).

Probably the most common techniques used to analyse archaeological glass today are XRF, SEM-EDS/WDS and EMPA (see Section 3.2.5). XRF analyses generally require a larger analysis area than SEM or EPMA. For example, to obtain data to establish compositional groupings in British iron age beads Henderson and Warren (1981: 83) carried out XRF analyses using an analysis area of 2mm, whilst the analysis area used by Sanderson *et al.* (1984: 55) to investigate 1st millennium British glass was a 3x4mm ellipse. In contrast to this, Henderson (1988: 79) used analysis areas ranging from 65-80µm diameter spots for his EPMA study of mixed alkali glasses, and EPMA analyses of French medieval glasses by Barrera and Velde (1989: 102) were obtained from analysis areas 20µm in diameter. The penetration depth of the electron beam for analytical SEM is approximately 30-50µm whilst in EPMA a much smaller layer of material is penetrated (approximately 3-5µm) (Henderson 2000: 17).

Published analyses of archaeological glasses using PIXE are less common than those carried out using XRF, SEM or EPMA. This may be due in part to the expense and availability of the equipment, but a number of medieval glasses have been analysed using this method (Kuisma-Kursula and Räisänen 1999, Kuisma-Kursula *et al.* 1997). PIXE is a very sensitive technique, capable of detecting low elemental concentrations. It is capable of analysing similar sample sizes as SEM or EPMA, and has a beam penetration of approximately 50µm (Henderson 2000).

In addition to the analytical techniques discussed above, neutron activation analysis (NAA) should also be mentioned. This technique usually requires a powdered sample (approximately 10-20mg (Frána *et al.* 1987: 72)) that is then irradiated, but can be carried out on a whole sample (Hancock *et al.* 1994). Elemental composition is determined by measurement of the speed of radioactive decay. The technique is extremely sensitive, accurate and precise and provides simultaneous measurement of a number of trace elements. It has been widely used for the analysis of archaeological ceramics (Buxeda I Garrigós *et al.* 2001, Hughes *et al.* 1991) and other siliceous materials such as faience (Aspinall *et al.* 1972). NAA has also been used for a number of studies of archaeological glasses. These include analyses of Bohemian glasses by Frána *et al.* (1987) and Mastalka and Venclova (1987), a provenance study of medieval Bulgarian glasses by Kuleff *et al.* (1985), and analysis of 16th-17th century North American trade beads by Hancock *et al.* (1994).

In summary it can be seen that with the introduction of new methods of analysis sample sizes have decreased whilst accuracy, precision and detection limits have increased. What must be remembered is that if the glass is not homogenous the use of small sample will increase the possibility of a significant bias in the results. The increasing popularity of obtaining compositional data from techniques such as SEM and EPMA, which analyse minute areas of glass means that it is imperative that the homogeneity of archaeological glasses now be assessed.

1.6 Research Aims

The aims of this research can be summarised as follows:

1. To determine which factors in the glassmaking process influence the formation of inhomogeneity.
2. To investigate the variables identified in (1) through the laboratory replication of medieval potash based glasses.
3. To determine the extent of inhomogeneities present in medieval glasses by an analytical investigation of comparative archaeological material.
4. To compare the results from (2) and (3) to establish how inhomogeneities are likely to have been formed.

5. To determine the effects that inhomogeneities may have on the way in which archaeological glasses are studied.

The archaeological material selected for this research is potash based glass produced in northern Europe during the 12th to early 17th centuries, and therefore encompasses both the medieval and post medieval periods. The transition between the two occurred during 16th century and has been assigned to a variety of dates (Gaimster and Stamper 1997: ix). For ease and simplification the term 'medieval' will be used in this thesis to refer to the whole period under study.

In northern Europe, the start of the medieval period saw a high demand for ecclesiastical glass combined with a limited availability of soda based (sodium rich) alkalis, such as *natron* (mineral hydrated sodium carbonate Na_2CO_3. 10 H_2O) (Newton and Davison 1989:56, Singer *et al.* 1979: 259-60). As a consequence of this, glassworkers are thought to have moved into forested areas in search of fuel, and potash rich plant ashes (such as beech and bracken ash) were utilised as alkali sources (Hunter 1981).

Medieval, potash based glasses have been selected for this research for the following reasons:

- There is textual evidence that gives information concerning raw materials and medieval glassmaking practices that is not seen in earlier periods (see Section 2.1.1). Therefore we know what was used when compared to glasses from earlier periods.
- A number of different plant species may have been used as alkalis in medieval glassmaking. These are very varied in composition and may therefore be more likely to exhibit different degrees of inhomogeneity (see Section 2.2.2).
- The excavated archaeological evidence for medieval glass production sites is more prevalent than in earlier periods (see Section 2.1.1) and therefore comparable material of known provenance is available.
- The raw materials for experimental replication can be obtained relatively easily and in quantity (see Section 4.3).

In order to determine which factors in the glassmaking process influence the formation of inhomogeneities the medieval glassmaking procedure must therefore be examined in detail. This is the objective of Chapter 2 where studies on homogeneity will be combined with archaeological and textual evidence for medieval glass production. The aim is to highlight the factors that are likely to exert the strongest influence on homogeneity. The results will be used to select which variables will be investigated in the experimental part of this research.

Prior to the production of any experimental glasses it is necessary to decide on a suitable methodology. This is set out in Chapter 3 and covers in detail aspects such as the preparation and selection of raw materials, crucibles and furnaces. In addition to this, a method of visually recording and interpreting the experimental frits and glasses is outlined. This is essential to ensure that the results obtained are consistent and can therefore be reliably compared to one another. Chapter 3 ends with a discussion of the established and traditional methods used for measuring homogeneity. This is an area that has primarily developed through the needs of the modern glass industry. Therefore, to select an appropriate method for archaeological glass we need to consider the additional limitations such as sample size and destruction. In addition to this, the method must provide both qualitative and quantitative results. This is vital to be able to relate the results of this work to the study of archaeological glass (see Section 1.3).

The laboratory replication of medieval glasses forms a large part of this research and is broken down into three main themes: raw materials (Chapter 4), fritting (Chapter 5) and melting (Chapter 6). Each chapter builds on the results from the previous chapters and determines how homogeneity is affected by each variable in medieval glassmaking. The overall aim of these three chapters is to obtain an integrated picture of how homogeneity is affected by the combination of all of these processes. The extent of homogeneity in the experimental glasses is determined qualitatively and quantitatively to ascertain:

- If inhomogeneity is present that is not visible to the eye.
- If the inhomogeneities are present, whether they will have a significant effect on measured glass composition (see Section 1.3).
- If certain elements exhibit more inhomogeneity than others in the glass.

- If certain glassmaking practices exert more of an influence on homogeneity than others.

The archaeological material selected for this research is from the medieval glassmaking areas of West Surrey/Sussex Weald (Kenyon 1967) and Staffordshire, England (Welch 1997), and Hils, near Grünenplan, Germany (Six 1976). The sites in these areas cover the period from 12th-17th century, and exhibit a wide range of glassmaking traditions. Chapter 7 discusses the background to this material, and why it is likely to represent different levels of inhomogeneity based on the findings of Chapters 2, and 4-6. Chapter 8 covers the analysis of the archaeological material and the results are discussed with respect to the evidence in Chapter 7.

Chapter 9 draws together all of the information on homogeneity gathered in the previous chapters and discusses the implications of this on a) the analysis and interpretation of compositional data from medieval glasses and b) medieval glassmaking practices. Finally the conclusions and further work based on the ideas and results produced during this research are presented.

CHAPTER 2

How the Variables in Medieval Glass Making Influence Homogeneity

2.1 Introduction

This chapter examines the variables involved in medieval glass production and determines what effect they have on homogeneity. Medieval glass production was a complex, high temperature process that can be broken down into 5 main sections:

1. Raw materials
2. Fritting
3. Melting
4. Working
5. Annealing

The choices and variables involved in glass making are more complex than the basic outline given above. Figure 2:1 illustrates how each stage of medieval glass production is affected by many different parameters such as the composition of raw materials, furnace temperatures and crucible dimensions. Homogeneity is influenced by a combination of all of these factors and some have a more significant effect than others. This chapter examines raw materials, fritting and melting in detail and uses the findings to select suitable parameters for the experimental part of this research (see Chapters 4-6). Working and annealing will also be briefly discussed but will not be investigated experimentally as they are less likely to effect homogeneity (see Sections 2.5 and 2.6).

Evidence of medieval glassmaking practices (see Section 2.1.1) will be combined with studies of homogeneity in modern glasses. The following literature review therefore contains references to some industry related, laboratory scale experiments. The heavy industrial bias of this data is noted and caution exercised in its use with respect to medieval glassmaking.

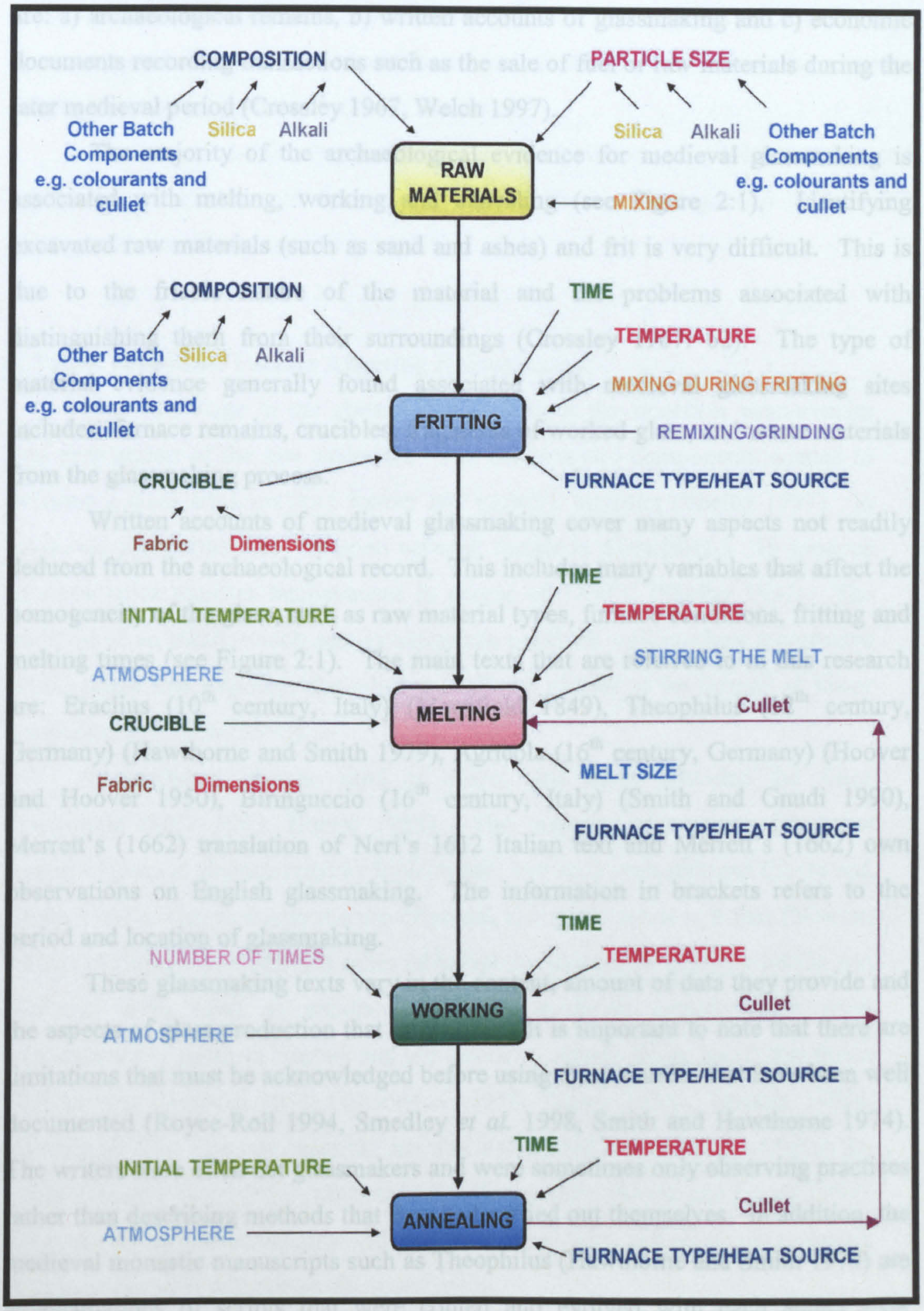


Figure 2:1 Factors affecting homogeneity at each stage of medieval glass production

2.1.1 Sources of Evidence for Medieval Glass Production Practices

The three sources of evidence for medieval glassmaking used in this research are: a) archaeological remains, b) written accounts of glassmaking and c) economic documents recording transactions such as the sale of fuel or raw materials during the later medieval period (Crossley 1967, Welch 1997).

The majority of the archaeological evidence for medieval glassmaking is associated with melting, working and annealing (see Figure 2:1). Identifying excavated raw materials (such as sand and ashes) and frit is very difficult. This is due to the friable nature of the material and the problems associated with distinguishing them from their surroundings (Crossley 1967: 62). The type of material evidence generally found associated with medieval glassmaking sites includes: furnace remains, crucibles, fragments of worked glass, and waste materials from the glassmaking process.

Written accounts of medieval glassmaking cover many aspects not readily deduced from the archaeological record. This includes many variables that affect the homogeneity of the glass, such as raw material types, furnace conditions, fritting and melting times (see Figure 2:1). The main texts that are referred to in this research are: Eraclius (10th century, Italy) (Merrifield 1849), Theophilus (12th century, Germany) (Hawthorne and Smith 1979), Agricola (16th century, Germany) (Hoover and Hoover 1950), Biringuccio (16th century, Italy) (Smith and Gnudi 1990), Merrett's (1662) translation of Neri's 1612 Italian text and Merrett's (1662) own observations on English glassmaking. The information in brackets refers to the period and location of glassmaking.

These glassmaking texts vary in the content, amount of data they provide and the aspects of glass production that they cover. It is important to note that there are limitations that must be acknowledged before using these sources that have been well documented (Royce-Roll 1994, Smedley *et al.* 1998, Smith and Hawthorne 1974). The writers were often not glassmakers and were sometimes only observing practices rather than describing methods that they had carried out themselves. In addition, the medieval monastic manuscripts such as Theophilus (Hawthorne and Smith 1979) are amalgamations of scripts that were copied and evolved with each author over centuries (Richards 1940). It is impossible to be certain if errors and omissions were made and these texts should therefore be used with care. However, even considering this they are a possible insight into the practices used in medieval glass production and this research makes use of these sources as they provide a starting point from which to work. Although the remit of this research is northern Europe (see Section 1.6) written texts from northern and southern Europe will be used. This is because documentary evidence is limited and there is a degree of correspondence between the practices described in texts from both locations.

Sections 2.2-2.6 therefore use a combination of documentary and archaeological evidence to discuss the factors affecting homogeneity in medieval glass production illustrated in Figure 2:1.

2.2 Raw Materials: Factors Affecting Homogeneity

The first stage in the glassmaking process is the selection, procurement and preparation of the raw materials. The fundamental components needed to produce a glass are a network former and network modifier (Shelby 1997). In medieval glasses the most common network former is silica (SiO_2). To produce vitreous silica requires temperatures in excess of 1700°C (Shelby 1997). The addition of an alkali, which acts as a network modifier, will produce a corrosive liquid phase that dissolves the silica and allows glasses to be formed at lower temperatures (Shelby 1997).

In medieval glasses, sand or quartz rich rocks provided the silica component (Brill 1963, Hunter 1985). The majority of northern European medieval glass is characterised by high potash, low soda compositions (Sayre and Smith 1967). This is due to the use of potash rich plant ashes as a flux (Newton 1980). Although the soda rich ashes of halophitic plants (for example barilla and rochetta) were used as alkalis during the medieval period, these were predominant in southern Europe and are therefore outside the scope of this thesis (Ashtor and Cevidalli 1983, Gerth *et al.* 1998, Turner 1956c, Zecchin 1997a, Zecchin 1997b). In some cases the ash was also treated before being added to the batch to form a '*salt*' (Neri (Merrett 1662), Biringuccio (Smith and Gnudi 1990). This research is concerned only with glasses formed from untreated raw materials and therefore salts will not be discussed here.

Lime (CaO) is also present in medieval glasses. It may have been added unintentionally, by the use of calcareous sands and lime rich plant ashes or intentionally, using limestone, dolomite, or ground up shells (Brill 1963, Henderson and Warren 1981). Together the combination of raw materials is called the *batch*.

2.2.1 Silica Sources

Medieval glassmaking texts suggest that sand and quartz pebbles were the main silica sources during this period, examples of this (in bold) are given in the following quotes.

> *'and a third part of* ***sand****, collected out of water, and carefully cleaned of earth and stones.'*
>
> Theophilus (Hawthorne and Smith 1979: 52, 53)

> *'Our Glass houses in London have a* ***very fine white sand*** *(the very same that's used for sand-boxes and scouring) from Maid-stone in Kent, and for Green-glasses, a* ***coarser*** *from Woolwich.'*
>
> (Merrett 1662: 261)

> *'****Stones*** *which are fusible, if they are white and translucent, are more excellent than the others, for which reason crystals take the first place. From these when pounded, the most excellent transparent glass* was *made in India.'*
> *'The second place is accorded to* ***stones*** *which, although not as hard as crystal, are yet just as white and transparent. The third is given to* ***white stones****, which are not transparent.'*
>
> Agricola (Hoover and Hoover 1950: 584, 585)

> *'When you would make fair, and fully perfect Crystal, see you have the* ***whitest Tarso****, which hath not black veins, nor yellowish like rust in it. At Moran they use the* ***pebbles*** *from Tesino, a stone abounding in that River.*
>
> Neri (Merrett 1662: 7)

An anonymous account of Venetian glassmaking dated to the early 14th/late 15th century also mention the use of hard white stones and pebbles from the rivers of Ticino and Adige in northern Italy (Jacoby 1993, Verità 1991). There is little archaeological evidence for silica sources (see Section 2.1.1). However, it has been suggested that glass waste containing fragments of white quartz pebbles from the glasshouses at Little Birches (14th and 16th century) (Welch 1997: 28) and Bagot's Park (16th century), Staffordshire (Crossley 1967: 63, Welch 1997: 28), may be evidence for the use of quartz as a raw material. White veined quartz from a local provenance was also found associated with the Monte Lecco glasshouse (15th/16th century), in the Genovese Appenines, Italy (Mannoni 1972). The descriptions of medieval glassmaking given in this section appear to suggest that there may be some geographical bias in the use of quartz rich stones in Italy compared with sand in northern Europe.

As can be seen from the quotes above, the source and quality of silica appears to have been an important issue to the medieval glassmaker, as this would affect the characteristics of the glass produced (D'Angelo 1976, Hawthorne and Smith 1979, Hoover and Hoover 1950, Merrett 1662). There is also documentary evidence describing the preparation of silica for glassmaking, such as grinding, washing and sieving. Examples of this (in bold) are given in the following quotes:

> *'Take then of the best Tarso, **pounded small**, and served as fine as flower,'*
>
> Neri (Merrett 1662: 7, 8)

> *'Now this sand must be **washed** from all it's unprofitable rerrestricity, and **forced**, and then this will make a white and good glass'*
>
> Neri (Merrett 1662: 18)

Washing the silica source and the use of high purity quartz rich pebbles instead of sand may have been a way of overcoming iron contamination. Glassmaking sands were (and still are) selected for their low iron concentrations but the presence of iron even at low levels (<0.5%) will impart a green tint to glass (Weyl 1951). The composition of the silica source would have depended on its origin. Sands often include feldspar and clay, both of which can attribute to the alumina and iron concentrations in the final glass and these may potentially influence homogeneity.

In addition to quality, it can be seen from the quotes above that silica particle size also appears to have been an important issue to the medieval glassmaker. In the 15th century, glassmakers in central Italy used pulverised pebbles formed by heating and quenching, or simply grinding the stone (Verità 1991). In 1423 a licence was granted to Stefano Michiel to supply nine metric tons of crushed pebbles to Murano glassmakers (Jacoby 1993: 75). Silica particle size is significant as it influences many aspects of the glassmaking process and will be discussed in detail in Section 2.2.1.1.

2.2.1.1 Silica Particle Size

To determine how silica particle size will influence homogeneity it is necessary to understand what happens during the melting process. Melting can be described in three stages (Plumat *et al.* 1963, Shelby 1997: 35):

1. The raw materials are heated to a temperature where they react and decompose. After the batch components have completely dissolved, the glass is said to be 'batch free'.
2. Evolved and trapped gases (such as seed and bubbles, see Section 1.1) are eliminated from the melt. The period taken to do this is known as 'refining time'. This starts during the melting process but will often continue after batch free time (Lyle 1945).
3. The melt continues to homogenise by diffusion until it becomes isotropic. In practice it would require extremely long times for this to happen unaided.

Stages 2 and 3 occur together until the melt is fully refined. The rise of bubbles and seed to the surface can aid homogenisation by turbulent mixing, if the melt is fluid enough to allow the bubbles to ascend. In small scale melts relatively rapid convection currents can move seed back into the melt, facilitating homogenisation but impeding refining (Plumat *et al.* 1963).

The particle size of the silica is important as if it is reduced then the batch free time decreases and the homogeneity of the glass will increase (Kreider and Cooper 1967). Assuming that there is no melting or batch segregation the most homogenous glass is therefore given by the smallest grain size. This has been documented in studies including those by Boffé and Letocart (1962), Cable (1958, 1960a, 1960b), Furuuchi (1959a, 1959b, 1959c), Ito and Uno (1955), Manring and Bauer (1964), Potts *et al.* (1944), and Tooley and Tiede (1944). In their work on soda-lime-silica glasses, Preston and Turner (1940) suggested that batch free time is inversely proportional to the sand grain surface area. From their work on soda-lime-silica glasses using a narrow range of sand grain sizes (776-65μm), Boffé & Letocart (1962) suggest that either the specific area or the size distribution of the particles could be the deciding factor for batch free time. They found that batches with a high proportion of the largest grains took longer to reach a batch free melt and it was therefore concluded that the size distribution of grains was the controlling variable (Boffé & Letocart 1962). This factor is also important when the comparative grain sizes of the other batch components are considered (see Section 2.2.3).

Small silica grain sizes are therefore beneficial in the production of a more homogeneous glass. However, grain size also influences refining time and this must be taken into consideration. If a melt is poorly refined it will contain large numbers of seed. Refining time is controlled by silica particle size since the seediness early in refining increases as the grain size decreases. Grain size affects the number, size distribution, and therefore, the refining rate (Cable 1958, 1960a, 1960b).

The finest sands although producing a very homogeneous glass with a fast batch free time, are therefore the most difficult to refine. Fine sand particles give rise to heavily concentrated fine interstices within the unmelted batch. When the batch begins to melt these gases (both atmospheric and those produced in the melt) are trapped as the particles begin to agglomerate and form many tiny bubbles (Shelby 1997: 39). Longer melt times and higher melt temperatures may facilitate the removal of these bubbles (see Sections 2.4.2 and 2.4.3) (Cable 1958, 1960a, 1960b). To avoid excessive refining periods a balance has to be achieved between refining time and batch grain size. The medieval glassmaker may have been more concerned with achieving a well refined, rather than homogeneous glass. Particle sizes and melt times would have therefore been probably chosen to optimise refining. However, inhomogeneity may have been an issue to the medieval glassmaker, as it would have made the glass difficult to anneal (see Section 2.6).

The shape and composition of the silica particles will also affect the way they react, which will affect homogeneity (Hlavác and Nademlynska 1969, Hrma 1982, Ito *et al.* 1954). Different silica sources such as water washed sands or crushed pebbles (see Section 2.2.1) may therefore influence homogeneity in different ways (Cable 1970).

2.2.2 Alkali Sources

Potassium rich plant ashes were the main alkali source in northern European medieval glass production. The term 'potash' is used to describe the ashes as well as the substance produced when the ashes are lixiviated (Rymer 1976). The main evidence for these alkali sources comes from written accounts of medieval glassmaking (see Section 2.1.1). A number of these texts refer to specific plants such as **beech** (*Fagus sp.*) by Theophilus (Hawthorne and Smith 1979: 52, 53) and **fern** (Polypodiaceae *sp.*) by Neri (Merrett 1662: 261) and Biringuccio (Smith and Gnudi 1990: 127). In addition to this, analyses of the ashes of modern versions of these plants have been used to extrapolate information about the types of plants being used by medieval glassmakers in different periods and locations (Wedepohl 1997).

Beech ashes are frequently associated with the production of northern European medieval glass, in particular German glass. This is due to the mention of beech (in bold), as both a flux and a fuel in the manuscripts of Theophilus (Hawthorne and Smith 1979) (see Section 2.1.1).

> *'If you have the intention of making glass, first cut many* ***beechwood*** *logs and dry them out. Then burn them in a clean place and carefully collect the ashes, taking care that you do not mix any earth or stones with them.'*
>
> Theophilus (Hawthorne and Smith 1979: 49)

> *'take* ***beechwood*** *logs completely dried out in smoke, and light large fires on each sides of the bigger furnace. Then take two parts of the ashes of which we have spoken before'*
>
> Theophilus (Hawthorne and Smith 1979: 52)

The manuscripts of Eraclius (Merrifield 1849) mention the use of glasses produced from *'faina'*. Merrifield (1849: 212) suggests that these are in fact the ashes of beech wood, the term relating to the French for beechnut 'faine'. These references are sometimes used to infer that beech was the preferential alkali source in all northern European medieval glassmaking. This may have been true in some regions but it is unlikely that this was always the case. For example, it has been noted that during the medieval glassmaking period, the Weald was not populated with large numbers of beech trees. It has therefore been suggested that the alkali source was probably oak, which was thought to be more abundant at that time (Wood 1965, 1982).

Fern appears to have been predominant in English and Italian glassmaking (Merrett 1662). In England the species of fern found is **bracken** (*Pteridium aquilinum*) (Stace 1991: 16), although it is referred to as fern in English medieval texts such as those by Harrison (1587: 128) and Norton (*c*1477) (Reidy 1975: 87). Crossley (1967) notes that documents exist confirming the sale of fern ashes to glassmakers at Bagot's Park, Staffordshire during the 16th century.

Ashes from other species including oak (*Quercus sp.*) and plants such as beans, brambles, rushes and millet may also have been used as alkali sources (Agricola (Hoover and Hoover 1950: 586), Neri (Merrett 1662: 15), Zecchin 1997b). It is difficult to determine whether a single or a mixture of ash species would have been used as an alkali source and Merrett (1662: 259) notes that English medieval glassmakers did use a combination of ashes. The percentage ash yield from burning wood or fleshy plants such as bracken is extremely low (approximately 2%, see Section 4.3.3.1). The medieval glass industry would have required very large quantities of vegetation to ensure a sufficient supply of alkali (Bezborodov 1975, Smedley *et al.* 1998). Crossley (1998) has therefore suggested that fuel ash may also have been commonly used to supplement or provide the whole of the alkali source. This would be beneficial, as it would reduce the total amount of wood required to maintain furnace temperatures and supply sufficient raw materials. The use of fuel ashes may have been essential to English glassmakers in the in the late 16th century to combat the rising cost of wood (Godfrey 1975).

In comparison to silica, medieval glassmaking texts make no reference to the use of ground alkali (see Section 2.2.1). One reason for this may correspond to the dominating role of the sand grain size in the melting process (see Section 2.2.1.1). Another reason may perhaps be that plant ashes were already in a mainly powdered form, although they are often of a predominantly larger grain size compared to that of sand (see Section 4.4). Ash particle size may not be critical, as it will melt during the early stages of the glass melting, due to the lower melting point of potassium based alkalis (approximately 900°C) compared to silica (in excess of 1700°C) (Lide 1999, Shelby 1997, Smedley *et al.* 1998). The smaller surface area to volume ratio and more refractory nature of the silica compared to the alkali component will mean that it is likely to dissolve into the melt at a slower rate.

It can be seen that identifying the exact ash types used in medieval glassmaking is difficult. The ashes used may have varied depending on factors such as geographical area, manufacturing traditions or the season. However, with respect to homogeneity, the chemical composition of the ash remains the critical factor. This will be discussed in Section 2.2.2.1.

2.2.2.1 Plant Ash Composition

The inland plant ashes, such as beech, bracken and oak, thought to be used in northern European medieval glassmaking (see Section 2.2.2) are rich in potassium and have low levels of sodium. The sum of these elements is taken here to equal the total alkali content. Increased alkali levels will allow the batch to melt more quickly, facilitating mixing and contact between the raw materials and therefore improving homogeneity (see Section 2.2.4). If a batch contains insufficient alkali to react with all of the silica then the glass will not fully melt and be inhomogeneous. The contents of silica and other refractory components, such as calcium carbonate in the plant ash are therefore also important. Plant ashes containing higher alkali levels and low levels of silica will probably produce more homogeneous glasses.

Plant ashes frequently contain high calcium levels and this may also influence homogeneity. Cable and Bower (1965) using glasses manufactured from laboratory reagents determined that soda-lime-silica glasses with high calcium contents (approximately 13%, added as calcium carbonate) exhibited poor homogenisation. Segregation occurred quickly with a bottom lime rich layer, and a silica rich top layer. All of the melts were inhomogeneous and required stirring to improve them (see Section 2.4.6). If this feature is also true for potash based glasses then medieval glasses with high lime levels may potentially be more susceptible to inhomogeneity. Plant ashes are made up of many different compounds and calcium may be present in a number of different forms (Smedley *et al.* 1998). These have different melting temperatures and therefore this may influence their effect on homogeneity.

The ashes of different plant species are elementally distinct (Geilmann *et al.* 1955, Sanderson and Hunter 1981, Turner 1956d). Three of the most commonly quoted ashes are beech, oak (Sanderson and Hunter 1981: Table 1) and bracken (Jackson and Smedley 2000: Table 2). Table II:1 and Table II:2 list the compositions of a number of published analyses for these ash types. As there is only one available analysis of bracken ash, an analysis of fern ash (Bezborodov 1975: Table V) is included for comparison, but unfortunately this is from an unknown location. Figure 2:2 illustrates the results of plotting the total alkali concentration against calcium for the different ashes. These were chosen, as according to the literature, they are the most significant with respect to homogeneity. They are also frequently used to link medieval potash glass and potash rich plant ash compositions (see Section 1.3) (Barrera and Velde 1989, Bezborodov 1957, Wedepohl 1997).

Figure 2:2 illustrates that a significant difference can be seen between the calcium and total alkali concentration of bracken (see Section 2.2.2) and the hard woods, beech and oak. The total alkali concentration of the bracken ash and fern ashes ranges from 39.52-47.4%, which is significantly higher than the beech and oak values (7.28-20.72%, from two samples). Based on the assumption that increased alkali levels will improve homogeneity, these bracken ashes are more likely to make a homogeneous glass than the beech or oak ashes. The bracken and fern ashes also contain marginally lower lime levels (9.02-14.1%) than the beech and oak ash (13.99-36.10%) (Table II:1 and Table II:2). The increased lime levels in the beech and oak ashes may also make them more susceptible to forming inhomogeneous glasses than the bracken ash. It should be noted that examining the alkali and lime values of Wealden beech and oak (Figure 2:2) shows that it is difficult to distinguish between these data even though they are from different species. The silica content of the ashes also has to be considered, as this will increase the overall silica levels in the batch. In the bracken and fern ashes this is 15.17% and 6.1% respectively (see Table II:2). Unfortunately there are no comparative results for this element for the Wealden oak and beech.

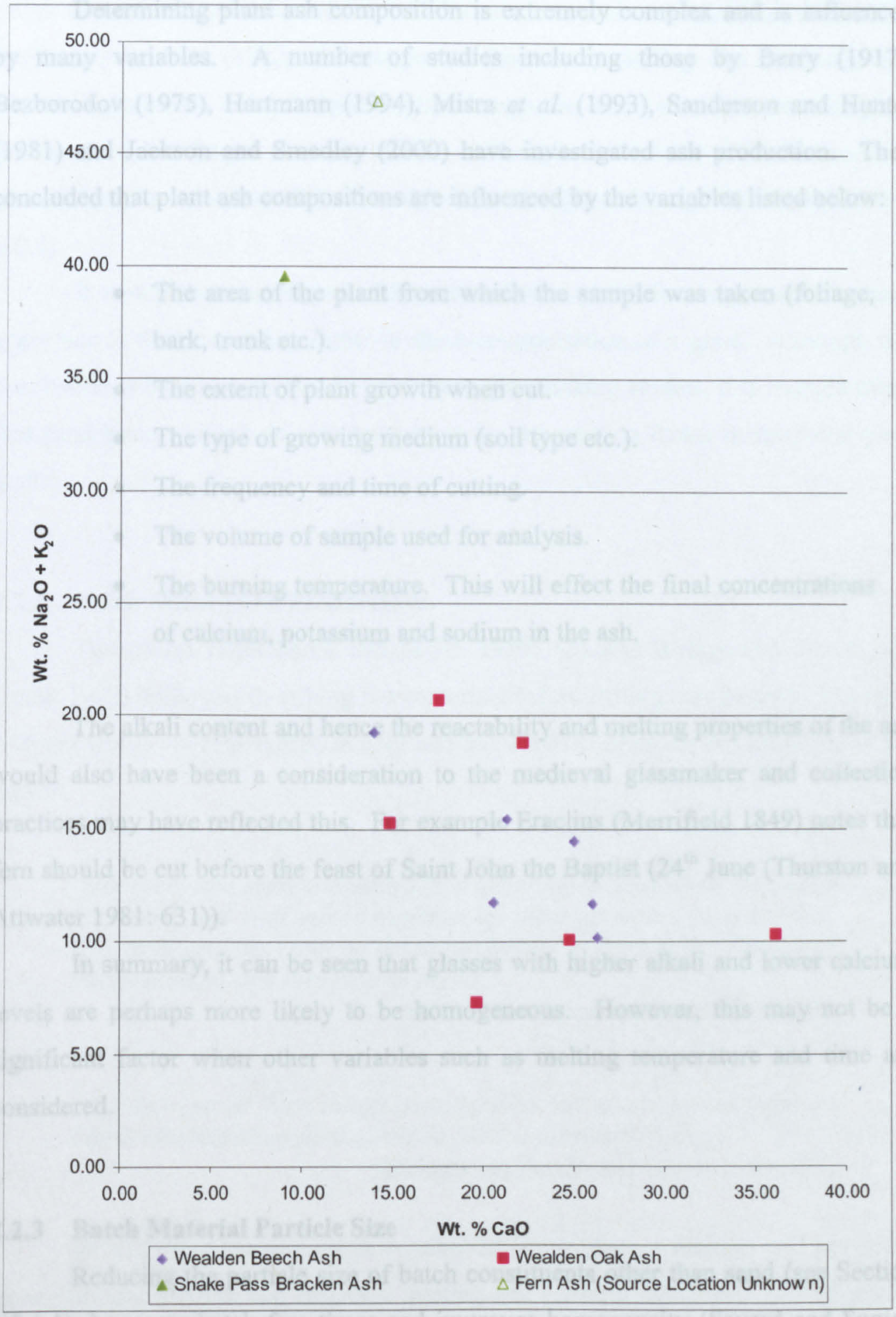


Figure 2:2 Total alkali content versus calcium content for a selection of English beech, oak (Sanderson and Hunter 1981: Table 1) and bracken ashes (Jackson and Smedley 2000: Table 2) and fern ashes (location unknown) (Bezborodov 1975: Table V) (see Table II:1 and Table II:2)

Determining plant ash composition is extremely complex and is influenced by many variables. A number of studies including those by Berry (1917), Bezborodov (1975), Hartmann (1994), Misra *et al.* (1993), Sanderson and Hunter (1981) and Jackson and Smedley (2000) have investigated ash production. They concluded that plant ash compositions are influenced by the variables listed below:

- The area of the plant from which the sample was taken (foliage, bark, trunk etc.).
- The extent of plant growth when cut.
- The type of growing medium (soil type etc.).
- The frequency and time of cutting.
- The volume of sample used for analysis.
- The burning temperature. This will effect the final concentrations of calcium, potassium and sodium in the ash.

The alkali content and hence the reactability and melting properties of the ash would also have been a consideration to the medieval glassmaker and collection practices may have reflected this. For example Eraclius (Merrifield 1849) notes that fern should be cut before the feast of Saint John the Baptist (24th June (Thurston and Attwater 1981: 631)).

In summary, it can be seen that glasses with higher alkali and lower calcium levels are perhaps more likely to be homogeneous. However, this may not be a significant factor when other variables such as melting temperature and time are considered.

2.2.3 Batch Material Particle Size

Reducing the particle size of batch constituents other than sand (see Section 2.2.1.1) decreases batch free times and improves homogeneity (Savard and Speyer 1993a, 1993b, Sheckler and Dinger 1990). More significantly, the minimum batch free time and refining time occurs when the particle sizes of all the batch components are well matched. Potts *et al.* (1944) found that when they reduced the grain size of one batch component, the shortest batch free time occurred when all the batch particle sizes were equal. The most significant change being with sand grain sizes rather than other batch materials such as limestone or soda ash (see Section 2.2.1.1). Boffé and Letocart (1962) also supported this theory finding that limestone and dolomite grain size did not significantly change the batch free time providing the grains were not larger than the sand. Although the alkalis used in medieval glassmaking have large particle sizes this is not thought to be significant (see Section 2.2.2).

It would therefore appear that in the choice of batch components, the sand grain size is the dominating factor in the homogenisation of a glass. Although this conclusion is based on the results of modern glassmaking studies, it is thought likely that sand grain size would also have been the dominating factor in medieval glass melts.

2.2.4 Batch Mixing and Preparation

Theophilus (Hawthorne and Smith 1979: 53) and Biringuccio (Smith and Gnudi 1990) both refer to mixing raw materials before fritting (see below). The most relevant words are highlighted in bold and the words in brackets are additions by the author.

> '***mix them*** (the sand and ashes) *in a clean place, and when they have been* ***long and well mixed together*** *lift them up with a long handled iron ladle and put them on the upper hearth in the smaller Section of the furnace so that they may be fritted.*'
>
> Theophilus (Hawthorne and Smith 1979: 53).

> '*and then put all these things* (sand/pebbles and alkali) ***mixed together*** *into a reverberatory furnace made for this purpose* (fritting)'
>
> Biringuccio (Smith and Gnudi 1990: 127)

Mixing the silica and ashes together before fritting or melting will provide a more intimate mixture and facilitate melting and refining reactions. A well mixed batch should therefore produce a more homogeneous glass. Glass technologists have examined batch mixing in detail. Such studies include Cable (1958), Fletcher (1963), Knight (1956a, 1956b, 1956c, 1956d), Poole (1963), and Sheckler and Dinger (1990). Although a well mixed batch may be achieved using relatively short mixing times (see Section 2.2.4.3), the uniform distribution of smaller quantities of substances throughout the batch, such as colourants and refining agents (if added at this stage), may not be so easy to achieve. This would therefore be a possible source of inhomogeneity in the finished glass. In archaeological glasses these minor components may not have been added to the batch but maybe later during the melt, for example the addition of colourants by the use of fully formed glass (cullet) (see Section 2.2.5) (Henderson 1985).

Therefore, mixing is dependent on the size, shape and other properties of the materials concerned. It may vary considerably depending on the different types of substances and sample sizes used (Cable 1969: 147-52, Poole 1963, Sheckler and Dinger 1990). In addition, the moisture content of the raw materials and the mixing method will all influence the extent to which a batch can be well mixed, these points are discussed in Sections 2.2.4.1 to 2.2.4.3.

2.2.4.1 The Effect of Moisture Content on Batch Mixing

Moisture content affects the extent of mixing within a batch (Cable 1958, Hartley 1963). Stanworth & Turner (1937) found that >4% water content was required to cause a significant effect on the rate of melting and refining of a glass batch. Damp raw materials may cause the agglomeration of silica fines and prevent the flow of raw materials, hindering mixing. A glass formed from a poorly mixed batch is therefore more likely to contain inhomogeneities (see Section 2.2.4). In addition to this, the water contained in wet materials would be heated up and evolved as steam. This would cause a small decrease in maximum furnace temperature at this time and influence homogeneity (see Section 2.4.2). Moisture may also react with batch components such as carbonates to form substances with different melting characteristics and therefore affect homogeneity.

In archaeological glass production a significant moisture content may have been unavoidable unless raw materials were left near the furnace prior to use. There is evidence to suggest that medieval glasshouses may have been covered (see Section 2.4.1) and raw materials may have been kept dry by storing them above the furnace.

2.2.4.2 The Effect of Particle Size on Batch Mixing

Particle size has an effect on melting (see Sections 2.2.1.1 and 2.2.3) and also on the extent of batch mixing. Experiments carried out on soda-lime-silica glasses by Tooley and Tiede (1946: 197) found that reducing sand grain size from 20-60mesh (850-250µm) to less than 200 mesh (75µm) reduced batch segregation. Manring and Bauer (1964) and Poole (1963) built on these experiments and suggested that if the batch materials were of similar particle sizes, this would enable good mixing, thereby producing a more homogeneous batch. Potts *et al.* (1944) also found that variation in raw material grain size resulted in the demixing or separation in the batch, but the addition of cullet reduced the problem (see Section 2.2.5). Using small silica grain sizes and other evenly matched raw materials might therefore translate to the formation of a more homogenous glass. In archaeological melts it has been seen that the use of smaller silica grain sizes may have been favoured (see Section 2.2.1.1). However, it is not known if all of the batch components would have been of similar sizes, or if and when cullet was added to the batch (see Figure 2:1).

2.2.4.3 The Effect of Mixing Times on Batch Mixing

Tooley and Tiede (1946) investigated the effect of different mixing times (1-30 minutes at 40 r.p.m.) on the homogeneity of 50g soda lime silica glass melts. They found that it was relatively easy to achieve a well assimilated batch with dry batch components but these experiments were carried out with laboratory reagents and medieval raw materials may behave differently. Tooley and Tiede (1946) suggest that the duration of batch mixing does not have a significant effect on the homogeneity of the glass obtained. This may not be because batch mixing is not important but that in conjunction with other variables such as melt temperature (see Section 2.4.2) it may not appear significant. Conversely, Cable (1998) notes that extended mixing times can lead to demixing within a batch. Even with well mixed batches there will always be inhomogeneity in the first liquids formed during the early stages of melting. The liquid formed at batch free time (see Section 2.2.1.1) is not close to the desired average composition and therefore further mixing is required to yield a homogeneous melt (Cable 1998: 1085).

2.2.5 Recycled Glass

The use of cullet is an extremely complex issue and it would not be possible to cover all of its implications for the glassmaking process here. However, there is documentary evidence that cullet was used in medieval glassmaking (Biringuccio (Smith and Gnudi 1990: 129)). Cullet can be split into two types:

a) **Local cullet**, this is glass made on the site where it is found and is therefore likely to have a similar composition to the glass being made there

b) **Foreign cullet**, this is glass that is brought into to the site from outside and is therefore likely to have a different composition to the glass being made on site.

If local cullet was used, continued recycling may produce glasses with very similar compositions but which may not have been made from the same raw materials (Crossley 1990, Hunter 1985, Price 1978). In this way the use of cullet could therefore increase the homogeneity of a melt. Conversely, foreign cullet could be a source of inhomogeneity if it had a different composition to the bulk material, or if a batch was composed entirely of cullet and contained glasses of many different compositions.

Manring and Conroy (1968) also noted that the particle size of cullet may influence homogeneity. If the particle size of the alkali component and cullet are similar, and the batch is dry to ensure good mixing (see Section 2.2.4.1), the rate of reaction of the alkali with the cullet is greater than with silica. A longer melt time is therefore required to dissolve the silica component of the batch and may be a potential source of inhomogeneity. However, this assumes the use of ground cullet and it is not certain what would occur if the glass were used untreated.

2.3 Fritting: Factors Affecting Homogeneity

2.3.1 Introduction

'Fritting' in archaeological glassmaking refers to a low temperature heat treatment (700-900°C) to promote a solid state reaction between raw materials (Turner 1956d). This leads to the elimination of gases but does not allow melting to occur. The substance formed is termed a 'frit' and this is ground and melted to form a glass (Biek and Bayley 1979). Frit will heat up faster than the batch, as it is a more effective conductor of heat. Therefore it appears to require a shorter melting period than producing a glass from unfritted raw materials (Smedley *et al.* 1998). Fritting will also reduce batch volume, eliminate volatile components and facilitate the homogenisation of the frit (Smedley *et al.* 1998). The latter is an important variable to be investigated in this research.

The use of frit and a fritting stage is referred to in written accounts of medieval glassmaking (see Section 2.1.1). The first reference is in the Mappae Clavicula (12th century) where the manufacture of glass using a two stage process is noted but there is some doubt as the whether this reference refers to glassmaking or metal slag (Smith and Hawthorne 1974). Theophilus (Hawthorne and Smith 1979), Agricola (Hoover and Hoover 1950), Biringuccio (Smith and Gnudi 1990) and Neri (Merrett 1662) describe various aspects of frit and the fritting process but it should be noted that Biringuccio (Smith and Gnudi 1990: 132) also describes the production of a glass without a fritting stage. Examples of documentary evidence that refer to fritting (in bold) are given below.

> *'When they* (sand and ashes) *begin to get hot,* ***stir*** *at once with the same ladle to* ***prevent them from melting*** *from the heat of the fire and agglomerating. Continue doing this for* ***a night and a day****'*
> Theophilus (Hawthorne and Smith 1979: 53).

> *'then put them* (raw materials) *into a 'calcar, which at first must be well heated, for if they be put into the calcar when it is cold, Fritt will never be made of them. At first for* ***an hour,*** *make a* ***temperate fire,*** *and always* ***mix*** *the Frit with the rake, that it may be well incorporated, and calcined, then the* ***fire must be increased,*** *alwaies* ***mixing*** *well the Fritt with the rake, for this is a thing of great importance, and you must alwaies do thus for* ***5 hours,*** *still continuing a* ***strong fire.****'*
> Neri (Merrett 1662: 8)

> *'The calcar is a kind of calcining furnace, the rake is a very long instrument of iron, wherewith the Fritt is* ***continually stirred,*** *both these are very well known and used in glass furnaces. At the end of* ***five hours,*** *take the Fritt out of the Calcar, which in that time (having had* ***sufficient fire,*** *and being* ***well stirred)*** *is made and perfected.'*
> Neri (Merrett 1662: 8)

There is a lack of archaeological evidence for fritting or frit. This is perhaps not surprising, as unless the glass production had failed it would have been converted to glass (Crossley 1990). Even if it was discarded, documentary evidence suggests that frit may have been friable and therefore would not remain in the archaeological record or be easily distinguished from its surroundings (see Section 2.1.1). Examples of excavated material referred to as 'frit' are from the glasshouse at St Weonards, Herefordshire (16th century) (Bridgewater 1963: 305) and the Hils glasshouses in Germany (12th-15th century) (Leiber 1990/1991), but the nature of these materials is not described. At Knightons glasshouse, Surrey (16th century) (see Section 7.2.2), (Wood 1982: Microfiche 9, 43) states that frit is present and is either a fused cindery or glassy material. An excavated crucible from the nearby site of Sidney Wood, Surrey (17th century) (see Section 7.2.3) is also described as being full of glassy material or frit ((Kenyon 1967: 52). Giannichedda *et al.* (2000) tentatively suggest that at a glasshouse in the Gargassa Valley, northern Italy (13-14th century) the fragments of vitreous fused glass pastes excavated may be frit. These descriptions are scant and varied and for the archaeologist there is no exact definition of what constitutes a frit. Crossley (1967: 62) has suggested that some excavated materials attributed as frit are actually waste products from glassmaking. In the medieval period there may have been many different forms of frit depending on the raw materials and production parameters used. The description of the excavated material is very varied and it may be that frit may benefit by being described by the percent of vitrification observed. The lack of material evidence means that, as with raw materials much of the information about frit has to be obtained from the results of experimental replication or written accounts of glassmaking. The influence of fritting on homogeneity will be discussed in Sections 2.3.2-2.3.5.

2.3.2 Fritting Temperature and Time

Fritting temperature and time is critical, as this will control the chemical reactions that occur on heating, and therefore determine to what extent the components decompose and/or melt. The range of temperatures and times used in medieval glassmaking would have been determined by the composition of the raw materials, the heat output of the furnace, and possibly the nature of the glass to be produced. Furnace design and the choice of fuel will affect the temperature, heat distribution and atmosphere within a furnace and hence the fritting reactions, which in turn influence homogeneity (Turner 1956d, Wood 1965). It is suggest by Turner (1956d) that a low heat is required to prevent complete fusion and liquefaction, but it must be high enough or maintained for long enough to cause granulation and a semi-vitreous condition.

Alkali composition (see Section 2.2.2.1) is important as potassium rich ashes melt at higher temperatures than sodium rich ones (Smedley *et al.* 1998). Written descriptions of medieval glassmaking allow an estimation of fritting temperatures and times. For example, Theophilus (Hawthorne and Smith 1979: 53) (see Section 2.3.1) states that a beech ash based frit should be heated for a day and a night and that that batch must not be allowed to melt in the heat of the fire. It has been assumed that this refers to 24 hours. Neri (Merrett 1662: 8) states that fern ash frits should be heated for a shorter time of 5 hours and refers to the heat being altered (see Section 2.3.1). It is important to note that the higher the fritting temperature the shorter the time required to produce the same effects. Although different fritting times are given for beech and bracken ash batches, they may have been carried out at different temperatures. The colour, vitrification, friability and texture of the frit may also have been a more suitable indicator than the length of time it was in the furnace.

Potash based frits have only recently been experimentally investigated. Royce-Roll (1994) fritted batches of beech wood ash and sand in a replica medieval furnace. This was done at 1150°C for 3 hours and the frit melted at approximately 1200°C for about 8 hours to form a glass. Smedley *et al.* (1998) also formed frit using beech wood ashes and sand. They found that temperatures above 700°C were enough to initiate a moderate chemical reaction between the ash and sand and that some liquid phases were formed above 900-1000°C. Theophilus (Hawthorne and Smith 1979) mentions the prevention of the mixture liquefying (see Section 2.3.3). Smedley *et al.* (1998) has suggested that fritting temperatures of below 1000°C were typical.

The liquefaction of the frit influences homogeneity. Fritting temperatures or times that are too high will prevent sufficient mixing of the raw materials and are more likely to form glasses containing batch relics and partially refined material. Further melting to dissolve the 'batch relics' is thought to have been ineffective at the temperatures thought to be obtainable in medieval furnaces and an inhomogeneous glass would be formed (Biek and Bayley 1979). This phenomenon has been observed in experiments by Smedley *et al.* (1998). Turner (1956d) and Smedley *et al.* (1998) both noted that if liquid phases form during fritting they could react with the refractory floor in the furnace or crucible. Refractory oxides can be dissolved into the reacting materials to create inhomogeneity. Conversely, fritting can also reduce refractory corrosion (Smedley *et al.* 1998). Ashes are extremely fine powders that can be easily transported into the furnace atmosphere by rapidly circulating flames etc. The ashes may come into contact with the furnace roof and the chemical reactions may form liquids that could drip into the open crucibles influencing the homogeneity of the melt. Fritting would diminish the chances of this occurring by increasing the effective density of the mixture. The consequences of refractory corrosion are discussed fully in Section 2.4.5.1.

2.3.3 Mixing During Fritting

Theophilus (Hawthorne and Smith 1979: 53) and Neri (Merrett 1662) describe the mixing of raw materials during fritting (see Section 2.3.1). Section 2.2.4 noted that homogeneity was likely to be improved by using a well mixed batch. Mixing the batch *during* the fritting process may be beneficial, as it would speed up reaction times between raw materials, shortening fritting times and forming a more intimate mixture due to closer contact between the particles. It is not known whether this practice would have also facilitated the homogeneity of the glass. Stirring the frit may decrease the contact with refractory surfaces and reduce the chances of inclusion of corrosion products (see Section 2.4.5.1). Conversely, if the frit was on the furnace floor (see Section 2.3.4), stirring may increase the chances of particles being abraded from the floor and transferred into the frit thus decreasing homogeneity. These conflicting arguments mean that it is difficult to confirm what effect mixing will have on homogeneity.

2.3.4 Fritting Vessel Dimensions

Neri (Merrett 1662) and Theophilus (Hawthorne and Smith 1979) state that fritting is carried out on the furnace floor. Spreading the mixture over the furnace floor may have allowed heat to penetrate more quickly and produced a more controlled temperature distribution, contact with the furnace atmosphere and hence a more uniformly fritted product. This practice may have therefore improved the quality and the homogeneity of the glass produced, although contact with the larger surface area of refractory material increases the possibility of the frit picking up inclusions from the furnace floor. Alternatively, the frit may have been produced in crucibles, but little excavated evidence exists to support this (see Section 2.3.1). However, there are fritting crucibles recorded from Egypt during the Roman period. Saleh *et al.* (1972) investigated two large (5 and 9 litres in volume) rectangular, crucibles that were found at Wadi Natrun. These are suggested as having been used in the production of soda based frit. Refractory corrosion from the crucible or furnace floor would also have depended on the nature of both the batch and the materials used to form the crucible or furnace and on the fritting time and temperature.

2.3.5 Grinding and Remixing Frit

It is generally assumed that frit is ground up and remixed before the melting stage (Biek and Bayley 1979, Royce-Roll 1994). Medieval glassmaking texts only refer to frit being broken up so that it can be placed into the glassmaking crucible and do not mention grinding or remixing (Biringuccio (Smith and Gnudi 1990: 128), Agricola (Hoover and Hoover 1950: 587)). If the frit were ground, a more homogeneous mixture would be formed as any silica rich areas are broken up and redistributed more evenly throughout the material. Grinding would reduce the volume of material if the frit contained bubbles and this would allow a larger charge to be melted in one go. Grinding the frit would require more labour and time but may have been advantageous if this facilitated melting. Alternatively, frit may not have required grinding if it was raked on the furnace floor and/or was not allowed to vitrify.

2.4 Melting: Factors Affecting Homogeneity

2.4.1 Introduction

The next stage of medieval glass manufacture is to form a batch free glass suitable for working into different shapes and forms using a variety of methods such as casting and blowing (Grose 1984). The raw materials, frit or cullet (or a combination of these) is placed in crucibles and heated at a high temperature until a molten glass is formed (Biek and Bayley 1979). Estimations of the temperatures required to do this for medieval, potash based glasses vary between 1200-1400°C (Turner 1956d: 295T, Wedepohl 1997: 254), and will be discussed in Section 2.4.2. There are a number of documentary sources that depict or describe medieval furnace design. The earliest picture of a medieval glass furnace is depicted in a manuscript dating to 1023 A.D. in Monte Cassino, Italy. It is thought to be a copy of one attributed to *De Universo* by Hrabanus Maurus, Bishop of Mainz (*c*.776-856 A.D.) who was an advisor to Charlemagne (Hunter 1981, Newton and Davison 1989: 111) (Plate 2:1).

Plate 2:1 A depiction of an early medieval glass furnace from the manuscript of Hrabanus Maurus dating to 1023 A.D. (Monte Cassino, Italy) (Codex i32) (Notarianni and Ferrari 1998: 4)

Charleston (1978) suggested that medieval glass furnaces could be split into two types based on their shape. The 'northern' furnace is characterised by rectangular foundations, and is frequently ascribed to northern Europe (Plate 2:2) This furnace is described by Theophilus (Hawthorne and Smith 1979: 49-52) who states that it was used in conjunction with a separate annealing furnace (see Section 2.6).

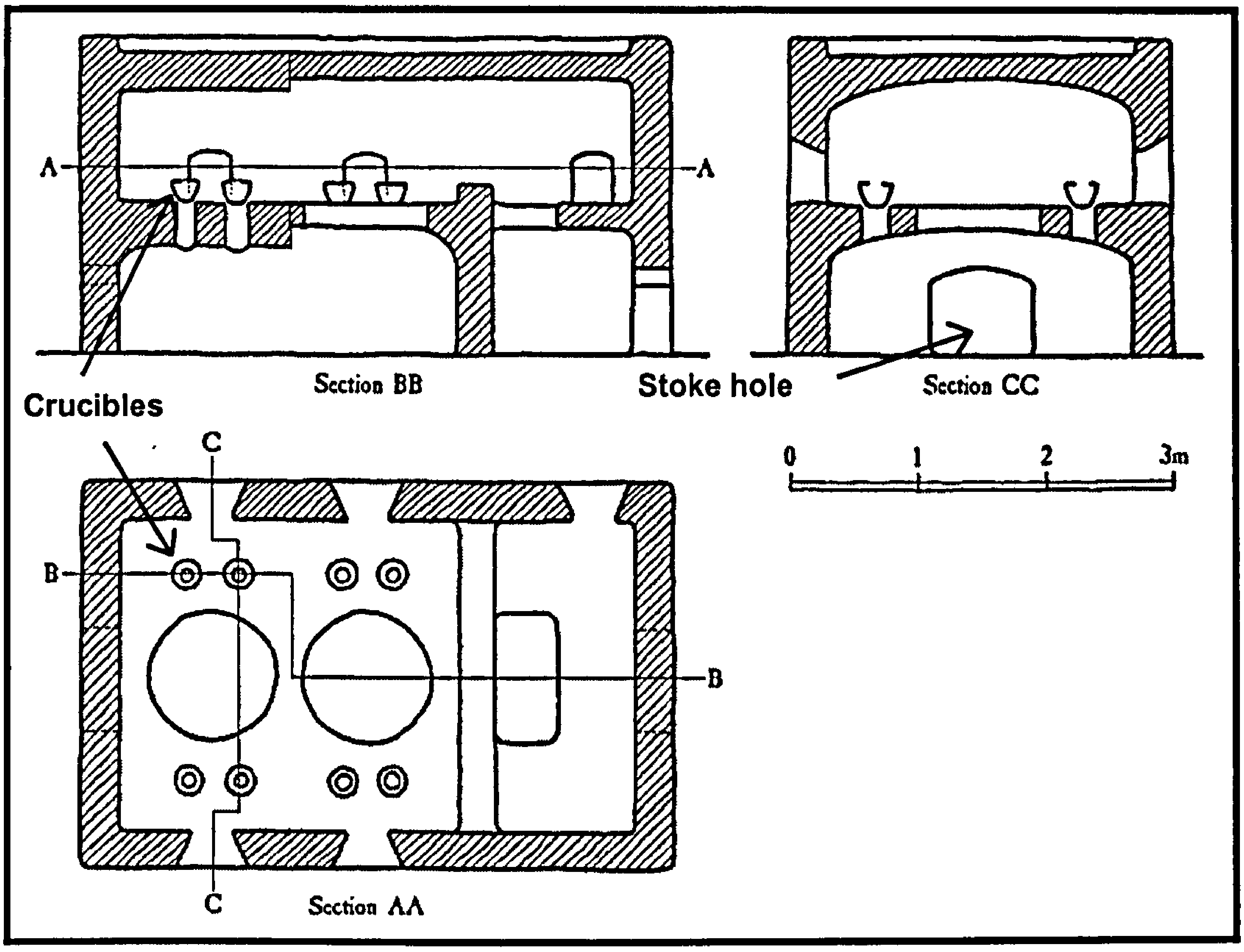
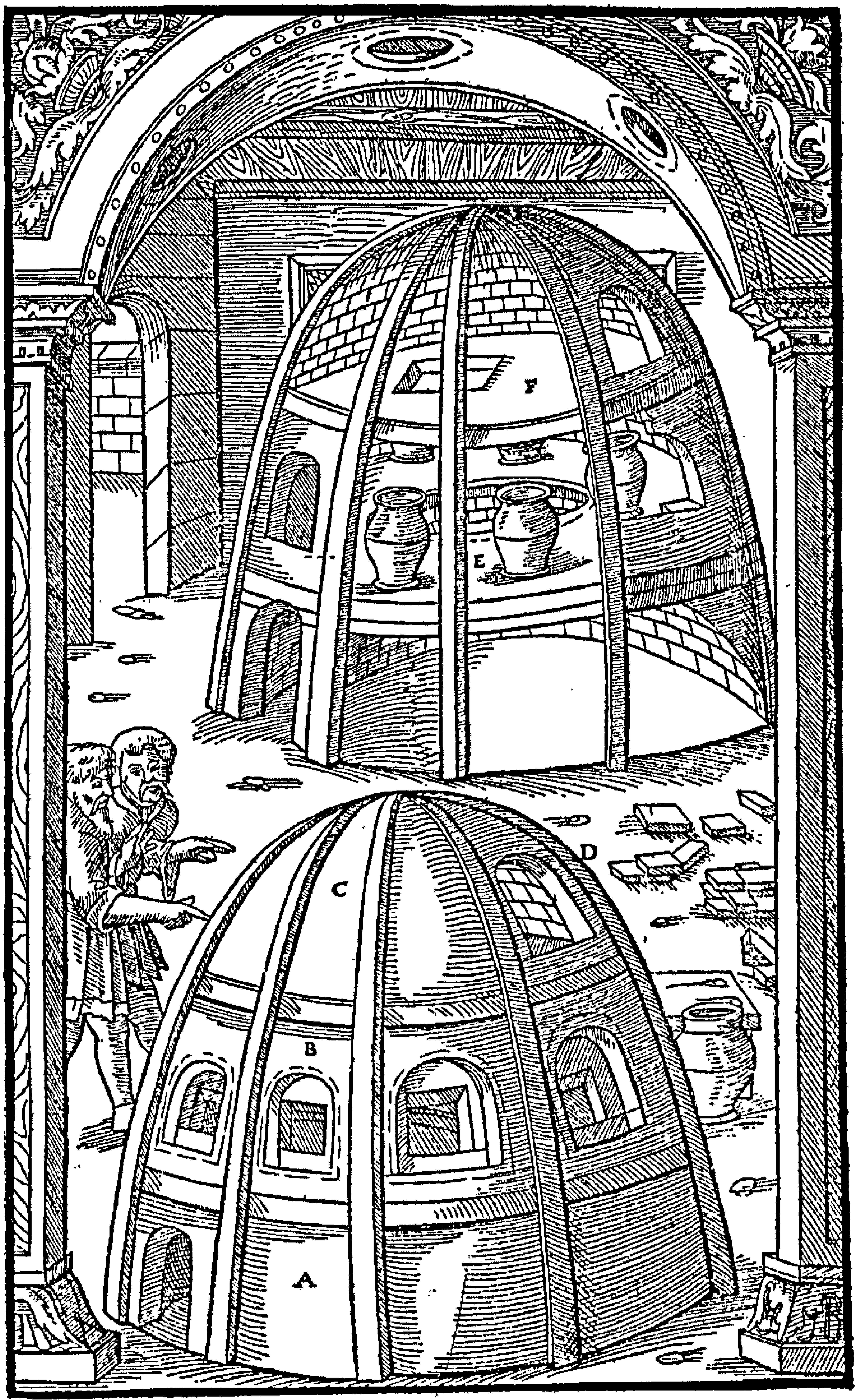


Plate 2:2 A suggested plan of a 'Northern' style glass furnace based on the writings of Theophilus (Hawthorne and Smith 1979: 49)

The 'southern' furnace type is characterised by a round base and domed shape, and is frequently linked with southern Europe. This furnace is described by Neri (Merrett, 1662: 240-8), Biringuccio (Smith and Gundi 1990: 128-9), and Agricola (Hoover and Hoover 1950: 586-92) from whom the illustration in Plate 2:3 is taken. Annealing was carried out in the upper part of the furnace and glass melting in the lower sections; separate furnaces for fritting or pot arching may also have been used.



A—Lower chamber of the other second furnace. B—Middle one. C—Upper one. D—Its opening. E—Round opening. F—Rectangular opening.

Plate 2:3 A 'Southern' style glass furnace (Agricola (Hoover and Hoover 1950: 589))

Excavated archaeological evidence for furnace structures is more common in the medieval period in comparison to earlier periods but remains are predominantly foundations and little information can be gleaned about superstructure. The evidence also suggests that there is more variation in furnace type than documented in medieval texts. For example, rectangular furnaces with proposed separate annealing ovens, linked to the northern type described above, are noted at Little Birches (14th and 16th centuries) (Welch 1997) and Bagot's Park, (16th century) (Crossley 1967) Staffordshire, and Knightons (Wood 1982). A more complex winged furnace design, in which fritting and annealing are thought to have been carried out, is found at Vann Copse, Surrey (16th century) (Kenyon 1967) and Hutton and Rosedale, (16th century) Yorkshire (Crossley and Aberg 1972). A number of these furnaces will be discussed in more detail in Chapter 7.

The nature of these furnace changes is important because they will influence variables such as temperature (see Section 2.4.2) and atmosphere (see Section 2.4.4) that have a direct affect on homogeneity. Cable (1997) suggests that the design of northern furnaces would have made it easier to melt higher temperature glasses and that the addition of fuel and removal of spent fuel would have been easier and interfered less with the working glassblowers compared to the design of the southern furnace. The position of the crucible with respect to the heat source in the furnace will influence the extent to which convection currents are set up, facilitating better mixing and therefore homogenisation. The crucibles from Bagot's Park and Kimmeridge, Dorset (17th century) appear to have been placed with one side overlapping the edge of the siege and may have facilitated this (Crossley 1987).

It can be seen that medieval furnace design is extremely varied and complex. The effects on homogeneity will be hard to predict and therefore this is beyond the scope of this research. However, the effects of altering parameters such as furnace temperature and crucible dimensions can be examined and these will be discussed in Sections 2.4.2 to 2.4.6.

2.4.2 Melting Temperature

The temperatures achieved in medieval furnaces depend on their design, age and the type and form of the fuel. Accurate prediction of the temperatures attained is difficult and it is also impossible to know whether the furnace would have always been operated at the maximum working temperature. The determination of temperatures was not noted in glassmaking until the 18th century, but Cable (1997) suggests that in qualitative terms the highest heats were known to form the best glasses. Cable and Smedley (1987) have suggested that temperatures of up to 1350°C may have been obtained in medieval furnaces based upon the softening and liquidus temperatures of glass from Hutton and Rosedale, Kimmeridge, and Bolsterstone, South Yorkshire (18th century). This method has also been used to identify melting temperatures in excess of 1320°C for glass samples from Little Birches, Staffordshire (White in Welch (1997: 49)). Experimental replication of medieval glasses from laboratory reagents by Wedepohl (1997: 254) have led him to suggest that to produce a homogeneous melt would have required temperatures in excess of 1400°C.

In isolation, increasing melting temperature will improve homogeneity, as the viscosity of the glass will decrease increasing the mobility of ions and therefore diffusion rates. Higher temperatures will also increase the quality of the glass produced as better refining is achieved using higher melt temperatures compared to longer melt times (see Section 2.2.1.1) (Cable 1997, Rindone 1957). However, higher furnace temperatures require higher fuel consumption, and lead to shorter crucible and furnace lives. These factors may have been an important consideration to the medieval glassmaker.

The use of different types of fuel in glass manufacture has been noted above and many references are made to the use of high quality, dry wood so as not to affect the quality of the glass (see Section 2.4.4) (Cable 1997, Crossley 1972, Verità 1991). The fuel source has a direct relation to the temperatures that would have been achieved in medieval glass production. Although, hard woods such as beech and oak have similar calorific values, the heat produced will depend on many factors such as water content, shape, and size (Tylecote 1986). The use of specific species, which have been carefully selected and prepared, are mentioned by Theophilus (Hawthorne and Smith 1979) and Neri (Merrett 1662). The dimensions of the wood and the way in which it was introduced to the furnace would determine any fluctuations in temperature. This can facilitate mixing within the melt and therefore improve homogeneity and refining (Crossley 1998). The effect of melting temperature is inter-linked with melt time and this will be discussed in Section 2.4.3.

2.4.3 Melting Time

Melt time would have been dependent on the composition and particle size of the raw materials, furnace temperature, the size of the melt, and the quality of the glass required. To determine maximum melt time, visual indicators such as bubbles on the surface of the melt may have been used. The glass may have been sampled to determine the workability of the melt, observe the colour or check the extent of refining and cord. Agricola (Hoover and Hoover 1950: 592) notes that the glassmaker will determine whether the glass is ready for blowing by pulling it up on the blowpipe to observe the appearance and behaviour of it.

In the following quotes Agricola (Hoover and Hoover 1950: 592) notes an improvement in glass quality with increasing melt time (in bold) up to 48 hours.

> *'The **longer** they remelt it (the glass), the purer and more transparent it becomes, the fewer spots and blisters there are, and therefore the glassmakers can carry out their work more easily.'*
>
> Agricola (Hoover and Hoover 1950: 592)

> *'those who only melt the material from which glass is made for **one night**, and then immediately make it up into glass articles, make them less pure and transparent than those who first produce a vitreous mass and then remelt the broken pieces for **a day and a night**. And, again, these make a less pure and transparent glass than do those who melt it again for **two days and nights**, for the excellence of the glass does not consist solely in the materials from which it is made, but also in the melting.'*
>
> Agricola (Hoover and Hoover 1950: 592)

48 hours would appear to be a relatively long melt time but the affect on homogeneity would depend on the temperature of the furnace and melt size. The improvement in the quality of the glass may be more significantly influenced by the breaking up and remelting of the glass than the increase in melt time (see Section 2.4.6). Increasing melt time will improve homogeneity and refining to a certain extent (see Section 2.2.1.1). In soda-lime-silica glasses Tooley and Tiede (1944) found that in 50g melts homogeneity improved quickly during the first 10 hours but increasing the melt time (up to 64 hours) was of little further benefit. Although these are not potassium based glasses it appears that increasing melt time improves homogeneity up to a point after which no further improvement is seen, and other

factors such as increased refractory corrosion (see Section 2.4.5.1) and volatilisation should be considered (Hrma 1982).

Volatilisation will tend to only affect the immediate surface layer but it can cause significant inhomogeneity if the density of the melt increases and parts of the surface layer sink into the main body (Cable 1998). Batch components such as those containing potassium, sodium, lead, halides or sulphur are more susceptible to volatilisation than others (Cable 1994). These factors make the contribution of volatilisation to inhomogeneity hard to predict (Cable 1998).

2.4.4 Furnace Atmosphere

Furnace atmosphere will alter depending on fuel type. The absorption of water, sulphur, oxygen and other furnace gases into the surface layer of the melt will alter the chemical composition of the layer (Cable 1994). This glass will probably have a different chemical composition compared to the bulk glass and when this is incorporated into the main body will be a source of inhomogeneity. In medieval glassmaking, references are made to the use of high quality, dry wood as a fuel source (Cable 1997, Crossley 1972, Hoover and Hoover 1950: 592, Merrett 1662). The deliberate choice of specific woods and their subsequent preparation may have been made to prevent contaminating the glass in open crucibles and/or for their ease of combustion (see Section 2.4.5).

2.4.5 Glass Making Crucibles

Crucible fabric and design (shape and size) both influence the glassmaking process. Each of these factors have a combined effect on inhomogeneity as they affect variables such as the rate of volatilisation from the melt surface, refractory corrosion and the extent of heat transfer and hence diffusion currents (internal mixing). It is known that certain clays and shapes were favoured in medieval glassmaking and the importance of this to homogeneity will be discussed in Sections 2.4.5.1 and 2.4.5.2.

2.4.5.1 Crucible Fabric

Molten glass is very corrosive and reactions at the crucible/glass interface will dissolve the ceramic fabric (Turner and Turner 1923). The dissolution of refractory impurities into the melt will impair the quality of the glass and make it less homogeneous. The following variables all contribute to the rate at which the dissolved impurities are distributed throughout the glass.

- Glass and crucible composition.
- Melt time.
- Melt temperature.
- The heat transfer and refractory properties of the crucible.
- The dimensions and surface area to volume ratio of the crucible.
- Diffusion within the melt.
- Stirring the glass melt.

To reduce the risk of damaging the melt, crucible fabrics that are more resistant to corrosion have been traditionally preferred by glassmakers (Preston 1943, Rosenhain 1919). The clay matrix of good refractory clays should contain high levels of silica and alumina (Firth *et al.* 1923). Non-plastics, especially silica, are frequently added to crucible clays to increase the refractory nature of the clay and to prevent the shrinkage, cracking and distortion of the body during drying (Tite *et al.* 1985). How effective they are depends on amount, grain size and their distribution throughout the ceramic body. Low levels of iron, calcium and magnesium oxides, and alkalis are also desirable, as these will all diminish the refractoriness and stability of the crucible (Rice 1987:51, Welch 1997).

The use of specific high refractory clays or addition of a quartz rich temper has been noted in many analyses and descriptions of medieval glass crucibles (Bezborodov 1957, Doherty 1993, Hurst 1969b, Kenworthy 1918, Mendera 1988). Petrographic analyses of crucibles from the 17th century glassmaking site at Kimmeridge, have shown the high refractory nature of the clay and have been estimated using refiring to be able to withstand temperatures of 1300-1350°C (Crossley 1987: 372). Examination and refiring of crucibles from Hutton and

Rosedale determined that the crucibles were most likely to be of local clay and would have withstood up to 1500°C (Crossley and Aberg 1972).

Theophilus (Hawthorne and Smith 1979, 53) describes the use of a specific clay for glassmaking crucibles and Biringuccio (Smith and Gnudi 1990: 128) notes that the refractory properties of the crucible clay are paramount. The crucibles must be able to withstand the hottest heat and are therefore only selected if they do not fracture or crack on preheating. The use of prefired and preheated pots appears to be a common practice in documented accounts of glassmaking (Theophilus (Hawthorne and Smith 1979: 53), Agricola (Hoover and Hoover 1950: 590) and Neri (Merrett 1662: 127)). The use of prefired pots is likely to be beneficial to homogeneity as the ceramic will be less prone to refractory corrosion (Firth *et al.* 1923). The medieval glassmaker may have been more concerned with obtaining a pot that would not crack and therefore loose the melt rather than the dissolution of the ceramic into the glass during melting.

2.4.5.2 Crucible Dimensions and Melt Size

Depending on the nature of the batch (i.e. frit, cullet or sand and ashes, see Section 2.3.5) crucible size will affect the amount of glass being produced at one time. The influence of melt size on homogeneity must be considered in conjunction with melting temperature and time. A small melt has relatively rapid convection currents that aid the removal of bubbles and facilitate homogenisation (Plumat *et al.* 1963). Large melts may homogenise faster than smaller ones at sufficiently high melt temperatures and times suggesting that melting temperature is the predominating variable. It is not clear whether the temperature and time required to produce a homogenous melt does increase proportionally with melt size (Cable 1969). Crucibles with a large surface area to volume ratio will be more likely to be subject to volatilisation (see Section 2.4.3) and reaction with the furnace atmosphere (see Section 2.4.4) that may influence homogeneity.

The dimensions of medieval glassmaking crucibles are very varied (Horat 1991). The description of crucible production by Theophilus (Hawthorne and Smith 1979: 53) is thought to suggest pots of an open, bowl design. No dimensions are given but the pots have inturned rims that may have been to prevent spillage and overflow of the glass (Hawthorne and Smith 1979: 54). Biringuccio (Smith and

Gnudi 1990: 129) describes crucibles that are almost 2 feet by 1.5 feet with a thickness of two digits, to produce a good quality glass the charge is heated for two days and stirred (see Section 2.4.6). Thick crucible walls were probably chosen for strength and crack resistance (see Section 2.4.5.1) but in contrast thick walls would have reduced thermal conductivity (reducing internal mixing by thermal currents (see Section 2.4.6)) and required higher melting temperatures and/or times.

Daniels (1950) estimates that the crucibles from the Woodchester glasshouse (16th century) could have contained 150-200lb (68-91Kg) of glass, and Bridgewater (1963) estimates 400lb (182Kg) for those at Glasshouse farm, St Weonards (16th century). Crossley (1988) suggests that medieval glass melts may never have been fully homogeneous and the glassmaker may have deliberately avoided the use of the glass at the bottom of the crucible. The use of tall thin crucibles may have been used to prevent this problem such as noted at Bagot's Park (Crossley 1967) and Little Birches (Welch 1997).

2.4.6 The Effect of Stirring the Melt on Homogeneity

Glass melts are too viscous to allow turbulent mixing and are subject to laminar flow that will stretch out inhomogeneities. This will aid their removal by diffusion but is not as efficient as turbulent mixing, which can be achieved by stirring (Cable 1998). Stirring molten glass is widely used to improve homogenisation in modern experimental melts (Cable 1996, Cable and Hakim 1973, Cooper *et al.* 1967, Joanni *et al.* 1989). The only reference to stirring in medieval glassmaking texts is made by Biringuccio (Smith and Gnudi 1990: 129) but it is not know what the stirrer was made from, or when and how often this was carried out. Neri (Merrett 1662: 148) refers to molten glass being poured into water and then being remelted several times to improve the quality of the glass produced. Stirring, or pouring and remelting will facilitate homogenisation through mixing (Tiede and Tooley 1945). However, to stir the melt, the furnace would have to be opened, causing heat loss and there may have also been contamination of the melt with material from the stirrer.

2.5 Working

To form artefacts from a molten glass it must be at the correct temperature to obtain the required viscosity for the forming method selected. For example a lower viscosity will be required to blow glass than to cast it (Grose 1984: 29). The molten glass will be heated for longer periods than were required to melt it and will therefore be subject to all the variables that affect homogeneity discussed in Section 2.4. However, it is thought unlikely that working will have such a significant effect on homogeneity as fritting and melting but several factors should be considered. Longer melting times will facilitate homogeneity by internal mixing. Conversely, extended melting times may form more inhomogeneities due to ceramic corrosion or loss of volatiles from the melt surface. However, these will probably be negligible in the glass composition as a whole.

The action of blowing the glass may cause some additional mixing close to the surface of the melt. This occurs each time the blowing iron is placed in the melt to gather a gob of glass. Modern glassmakers twist the blowing iron as the glass is gathered to increase the quantity of glass that is collected. This action may facilitate homogenisation by mixing but also introduce inhomogeneities as the melt surface is mixed in with the bulk mass. If the glass does contain inhomogeneities then the production technique will influence their distribution, blowing the glass will stretch the inhomogeneities over a wider area than in thicker, cast glass. Areas that are rich in silica have a higher viscosity and will not flow as well as the rest of the glass. Due to this, successfully manipulating an inhomogeneous glass is difficult (particularly in blown glass), and melts of this nature may have been discarded or remelted. Therefore it is unlikely that these glasses would be found as finished artefacts.

2.6 Annealing

Annealing removes the internal stresses formed in a glass during working and is the final stage in the glassmaking process. The stresses are formed by temperature gradients produced as the artefact is repeatedly heated and cooled. If a glass is not annealed it will be brittle and shatter when touched (Shelby 1997). To remove these stresses an even temperature must be created throughout the whole body of the glass and the temperature lowered so the centre cools at the same rate as the surface (Shelby 1997). The annealing time and temperature vary according to glass type, the variation of thickness in the object and its position in the furnace.

Annealing is carried out at relatively low temperatures (400-600°C) compared to the rest of the production process (Shelby 1997: 109). Although annealing does not influence homogeneity, the success of annealing **is** affected by homogeneity. An inhomogeneous glass will contain regions of different compositions and therefore also a range of thermal expansions. As the glass cools, the different regions will contract at different rates causing breakage. The resulting cullet may have been remelted or discarded.

2.7 Selection of Experimental Variables and Conclusions

This chapter illustrates that the variables influencing homogeneity in medieval glass production (Figure 2:1) are very complex and frequently inter-linked producing combined effects. Within the scope of this research it is not possible to investigate every parameter and all the possible relationships. A number of variables are also constrained by the time and equipment available in this research. Allowing for these factors, the experimental variables that have been selected for investigation in the experimental part of this research (Chapters 4-6) are those believed to have potentially the most significant effects on homogeneity. These are summarised in Table 2:1, and Figure 2:3 illustrates how these correspond to Figure 2:1 where all the variables that influence homogeneity were depicted.

Stage of Glass Production	Variable to be Investigated
Raw Materials	Sand Grain Size
	Mixing
	Variation in Alkali Component
Fritting	Temperature
	Time
	Stirring
	Crucible Dimensions
	Crushing and Remixing Frit
Melting	Production of a Glass Without Fritting
	Time
	Temperature
	Crucible Dimensions
	Crucible Fabric
	Melt Size
	Furnace Atmosphere

Table 2:1 Summary of experimental variables to be investigated in Chapters 4-6

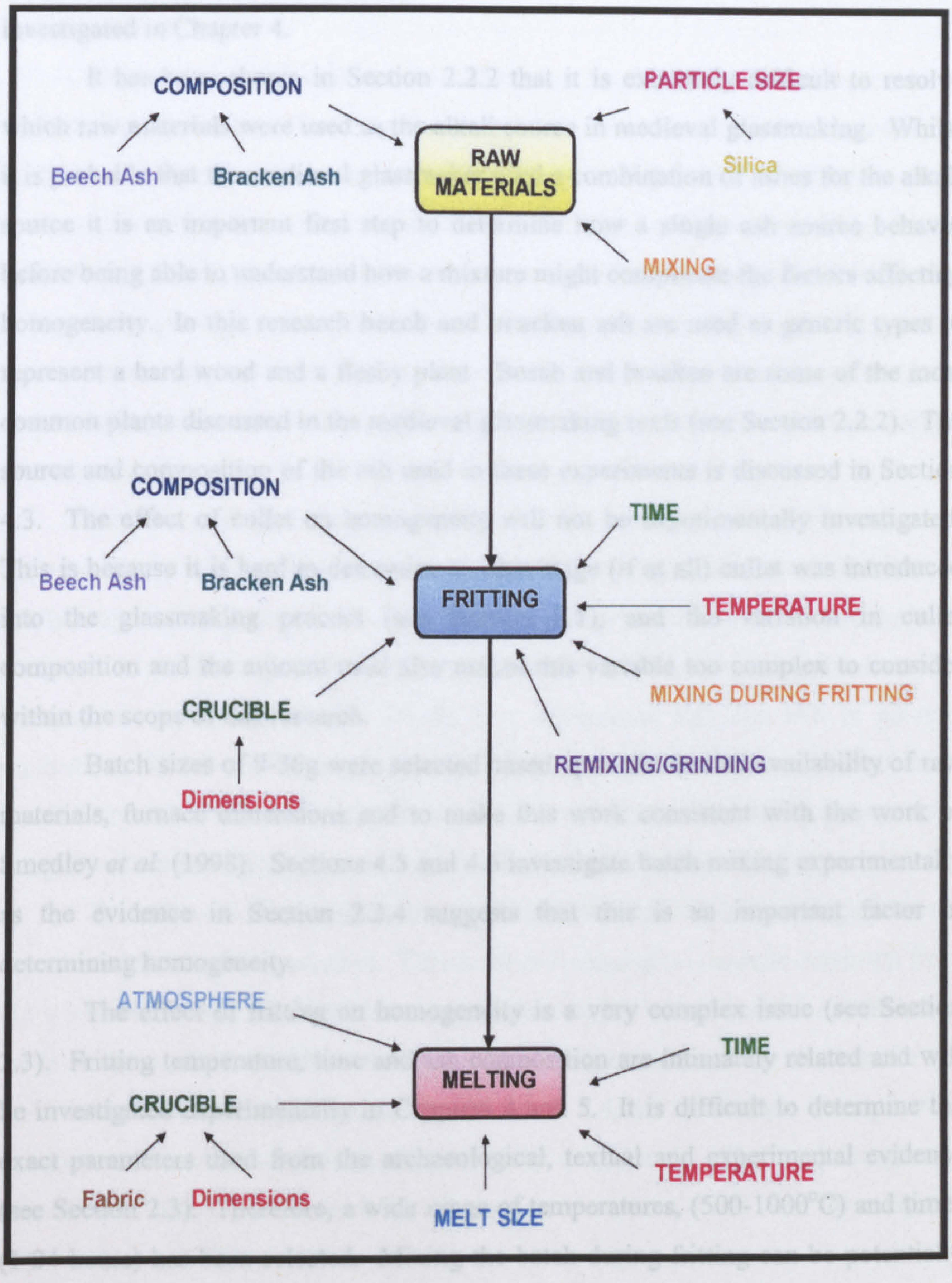


Figure 2:3 A schematic representation of the experimental variables to be investigated in Chapters 4-6

To avoid introducing unknown variables that may affect homogeneity into the experimental part of this research, the silica source was selected to have a known composition and particle size distribution (see Section 4.2). Section 2.2.1.1

determined that particle size will significantly influence homogeneity and this will be investigated in Chapter 4.

It has been shown in Section 2.2.2 that it is extremely difficult to resolve which raw materials were used as the alkali source in medieval glassmaking. Whilst it is probable that the medieval glassmaker used a combination of ashes for the alkali source it is an important first step to determine how a single ash source behaves before being able to understand how a mixture might complicate the factors affecting homogeneity. In this research **beech** and **bracken** ash are used as generic types to represent a hard wood and a fleshy plant. Beech and bracken are some of the most common plants discussed in the medieval glassmaking texts (see Section 2.2.2). The source and composition of the ash used in these experiments is discussed in Section 4.3. The effect of cullet on homogeneity will not be experimentally investigated. This is because it is hard to determine at what stage (if at all) cullet was introduced into the glassmaking process (see Section 2.1), and the variation in cullet composition and the amount used also makes this variable too complex to consider within the scope of this research.

Batch sizes of 9-36g were selected based upon the limited availability of raw materials, furnace dimensions and to make this work consistent with the work of Smedley *et al.* (1998). Sections 4.5 and 4.6 investigate batch mixing experimentally as the evidence in Section 2.2.4 suggests that this is an important factor in determining homogeneity.

The effect of fritting on homogeneity is a very complex issue (see Section 2.3). Fritting temperature, time and ash composition are intimately related and will be investigated experimentally in Chapters 4 and 5. It is difficult to determine the exact parameters used from the archaeological, textual and experimental evidence (see Section 2.3). Therefore, a wide range of temperatures, (500-1000°C) and times (1-24 hours) has been selected. Mixing the batch during fritting can be potentially beneficial to the formation of a homogeneous glass (see Section 2.3.3); this is investigated in Chapter 5. Crushing and mixing the frit prior to melting should also facilitate homogeneity (see Section 2.3.5), and is investigated in Chapter 5.

The choice of melting temperature and time are important parameters with respect to homogeneity (see Section 2.4.2 and 2.4.3). After trials (see Section 4.7) two melting temperatures of 1200 and 1300°C were selected for this research. These are thought to cover the possible temperatures that were obtained in medieval furnaces estimated from experimental work and also the temperatures that the raw materials melted at.

The effect of different crucible fabrics on homogeneity is a complex issue (see Section 2.4.5.1). The structure, chemical and physical characteristics of medieval crucibles are very varied and therefore it is impossible to reproduce these here. Therefore, two compositionally known, high refractory crucible fabrics (mullite and alumina) (see Appendix A) will be used to provide a possible indication of how homogeneity might be influenced by a change in crucible composition rather than to imitate any archaeological crucibles. The use of a known fabric composition should eliminate unknown variables being introduced into the experimental procedure.

An indication of scaling up melt size will be investigated by using melt sizes between 9-36g. Larger experimental melts could not be made due to the limited availability of raw materials (see Section 4.3.3.1). Melt size is influenced by melt temperature and time (see Section 2.4.5.2) and the effect of altering these can be investigated on smaller melts. Whilst it is understood that this will in no way replicate medieval melt sizes (see Section 2.4.5.2) it will provide an indication of possible trends. The effects of different surface area to volume ratios produced by using crucibles of varying sizes will also be examined in Section 6.1.3.

The effect of stirring the melt on homogeneity will not be investigated in the experimental part of this research. This is for two reasons: a) ceramic corrosion from the stirrer blade may introduce inhomogeneities, b) the volume of the experimental melts is too small to enable a conventional laboratory stirrer to be used or for the melt to be poured and remelted (see Section 2.4.6). Although the operating parameters for medieval glass furnaces are very complex the effect on homogeneity caused by altering the melting furnace atmosphere will be investigated experimentally in Chapter 6.

Working and annealing are also factors that influence homogeneity albeit to a lesser extent. They are not investigated here, as this would require the production of large quantities of experimental glasses. This is not within the scope of this research due to constraints on raw materials and laboratory equipment. However, the relationship between working and homogeneity must be considered as fragments of medieval worked glass (vessel and window) are analysed in Chapter 8.

Before investigating the variables discussed above it is important to set out the methodology that will be used to examine the experimental glasses formed. This will now be discussed in Chapter 3.

CHAPTER 3

Methodology for Examining the Experimental and Archaeological Glasses

3.1 Introduction

This chapter describes the standard set of parameters that were developed to record the experimental frits and glasses produced in Chapters 4-6 and the archaeological material investigated in Chapter 8. A suitable method for measuring inhomogeneity was also required and this is discussed in Section 3.2. The different methods used to depict the visual and microscopic results are described in Section 3.3. In some cases the qualitative nature of the observations meant that it was hard to quantify the results, but where possible a systematic recording process has been used.

3.2 Methods of Measuring Homogeneity

A suitable method was required to determine the extent of homogeneity in the experimental and archaeological glasses in this research. To quantitatively describe the homogeneity of a sample a minimum of two parameters are required. These are, **intensity,** which is the magnitude of deviation of the property from the average value, and the **scale,** which is the size of the sample used or of the inhomogeneity itself (Cable and Bower 1965: 197). In this research it is important that inhomogeneity can be described in parameters that correspond to the compositional study of archaeological glass (see Section 1.3). It is therefore vital that the measuring method selected provides the following data:

- **Composition**

  This is the relative compositional difference between inhomogeneities and the glass matrix. These data determine to what extent the inhomogeneity is likely to exert a bias on compositional results (see Section 1.3).

- **Size**

  If the sample size and/or analysis area is significantly smaller than the size of the inhomogeneities then the data obtained may not be representative of the true glass composition (see Section 1.5).

- **Position**

  If the glass has widely and unevenly distributed inhomogeneities then the sample selected for analysis may also not be representative of the true glass composition.

Several techniques have been developed to measure the homogeneity of glass. These techniques arose from industrial applications where homogeneity is very important, as it can adversely affect the mechanical and optical properties of a glass (see Section 1.2) (Anon 1961, Cable and Bower 1965, Imagawa 1973). These industrial methods are not constrained by the amount of material available or the possible destruction of the sample during testing, as is the case in this study. Therefore, the application of these techniques to archaeological samples is not always appropriate. The following sections describe some of the methods that have been developed for measuring homogeneity and summarise their suitability for the glasses in this research.

3.2.1 Visual Examination and Shadow Patterns

The presence of cord in a glass will leave flow patterns that frequently can be detected visually (see Section 1.1). The ease with which this can be seen depends on the size and colour of the inhomogeneity, and the thickness of sample. Placing glass samples against contrasting backgrounds has been used to facilitate observation (Anon 1961).

Inhomogeneity can also be recorded using either an ordinary photograph or a shadow pattern. A shadow of the glass is cast onto a screen or photographic plate and the smaller the source of light used the sharper the shadow. Examples of this type of apparatus are described by Spencer and Badger (1924), Seddon (1937) and Jebsen-Marwedel (1959). Any irregularities on the glass surface will appear as light and dark streaks on the photographic plate. The flow patterns in a glass can be observed without the interference of surface markings by submerging the test piece into a liquid of identical refractive index (Anon 1961, Wright 1921). These methods are non-destructive and provide a visual indication to the extent of inhomogeneity on a macro scale. However, the compositional difference between the bulk glass and inhomogeneity is not obtained and the sample size is large (several centimetres). Therefore this method is not suitable for the archaeological samples in this research.

3.2.2 Density Spread Technique

The density spread technique was developed by Turnbull (1941), and Turnbull and Ghering (1941). It involves the crushing and centrifuging of a sample of glass to determine the spread of density distribution throughout the particles. The disadvantages of this method are that it is laborious and does not give information about the precise distribution or composition of inhomogeneities throughout the glass. The scale of the inhomogeneities can sometimes be determined if they are in the same order of magnitude as the glass particles. Thus, this method is only suitable for determining the *relative* intensity of the inhomogeneities in a glass (Cable and Bower 1965). This method is unsuitable for archaeological glasses due to the destruction of a large sample (approximately 10g (Turnbull 1941, Turnbull and Ghering 1941)) and the limited value of the information that it yields.

3.2.3 The Christiansen-Shelyubskii Method

This method is derived from the principle of the Christiansen Filter (Christiansen 1884a, 1884b) and the interpretation of this by Raman (1949) and Schilling and Weiss (1966: 66). The fundamental principles of this technique are discussed by Hense (1987a, 1987b). The basic apparatus consists of a long, optical cell filled with grains of the crushed glass sample suspended in a liquid of matching refractive index. A suitably dimensioned cell will allow a beam of white light to pass through undeviated giving a virtually monochromatic beam of white light, this is known as a Christiansen Filter (Hense 1987a, 1987b). If the refractive indices of the glass and liquid differ then the light will be refracted and will scatter each time it passes a glass liquid boundary. This effect can be used to measure the homogeneity of a glass and essentially gives the homogeneity factor as the standard deviation of the refractive index (Tenzler and Frischat 1995).

Shelyubskii (1960) developed this principle and Cable and Bower (1965) produced a simple apparatus to carry out experiments using this technique. Their method was easy to use but although it gave the intensity of the homogeneities it did not give their distribution and orientation. Further development of Shelyubskii's technique by Imagawa (1973), Sakaino *et al.* (1978) and Cable and Walters (1980) refined the accuracy of the method. Coloured glasses require a further modification to account for the absorption of the glass, which will lower the transmission values and simulate a higher inhomogeneity (Budd and Blanchard 1966, Inoue *et al.* 1981). The Christiansen-Shelyubskii technique is not suitable for archaeological glass samples. This is due to the destruction of the sample, the sample size (approximately 2g (Budd and Blanchard 1966: 13)) required, the lack of information about the distribution of inhomogeneities, and the modifications that would be required for coloured glasses.

3.2.4 Etching and Interferometry

This technique was originally devised and then developed by Löffler (1954) to provide a way of examining individual inhomogeneities. It can also provide the parameters necessary for the quantitative measurement of the homogeneity of a sample. The method involves a test piece of glass being placed in dilute hydrofluoric acid. The rate of attack of this acid on soda-lime-silica glasses is very sensitive to changes in chemical composition and the etching of an inhomogeneous glass sample will therefore produce regions of differing depths. The differences, which are of the order of a few wavelengths of light, can be measured using an interferometer. The pattern of interference fringes produced provides the difference in depth of etching (intensity of the inhomogeneity), the size of the inhomogeneities (scale) and the distribution of inhomogeneities throughout the sample (Cable and Bower 1965, Cable and Hakim 1973). The depth of etching does not define the exact chemical composition of the inhomogeneity even though the depth does depend on composition.

The main problem that exists with the application of this technique to potash rich archaeological glasses is that calibration would be required to determine the attack rates on potassium-lime-silica glasses. Although the method identifies the position of inhomogeneities in the sample it does not supply their chemical composition. In addition, the highly corrosive acids that destroy the samples also make this method inappropriate for this research.

3.2.5 SEM (EDS/WDS) and EPMA

SEM and EPMA can be used to examine inhomogeneity both qualitatively and quantitatively (Adams *et al.* 1966). The EPMA works by focusing an electron beam onto a small area of the sample and collecting the emitted X-rays. Qualitative analysis is possible as each element has a characteristic X-ray spectrum and therefore each line obtained can be identified by its wavelength. These results can then be quantified by comparing the intensities of the lines obtained from the sample with those produced from standards of known compositions. To collect the spectra an EPMA will often have an energy dispersive spectrometer (EDS) in addition to a number of wave dispersive spectrometers (WDS) attached to it. The EDS collects the spectra in parallel and gives a rapid and convenient way of obtaining the overall composition of a sample. In comparison the WDS focuses on one wavelength at a time and therefore some EPMA machines will have a number of spectrometers attached to them working in series. Although the analysis time is generally slower the precision, accuracy and limits of detection are generally improved (Reed 1996).

The SEM is primarily an electron imaging tool. It works in a very similar way to the EPMA except the beam is scanned over a small area of the sample, by changing the type of detection either a topographical or a compositional contrast (using backscattered electrons) image can be obtained (Goodhew *et al.* 2001). An SEM can also be modified to carry out compositional analysis by attaching an X-ray spectrometer. Such instruments are often referred to as SEM-EDS or SEM-WDS depending on the type of spectrometer attached. In archaeological glass analyses, SEM-EDS is generally more common (see Section 1.5) (Reed 1996).

Backscattered imaging (usually with a SEM but sometimes available on EPMAs) can successfully identify the presence of inhomogeneities (Adams *et al.* 1966: 99). Plate 3:1 illustrates two images taken from the same piece of inhomogeneous glass attached to a crucible fragment (to the bottom right of the picture). The left hand secondary electron image is topographical and it can be seen that the structural properties of the crucible are shown clearly, whilst the translucent glass (which has no structure) appears as all one colour. The right hand image was taken in backscattered electron mode. The intensity of the colours is proportional to the composition of the material, brighter regions corresponding to a higher mean atomic mass than darker areas (Chescoe and Goodhew 1990, Reed 1996). The contrast of the backscattered image in Plate 3:1 has been adjusted to reflect the compositional differences in the glass rather than the crucible. The dark and light areas indicated on the image indicate the presence of inhomogeneities. However, it should also be noted that in some cases an inhomogeneous sample will not exhibit any colour contrast on a backscattered image. This can occur in multi-element materials, such as glass, when regions of the same sample have different elemental proportions but the same mean atomic mass (Goodhew *et al.* 2001).

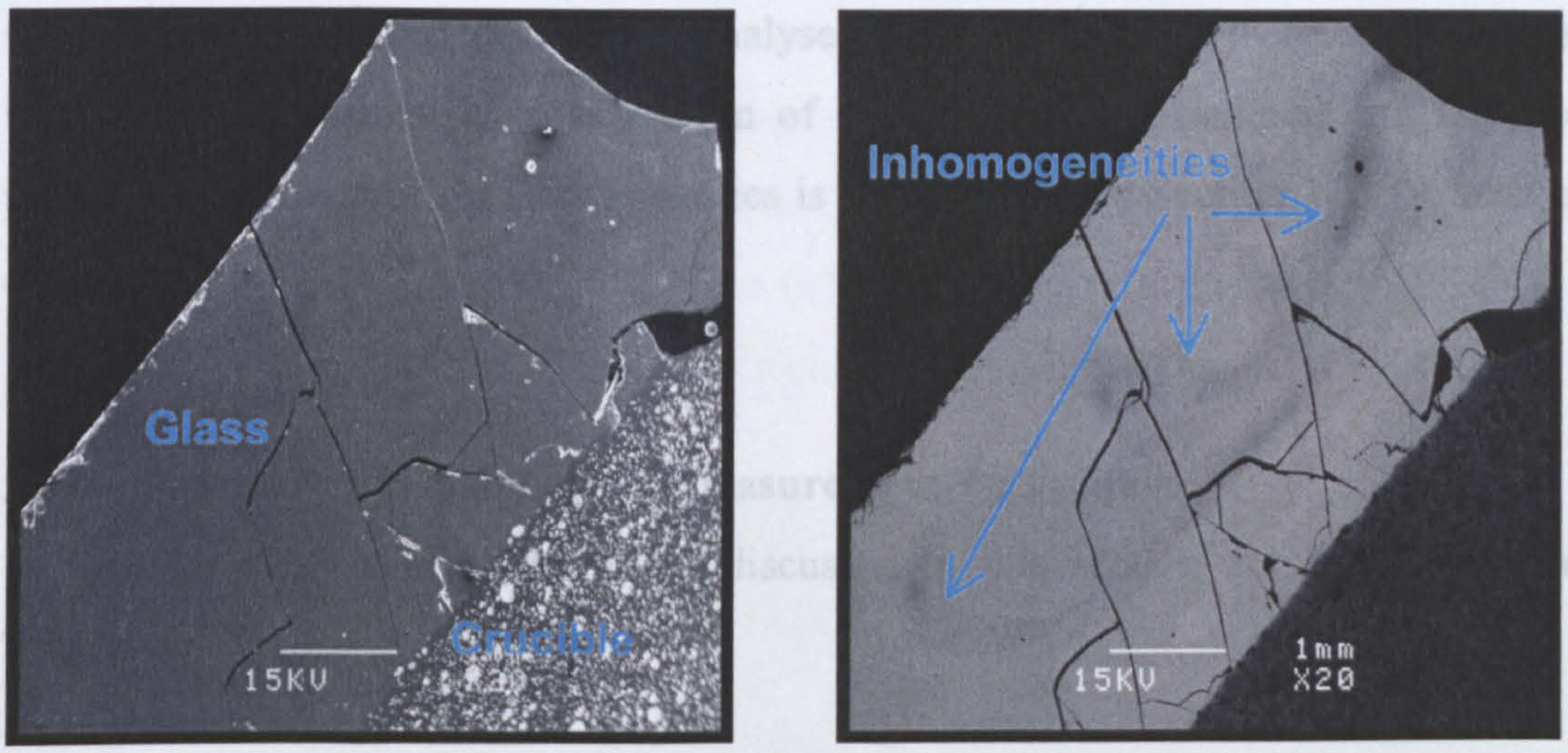


Plate 3:1 A comparison between a secondary electron (Left) and backscattered (Right) SEM image of an inhomogeneous glass sample (Br68, Table V:19)

Once the presence of these inhomogeneities has been identified the difference between the bulk glass composition and the inhomogeneity can be quantified by analysis using an SEM-EDS/WDS or EPMA. Depending on the information required this could take the form of spot or line analyses, or elemental mapping. These techniques have not been widely used to examine inhomogeneity. Adams *et al.* (1966) obtained qualitative and semi-quantitative data on inhomogeneous borosilicate glasses using SEM backscattered images and EPMA line scans. In archaeological glasses only a small number of published studies of archaeological glasses have noted the presence of inhomogeneities (see Section 1.3). In all of these cases a combination of SEM and EPMA was used to identify and quantify the inhomogeneities present (Brill and Moll 1963, Cox and Ford 1989, Giannichedda *et al.* 2000, Riccardi *et al.* 1999).

The use of SEM and EPMA provides a relatively fast and easy way of identifying the presence and composition of inhomogeneities in small (generally several millimetres or less) glass samples. Although these techniques are 'non-destructive', sample preparation can require the removal of very small samples from the original material (see Section 1.5). Due to the limited size of archaeological material usually available for analysis this would seem to be an advantage. However, if large scale inhomogeneities are present they will not be identified in small samples (see Section 1.3). These techniques are also specialised and expensive, and if large samples are available they cannot always be accommodated. Only one surface of the glass can be analysed at a time, and it is therefore important to ensure that a suitable cross section of the material is examined and that the possible orientation of the homogeneities is considered (see Section 1.3) (Adams *et al.* 1966: 98).

3.2.6 Summary of Homogeneity Measurement Techniques

The measurement techniques discussed in this section are summarised in Table 3:1.

Method of Measuring Inhomogeneity	Composition of Inhomogeneity	Distribution of Inhomogeneities	Position of Inhomogeneities	Sample Destruction	Sample Size Larger than 1g?
Visual Examination and Shadow Patterns	No	Yes	Yes	No	Yes
Density Spread Technique	No	No	No	Yes	Yes
Christiansen – Shelyubskii Method	No	No	No	Yes	Yes
Löffler's Etching and Interferometry	No	Yes	No	Yes	No
SEM and EPMA	Yes	Yes	Yes	Yes	No

Table 3:1 A comparison of homogeneity measurement techniques and the different parameters that they measure

The most suitable method for assessing inhomogeneity in the experimental and archaeological glasses in this research is backscattered SEM imaging coupled with SEM-EDS/WDS or EMPA analysis. The use of these techniques fulfils the criteria set out in Section 3.2 as the position, scale and the composition of inhomogeneities can be obtained, and this is also an easy and practical technique. Most importantly, it has been seen that SEM and EPMA are widely used for the compositional analysis of archaeological glasses (see Section 1.5). The significance of inhomogeneity on this type of analysis can therefore be assessed.

3.3 Measurement of Results in Chapters 4-6 and 8

3.3.1 Visual Observations

A standard method was developed for recording the features observed in the experimental frits and glasses produced in Chapters 4-6. All the material produced was examined visually with a hand lens (x10) and a range of parameters recorded. These differed between frits and glasses and are listed in Table 3:2.

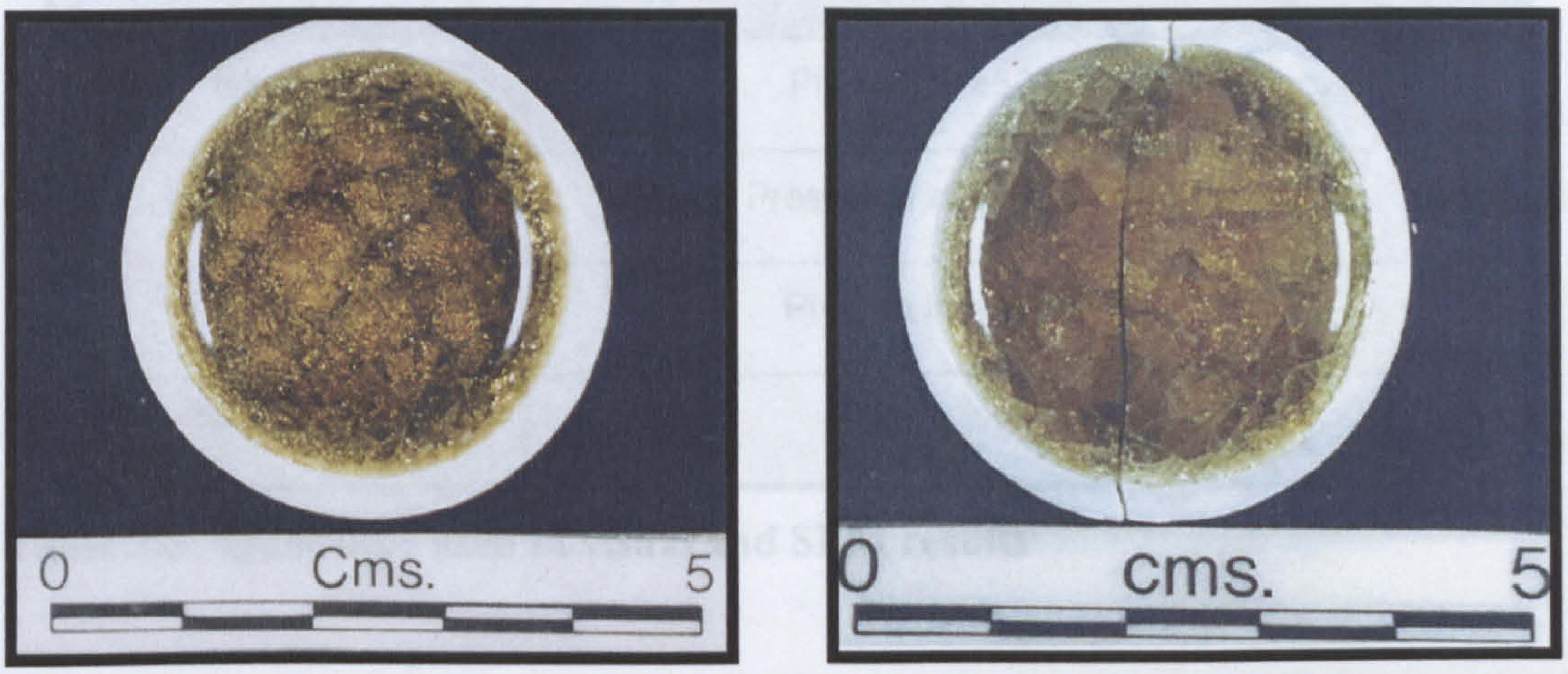
Material	Observation Recorded
Frit	**Colour**
	Percentage change in batch volume from unheated to heated batch
	Presence of any unreacted batch (loose raw materials)
	Friability of the product
	Extent of vitrification within the product
Glass	**Colour**
	Presence of any unreacted batch
	Presence of any batch relics (white crystalline inclusions within the glass)
	Presence of any opacity* (a cloudy appearance in the glass)
	Presence of any crystalline substances on the glass surface*

* Only present in bracken ash glasses

Table 3:2 Visual observations recorded for experimental glasses and frits

An example of a visually homogeneous glass, and glasses with batch relics, opacity and the crystalline substance can be seen in Plate 3:2. Glasses containing batch relics that were visible to the eye were taken to be **visually inhomogeneous**.

The percentage reduction in batch volume was calculated by recording the volume of each batch before and after heat treatment. The extent of friability, vitrification and colour were subjective observations.



Visually homogenous bracken glass (Br116, Table V:23)

Bracken glass with opacity (Br147, Table V:27)

Bracken glass with crystalline substance and batch relics (Br79, Table V:19)

Beech glass with batch relics (Be144, Table VI:5)

Plate 3:2 Examples of batch relics, opacity and white crystalline substance in experimental beech and bracken glasses

Batch relics, opacity and the crystalline substance were found to vary considerably in quantity in different glasses. In order to quantify the variation between samples a set of parameters was created and are listed in Table 3:3. It can be seen from Plate 3:2 that the beech ash glasses are very deeply coloured and although it was visually easy to see batch relics and inhomogeneity, representing this photographically was frequently difficult.

Symbol	Occurrence
High (H)	Present in ≥50%of the glass
Medium (M)	Present in ≥25-<50% of the glass
Low (L)	Present in <25% of the glass
None (NV)	Not visible in the glass

Table 3:3 Qualifiers used in visual and SEM results

The archaeological glasses investigated in Chapter 8 were initially examined using a hand lens (x10), and their colour, condition (the presence of weathering products) and the presence of any opacity recorded. Following visual examination the archaeological and experimental glasses were subjected to SEM and/or EPMA analysis and this is described in Section 3.3.2.

3.3.2 Scanning Electron Microscopy and Electron Microprobe Analysis

3.3.2.1 Instrumentation

The SEM and EPMA analyses were carried out at the NERC Electron Microprobe Facility in the Department of Earth Sciences, University of Manchester. A JEOL JSM6400 analytical scanning electron microscope fitted with an Oxford Instruments, energy dispersive spectrometer was used for imaging. Towards the latter part of this research the detector on the SEM was replaced with a PGT X-ray Analysis System. The Cameca SX100 electron microprobe was not commissioned until near the end of this research. It was then used in conjunction with the SEM to provide elemental mapping and line scans.

3.3.2.2 Sample Selection and Preparation

The aim of sampling the experimental glasses for imaging and analysis was a) to ensure that the piece removed would be as representative of the whole glass as possible, and b) to look at the extent of inhomogeneities produced when variables in the glassmaking process were altered. The ideal situation would have been to examine the whole glass, because the size and distribution of any inhomogeneities was not known (see Section 1.5). However, this was not possible due to the large number of glasses to be analysed (over 350) and the size constraints of the SEM and EPMA sample holders (26mm diameter).

Vertical cross sections of the experimental glasses were selected for analysis, as these are likely to exhibit a higher incidence of inhomogeneity (see Section 1.5). The area of glass available for analysis in most cases was approximately 2cm by 0.5cm. In the case of the archaeological material (Chapters 7 and 8) the dimensions of the artefact and the quantity that could be removed for analysis limited the sample size. Where possible the largest cross section obtainable was selected but care was taken to remove a sample where the surface to be analysed would not have been altered by weathering or corrosion (see Section 1.3). Samples of both the experimental and archaeological glasses were mounted in Presi Mecaprex MA 2 epoxy resin, ground using Buehler silicon carbide papers (400, 800 and 2500 grades) and then polished using Buehler Metadi diamond spray to 0.25μm. The samples were coated with a layer of carbon to ensure good conductivity during analysis.

It is important to note that the sample sizes used are substantially larger than those **usually** examined in compositional analyses of archaeological glasses using SEM and EPMA (see Section 1.5). Thus, by examining a larger area it will be possible to determine how inhomogeneity will influence compositional results if only a small sample is analysed. This has important implications for archaeological research (see Section 1.5).

3.3.2.3 Imaging

The mounted, polished and coated samples were examined using the SEM in secondary and backscattered electron modes (see Section 3.2.5). The SEM was operated at 15kV with a beam current of 1.5nA at a working distance of 15mm and a take off angle of 40° for the Oxford Link detector, and 30° for the PGT detector (see

Section 3.3.2.1). Each sample was examined carefully and any inhomogeneities recorded and photographed. All the images in this thesis were taken when the SEM was fitted with the PGT detector (see Section 3.3.2.1). The glasses were divided into three categories based on the electron imaging results:

1. Inhomogeneous glasses with silica relics (Plate 3:3).
2. Inhomogeneous glasses with no silica relics (Plate 3:4).
3. Homogeneous glasses (Plate 3:4).

A variation was observed in the number of silica grains and the extent of inhomogeneity within the glasses in the first two categories (Plate 3:3 and Plate 3:4). These were split into categories of high, medium, low and none visible using the same parameters as listed in Table 3:3. It should be noted that the homogeneous glasses in (3) are those where no grey level contrast was visible on the backscattered image (see Plate 3:4). Although it was seen in Section 3.2.5 that these glasses could still be inhomogeneous it is thought that the likelihood of many samples exhibiting this phenomenon is low. However, quantitative analysis (see Section 3.3.2.5) will be used to determine the extent to which elemental composition varies in 'homogeneous' samples.

3.3.2.4 Elemental Mapping

Elemental mapping was carried out on one archaeological sample (see Section 8.3.1). The technique allows a small area of the sample to be scanned for a set number of elements. The results are given in the form of images where changes in elemental concentration in the area scanned are represented by different colours (Reed 1998). Elemental mapping was carried out using the EPMA with an accelerating voltage of 20kV and a beam current of 100nA.

3.3.2.5 Compositional Analysis

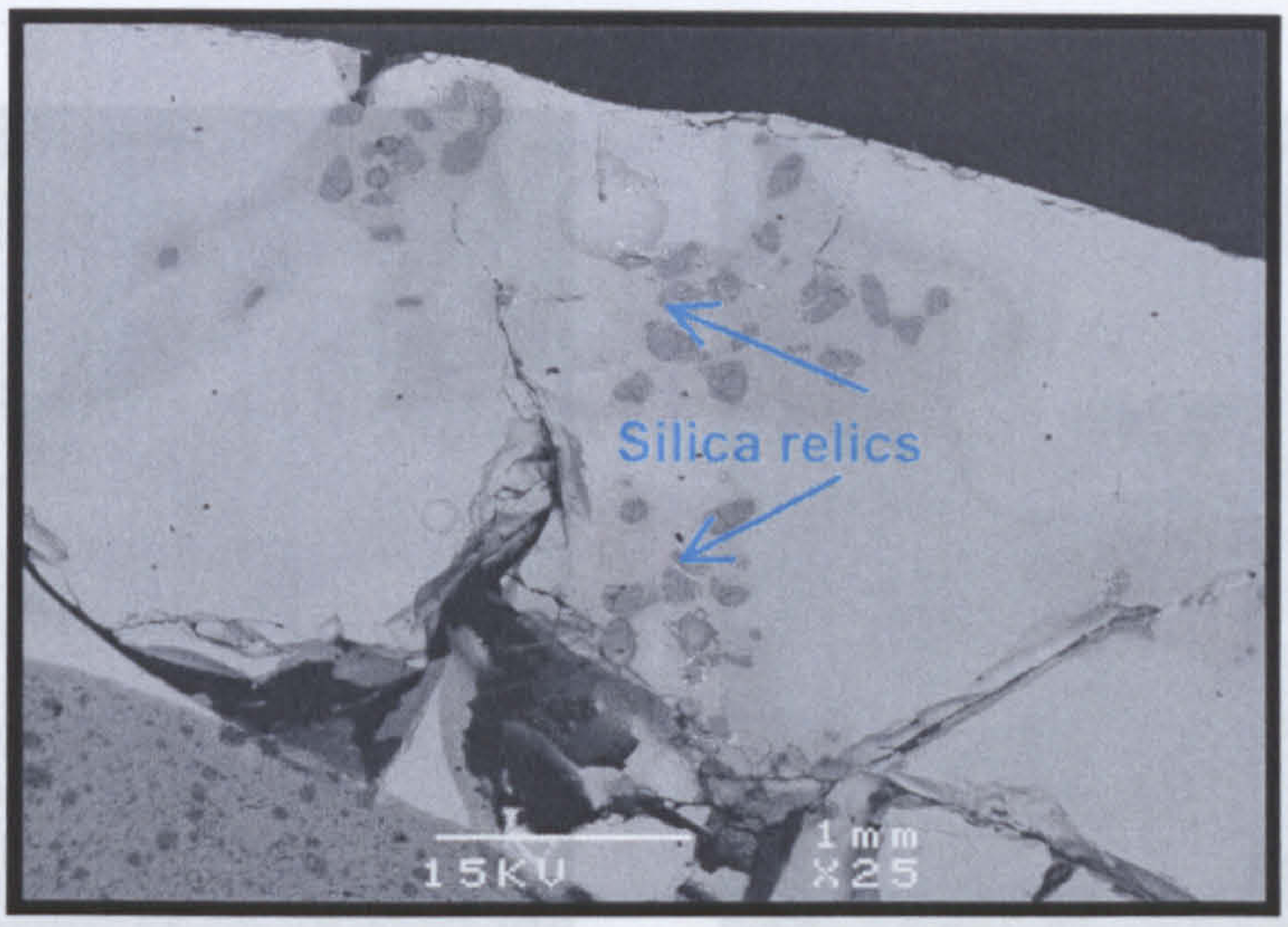
The chemical analysis of the experimental and archaeological glasses was carried out using the EPMA (see Section 3.3.2.1). The basic operating parameters are described in Table III:1. A defocused beam of approximately 10-20μm in diameter was used, with a beam current of 6nA and an accelerating voltage of 15kV. To optimise results for the volatile elements these were counted first using short count times. The data obtained from the EPMA is automatically corrected using an internal ZAF correction program.

The EPMA was calibrated with known mineral and metal standards for each element to be detected (Table III:1). Corning D, a potash based, glass standard that is comparable with medieval glass compositions was then used to ensure that the system was set up correctly for the glasses to be analysed, and that matrix effects were minimised (Table III:2) (Brill 1972: Table IV). The EPMA data obtained for this thesis was collected over 5 runs. On each occasion the same standardising procedure was carried out and Corning D was analysed before, during and after the unknown samples were analysed. Initially it was not possible to obtain data for chlorine, cobalt or copper. Analysis of chlorine became possible after run 1 but cobalt and copper were only available for runs 4 and 5.

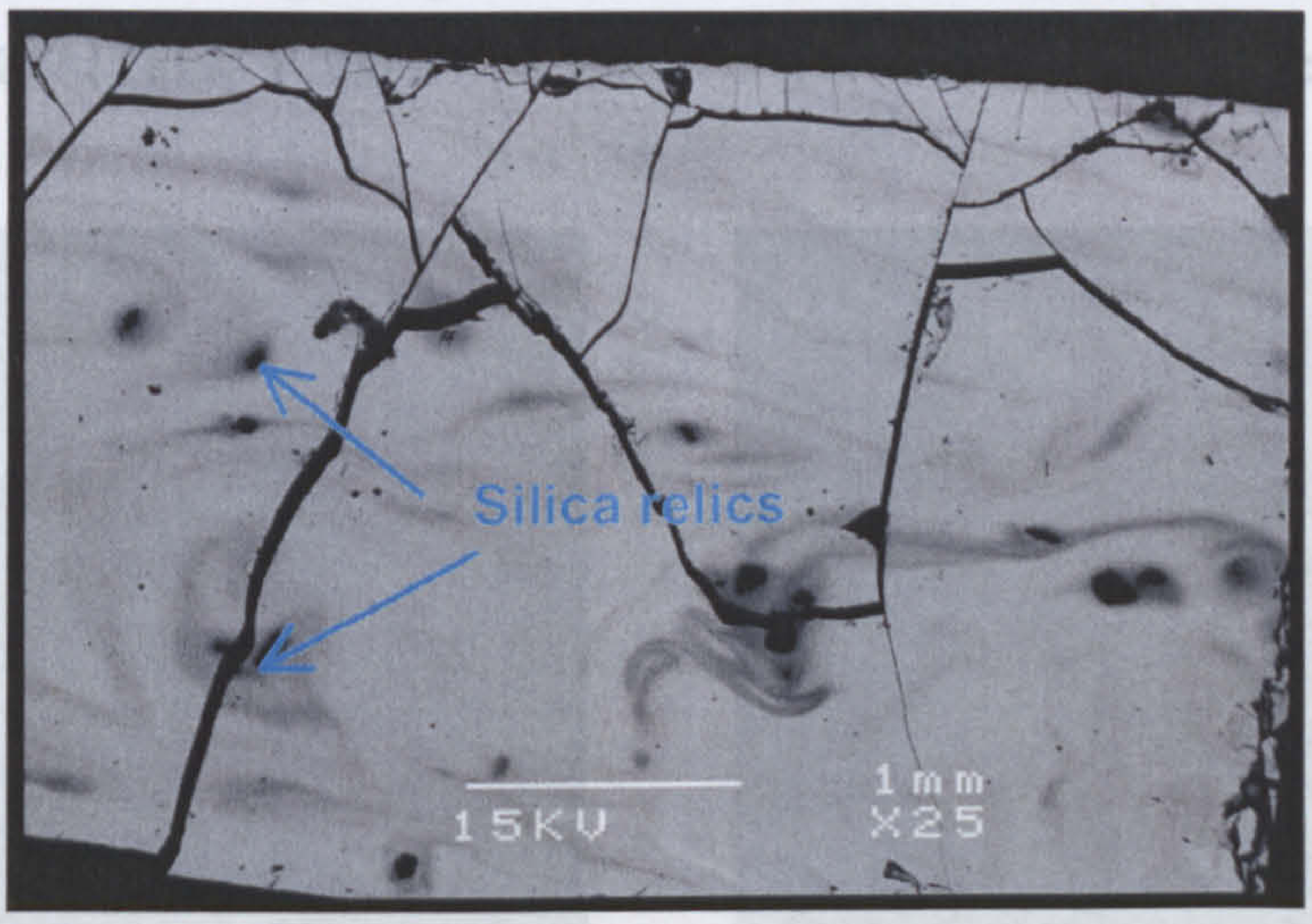
The Corning D analyses for each run were averaged and are recorded in Table III:3. The difference between the published (Table III:2) and recorded values was then calculated and the data obtained from the archaeological and experimental glass samples corrected by this factor (using the data from the relevant run). The average and 2 sigma values from the Corning D data for each run is listed in Table III:3. The relative variation in the data can be observed by comparing the values of the coefficient of variation (standard deviation/mean), this is expressed as a percentage and recorded in Table III:4. The average lower limit of detection (see Appendix B) for each element on each run and over the entire data set is listed in Table III:5.

It can be seen from a comparison between the published values of Corning D (Table III:2) and the data obtained from each run (Table III:3, Table III:4 and Table III:6) that the data exhibits a good degree of accuracy and precision for the majority of the elements analysed. It should be noted that although the values obtained for iron have a good accuracy there is a significant variation in precision between each run. A significant variation in precision between each run can also be seen in the chlorine values. Although the level of chlorine in Corning D is significantly greater than the lower limit of detection of the EPMA for this element the data obtained from the Corning D analyses also have poor accuracy. The values obtained for aluminium are approximately 0.5Wt.% lower and the concentrations of phosphorus (with the exception of run 1) are approximately 0.5Wt.% higher than the expected values from Corning D. However, the small standard deviation of the coefficient of variation for these elements (Table III:6) shows that this data does have good precision. The levels of sulphur and cobalt in Corning D are too close to the lower limits of detection of the EPMA (Table III:5) for the values obtained to be confirmed or refuted.

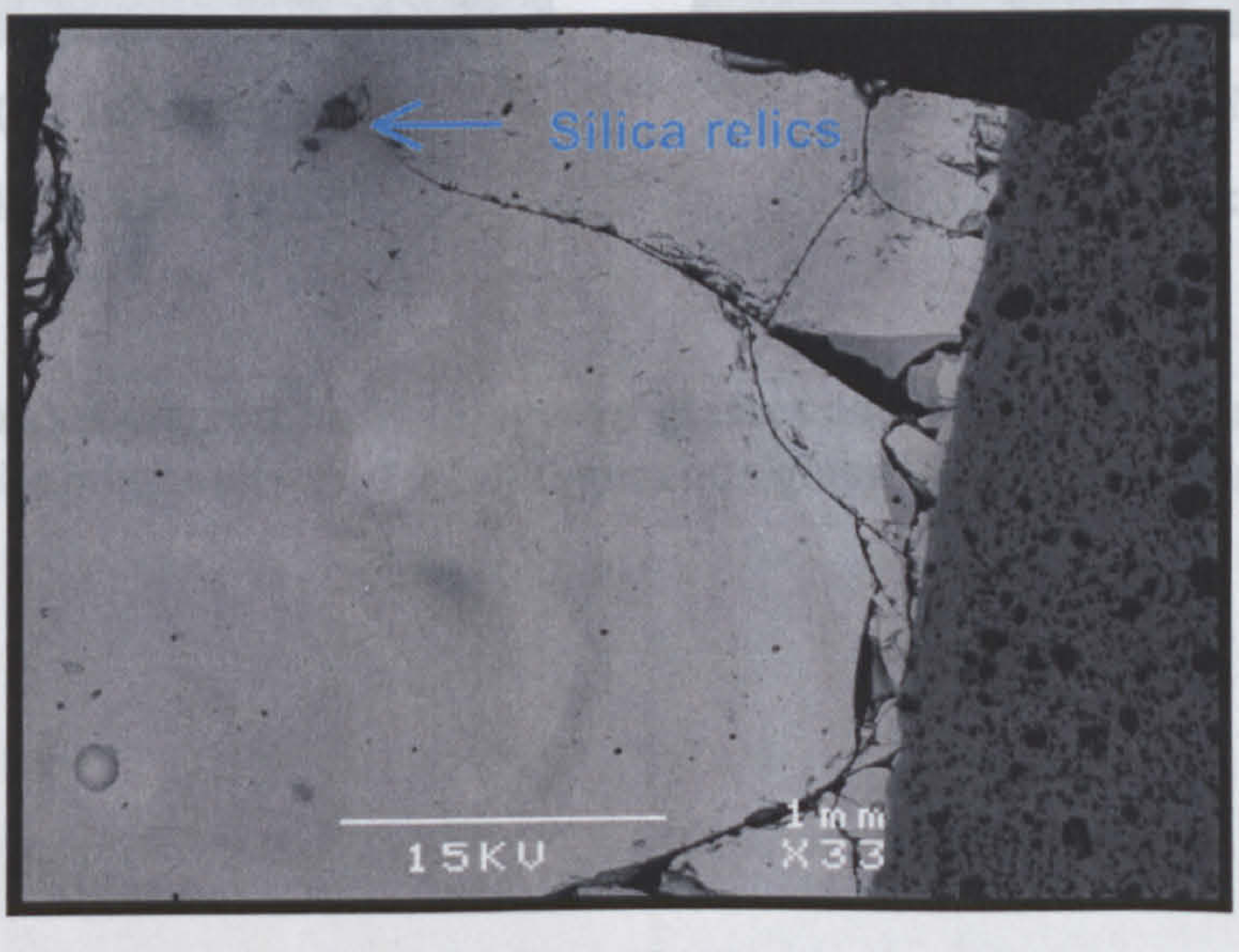
Analyses of the unknown samples were carried out using the same techniques and conditions as the Corning D standards. Therefore, in cases where the concentration of the elements in the unknown is similar to that of the standard they should both be subject to the same standard deviation. In this research the 2 sigma values for Corning D (Table III:3) and the lowest detectable limits (Table III:5) obtained from each data run will be used.



High (H) Quantities of Silica Relics (Be70, Table IV:20)

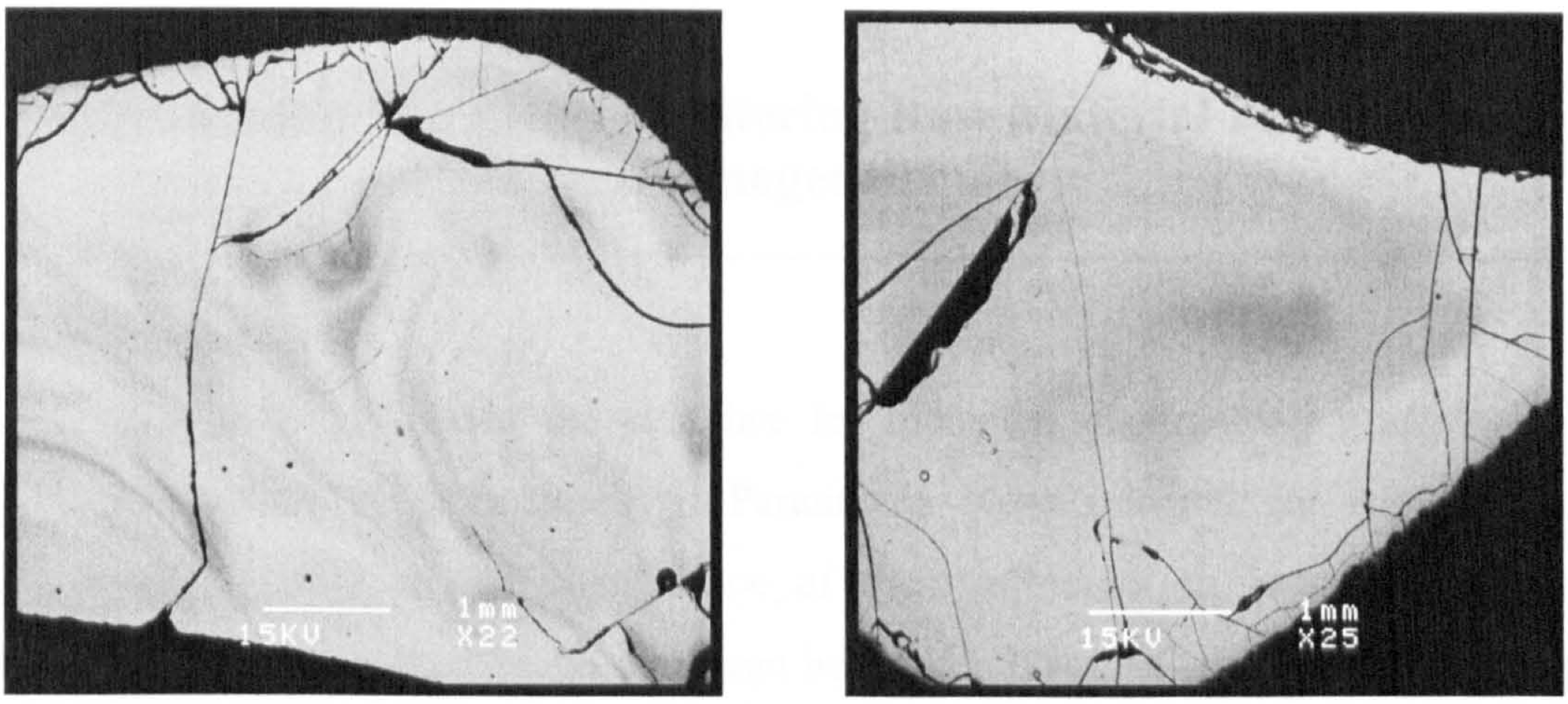


Medium (M) Quantities of Silica Relics (Be101, Table V:16)



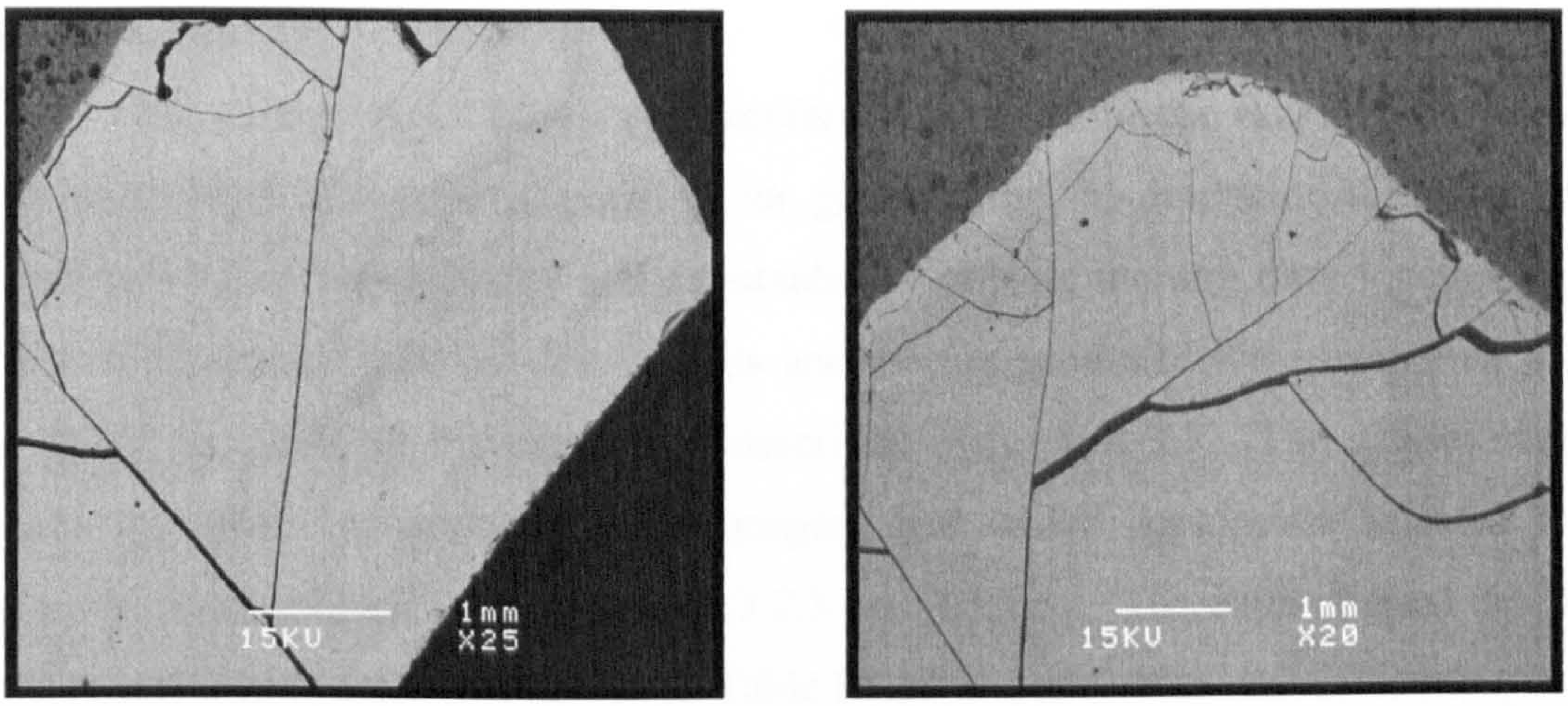
Low (L) Quantities of Silica Relics (Br)

Plate 3:3 Backscattered SEM images of inhomogeneous beech and bracken glasses containing varying quantities of silica relics (Table 3:3)



High (H) Inhomogeneity
Br147 (Table V:28)

Medium (M) Inhomogeneity
Br45 (Table IV:24)



Low (L) Inhomogeneity
Be84 (Table IV:20)

Homogeneous (NP)
Br37 (Table IV:22)

Plate 3:4 Backscattered SEM images of glasses containing different levels of inhomogeneity and a homogeneous glass for comparison (Table 3:3)

CHAPTER 4

Experimental: The Effect of Altering Raw Material Parameters on Homogeneity

4.1 Introduction

Chapter 2 discussed the evidence for medieval glassmaking practices and their relationship to homogeneity. Parameters were selected for experimental investigation based on the significance of their influence on homogeneity (see Section 2.7). This experimental work can be broken down in to three main themes: **raw materials** (this Chapter), **fritting** (Chapter 5) and **melting** (Chapter 6). However, it will be seen that there are many links and interactions between the variables involved in each stage and that it is often difficult to draw a distinction between each one.

The aims of this Chapter are therefore to: a) describe the raw materials used in this research and their preparation for glassmaking, b) determine the effect of batch mixing on homogeneity and c) establish a suitable melting time for each ash used in Chapters 5 and 6. All the frits and glasses produced were examined and recorded according to the parameters described in Section 3.3. The glasses were examined using backscattered SEM imaging and where appropriate selected for compositional analysis (see Sections 3.3.2.3 and 3.3.2.5). The experimental details and results are recorded in Table IV:1-Table IV:24.

4.2 Sand

The influence of the silica source on homogeneity has been discussed in Section 2.2.1. Loch Aline L30A commercial grade sand (commonly used in the modern UK lead crystal glass industry) was chosen to provide a known source with uniform chemical and physical properties, which would avoid introducing unknown variables that may affect the homogeneity of the experimental glasses. The compositional analysis (by XRF) is given in Table 4:1 and the typical distribution of particle sizes in Table 4:2 (Tilcon 1999: 1). This data indicates that the sand is of high purity and has a limited range of grain sizes.

Chemical Composition	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	MgO	Loss on Ignition
Oxide Wt.%	99.8	0.05	0.009	<0.05	<0.01	<0.02	<0.05	0.07

Table 4:1 Chemical composition of standard grade Loch Aline sand (L30A) (Tilcon 1999: 1)

	Particle Size (B.S. 410 Test Sieves) /µm							
	>500	>425	>355	>250	>180	>125	>90	<90
Typical %	Nil	0.2	3.0	36.0	53.7	6.4	0.5	0.1
Specification Limits %	Nil	1.0max	N/a	n/a	n/a	N/a	0.6max	n/a

Table 4:2 Typical distribution of particle sizes in Loch Aline standard grade sand (L30A) (Tilcon 1999: 1)

Sand grains of known particle sizes were required for all of the following experiments. To limit variations in the raw material, a single batch of L30A sand was prepared. A large sample of sand (3.0Kg) was ground for 24 hours using a ball mill containing alumina milling media (1.5Kg). The resultant sand was then sieved (B.S. 410 Test Sieves) to produce different grades ranging from ≤45µm-≥425µm grain diameter. The sand was sieved in quantities of 100g to ensure it was all subjected to the percussion action of the sieve shaker and to prevent contamination of larger grain sizes with smaller ones. The sieving stage was repeated three times for each grade to ensure consistent results. Each grade was washed repeatedly with copious amounts of water until no more fines could be observed in the decanted liquor. The sand was then heated to 105°C for 12 hours to remove the remaining water. The grades of sand produced for these experiments are listed in Table 4:3.

Milled Sand Particle Size (B.S. 410 Test Sieves) /µm						
≥425->250	≤250->180	≤180->150	≤150->75	≤75->63	≤63->45	≤45

Table 4:3 Particle sizes of milled Loch Aline standard grade sand (L30A) produced for use in this research

4.3 Beech and Bracken Ash

4.3.1 Ash Preparation

The use of beech and bracken ashes in medieval glassmaking has been described in Section 2.2.2, and the reasons why they have been chosen for these experiments discussed in Section 2.7. At least two kilograms of beech tree ash was required to produce the glasses for the experimental part of this project (Chapters 4-6). It would have been preferable to use a single source of beech ash but this was not possible due to the large amount of wood required (see Section 4.3.3.1). Experiments in Section 4.6 used beech ash obtained from branches and twigs (brash) prepared by Smedley *et al.* (1998). This was collected from a single tree of an unknown age, the burning parameters are listed in Table IV:1.

The majority of experiments (Sections 4.7-6.1.4) used beech ash produced during the period of this research. Wood was collected in April 1999 from Whitely Woods, Sheffield (SK305 847). The tree had been cut down for at least one year prior to collection and consisted of 490.0Kg of trunk wood (30-40cm diameter) (Plate 4:1). The wood was analysed by the Sheffield Dendrochronology Laboratory and confirmed as being from a 120 year old beech tree.

Plate 4:1 Billeted beech trunk wood ready for ashing

The wood was allowed to dry indoors for six months before it was burnt and during this period approximately 200Kg was stolen! This meant that the weight loss from wet to dry wood could not be assessed. The dry wood was billeted, weighed and ashed inside a garden incinerator using a blowtorch to initiate burning. The burnt material from each sample was allowed to cool before being sieved (2mm B.S. 410 Test Sieve). The resulting fractions were weighed and the results recorded in Table IV:1.

A single **bracken** ash source was used in all of these experiments. This was beneficial as it allows more reliable comparisons between the different experimental glasses. The bracken was collected from Snake Pass, Derbyshire (SK084 924) and is described in Jackson and Smedley (2000: 336) (Table IV:2).

4.3.2 Compositional Analysis

The compositional analyses by XRF of the beech ash collected by Smedley *etal.* (1998: 149), and the bracken ash collected by Jackson and Smedley (2000: Table 2) are reported in Table IV:3 and Table II:2 respectively. Samples of ash from the beech trunk wood ashed during this research (Table IV:1) were collected for analysis. The original XRF unit used by Smedley *etal.* (1998) and Jackson and Smedley (2000) was not available. Therefore, initial attempts to analyse the ash were made using ICP-AES, at the NERC facility, Department of Geology, Royal Holloway, University of London. A variety of sample preparations were tried based on either a nitric acid digest or a nitric followed by hydrofluoric acid digest. The mixture of organic and inorganic matter in the samples meant that it was impossible to obtain a complete dissolution, and filtration was required to produce a solution suitable for the ICP-AES. It was not possible to obtain repeatable results due to the difficulty in controlling the rate of sample dissolution into the acid. In order to overcome these problems, XRF analysis was attempted as the ash could be analysed without putting it into solution. An EDAX Eagle micro-probe (35 kV, 620μA) was used with an analysis time of 100 seconds. The beam was directed by a 300 micron capillary that attenuated X-rays over about 20 KeV and the samples were prepared as compressed powder pellets. Unfortunately, the facilities were not available to enable the analysis of all of the ash samples and therefore a representative group was chosen. It should be noted that the results obtained (Table IV:3) are semi-quantitative as no suitable matrix matched standards were available.

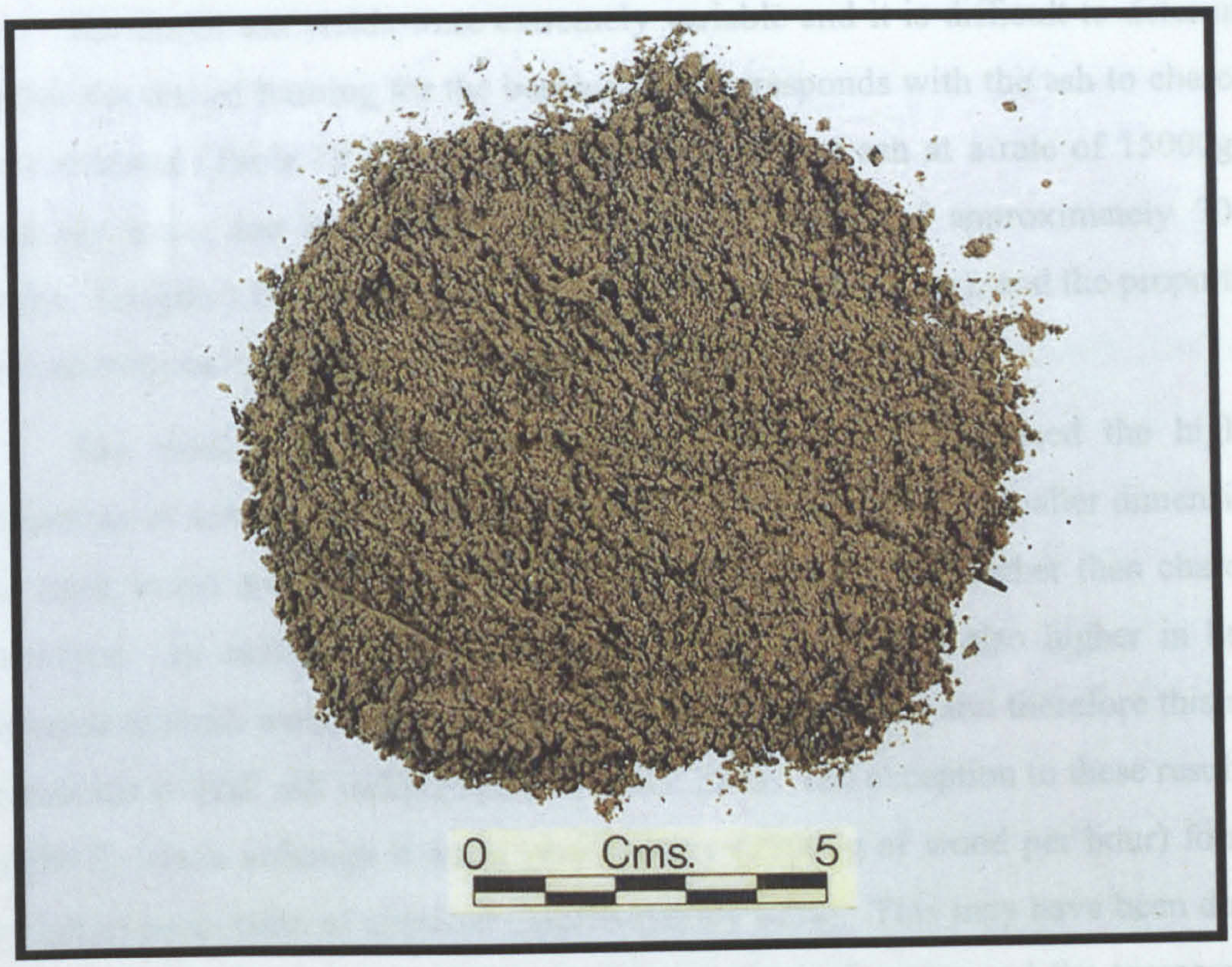
4.3.3 Results and Discussion

4.3.3.1 Burning Times and Ash Yields for Beech and Bracken

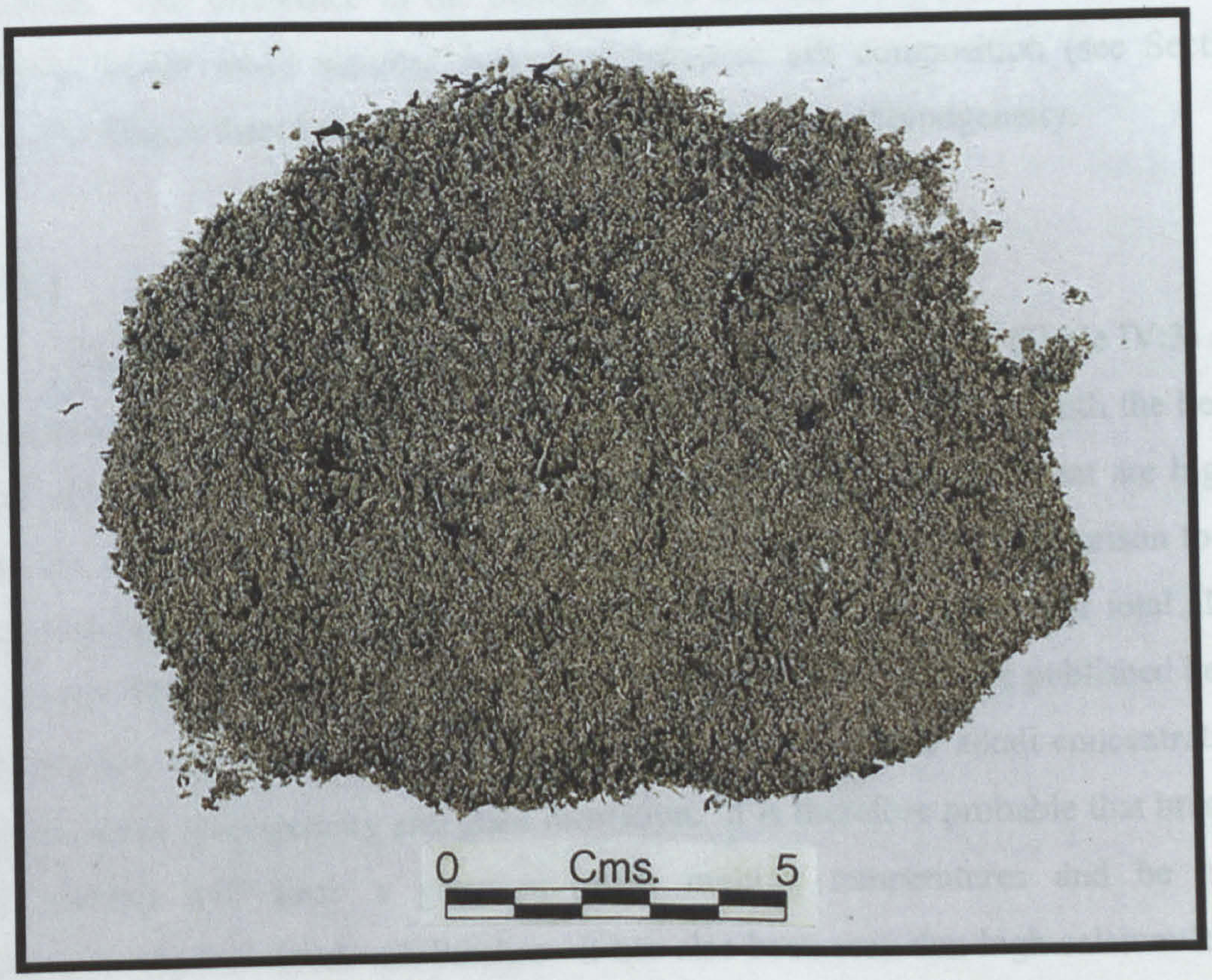
Initially the beech wood burning was carried out inside the Department of Engineering Materials, University of Sheffield. This was to ensure constant conditions for each ashing and avoiding factors such as wind and rain. The heat and flames, approximately 2m high, meant that the following experiments had to be done outdoors for safety.

Obtaining a stable flame was initially difficult but once burning was established the wood burnt very fast and fiercely. The burning times recorded in Table IV:1 are the periods when flames could be seen but it should be noted that the ashes and charcoal took much longer (up to 8 hours in some cases) to cool to air temperature. The beech ash formed was a pale grey/brown fine powder (Plate 4:2). The bracken ash was dark grey in colour, had a coarser texture and was more vitrified than the beech ash (Plate 4:2). The presence of small quantities of charcoal could be seen in both ashes.

The results from the burnings of beech and bracken are recorded in Table IV:1 and Table IV:2. The percentage yield of ash is very low for all the samples (approximately 0.5-1.5 Wt.%). These results are in agreement with the findings of studies such as Berry (1917), Bezborodov (1975) and Smedley *et al.* (1998) (see Section 2.2.2). They confirm that a large volume of vegetation is required to produce an adequate supply of ash for glass production. These low yields may have meant that glassmakers could have used fuel ashes as a supplement. This brings additional problems in relating the chemical composition of a glass to the composition of the raw materials from which it was made (see Section 2.2.2.1).



Beech Ash



Bracken Ash

Plate 4:2 Beech ash (Trunk Wood, Sample 1 Table IV:1) and Snake Pass bracken ash (Table IV:2)

The beech ash yields were extremely variable and it is difficult to determine whether the rate of burning for the beech wood corresponds with the ash to charcoal ratios obtained (Table IV:1). Samples 3-5 all produced ash at a rate of 15000g of wood per hour, and had similar ash to charcoal ratios of approximately 70:30 percent. Sample 1 burnt more slowly (12500g of wood per hour), and the proportion of ash to charcoal was increased (approximately 40:60).

The brash wood burnt by Smedley *et al.* (1998) produced the highest proportions of ash to charcoal (approximately 85:15). Brash has smaller dimensions than trunk wood and will therefore burn faster facilitating ash rather than charcoal production. In addition to this the ratio of bark to wood is also higher in brash compared to trunk wood. Bark produces more ash than wood and therefore this may increase the overall ash yields (Tylecote 1986: 223). The exception to these results is Sample 2, which although it burnt very quickly (25000g of wood per hour) formed the highest proportion of charcoal (approximately 62%). This may have been due to factors such as the rate that wood was fed into the incinerator and the temperature achieved. The difference in the burning rates and ash to charcoal ratios for the different beech wood samples may also influence ash composition (see Section 2.2.2.1). This is therefore another factor that will influence homogeneity.

4.3.3.2 Ash Composition

Figure 4:1 illustrates the elemental composition of the beech (Table IV:3) and bracken ashes (Table II:2) used in this research (see Section 4.3.1). Both the beech brash and trunk ashes have calcium levels (in excess of 31% CaO) that are higher than the total alkali concentration (less than 24% K_20+Na_2O). In comparison to the beech, the bracken ash contains lower calcium (9.02% CaO) and higher total alkali levels (39.52% K_2O+Na_2O). These trends are in agreement with the published beech and bracken ash analyses discussed in Section 2.2.2.1. Higher alkali concentrations will facilitate homogeneity and glass formation. It is therefore probable that bracken ash batches will form a glass at lower melting temperatures and be more homogeneous than beech ash batches. It has also been seen that high calcium levels may have a detrimental effect on homogeneity (see Section 2.2.2.1) and therefore this may be evident in glasses produced from the beech ashes.

The beech brash and bracken ash have higher silica levels (18.0 and 15.17% SiO_2 respectively) than the beech trunk wood ash (2.55% SiO_2). This will increase the total silica component of the batch and increase the amount of alkali required to form a homogeneous glass. However, as the bracken ashes have a significantly higher total alkali content than the beech brash ashes the increased silica levels are less likely to cause inhomogeneity in the bracken compared to beech brash glasses.

There are significant differences between the composition of the beech brash and trunk ash. Although both of the trees are from the same geographical area it is well documented that the part of the tree burnt will affect the composition of the ash (see Section 2.2.2.1). The higher phosphate concentration in the beech brash ash (15.3% P_2O_5) compared to the trunk ash (4.16% P_2O_5) may be due to the higher proportion of bark to wood, as bark contains a higher proportion of phosphates (Tylecote 1986: 223). In comparison to these wood ashes, the phosphate concentration in the bracken ash (as fleshy plant see Section 2.2.2) is 7.55% P_2O_5. The magnesium level in the three ash types is also very varied. The beech trunk wood contains the highest levels (11.63% MgO) and the bracken ash the lowest (4.88% MgO) with the beech brash ash falling in between (6.95% MgO). Although there are significant differences in the phosphate and magnesium concentrations of the three ash types the potential affects of these on homogeneity are not known. Phosphoric oxide can act as a network former (see Section 2.2) (Shelby 1997: 27), but it is not certain whether this will influence homogeneity. The three ash types have low levels of alumina (0.46-1.01% Al_2O_3). Although alumina can increase the melting point of a batch, which would affect homogeneity (see Section 2.4.2) (Shelby 1997: 28), it is thought unlikely that it will be so significant when present at these low levels.

The beech brash and trunk ashes contain approximately 6.2% and 7.23% manganese oxide respectively. High levels of manganese are well documented in beech ashes (see Section 2.2.2.1) and will impart a purple colour to the glass. The high levels of iron (3.55%) in the bracken ash mean that the glass formed is likely to be green or blue. However, the colour of the glasses formed from both these ashes will depend on factors such as melting temperature, time, furnace atmosphere, and the presence of internal redox agents (Sellner *et al.* 1979, Weyl 1951).

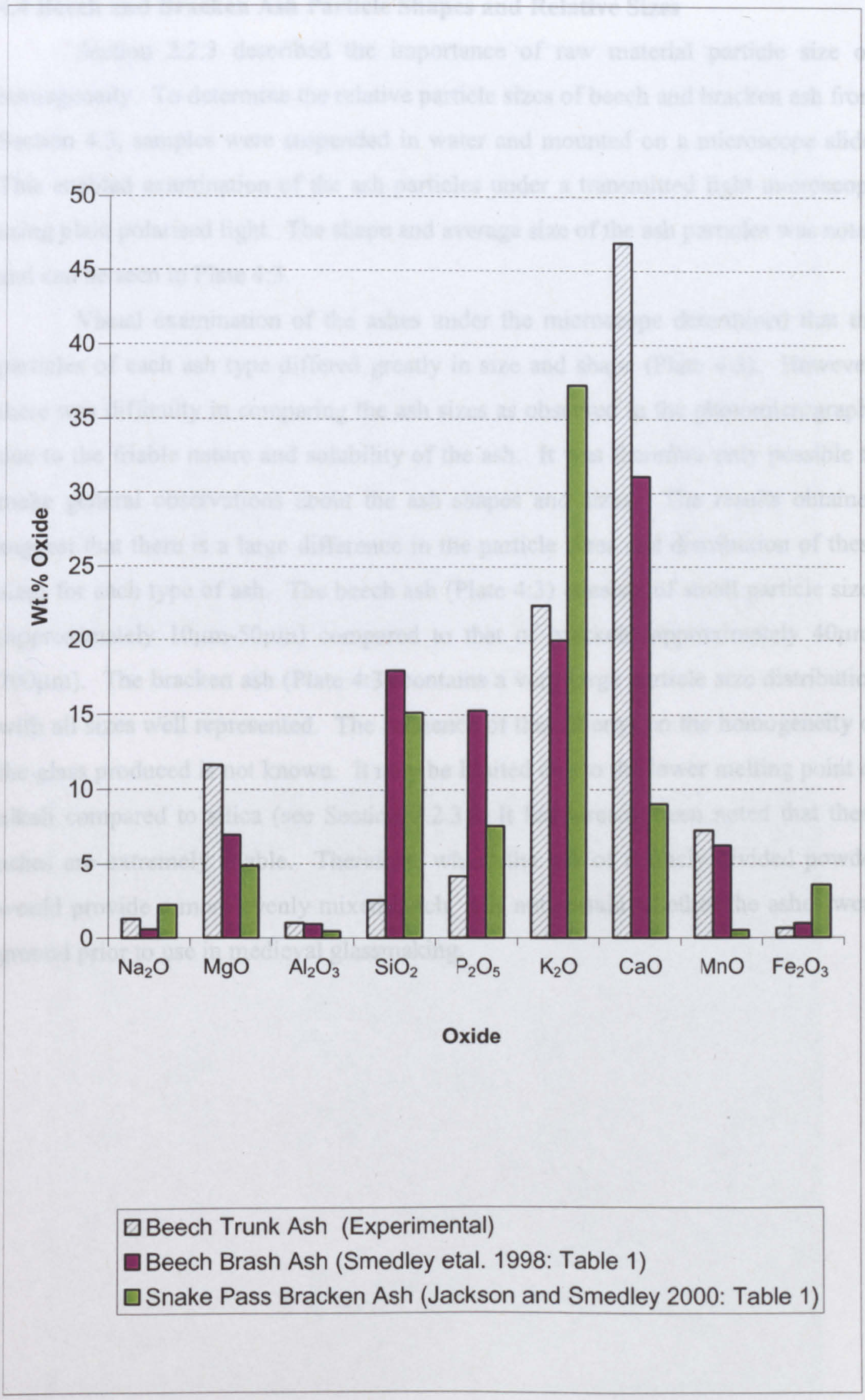
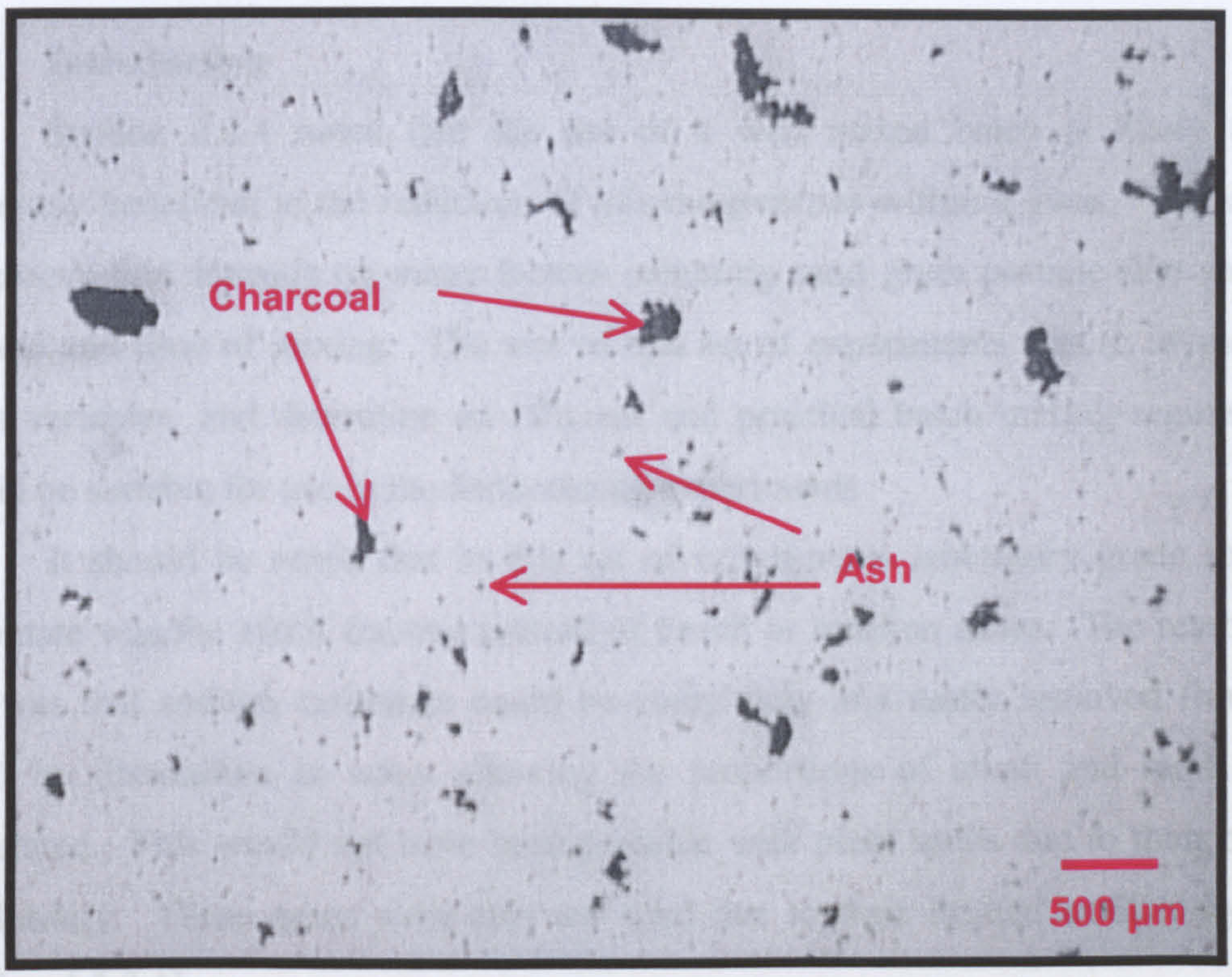


Figure 4:1 A comparison of the composition of beech and bracken ashes used in this research (Table II:2 and Table IV:3)

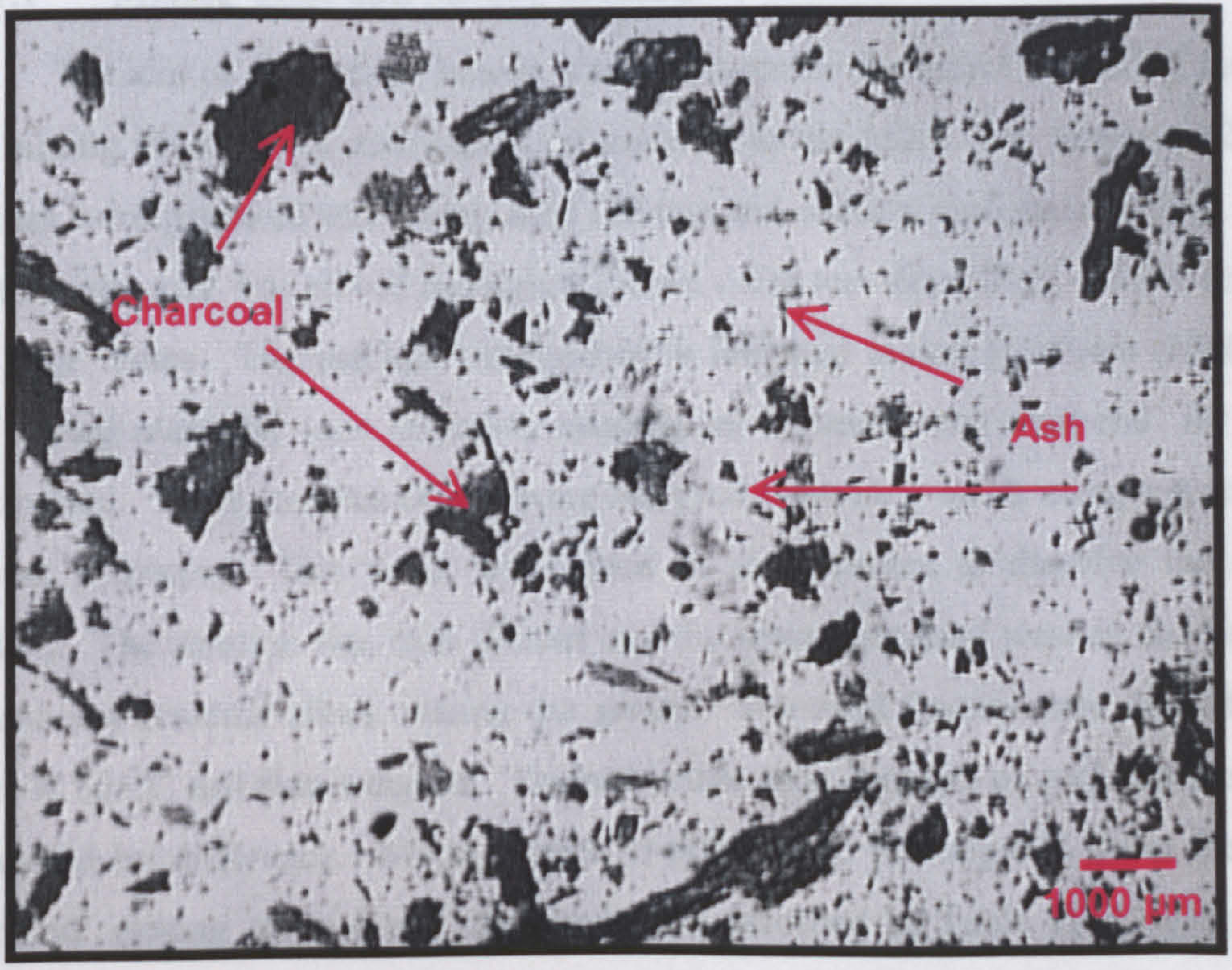
4.4 Beech and Bracken Ash Particle Shapes and Relative Sizes

Section 2.2.3 described the importance of raw material particle size on homogeneity. To determine the relative particle sizes of beech and bracken ash from Section 4.3, samples were suspended in water and mounted on a microscope slide. This enabled examination of the ash particles under a transmitted light microscope using plain polarised light. The shape and average size of the ash particles was noted and can be seen in Plate 4:3.

Visual examination of the ashes under the microscope determined that the particles of each ash type differed greatly in size and shape (Plate 4:3). However, there was difficulty in comparing the ash sizes as observed in the photomicrographs due to the friable nature and solubility of the ash. It was therefore only possible to make general observations about the ash shapes and sizes. The results obtained suggest that there is a large difference in the particle sizes and distribution of these sizes for each type of ash. The beech ash (Plate 4:3) consists of small particle sizes (approximately 10µm-50µm) compared to that of bracken (approximately 40µm-200µm). The bracken ash (Plate 4:3) contains a very large particle size distribution with all sizes well represented. The influence of this (if any) on the homogeneity of the glass produced is not known. It may be limited due to the lower melting point of alkali compared to silica (see Section 2.2.3). It has already been noted that these ashes are extremely friable. Therefore, whilst the use of a finely divided powder would provide a more evenly mixed batch, it is not certain whether the ashes were ground prior to use in medieval glassmaking.



Beech Trunk Wood Ash (Table IV:1)



Snake Pass Bracken Ash (Jackson and Smedley 2000)

Plate 4:3 Beech trunk wood ash and bracken ash particle sizes

4.5 Batch Mixing Experiments

4.5.1 Introduction

Section 2.2.4 noted that the use of a well mixed batch is likely to be extremely beneficial in the reduction of inhomogeneities within a glass. The ability to achieve this depends on many factors including sand grain particle size and the method and time of mixing. The aim of this set of experiments was to investigate these variables, and determine an efficient and practical batch mixing regime that would be suitable for use in the forthcoming experiments.

It should be noted that in this set of experiments laboratory grade sodium carbonate was the alkali fraction instead of beech or bracken ashes. The reason for this was that sodium carbonate could be completely and easily removed from the batch by dissolution in water allowing the proportions of alkali and sand to be calculated. This would not have been possible with plant ashes due to their partial insolubility. These ashes were also not used due to their limited availability (see Section 4.3.3.1).

4.5.1.1 Mixing Time and Mixing Method

The aim of these experiments was to determine the effect of mixing method and mixing time on the distribution of material in the batch (see Section 2.2.4.3). Batches were prepared containing sand (50.0g) and sodium carbonate (50.0g). The sodium carbonate was sieved through a 250μm mesh test sieve (B.S. 410) to remove any large lumps. The batches were placed in identical sealed glass jars (1000cm^3) and rotated manually (one complete rotation per second), 'end over end' for a set time period. Three samples of 20g were removed from each batch using a spatula to prevent demixing. Hot water was added to the samples to dissolve the alkali fraction. The solution was then filtered and the remaining sand washed carefully to remove any residual alkali coating the grains. The sand fraction was dried for 12 hours at 105°C and then weighed. The respective soda contents of each sample were calculated by difference. Mixing times (0-600s) were investigated using the 'end over end' mixing method and the results are recorded in Table IV:4. Duplicate experiments were then carried out using the CB1 mixing method. This involved placing each batch in a large crucible (CB1, see Appendix A, Figure B:1, Table B:2) and manually stirring it using a wooden spatula (15cm long, 1cm width). The results are recorded in Table IV:5.

The results in Table IV:4 and Table IV:5 show that whatever mixing method or time is used the samples removed from the batch appear to contain almost equal amounts of sand and soda. However, when the range of results for each set of samples is looked at in detail a few general trends can be observed. Figure 4:2 illustrates the change in distribution of the batch components with increased mixing time and different mixing methods. Each point on the graph represents an average of three measurements.

Mixing the batch even for very short periods (30seconds) using either the end over end or the CB1 method significantly improves the even distribution of the batch components in each sample (1.8-4.8% respectively) compared to no mixing at all (12.5-26.4g). Increasing stirring times to 60s gives an improvement in batch distribution in the end over end samples (1.1%) but no change in the CB1 samples compared to those produced at 30s using the same method. Increasing stirring times to 300 and 600s continues to improve the distribution of sand and soda in the CB1 samples but introduces demixing in the 'end over end' samples (see Section 2.2.4.3). These experiments have shown that the two methods have different rates of mixing. The 'end over end' method is more efficient producing a well mixed batch faster, as it has a more vigorous mixing action within a larger mixing area compared to the stirring action in the smaller CB1 crucible. A practical batch mixing regime was required for future experiments in this chapter as well as Chapters 5 and 6. Based on the results from this section the 'end over end' method and a mixing time of sixty seconds were selected.

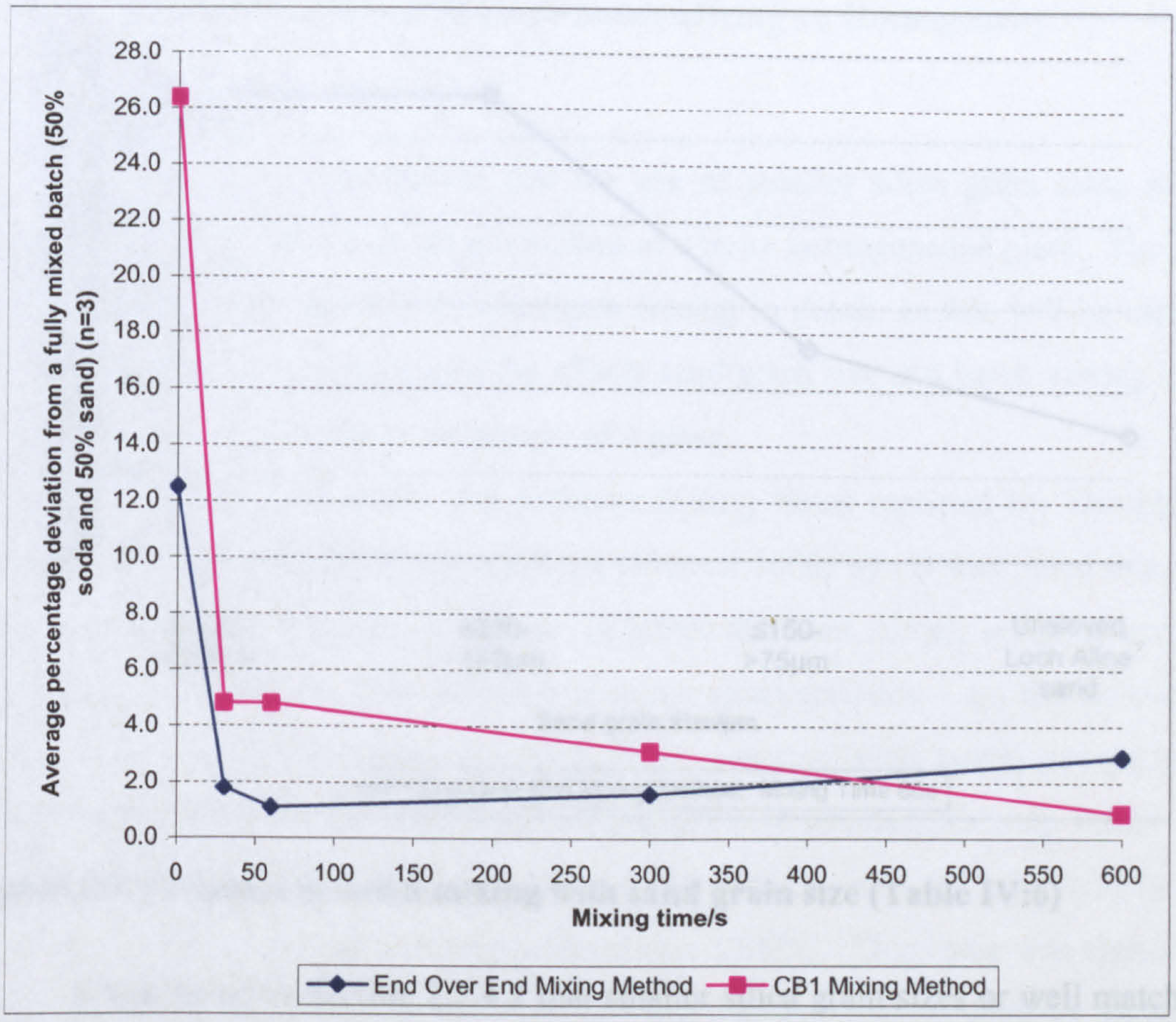


Figure 4:2 Variations in batch mixing with mixing time and method (Table IV:4 and Table IV:5)

4.5.1.2 Sand Grain Size

Experiments were carried out to determine the effect of sand grain size on mixing (see Section 2.2.4.2). Batches were prepared using unsieved sand (Table 4:2) and a range of sand grain sizes (≥450->75µm) (Table 4:3). The values for the ≥450->250 sand grain size samples were obtained from the results of the experiments in Section 4.5.1.1. The results are recorded in Table IV:6 and are illustrated in Figure 4:3.

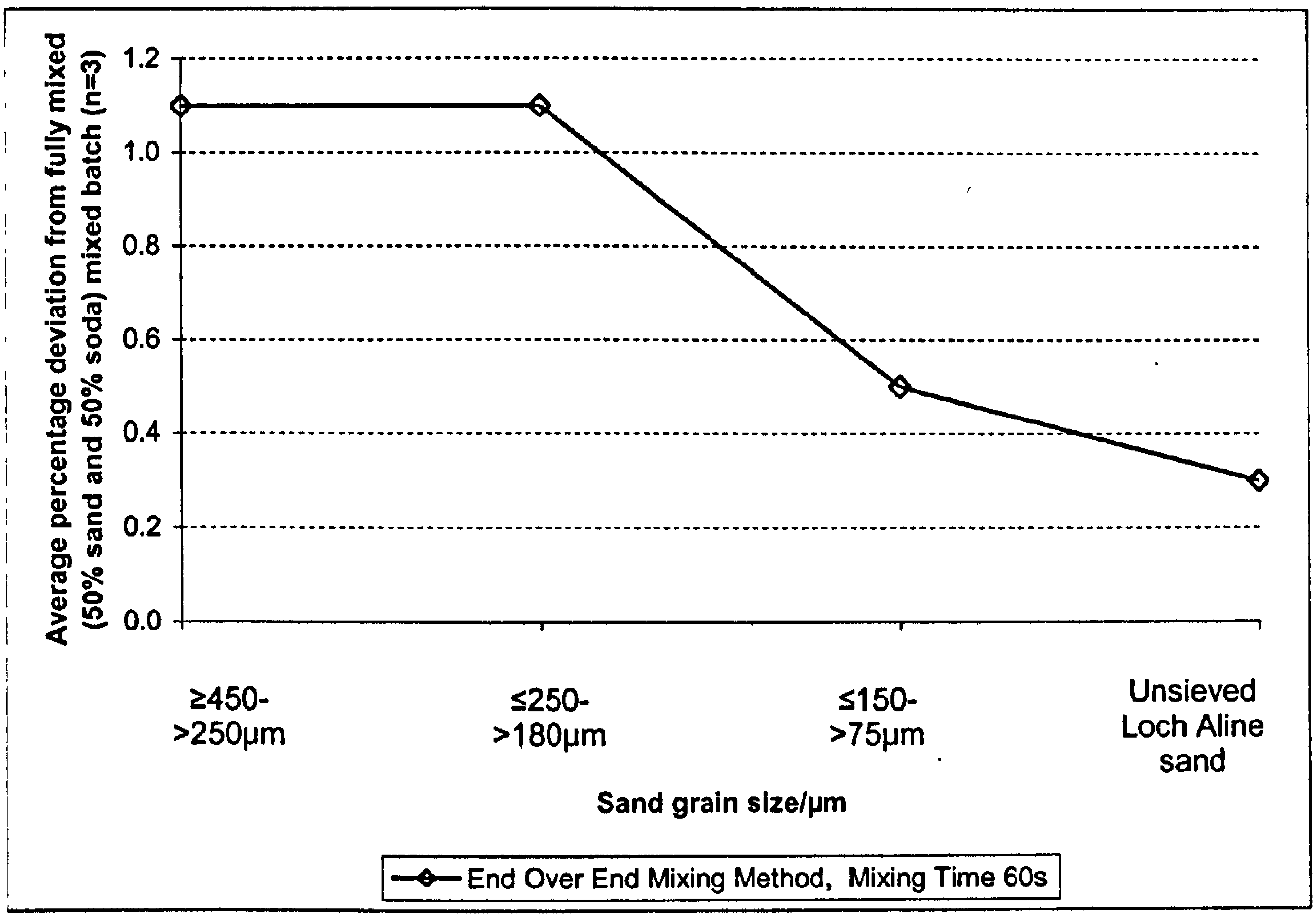


Figure 4:3 Variation in batch mixing with sand grain size (Table IV:6)

It was noted in Section 2.2.4.2 that smaller silica grain sizes or well matched batch grain sizes facilitated batch mixing. Figure 4:3 shows that better mixing appears to be achieved with decreasing sand grain size although the differences are small. However, the best distribution was obtained when using unsieved, multi grain sized sand and this is therefore not in agreement with the published results discussed in Section 2.2.4.2. Reasons for the improved mixing when using the unsieved sand could be that better packing is achieved when a mixture of grain sizes is used or a sampling bias in the results.

4.5.2 Summary and Discussion of Batch Mixing Experiments

These basic mixing experiments have shown that successful mixing of the batch components occurs rapidly when using dry materials and does not appear to be significantly affected by the use of different sand grain sizes and mixing methods. If the batch is not mixed, it may not actually be a major source of inhomogeneity due to other factors involved in the production of a glass (see Section 2.2.4.3) (Tooley and Tiede 1946). The particle size of raw materials may actually be more important in the later stages of melting and refining (see Section 2.2.3). Therefore the effect of mixing and particle size will be investigated in Section 4.6.

4.6 The Effect of Sand Grain Size and Batch Mixing on Homogeneity

4.6.1 Introduction

Section 2.2.1.1 determined that the use of smaller silica grain sizes and a mixed batch are beneficial in the production of a more homogeneous glass. The aim of these experiments was not to investigate fritting in detail, as this will be carried out in Chapter 5, but to investigate the effects sand grain size and batch mixing have on fritting, melting, and the homogeneity of a glass.

Section 2.3.2 discussed the different fritting times reported by Theophilus (Hawthorne and Smith 1979: 53) and Neri (Merrett 1662: 8). It was noted that this disparity could be a function of the use of either different fritting temperatures, or different raw materials with different melting characteristics. In the following experiments the fritting times and temperature were selected based on work by Smedley *et al.*(1998: 154), and these parameters kept constant for both beech and bracken batches to enable the observation of any differences in the behaviour of the two ashes. The melting temperature selected was 1300°C. This value was chosen as it is thought that this would be sufficient to form a glass based on work by Smedley *etal.* (1998: 152), and also be within the temperatures assumed to be achievable in medieval furnaces (see Section 2.4.2).

4.6.2 Experimental

The following experiments were carried out to investigate the differences between glasses formed using mixed (see Section 4.5) and unmixed batches. Bracken and beech ash based batches were prepared using differing sand grain particle sizes. Four identical batches were prepared for each ash and sand grain size. The ash particle size was variable (see Section 4.4). Two batches were mixed, the other two left unmixed.

A standard batch composition of 2 parts alkali, to 1 part silica, by weight was used in all of the experiments in this section. The choice of this ratio and the use of weight rather than volume was based on the results of the experimental work carried out by (Smedley *et al.* 1998). L30A sand (Section 4.2) was the silica source (5.00g), and either beech or bracken ash (10.00g) was used to provide the alkali (Section 4.3). Where specific sand grain sizes are quoted they refer to those described in Section

4.2, Table 4:3. Where it is stated that the batch is mixed, the procedure used was the 'end over end' method for a period of 60s (see Section 4.5.1.1).

A schematic representation of this set of experiments can be seen in Figure 4:4 and the experimental details for both the bracken and beech ash batches are recorded in Table IV:8 and Table IV:11. All the frits and glasses produced were examined visually and the results recorded in Table IV:9 and Table IV:12.

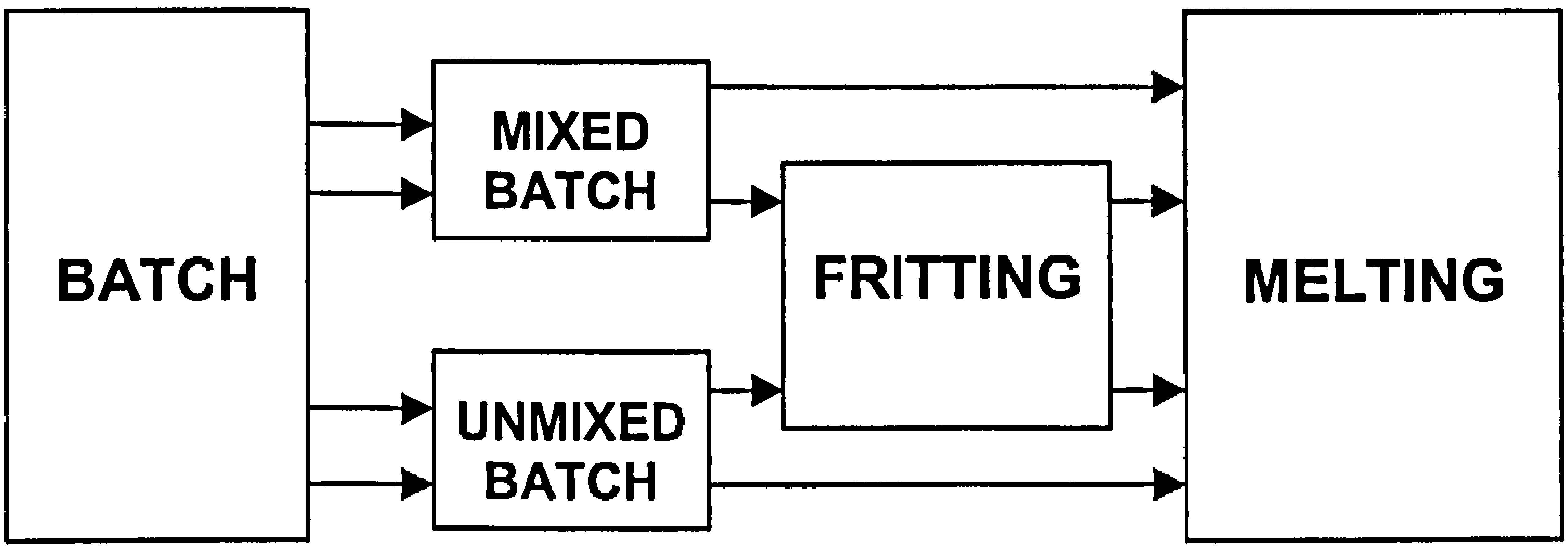


Figure 4:4 A Schematic representation of batch mixing and sand grain size experiments

4.6.2.1 Fritting

One mixed and one unmixed batch of each ash type (beech and bracken) and sand grain size was subjected to a fritting procedure (see Section 2.3) before the glass melting stage. These samples were heated in mullite crucibles (CON 9) at 900°C for 24 hours. The crucibles are conical in shape, approximately 5.5cm in height and have a volume of 43ml (for a full description see Appendix A). The crucibles were then allowed to cool on the back of the furnace to decrease the risk of cracking due to thermal shock. Two sets of identical frits were produced, one was removed from the crucible for examination and the other was left *in situ* for the subsequent melting stage. These experiments did not investigate the effect on homogeneity of grinding and mixing frit before the melting stage. This will be covered in Section 5.5.

4.6.2.2 Melting

All the batches were melted at 1300°C for 1 hour in an electric furnace (see Appendix A). The unfritted batches were added to preheated crucibles (1000°C) in one charge. The fritted samples were left in their crucibles and were preheated on the back of the melting furnace for thirty minutes to prevent the crucibles cracking due to thermal shock on insertion into this furnace. After removal from the melting furnace the crucibles were allowed to cool on the back of the furnace before being examined.

4.6.3 Results

4.6.3.1 Unmixed and Unfritted Batches

The unmixed, unfritted **beech ash** batches did not form glasses (Table IV:9). The batch was pale grey/green and had reduced in volume by approximately 25%. The batch fell apart when removed from the crucible (Plate 4:4). It contained loose powder except at the sand ash interface where some vitrification was visible, this vitrification **increased** with **decreasing** sand grain size.

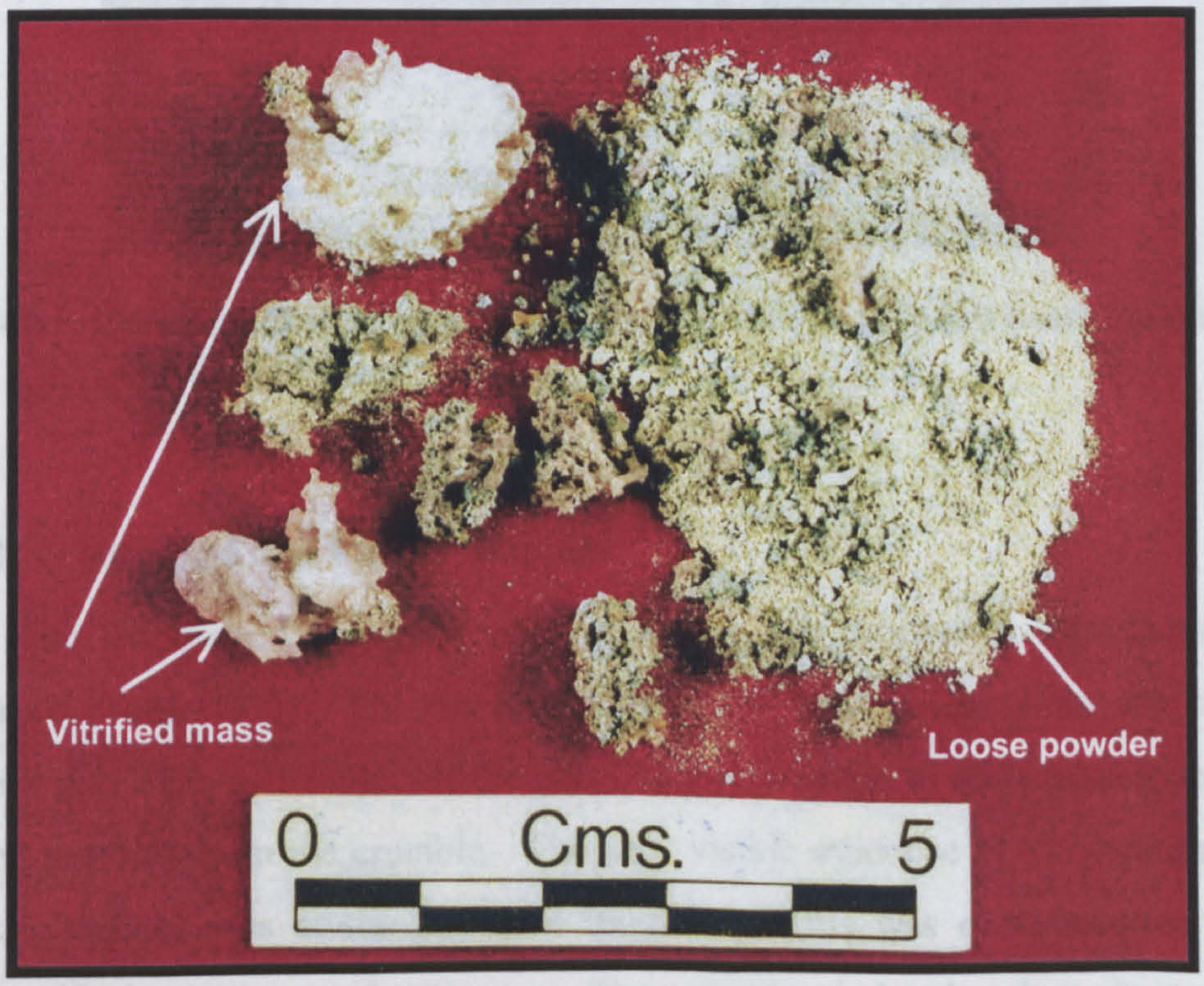


Plate 4:4 Unmixed, unfritted beech (Be5, Table IV:9) ash batch heated at 1300°C for 1 hour

All the unmixed and unfritted **bracken ash** batches in this set of experiments formed a visually homogeneous, dark green glass (Plate 4:5, Table IV:12). Visual examination showed that there appeared to be no difference in the samples produced using differing sand grain particle sizes. All the glasses were observed to have a ring of a white crystalline substance (see Section 3.3.1) around the top of the glass (Plate 3:2) and no batch relics could be detected. The SEM images obtained from samples of these glasses determined that in all cases the glass appeared to be **homogeneous**.

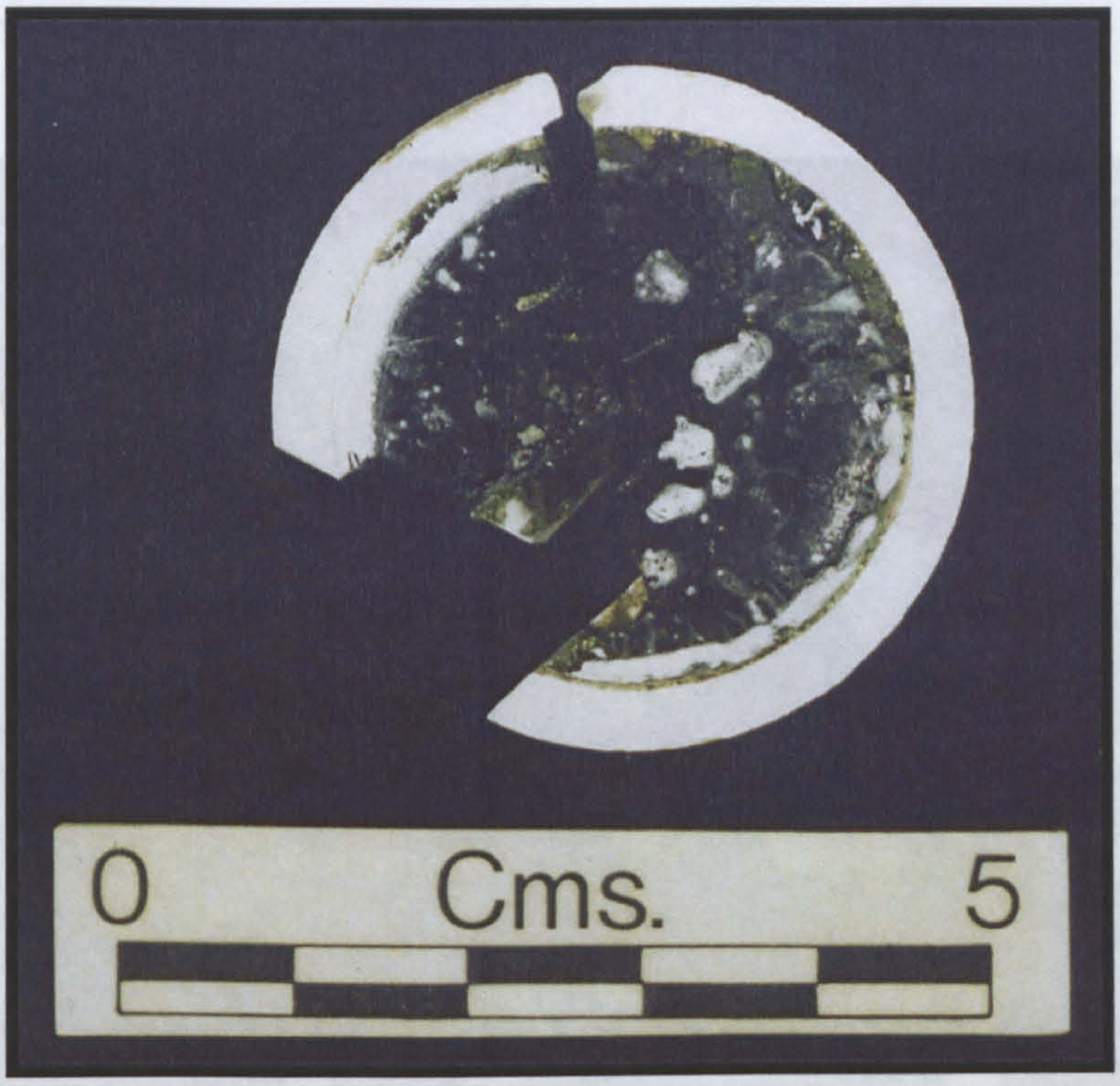
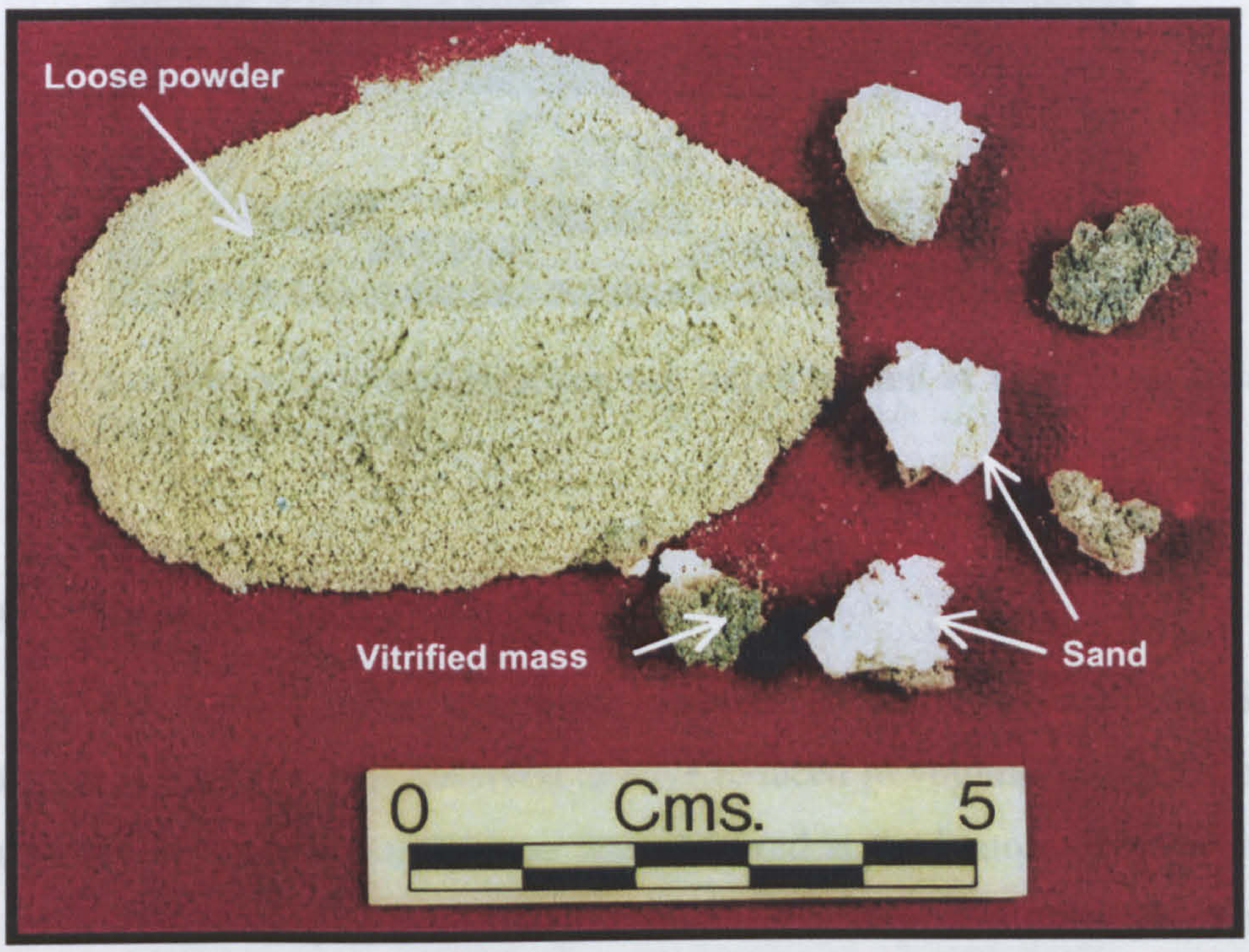


Plate 4:5 Unmixed, unfritted bracken (Br5, Table IV:12) ash batch heated at 1300°C for 1 hour

4.6.3.2 Unmixed and Fritted Samples

The frit formed from the unmixed **beech ash** batches was predominantly grey/green (Table IV:7). The frit formed from the unmixed **bracken ash** batches was dark grey (Table IV:10). All the frits mainly consisted of loose powder and fell apart on removal from the crucible. The only visible evidence of vitrification (pale purple in colour) was at the ash sand interface. This was observed to increase slightly with decreasing sand grain size. The reduction in batch volume between the raw materials and the frit was approximately 25%, in the beech ash batches and 30% in the bracken ash batches.

The unmixed and fritted **beech ash** batches did not form glasses when heated at 1300°C for 1 hour (Plate 4:6, Table IV:9). The only vitrification observed was the same as has been seen in the frit at the interface between the sand and ash. The thin layer of semi-vitrified product was greater than that observed in the frit and the extent of vitrification **increased** with **decreasing** sand grain size. The extent of vitrification in these samples was less than that observed in the unmixed and unfritted samples (Section 4.6.3.1).



Beech Ash Batch

Plate 4:6 An unmixed, fritted beech (Be6, Table IV:9) ash batch heated at 1300°C for 1 hour

All the unmixed and fritted **bracken ash** batches (Table IV:12) in this set of experiments did not form complete glasses and the extent of vitrification **increased** with **decreasing** sand grain size. Visual examination of the product showed that in all cases it was opaque brown, semi-vitrified and contained copious batch relics (Plate 4:7). Examination with the SEM determined that homogeneity **increased** with **decreasing** sand grain sizes.

Plate 4:7 An unmixed, fritted bracken ash batch heated at 1300°C for 1 hour (Br6, Table IV:12)

4.6.3.3 Mixed and Unfritted Batches

The mixed and unfritted **beech ash** batches (Table IV:9) did melt but failed to form a glass. The batch was observed to have reduced in volume by approximately 75% and an opaque, pale purple mass was observed at the bottom of each crucible (Plate 4:8). No loose powder could be observed in any of the samples and the substance could not be removed from the crucible. The extent of vitrification **increased** with **decreasing** sand grain size and a small quantity of pale purple glass was observed to have formed around the edges of the crucible in those samples produced using sand grain sizes ranging from ≤180µm-≤45µm.

All the mixed and unfritted **bracken ash** batches (Table IV:12) in this set of experiments formed a visually homogeneous, dark green glass (Plate 4:8). Visual examination showed that there appeared to be no difference in the samples produced using differing sand grain particle sizes. No significant visual differences could be detected between the glasses produced in this section and those produced from unmixed and unfritted batches (see Section 4.6.3.1). All these glasses were observed to have a ring of a white crystalline substance around the top of the glass and were found to be **homogeneous** on examination under the SEM.

Beech Ash Batch

Bracken Ash Batch

Plate 4:8 A mixed, unfritted beech (Be7, Table IV:9) and bracken (Br7, Table IV:12) ash batch heated at 1300°C for 1 hour

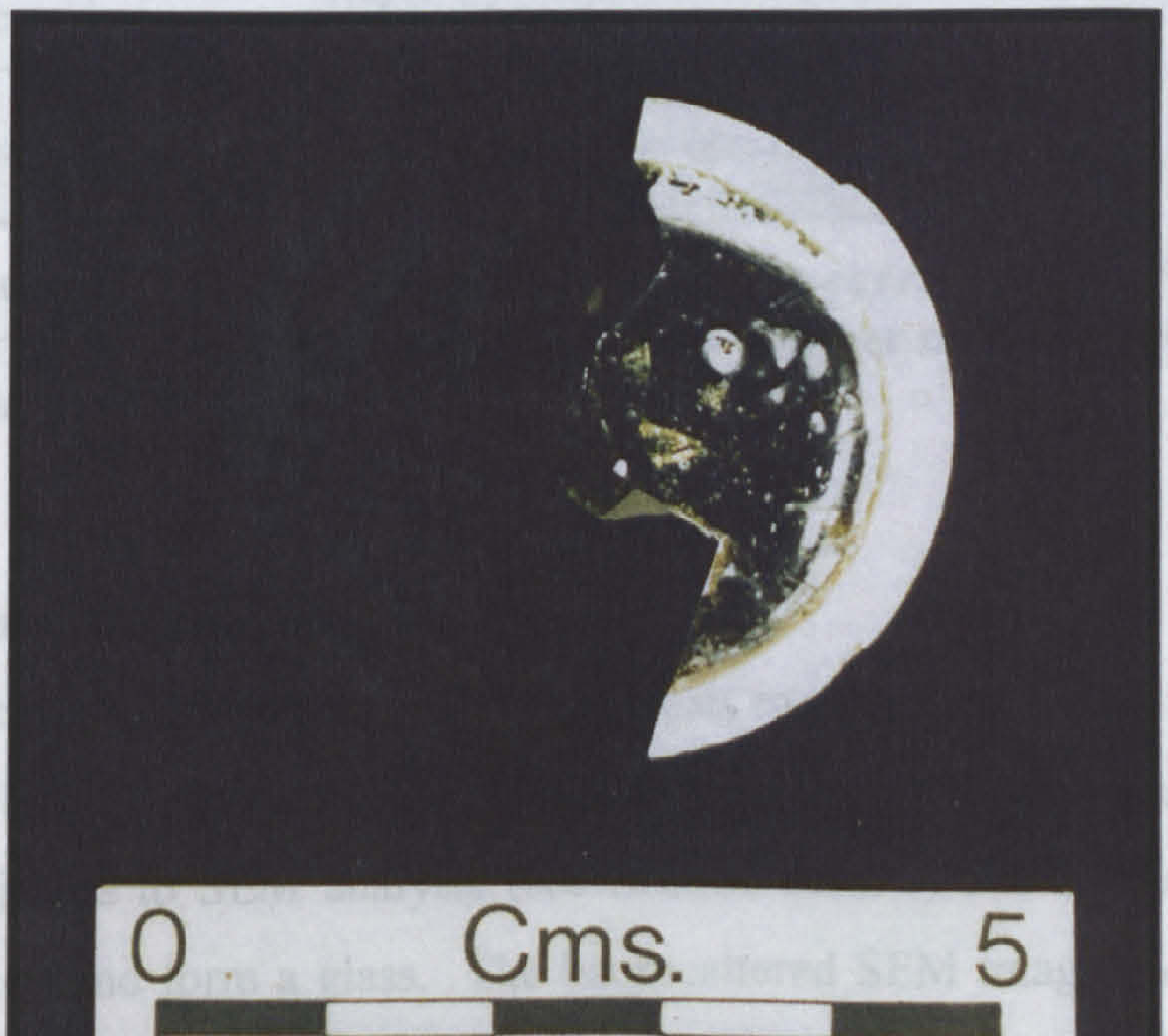
4.6.3.4 Mixed and Fritted Samples

The frit formed from the mixed **beech ash** was pale purple in colour (Table IV:7). The **bracken ash** batches were a darker purple with a dark green surface layer (Table IV:10). All the frits occupied approximately 50% of the original batch volume and contained extensive vitrification. They had shrunk away from the sides of the crucible and were difficult to completely remove from the crucible. The beech batches could not be broken up completely by hand. The bracken ash batches were completely vitrified and could only be broken using a hammer.

The mixed and fritted **beech ash** batches (Plate 4:9, Table IV:9) did not completely melt but the extent of vitrification increased with decreasing sand grain size. Vitrification was **less** than that observed in the identical **unfritted** batches (Section 4.6.3.3). A small amount of glass was again observed in samples produced using sand grain sizes of 75µm or less.

The mixed and fritted **bracken ash** batches (Table IV:12) made using the smallest sand grain sizes (≤75->63µm and ≤63->45µm) produced visually batch free but highly opalescent, pale green glasses (Plate 4:9). The batches containing larger sand grain sizes (≥425->75µm) did not melt completely. Visual examination of the partially formed, opaque brown glass showed that it contained copious batch relics. This was visually identical to the product formed by the unmixed and fritted batches (Plate 4:6, Section 4.6.3.2). The extent of vitrification in the opaque brown substance **increased** with **decreasing** sand grain size. Backscattered SEM imaging determined that the pale green glasses were homogeneous and that the opaque brown material became more homogeneous with **decreasing** sand grain sizes. The decrease in inhomogeneities occurred at comparatively larger sand grain sizes than those in glasses made from unmixed fritted batches (Section 4.6.3.2).

Beech Ash Batch



Bracken Ash Batch

Plate 4:9 A mixed, fritted beech (Be8, Table IV:9) and bracken (Br8, Table IV:12) ash batch heated at 1300°C for 1 hour

4.6.3.5 Crystalline Substance Found on Bracken Glasses

Many of the bracken glasses produced in these experiments had a very fluid liquid layer on top of the melt, which on cooling, formed a pale pink or white crystalline substance (Plate 3:2). The substance was observed to flake off the surface of the glass very easily and deliquesce if left in contact with air for a few days. This material was not seen on any of the beech glasses produced.

The crystalline substance was removed from the surface of a selection of bracken glasses. A sample of each of these was subjected to the standard chemical qualitative tests listed in Table 4:4 (Briggs and Stewart 1928) to determine the nature of the cations and anions present. The experimental parameters and the results observed at all stages were noted in Table 4:4 and it was concluded from these that this substance was likely to be potassium sulphate.

Test	Observations	Deductions
Add aqueous barium chloride	The colourless solution forms a white precipitate.	CO^{2-}, SO_3^{2-}, SO_4^{2-}, $Cr_2O_4^{2-}$ present
Add dilute hydrochloric acid	The white precipitate remains.	SO_4^{2-} only present
Flame test	The white crystalline substance burns to give an orange/lilac flame. This appears lilac when viewed through blue glass.	K^+ present

Table 4:4 Results of the qualitative chemical tests carried out on the white crystalline substance observed on a number of the bracken ash glasses

4.6.4 Summary of Results

The results of the beech and bracken ash experiments in this section (Table IV:9 and Table IV:12 respectively) are summarised below. The beech ash batches were not subjected to SEM analysis (see Section 3.3.2.2) due to their inability to completely melt and form a glass. The backscattered SEM imaging of the bracken ash glasses confirmed the visual observations made in all cases with respect to homogeneity.

- Melting temperatures of 1300°C and times of 1 hour are not sufficient for any of the **beech ash** batches to fully melt and form a glass. In contrast, all of the unmixed or mixed, unfritted **bracken ash** batches formed a glass. No difference in homogeneity could be detected visually or using the SEM between the unmixed or mixed, unfritted bracken glass types.

- The use of smaller sand grain sizes (≤180µm->45µm) does appear to improve the extent of vitrification in the finished product in both fritted and unfritted batches.
- **Mixing** the batch **improves** the extent of vitrification in the finished product in both fritted and unfritted batches for **both ash types.**
- The inclusion of a fritting stage (24hr at 900°C) does **not** facilitate the production of a glass at melting temperatures of 1300°C for 1 hour when compared to unfritted batches for **both ash types.** In bracken glasses the exception to this occurs when using a mixed batch and small sand grain sizes (≤75->45µm).
- The glasses formed from bracken ash frit are paler in colour than those formed from unfritted batches and contain extensive opacity. No difference in homogeneity can be seen under the SEM between the two types.

4.6.5 Discussion

4.6.5.1 Batch Mixing

Although many of the beech and bracken ash batches in these experiments did not form completely batch free glasses they did exhibit several general trends in the results. Mixing the raw materials prior to fritting or melting does increase the extent of vitrification and the homogeneity of the finished glass. Theophilus (Hawthorne and Smith 1979: 53) and Biringuccio (Smith and Gnudi 1990) both refer to batch mixing in their observations on medieval glassmaking practices. It would therefore appear that the glassworkers knew of the significance of this stage in the glassmaking process (see Section 2.2.4). Mixing the batch will ensure a more intimate combination of the alkali and silica, facilitating reactions between the raw materials. This is applicable to both glasses made from unfritted or fritted batches and reduces the likelihood of forming inhomogeneities such as silica rich inclusions within the melt (see Section 2.3.2) (Crossley 1972).

4.6.5.2 Sand Grain Size

In addition to the benefits of batch mixing, decreasing the sand grain particle size increased the extent of homogeneity and glass formation within the batches. These results are comparable with those discussed in Section 2.2.1.1. Decreasing the size of the silica grains increases the surface area to volume ratio and therefore the area over which the alkali can attack the silica, ensuring a faster and more complete melt. Combining the use of a small silica grain size and a mixed batch therefore increases the probability of forming a relatively batch free and homogeneous glass.

It has been seen that there was a deliberate selection of smaller silica grain particle sizes in medieval glass manufacture, as mentioned by Neri (Merrett 1662), Theophilus (Hawthorne and Smith 1979) and Biringuccio (Smith and Gnudi 1990) (see Section 2.2.1). This choice was probably not due solely to the increased homogeneity of the finished glass, but is more likely to be linked with the shorter melting times obtained which would reduce fuel requirements.

The correlation between refining time and sand grain size must also be considered. In Section 2.2.1.1 it was noted that the use of very small grain sizes would cause an increase in refining time. In these experiments the glass that was formed contained little seed and appeared to be relatively well refined. However, it must be noted that these experimental melts are very small compared to the evidence for medieval glass melting (see Section 2.4.5.2) and are therefore likely to exhibit much faster rates of homogenisation and refining (see Section 2.2.1.1) (Plumat *et al.* 1963). The production of glass on a larger scale may therefore have needed to address the question of refining as large quantities of seed would have affected the visual appearance and overall quality of the glass and increase the melting time required. The medieval glassmaker may therefore have had to balance grain size against refining time. This would have depended on the quality of the glass desired and the extra time required to prepare the batch for melting (for example pulverising quartz pebbles) if the dimensions of the raw materials were not small enough.

4.6.5.3 Fritting

In both the beech and bracken ash batches the fritting stage can be seen to have significantly altered the appearance of the batch when compared to the raw materials. The beech ash batches were initially a pale brown colour (caused by the ash). On heating, the mixed batches changed to pale purple, caused by the presence of manganese in the ashes (approximately 6%, Table IV:3). The colour change occurs as the Mn^{3+} ion is altered with increasing temperatures (Smedley *et al.* 1998). In comparison, the unmixed batches turned a pale green colour on heating except at the sand/ash interface where the purple colour was again present. The reason for the green colour is not certain, but this may be due to the removal of the organic component of the ash as it is heated causing the overall colour of the batch to lighten.

In the mixed batches the grey bracken ash also formed a predominantly purple coloured frit. The manganese concentration is much lower in this ash type (approximately 0.5%, Table IV:3) and it is not certain whether this element is responsible for the colour change here. The difference in colour between the body (purple) and the surface (dark green) of the frit may be caused by the reaction between the batch and the furnace atmosphere. The frit was heated in air and the conditions inside the furnace are neutral to oxidising. In contrast the environment inside the frit is likely to be reducing as the ash contains organic material that will burn to release carbon dioxide at temperatures greater than about 400°C (Lide 1999). The change in atmosphere is probably responsible for the difference in colour between the surface and the body.

In the unmixed bracken batches the bracken ash remained grey in colour but had become paler with heating, as with the unmixed beech batches the purple colour was observed at the raw material interface where the materials had begun to react. It would therefore appear that in both these ash types the colour change is a direct result of the reaction between the ash and sand.

In addition to the difference in colour, a comparison of the fritted beech and bracken ash batches shows bracken exhibits a greater change in batch volume and vitrification when compared to the same samples produced from beech. This is due to the differences in the composition of the two ash types, it can be seen from Table IV:3 that bracken contains a much higher total alkali concentration (approximately 37-53%) than beech ash (approximately 20%). Potassium and sodium compounds will melt at temperatures in the region of approximately 700-1000°C and begin to react with silica in the batch (Lide 1999, Smedley *et al.* 1998). The higher the alkali concentration in the batch the faster the speed of these reactions will be. This therefore leads to a more noticeable difference in the vitrification.

The evidence for fritting in medieval glassmaking has been well documented by many authors in antiquity such as Theophilus (Hawthorne and Smith 1979) and Neri (Merrett 1662) and the potential benefits of including a fritting stage in glass production have been discussed in Section 2.3. It was noted that fritting had many advantages including a reduction in batch volume and in the temperature required to melt the batch, eliminating waste gases and allowing carbon and volatiles to be burnt off (Smedley *et al.* 1998). The results from these experiments confirm that with both ashes the batch volume and the friability (and therefore the removal of volatile components) of the fritted product are significantly reduced. It can also be seen that the use of a mixed batch is vital to ensure a more comprehensive reaction between the alkali and sand fractions even at lower temperatures.

The most unexpected observation in these experiments however, was that the use of a fritted batch generally appears **not** to have facilitated glass formation and has increased the quantities of inhomogeneities observed in the finished glass. This behaviour occurred in both beech and bracken ash batches and the reasons for this are not certain. It should be noted that the comparative experiments carried out by Smedley *et al.* (1998) with the same beech ash did find that the fritted batches produced glasses. It may therefore be that there was some unknown experimental error in the furnaces or materials used here. The former can probably be ruled out as the furnaces are calibrated regularly. However, it was noted in Section 2.2.2.1 that plant ash compositions can be very variable and this may be one reason for the results obtained. It would be interesting to determine the composition of the fritted product and determine if any significant differences could be seen. The melting behaviour of the beech brash ash will be examined in Section 4.7.

In addition to the reasons given above, there are many other factors that may have influenced the unexpected fritting results obtained in these experiments. The fritting parameters chosen were only an approximation to those described by Theophilus (Hawthorne and Smith 1979: 53), who noted that in addition to the batch being heated for twenty four hours that it should be continuously stirred. This latter instruction was not carried out here, as the practicalities of stirring the ashes for this length of time could not be overcome due to safety problems in working with hot open furnaces. The results may therefore be a reflection of this but there are other factors to consider. Theophilus' description also implies that the batch is placed on the furnace floor and raked. It is therefore not held in a crucible and this may have an important affect on the contact between raw material particles, the furnace atmosphere, the surface area to volume ratio of the batch, and heat transfer. The shape and fabric of the fritting crucibles used in these experiments will have had an effect on all of the variables mentioned and therefore may be responsible for the results obtained.

The main reason for the formation of more inhomogeneities in fritted compared to unfritted batches is thought to be due to the loss of some of the volatile alkali component. If significant amounts are lost during the fritting process then there may not be enough to melt all the silica to form a glass (Shelby 1997). It appears that fritting is a very complex procedure and further experiments are required to determine whether variables such as stirring the frit or changing crucible dimensions will affect the glass produced.

It can be observed from the results of these experiments that the fritting stage of glass production is complex and dependent on a complex combination of factors and these will be investigated further in Chapter 5.

4.6.5.4 Melting

The comparison between the results from the beech and bracken ash batches in these experiments show that different melting parameters (such as temperature and time) are required for different raw materials. Bracken ash glasses melt at a lower temperature than the equivalent beech ash glasses and, as with the fritting reactions, this is due to their higher total alkali concentrations. The faster the batch melts the more time is available for internal thermal mixing and therefore the more homogeneous the glass is likely to be. In addition to this, a well mixed batch and smaller sand grain sizes will increase the reaction speed of the raw materials, decreasing melting time and therefore facilitating homogenisation.

The colour of the glasses formed varied with the ash used and is dependent on the amounts and types of transition elements present in the batch. It is also influenced by many other factors including melting temperatures, times, and furnace atmosphere. The green colour of the bracken glasses was caused by the presence of iron in the ashes (between 0.5-3.5%, Table IV:3) (Weyl 1951). The two fritted batches that formed were significantly paler in colour than those formed from unfritted batches. It is not certain why this occurs but the change in hue may be due to the loss of some of the batch components during fritting. The colour change is important, as it may have been another reason for the inclusion of a fritting stage. The small amount of beech ash glass formed was pale purple in colour, and as with the frit, this is caused by the presence of the trivalent manganese ion in the ashes.

The bracken glasses formed in these experiments did have a tendency to form a white crystalline substance that is probably potassium sulphate (Table 4:4). If the batches had been scaled up and melted in large quantities then the volume of this would presumably have increased and would have had to be removed before the glass could be worked. The amount of potassium sulphate formed might be expected to reduce with the inclusion of a fritting stage, as potassium based components are very volatile and therefore more likely to be easily lost. However, it can be seen that the quantities observed on fritted glasses were equal to that seen on the unfritted glasses. Further investigation into the behaviour of this substance with different fritting and melting parameters will be carried out over the following sections. It is important to note that whilst this product would appear to be an undesirable side effect in the manufacture of bracken glasses it does not appear to affect the actual homogeneity of the glass.

In addition to the white crystalline substance, extensive opacity was observed in the two fritted bracken ash glasses. In archaeological glasses opalescence (usually observed as a grey/blue colouration) is thought to be due to the formation of calcium phosphate from phosphate rich plant ashes or apatite rich sands (Crossley 1972). The opacity visible in the experimental glasses does not appear to be grey/blue in colour, and imparts a milky appearance to the original glass. It does also not appear to be influencing the homogeneity of the glass but may be another unwanted consequence of forming glasses from bracken ashes. Further compositional information is required to determine the nature of the opacity in these glasses and this will be carried out in Chapter 6.

4.6.6 Conclusions

A summary of the main conclusions derived from this set of experiments is listed below:

- Mixing the batch will facilitate the production of a more homogeneous glass.

- Smaller sand grain sizes improve glass formation and therefore homogeneity. However, this has to be balanced against refining time and therefore the quality of the glass desired.
- Sand grain size and mixing may not significantly influence homogeneity if the ash is very reactive.
- The inclusion of a fritting stage increases inhomogeneity.
- The inclusion of a fritting stage is not always necessary to produce a glass.
- Beech ash batches required a higher melting temperature than bracken batches to form a glass.
- Beech and bracken ashes have specific fritting and melting requirements.

The unusual results obtained from the glasses made using a fritting stage suggests that fritting is a very complex variable that will require further experimental investigation. This will be carried out in Chapter 5. Before this can be done it is important to establish a melting temperature and time that will melt the beech ash batches into glasses. The relationship between ash type, melting temperature and time is therefore the focus of Section 4.7.

4.7 Stages of Melting, an Evaluation of Glass Melting Temperature and Time

4.7.1 Introduction

The results of Section 4.6 determined that at melting temperatures of 1300°C most of the glasses were not batch free after 1 hour. To be able to investigate inhomogeneity in Chapters 5 and 6 a melting time has to be selected that will form a glass. The following sets of experiments were therefore designed to determine at what times and temperatures these glasses became batch free. These experiments used the beech brash ash produced by Smedley *etal.* (1998) (used in Section 4.6), the beech trunk wood ash produced during this research (used in Chapters 5 and 6), and the bracken ash produced by Jackson and Smedley (2000) (see Section 4.3).

4.7.2 Experimental

The batch composition used in Section 4.6.2 was altered for all the following experiments in this Chapter. The parameters were the same except the total batch weight was reduced from 15.00g to 9.00g (3.00g sand, 6.00g ash). This new value was chosen to conserve raw materials (see Section 4.3.3.1). The sand grain size used was ≤250->180μm (B.S. 410 Test Sieves) and the batch was mixed. A single sand grain size was chosen, as it was important to maintain a standard throughout all the following experiments to avoid introducing additional unknown variables. The mixing procedure used was the 'end over end' method for a period of 60s (see Section 4.5.1.1). Unless otherwise stated, these batch parameters were also used in Chapters 5 and 6.

The batches were added in one stage to preheated mullite crucibles (CON9, see Appendix A). They were not fritted before melting as the results from Section 4.6 suggested that fritting is an extremely complex variable and this will be investigated in detail in Chapter 5. Batches of each ash type were subjected to differing melting temperatures (1200°C and 1300°C) and times (0.083-66hrs) in an electric furnace. The crucibles were then removed and left to air cool on the back of the furnace. The experimental parameters and the visual results of the glasses produced in this section are recorded Table IV:13 to Table IV:24.

4.7.3 Results for Beech Ash Batches

The difference in the melting behaviour of the beech brash and trunk wood ash batches at 1200°C and 1300°C is illustrated in Figure 4:5.

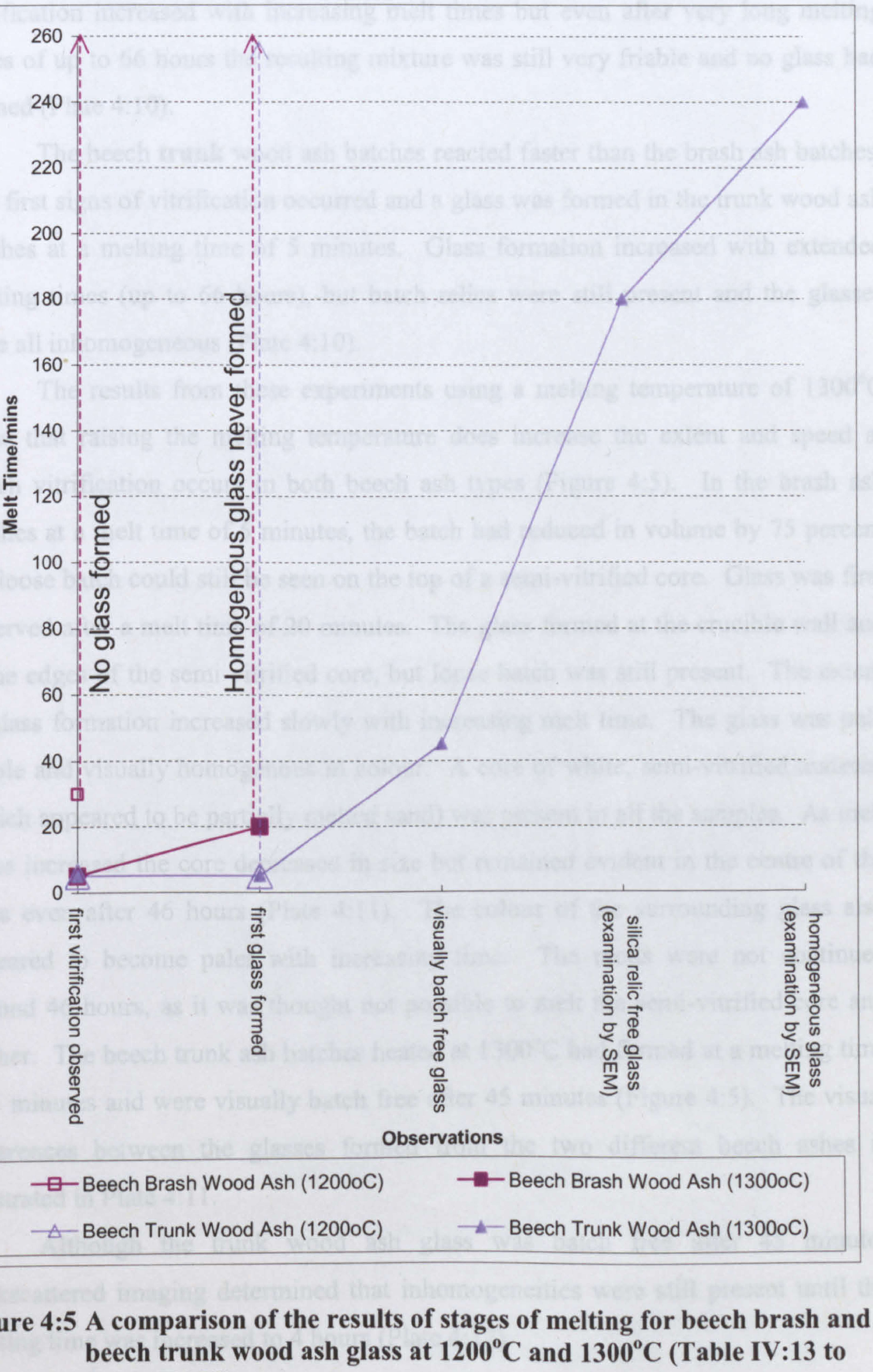


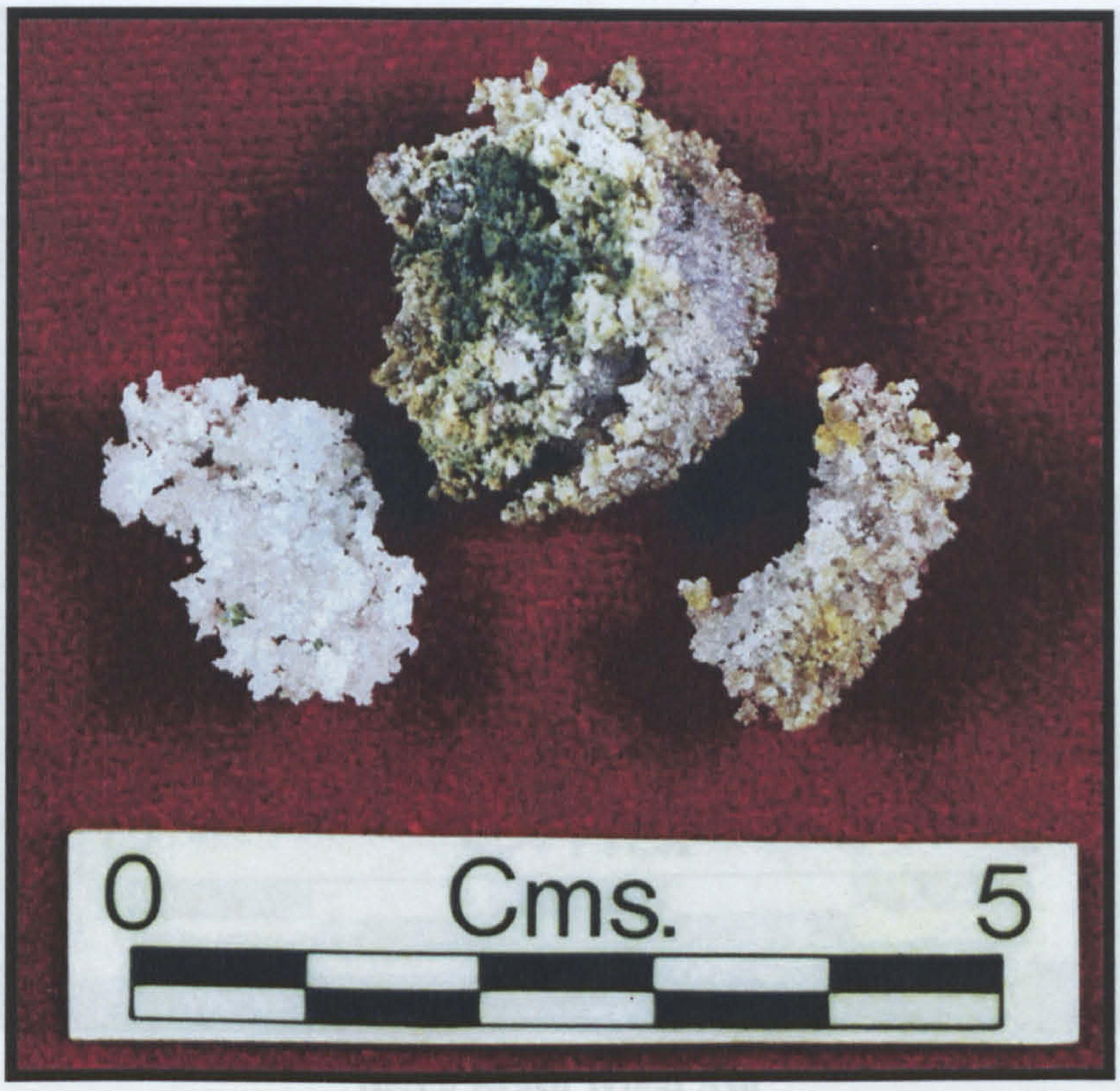
Figure 4:5 A comparison of the results of stages of melting for beech brash and beech trunk wood ash glass at 1200°C and 1300°C (Table IV:13 to Table IV:20)

The beech **brash** ash did not form a glass at a melting temperature of 1200°C. At melt times between 5 and 20 minutes no visible melting could be observed. Vitrification was observed in the centre of batches heated for times greater than 20 minutes but the resulting substance was still extremely friable. The extent of vitrification increased with increasing melt times but even after very long melting times of up to 66 hours the resulting mixture was still very friable and no glass had formed (Plate 4:10).

The beech **trunk** wood ash batches reacted faster than the brash ash batches. The first signs of vitrification occurred and a glass was formed in the trunk wood ash batches at a melting time of 5 minutes. Glass formation increased with extended melting times (up to 66 hours), but batch relics were still present and the glasses were all inhomogeneous (Plate 4:10).

The results from these experiments using a melting temperature of 1300°C show that raising the melting temperature does increase the extent and speed at which vitrification occurs in both beech ash types (Figure 4:5). In the brash ash batches at a melt time of 5 minutes, the batch had reduced in volume by 75 percent but loose batch could still be seen on the top of a semi-vitrified core. Glass was first observed after a melt time of 20 minutes. The glass formed at the crucible wall and at the edges of the semi-vitrified core, but loose batch was still present. The extent of glass formation increased slowly with increasing melt time. The glass was pale purple and visually homogenous in colour. A core of white, semi-vitrified material (which appeared to be partially melted sand) was present in all the samples. As melt times increased the core decreased in size but remained evident in the centre of the glass even after 46 hours (Plate 4:11). The colour of the surrounding glass also appeared to become paler with increasing time. The melts were not continued beyond 46 hours, as it was thought not possible to melt the semi-vitrified core any further. The beech trunk ash batches heated at 1300°C had formed at a melting time of 5 minutes and were visually batch free after 45 minutes (Figure 4:5). The visual differences between the glasses formed from the two different beech ashes is illustrated in Plate 4:11.

Although the trunk wood ash glass was batch free after 45 minutes backscattered imaging determined that inhomogeneities were still present until the melting time was increased to 4 hours (Plate 4:12).

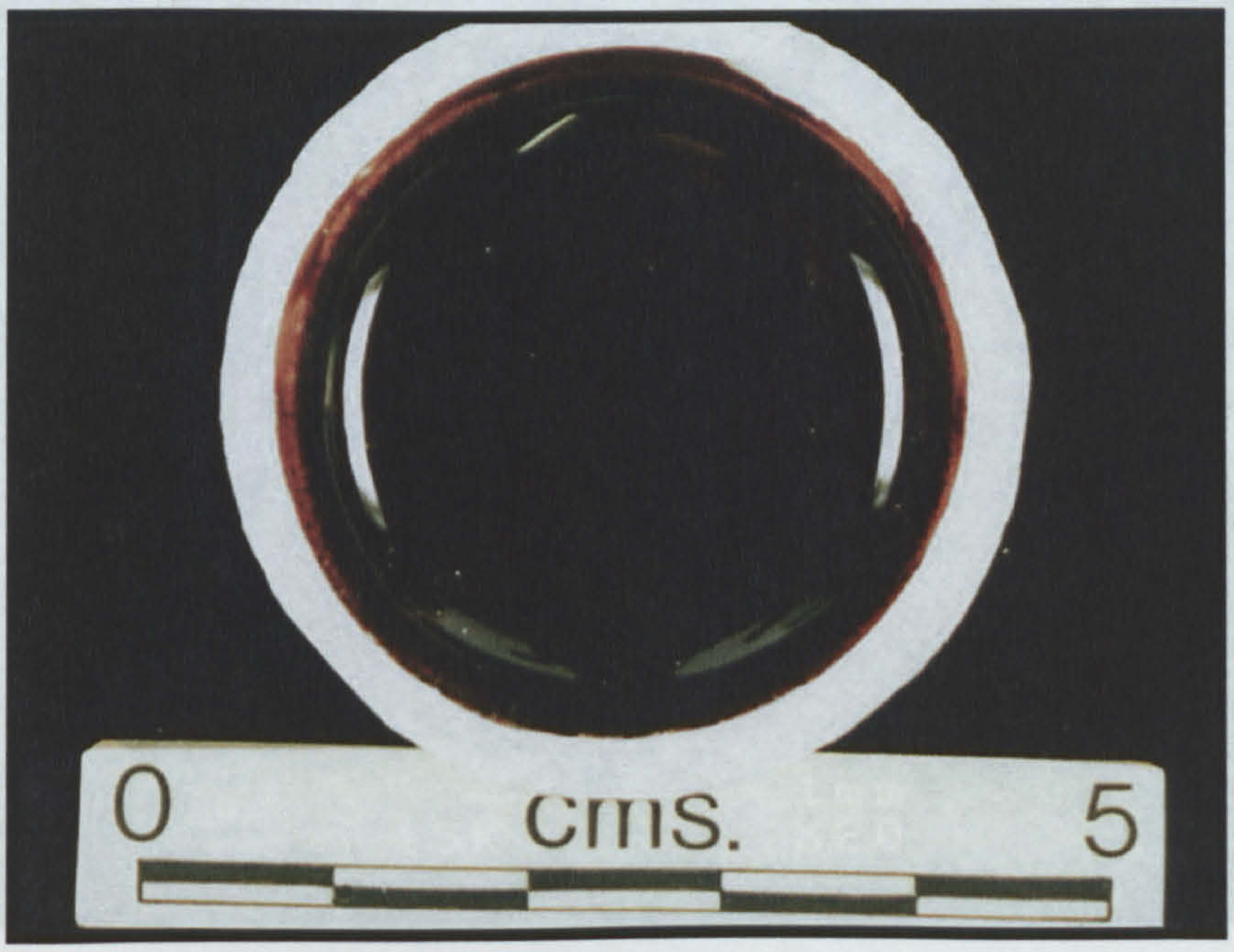


Beech Brash Wood Ash

Beech Trunk Wood Ash

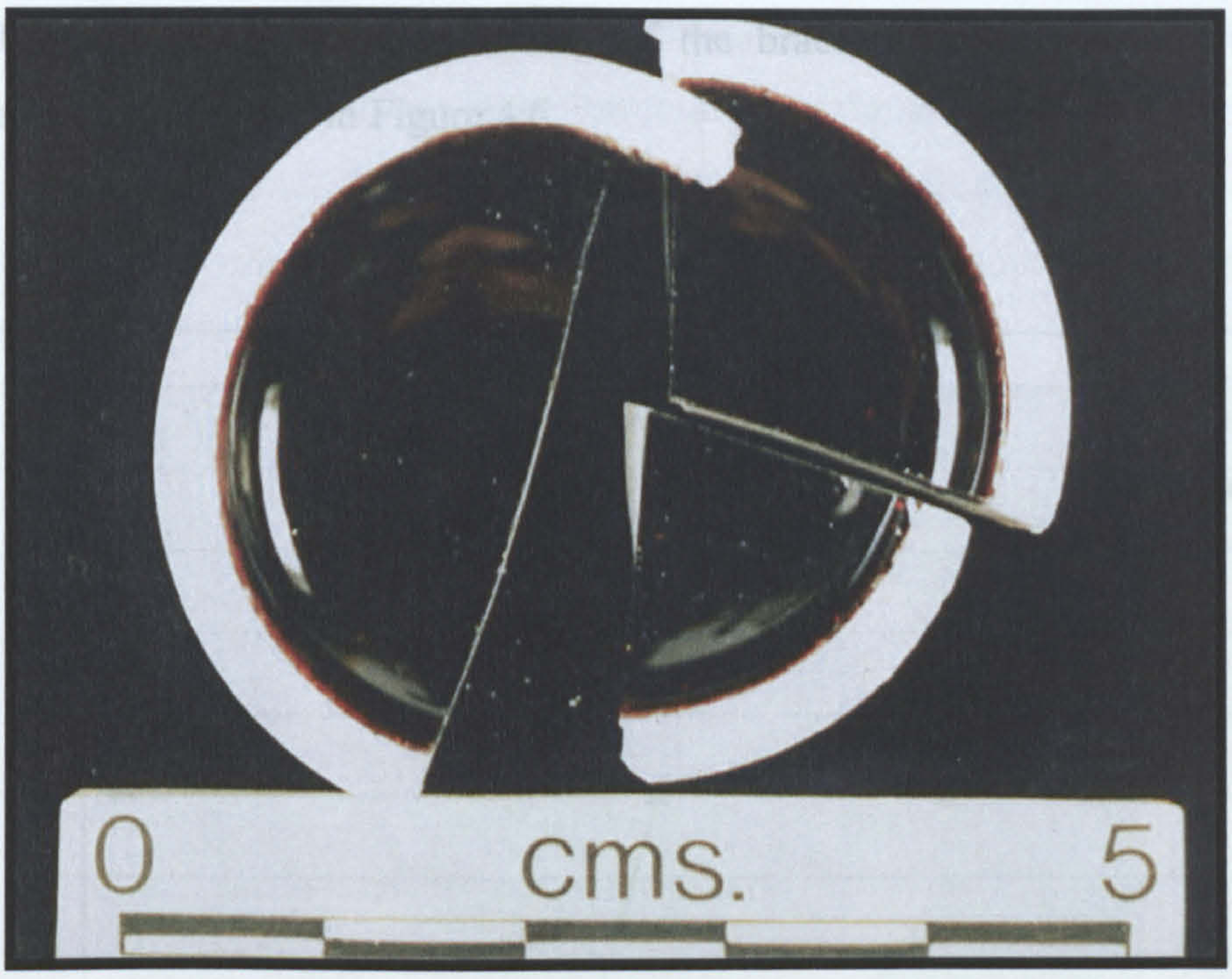
Plate 4:10 **A comparison of beech brash and trunk wood ash batches heated at 1200°C for 66 hours (Be36, Table IV:14 and Be48, Table IV:16)**

Beech Brash Wood Ash

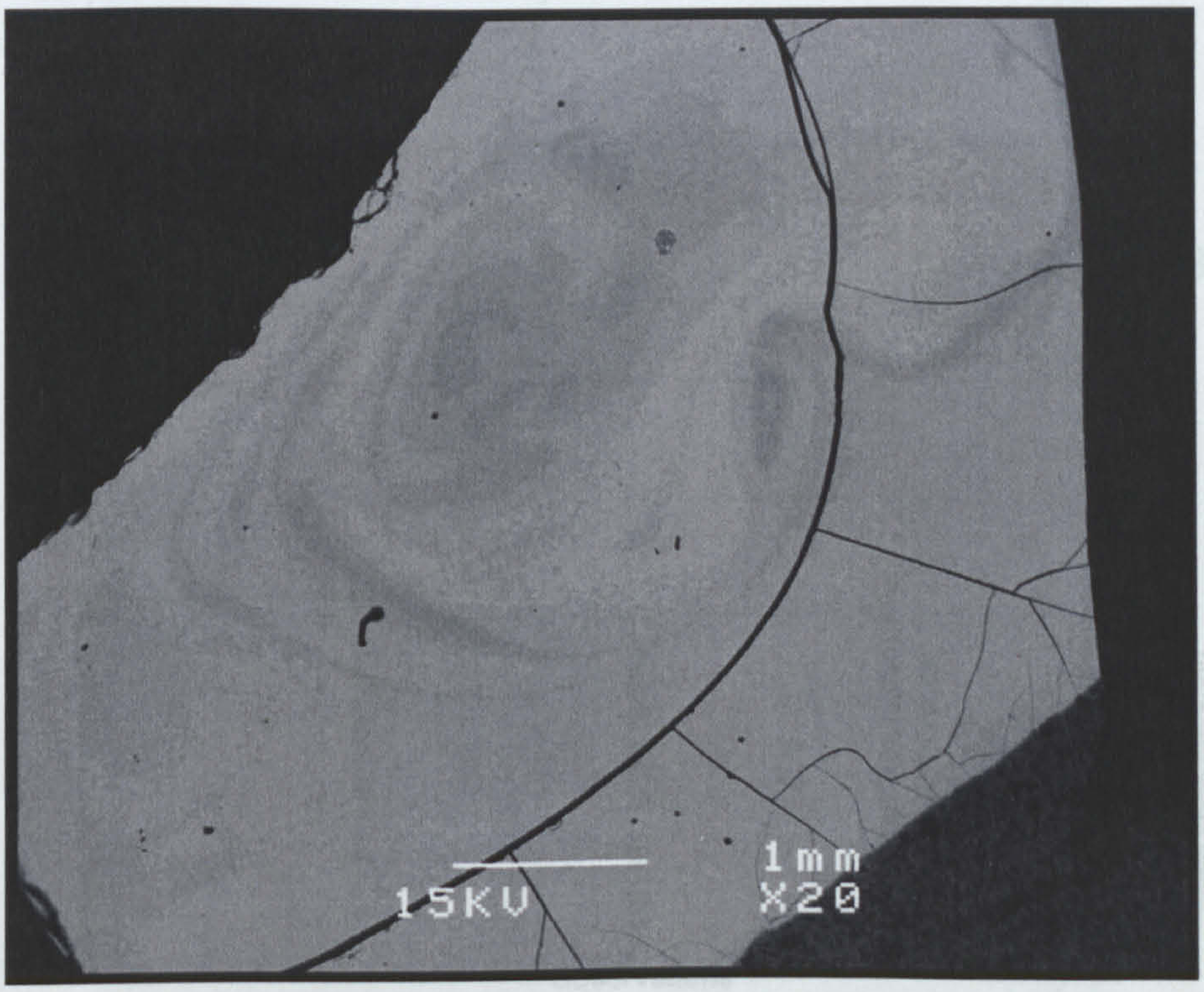


Beech Trunk Wood Ash

Plate 4:11 A comparison of a beech brash wood ash batch heated at 1300°C for 46 hours (Be69, Table IV:18) and a beech trunk wood ash batch heated at 1300°C for 4 hours (Be85, Table IV:20)



Visually Batch Free Glass



Backscattered SEM Image Illustrating Medium Inhomogeneity

Plate 4:12 A comparison of optical and backscattered SEM images of a beech trunk ash glass melted at 1300°C for 0.75 hours (Be78, Table IV:20)

4.7.4 Results for Bracken Ash Batches

The difference in the behaviour of the bracken ash at different melting temperatures is illustrated in Figure 4:6.

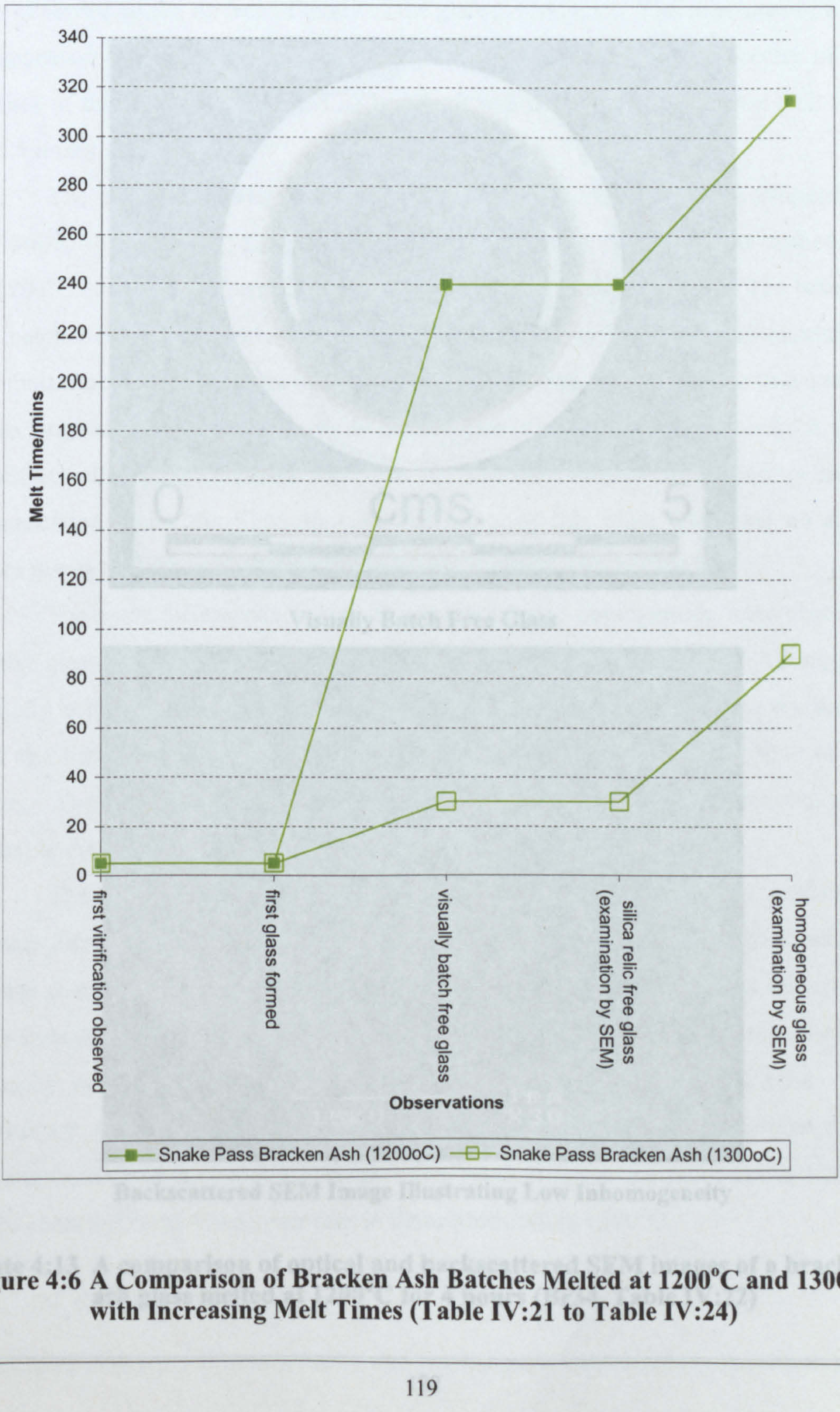
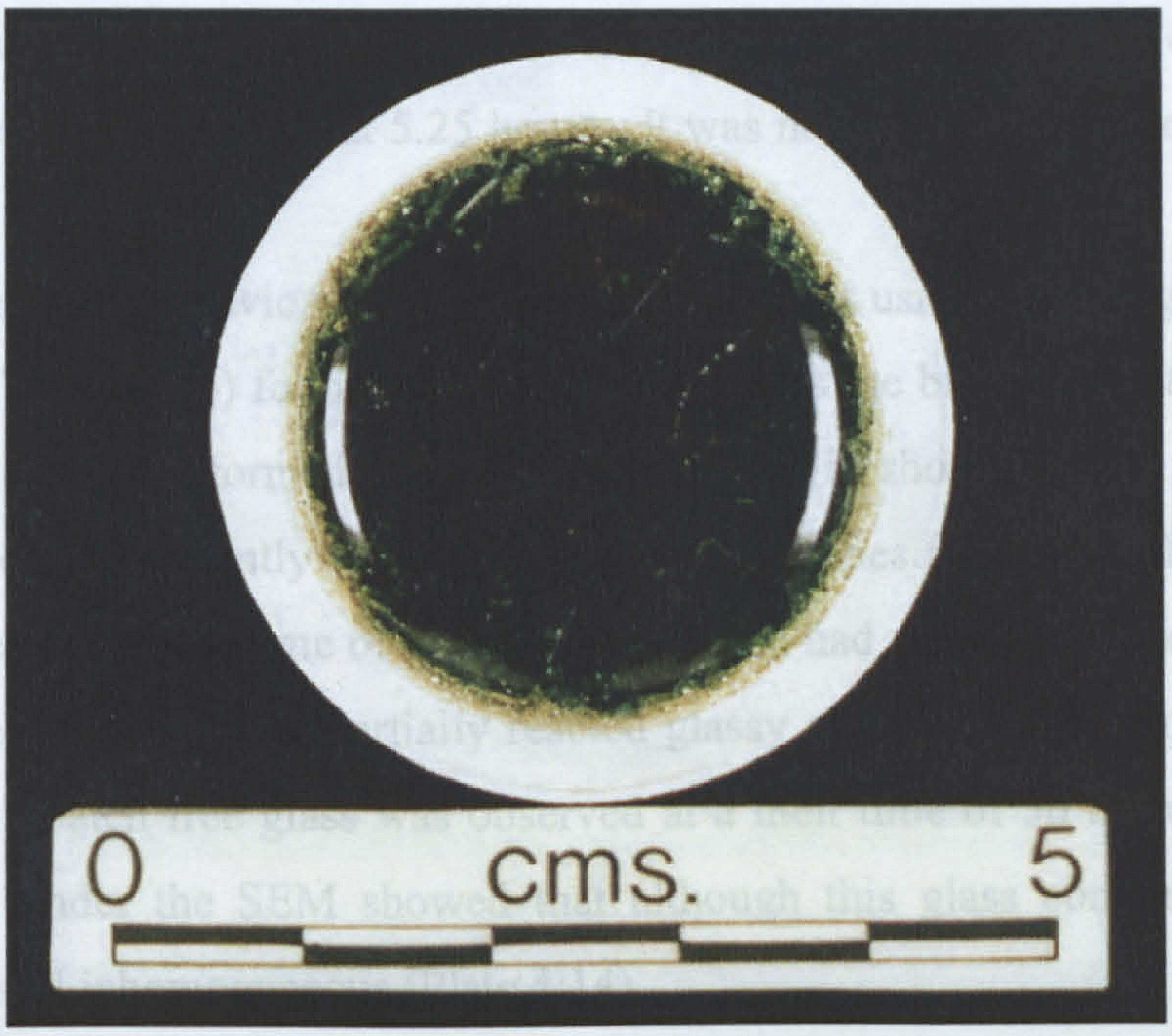
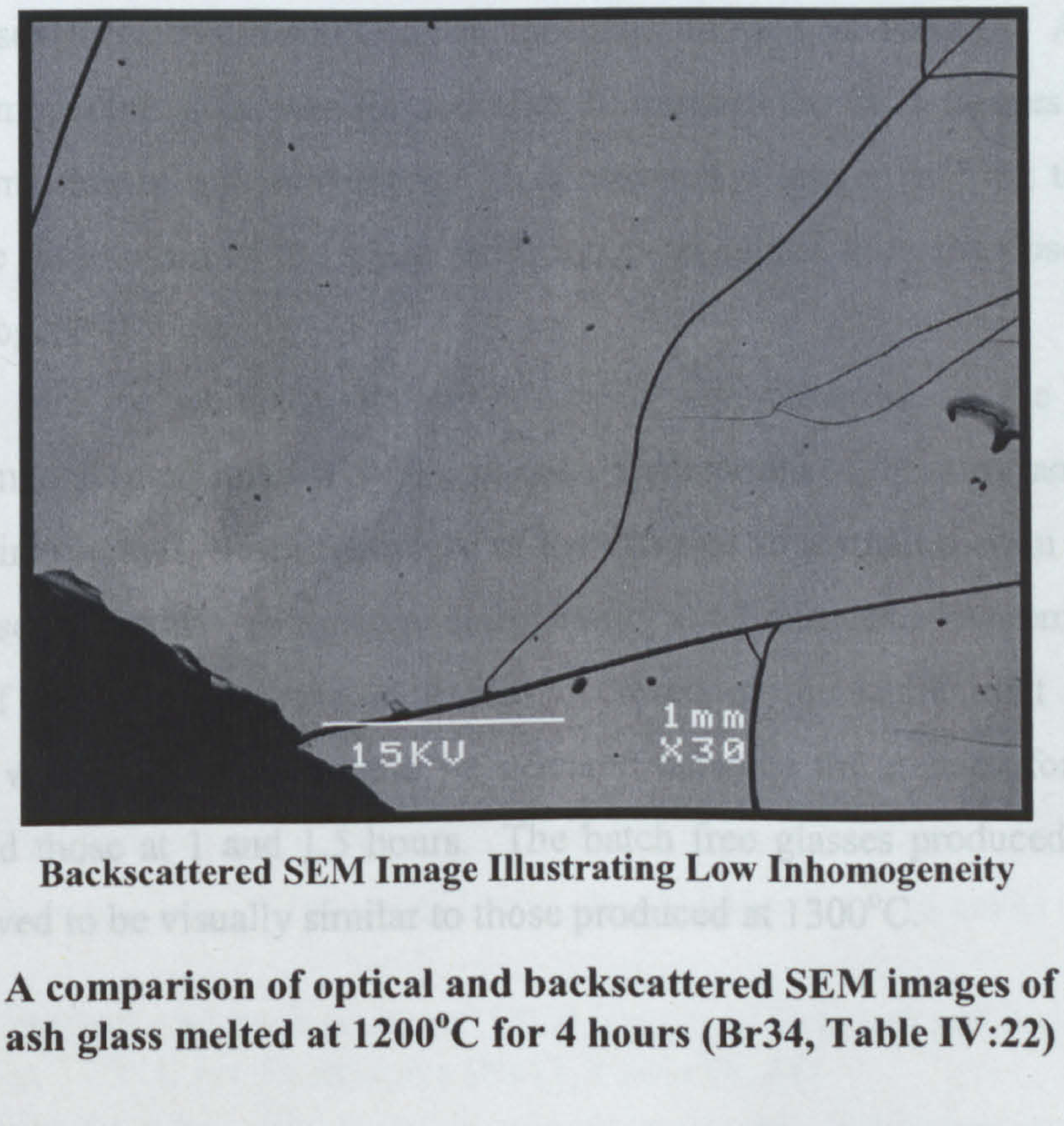


Figure 4:6 A Comparison of Bracken Ash Batches Melted at 1200°C and 1300°C with Increasing Melt Times (Table IV:21 to Table IV:24)

The results obtained from these experiments using a melting temperature of 1200°C (Table IV:22) determined that the bracken ash batches were extremely reactive. Copious white fumes were emitted from the batch during the first 10 minutes of the melt time. The batch reduced by a quarter in size within 5 minutes. The time taken to produce a dark green batch free glass was 4 hours (Plate 4:13).



Visually Batch Free Glass



Backscattered SEM Image Illustrating Low Inhomogeneity

Plate 4:13 A comparison of optical and backscattered SEM images of a bracken ash glass melted at 1200°C for 4 hours (Br34, Table IV:22)

Backscattered SEM imaging showed that low levels of inhomogeneity were still present after a melting time of 4 hours (Plate 4:13). The backscattered imaging confirmed that visual homogeneity coincided with the removal of the silica relics, but that complete removal of inhomogeneity required a melting time of 5.5 hours.

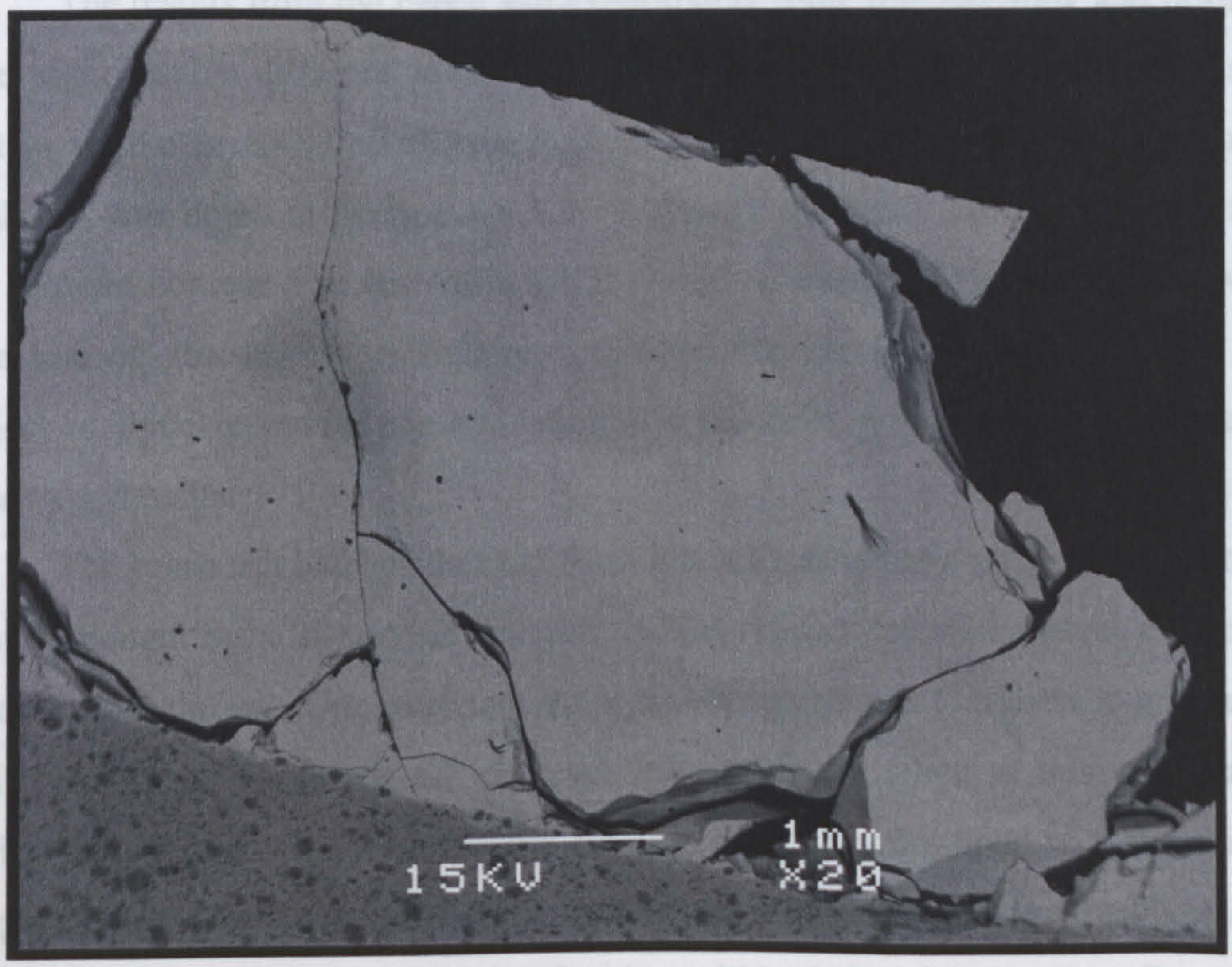
A pink or white crystalline substance (identical to that seen in Section 4.6.3) was observed on the surface of many of the glasses produced. The substance initially disappeared at melt times greater than 2 hours but reappeared in the centre of the surface of the glass produced at 5.25 hours. It was not present at the next melt time of 5.5 hours.

The melting behaviour in this set of experiments using a melting temperature of 1300°C (Table IV:24) followed the same pattern as the bracken melts carried out at 1200°C except fully formed glasses were produced in shorter times. The bracken ash batches reacted violently emitting copious white fumes for the first 10 minutes of the melt time. At a melt time of 5 minutes the batch had reduced in size to a quarter of its original volume and a partially reacted glassy substance had formed. A dark green visually batch free glass was observed at a melt time of 30 minutes or more. Examination under the SEM showed that although this glass contained no silica relics it was still inhomogeneous (Plate 4:14).

The same differences in visual and microscopic homogeneity were observed in the glasses formed at 1300°C as in the glass formed at 1200°C. Although a visually homogenous glass was formed after 30 minutes the SEM images confirmed that the formation of a homogeneous glass required a longer melting time of 1.5 hours. The dissolution of the silica relics again coincided with the observation of visual homogeneity.

The pink or white crystalline substance was observed on the surface of glasses formed at melt times of 5-50 minutes. The amount of this substance reduced in size (shrinking away from the edges of the crucible to a small disk in the centre) with increased melt time, completely disappearing at 55 minutes. The removal of the majority of bubbles from the melt also occurred at the same melt time. No significant visual differences could be detected between the glasses formed at 55 minutes and those at 1 and 1.5 hours. The batch free glasses produced at 1200°C were observed to be visually similar to those produced at 1300°C.

Visually Batch Free Glass



Backscattered SEM Image Illustrating Medium Inhomogeneity

Plate 4:14 Optical and backscattered SEM images of bracken ash batch heated at 1300°C for 30 minutes (Br43, Table IV:24)

4.7.5 Discussion

4.7.5.1 Beech Ash

The trunk ash reacts faster and therefore forms more homogeneous glasses than the brash ash. However, even when melting for lengthy time periods melting temperatures of 1200°C are not sufficient for either ash to form a homogeneous glass. Increasing the melting temperature to 1300°C improves the quantity and homogeneity of glass formed. Section 4.3.3.2 noted that beech ashes have a lower total alkali content than bracken ashes and are therefore more likely to require higher melting temperatures to form a homogeneous glass. The results from these experiments suggest that this is the case. Cable and Smedley (1987) have suggested that temperatures of up to 1350°C may have been produced in wood fired furnaces (see Section 2.4.2). It is not certain whether these temperatures were achievable in medieval furnaces, but if glasses were being produced from beech ashes, then higher temperatures may have been required. Unfortunately it was not possible to determine the melting behaviour of beech ash glasses at temperatures higher than 1300°C due to time and raw materials constraints but this is area for further work.

The results from the beech ash experiments show that the trunk and brash ash have significantly different melting behaviours. This is surprising as the ashes contain similar levels of alkali (see Section 4.3.3.2). The unusual behaviour of the brash ash was noted in Section 4.6.5.3. Although the brash ash has a higher silica and calcium content than the trunk ash it would be expected that both ashes would have formed glasses. It is therefore assumed that the brash ash must have been subject to some unknown contamination and therefore it is not used in the rest of these experiments.

The brash ash batches that did form glasses contained a semi-vitrified core of what is thought to be silica rich material. Silica relics were also present in many of the trunk ash glasses. One explanation for this occurrence is that there is not enough alkali present in the beech ash to react fully with the silica at this temperature. During the melting stage the available alkali is gradually combined with the silica in the production of a glass. If there is insufficient alkali available to dissolve all the silica in the batch then the remaining fraction will be left as batch relics. To remove silica rich areas within a glass higher melting temperatures are required. These will facilitate a faster and more turbulent melting reaction ensuring a more intimate mixture between the silica and alkali. To avoid the inclusion of batch relics it is therefore beneficial for the raw materials to react quickly. This will be facilitated by the use of higher melting temperatures, mixed batches, small silica grain sizes and raw materials with high alkali concentrations.

Although visually homogeneous glasses were formed using trunk wood ash, the SEM images confirmed that inhomogeneities were still present that required extended melting times to remove. It is important to note that the medieval glassmaker would not have been able to observe these microscopic differences in composition. It is therefore possible that glass may have been worked before it was homogeneous. The batches used in these experiments are also very small in comparison to medieval melts (see Section 2.4.5.2). The times required for the experimental melts to become not only batch free but also compositionally homogenous may therefore be much less than that required for medieval glass production. The influence of increasing batch size on homogeneity will be investigated in Section 6.1.3.

Despite the presence of the many silica relics in the brash ash glasses, the glass formed contained very little seed. This is important to note, as it is therefore possible that although the beech ashes will probably require higher and longer melting times to become batch free, they may not then require extra refining time (see Section 2.2.1.1). However, another reason for the lack of seed may be the presence of manganese in the glass that acts as a very efficient refining agent (Weyl 1951).

The trunk ash glass is dark purple and the brash ash glass pale purple. The two ashes contain similar manganese contents. It is therefore surprising that, as they have been melted in the same way, that they should produce significantly different colours of glass. This again suggests that the brash ash has been contaminated. The colour of the brash ash glasses was observed to lighten as the melt time increased. It has already been seen that the purple colouration is due to the presence of the manganese in the ash (see Section 4.6.5.4). The purple Mn^{3+} ions exist in equilibrium with pale yellow/brown, Mn^{2+} ions. In oxidising conditions the equilibrium will shift towards the trivalent ion and the purple colour will increase. Increasing the melt times will cause the internal melt conditions to become more reducing. This will shift the equilibrium back towards the production of the divalent, manganous ions, producing a paler glass (Weyl 1951). Therefore the brash ash glasses become paler with increasing melt times.

4.7.5.2 Bracken Ash

The results from Section 4.6 demonstrated that bracken ash batches required lower melt temperatures and shorter times to form a glass than their beech equivalents. In addition to this, it can be seen that at lower temperatures (1200°C) longer melting times will be required to form a batch free bracken glass (240 minutes) and that at 1300°C a batch free glass is formed after only 30 minutes. These results confirm that the bracken ash is extremely reactive and will form a visually homogeneous glass very readily.

The observations on the bracken ash glasses also confirm that visual homogeneity does not mean that inhomogeneities are not present which will require extended melting times to remove. The bracken batches form a glass faster than the beech batches but may then require additional refining time to produce a seed free melt. This needs to be considered, as extra refining time will allow the melt to become more homogeneous. The batch free times recorded in these experiments are not necessarily the times required to produce a glass suitable for working.

The white crystalline substance produced on the surface of the bracken ash glasses is the same as was observed in the previous set of experiments and is therefore probably potassium sulphate (see Section 4.6.5.4). It was observed that longer melt times facilitate the removal of the white substance. This is probably due to the volatile nature of the material (see Section 4.6.5.4).

4.7.6 Conclusions

The results in these experiments exhibit many of the same trends observed in the batch mixing and sand grain size experiments in Section 4.6. However, the most evident observation is that bracken ash batches exhibit a faster melting behaviour than their beech equivalents. A summary of the main conclusions made from these experiments is given below:

- Increasing melt time improves homogeneity and refining.

- Increasing melt temperature improves homogeneity and refining.
- If silica rich areas (silica relics) are formed in a melt they are difficult to remove and will remain as a potential source of inhomogeneity.
- If a glass is visually homogeneous it may still contain inhomogeneities that can only be detected using backscattered SEM imaging.
- Melting parameters (temperature and time) are specific to the raw materials in the batch.
- Beech ash glasses require a higher melting temperature than bracken ash glasses.

These results provide a set of guide lines about the melting behaviour of beech and bracken batches. This will be built upon in Chapter 6 but first the behaviour of beech and bracken ash frit will be investigated in Chapter 5.

CHAPTER 5

Experimental: The Effect of Fritting Variables on Homogeneity

5.1 Introduction

It was concluded in Chapter 4 that the inclusion of a fritting stage in glass production did not improve homogeneity, or facilitate the formation of glasses at lower melting temperatures as was expected. The aim of this Chapter is to carry out a detailed investigation of how altering the fritting parameters such as temperature, time and crucible dimensions, affects the homogeneity of the glass formed. The Chapter is in two parts: a) the production of beech and bracken ash frits using different fritting parameters and b) melting the frits produced in (a) into glasses. The evidence for fritting in medieval glassmaking and the reasons why specific fritting variables were chosen for experimental investigation has been discussed in Sections 2.3 and 2.7.

The experiments in this chapter were initially carried out using bracken ash, as a new supply of beech ash was being located (see Section 4.3). The results from these and experiments using the new beech ash source (see Section 4.7) exhibited well defined melting characteristics. These observations were therefore used to plan the experimental schedule for the beech ash in this Chapter. The same maximum and minimum values for temperature and time were used as for the bracken fritting experiments but with fewer intermediate values. All the experimental details and results from this Chapter are tabulated in Table V:1-Table V:32.

5.2 Fritting Temperature and Time

These experiments were carried out using the standard mixed batch of beech or bracken ash (2 parts) and sand (1 part) as described in Section 4.7.2. Identical batches were placed in mullite crucibles (CON9) and heated in air in an electric muffle furnace (Appendix A) at differing temperatures (500-1000°C) and times (1-24hr). The colour, decrease in batch volume and friability of the finished product (in these experiments called 'the frit') and the experimental parameters are recorded in Table V:1 to Table V:4. Unless otherwise stated, the batch composition and furnace parameters used here were also used for the experiments in Sections 5.3 and 5.4.

Samples of the beech and bracken frits produced were analysed by ICP-AES and XRF. The operating parameters and sample preparation were as described in Section 4.3.1. The frit was crushed and thoroughly mixed to ensure that a representative sample as possible was removed for analysis. Repeatable results could not be obtained from ICP-AES due to problems with the extent of sample dissolution (see Section 4.3.1). XRF analysis was therefore used instead and the results recorded in Table V:5 and Table V:6. The frit samples selected for XRF analysis were unfortunately limited in number. Samples were therefore chosen to represent regions where significant change occurred in the fritting behaviour of the two ash types. Although the beech ash frits produced at 1000°C were analysed, the bracken frits produced at the same temperature were extremely vitreous and it was difficult to obtain a representative sample free of refractory contamination. Therefore, bracken ash frits produced at 900°C were selected as they exhibited the same degree of vitrification as the beech ash frits formed at 1000°C.

5.2.1 Results

5.2.1.1 Colour

Figure 5:1 is a schematic representation of the changes in the colour of the **beech** ash batch with temperature and time. The original batch was the same pale grey/brown colour as the ash (Plate 4:2). Heating the batch to 500°C caused a visible change in colour. At temperatures ranging from 500-600°C the colour was paler than the original batch but at temperatures from 700°C upwards the colour became darker. This change became more marked with increasing times and temperatures until at 800°C the frit was dark brown/black in colour. Granular grains of a blue/green material were observed inside the frit. Raising the temperature and time further (800-1000°C) caused the number of these specks to increase. The maximum fritting temperature and time investigated (1000°C for 24 hours) gave a shiny black/purple frit, which contained many green, blue and white specks. A selection of the frits produced can be seen in Plate 5:1.

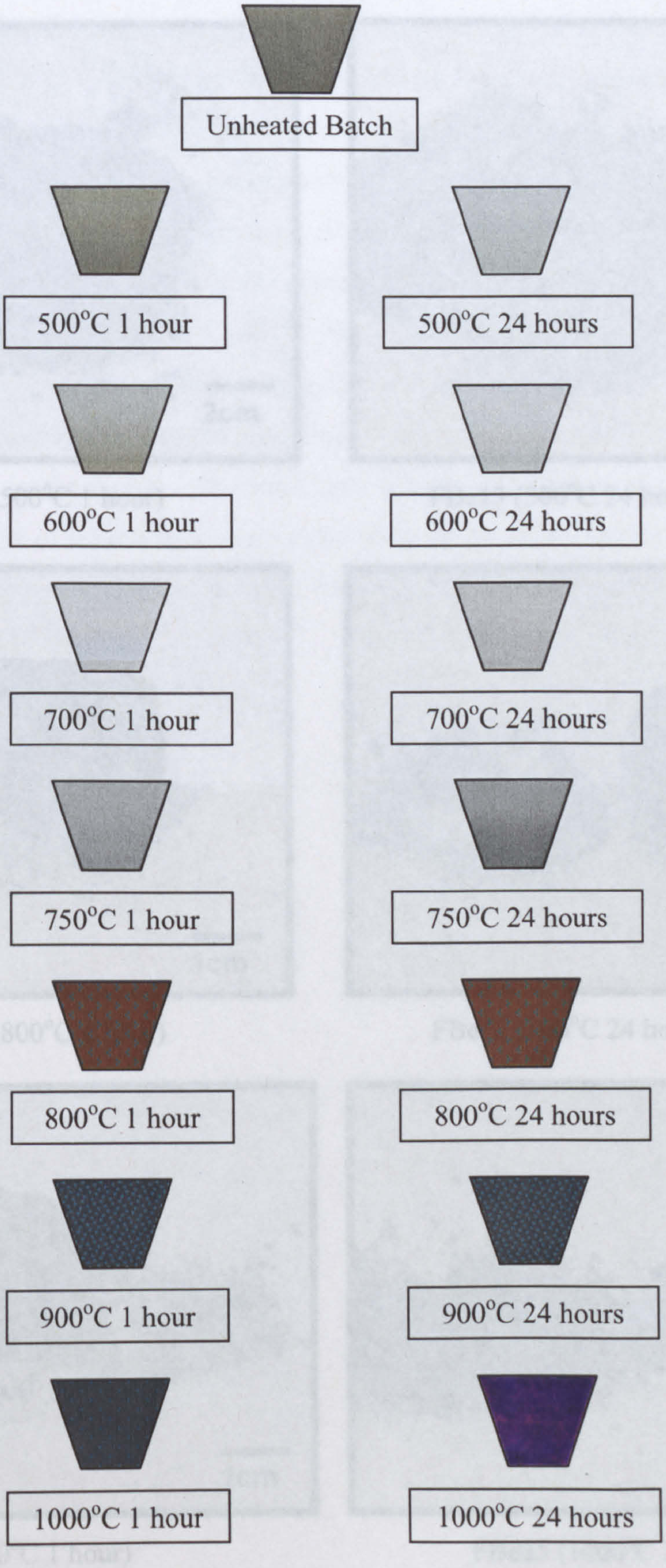
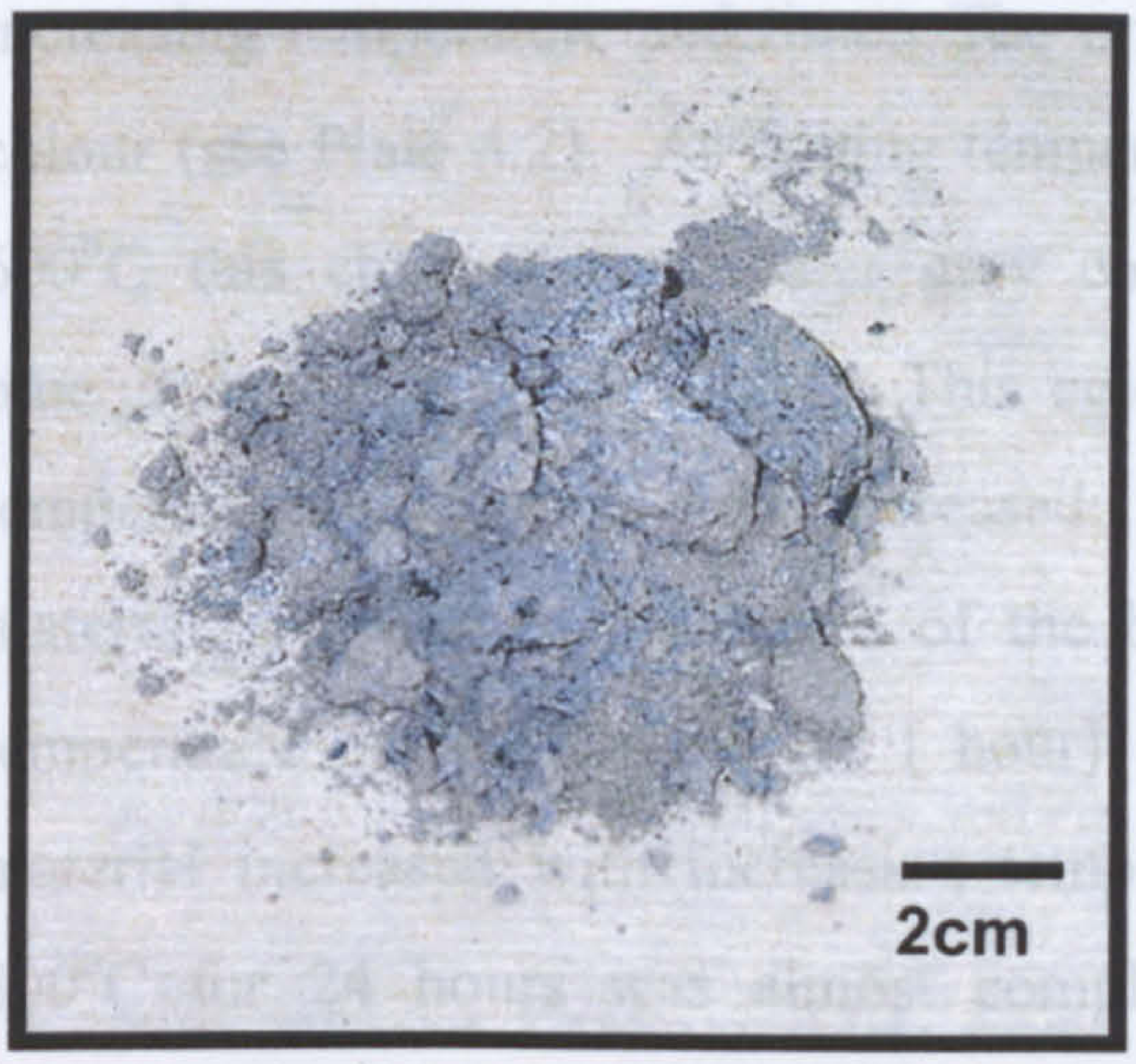
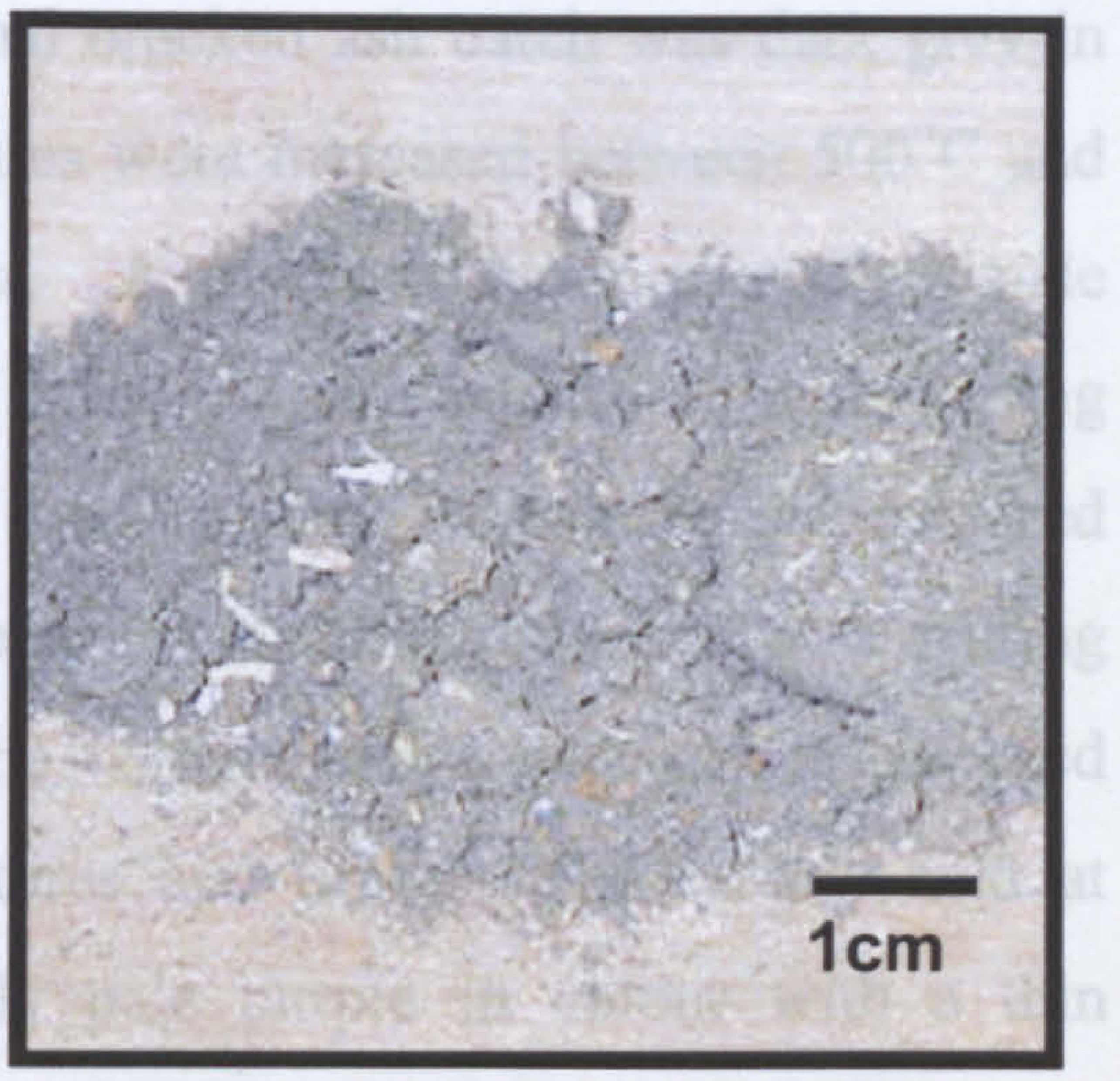


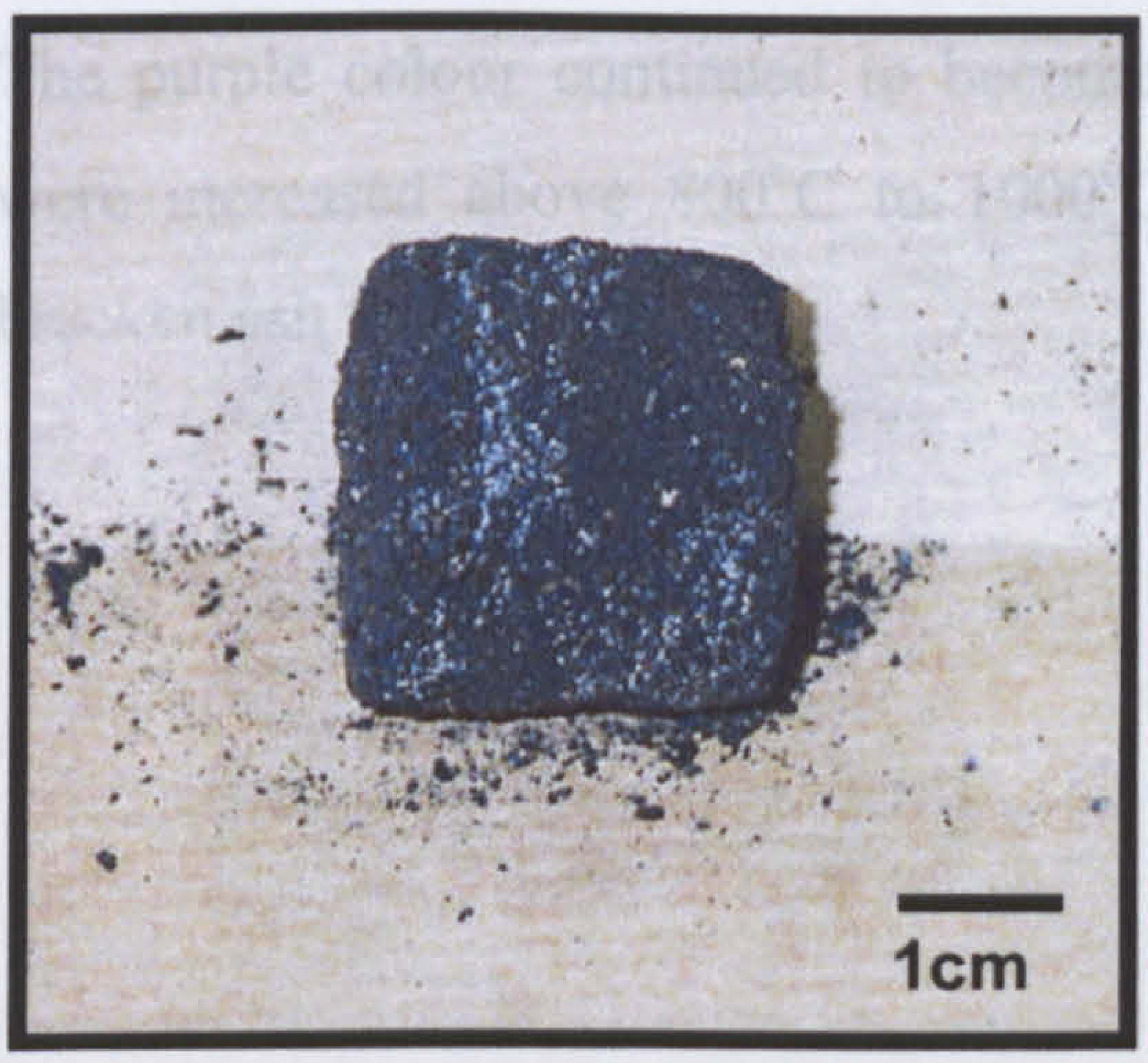
Figure 5:1 A schematic representation of change in beech ash frit colour with temperature and time (Table V:2)



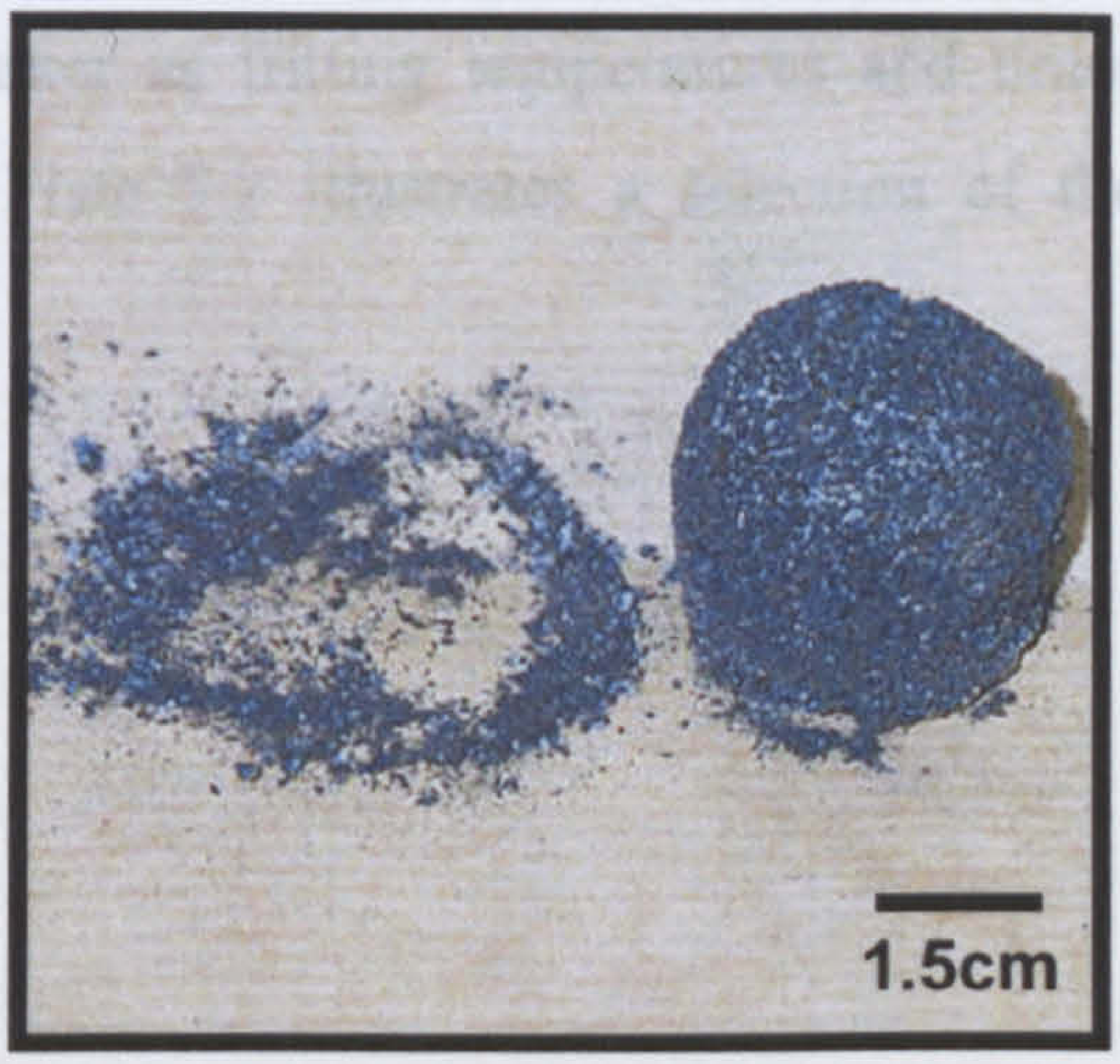
FBe12 (500°C 1 hour)



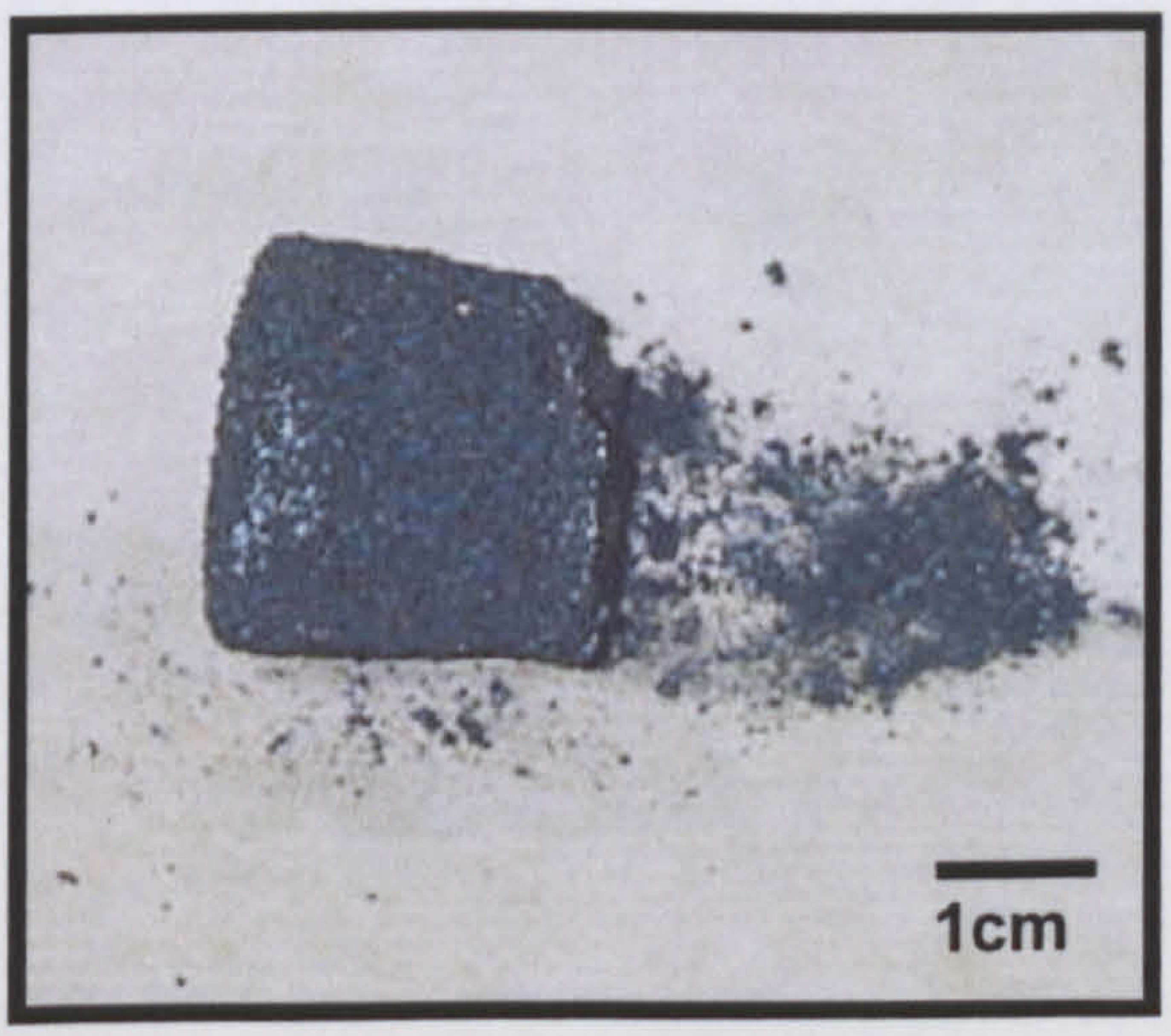
FBe13 (500°C 24 hours)



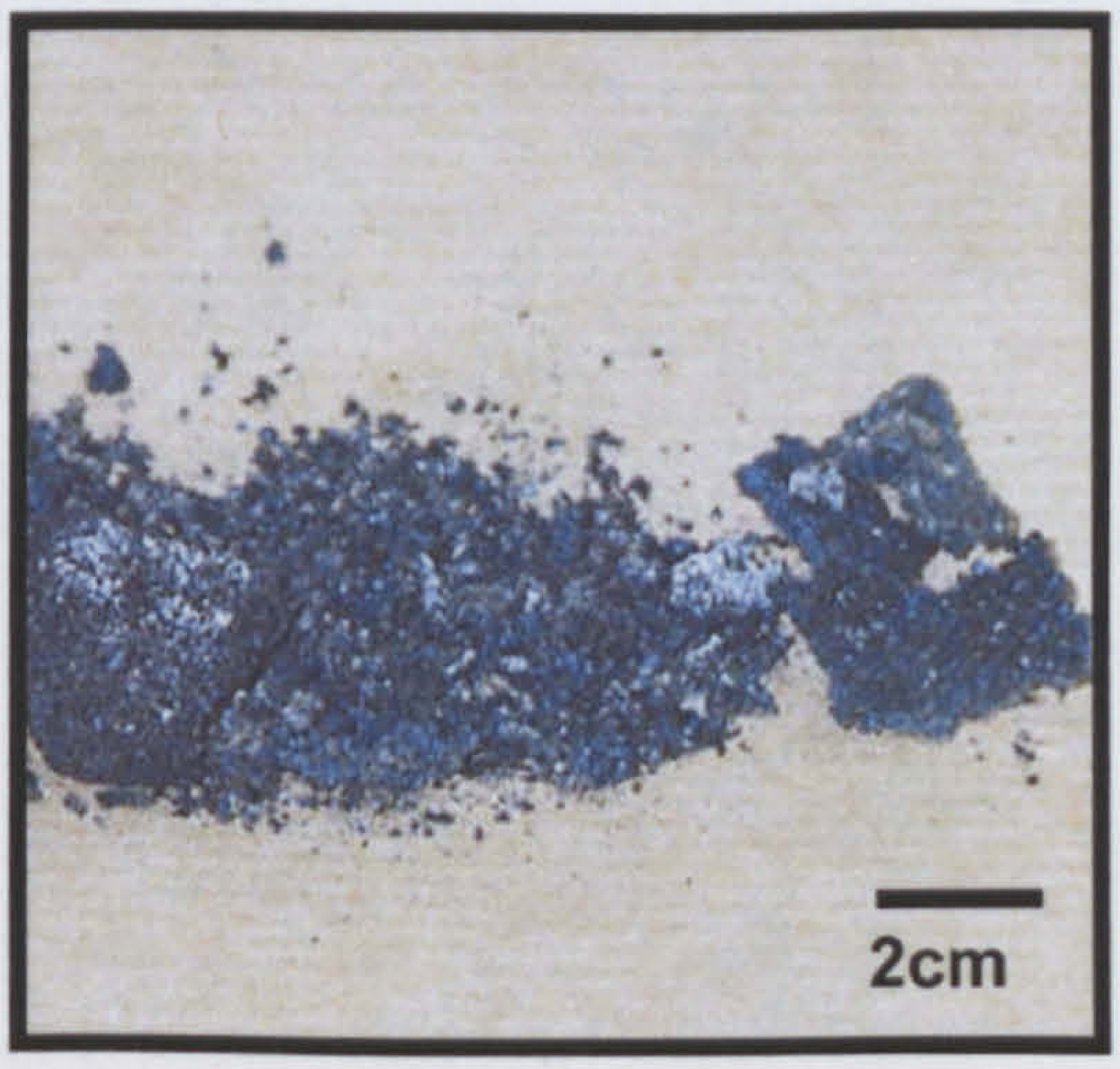
FBe20 (800°C 1 hour)



FBe21 (800°C 24 hours)



FBe24 (1000°C 1 hour)



FBe25 (1000°C 24 hours)

Plate 5:1 A selection of beech ash frits (Table V:2)

Figure 5:2 illustrates the change in colour of the **bracken** ash frits with increasing temperature and time. The original bracken ash batch was dark grey in colour (see Plate 4:2). As fritting temperatures were increased between 500°C and 600°C this changed to a paler grey colour. A marked colour change to pale blue/green occurred at 700°C. This colour became more intense as both fritting temperatures and times were increased. A small volume of pale purple coloured material appeared in the centre of the blue/green material produced at a fritting temperature of 700°C (held for 1 hour). The volume of the pale purple coloured material increased with increasing temperatures and times. The sample held at 800°C for 24 hours was almost completely pale purple in colour with a thin green/blue layer on the surface. The main body of material was dark purple in colour with white specks of what was thought to be silica rich material throughout the frit. The purple colour continued to become darker as fritting temperatures and times were increased above 800°C to 1000°C. Plate 5:2 illustrates a selection of the bracken ash frits.

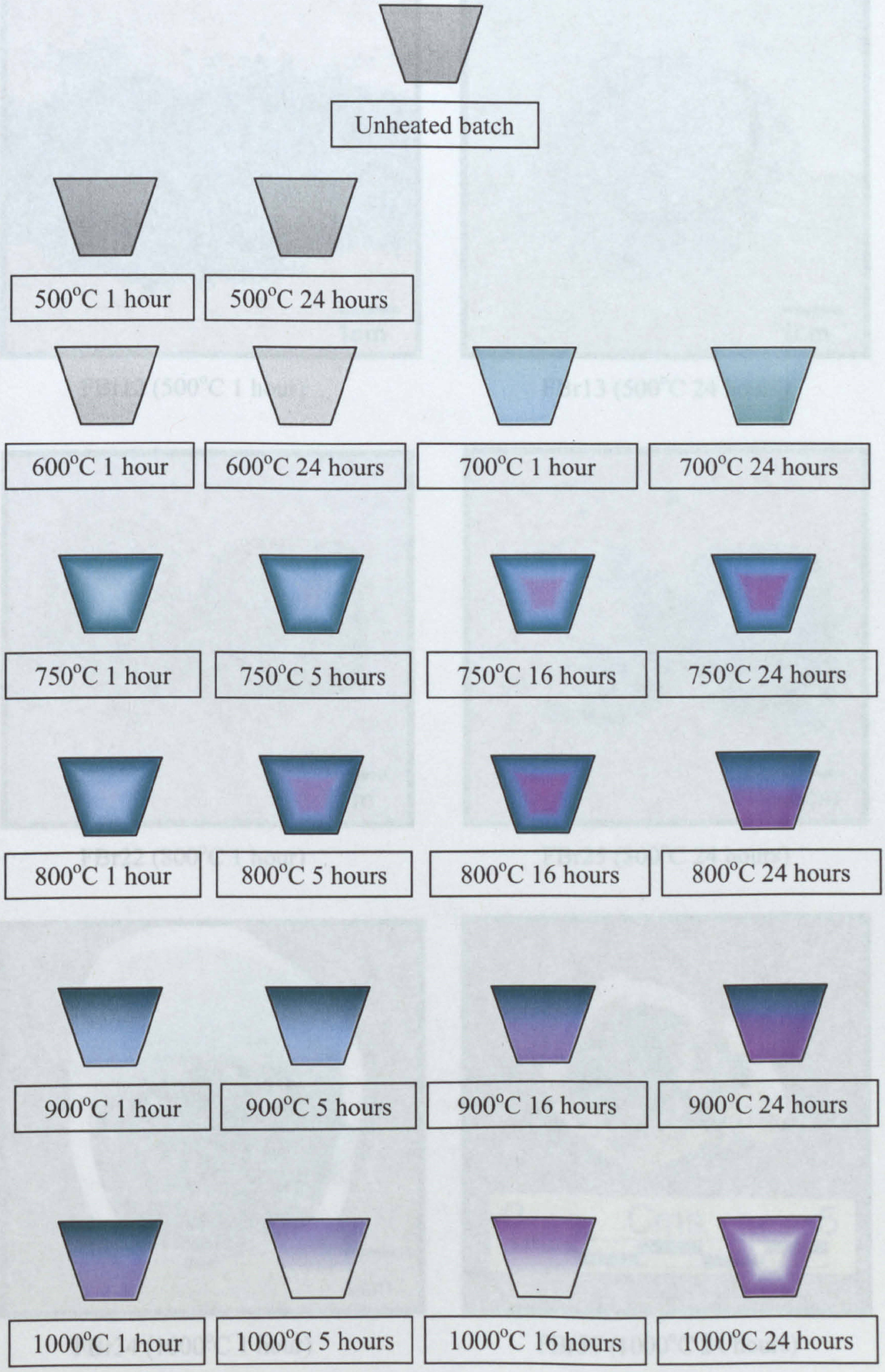
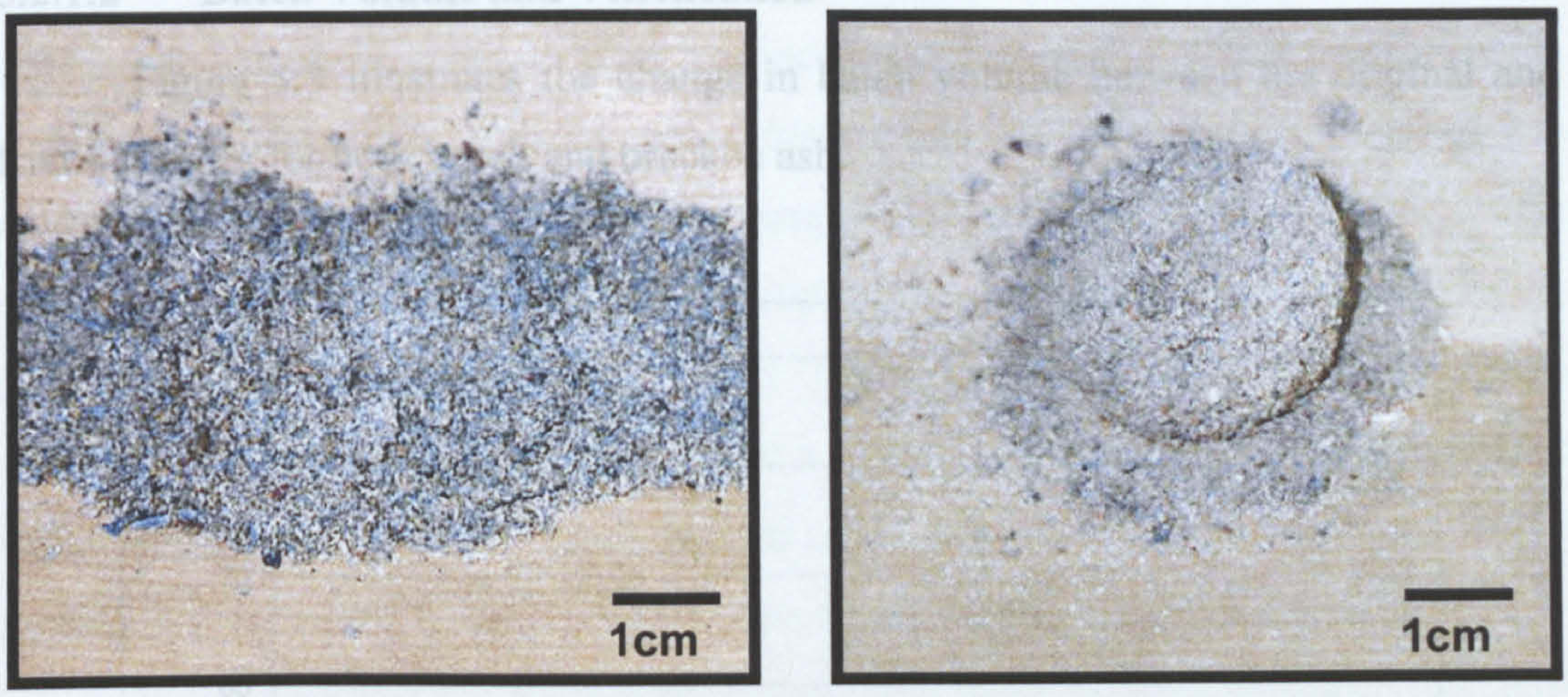
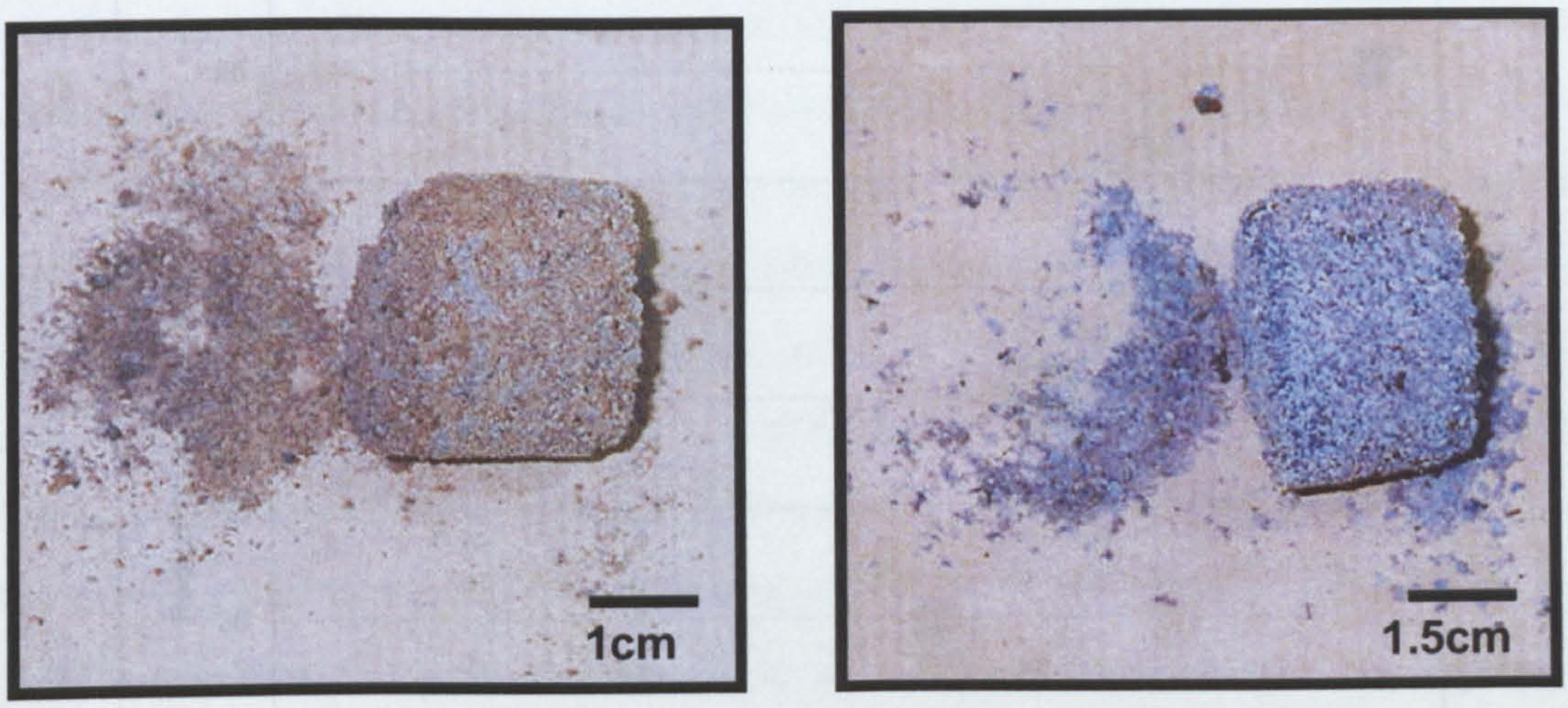


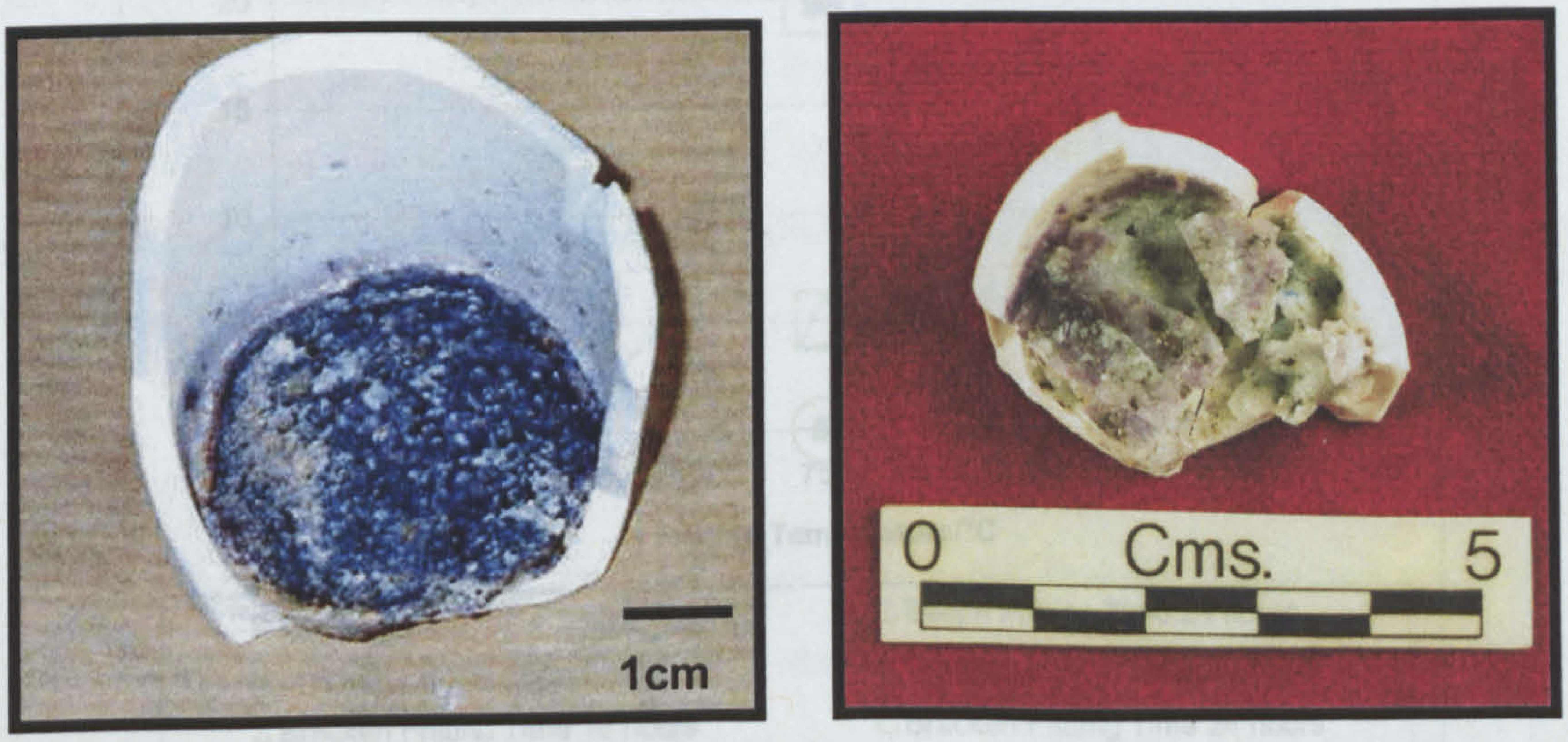
Figure 5:2 **A schematic representation of change in bracken ash frit colour with temperature and time (Table V:4)**



FBr12 (500°C 1 hour) FBr13 (500°C 24 hours)



FBr22 (800°C 1 hour) FBr25 (800°C 24 hours)



FBr34 (1000°C 1 hour) FBr37 (1000°C 24 hours)

Plate 5:2 A Selection of Bracken Ash Frits (Table V:4)

5.2.1.2 Batch Volume and Vitrification

Figure 5:3 illustrates the change in batch volume between the original and fritted batches for both beech and bracken ash.

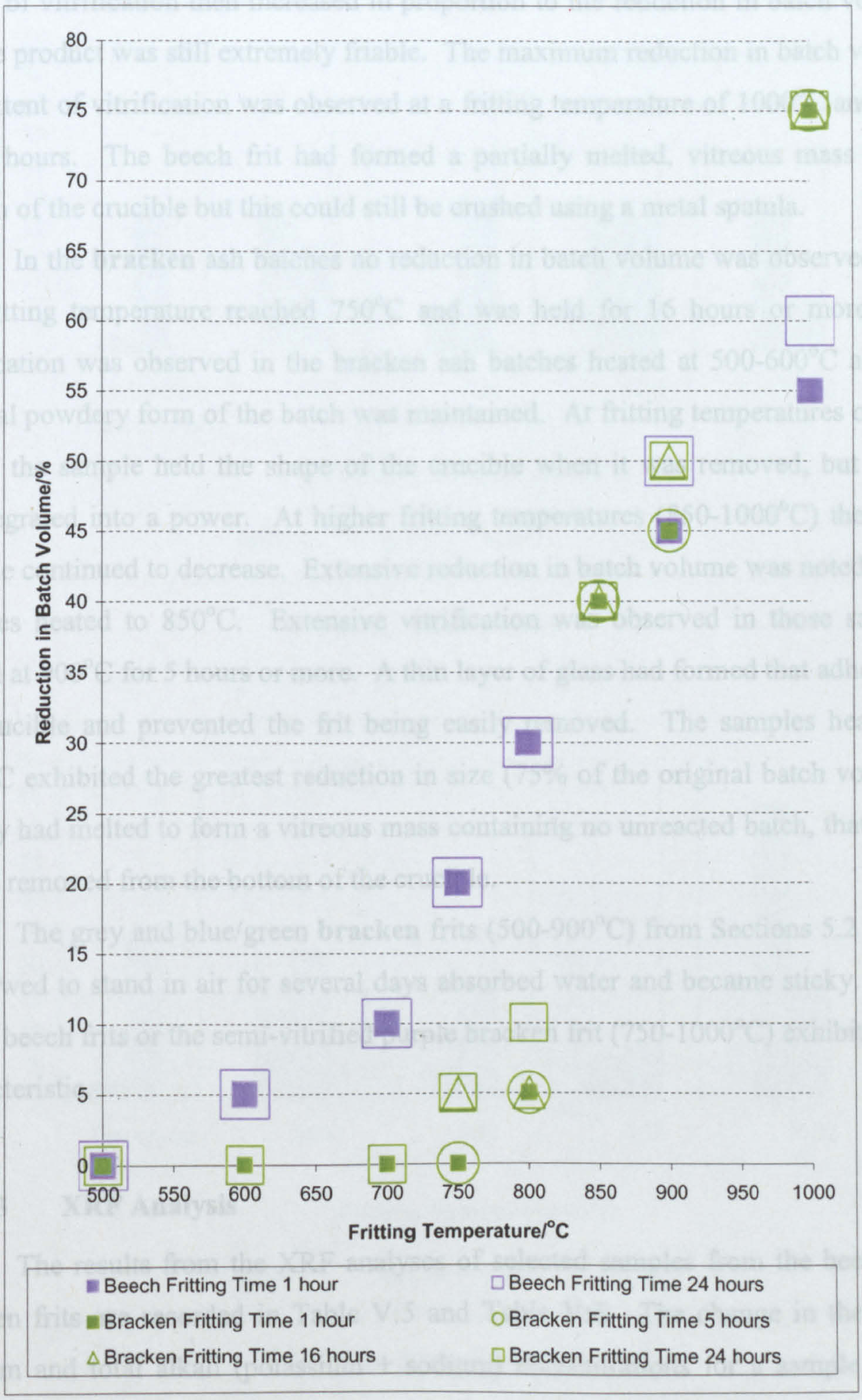


Figure 5:3 A comparison of the change in batch volume with fritting temperatures and times for beech and bracken ash batches

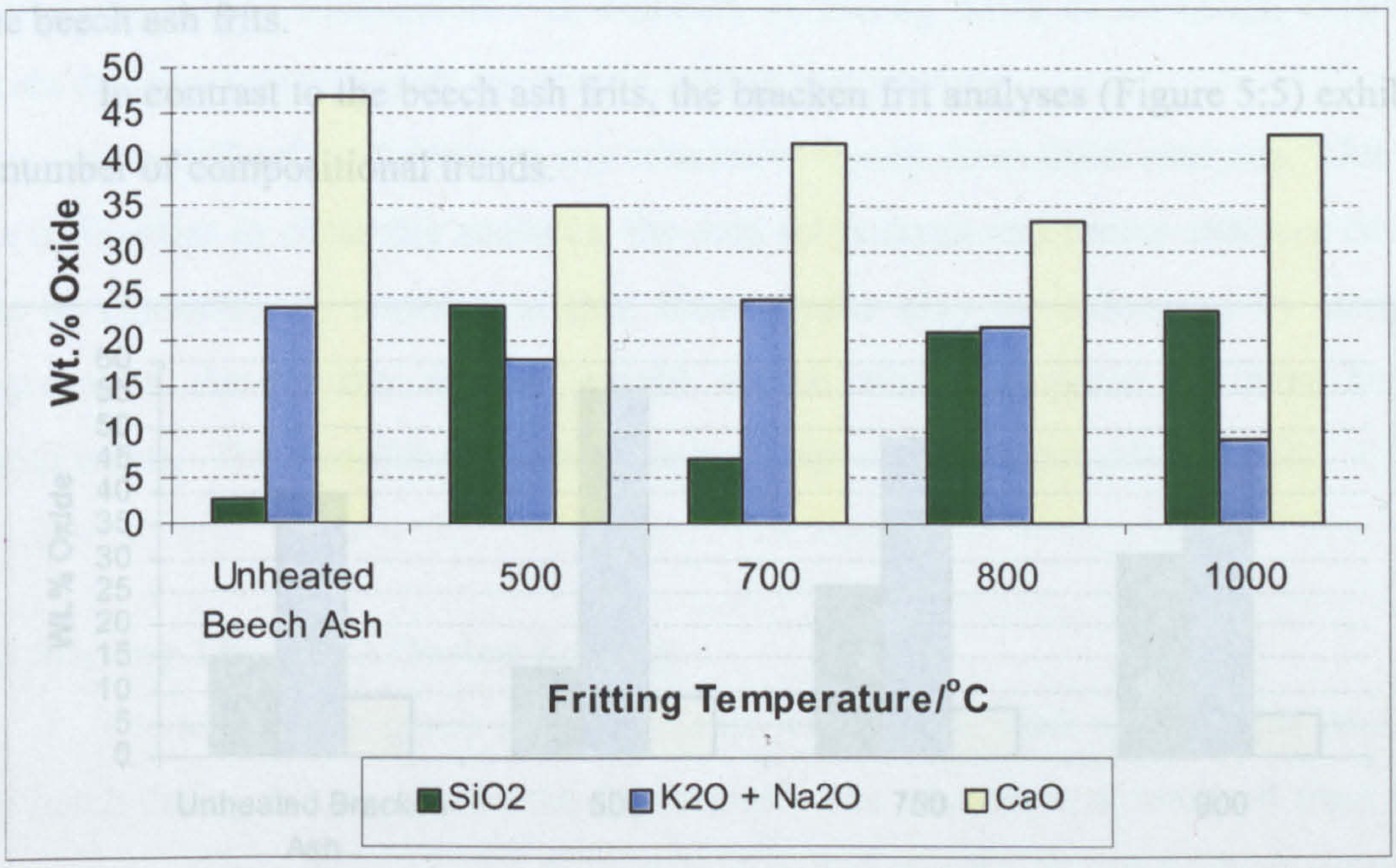
In the **beech** ash batches there was no visible change in percentage batch volume until the fritting temperature was increased to 600°C. The batch volume then decreased in proportion to the increased fritting temperature and time. The batches remained in a powered form until the temperature was raised above 700°C. The extent of vitrification then increased in proportion to the reduction in batch volume, but the product was still extremely friable. The maximum reduction in batch volume and extent of vitrification was observed at a fritting temperature of 1000°C and time of 24 hours. The beech frit had formed a partially melted, vitreous mass at the bottom of the crucible but this could still be crushed using a metal spatula.

In the **bracken** ash batches no reduction in batch volume was observed until the fritting temperature reached 750°C and was held for 16 hours or more. No vitrification was observed in the bracken ash batches heated at 500-600°C and the original powdery form of the batch was maintained. At fritting temperatures of 700-750°C the sample held the shape of the crucible when it was removed, but easily disintegrated into a power. At higher fritting temperatures (850-1000°C) the batch volume continued to decrease. Extensive reduction in batch volume was noted in the samples heated to 850°C. Extensive vitrification was observed in those samples heated at 900°C for 5 hours or more. A thin layer of glass had formed that adhered to the crucible and prevented the frit being easily removed. The samples heated to 1000°C exhibited the greatest reduction in size (75% of the original batch volume), as they had melted to form a vitreous mass containing no unreacted batch, that could not be removed from the bottom of the crucible.

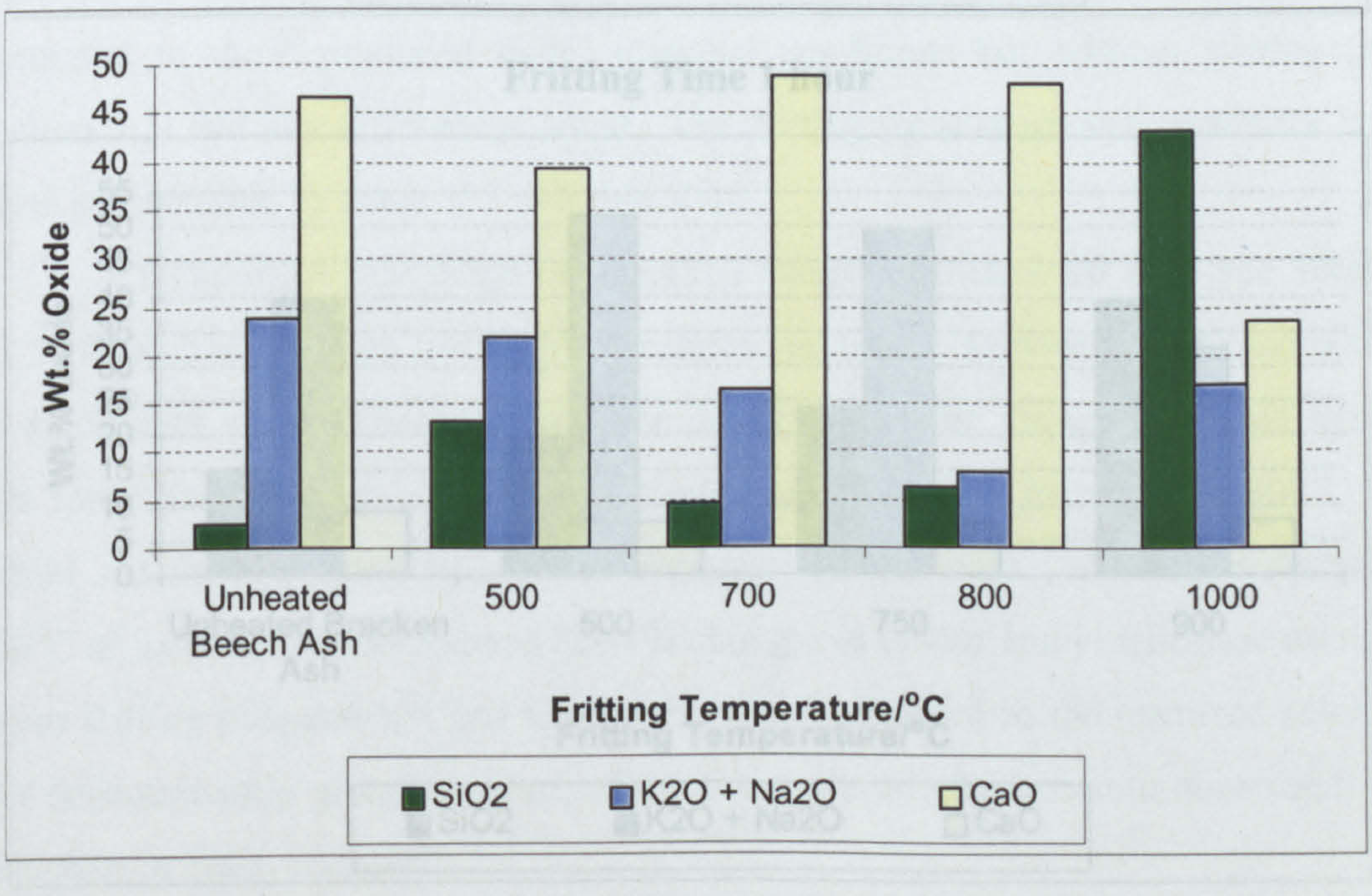
The grey and blue/green **bracken** frits (500-900°C) from Sections 5.2 to 5.4, if allowed to stand in air for several days absorbed water and became sticky. None of the beech frits or the semi-vitrified purple bracken frit (750-1000°C) exhibited this characteristic.

5.2.1.3 XRF Analysis

The results from the XRF analyses of selected samples from the beech and bracken frits are recorded in Table V:5 and Table V:6. The change in the silica, calcium and total alkali (potassium + sodium) concentrations for a sample of the beech and bracken ash frits are illustrated in Figure 5:4 and Figure 5:5 respectively. These elements have been selected as they are thought to have a significant influence on homogeneity (see Section 4.3.3.2). It was expected that the frits would contain higher silica levels than their respective ashes due to the addition of the sand component in the batch.



Fritting Time 1 hour

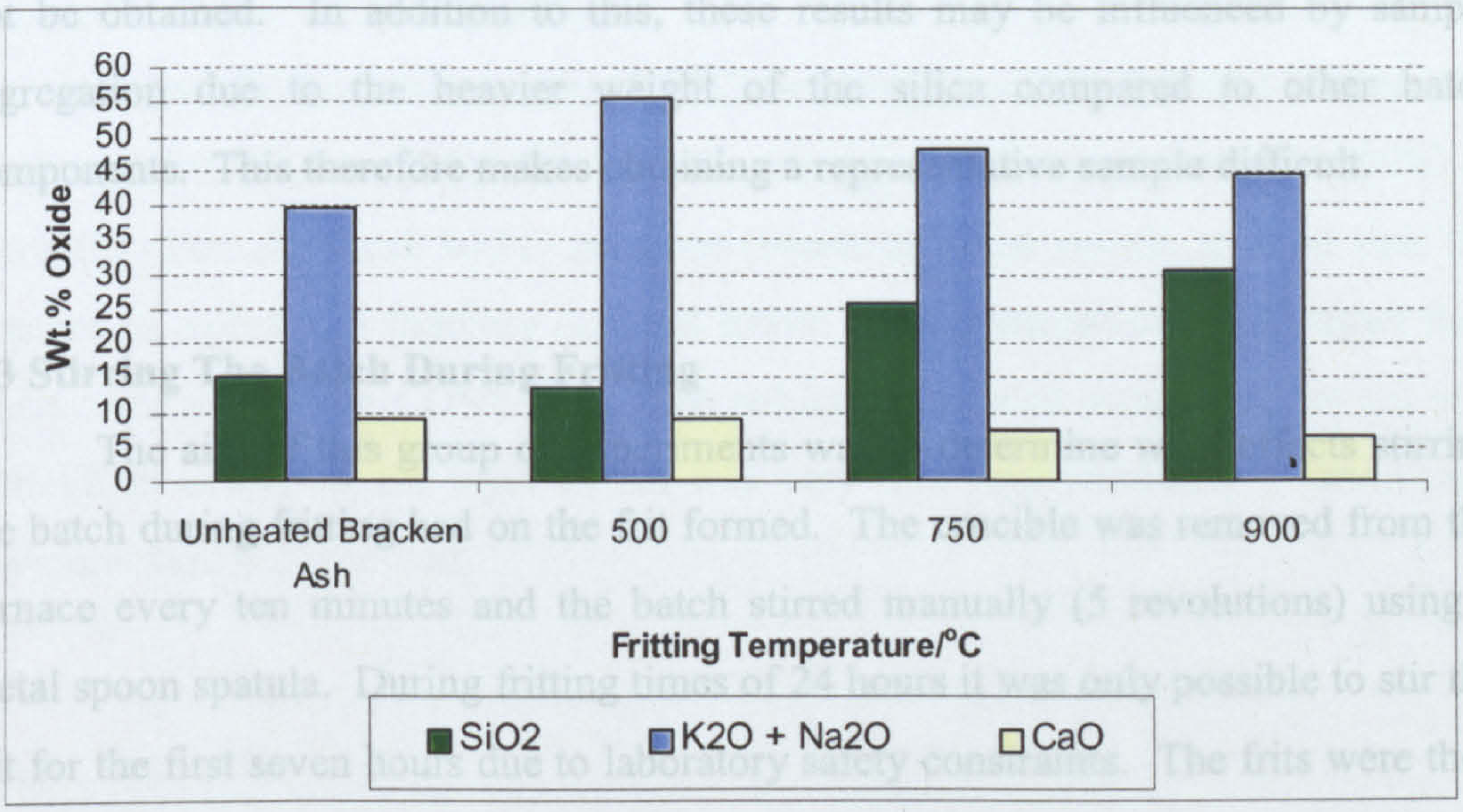


Fritting Time 24 hours

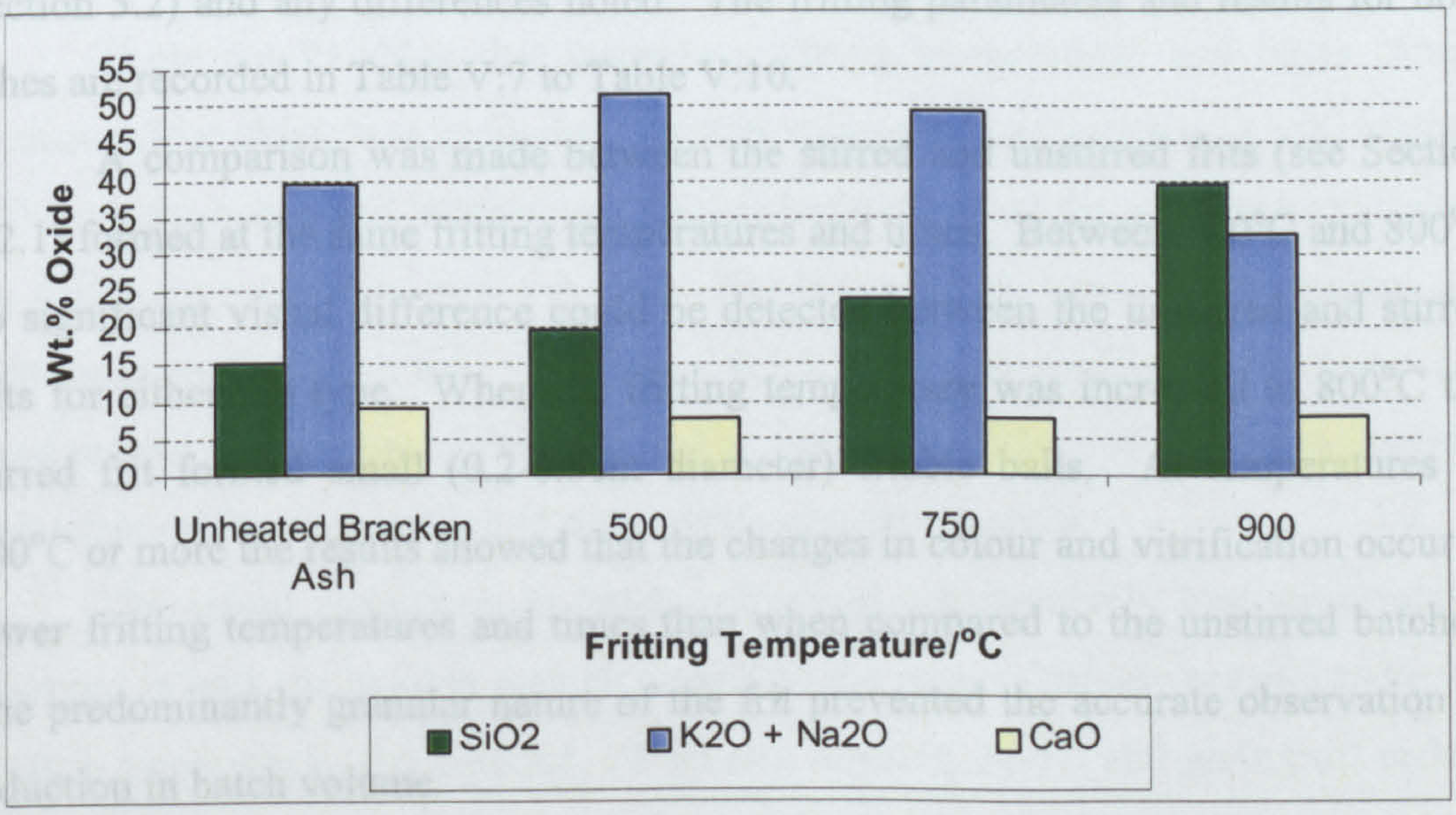
Figure 5:4 A comparison of silica, calcium and total alkali concentrations (by XRF) in beech ash frits and unheated beech ash (Table V:5)

It can be seen from Figure 5:4 that the silica levels are higher in both sets of beech frits compared to the unheated ash. The silica level increases at a fritting temperature of 500°C but then decreases as the temperature is increased. There appears to be no observable pattern in the total alkali and calcium oxide values for the beech ash frits.

In contrast to the beech ash frits, the bracken frit analyses (Figure 5:5) exhibit a number of compositional trends.



Fritting Time 1 hour



Fritting Time 24 hours

Figure 5:5 A comparison of silica, calcium and total alkali concentrations (by XRF) in bracken ash frits and unheated bracken ash (Table V:6)

It can be seen that in bracken ash frits made at 1 and 24 hours the levels of silica increase and the total alkali decreases with an increase in the fritting temperature. The change in calcium values is less significant than observed in the silica or alkali concentrations. At a fritting time of 1 hour, calcium decreases with increasing fritting temperature. In contrast, at fritting times of 24 hours, calcium oxide decreases slightly with increasing fritting temperatures.

It is difficult to determine any conclusive results from these analyses. Due to the difficulties in obtaining analyses, the data set is small and repeat analyses could not be obtained. In addition to this, these results may be influenced by sample segregation due to the heavier weight of the silica compared to other batch components. This therefore makes obtaining a representative sample difficult.

5.3 Stirring The Batch During Fritting

The aim of this group of experiments was to determine what effects stirring the batch during fritting had on the frit formed. The crucible was removed from the furnace every ten minutes and the batch stirred manually (5 revolutions) using a metal spoon spatula. During fritting times of 24 hours it was only possible to stir the frit for the first seven hours due to laboratory safety constraints. The frits were then compared to those produced under identical conditions but without stirring (see Section 5.2) and any differences noted. The fritting parameters and results for both ashes are recorded in Table V:7 to Table V:10.

A comparison was made between the stirred and unstirred frits (see Section 5.2.1) formed at the same fritting temperatures and times. Between 500°C and 800°C no significant visual difference could be detected between the unstirred and stirred frits for either ash type. When the fritting temperature was increased to 800°C the stirred frit formed small (0.2-0.5cm diameter) friable balls. At temperatures of 800°C or more the results showed that the changes in colour and vitrification occur at lower fritting temperatures and times than when compared to the unstirred batches. The predominantly granular nature of the frit prevented the accurate observation of reduction in batch volume.

5.4 Fritting Crucible Dimensions

The aim of these experiments was to determine how altering the surface area to volume ratio of the batch would affect the nature of the frit formed. The fritting crucible used in these experiments was a small mullite tray approximately 80mm wide, 125mm in length and 15mm high (see Appendix A). Beech and bracken ash frits were produced at a selection of fritting temperatures and times. The frits were then compared to those produced under identical conditions in CON9 crucibles (see Section 5.2) and any differences noted. The fritting parameters and results are recorded in Table V:11 to Table V:14.

At low fritting temperatures (500°C) no change could be detected between the small tray frit and the CON9 frit for both ash types. At temperatures of 600°C or more (bracken ash) and 800°C or more (beech ash) the results showed that the changes in colour and friability occur at lower fritting temperatures and times than when compared to the CON9 frits. The reduction in batch volume of the frit was difficult to assess, as the layer of frit was very thin (approximately 2-3mm), and therefore were not recorded.

5.4.1 Discussion

5.4.1.1 Fritting Temperature and Time

These results show that increasing fritting temperatures and times caused distinct colour changes, a reduction in batch volume and an increase in vitrification. Although the beech and bracken ash batches both exhibited the same general trends, the frits were specific to each ash type. The higher alkali levels of the bracken ash (compared to the beech ash, see Section 4.3.3.2) are responsible for the faster and more extensive reactions of these frits. The fritting behaviour of a batch is therefore dependent on the composition of the constituent raw materials.

The initial reductions in batch volume at comparatively low temperatures observed in both the batches may be caused by the removal of any organic and other volatile components, for example, carbonates forming oxides and giving off carbon dioxide. Depending on the reactivity of the ash component increasing fritting temperature and time facilitates further reduction in batch volume as the raw materials react and start to vitrify. It can be seen from Figure 5:3 that the beech batches reduce in size almost proportionally with increasing fritting temperatures and time and the extent of vitrification in the batches was never enough to prevent the frit being crushed easily by hand. In comparison the volume of the bracken ash based material is reduced only slightly at lower fritting temperatures (500-800°C) but then drops significantly at temperatures of 850°C and 1000°C. The major changes in the vitrification of the batch also occur at approximately these temperatures and times and there is therefore only a narrow window in which these changes occur. In comparison to the beech ash, the frit formed is much harder and at high temperatures (approximately 900°C) impossible to crush by hand. It is generally assumed that in medieval glass production the frit was crushed and ground up before it was melted (see Section 2.3.5). This would have a significant effect on the homogeneity of the glass formed and this will be investigated in Section 5.5.

5.4.1.2 Stirring the Batch During Fritting

The results of these experiments for both ash types show that stirring the batch during fritting does appear to facilitate the production of a more vitrified product with a greater reduction in batch volume and volatility in comparison to unstirred frits prepared using the same temperatures and times. The faster reaction times are probably due to the stirring procedure improving the contact between the batch components. In Section 2.3.3 it was noted that Theophilus (Hawthorne and Smith 1979, 53) stated that frit should be stirred during production until it formed small balls. The results from these experiments show that this will only occur if fritting temperatures and times are raised to a point where sufficient vitrification occurs to bind the frit together. It is thought that his observations are based on beech ash glasses but in these experiments this event appears to occur in both beech and bracken ash batches and at approximately the same temperature (800°C).

Stirring the frit will also ensure that there is a more even contact of the raw materials with the furnace atmosphere, compared to just one surface for the unstirred frit. This is probably the reason why the stirred frits are all one colour compared to the unstirred samples which exhibit differences between the surface and the body of the frit. Whether the increased reaction of the frit with the furnace atmosphere will have any affect on the finished glass is uncertain. Stirring the frit may lead to an increase in contact with the crucible walls and may increase the chances of refractory contamination within the glass, which may therefore be a possible source of inhomogeneity in the glass produced.

It would therefore seem that although stirring the frit requires more labour and a possible increase in heat loss from the furnace it may have been beneficial in the reduction of batch volume and the production of a glass. Factors such as reactions with the furnace atmosphere and refractory materials mean that it is not certain if stirring would be beneficial in the production of a more homogeneous glass. The glasses formed from mixed batches in Section 4.6 showed that a more intimate mixture of raw materials assisted the production of a more homogeneous glass. It will be interesting to determine whether stirring the frit has the same effect and this will be carried out in Section 5.5.3.

5.4.1.3 Fritting Crucible Dimensions

It can be seen from the results of these experiments that for both the beech and bracken ash batches the increase in crucible surface area to volume ratio facilitates the speed of reactions in the frit. In these experiments the batch is more thinly spread over a wider area and therefore the raw materials heat up more rapidly and have more contact with the furnace atmosphere. The reactions in the batch are therefore more likely to be faster. The benefits of this may be that the batch forms a more even fritted product and that this will then transpose to a more homogeneous glass. However, the increased contact with the crucible may increase the likelihood of refractory contamination and therefore possible inhomogeneity (see Section 2.3.4).

Section 2.3.4 noted that the evidence for archaeological fritting crucibles is limited and it is therefore not certain what crucible dimensions were used or, as Theophilus (Hawthorne and Smith 1979) suggests, whether fritting was carried out on the furnace floor. Frit produced on the furnace floor is likely to have had a larger surface area to volume ratio than that produced in a crucible. This would therefore speed up the rate of the fritting reactions. The choice of method may therefore influence homogeneity but if the frit was subjected to stirring then the influence of the crucible dimensions may have been in effect cancelled out.

5.4.2 Conclusions

The results from this set of experiments have built substantially on the previous fritting work in the batch mixing experiments (see Section 4.6). The results from both sets of experiments have shown that frits formed using different conditions and ashes are very different in nature. It would appear that the fritting stage has to be modified depending on the type and proportions of raw materials being used. The main conclusions drawn from these experiments are summarised below.

- The changes observed in a frit are specific to the raw materials in the batch.
- Batch volume reduces with increased fritting temperature and time.
- Vitrification increases with increased fritting temperature and time.
- Friability decreases with increased temperature and time.
- Stirring the frit facilitates faster reactions between the raw materials.
- Increasing the surface area to volume ratio of the fritting crucible facilitates faster reactions between the raw materials.

Now that the behaviour of the beech and bracken ash frits has been characterised it is possible to establish how different frits can be related to the homogeneity. This will be carried out in Section 5.5. The results can then be combined with those here to determine which fritting parameters are more likely to have been successful in the production of a homogeneous glass and how this relates to the use of different raw materials.

5.5 Melting Beech and Bracken Glasses From Their Frits

5.5.1 Introduction

The aim of these experiments was to observe how the use of the different fritting parameters affected the final homogeneity of the glass formed. The fritted batches produced in Section 5.2 to 5.4 were melted at 1200°C or 1300°C for five hours. A selection of bracken frits was also melted at 1250°C. The range of temperatures and melt time was chosen based on the results of the stages of melting experiments (see Section 4.7).

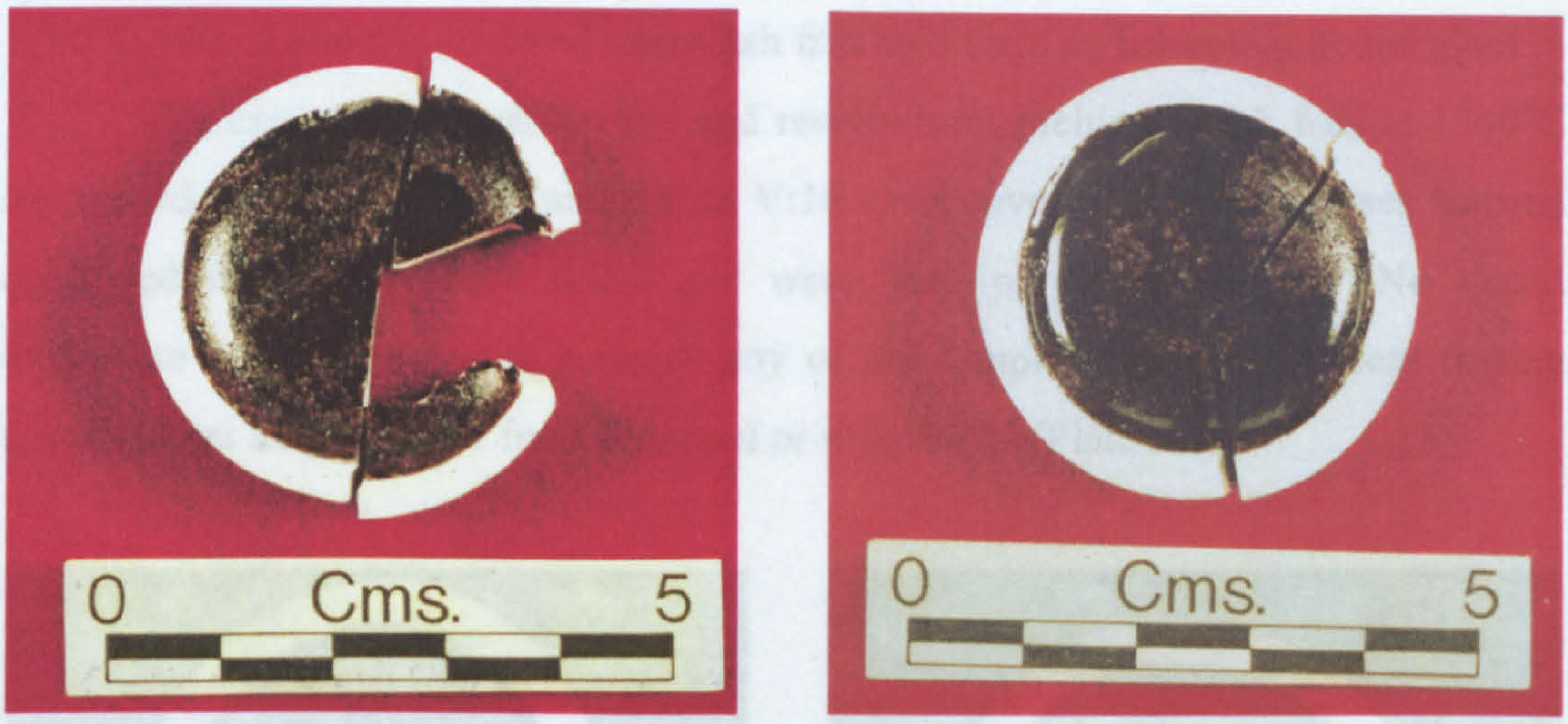
The cooled frit was removed from the fritting crucible, crushed, mixed and placed in a mullite crucible (CON 9). To prevent the crucible cracking from thermal shock it was preheated on the back of the furnace for thirty minutes before melting. A preheated crucible containing the frit was placed in an electric furnace for 5 hours and then removed and left to cool on the back of the furnace for thirty minutes. The experimental parameters and the results from these experiments are recorded in (Table V:15 to Table V:32). It should be noted that it was not possible to crush any of the bracken ash frit made at 1000°C (1-24 hours) because the frit had become a hard, vitreous mass which could not be removed from the crucible.

Duplicate fritted samples were prepared using the same parameters as detailed in section 5.2. The frit was **not** crushed and mixed, and remained in the fritting crucible before being melted (as described above). The aim of this set of experiments was to determine whether the smaller particle size caused by crushing the frit will provide a more intimate mixture, thereby facilitating the formation of a more homogeneous glass.

5.5.2 The Effect of Fritting Temperature and Time on Homogeneity

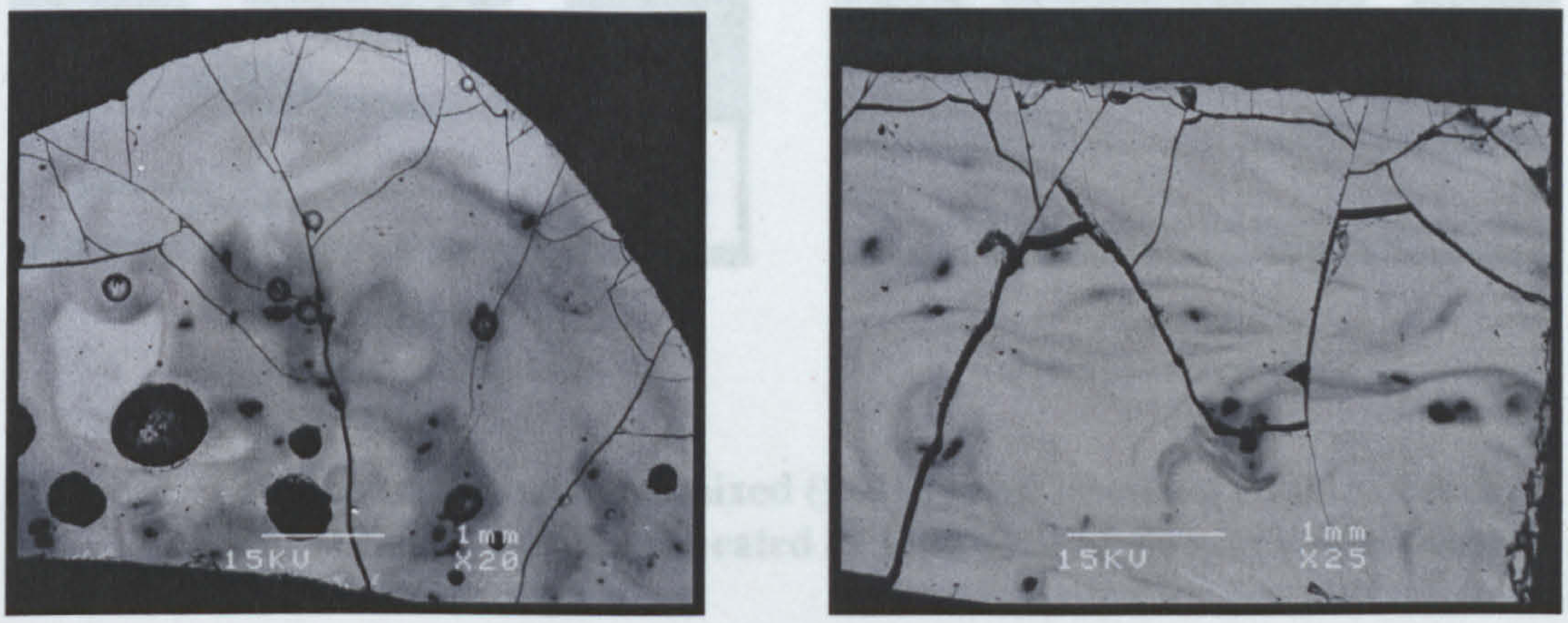
5.5.2.1 Beech Glasses

The experimental parameters and results from the beech ash frits heated at 1200°C can be seen in Table V:15 and Table V:16 respectively. All of the samples produced using either the mixed or the unmixed frit consisted of a dark purple glass containing batch relics. The number of relics increased with increasing fritting temperatures and times. The glasses formed using frits made at 500°C from either unmixed or mixed frit were visually identical and contained low levels of batch relics. Melting frits formed at 600°C-1000°C produced glasses containing increased levels of batch relics. At these fritting temperatures the glasses made from **unmixed** frits contained **fewer** batch relics than those made from identical **mixed** frits (Plate 5:3).



Mixed Frit
High levels of batch relics
Fritting 1000°C 24 hours
(Be93)

Unmixed frit
Medium levels of batch relics
Fritting 1000°C 24 hours
(Be101)



Backscattered SEM Images

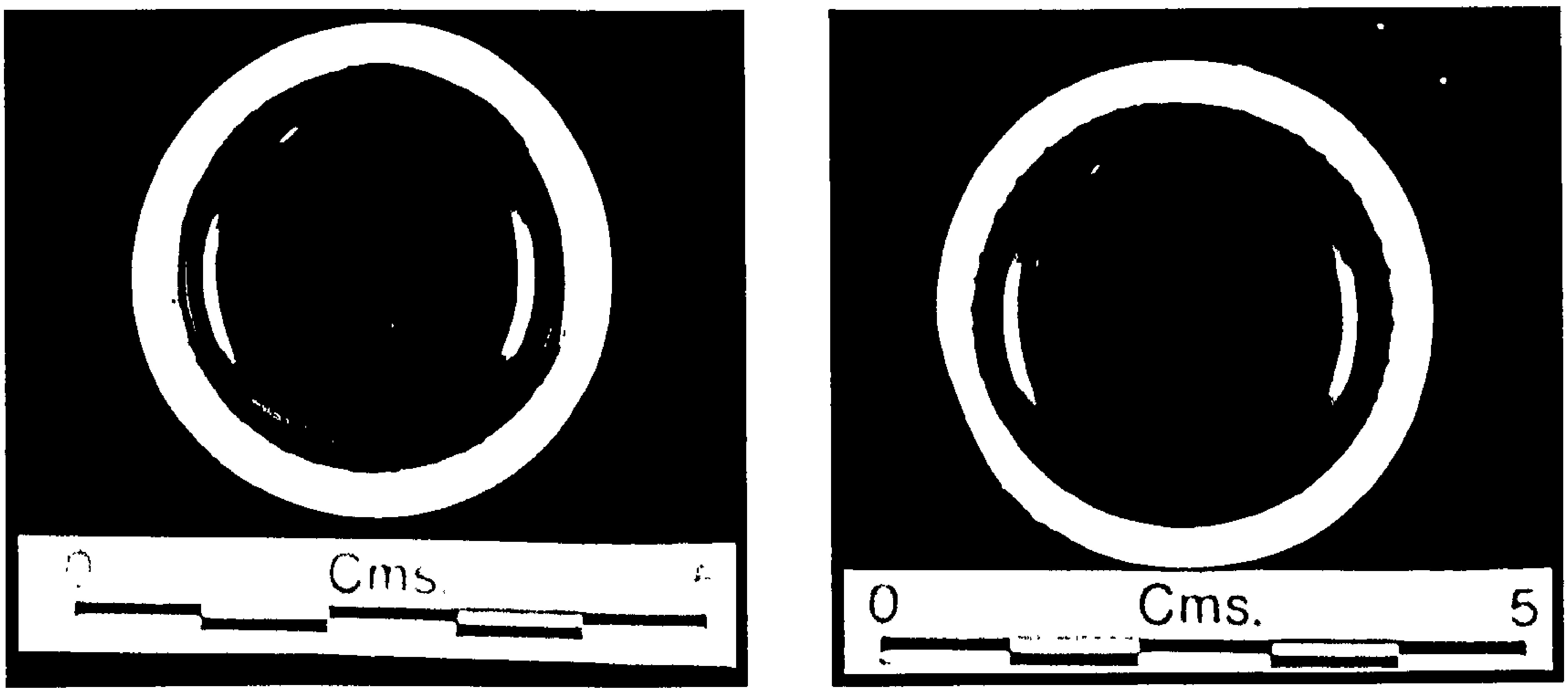
High levels of batch relics
High levels of inhomogeneity
(Be93)

Medium levels of batch relics
Medium levels of inhomogeneity
(Be101)

Plate 5:3 A comparison between optical and backscattered SEM images of mixed (Be93) and unmixed (Be101) beech frits (1000°C, 24 hours) heated at 1200°C for 5 hours (Table V:16)

The SEM results confirm the visual observations made of the beech glasses produced at 1200°C (Plate 5:3). In a small number of samples the levels of inhomogeneity noted using the SEM are lower than the levels of batch relics recorded visually. The SEM samples were selected to be as representative of the whole glass as possible but it is likely that in some cases this was not always achieved. The visual and SEM observations confirm that at melting temperatures of 1200°C, mixed and the unmixed beech ash frits will form an **inhomogeneous** glass.

The experimental parameters and results from melting beech frits at 1300°C are recorded in Table V:17 and Table V:18 respectively. All the glasses formed contained no visible batch relics and were dark purple in colour. No visual difference could be detected between any of the samples made at different fritting temperatures and times, or from unmixed or mixed frits (Plate 5:4).

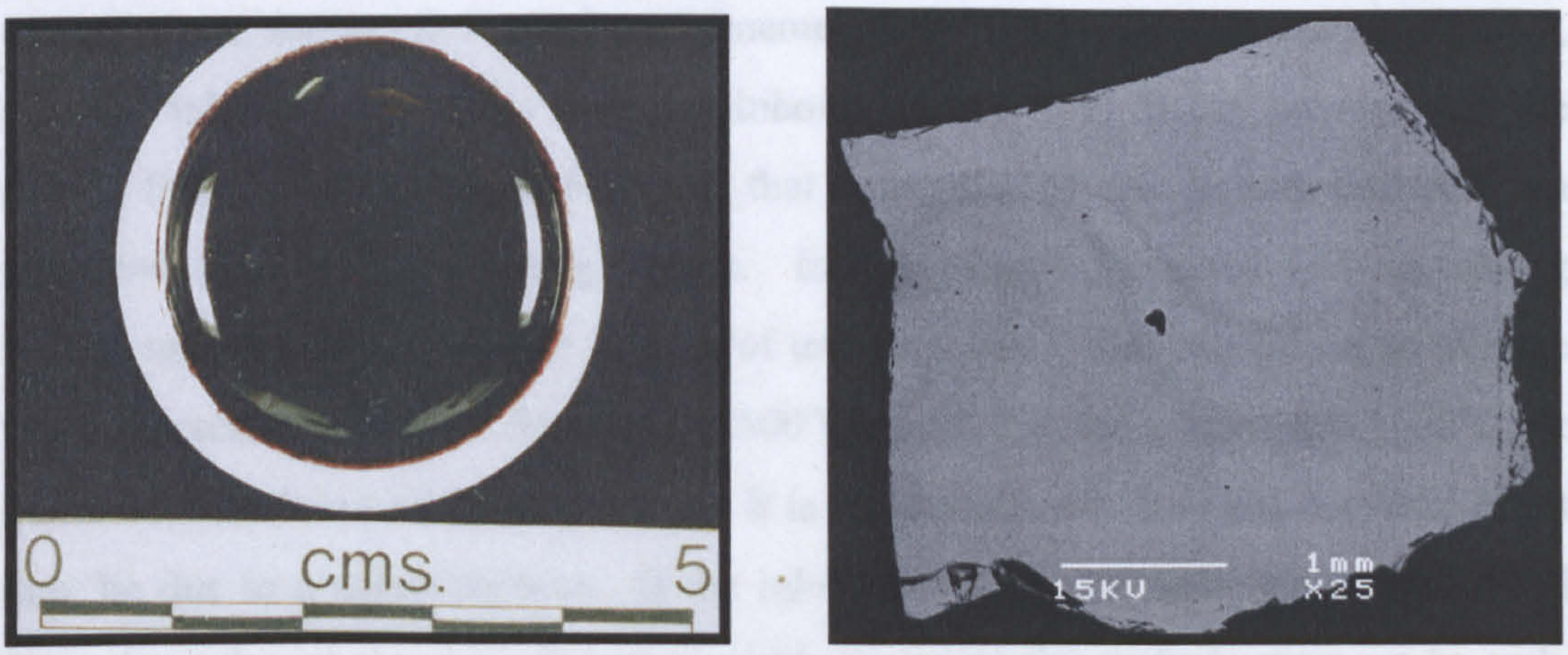


Mixed Frit
Homogeneous Glass
(Be107)

Unmixed frit
Homogeneous Glass
(Be115)

Plate 5:4 A comparison between mixed (Be107) and unmixed (Be115) beech frits (1000°C, 24 hours) heated at 1300°C for 5 hours (Table V:18)

The SEM results confirmed the absence of any batch relics in any of the beech glasses produced at 1300°C but identified the presence of **inhomogeneities** in a number of samples. The backscattered SEM image obtained from the visually homogeneous glass Be96 (Plate 5:5) shows that the glass contains medium levels of inhomogeneity.



Visually Homogeneous Glass

Backscattered SEM Image with Medium Levels of Inhomogeneity

Plate 5:5 A visually homogeneous beech glass (Be96) and a backscattered SEM image of a sample of the glass illustrating the presence of medium inhomogeneity

The extent of the inhomogeneities in the beech glasses produced at 1300°C are illustrated in Figure 5:6.

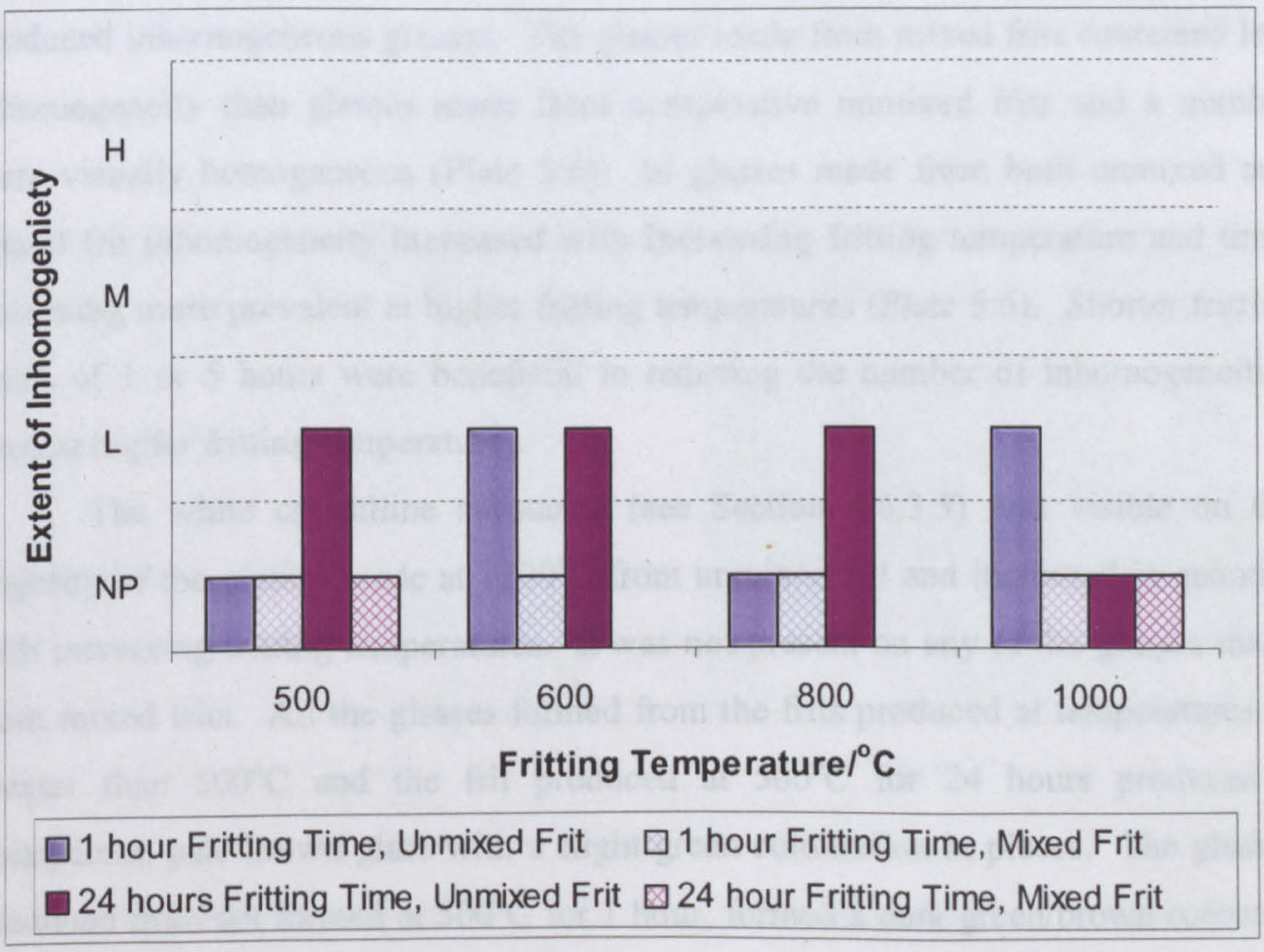


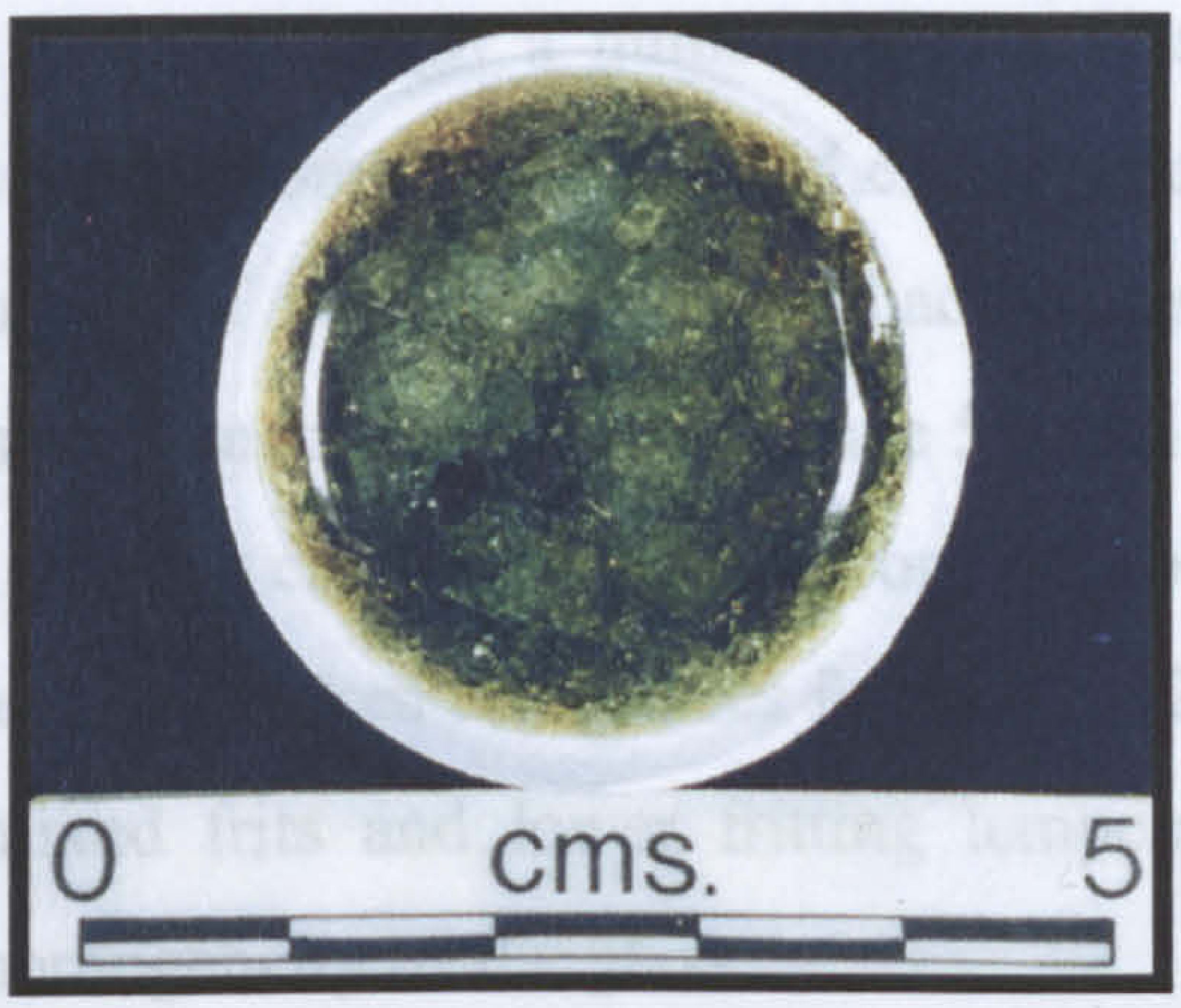
Figure 5:6 A comparison between glasses made from mixed and unmixed beech frit at 1300°C (Table V:18)

The symbols on the y-axis of Figure 5:6 correspond to the parameters described in Section 3.3.2.3: homogeneous glass (NP), low inhomogeneity (L), medium inhomogeneity (M) and high inhomogeneity (H). It can be seen that the **mixed** frits are all **homogeneous** but that a number of the glasses formed from **unmixed** frit contain **inhomogeneities**. Inhomogeneity increases with increasing fritting temperature, times and the use of unmixed frits. The exceptions to this are those glasses formed from frit made at 500°C and 800°C for 1 hour, and 1000°C for 24 hours, which are all homogeneous. It is not certain why this has occurred but it may be due to a sampling bias. If the inhomogeneities are not equally distributed throughout the whole glass then the sample removed for analysis may not be truly representative. The exact locations of inhomogeneities cannot be located during sampling as they cannot be visually resolved. Therefore this problem may be difficult to avoid.

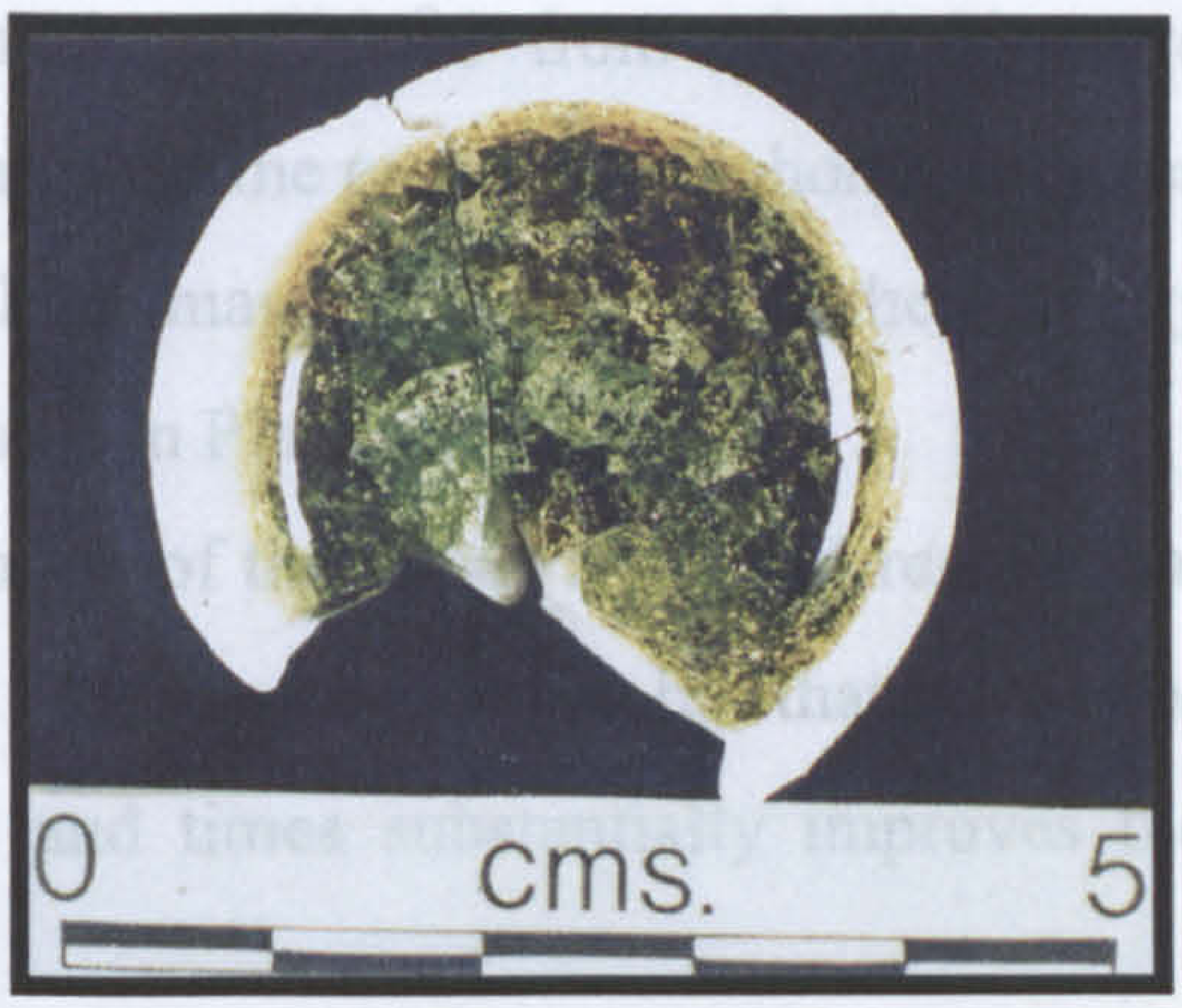
5.5.2.2 Bracken Glasses

The experimental parameters and results from bracken frits melted at 1200°C are recorded in Table V:19 and Table V:20 respectively. The **unmixed** frits all produced inhomogeneous glasses. The glasses made from mixed frits contained less inhomogeneity than glasses made from comparative unmixed frits and a number were visually homogeneous (Plate 5:6). In glasses made from both unmixed and mixed frit inhomogeneity **increased** with **increasing** fritting temperature and time, becoming more prevalent at higher fritting temperatures (Plate 5:6). Shorter fritting times of 1 or 5 hours were beneficial in reducing the number of inhomogeneities even at higher fritting temperatures.

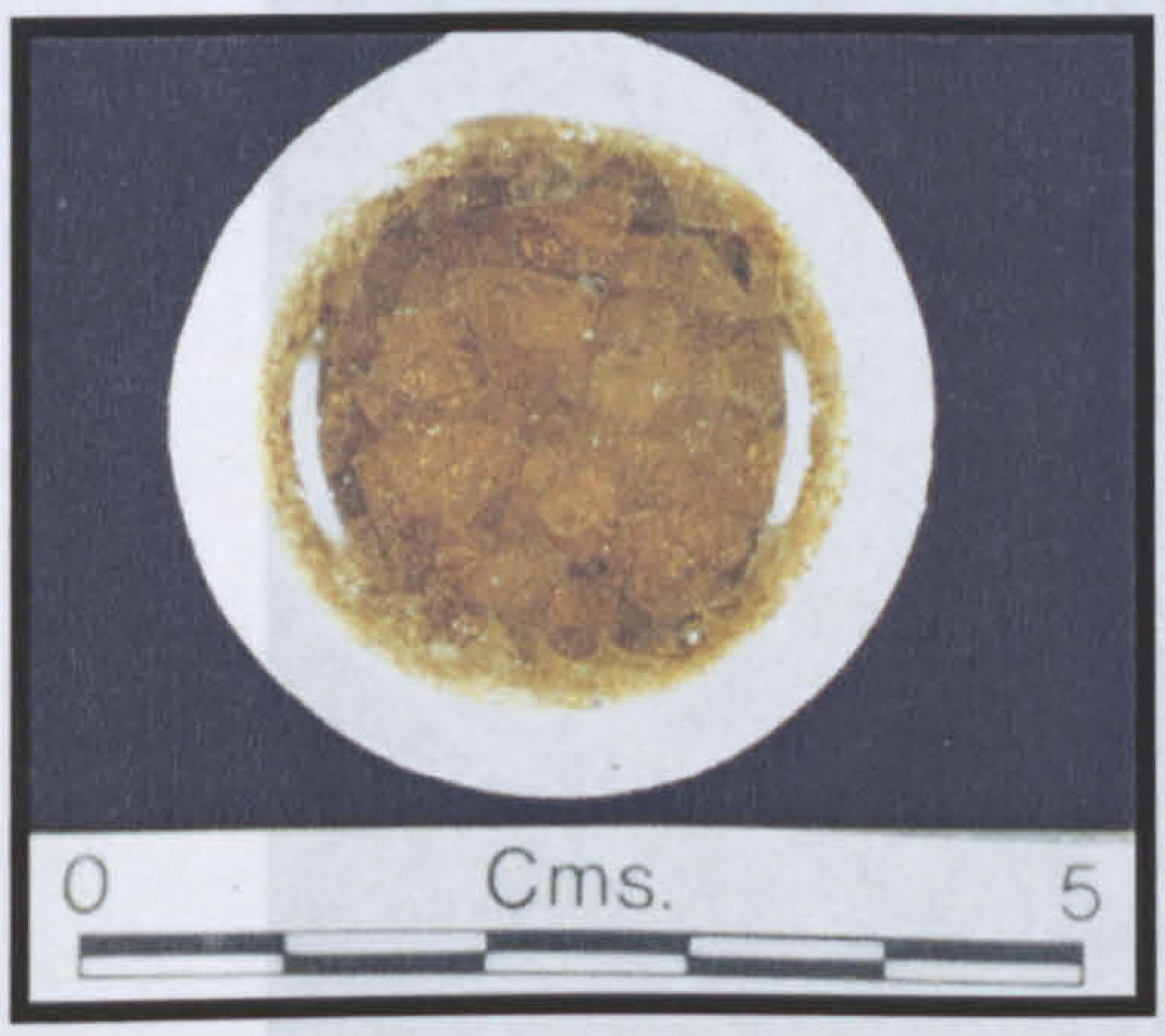
The white crystalline substance (see Section 4.6.3.5) was visible on the majority of the glasses made at 1200°C from unmixed frit and increased in quantity with increasing fritting temperatures. It was **not** present on any of the glasses made from mixed frits. All the glasses formed from the frits produced at temperatures of greater than 500°C and the frit produced at 500°C for 24 hours produced a transparent, pale brown glass with a slight green colouration in places. The glasses produced from frit formed at 500°C for 1 hour, formed a dark green/brown coloured glass (Plate 5:6).



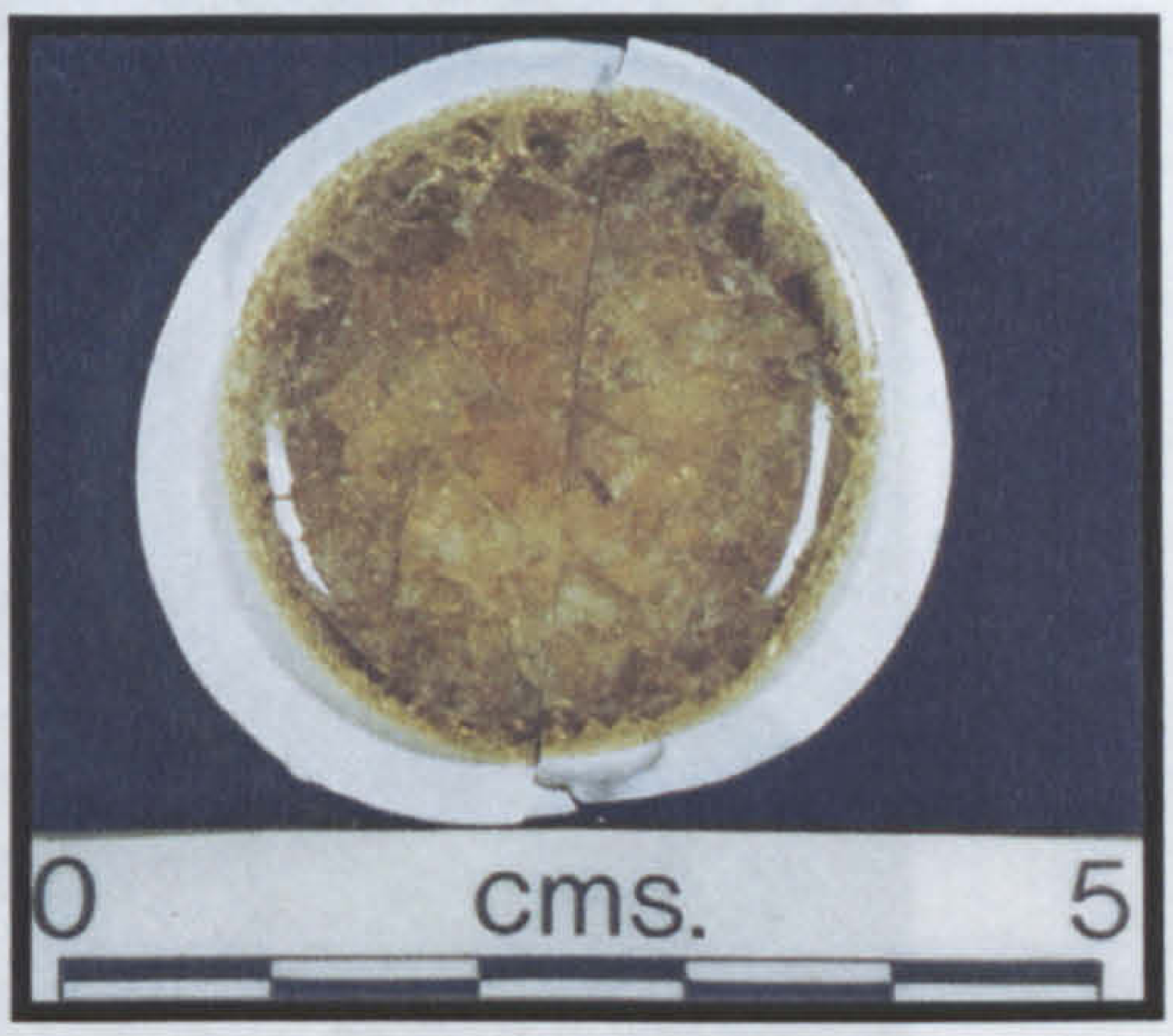
Frit 500°C 1 hour
Visually homogeneous glass (Br51)



Frit 900°C 1 hour
Medium levels of batch relics and low opacity (Br71)

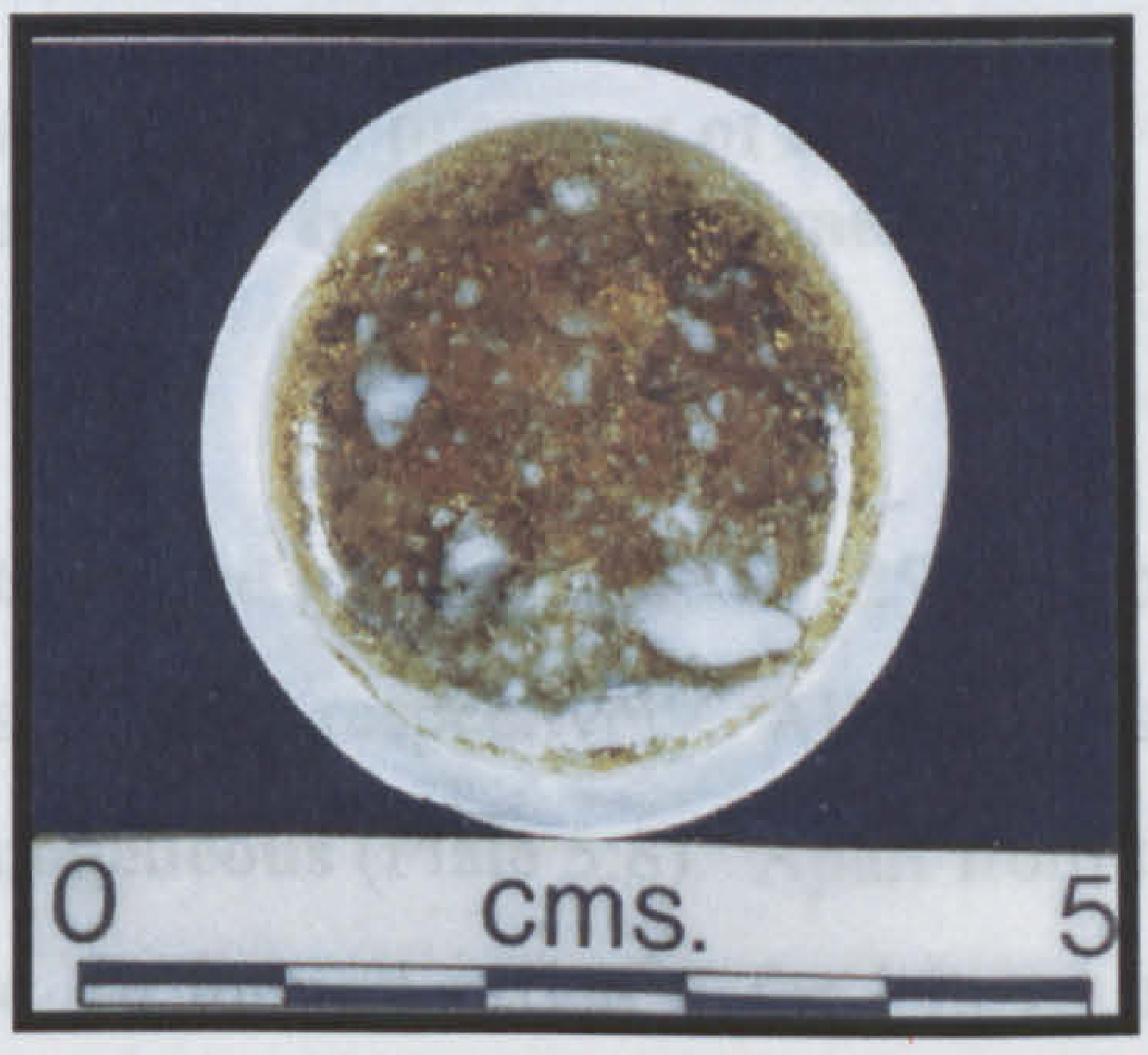


Frit 900°C 1 hour
Visually homogeneous glass (Br67)



Frit 900°C 1 hour
Medium levels of batch relics and high opacity (Br77)

Frit 900°C 24 hours
Medium levels of batch relics and low opacity (Br70)



Frit 900°C 1 hour
High levels of batch relics and high opacity (Br80)

Glasses Made From Mixed Frits **Glasses Made From Unmixed frits**

Plate 5:6 A comparison between glasses made at 1200°C (5 hours) from mixed and unmixed bracken frits made at different fritting temperatures and times (Table V:20)

Although a number of the glasses made at 1200°C from mixed frit were visually homogeneous, SEM examination confirmed the presence of inhomogeneities in **all** of the glasses. The backscattered SEM image obtained from the visually homogeneous glass Br51 (Plate 5:6) is illustrated in Plate 5:7.

It can be concluded from the combination of the visual and SEM results that all the bracken ash glasses formed at 1200°C are **inhomogeneous** but that the use of mixed frits and lower fritting temperatures and times substantially improves the homogeneity of the glass.

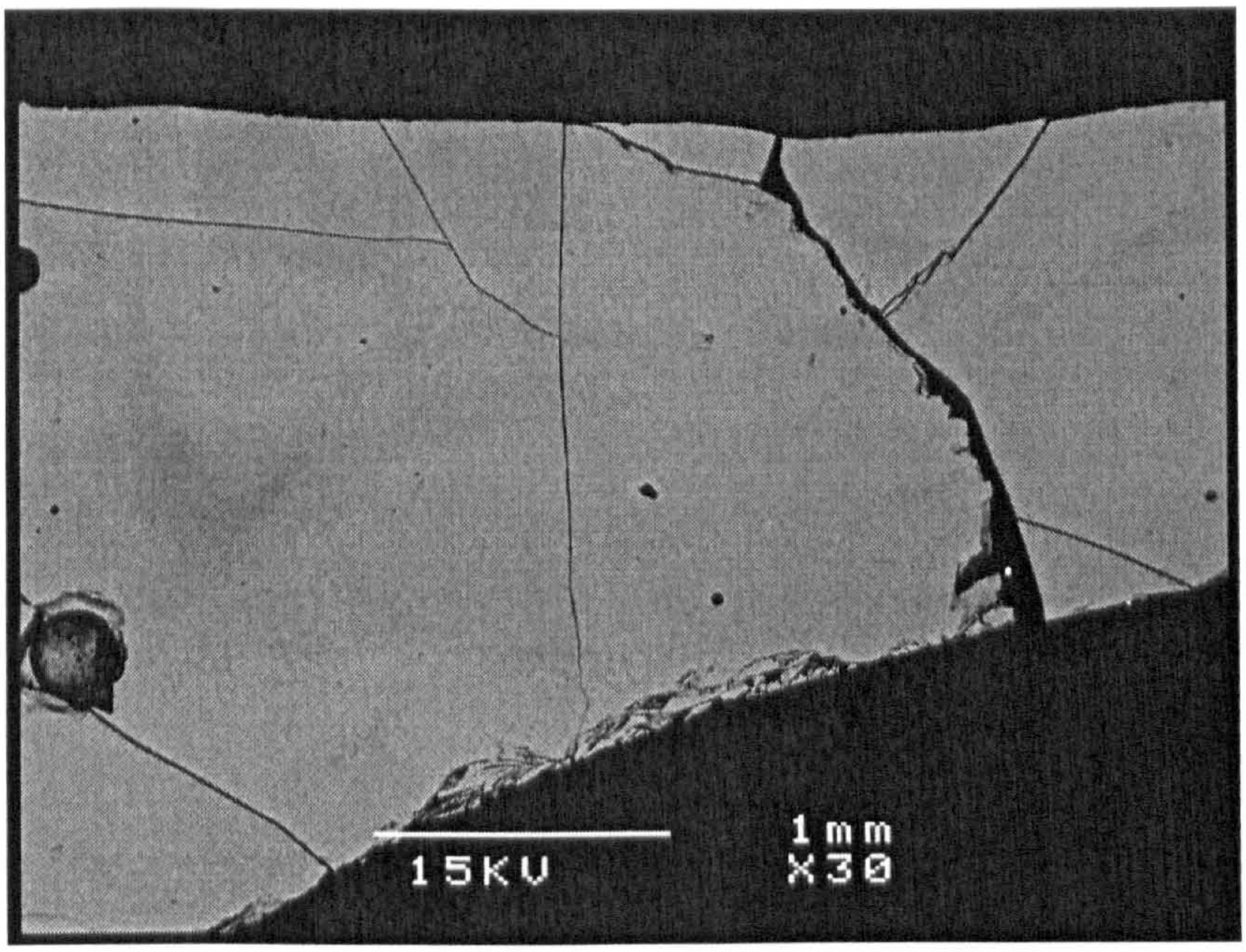
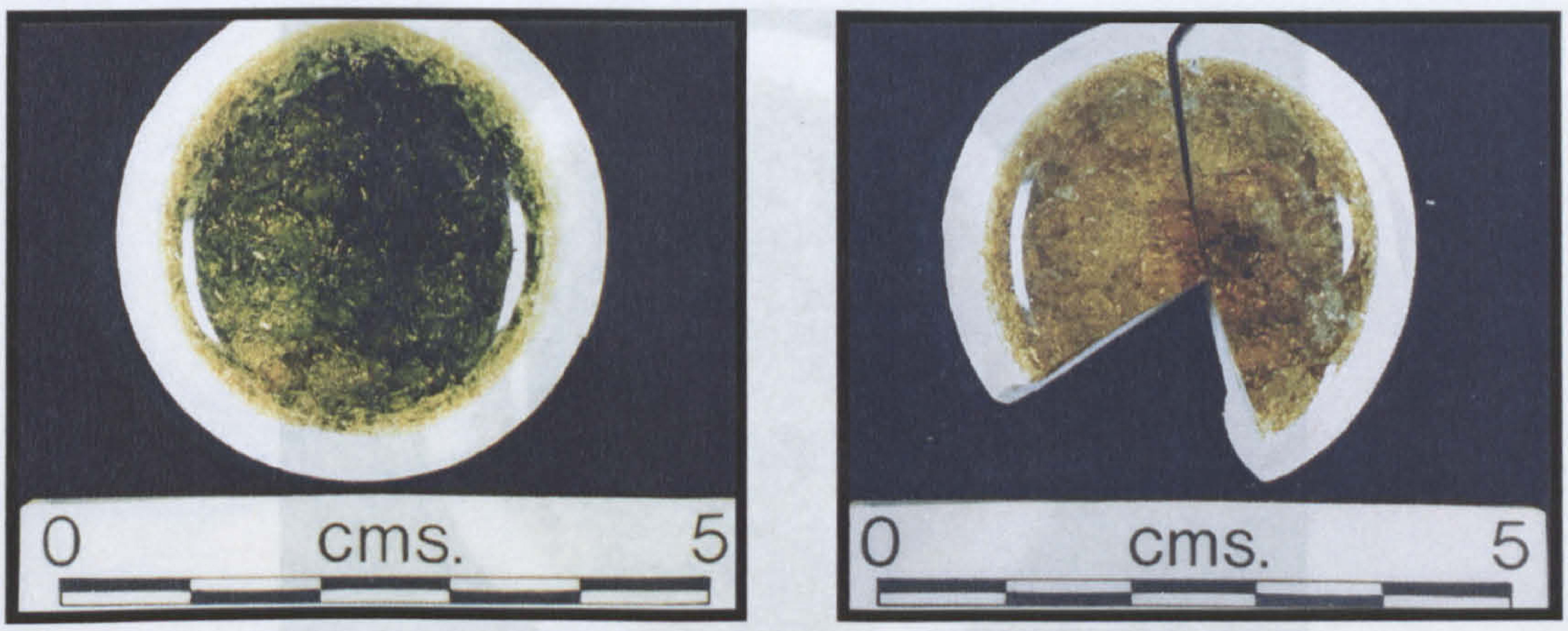


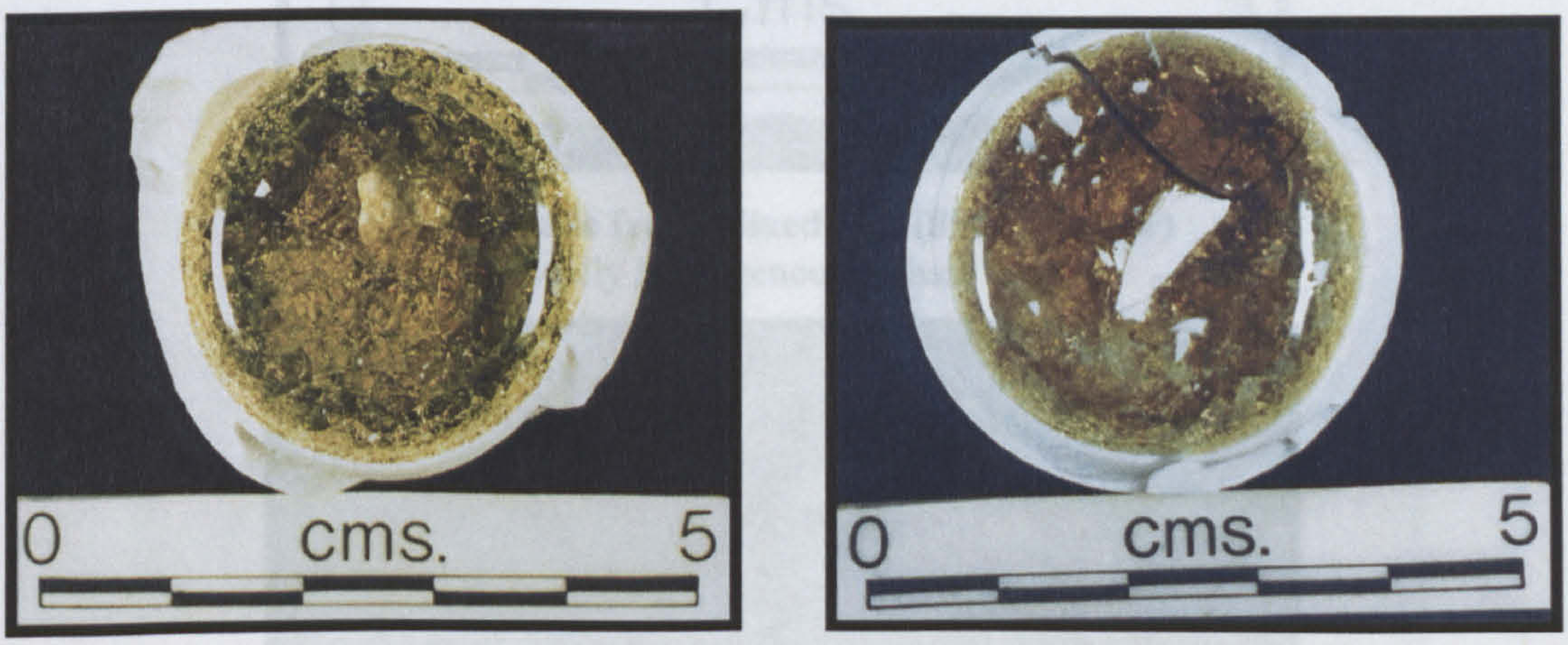
Plate 5:7 A backscattered SEM image illustrating the presence of low inhomogeneity in a visually homogeneous bracken glass melted at 1200°C (Br51) (Plate 5:6)

The experimental parameters and results for the glasses made at 1250°C from bracken frits are recorded in Table V:21 and Table V:22 respectively. All the glasses formed from the **mixed** frits were visually **homogeneous** (Plate 5:8). Apart from the colour of Br85 (which was melted from mixed frit formed at 600°C for 1 hour), no visual difference was observed between glasses formed using differing fritting times and temperatures. To conserve raw materials, only a small number of unmixed bracken frits were melted at 1250°C, and therefore the main fritting temperatures were based upon the previous results in this Chapter. The glasses made from **unmixed** frits produced at 600°C, 700°C and 900°C for 1 hour, and 1000°C for 24 hours were **inhomogeneous** (Plate 5:8). The glasses made from unmixed frits produced at 1000°C for 1, 5, and 16 hours were all visually homogeneous, and visually identical to those produced from mixed frits at the same temperatures and times. Slight opacity was visible in Br106, although this was the only glass formed at 1250°C to show this characteristic.



Frit 600°C 1 hour
Visually homogeneous glass (Br85)

Frit 600°C 1 hour
Low levels of batch relics (Br102)



Frit 900°C 1 hour
Visually homogeneous glass (Br98)

Frit 900°C 1 hour
Low levels of batch relics and crucible fragments (Br104)

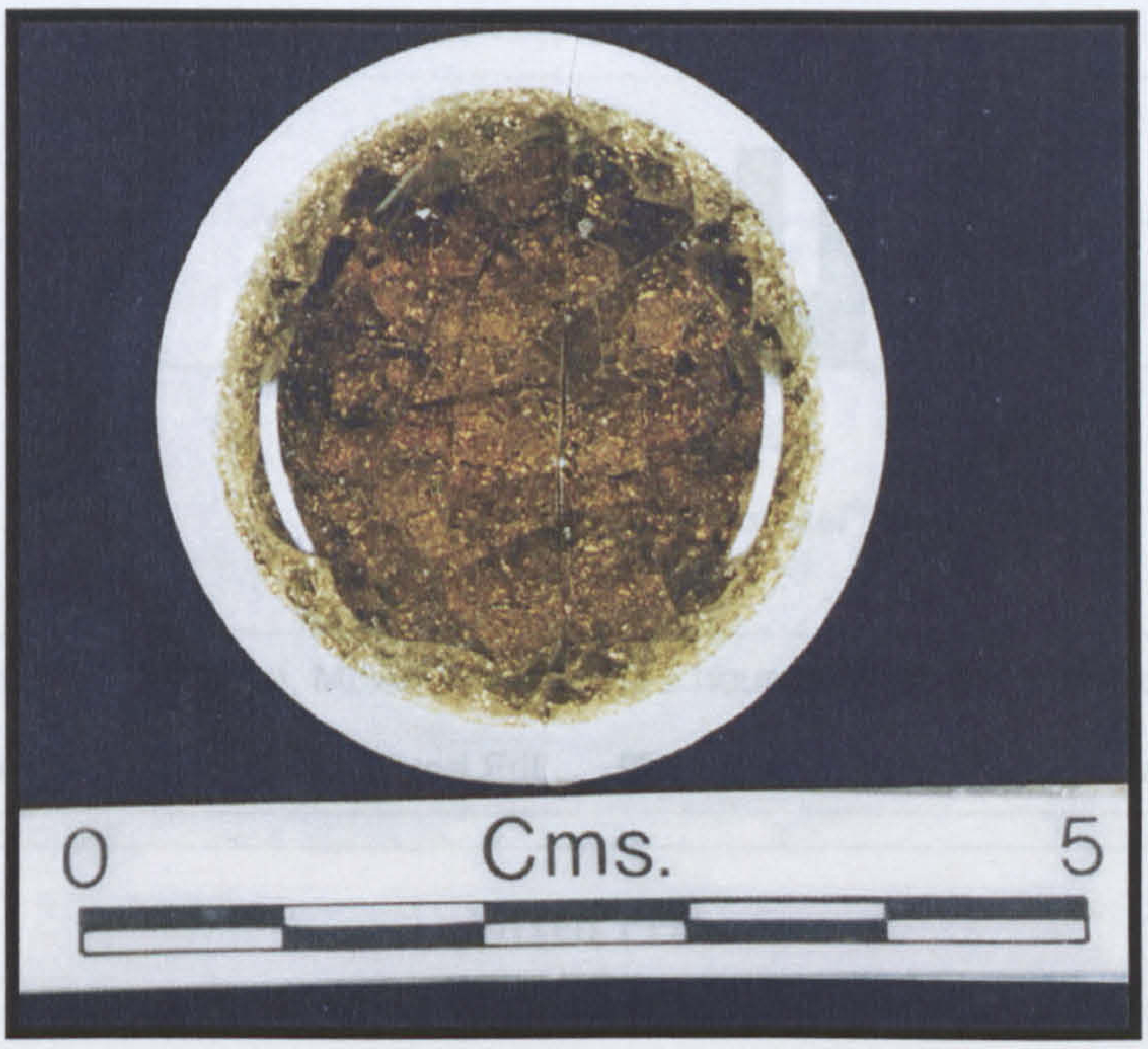
Glasses Made From Mixed Frits

Glasses Made From Unmixed frits

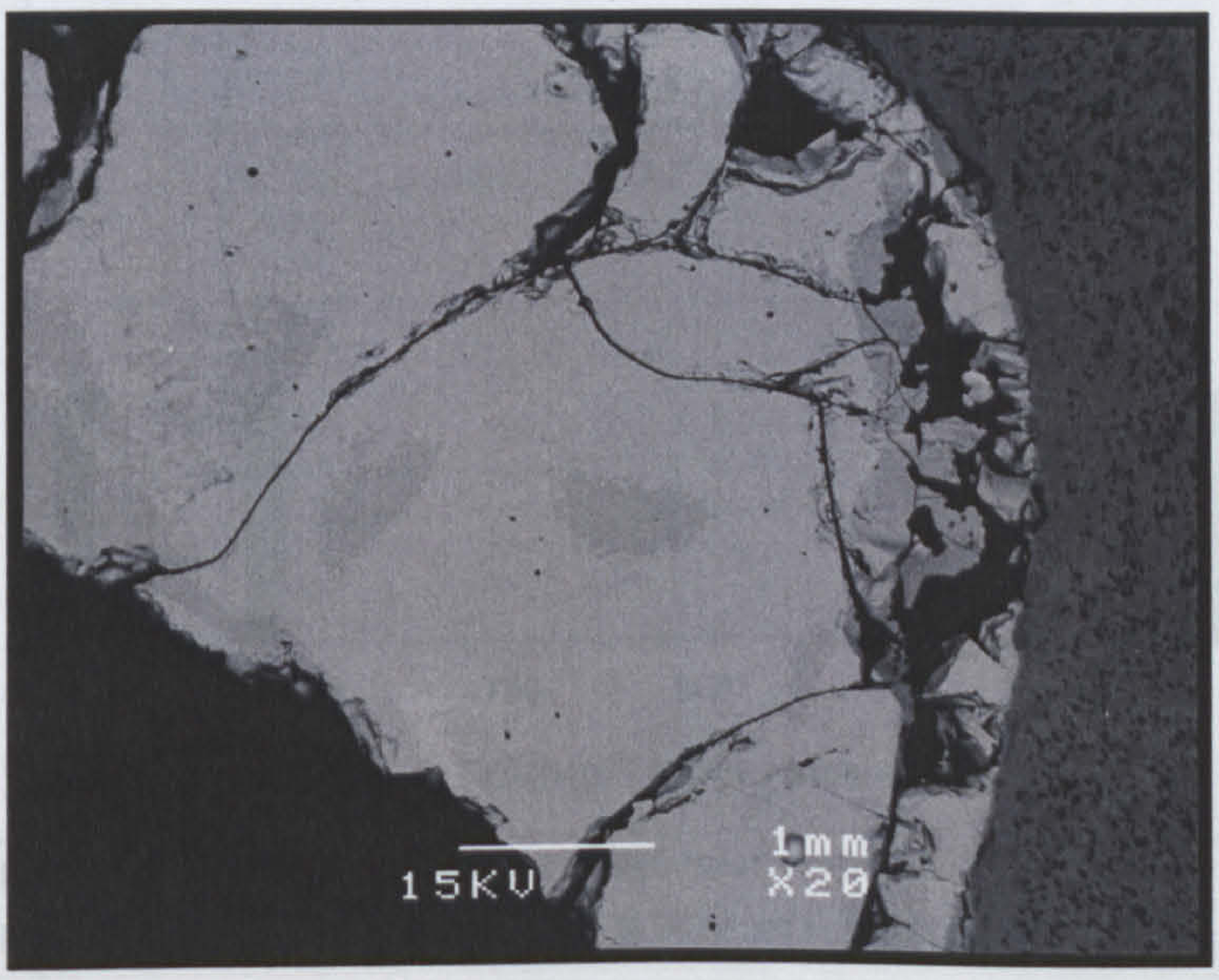
Plate 5:8 A comparison between glasses made at 1250°C (5 hours) from mixed and unmixed bracken frits made at different fritting temperatures and times (Table V:22)

The majority of the glasses formed at 1250°C formed a glass, which was a slightly darker brown/green colour than those produced at 1200°C (Plate 5:6). The exceptions to this were Br 85 and Br102 formed from frits produced at 600°C for 1 hour and Br 103 formed from unmixed frit produced at 700°C for 1 hour. These were a darker green colour than the rest of the glasses produced at 1250°C.

The SEM results for the bracken glasses formed at 1250°C confirm that a number of the visually homogeneous glasses from both the **mixed** and **unmixed** frits contain inhomogeneities that are **only** visible under the SEM (Plate 5:9).



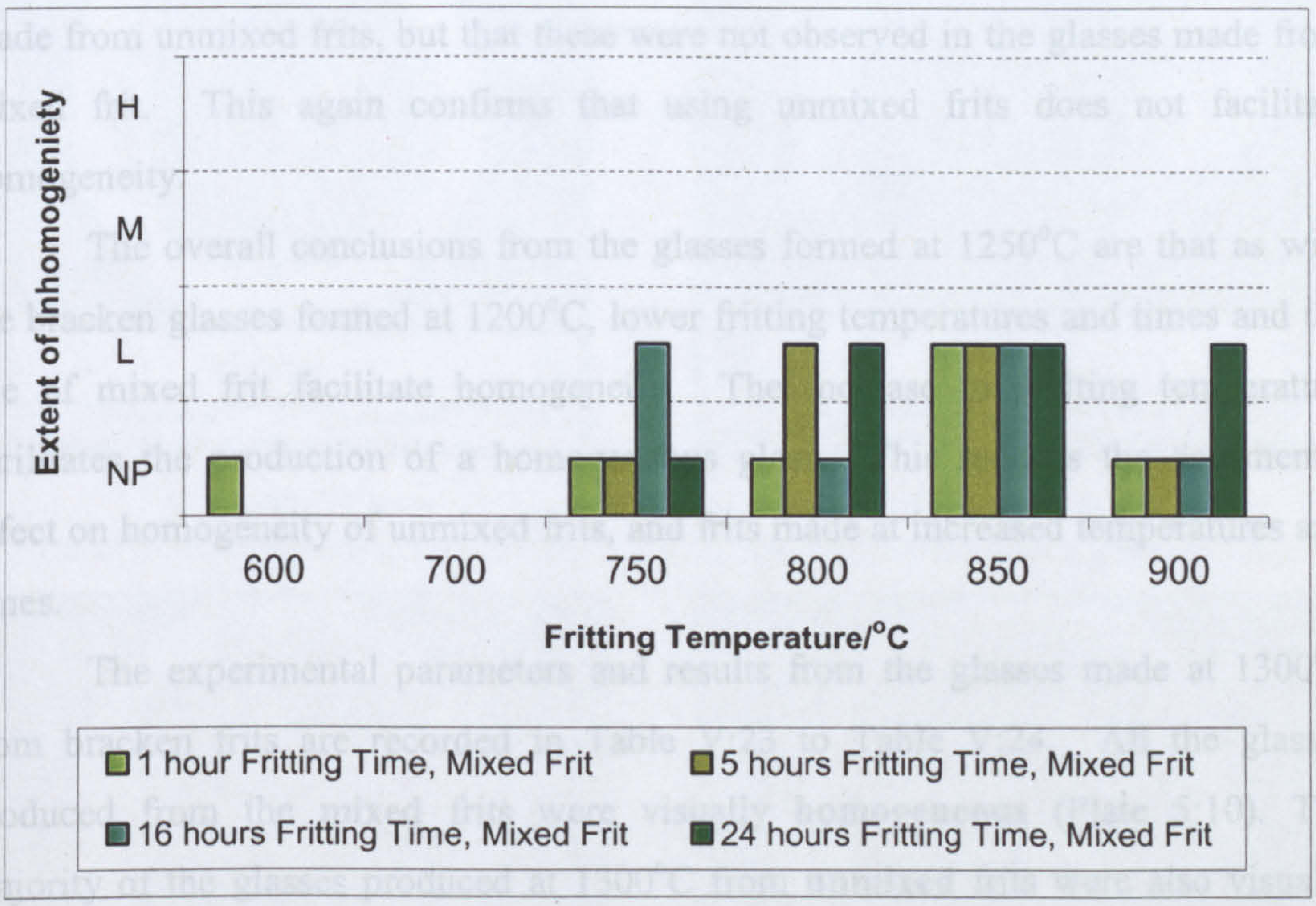
Glass Made from Mixed Frit (850°C 1 hour)
Visually homogeneous glass (Br94)



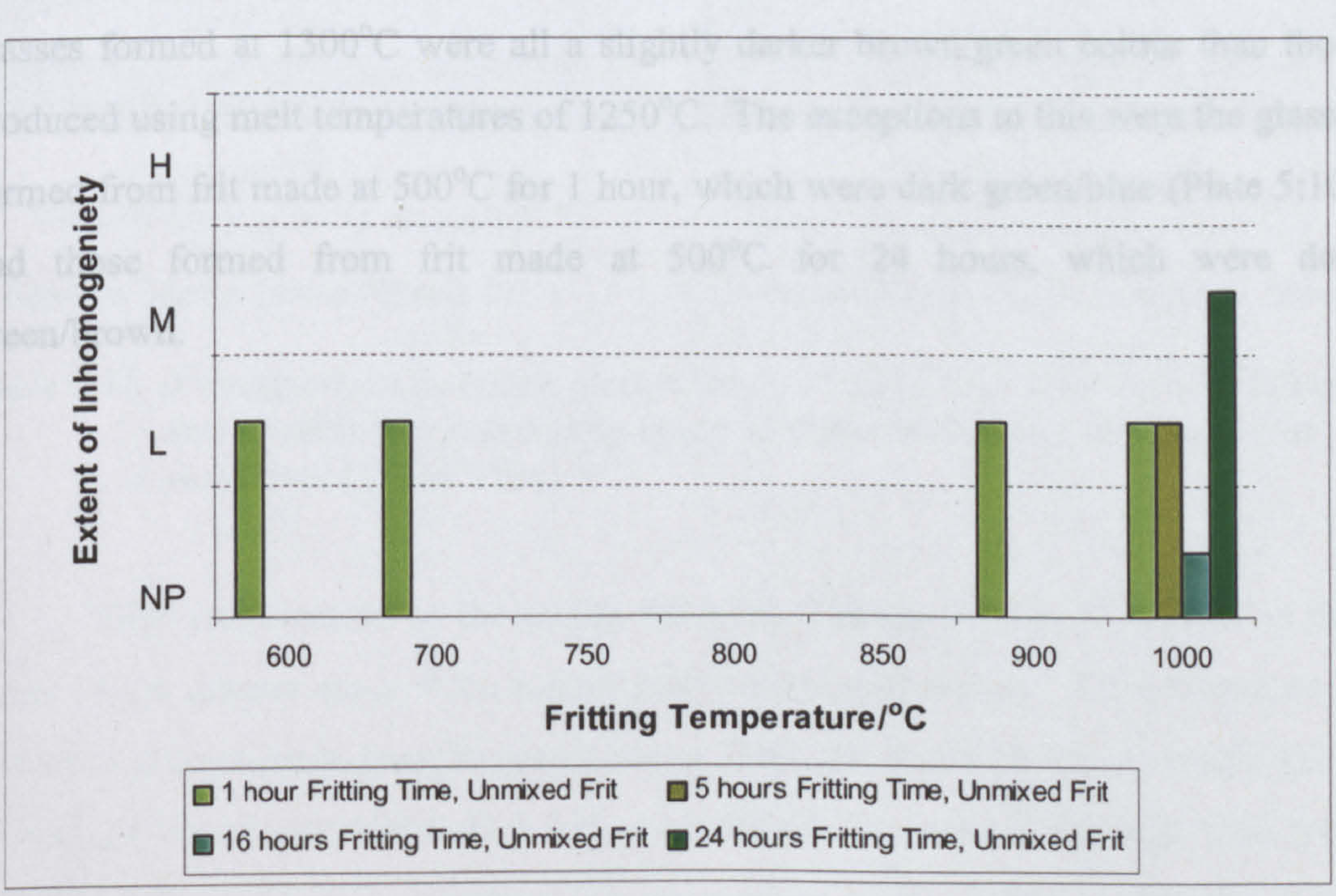
Backscattered SEM Image of Br94 with Low Inhomogeneity

Plate 5:9 A visually homogeneous bracken glass melted at 1250°C (Br94) and a backscattered SEM Image of a sample of the glass illustrating the presence of low inhomogeneity

The presence of these inhomogeneities increases in glasses made from frits produced at higher fritting temperatures and times (Figure 5:7).



Mixed Frit



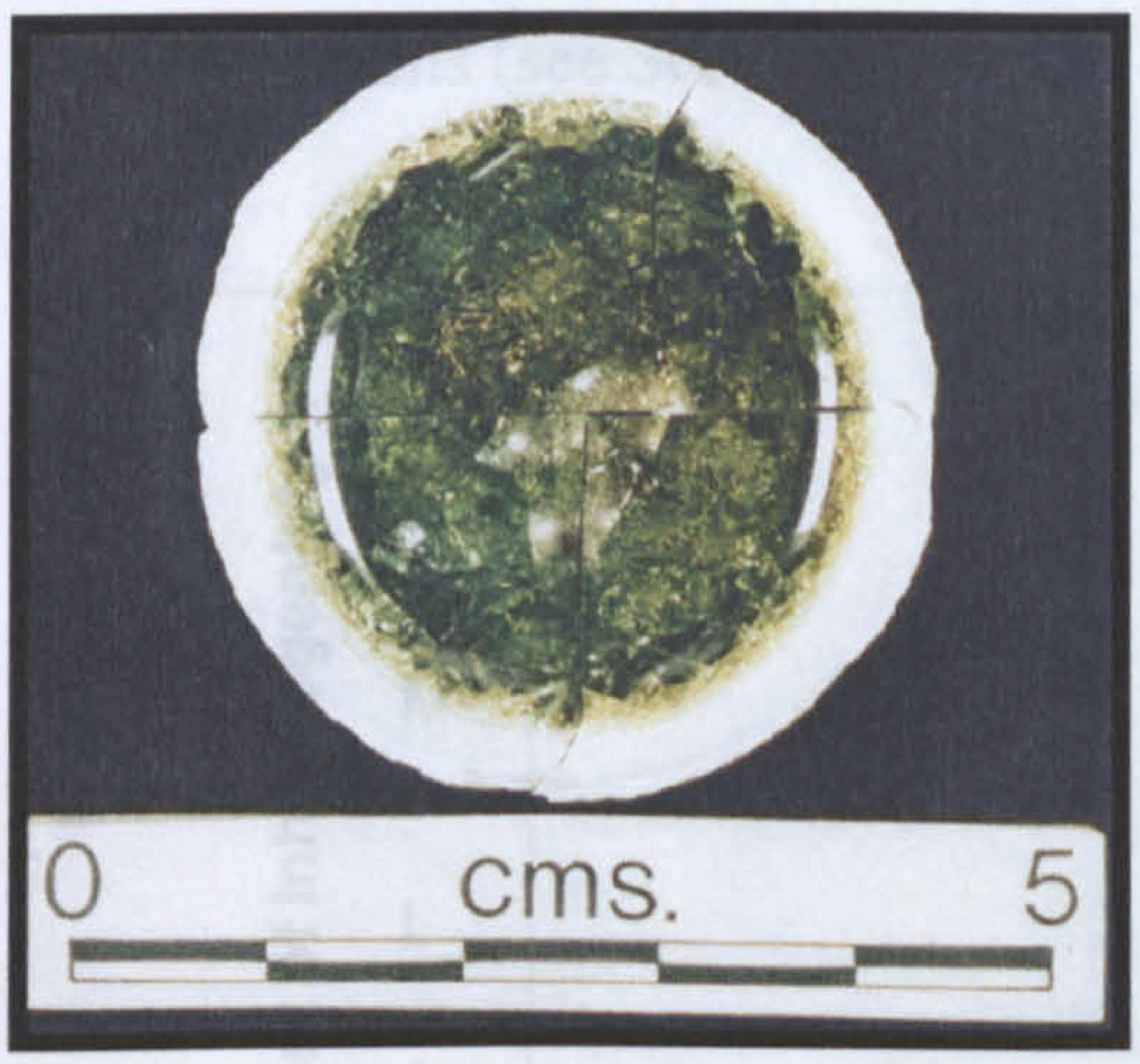
Unmixed Frit

Figure 5:7 A comparison between glasses made from mixed and unmixed frit melted at 1250°C for 5 hours (Table V:22)

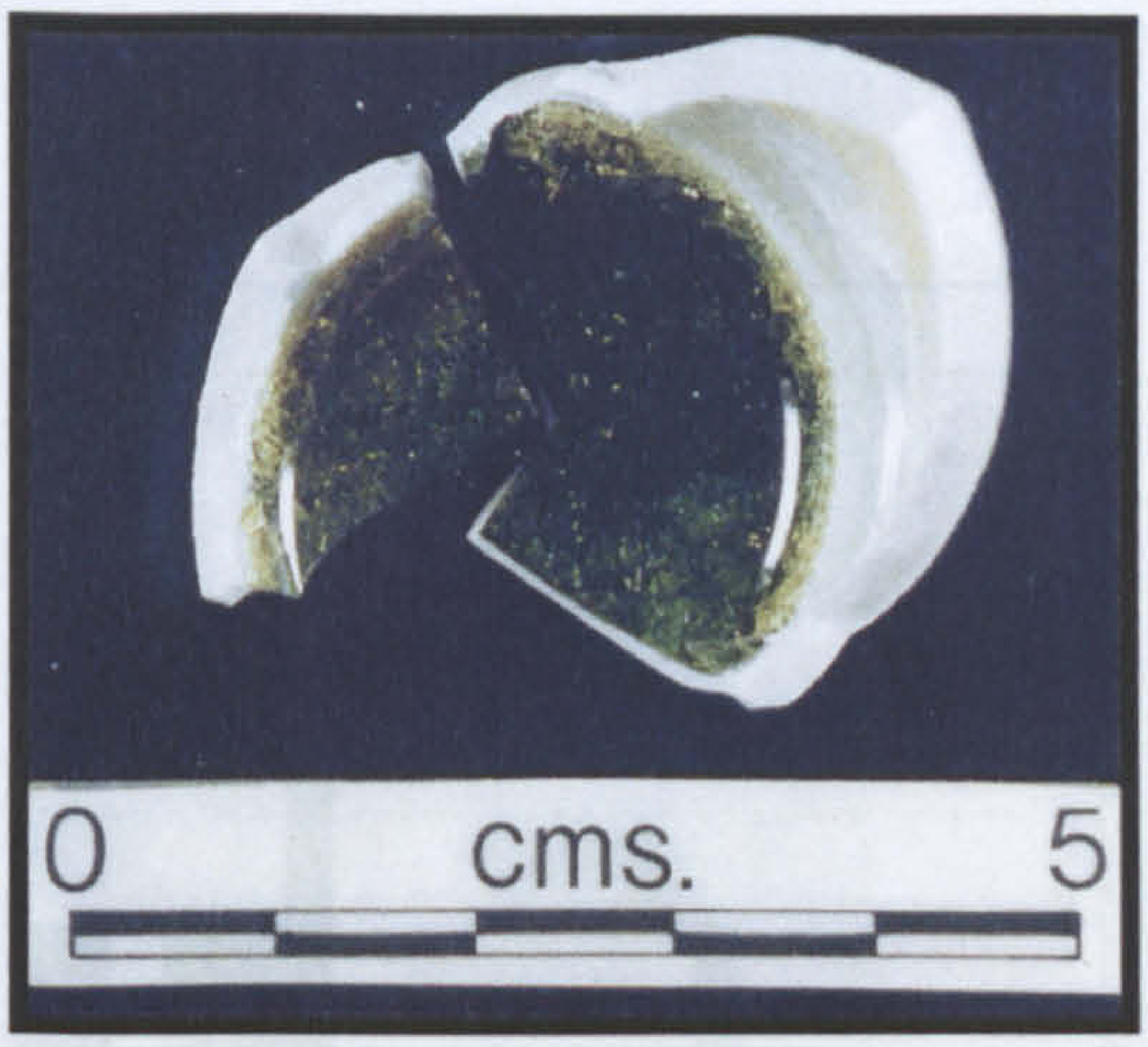
Although there are a small number of glasses made from the unmixed frits they contain comparatively more inhomogeneities than glasses formed from mixed frits. SEM examination also showed that silica relics are apparent in the glasses made from unmixed frits, but that these were not observed in the glasses made from mixed frit. This again confirms that using unmixed frits does not facilitate homogeneity.

The overall conclusions from the glasses formed at 1250°C are that as with the bracken glasses formed at 1200°C, lower fritting temperatures and times and the use of mixed frit facilitate homogeneity. The increase in melting temperature facilitates the production of a homogeneous glass. This reduces the detrimental effect on homogeneity of unmixed frits, and frits made at increased temperatures and times.

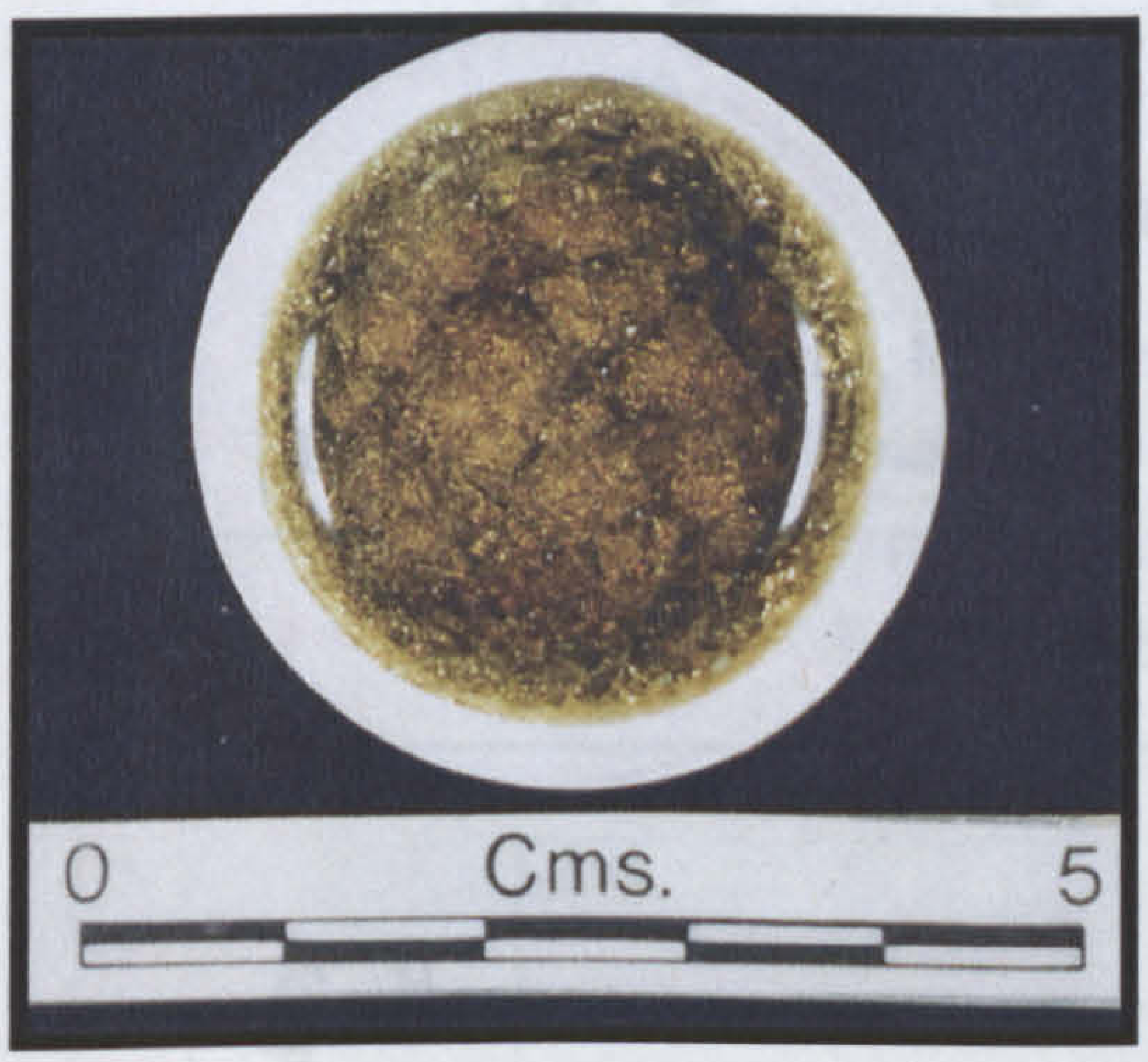
The experimental parameters and results from the glasses made at 1300°C from bracken frits are recorded in Table V:23 to Table V:24. All the glasses produced from the **mixed** frits were visually **homogeneous** (Plate 5:10). The majority of the glasses produced at 1300°C from **unmixed** frits were also visually **homogeneous** (Plate 5:10) except those formed from frits made at 900°C and 1000°C for 1 hour and 1000°C for 16 hours which contained low levels of batch relics. The glasses formed at 1300°C were all a slightly darker brown/green colour than those produced using melt temperatures of 1250°C. The exceptions to this were the glasses formed from frit made at 500°C for 1 hour, which were dark green/blue (Plate 5:10), and those formed from frit made at 500°C for 24 hours, which were dark green/brown.



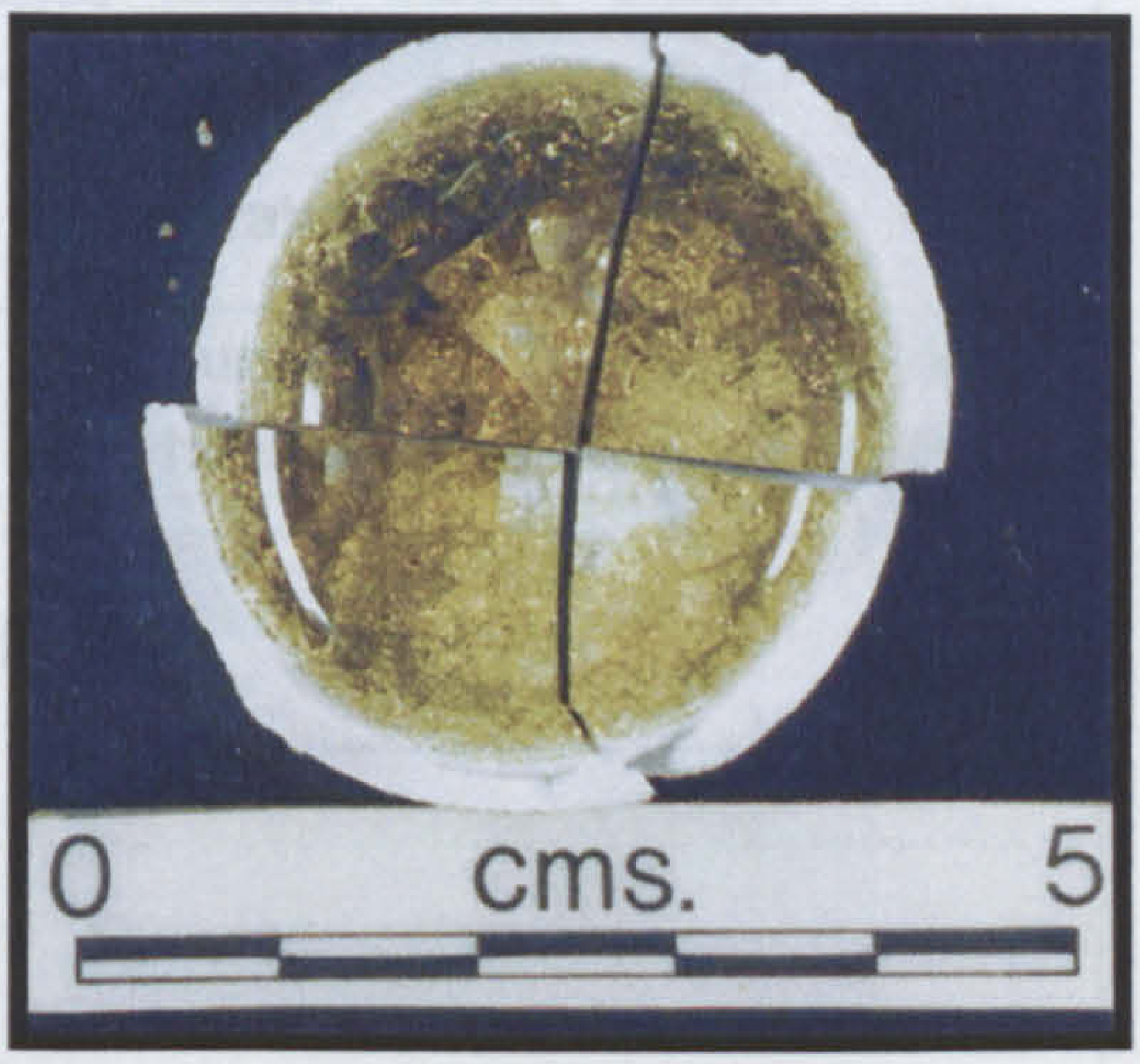
Frit 500°C 1 hour
Visually homogeneous glass (Br109)



Frit 500°C 1 hour
Visually homogeneous glass (Br128)



Frit 800°C 1 hour
Visually homogeneous glass (Br116)



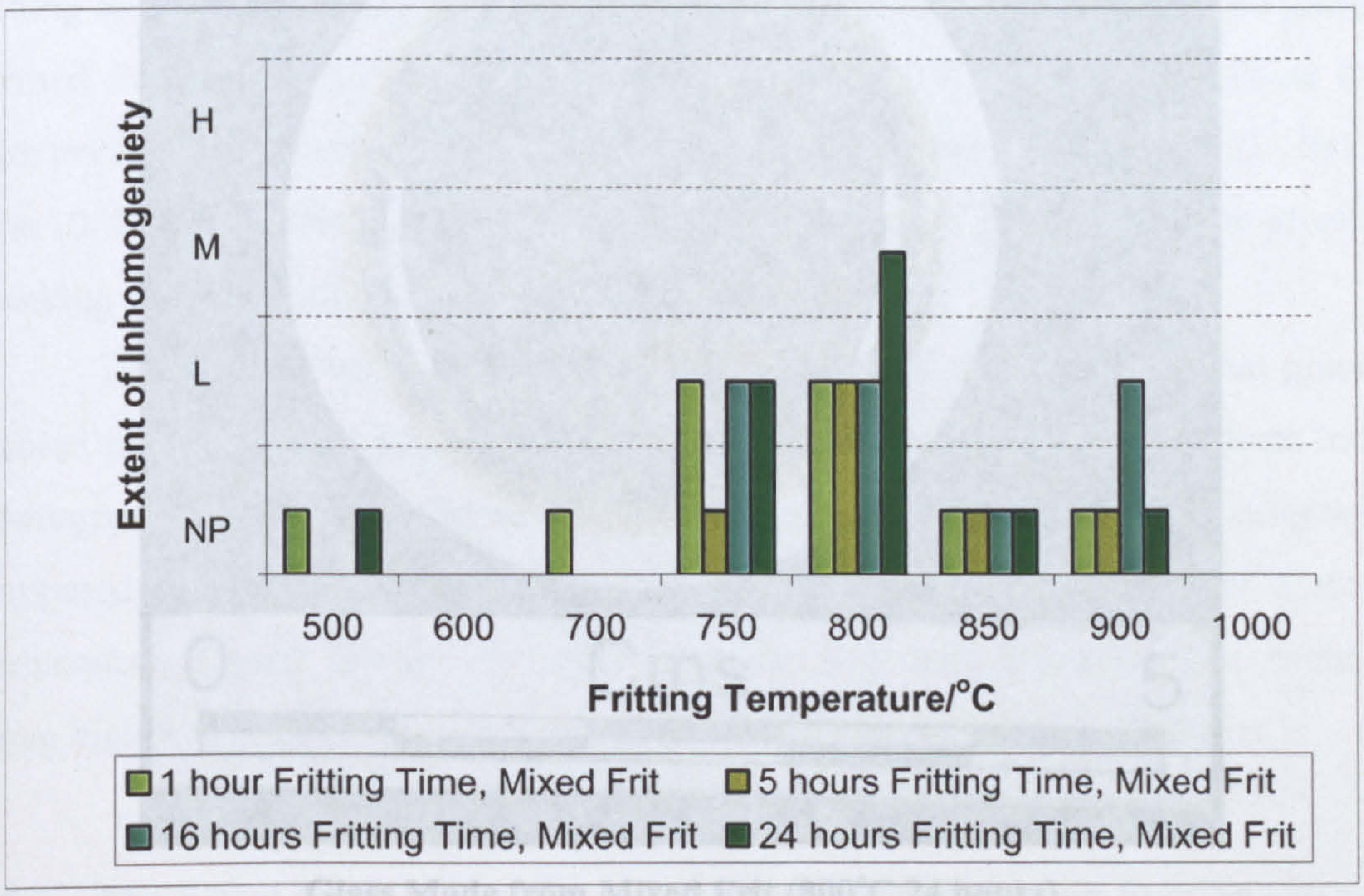
Frit 800°C 1 hour
Visually homogeneous glass (Br132)

Glasses Made From Mixed Frits

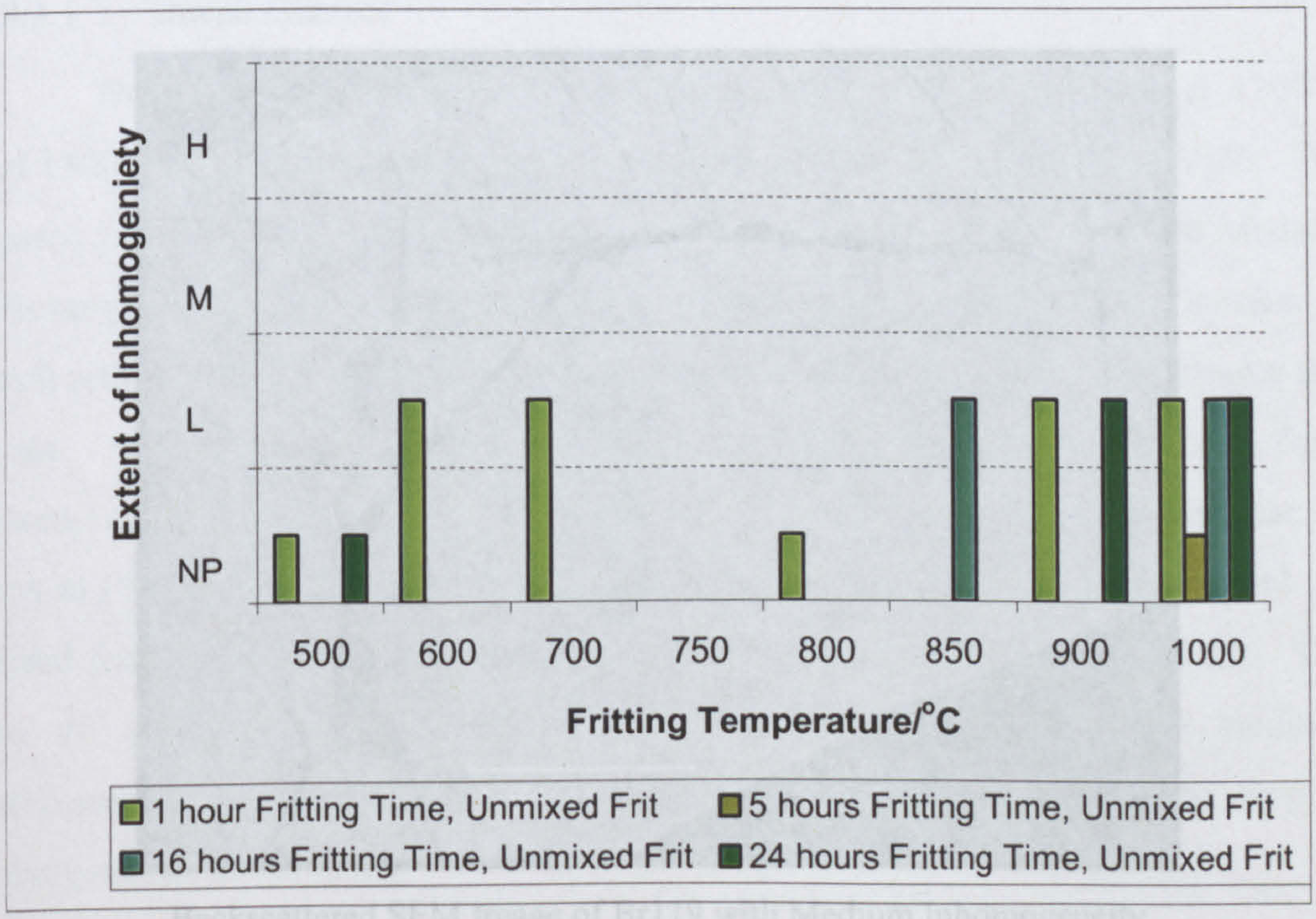
Glasses Made From Unmixed frits

Plate 5:10 A comparison between glasses made at 1300°C (5 hours) from mixed and unmixed bracken frits made at different fritting temperatures and times (Table V:24)

SEM examination of the mixed frit glasses made at 1300°C confirmed that many of the glasses made from mixed frits were homogeneous. The exceptions to this were glasses made from frit produced at 750°C (1, 5 and 16 hours), 800°C (1, 5, 16 and 24 hours) and 900°C (1 hour) produced glasses, which although they were visually homogeneous, contained **inhomogeneity** only visible under the SEM (Figure 5:8, Plate 5:11). These results do not appear to follow the general trend of increasing inhomogeneity with increased fritting temperatures and times as observed in the glasses produced at 1200 and 1250°C. This may be due to a sampling bias in the SEM results (see Section 5.5.2.1).

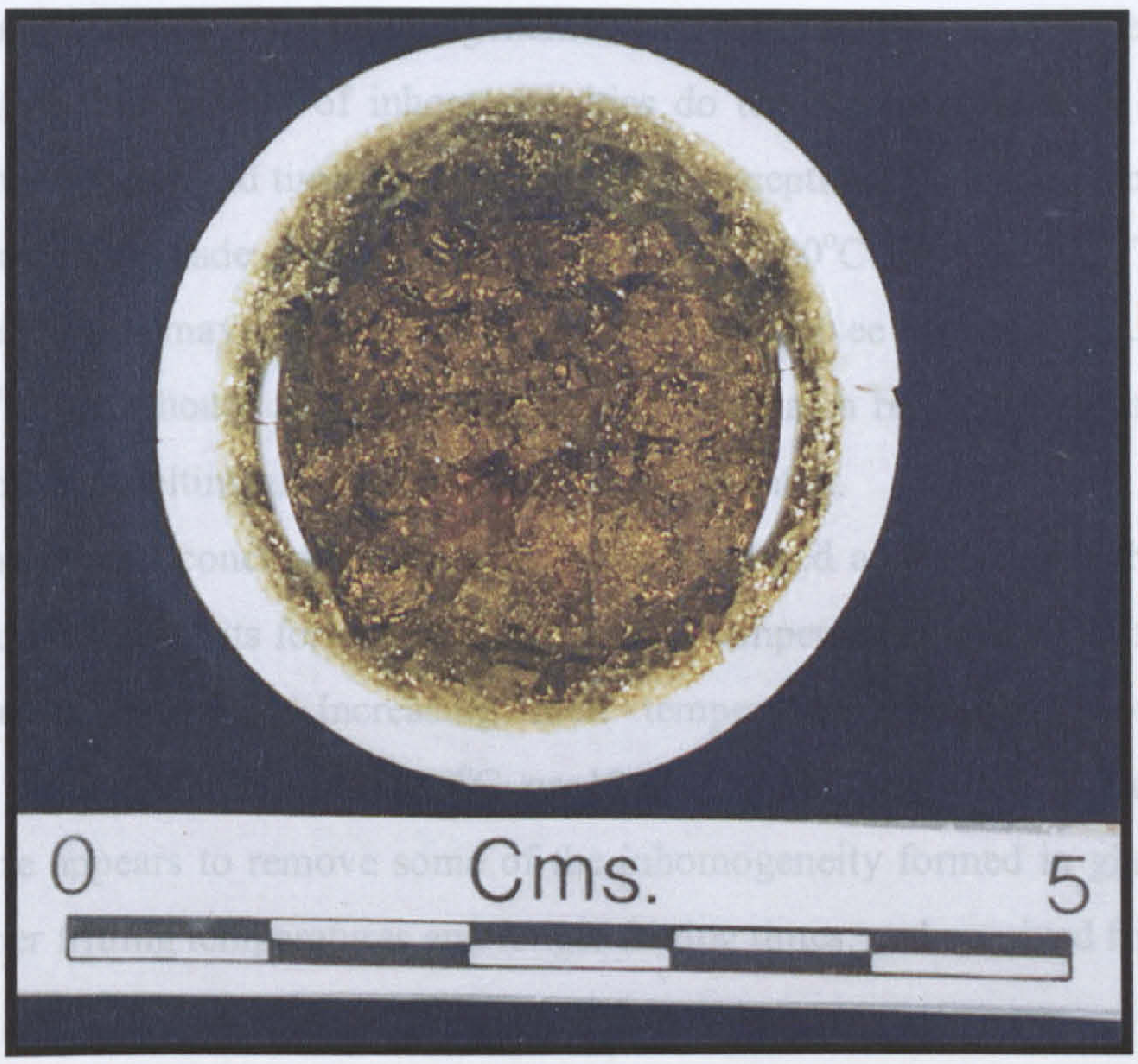


Mixed Frit

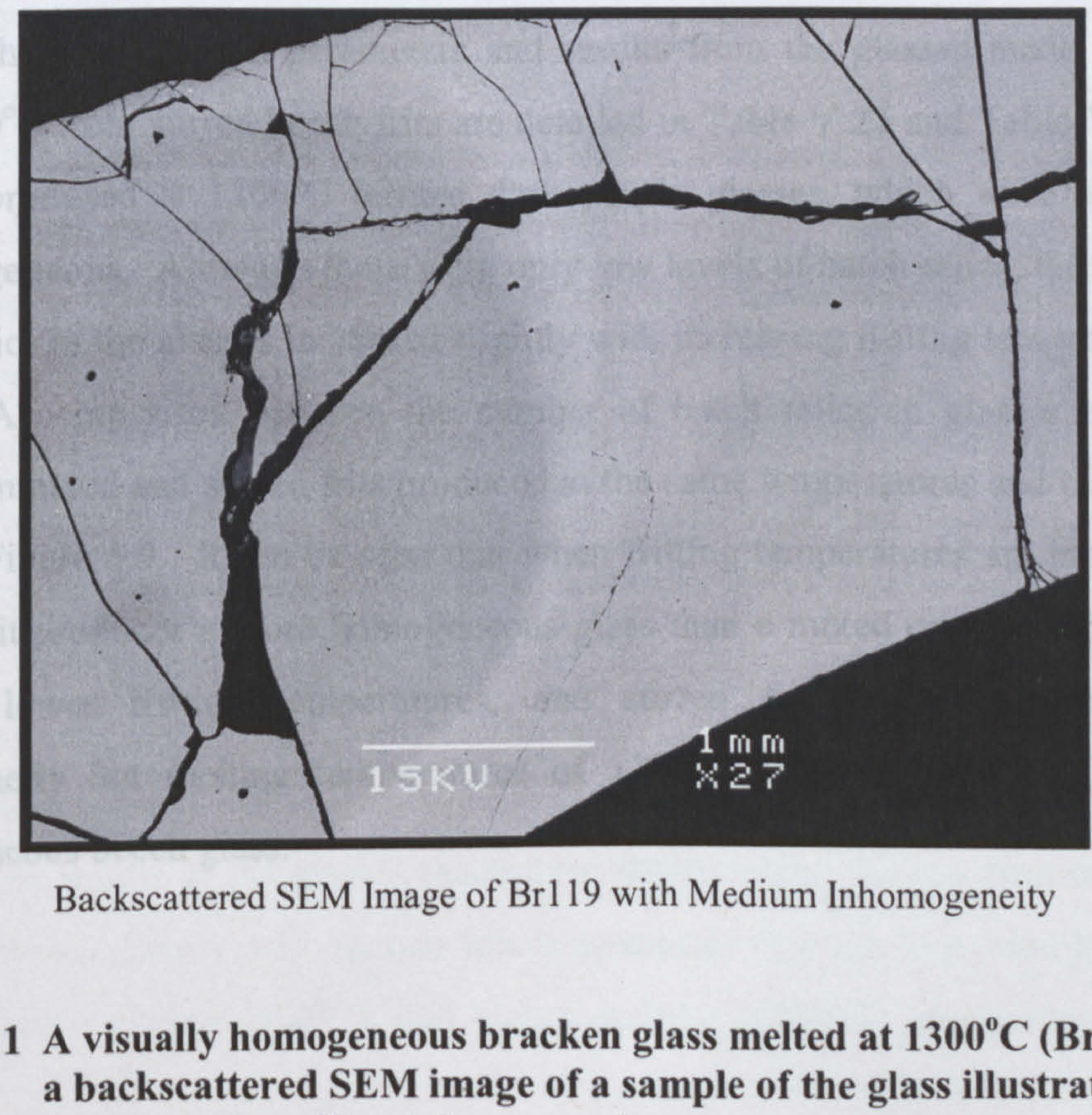


Unmixed Frit

Figure 5:8 A comparison between glasses made from mixed and unmixed frit melted at 1300°C for 5 hours (Table V:24)



Glass Made from Mixed Frit (800°C 24 hours)
Visually homogeneous glass (Br119)



Backscattered SEM Image of Br119 with Medium Inhomogeneity

Plate 5:11 A visually homogeneous bracken glass melted at 1300°C (Br119) and a backscattered SEM image of a sample of the glass illustrating the presence of medium inhomogeneity

The SEM results from the glasses made from unmixed frits melted at 1300°C contain comparatively more inhomogeneities than those formed from mixed frits. In these samples the number of inhomogeneities do tend to increase with increasing fritting temperatures and times (Figure 5:8). The exceptions to this are those glasses formed from frits made at 800°C for 1 hour, and 1000°C for 5 hours. These two unexpected results may again be due to a sampling bias (see Section 3.3.2.2). Br136 (frit 1000°C for 1 hour) contains a high quantity of batch relics due to the crucible breaking during melting and the loss of much of the batch.

The overall conclusions from the glasses formed at 1300°C are that glasses formed from **mixed** frits formed at **lower** fritting temperatures and times form more **homogeneous** glasses. Increasing melt temperature **improves** homogeneity compared to frits melted at 1200°C or 1250°C. The use of a higher melting temperature appears to remove some of the inhomogeneity formed in glasses made using higher fritting temperatures and longer fritting times, and unmixed frits.

5.5.3 The Effect on Homogeneity of Stirring the Batch During Fritting

5.5.3.1 Beech Glasses

The experimental parameters and results from the glasses made at 1200°C and 1300°C from stirred beech frits are detailed in Table V:25 and Table V:26. The glasses produced at 1200°C formed dark purple glasses, which were all visually **inhomogeneous**. Although there were only low levels of batch relics, the number of batch relics in the glasses increased slightly with increasing fritting temperatures and times. A comparison between the number of batch relics in glasses made from mixed, unmixed and stirred frits produced at the same temperatures and times can be seen in Figure 5:9. It can be seen that when fritting temperatures are increased the stirred frit produces a more homogeneous glass than a mixed or unmixed frit. The use of lower fritting temperatures, and stirred frit will therefore facilitate homogeneity but melting temperatures of 1200°C are **not** sufficient to form a homogeneous beech glass.

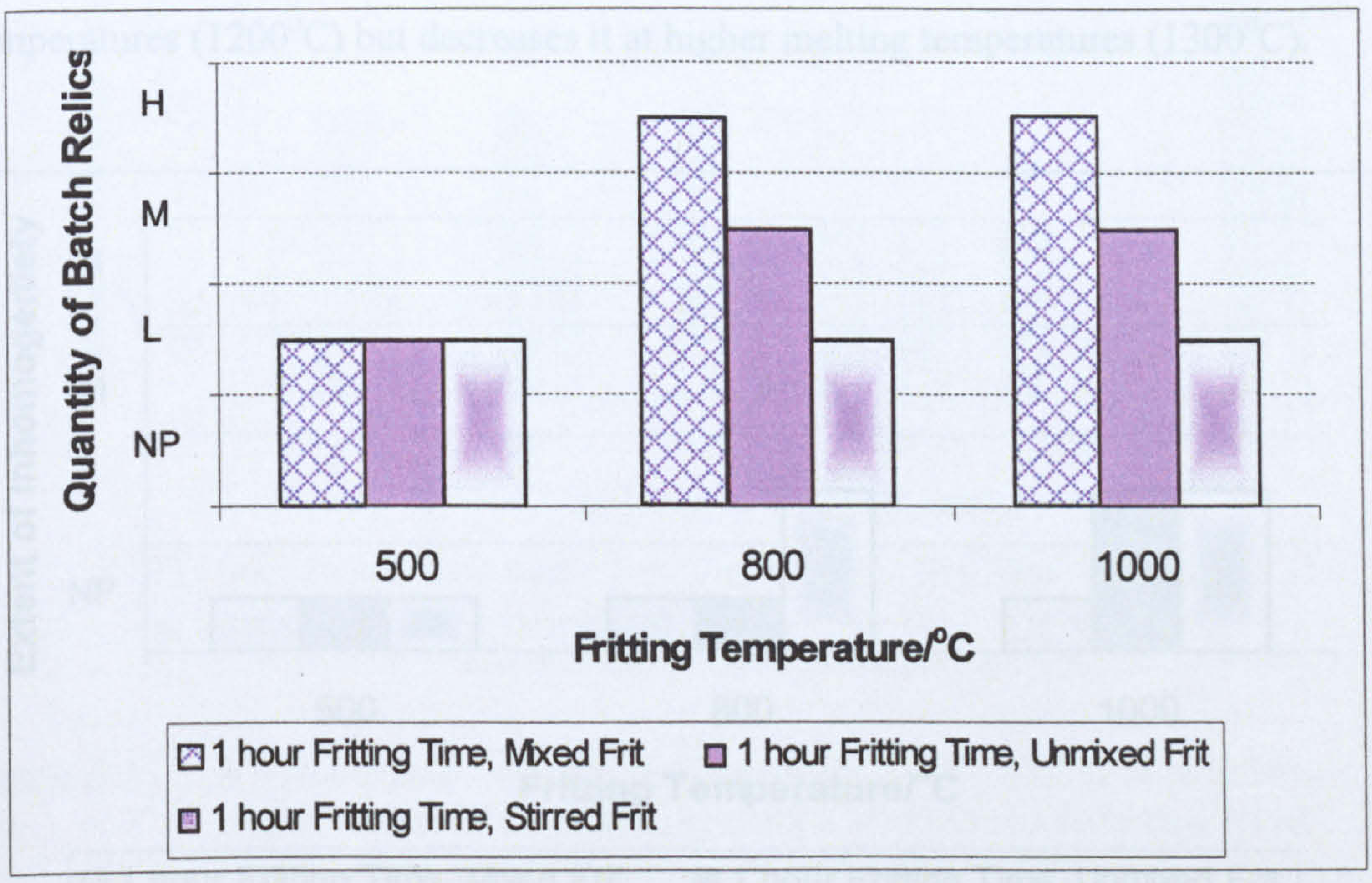


Figure 5:9 **A comparison between the visual homogeneity of glasses made from mixed, unmixed and stirred beech frits melted at 1200°C for 5 hours (Table V:16 and Table V:26)**

The glasses formed from stirred beech frits melted at 1300°C all formed visually **homogeneous**, dark purple glasses. No visual difference could be detected between the samples produced at different fritting temperatures and times. The SEM results determined that low levels of **inhomogeneity** were present in the glasses formed from frits heated at 800°C and 1000°C for 1 hour. A comparison between the homogeneity of glasses made from mixed, unmixed and stirred frits produced at the same temperatures and times can be seen in Figure 5:10. It can be seen that as in the glasses made at 1200°C there is no difference between the homogeneity of the glasses made from mixed, unmixed or stirred frits produced at 500°C for 1 hour. Increasing fritting temperature to 800°C decreases homogeneity, and in contrast to the results obtained at 1200°C the stirred frit forms a more inhomogeneous glass than the mixed or unmixed frit. At a fritting temperature of 1000°C only the mixed frit forms a homogeneous glass.

The results of the glasses made from stirred beech frits confirm that visually homogeneous glasses may contain inhomogeneities that are only visible using the SEM. Lower fritting (500°C), and higher melting (1300°C) temperatures facilitate homogeneity, and stirring the frit increases homogeneity at lower melting temperatures (1200°C) but decreases it at higher melting temperatures (1300°C).

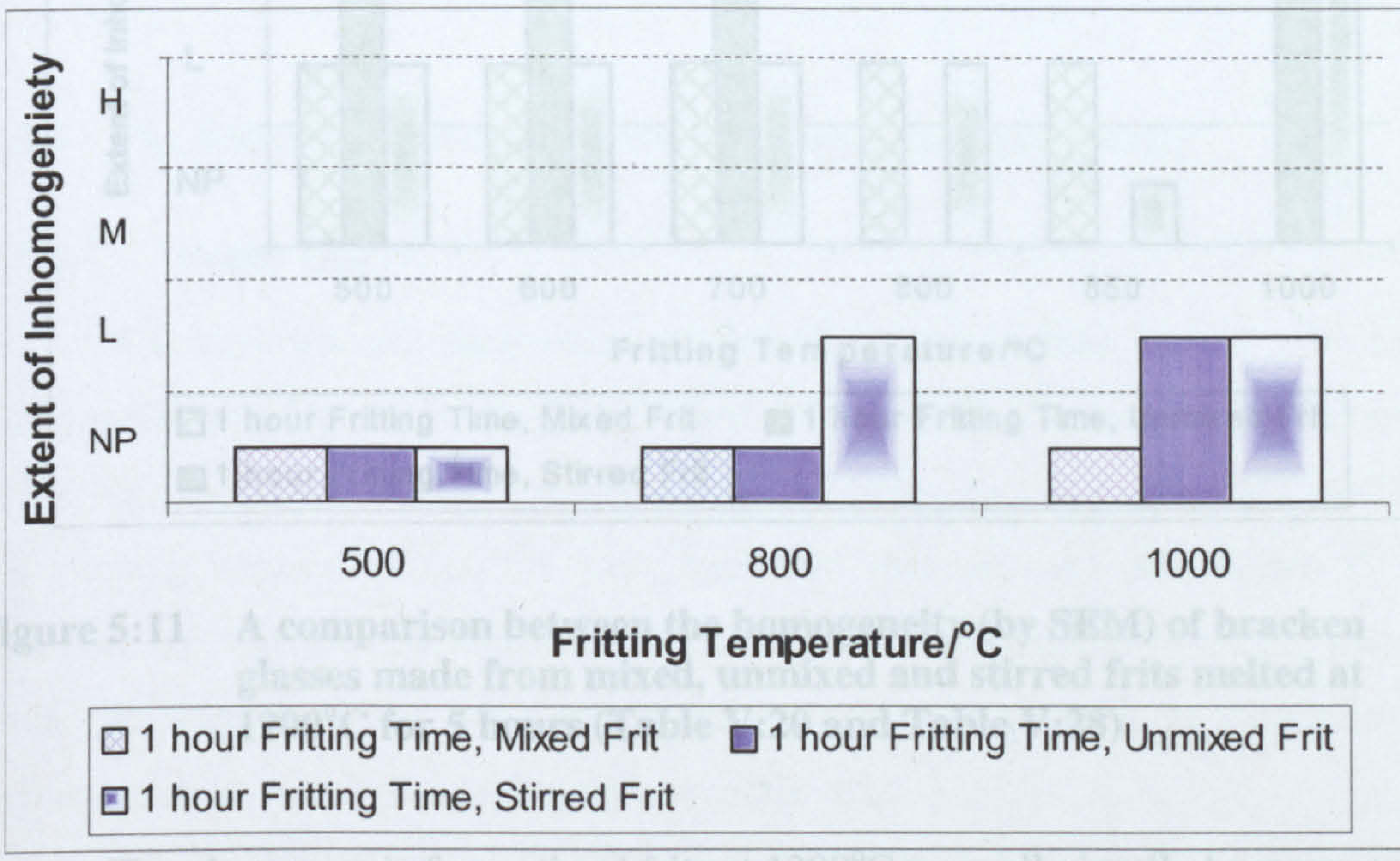


Figure 5:10 A comparison between the homogeneity (by SEM) of glasses made from mixed, unmixed and stirred beech frits melted at 1300°C for 5 hours (Table V:18 and Table V:26)

5.5.3.2 Bracken Glasses

The experimental parameters and results from the glasses made at 1200°C and 1300°C from stirred bracken frits can be seen in Table V:27 and Table V:28. All the glasses formed were visually homogeneous, but many contained inhomogeneities that were only visible using the SEM. The glasses were the same colour as those formed from unstirred frits at the same melting temperatures (see Section 5.5.2.2). Figure 5:11 illustrates the differences in homogeneity between glasses formed at 1200°C from stirred, mixed and unmixed frits made at identical fritting temperatures and times. The stirred and mixed frits form glasses containing the same levels of inhomogeneity, which is less than those in the glasses made from unmixed frits. The exception to this is seen at a fritting temperature of 850°C (1 hour), where the stirred frit forms a more homogeneous glass than the mixed frit; and fritting temperatures of 1000°C, where the glass formed was very inhomogeneous and identical to that formed from the unmixed frit.

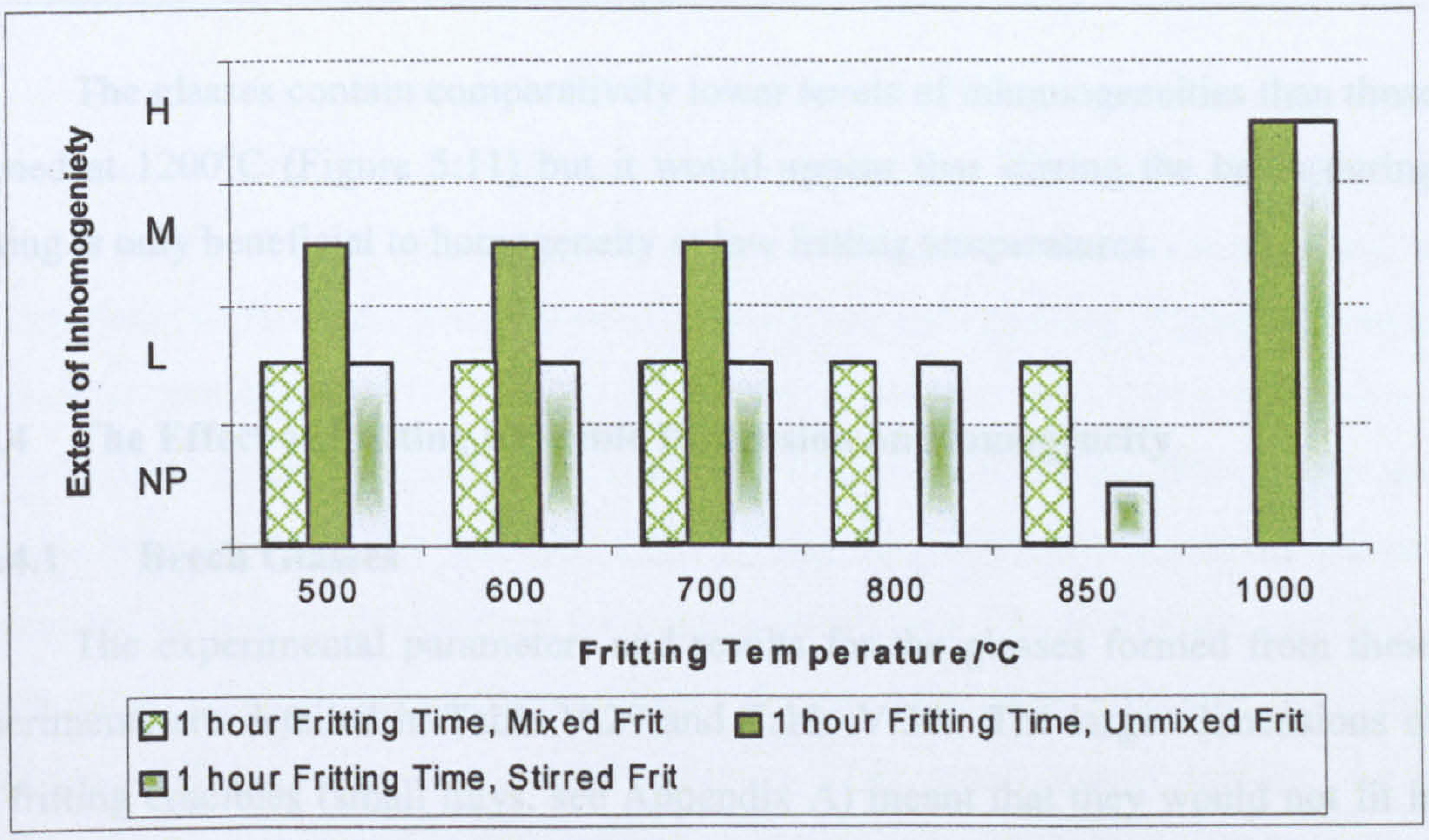


Figure 5:11 **A comparison between the homogeneity (by SEM) of bracken glasses made from mixed, unmixed and stirred frits melted at 1200°C for 5 hours (Table V:20 and Table V:28)**

The glasses made from stirred frits at 1300°C were all visually homogeneous. The glasses formed from frits made at 700°C and 1000°C for 1 hour contained low levels of inhomogeneity that were only visible using the SEM. The effect on homogeneity of melting stirred, mixed and unmixed frits at 1300°C is illustrated in Figure 5:12.

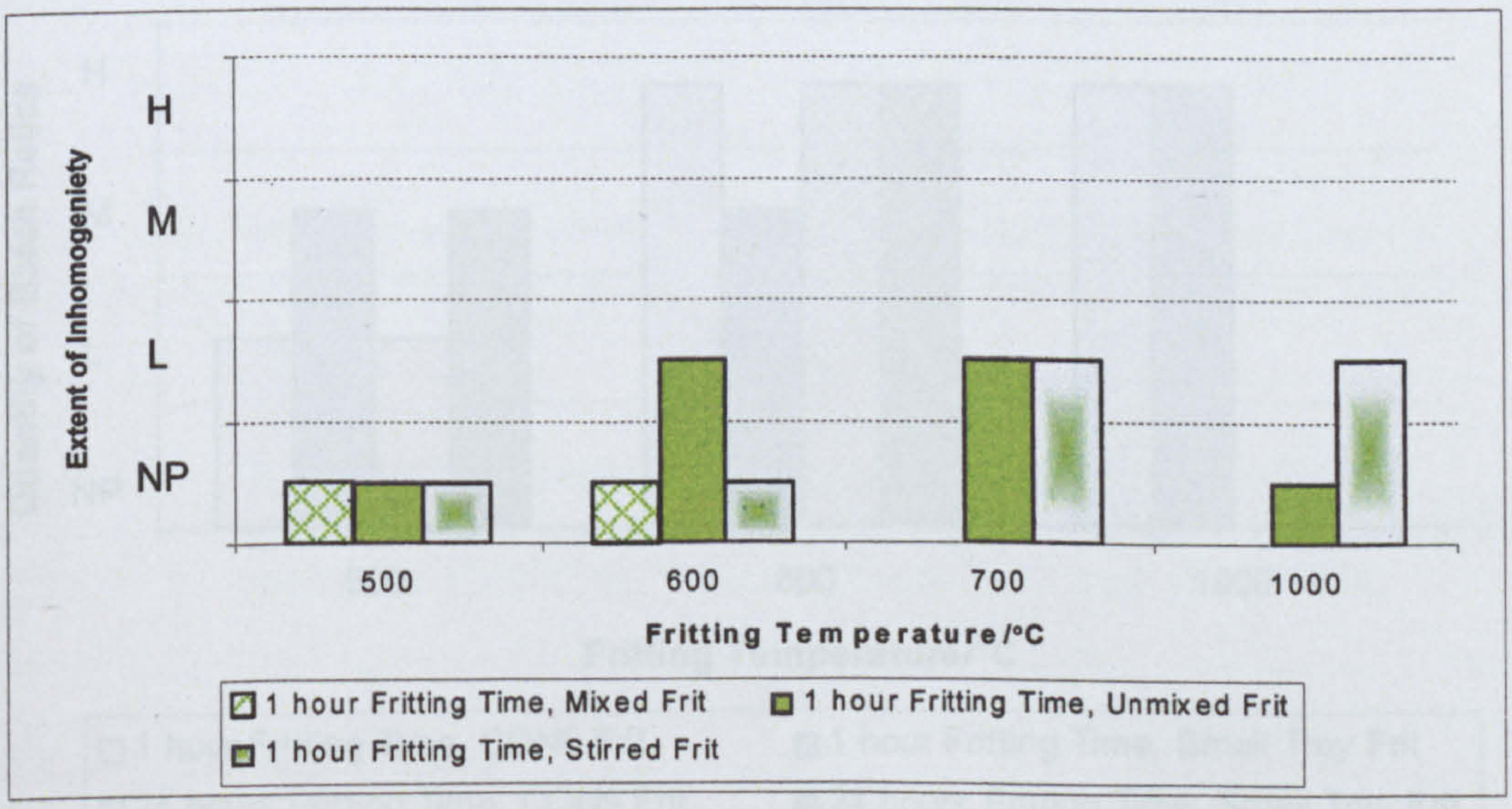


Figure 5:12 **A comparison between the homogeneity (by SEM) of bracken glasses made from mixed, unmixed and stirred frits melted at 1300°C for 5 hours (Table V:24 and Table V:28)**

The glasses contain comparatively lower levels of inhomogeneities than those formed at 1200°C (Figure 5:11) but it would appear that stirring the batch during fritting is only beneficial to homogeneity at low fritting temperatures.

5.5.4 The Effect of Fritting Crucible Dimension on Homogeneity

5.5.4.1 Beech Glasses

The experimental parameters and results for the glasses formed from these experiments are detailed in Table V:29 and Table V:30. The larger dimensions of the fritting crucibles (small trays, see Appendix A) meant that they would not fit in the melting furnace. The frits were therefore removed and placed into CON9 crucibles for the glass melting stage. The frit had to be broken to enable transfer from one crucible to the other and it was therefore not possible to determine the behaviour of unmixed frits in this set of experiments.

All the frits melted at 1200°C formed visually **inhomogeneous** dark purple glasses. The extent of inhomogeneity increased with increasing fritting temperatures and times. The difference between the glasses made from frits formed in small trays and CON9 crucibles is illustrated in Figure 5:13.

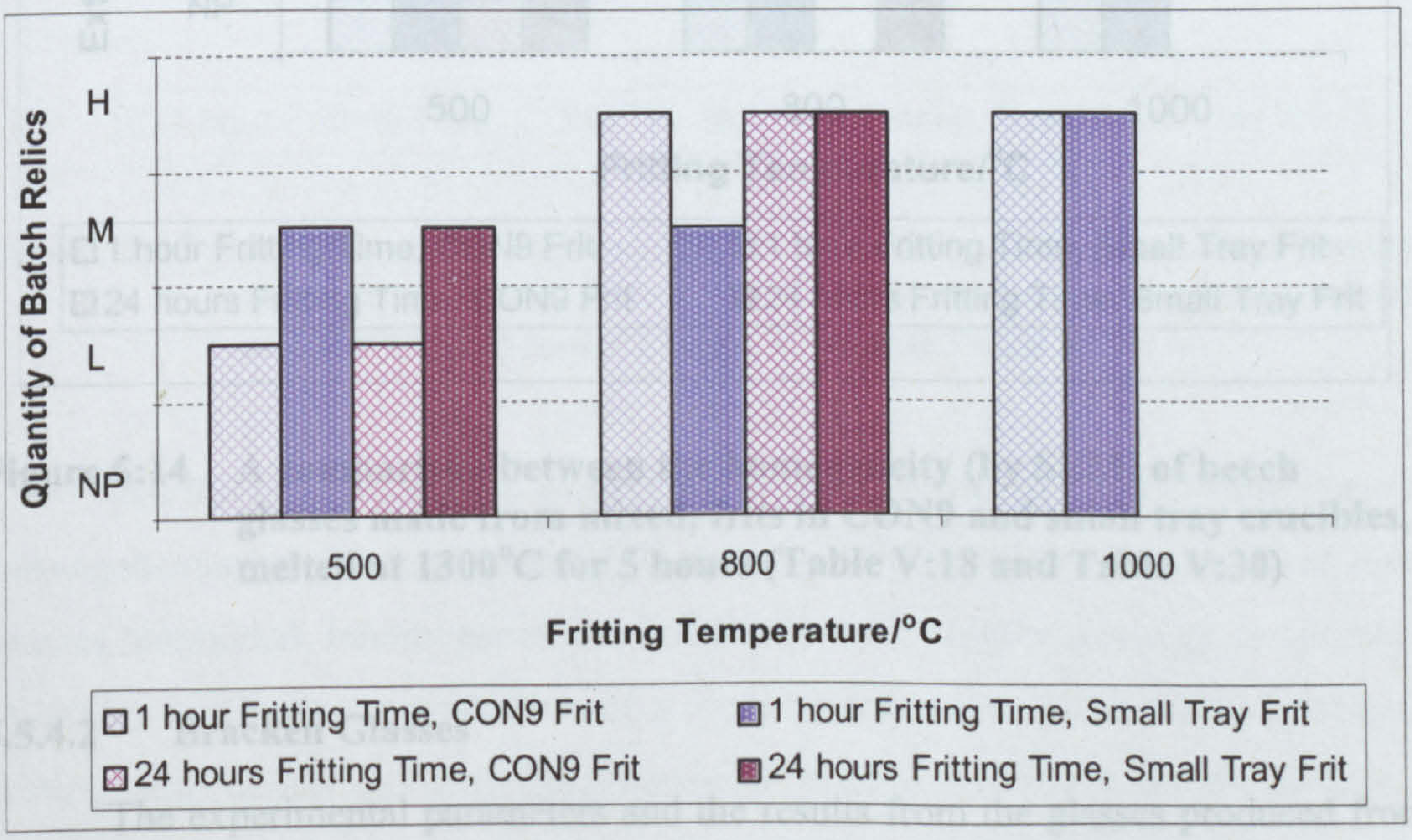


Figure 5:13 A comparison between the visual homogeneity of beech glasses made from mixed, frits in CON9 and small tray crucibles, melted at 1200°C for 5 hours (Table V:16 and Table V:30)

At a fritting temperature of 500°C the use of fritting crucibles with larger surface area to volume ratios will decrease homogeneity. This effect appears to be cancelled out by the use of higher fritting temperatures and longer fritting times, as no significant difference can be detected between the homogeneity of glasses formed from either crucible type.

All the glasses formed from small tray frits at 1300°C were dark purple and visually homogeneous. Backscattered SEM imaging confirmed that all the glasses (except the sample produced from frit made at 800°C for 1 hour) contain low levels of inhomogeneity. A comparison of these glasses with those produced from frits made in CON9 crucibles is illustrated in Figure 5:14. It can be seen that the use of smaller surface area to volume fritting crucibles and an increased melting temperature facilitates the formation of a more homogeneous glass.

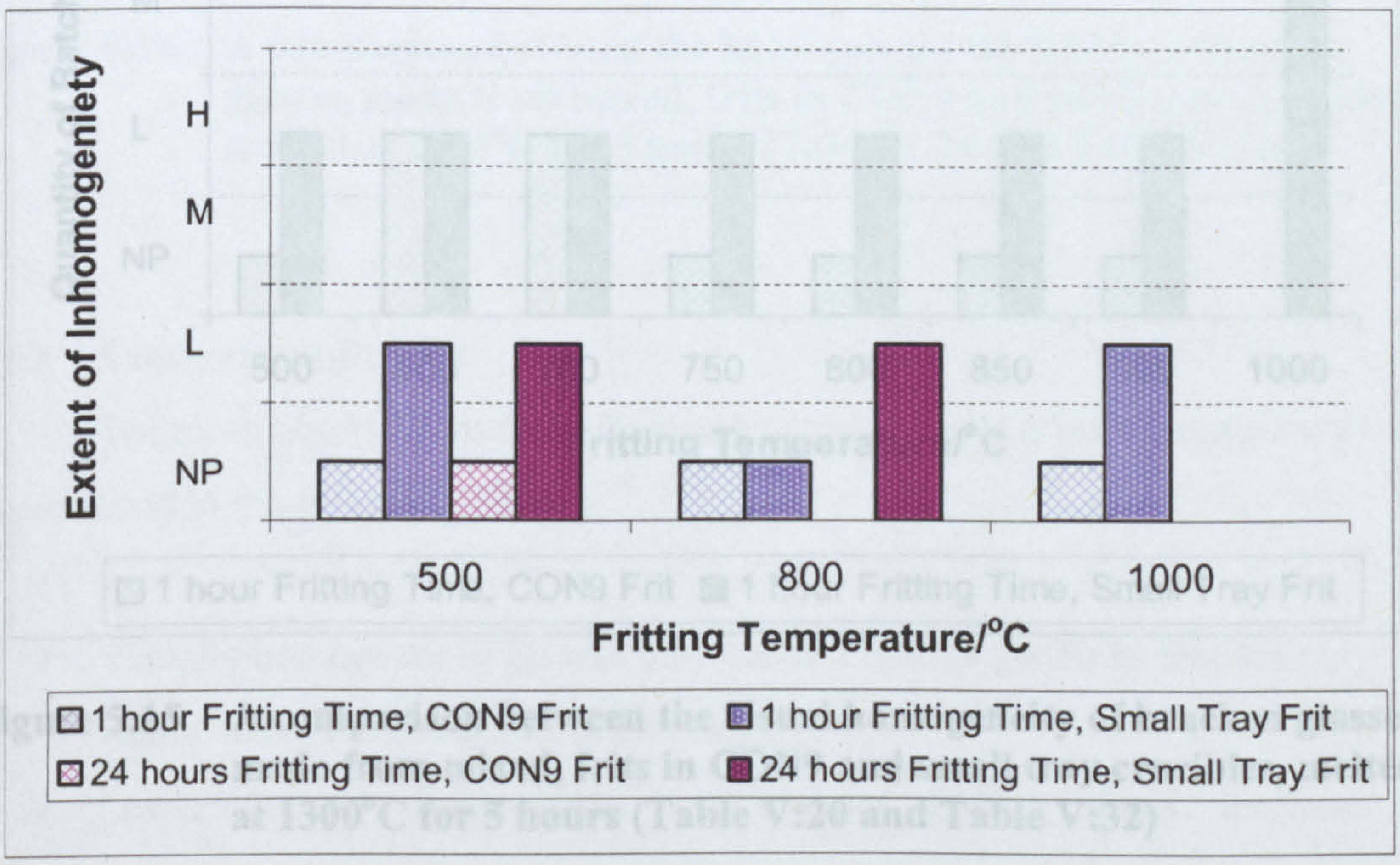


Figure 5:14 A comparison between the homogeneity (by SEM) of beech glasses made from mixed, frits in CON9 and small tray crucibles, melted at 1300°C for 5 hours (Table V:18 and Table V:30)

5.5.4.2 Bracken Glasses

The experimental parameters and the results from the glasses produced from bracken frits made in varying surface area to volume ratio crucibles are recorded in Table V:31 and Table V:32. The behaviour of unmixed frits could not be investigated as the frit broke up on transfer from the fritting to the melting crucible (see Section 5.5.4.1). The colour of all the glasses formed in this set of experiments was identical to that of those formed from comparative CON9 frits in Section 5.5.2.2.

All the glasses formed at 1200°C were visually **inhomogeneous**. Figure 5:15 illustrates the difference in the number of batch relics in glasses formed from frits made in CON9 and small trays. The glasses made from CON9 frits are generally more homogeneous than the glasses made from small tray frits. The larger surface area to volume ratio of the small tray has therefore had an adverse effect on homogeneity. The trend of increasing inhomogeneity with increasing fritting temperatures is only observed at 1000°C.

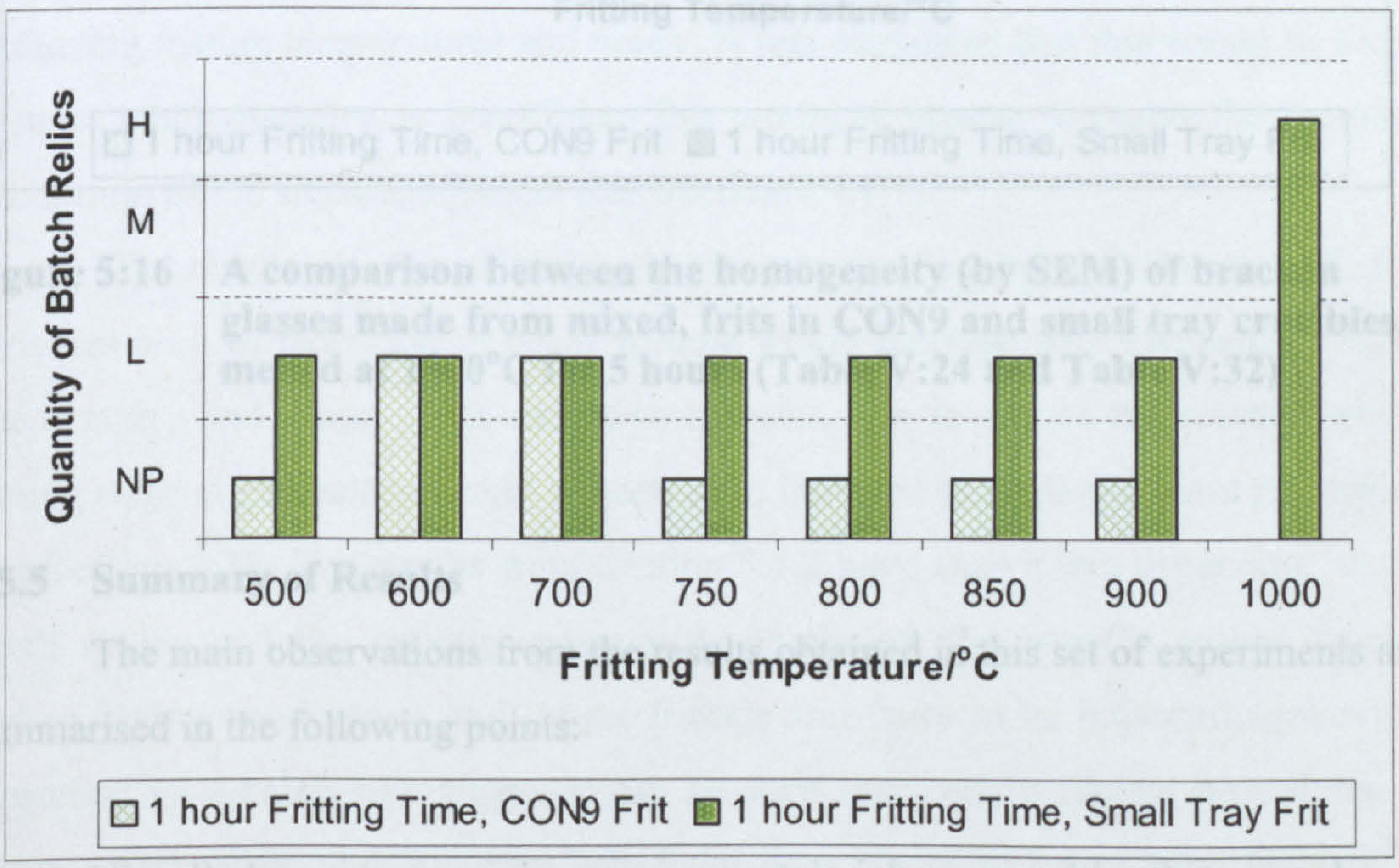


Figure 5:15 A comparison between the visual homogeneity of bracken glasses made from mixed, frits in CON9 and small tray crucibles, melted at 1300°C for 5 hours (Table V:20 and Table V:32)

All the bracken glasses made from small tray frits at 1300°C were visually **homogeneous** but backscattered SEM imaging confirmed that a number of these glasses contained inhomogeneities. The use of a higher melting temperature (1300°C) facilitates the production of a more homogeneous glass, whilst increasing fritting temperatures increases inhomogeneity. Figure 5:16 illustrates the difference between glasses formed from frits made in CON9 crucibles and small trays. The glasses formed from frits made in small trays contain comparatively more homogeneities than those made from frits formed in CON9 crucibles

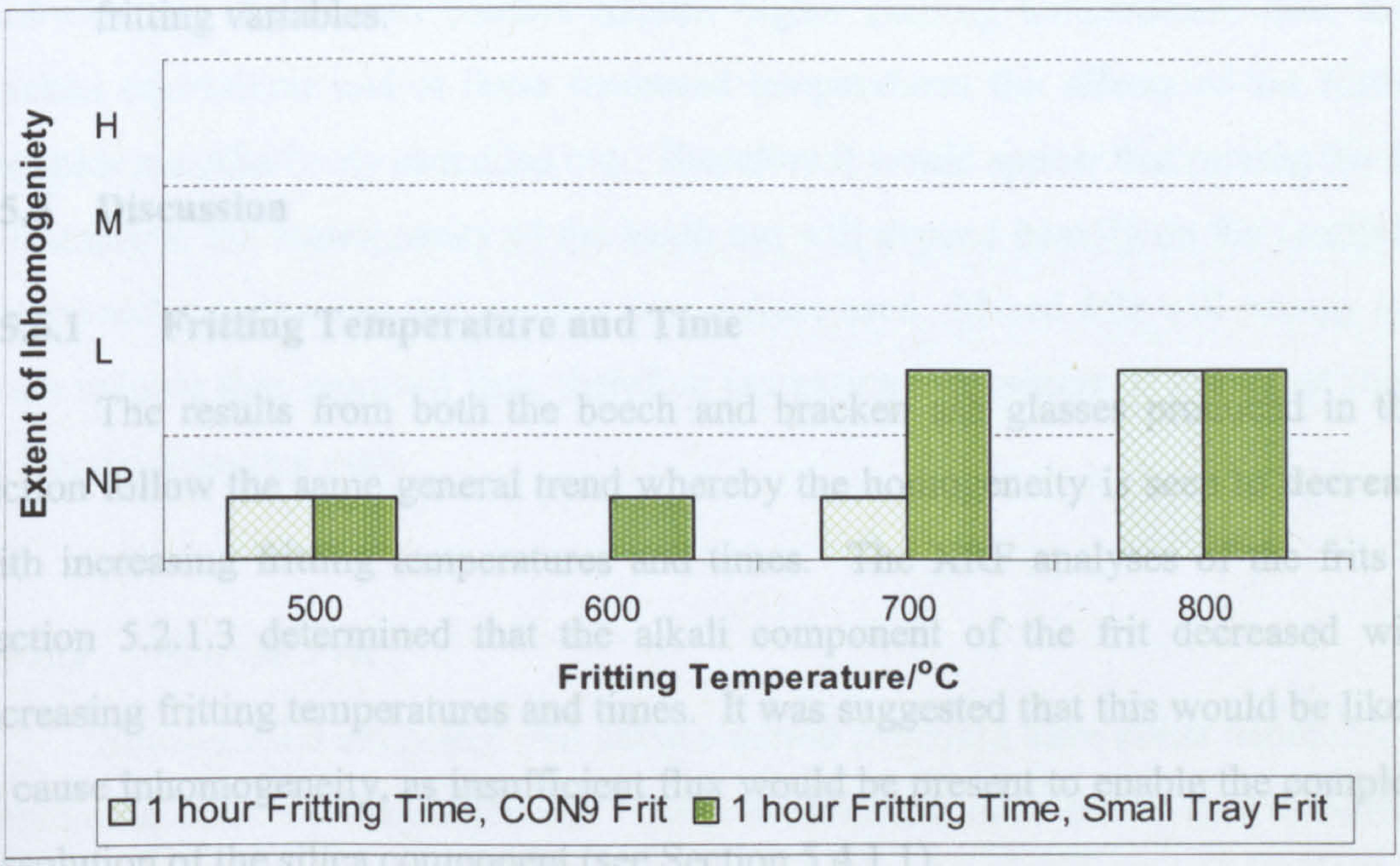


Figure 5:16 A comparison between the homogeneity (by SEM) of bracken glasses made from mixed, frits in CON9 and small tray crucibles, melted at 1300°C for 5 hours (Table V:24 and Table V:32)

5.5.5 Summary of Results

The main observations from the results obtained in this set of experiments are summarised in the following points:

- Visually homogeneous glasses may contain inhomogeneities that are only visible using backscattered SEM imaging.
- Lower fritting temperatures and shorter fritting times increases homogeneity in both ash types.
- Mixing the frit prior to melting increases homogeneity in both ash types.
- The use of stirred frit increases homogeneity at melting temperatures of 1200°C but increasing this to 1300°C gives inconclusive results for both ash types.
- The use of smaller surface area to volume ratio crucibles increases homogeneity.
- Increasing melting temperature increases homogeneity in both ash types.

- Increasing melting temperatures may cancel the effects of some of the fritting variables.

5.5.6 Discussion

5.5.6.1 Fritting Temperature and Time

The results from both the beech and bracken ash glasses produced in this section follow the same general trend whereby the homogeneity is seen to **decrease** with increasing fritting temperatures and times. The XRF analyses of the frits in Section 5.2.1.3 determined that the alkali component of the frit decreased with increasing fritting temperatures and times. It was suggested that this would be likely to cause inhomogeneity, as insufficient flux would be present to enable the complete dissolution of the silica component (see Section 5.4.1.1).

The results of the fritting experiments in Section 4.6 determined that variables such as reduction in batch volume would increase with increasing fritting temperatures and times. This reduction in batch size is one of the reasons why a fritting stage is generally thought to have been included in medieval glass production (see Section 2.3). The results from Section 5.5.2 have shown that depending on the alkali source and the melting temperature employed, the benefits gained from a higher fritting temperature and longer fritting time have to be balanced against the formation of a batch free glass. It can be seen that certain fritting procedures or heating parameters may be more beneficial than others and that these have to be altered according to the composition of the batch.

5.5.6.2 Mixed and Unmixed Frits

Mixing the frit before melting is thought to allow a more intimate mixture of the raw materials enabling a more extensive and even reaction between the silica and alkali and therefore facilitating the formation of a more homogeneous glass (see Section 2.3.5). The results of these experiments have shown that in bracken ash glasses this does occur, and the mixed frits form more homogeneous glasses than unmixed frit at the same fritting and melting parameters. It would therefore seem that for bracken ash batches this stage is very beneficial in the production of a homogenous glass.

In beech ash glasses the effect of mixed frits on homogeneity was inconclusive. Beech ash batches require higher melting temperatures than their bracken equivalents and at these increased temperatures the affects of the fritting variables are effectively cancelled out. Therefore it would appear that mixing the frit will improve the homogeneity of the batch but will depend heavily on the reactivity of the batch components and melting temperature used. Mixed frits will occupy less batch volume than unmixed frits, therefore increasing the volume of glass that could be formed from one melt.

5.5.6.3 Stirred Frit

Section 2.3.3 suggested that using a stirred frit could have either beneficial or detrimental effects on homogeneity. These experiments have shown that at melting temperatures of 1200°C using stirred frit produces similar improvements in homogeneity as mixing the frit before melting (see Section 5.5.6.2). The formation of a more intimate mixture of raw materials by **either** mixing method enables a more even interaction between the silica and alkali and facilitates homogeneity. The inconclusive results obtained at melting temperatures of 1300°C may be due to the more prevalent effect on homogeneity of the increased melting temperature. The possibility of refractory contamination with modern crucibles is very slight and it is not though that this would be a significant source of inhomogeneity in these experiments.

5.5.6.4 Fritting Crucible Dimensions

It has already been mentioned in Section 2.4.5.2 that it might be expected that the larger surface area to volume ratio of the fritting crucibles would cause a greater loss of the volatile components from the frit compared to those frits formed in crucibles with smaller surface areas. The fritting experiments in Section 5.4.1.3 shows that this hypothesis was correct and the larger crucible surface area facilitated a faster fritting reaction. When these frits were melted to form a glass (see Section 5.5.4) the results confirmed that the loss of volatiles had left insufficient alkali to form a homogeneous glass. The use of a larger surface area is therefore similar to the use of increased fritting temperatures and times and is therefore detrimental to the production of a homogeneous glass.

5.5.6.5 Melting Temperature

The most significant trend observed from the results of these experiments is the marked **increase** in homogeneity with **increasing** melt temperature. The higher temperature will aid the faster reaction of the silica and alkali components and help prevent segregation of the batch and the formation of silica rich areas which it is then difficult to remove even with extended melting times (see Section 4.7.5). Once the batch is fluid the increased temperature will lower the viscosity of the melt, facilitating the removal of bubbles and seed and speeding up homogenisation due to increased mixing by thermal currents within the molten glass. The use of higher melting temperatures will therefore not only enable the production of a more homogeneous glass but also one that is better refined and of an improved quality. The results from this Chapter also confirm that the beech ash batches require higher melting temperatures than bracken ash batches. This is due to the lower alkali content of the beech ash and has been discussed in Section 4.7.5.

The results from this Chapter show that the use of higher melting temperatures allows a larger tolerance of the parameters used in the preparation and fritting of the batch. For example, beech or bracken frit formed at high temperatures (1000°C) for long times (24 hours) will not form a homogeneous glass at a melting temperature of 1200°C, but will if the melting temperature is increased to 1300°C. If it is the loss of the alkali component in frits formed at high temperatures and long times which prevents the complete dissolution of the silica component of the batch (see Section 5.5.6.1) then the increase in melting temperature will compensate for this by allowing more silica to dissolve using less flux.

5.5.6.6 The Effect of Sampling Bias in Visually Homogeneous Glasses

The general trend in the results from this Chapter is that inhomogeneity increases with increasing fritting temperatures and times and decreasing melting temperature. However, it can be seen that there are some instances where the levels of inhomogeneity observed under the SEM do not follow this general pattern. The most likely reason for these anomalies is that the area removed for SEM analysis was not representative of the whole glass. It has been determined that inhomogeneities are present in visually homogeneous glasses but the position and distribution of these microscopic inhomogeneities (if present) could not be seen whilst sampling. Therefore although a large sample was removed for SEM analysis (see Section 3.3.2.2) in some cases the area sampled may not have been representative of the glass.

To remove this possible bias it would have been beneficial to carry out multi sampling and also to be able to produce each glass more than once in order to ensure repeatable results. This was not possible due to constraints on time and raw materials and as the general trends results appear to be relatively constant it is thought that, within the limitations of laboratory replication, these results constitute a good representation of the processes that are being investigated.

5.5.7 Conclusions

The conclusions from these experiments are summarised in the points below:

- Visually homogeneous glasses may contain inhomogeneities that are only visible under the SEM.
- Increasing melting temperatures will increase homogeneity in both ash types and will generally cancel out the effects of factors which appear to cause inhomogeneities, such as increased fritting temperatures or times.
- Fritting does not always facilitate the production of a homogeneous glass.
- Increasing fritting temperatures and times will increase inhomogeneity.
- Mixing the frit before melting and/or stirring the batch during fritting will improve homogeneity.
- Smaller surface area to volume ratio fritting crucible dimensions will increase homogeneity.
- Beech ash batches require higher melting temperatures than bracken.

It can be concluded from the results of these experiments that the choice of fritting and melting variables has to be selected depending on the composition of the raw materials. It can also be seen that effects of many of the fritting variables are removed by the use of higher melting temperatures and it would appear that this is one of the most significant factors in the production of a homogeneous glass. In addition to melting temperature it can be seen from Figure 2:1 that there are many other variables in the melting stage that will influence homogeneity and a number of these will be investigated in the next Chapter.

CHAPTER 6

Experimental: The Effect of Melting Variables on Homogeneity

6.1 Introduction

The effects of the melting stage on the homogeneity of medieval glasses were considered in Section 2.4. The aim of the experiments in this Chapter is to determine the effect on homogeneity of altering melting conditions, such as crucible dimensions, fabric and furnace atmosphere. It was not possible to experimentally investigate all of the variables associated with melting within the time scale of this research. Therefore a limited number of parameters had to be selected. The reasons behind these choices have been discussed in Section 2.7.

Beech and bracken ash batches were made up to the standard batch composition and mixing parameters given in Section 4.7.2. The constraints on raw materials meant that it was not possible to use both mixed and unmixed frits in these experiments. Mixed frits were selected as the experiments in Section 5.5.2 had determined that these were more likely to form homogeneous glasses. Glasses were also produced using unfritted batches to provide a comparison to the fritted glasses produced in Chapter 5. All the glasses were examined and described according to the parameters described in Section 3.3.

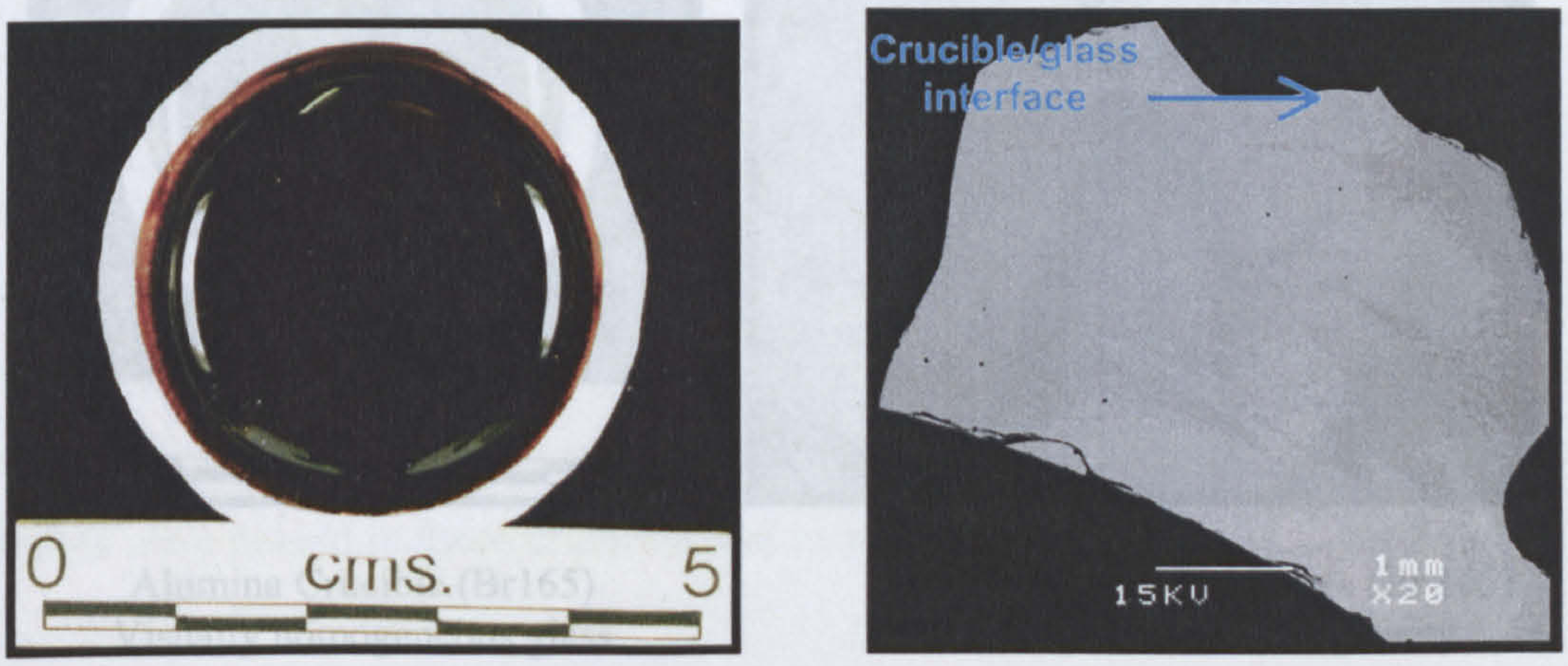
The results of the experiments in Chapter 5 determined that increasing fritting temperature and time appears to have a direct relationship to inhomogeneity.

6.1.1 The Effect of Melting Crucible Fabric on Homogeneity

It was not possible to replicate archaeological crucible fabrics, due to their complex nature, and diverse fabric types (see Section 2.4.5.1 and 2.7). Therefore, these experiments will determine how homogeneity is affected by the use of simple, modern refractory fabrics: alumina and mullite (see Appendix A). Mullite crucibles have been used in all of the experiments in Chapters 4 and 5. These experiments were carried out using unfritted batches placed in CON9 crucibles of each fabric type and heated at 1200°C and 1300°C for 5 hours.

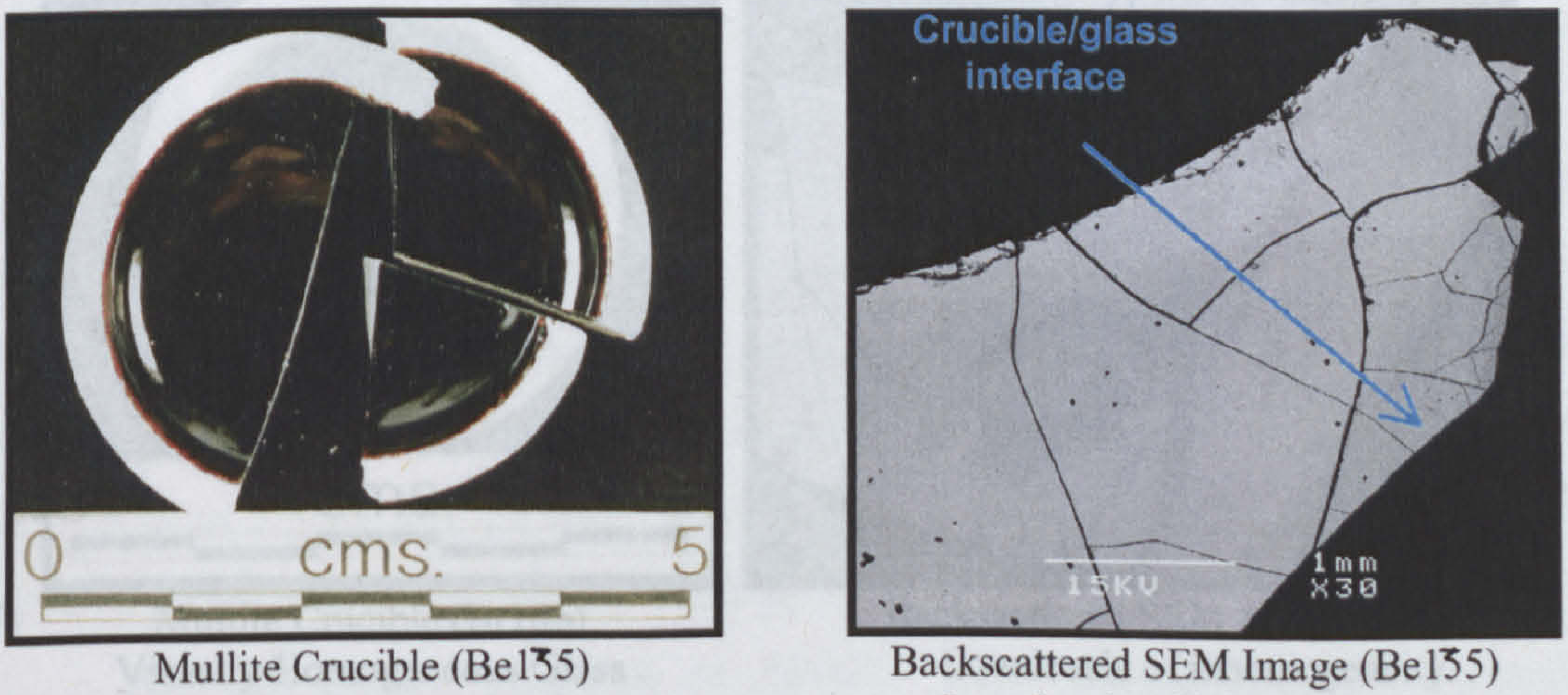
6.1.1.1 Beech Glasses

The experimental parameters and results from these experiments are detailed in Table VI:1 and Table VI:2 respectively. The unfritted beech glasses produced at 1200°C were dark purple and visually **inhomogeneous**. No difference could be observed either visually or under the SEM between the glasses formed in either mullite or alumina crucibles. The beech glasses produced at 1300°C were dark purple and visually **homogeneous**. Backscattered SEM imaging showed that both glasses contained a low level of inhomogeneity (Plate 6:1). It can be concluded from these experiments that changing melting crucible fabric from mullite to alumina does not have an effect on homogeneity.



Alumina Crucible (Be134)
Visually homogeneous glass

Backscattered SEM Image (Be134)
Low levels of inhomogeneity



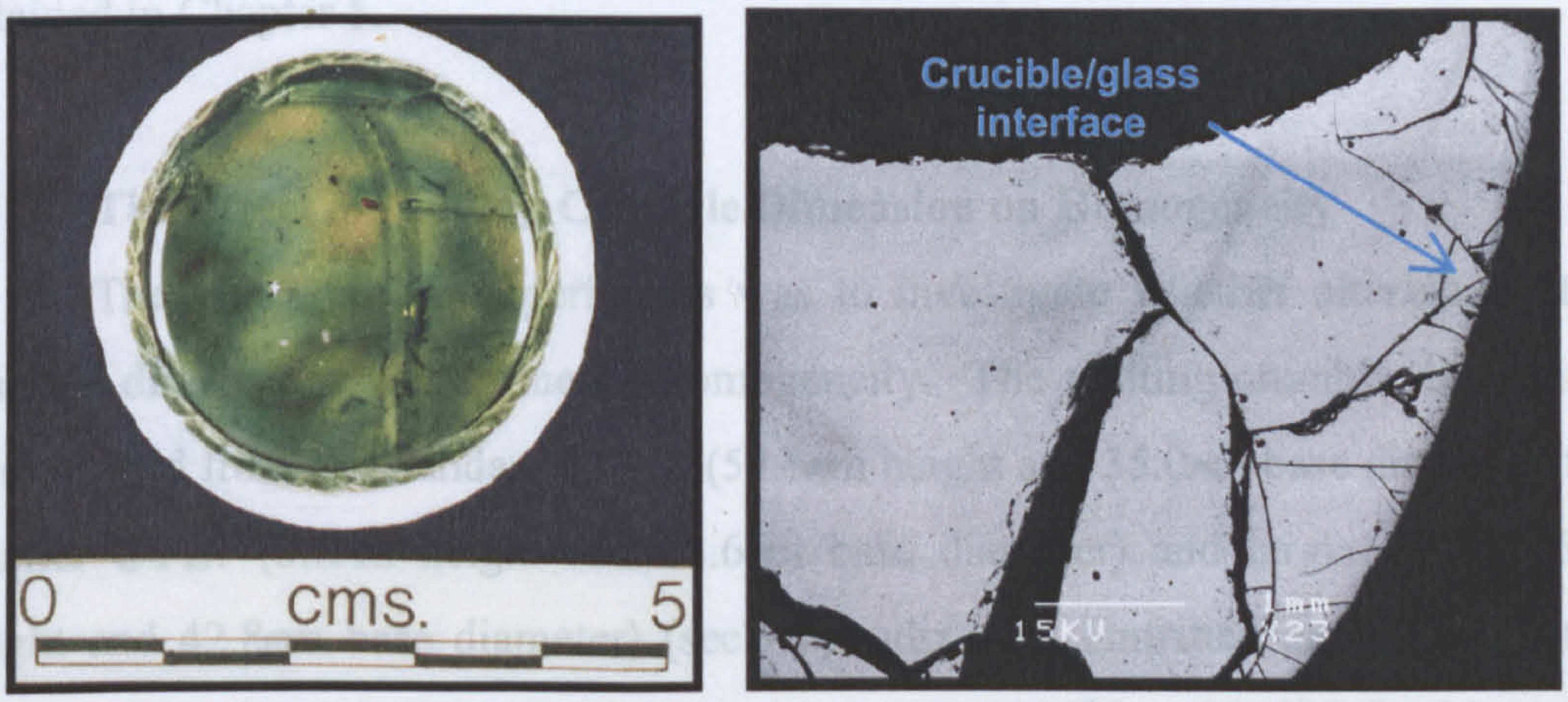
Mullite Crucible (Be135)
Visually homogeneous glass

Backscattered SEM Image (Be135)
Low levels of inhomogeneity

Plate 6:1 A comparison between the visual and microscopic homogeneity of unfritted bracken glasses made in alumina and mullite crucibles at 1300°C for 5 hours (Table VI:2).

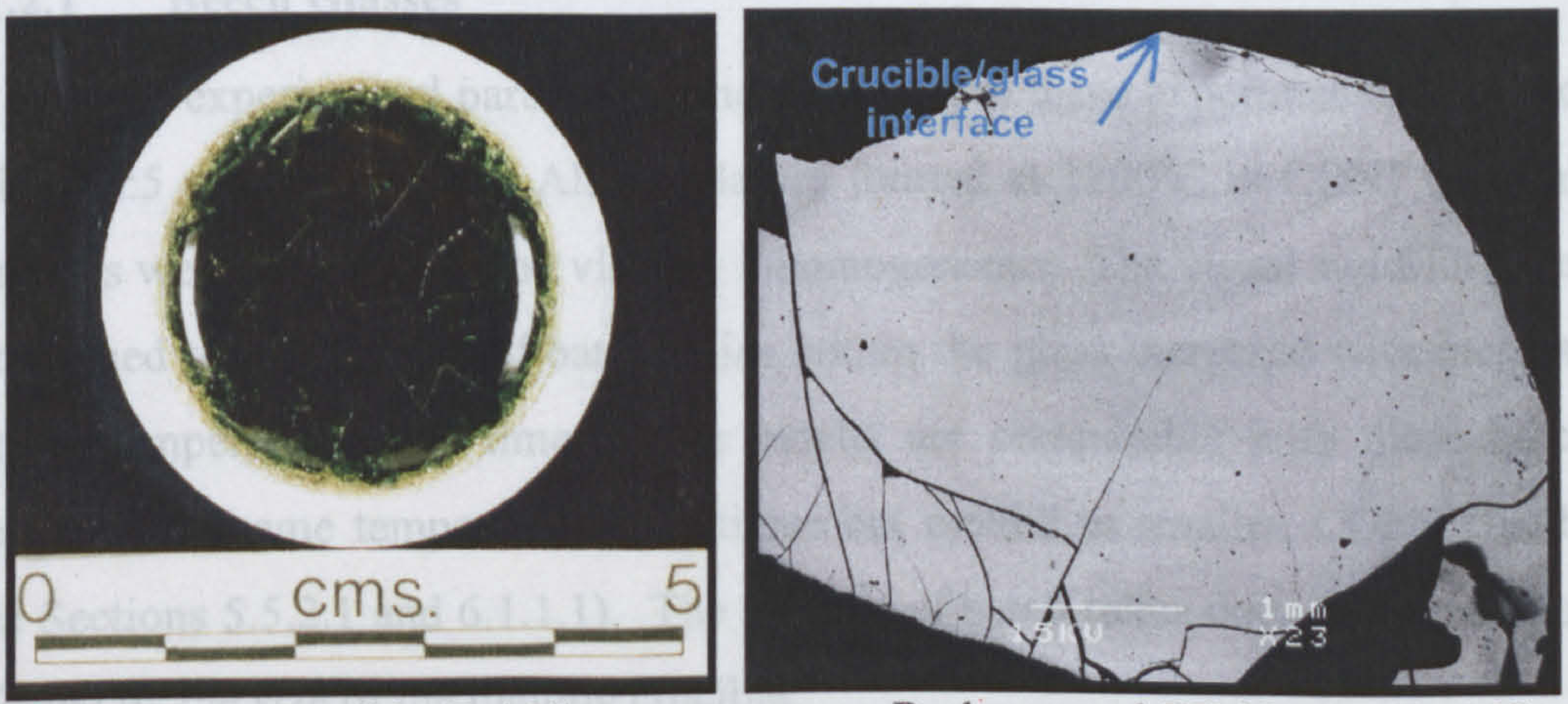
6.1.1.2 Bracken Glasses

The experimental details and results for the bracken glasses produced in alumina and mullite crucibles are recorded in Table VI:3 and Table VI:4. All the bracken glasses formed at 1200°C and 1300°C in mullite crucibles were dark green and visually homogeneous. All the glasses made at 1200°C and 1300°C in alumina crucibles were very mottled in appearance. Blue, brown and yellow streaks could be observed to be running through the predominantly green glass. The bright white colour of the alumina made these colours easier to observe (Plate 6:2).



Alumina Crucible (Br165)
Visually homogeneous glass

Backscattered SEM Image (Br 165)
Low levels of inhomogeneity



Mullite Crucible (Br166)
Visually Homogeneous Glass

Backscattered SEM Image (Br 166)
Low levels of inhomogeneity

Plate 6:2 A comparison between unfritted bracken glasses produced in alumina and mullite crucibles at 1200°C for 5 hours (Table VI:4)

Backscattered SEM imaging determined that both the bracken glasses made in alumina and mullite glasses at 1200°C contained the same low levels of inhomogeneity. The different colours of the alumina crucible glass did not relate to any differences in the colours on the SEM images. These colour changes are therefore **not** related to the presence of inhomogeneities. Both the glasses formed at 1300°C were **homogeneous** under the SEM. It can therefore be concluded that using either alumina or mullite as a crucible fabric does **not** significantly alter the homogeneity of the glass produced, but may alter its visual appearance. The increase in homogeneity with increasing melting temperature is comparable to the results obtained in Chapter 5.

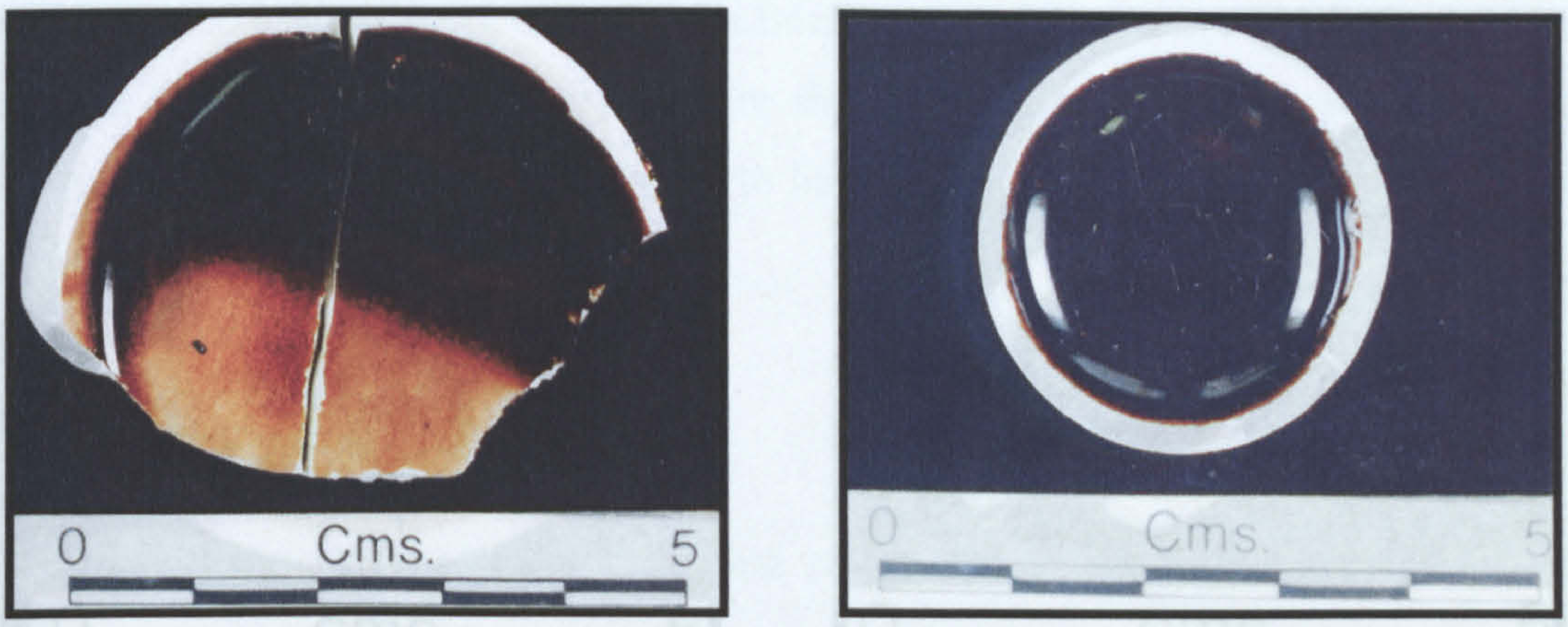
6.1.2 The Effect of Melting Crucible Dimension on Homogeneity

The aim of these experiments was to investigate whether altering melting crucible dimensions will influence homogeneity. The melting crucible dimensions were altered from the standard CON9 (54.5mm height and 35.0mm base diameter) to a smaller CYL7 (3.6mm height and 28.6mm base diameter) and larger CON7 (60.3 height and 42.8mm base diameter) (see Appendix A). Unfritted and mixed fritted batches were placed in these crucibles and heated at 1200°C or 1300°C for 5 hours.

6.1.2.1 Beech Glasses

The experimental parameters and results from these experiments are listed in Table VI:5 and Table VI:6. All the glasses formed at 1200°C in CON7 and CYL7 crucibles were dark purple and visually inhomogeneous. The visual and SEM results determined that the extent of batch relics within the glass increased with increasing fritting temperatures and times. The results are comparable with those batches melted at the same temperatures and times but melted in smaller, CON9 crucibles (see Sections 5.5.2.1 and 6.1.1.1). The number of batch relics does **not** appear to be affected by the size of the melting crucible.

All the glasses produced at 1300°C were dark purple and visually homogeneous (Plate 6:3). A comparison was made between these glasses and those melted in smaller, CON9 crucibles melted at comparable temperatures and times (see Sections 5.5.2.1 and 6.1.1.1). No difference could be detected visually or in backscattered SEM mode between the two sets of glasses.



Beech Glass CON7 Crucible
Visually Homogeneous Glass (Be146)

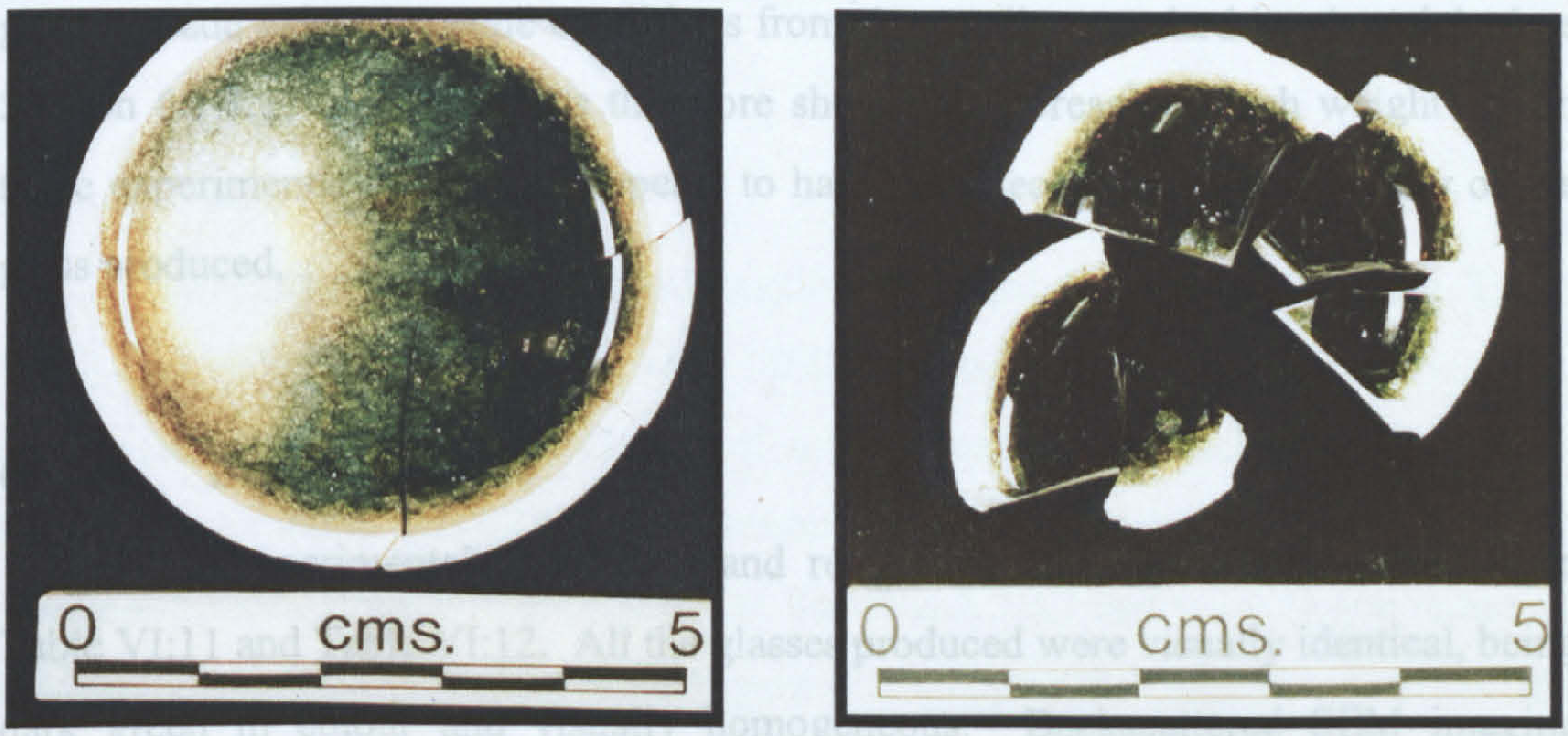
Beech Glass CYL7 Crucible
Visually Homogeneous Glass (Be147)

Plate 6:3 A comparison between unfritted beech glasses melted in CON7 and CYL7 melting crucibles at 1300°C for 5 hours (Table VI:6)

6.1.2.2 Bracken Glasses

Bracken glasses were produced in CON7 and CYL7 crucibles. The experimental details and results are recorded in Table VI:7 and Table VI:8. The glasses formed at melting temperatures of 1200°C from bracken frits were a brown/green colour and visually inhomogeneous. The level of inhomogeneity increased with increasing fritting temperature. The unfritted batches produced darker green/brown, visually homogeneous glasses but examination using the SEM determined that they contained low levels of inhomogeneity. The results were comparable to the glasses made from the same batches using CON9 crucibles (see Sections 5.5.2.2 and 6.1.1.2). The glasses formed at a melting temperature of 1300°C were all **visually homogeneous,** but examination using the SEM determined that those formed from frits made at 500°C for 1 hour contained low levels of **inhomogeneity**.

No difference could be detected either visually or microscopically between any of the glasses made using the same batches in different sized crucibles at either melting temperature (Plate 6:4). The results are also comparable to the glasses made from the same batches using CON9 crucibles (see Sections 5.5.2.2 and 6.1.1.2). It can be concluded from these results that altering the melting crucible size within these experimental parameters does not affect homogeneity.



Bracken Glass CON7 Crucible
Visually Homogeneous Glass (Br169)

Bracken Glass CYL7 Crucible
Visually Homogeneous Glass (Br170)

Plate 6:4 A comparison between unfritted bracken glasses melted in CON7 and CYL7 melting crucibles at 1200°C for 5 hours (Table VI:8)

6.1.3 The Effect of Melt Size on Homogeneity

The aim of these experiments was to determine how increasing the total batch weight would influence homogeneity. Due to the limitations of the furnace dimensions it was not possible to replicate a batch that would fill a typical medieval glassmaking crucible (see Section 2.4.5.2 for a discussion of the archaeological evidence for crucible dimensions). For these reasons only unfritted glass made from 6g sand and 12g ash, and 12g sand and 24g ash (standard batch weight = 3g sand, 6g ash) was produced. The ash to sand ratio and the rest of the batch parameters remained as described in section 4.7.2, and the furnace parameters used are as described in Section 6.1.1. The results from both the beech and bracken ash glasses are described in Section 6.1.3.1 and 6.1.3.2.

6.1.3.1 Beech Glasses

The experimental parameters and results for these glasses are detailed in Table VI:9 and Table VI:10. The glasses produced at 1200°C were dark purple in colour and visually inhomogeneous. Backscattered SEM imaging determined that these glasses were also inhomogeneous on a microscopic level. The glasses produced at 1300°C were both visually and microscopically homogeneous At either melting temperature no difference could be determined between the glasses made from different batch sizes. The glasses are also the same as those glasses made using the same conditions from the smaller standard batch weight (see Section 6.1.1.1). These results therefore show that increasing batch weight within these experimental parameters appears to have no affect on the homogeneity of the glass produced.

6.1.3.2 Bracken Glasses

The experimental parameters and results for these glasses are detailed in Table VI:11 and Table VI:12. All the glasses produced were visually identical, being dark green in colour and visually homogeneous. Backscattered SEM imaging determined that both the glasses formed at 1200°C contained low levels of inhomogeneity, but those formed at 1300°C were homogeneous. The results are the same as those glasses made using the same conditions from the smaller standard batch weight (see Section 6.1.1.2). These results therefore show that as with the beech, increasing batch weight within these experimental parameters appears to have no affect on the homogeneity of the glass produced.

6.1.4 The Effect of Melting Furnace Atmosphere on Homogeneity

The aim of these experiments was to investigate how furnace atmosphere influences homogeneity. A gas fired melting furnace (see Appendix A) was used to provide a reducing atmosphere. It was not possible to determine the degree of reduction by measuring the partial pressure of oxygen so the position, colour and shape of the flame was used to estimate the furnace conditions instead. A combination of unfritted and crushed fritted batches were placed in separate mullite crucibles (CON9) and preheated on the edge of the furnace for 1 hour to reduce the chance of cracking due to thermal shock. The batches were then heated at 1200°C and 1300°C for 5 hours, removed from the furnace and allowed to air cool.

These melts had to be repeated several times, as the crucibles were very susceptible to thermal shock. Preheating the crucibles did not appear to be as effective at preventing this problem as when using an electric furnace (neutral furnace atmosphere). The reasons for this may have been due to hot spots caused by uneven contact between the crucible fabric and flames. The results for the beech and the bracken glasses are given in Section 6.1.4.1 and 6.1.4.2.

6.1.4.1 Beech Glasses

The experimental details and results are listed in Table VI:13 and Table VI:14. Melting temperatures of 1200°C produced dark purple, visually inhomogeneous glasses. The degree of inhomogeneity increased with increasing fritting temperature. The difference between the visual homogeneity of glasses from identical batches formed in a neutral (see Sections 5.5.2.1 and 6.1.1.1) and reducing furnace atmosphere is illustrated in Figure 6:1. Where the batches are fritted the fritting time was 1 hour. The two glasses are the same, with the exception of the glasses produced from frit made at 500°C for 1 hour. In both types of furnace conditions homogeneity is less in the unfritted compared to fritted glasses. These results show that it is difficult to determine any significant difference between the results from either furnace atmosphere and at melting temperatures of 1200°C beech glasses will be **inhomogeneous**.

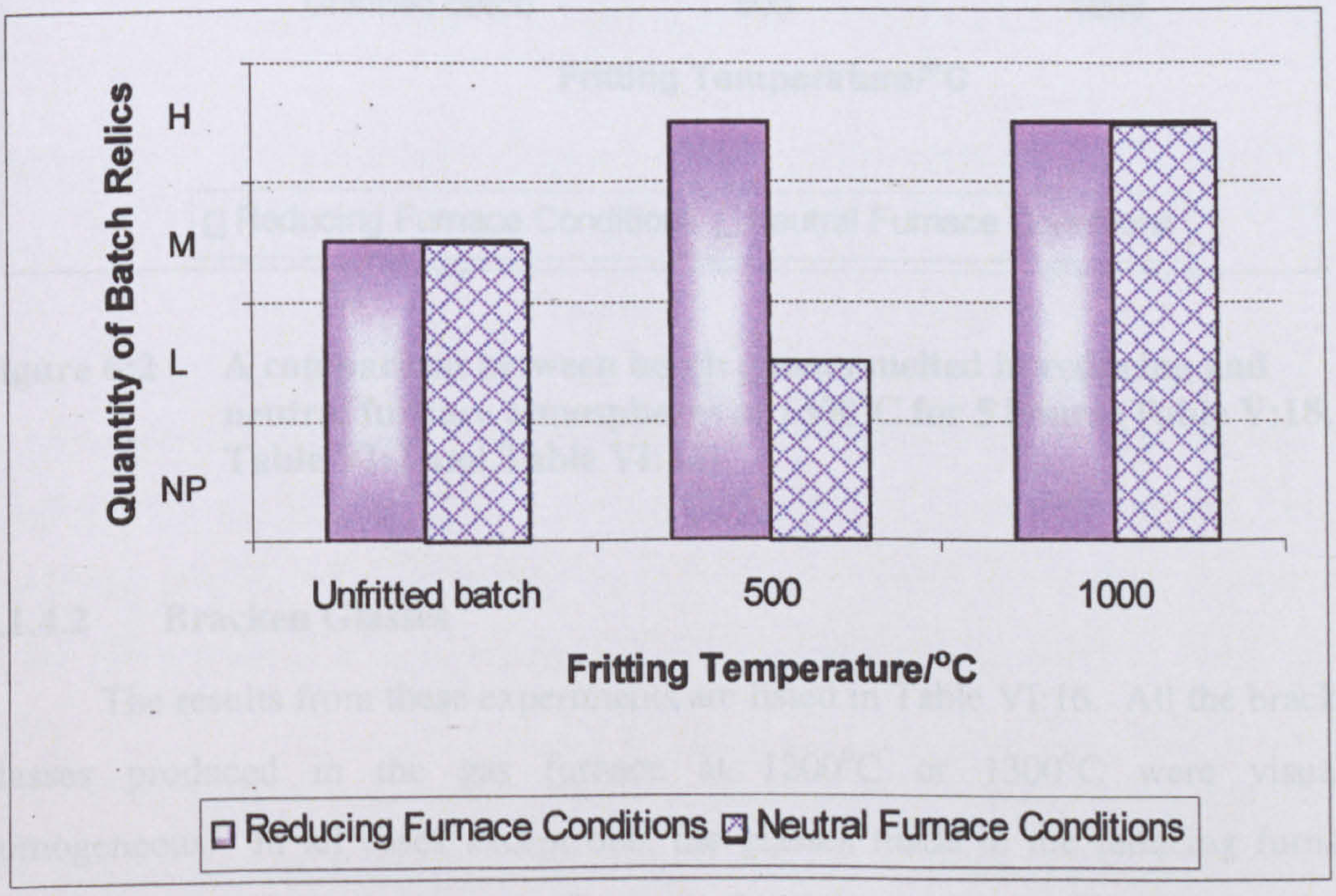


Figure 6:1 A comparison between unfritted and fritted beech glasses melted in reducing and neutral furnace atmospheres at 1200°C for 5 hours (Table V:16, Table VI:2 and Table VI:14)

The beech glasses produced at 1300°C in a reducing atmosphere were all dark purple and visually homogeneous. SEM examination confirmed that they were all microscopically homogeneous except for the glass formed from frit made at 500°C for 1 hour. The difference in microscopic homogeneity between these glasses and those made in neutral furnace atmospheres from identical batches (see Sections 5.5.2.1 and 6.1.1.1) is illustrated in Figure 6:2. The variable homogeneity of the glasses show that it is difficult to draw any definite conclusions as to whether the formation of a homogenous glass will be facilitated by the use of a reducing furnace atmosphere.

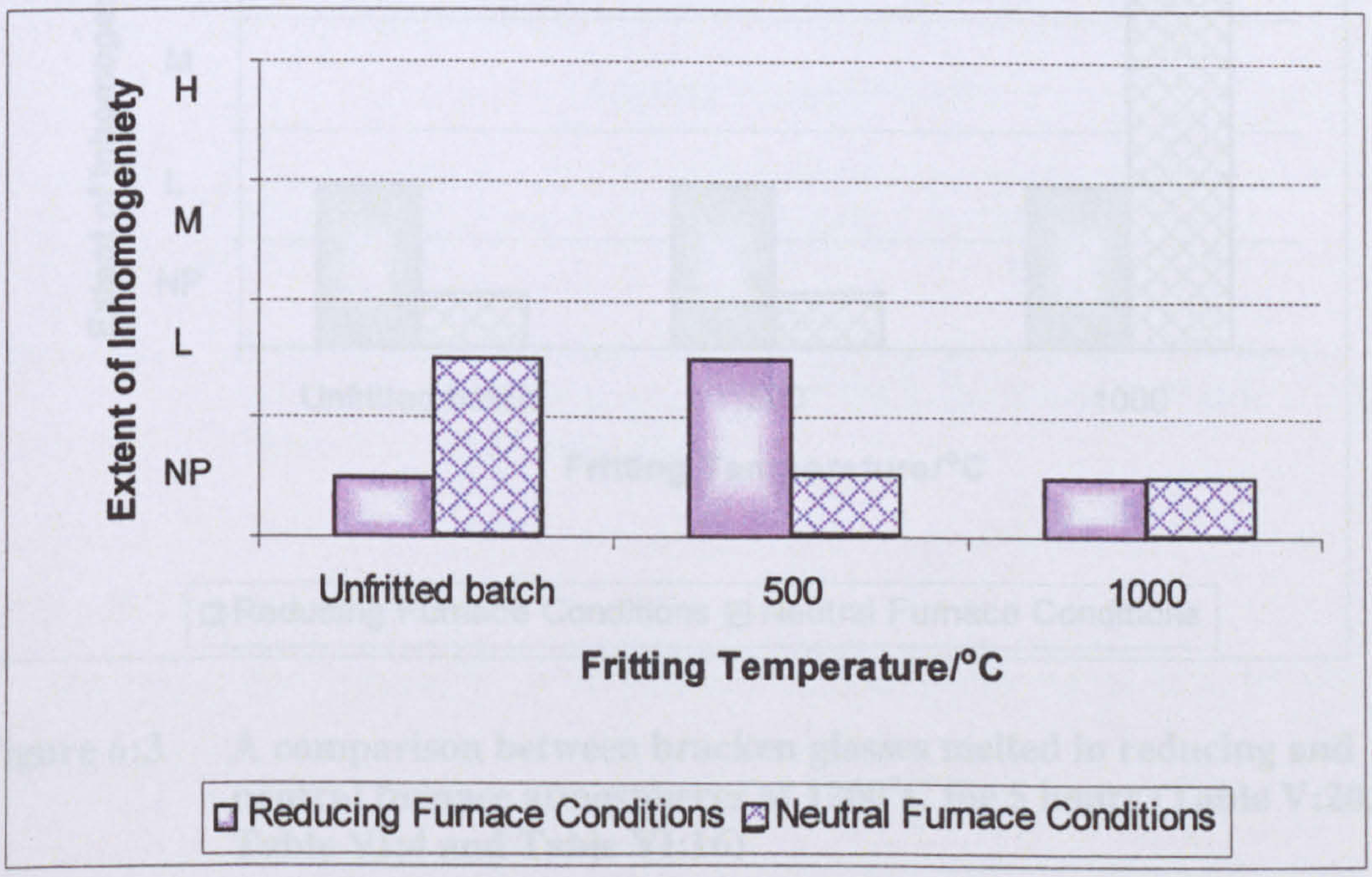


Figure 6:2 **A comparison between beech glasses melted in reducing and neutral furnace atmospheres at 1300°C for 5 hours (Table V:18, Table VI:2 and Table VI:14)**

6.1.4.2 Bracken Glasses

The results from these experiments are listed in Table VI:16. All the bracken glasses produced in the gas furnace at 1200°C or 1300°C were visually homogeneous. In all cases except one, the glasses made in the reducing furnace atmospheres were a darker green/brown colour than those made in the electric furnace (see Sections 5.5.2.2 and 6.1.1.2). The exception was the glass produced in the gas furnace from frit, which had been heated at 500°C for 1 hour. This glass was a green/brown colour compared with the blue/green colour of the one made in a neutral furnace atmosphere. Where the batch was fritted the fritting time was 1 hour.

The SEM results show that all the glasses made at 1200°C in the reducing furnace conditions contain inhomogeneities. The levels of homogeneity differ to those seen in the same glasses produced in neutral furnace conditions, this is illustrated in Figure 6:3.

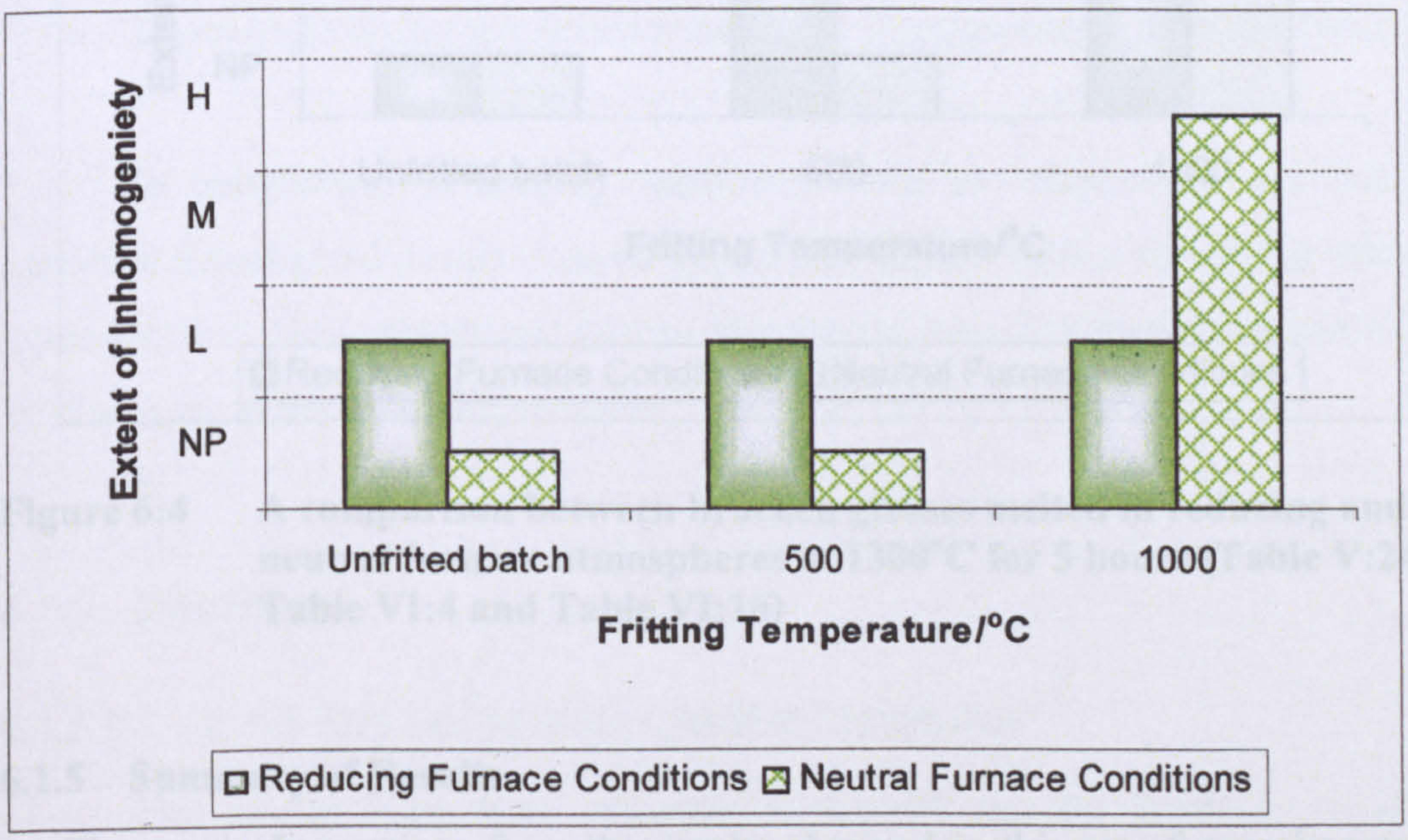


Figure 6:3 **A comparison between bracken glasses melted in reducing and neutral furnace atmospheres at 1200°C for 5 hours (Table V:20, Table VI:4 and Table VI:16)**

Increasing the melting temperature to 1300°C reduced the level of inhomogeneity. The levels of homogeneity in the glasses made in reducing furnace conditions are the same as those seen in the same glasses produced in neutral furnace conditions (Figure 6:4). The exception to this is the higher levels of inhomogeneity in the glass made in a reducing furnace atmosphere from frit made at 500°C for 1 hour.

The variable homogeneity of the bracken glasses in these experiments show that it is difficult to draw any definite conclusions as to whether the formation of a homogenous glass will be facilitated by the use of a gas furnace.

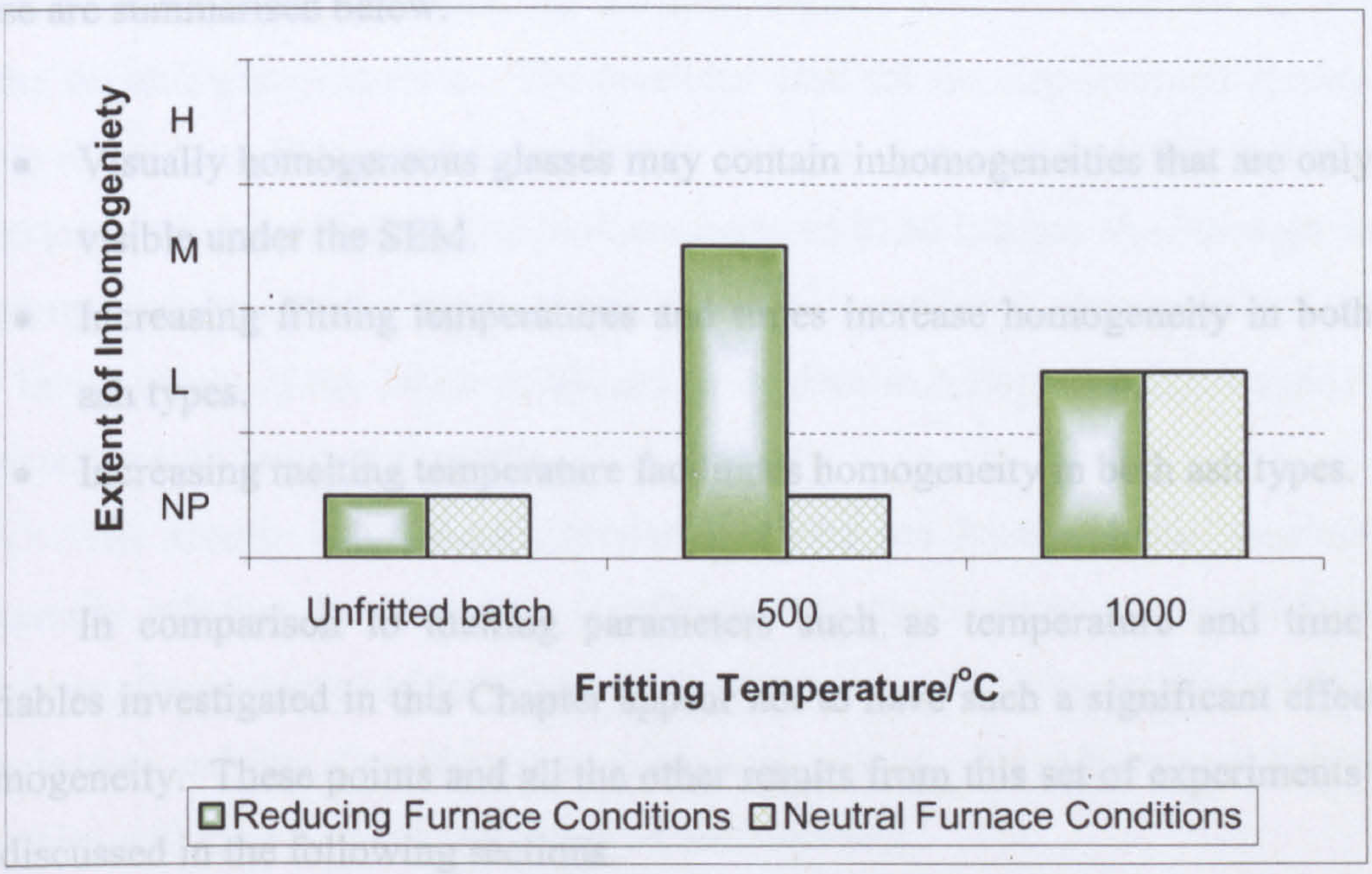


Figure 6:4 **A comparison between bracken glasses melted in reducing and neutral furnace atmospheres at 1300°C for 5 hours (Table V:24, Table VI:4 and Table VI:16)**

6.1.5 Summary of Results

The main observations from the results obtained in this set of experiments are summarised below:

- Altering the melting crucible fabric (using mullite and alumina) does **not** affect homogeneity in beech ash glasses.
- Altering the melting crucible fabric affects the visual appearance of the bracken glasses but does not affect homogeneity.
- Homogeneity is **not** affected by variations in melting crucible dimensions (using CON9, CON7and CYL7 crucibles) for either ash type.
- Homogeneity is not affected by an increase in melt size within the experimental limits (9-36g total batch weight) does not affect homogeneity in either ash type.
- Altering the furnace atmosphere does not give a conclusive change in homogeneity in either ash type.

The results from this Chapter also confirm many of the results from Chapter 5 these are summarised below.

- Visually homogeneous glasses may contain inhomogeneities that are only visible under the SEM.
- Increasing fritting temperatures and times increase homogeneity in both ash types.
- Increasing melting temperature facilitates homogeneity in both ash types.

In comparison to melting parameters such as temperature and time the variables investigated in this Chapter appear not to have such a significant effect on homogeneity. These points and all the other results from this set of experiments will be discussed in the following sections.

6.1.6 Discussion

6.1.6.1 Batch Size and Melting Crucible Dimensions

The results from these experiments suggest that no difference could be detected in the homogeneity of glass produced in melting crucibles with variable dimensions or small (9.00g) and large (36.00g) batch sizes. The experimental melts are much smaller than archaeological examples (see Section 2.4.5.2) and therefore can homogenise comparatively quickly. However, scaling up the melts in these experiments has not produced inhomogeneity. On the basis of these results it is difficult to determine whether batch size and crucible dimensions do have a significant influence on homogeneity. It is thought likely that the other factors such as melting temperature may be more influential, and that longer melting times would be required with increasing melt size.

6.1.6.2 Crucible Fabric

The aim of this set of experiments was not to replicate archaeological crucible fabrics but to investigate how altering the crucible fabric would affect homogeneity. The results from both the beech and bracken experiments determined that no conclusive correlation between homogeneity and crucible fabric could be observed. The highly corrosive nature of molten glass has been mentioned in Section 2.4.5.1 and it was noted that the most obvious point for this to be observed is at the ceramic/glass interface. The crucibles used for the experimental glasses are made of modern, highly refractive fabrics and the ceramic dissolution would have been too small to be observed on the backscattered SEM images. It is thought that it is more likely to observe these inhomogeneities in medieval glass crucibles due to the lesser nature of the fabric compared to modern materials, and the longer times required to melt larger scale melts.

The results from these experiments have not been able to conclusively determine whether homogeneity is affected by the change in crucible fabric. However, the properties of the clay, such as thermal conductivity, will influence melt temperature and therefore the extent of internal mixing. It has been seen that these variables will have a significant affect on homogeneity.

The choice of crucible fabric did affect properties of the glasses other than homogeneity. It was noted in Section 2.6 that none of the experimental glasses were subjected to annealing and therefore they would be liable to crack due to the presence of internal stresses formed on cooling. The glasses formed in the alumina crucibles all exhibited much less cracking and this is due to the greater insulating properties of this fabric in comparison to mullite. The bracken glasses formed in alumina crucibles were very mottled in colour but this was not linked to the presence of inhomogeneities. It was probably due to the presence of iron in different oxidation states (see Section 5.5.6.1). The alumina is also a bright white colour and it may therefore be that these colour differences are present in the mullite melts but cannot be so easily observed.

6.1.6.3 Melting Furnace Atmosphere

A comparison of the results obtained from the beech and bracken glasses produced in reducing and neutral furnace atmospheres did not produce conclusive results. It was difficult to regulate the temperature in the gas furnace as accurately as in the electric furnace (see Appendix A) and fluctuations in the temperature of the gas furnace may therefore have influenced the differences observed between the two sets of glasses. It is likely that if furnace atmosphere does have any effect on homogeneity it would be effectively removed by variables such as fritting and melting temperatures.

The reducing furnace atmosphere will influence glass colour depending on the colouring agents present in the melt. This was apparent in the bracken ash glasses made in a reducing furnace atmosphere, which are browner compared to those made in neutral conditions. The colour change is again due to the balance of Fe^{2+} and Fe^{3+} ions in the melt (see Section 5.5.6.1). The beech ash glasses produced in reducing and neutral furnace conditions were both dark purple, and no colour difference could be observed between identical melts produced in either furnace type. The reducing conditions are not sufficient to shift enough of the purple Mn^{3+} ions to yellow $Mn^{2+}$and cause a colour change, therefore the glass remains purple (see Section 4.7.5.1).

6.1.6.4 Melting Fritted and Unfritted Batches

It was noted in Section 2.3.1 that the inclusion of a fritting stage in medieval glass production is usually attributed to the reduction in melting temperature required when compared to melting unfritted raw materials. The results of the experiments in this and Chapters 4 and 5 have shown that unfritted beech and bracken ash batches will form glasses at the same melting temperatures. However, further experiments would be required to determine whether the behaviour of the two batch types is comparable as melting temperatures are reduced.

Glasses produced from unfritted raw materials tend to be more homogeneous than glasses formed from fritted batches. This may be because fritting forms compounds that require different melting temperatures and times, or because regions are formed in the frit that contain high levels of silica that would be difficult to melt. In addition to this, alkali may also be lost in the fritting stage (see Section 5.5.6.1). If this occurs then there may be insufficient alkali to react with all the silica present. The unfritted **bracken** glasses are much darker in colour than the fritted glasses, but there is no colour difference between unfritted and fritted **beech** ash glasses.

6.2 Overall Summary and Conclusions from Chapters 4-6

Standard batches were used in these experiments to ensure repeatability between melts, and differing proportions of ash to sand and other sources of alkali have not been investigated here. Beech and bracken ashes have been used as generic alkali types, but many other species (for example oak) or combinations of species may have been used in medieval glass manufacture (see Section 2.2.2). These differences in plant ashes will affect the batch composition and hence have an effect on ease of melting. Specific conditions would have had to been used for each batch. However, for the majority of the glassmaking variables investigated here, common trends can be observed in the behaviour of both ash types. Therefore, the behaviour of other batches may also follow similar trends.

In addition to the information on homogeneity these experiments have also provided information on the stages of glass production (such as batch mixing and fritting) that are not well represented in the archaeological record. It has been seen that fritting in particular is a very complex stage in glass production and will have a significant effect on variables such as batch volume or glass colour depending on the operating parameters and the ash types used.

Finally it can be seen that to produce a homogeneous glass is difficult. It requires considerable knowledge and experience of raw materials and the glass making process. However, the production of a visually homogeneous glass does not mean that it is microscopically homogeneous. This has implications when the composition of the glass is considered. The size and position of the sample removed for analysis, and the location of analyses on that sample will all have an influence the composition obtained. This has important implications for the study of archaeological glasses (see Section 1.3).

The main conclusions from the beech and bracken glasses produced in Chapters 4-6 are summarised in Table 6:1.

Stage of Glass Production	**Variable**	**Homogeneity**	
		Beech	**Bracken**
Raw Materials	Smaller Sand Particle Sizes	Improved	Improved
	Mixing the Raw Materials Before Fritting and/or Melting	Improved	Improved
Fritting	Fritting Crucibles with Smaller Surface Area to Volume Ratios	No change	Improved
	Lower Fritting Temperatures	Improved	Improved
	Shorter Fritting Times	Improved	Improved
	Stirring During Fritting	Improved	Improved
	Mixing the Frit Before Melting	Inconclusive	Improved
Melting	Higher Melting Temperatures	Improved	Improved
	Longer Melting Times	Improved	Improved
	Variation in Melting Crucible Dimensions	No Change	No Change
	Crucible Fabric	No Change	No Change
	Oxidising or Reducing Melting Furnace Atmosphere	Inconclusive	Inconclusive
	Increased Melt Size	No Change	No Change

Table 6:1 Summary of Experimental Results

CHAPTER 7

Selection of Comparative Archaeological Material

7.1 Introduction

The results from Chapters 4-6 have determined that inhomogeneity will vary depending on the glass making parameters used, and that certain factors, such as raw material composition and melting temperatures, will have a more significant effect than others. It is therefore necessary to select comparative archaeological material that represents glassmaking practices that are relevant to homogeneity. The following criteria were therefore used as the basis for selecting the archaeological material for this research:

1. Sites that are producing glass from raw materials (sand and ashes) rather than remelting cullet, as this material will be more likely to exhibit inhomogeneity (see Section 2.2.5).
2. Documented use of different alkali sources relevant to those used in this research, as it can be seen from Chapters 4 to 6 that this has a significant effect on homogeneity.
3. Extensive excavated evidence of factors that will influence homogeneity such as crucible sizes and fabric, and furnace types (see Chapter 2).
4. A range of periods and geographical locations. This increases the possibility of covering different technologies (such as alkali type (see Section 2.2.2)) that may affect homogeneity.
5. A wide range of material including worked and finished glass, crucibles and waste products. The waste and crucible glasses are very important, as these are more likely to contain inhomogeneities (see Section 2.4.5.2).
6. A large assemblage of glass from which to sample from and the ability to remove relatively large samples for analysis (see Section 3.3.2.2).
7. Well documented excavation.
8. The date of the site fits into the period under study (12th to 17th centuries).

The following medieval glassmaking regions were therefore selected: the Surrey/Sussex Weald and Staffordshire, England, and Hils, near Grünenplan, northern Germany. These sites are thought to represent the use of different alkali sources. Oak in the Weald, bracken in Staffordshire and beech in Hils (see Section 2.2.2 and below). They contain a large number of excavated glass production sites that together cover the period from 12th-17th century. There is documentary evidence (such as land leases and sales of fuel and raw materials) associated with some of the sites, as well as a wide variety of archaeological remains including furnace structures, crucible fragments, worked and finished glass fragments, and cullet. This data is important as it provides evidence for glassmaking practices. The sites chosen from each region are listed below:

The Weald

- Blunden's Wood (14th century) (Wood 1965).
- Knightons (16th century) (Wood 1982).
- Sidney Wood (17th century) (Kenyon 1967).

Staffordshire

- Little Birches, Wolseley (14th and 16th centuries) (Welch 1997).

Hils

- Glasshouses A2-A18 (12th-15th centuries) (Six 1976).

The specific reasons for these choices and the details of glass production at each site will be discussed in Sections 7.2 to 7.4.

7.2 The Medieval Glass Industry in the Weald

The Wealden glass industry has been studied extensively. The first excavations were carried out by Winbolt (1932, 1933), and were built on by Kenyon (1959, 1967). Glass production probably took place in the Weald at the start of the 13th century and continued until the mid 17th century. There were over forty glasshouses in operation during this period (Figure 7:1 and Table VII:1) but documentary and archaeological evidence is limited until the mid 16th century (Kenyon 1967).

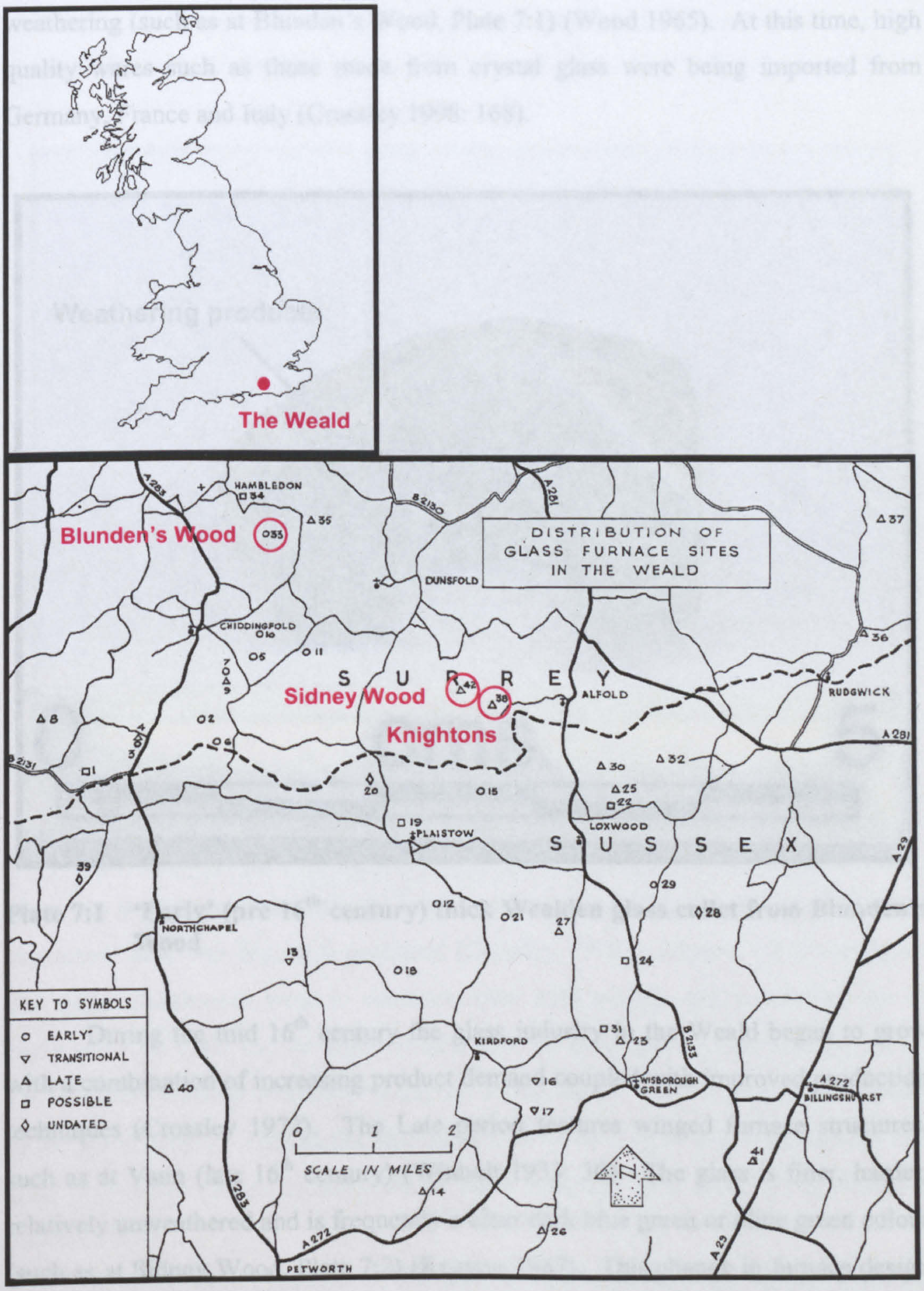


Figure 7:1 Map of glass furnace sites in the Weald (Table VII:1) after (Kenyon 1967)

Wealden glass and glass sites are frequently referred to using the terms 'Early' (pre 16th century) or 'Late' (post 16th century) (Kenyon 1967). The Early period is characterised by rectangular, 'northern' style glass furnaces (see Section 2.4.1), and thick glass that is frequently milky in appearance and more prone to weathering (such as at Blunden's Wood, Plate 7:1) (Wood 1965). At this time, high quality wares such as those made from crystal glass were being imported from Germany, France and Italy (Crossley 1998: 168).

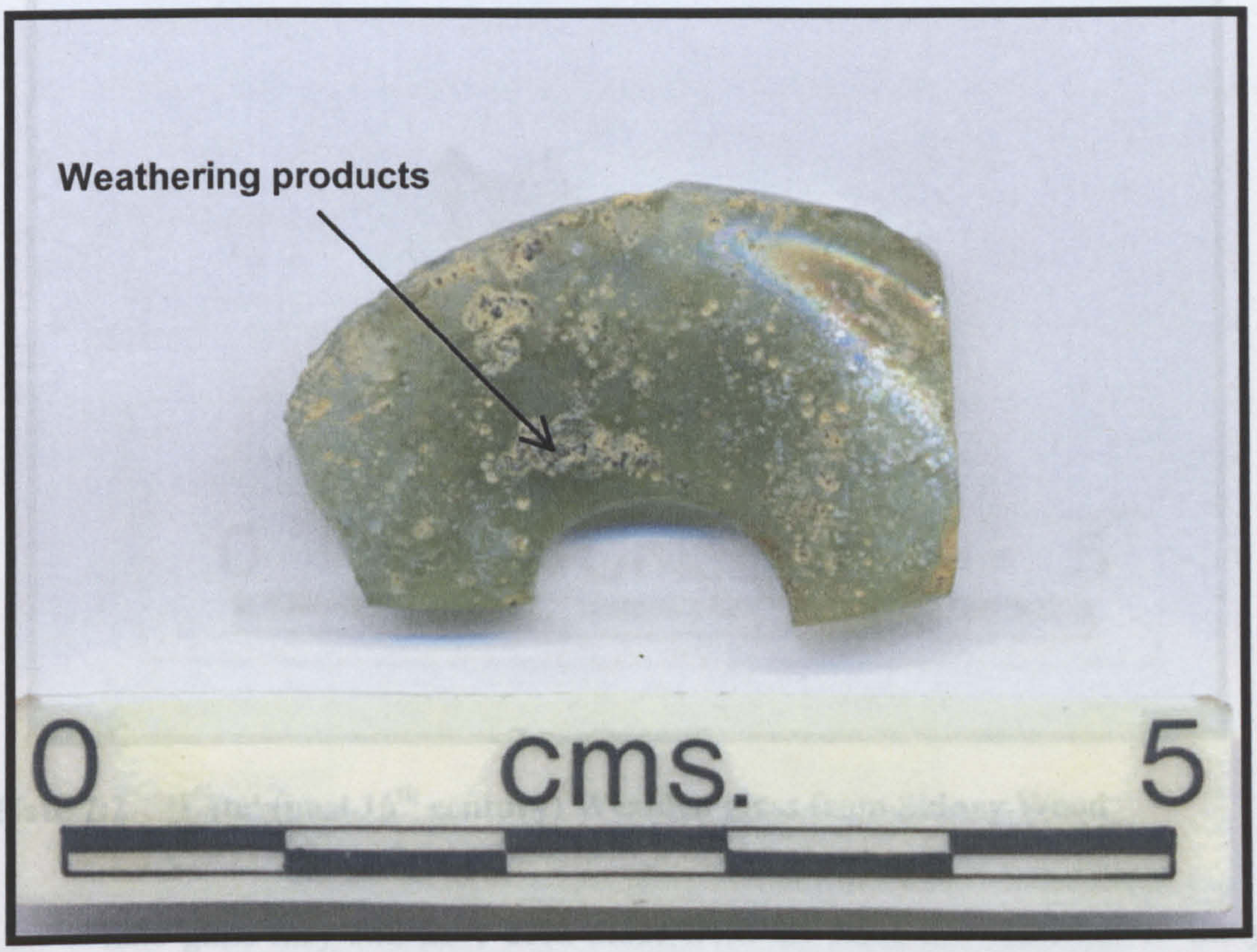


Plate 7:1 'Early' (pre 16th century) thick Wealden glass cullet from Blunden's Wood

During the mid 16th century the glass industry in the Weald began to grow with a combination of increasing product demand coupled with improved production techniques (Crossley 1972). The Late period features winged furnace structures, such as at Vann (late 16th century) (Winbolt 1933: 30). The glass is finer, harder, relatively unweathered and is frequently a clear dark blue green or olive green colour (such as at Sidney Wood, Plate 7:2) (Kenyon 1967). This change in furnace design reduced fuel costs and facilitated the manufacture of a higher quality glass that could be sold without increasing prices. These technological advances are frequently attributed to the influx of immigrant glassworkers from Lorraine and Normandy in northern France. Many of these workers came to live in the Chiddingfold area and the first recorded arrival is dated to 1567 (Crossley 1990, 1998, Kenyon 1967). However, the increased demand for high quality glass may have forced the English glassmakers to respond and adapt their production methods (Crossley 1972, 1990, Kenyon 1967: 13, Welch 1997).

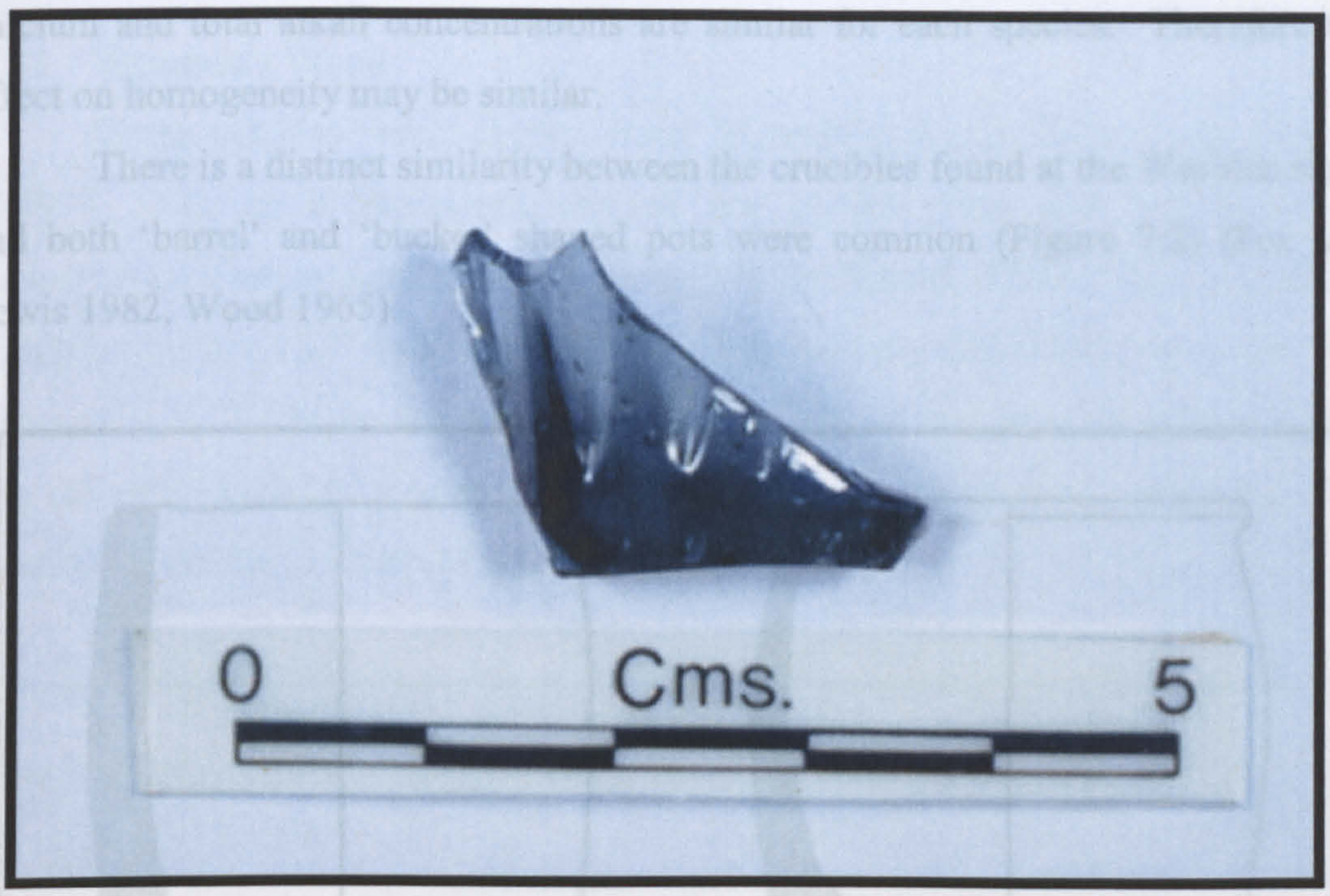


Plate 7:2 'Late' (post 16th century) Wealden glass from Sidney Wood

Late glass may still have been made from the same raw materials as Early glass, but production practices may have been improved so that a more uniform and consistent glass was regularly produced (Crossley 1972). Kenyon (1967) suggests that some glasshouses were in operation over both periods and a combination of Early and Late glass can be found at sites such as at Knightons (see Section 7.2.2). The Wealden industry eventually collapsed during the 17th century due to the scarcity of the wood supply. This meant that other fuels such as coal had to be utilised and glass production moved to areas where these materials were more easily available (Hunter 1981).

There is some evidence for the types of raw materials used by the Wealden glassmakers. Local sand sources such as those at Hambledon Common, near Chiddingfold may have been utilised (see Figure 7:1) (Crossley 1988, Kenyon 1967:

35). Plant ashes may have been obtained from a local source, as the medieval glassmaking areas in the Weald were heavily forested at this time (Crossley 1998). The environmental evidence suggests that oak and not beech trees were predominant during the medieval period (Sanderson and Hunter 1981), and therefore it is likely that oak may have been the main alkali source used (see Section 2.2.2). Although this ash was not used in the experimental part of this research (Chapters 4-6) it can be seen from the analyses of Wealden oak and beech in Section 2.2.2.1 that the calcium and total alkali concentrations are similar for each species. Therefore the effect on homogeneity may be similar.

There is a distinct similarity between the crucibles found at the Wealden sites, and both 'barrel' and 'bucket' shaped pots were common (Figure 7:2) (Fox and Lewis 1982, Wood 1965).

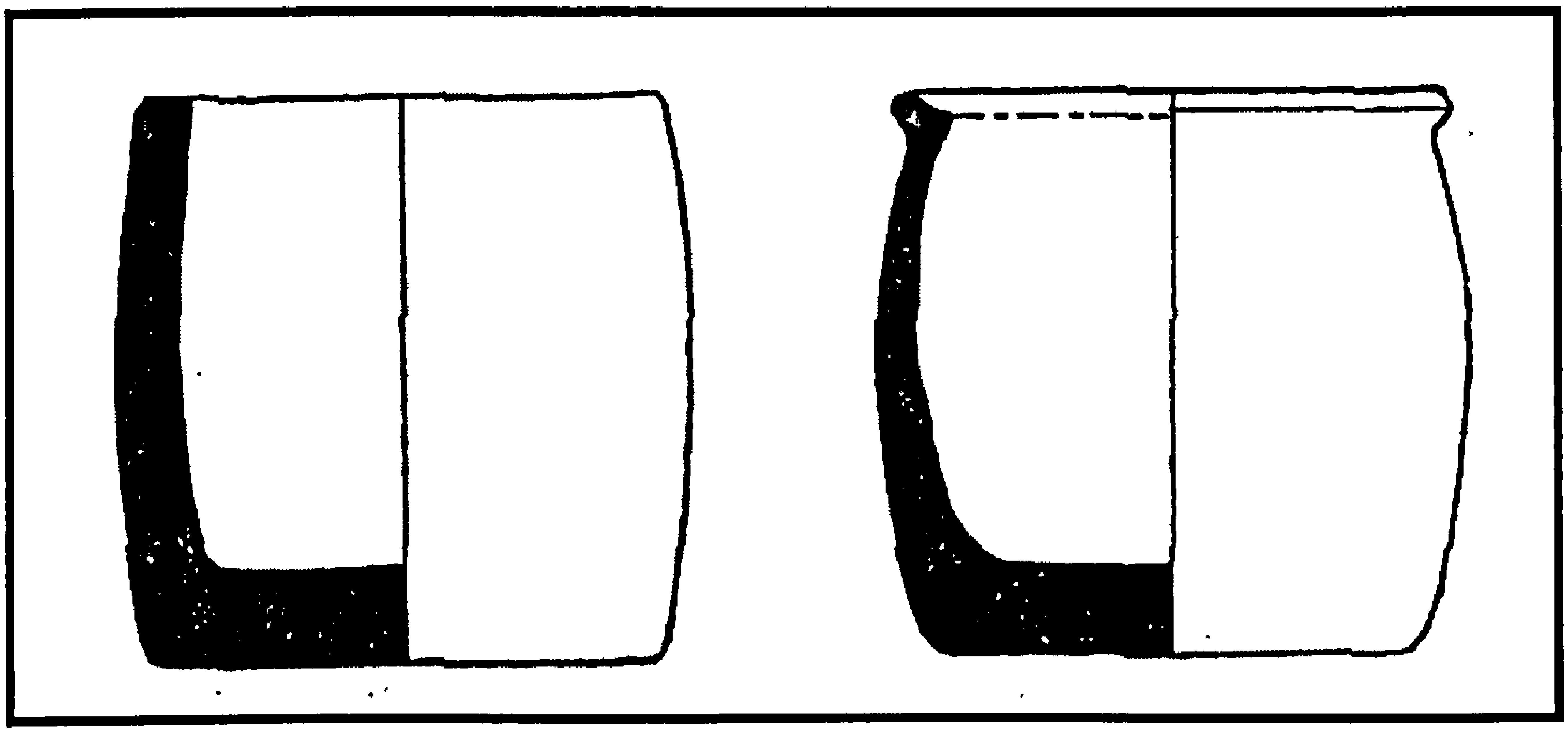


Figure 7:2 **Medieval Wealden glass crucibles from Blunden's Wood glasshouse, barrel (right) and bucket (left) shaped (Wood 1965: Figure 8)**

The crucibles range in size but Kenyon (1967: 49-51) suggests that the commonest forms were approximately 25-40cm in height and diameter with walls ranging from approximately 0.5-3cm in thickness. The rim shapes are varied and this has been attributed to the signature of different potters. The Wealden crucibles have good refractory properties and Kenyon (1967) suggests that the importance of obtaining the correct crucible fabric to withstand high temperature and resist refractory corrosion was well known (see Section 2.4.5.1). The crucible fabric and dimensions are important, as these will affect homogeneity (see Sections 2.4.5 and

6.1.6). Merchant (1998: 79,90,102) suggests that although Wealden clays would have been suitable for use as glass crucibles due to their good refractory properties, his analyses of Blunden's Wood, Knightons and Sidney Wood crucibles could not ascertain the exact clay sources used.

The Wealden glasshouses selected for this research span the Early to Late medieval periods, and will be discussed in Sections 7.2.1 to 7.2.3.

7.2.1 Blunden's Wood

Glass samples were chosen from Blunden's Wood, Hambledon, Surrey (SU974 374), as it represents one of the earliest sites and has the most comprehensive remains of glass manufacture in the Weald. The site has been dated to approximately 1330 and has remained comparatively undisturbed since the last phase of use. It was excavated in 1960 by E. S. Wood and provides a rare insight into the early phases of medieval glass production in this region (Wood 1965). The location of the site is illustrated in Figure 7:3.

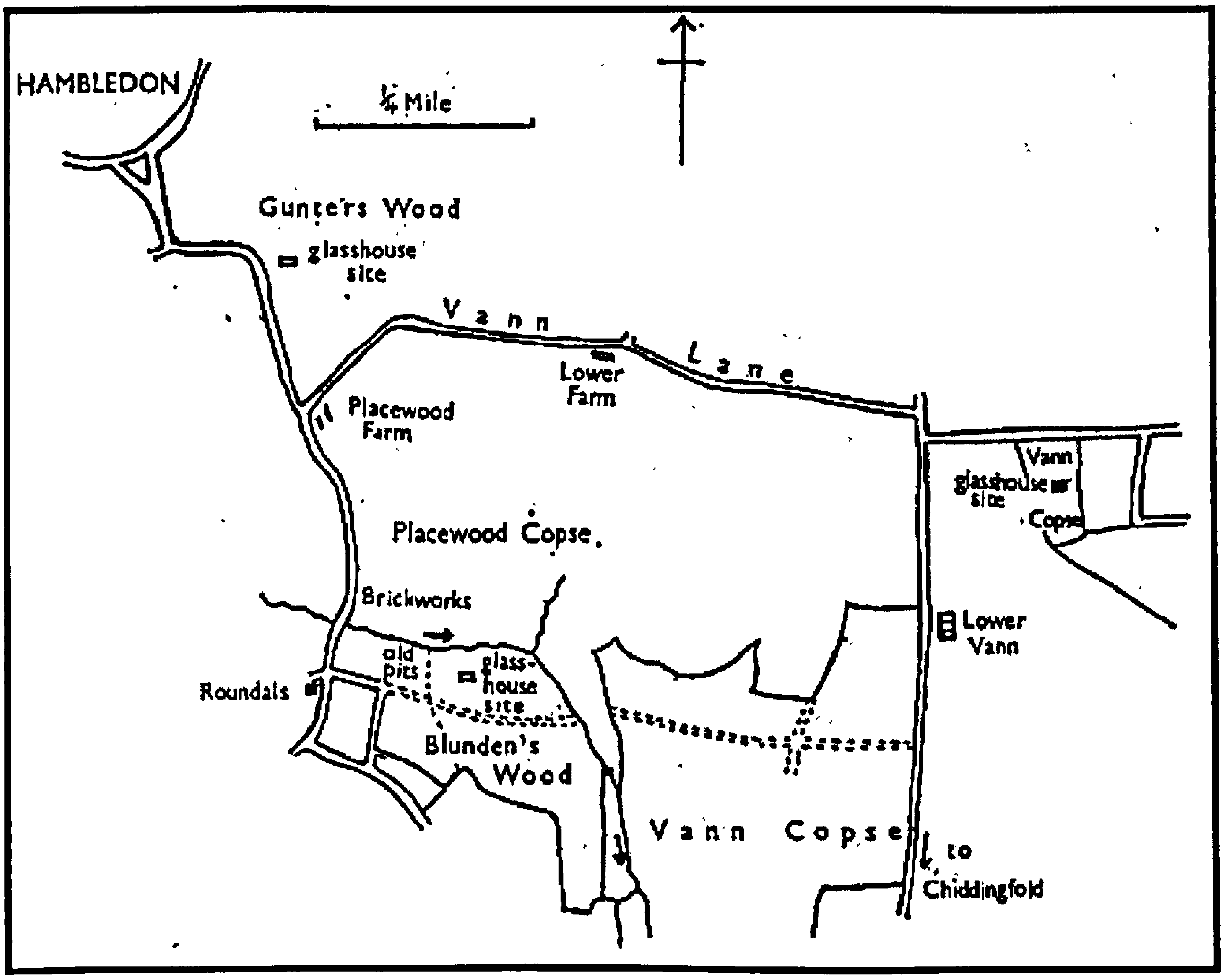


Figure 7:3 Map of the Hambledon area showing Blunden's Wood glasshouse (Wood 1965: Figure 1)

Blunden's Wood had three furnaces structures and these are illustrated in Figure 7:4. Furnace A was rectangular and of the northern type. It is thought to have been the main melting furnace due to the large amount of waste glass and scum or gall found associated with it. The sieges each contained two slight depressions that are thought to have been sites for crucibles. It is unusual in design as it contains what Wood (1965: 59) suggests is a cavity wall, which may have provided extra thermal insulation. This feature was also found at the 16th century furnace in Jamestown, Virginia (Harrington 1952). However, Ashurst and Wood (1973) suggest an alternative design, with no insulation cavity and an outer wall continuous to the sieges.

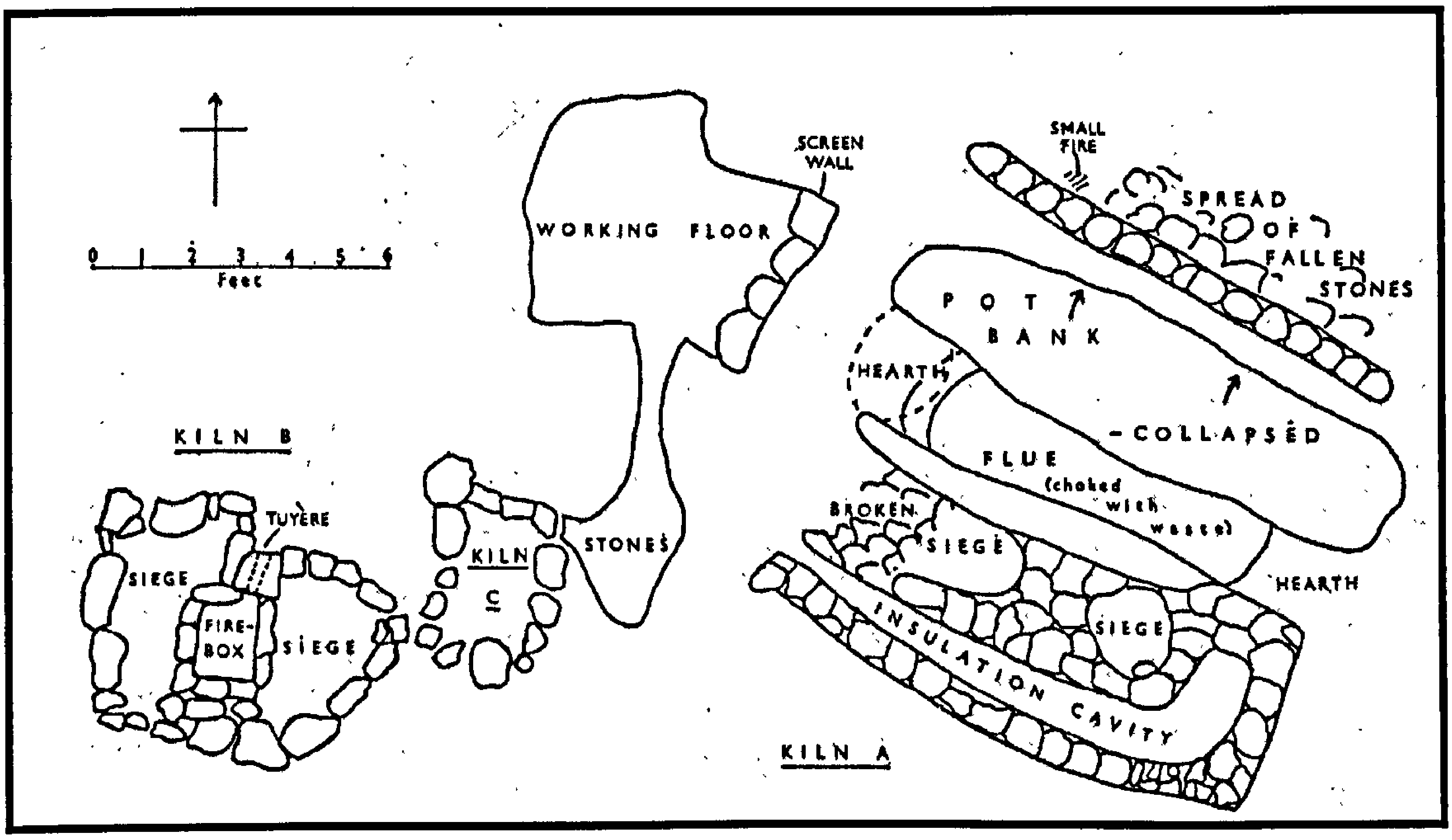


Figure 7:4 Excavation plan of Blunden's Wood glasshouse (Wood 1965: Figure 2)

Furnace B was circular and consisted of two chambers connected by a firebox. It is thought possibly to have resembled a beehive in shape. The function of this furnace is not certain. Glass was found attached to the structure in the eastern cavity and many crucible and glass fragments were found associated with the furnace. Furnace C was the smallest in size and situated between furnaces A and B. Wood (1965: 64) has suggested that furnace B may have been used for both fritting (east cavity) and annealing (west cavity) whilst furnace C may have been for firing and preheating crucibles. Wood (1965: 64) also notes that annealing may have been carried out in the roof of furnace A, although the superstructure was not excavated. There is a fragment of a possible frit type material attached to a crucible from Blunden's Wood. Analysis by Merchant (1998: 79, 168) found that it did consist of sand that had reacted with an alkali and he suggested that this would have occurred at a maximum temperature of 900°C. However, due to the problems of identification (see Section 2.3.1) it cannot be certain whether this material really is frit.

Window and vessel glass was produced at Blunden's Wood and although some imported cullet was also found, the majority of the pieces are typical of local manufacture based on abundance (Wood 1965). The glass is of the Early type and is weathered to varying degrees. It ranges in colour from pale green yellow to pale blue green and in some cases is slight opaque (Wood 1965). Analyses of Blunden's Wood glass by Merchant (1998: Tables 6.10 and 6.12) and Waterton (in Wood (1965: 71)) confirm that the glass has a typical medieval potash-lime composition with approximately 10-14 Wt.% total alkali and 11-17Wt.% lime (Table VII:2). Merchant (1998: 147) suggests that the high calcium levels may be due to the intentional addition of limestone or the use of calcium rich plant ashes. It can be seen from Section 2.2.2.1 that beech and oak ashes both contain relatively high calcium levels, but the Weald was also a well known source of lime during the medieval period (Godfrey 1975). It was noted in Section 2.2.2.1 that high calcium levels could be a source of inhomogeneity but this will depend on other factors such as melting temperatures.

Wood (1965: 68) notes that a fragment of glass from Blunden's Wood could be melted at 1150°C. He therefore suggests that it may have been produced between 1200-1250°C. Merchant (1998: 32) suggests from the results of crucible analyses that glass melting temperatures at Blunden's Wood were in excess of 1000°C and more likely between 1200-1300°C. It was noted above and in Section 7.2 that oak may have been used as the alkali component in Blunden's Wood glass, and it was suggested in Section 2.2.2.1 that oak may have similar effects on homogeneity as beech ash. The experimental results in Chapters 4-6 have shown that at 1300°C, small beech ash batches can produce a homogeneous glass, but at 1200°C the glass is very inhomogeneous. Therefore, based on the suggested melting temperatures above, the glass produced at Blunden's Wood may be likely to contain inhomogeneity, especially when the larger crucible dimensions and melt size are taken into consideration (see Section 2.4.5).

Unusually for the Weald, the majority of the crucibles found at Blunden's Wood were barrel, not bucket shaped (see Figure 7:2). The crucibles were approximately 10-15" (25-37.5cm) diameter, and 12-15" (30-37.5cm) in height, with walls of 0.25"–1" (0.6-2.5cm), and thicker bases (1.75-2" (4.3-5cm)) Wood (1965: 68-9). These large crucible dimensions (over 100 times larger in volume than a standard experimental CON9 crucible, see Appendix A) means that the melt size, and the thermal conductivity of the crucible fabric will have a greater affect on homogeneity (see Section 2.4.5.2) than in the experimental melts (Chapters 4-6).

The fourteen samples selected from Blunden's Wood are recorded in Table VII:3. They predominantly consist of crucible and waste glass fragments, as these are more likely to exhibit inhomogeneity (see Section 2.4.5.2). Bottle glass and a number of possible window glass or locally produced cullet fragments were also selected to provide a comparison to the waste material.

7.2.2 Knightons

The 16th century glass site at Knightons, Alford, Surrey (TQ 0170 3140), is situated in Sidney Wood (see Figure 7:5) (Wood 1982). The last use of the site has been dated to approximately 1550, shortly before the documented arrival of the French immigrant glass workers in the Weald in 1567, and Knightons is therefore thought to represent the change over between the old and new techniques in the region (see Section 7.2) (Crossley 1990).

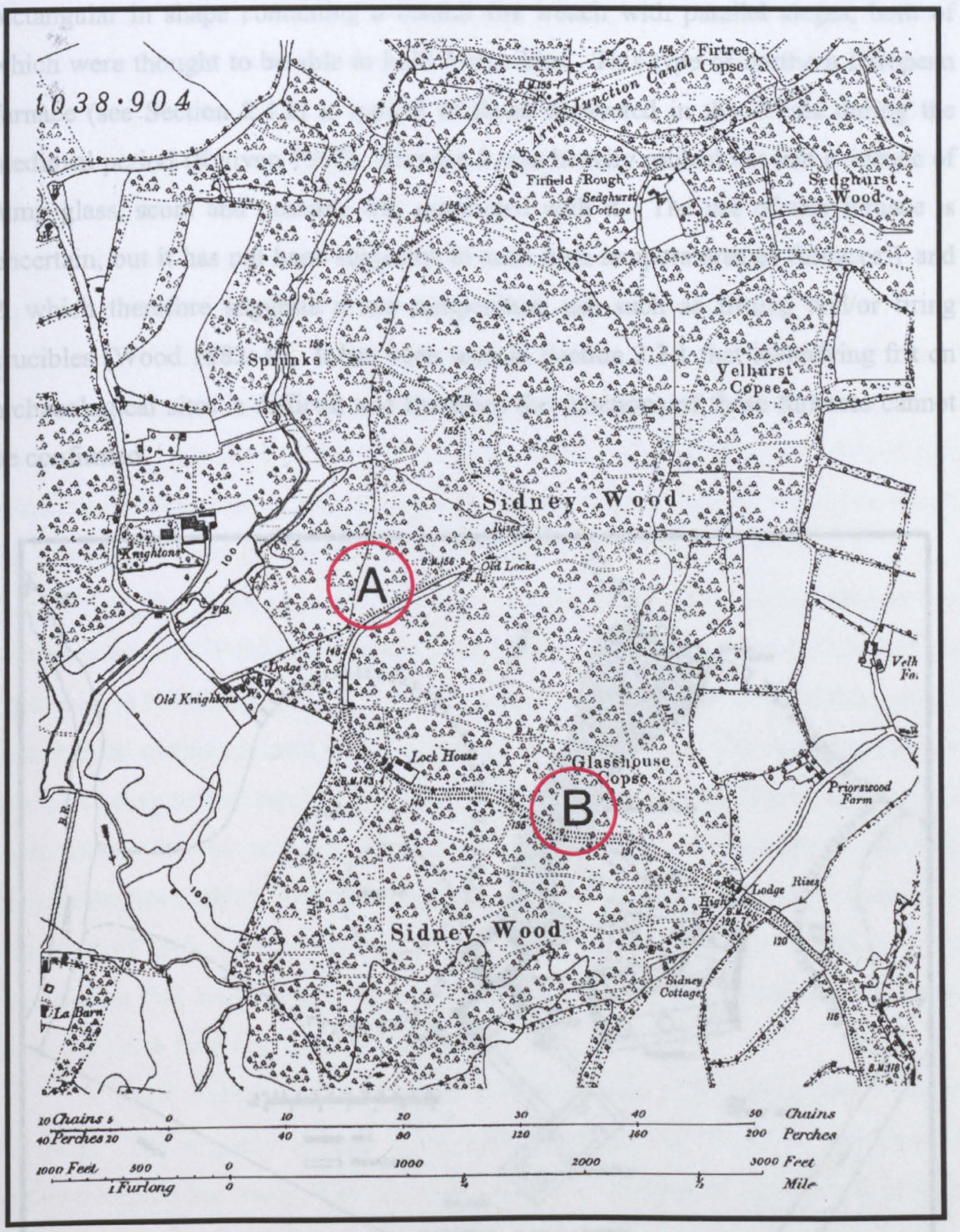


Figure 7:5 Map of Sidney Wood showing Knightons (A) and Sidney Wood (B) glasshouses (Wood 1982:9)

The excavations at Knightons uncovered four furnaces, all constructed from local materials. These are illustrated in Figure 7:6. Wood (1982) suggests that furnace 1 was the main working furnace due to its central position and structure. Furnace 2 (a slightly smaller but very similar furnace) replaced furnace 1 at some time during the operation of the site. The furnaces were single chamber and rectangular in shape containing a central fire trench with parallel sieges, both of which were thought to be able to hold 3 crucibles. This type of northern European furnace (see Section 2.4.1) is typical of those excavated in the Weald during the medieval period (Kenyon 1967). Furnace 3 was heavily robbed but had evidence of lump glass, scum and possible frit, associated with it. The use of this furnace is uncertain, but it has not been subjected to such high temperatures as furnaces 1 and 2, which therefore suggests a low temperature use such as fritting and/or firing crucibles (Wood 1982: 9). It has been seen in Section 2.3.1 that identifying frit on archaeological sites is difficult and therefore the functions of these furnaces cannot be confirmed.

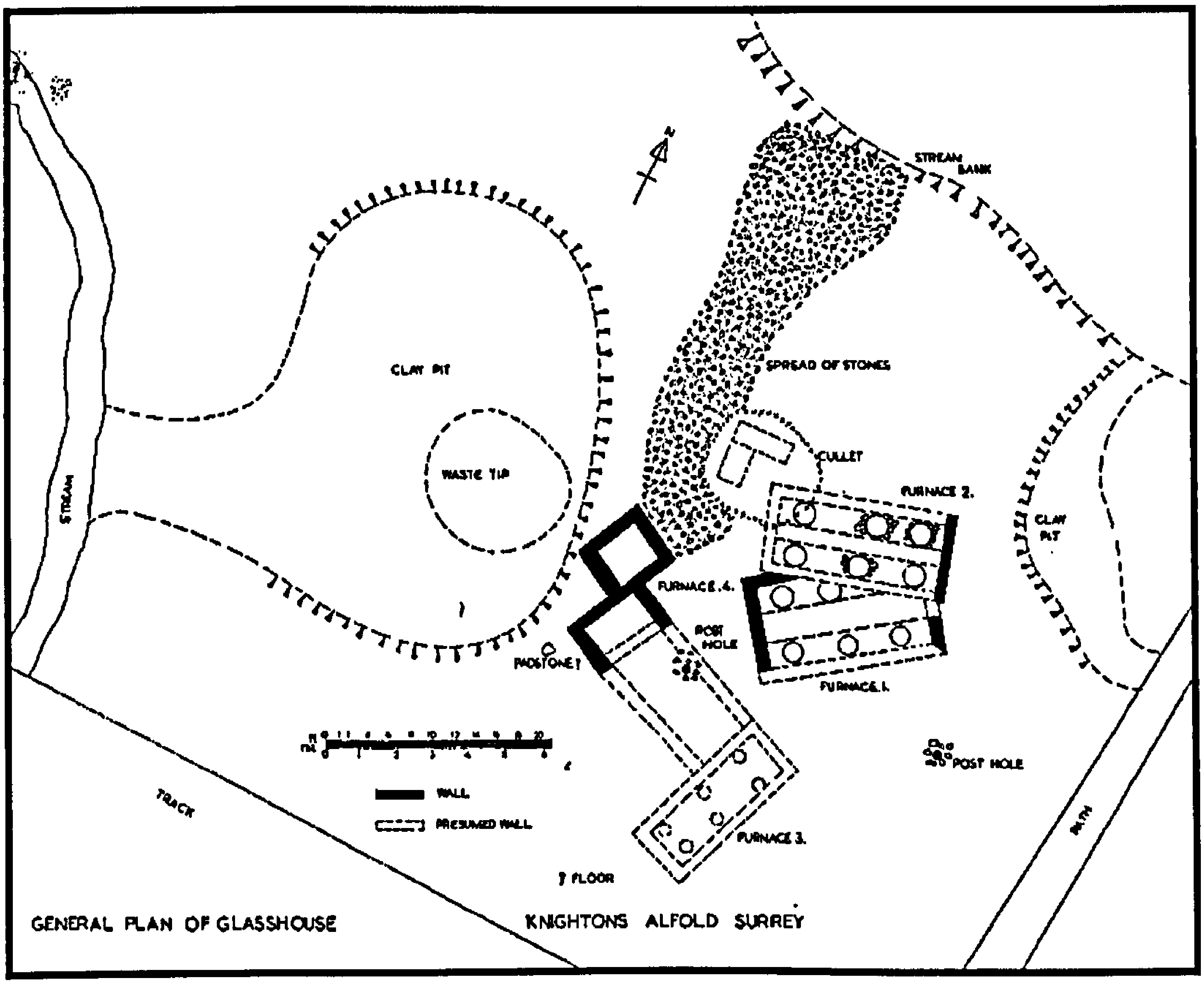


Figure 7:6 Site plan of Knightons glasshouse (Wood 1982: Figure 3)

Wood (1982) suggests that furnace 4 was the annealing furnace, although it may have also have also been used for pot arching. It consisted of two square chambers with a connecting passage, appeared not have reached high temperatures and contained fragments of crucible and crown and vessel glass. This furnace may have been specifically designed to hold sheets of crown glass on racks and each chamber used alternately in order to enable constant production. Figure 7:6 shows that furnaces 3 and 4 may have been connected. This may be evidence of French workmanship, as the trend in winged furnace design (such as at Vann) was to reduce fuel requirements by recycling the hot air from one part of the furnace into another (Hurst 1969a).

The two clay pits on the site appeared to have been used for building and repairing the furnaces. The site also had a trench connected with run offs to a stream that may have been used for washing raw materials or mixing clay. The presence of tile fragments and post holes suggests that the working area of the site may have been covered by a roof (Wood 1982). This may have prevented the fuel and raw materials becoming wet. This is important, as the use of dry batch materials would have facilitated homogeneity (see Section 2.2.4.1).

The glass at Knightons is predominantly the Early type, and is similar to that seen at Blunden's Wood (see Section 7.2.1). There is also a small proportion of Late type glass at Knightons (see Section 7.2), which contradicts the original date for the introduction of this material (1567) (Kenyon 1967). Wood (1982: 44) suggests that this glass may be the result of the local industry attempting to improve quality, or more likely due to an early French influence either at Knightons or another glasshouse from which cullet has been obtained. The glass produced at Knightons consisted of both window and vessel fragments and is typical of artefacts being produced at that time period. In addition to this, evidence of pontils and blowing irons were also found on the site (Wood 1982).

A cullet store was found which contained over 12000 fragments of glass (61.5Kg). The majority of these pieces were from the site. These were weathered and represented the Early Wealden type glass. In addition to these some foreign pieces were also noted (Wood 1982: 11). A waste tip was excavated containing fragments of many of the vessels found in the annealing furnace; glass from here may have been used as in house cullet for which the behaviour of the glass was known.

Analyses of Early Wealden glass from Knightons by Merchant (1998: Table 6.10 and 6.12) are given in Table VII:4, the glass composition is similar to that from Blunden's Wood (see Section 7.2.1) with total alkali levels ranging from 11.44-12.49Wt.%, and lime from 14.49-16.08Wt.%. There is no evidence of the raw materials used at Knightons but Wood (1982: Microfiche 49) suggests that oak may have been used. There have been no attempts to obtain furnace operating or glass melting temperatures. The melting furnace design and glass composition at Knightons is very similar to Blunden's Wood, and therefore the temperatures given in Section 7.2.1 may be comparable. However, Knightons was one of the last rectangular style furnaces in operation in the Weald (see Section 7.2) (Wood 1982: 44). Furnace technologies may therefore have been more advanced than at Blunden's Wood (see Section 7.2.1), increasing melting temperatures and facilitating homogeneity (see Section 2.4.2).

There are a large number of crucible fragments associated with the furnaces at Knightons, but few are large enough to determine the original form. Wood (1982: Microfiche 26) notes they fall into two groups. Thick walled (2-2.8cm with a base of up to 5cm) bucket shaped (28-33cm base diameter with a rim diameter of up to 40cm) and thin walled (1.1-1.8cm) barrel shaped (approximately 24cm base diameter, 32-38 rim diameter, suggested height 40-45cm). The large size of these crucibles will affect melt size and thermal transfer and influence homogeneity, as at Blunden's Wood (see Section 7.2.1).

Twenty one samples of glass waste, crucible fragments and window glass were selected for analysis in Chapter 8 (Table VII:5). The glass was all of the Early type as no Late glass or vessel glass was available.

7.2.3 Sidney Wood

Unfortunately, the 16th–17th century glass site at Sidney Wood (TQ 0220 3372) (see Figure 7:5) is not as well documented as Blunden's Wood or Knightons (see Sections 7.2.1 and 7.2.2). It is thought to be the glasshouse cited on the Norden maps of 1594 and 1607 and also Speed's maps of 1611-2 and 1676 (Kenyon 1967: 203). One, large (approximately 30-40 (9-12m) by 15-20 feet (4.5-6m)) rectangular furnace was excavated by Winbolt (1933: 38) and this contained the remnants of sieges covered in fused glass. The large size of the furnace leads Kenyon (1967: 81) to suggest that there may have actually been more than one furnace present. However, since the excavations were fragmentary it is difficult to assess the nature of the furnace or furnaces.

Although only a small quantity of heavily fragmented material was found at Sidney Wood, it is of the highest quality glass seen in the Weald (Plate 7:2) (Kenyon 1967: 206). Window and vessel glass were produced, and Winbolt (1933) also documents lumps of raw blue glass and glass tubes at the site. Kenyon (1967: 217) suggests that this glass (along with glass from Brookland and Glasshouse Lane) may possibly have been the last ever produced in the Weald and that a significant increase in quality had taken place over the period *c.*1579-1618.

Analyses of Sidney Wood vessel glass (Kenyon 1967: 39) can be seen in Table VII:6 (Samples 1-6 and 9-10). The vessel glass composition is different to the Blunden's Wood and Knightons samples (see Table VII:2 and Table VII:4), with a lower total alkali (approximately 5-6%) and higher lime content (approximately 21-25%). Higher melting temperatures would have been required to produce this glass composition (see Section 2.2.2.1), and this suggests that the furnace temperatures at Sidney Wood were probably greater than those archived at Blunden's Wood and Knightons (see Sections 7.2.1 and 7.2.2). The high calcium levels would be detrimental to homogeneity (see Section 2.2.2.1) but may have been compensated for by increased melting temperatures (see Section 2.4.2). The higher lime levels could have been relatively easily achieved by the intentional addition of limestone, which is prevalent in the Weald (Godfrey 1975) or the addition of calcium rich plant ashes (Merchant 1998). However, lowering the alkali component of the glass would require less plant ashes, which may have been enforced by the high demand and competition for wood in the Weald at this time (Godfrey 1975).

Many fragments from varying sized crucibles were found associated with the site and a complete crucible containing material described as frit or glass is illustrated in Plate 7:3 (Kenyon 1967: 52). Merchant (1998:102) notes that the Sidney Wood crucible fabric is denser than the Blunden's Wood or Knightons crucibles (see Sections 7.2.1 and 7.2.2), but that refiring experiments have shown that it has good refractory properties. It can be seen from Table VII:6 that the composition of the crucible glass (Samples 7-8) is significantly different to the vessel glass. Merchant (1998: 206) notes this anomaly and suggests that due to the paucity and poor standard of excavation at Sidney Wood the crucibles may not belong to this site.

Merchant (1998: 102) notes that the Sidney Wood crucibles are grey in colour and suggests that this might be an indication of a reducing furnace atmosphere. This may also be a reason for the blue hue of Sidney Wood glass compared Blunden's Wood and Knightons glass, which is green. The blue colour is caused as the oxidation state of iron is reduced (Weyl 1951: 95). However, reducing conditions can also be produced by increased melting temperatures and times as well as internal redox agents (see Section 4.3.3.2).

Plate 7:3 A crucible from Sidney Wood (Kenyon 1967: Plate IV)

A final and very important point to note about Sidney Wood is that Winbolt (1933) notes the presence of coal clinker at the site and suggests that wood and coal may have both been sources of fuel. Coal fired furnaces appeared at the start of the 17th century due to the lack of coppiced wood and this scarcity was particularly prevalent in the Weald (Crossley 1988). However, glassmaking moved away from the Weald to coal producing areas (see Section 7.2) and it is not certain whether Sidney Wood was being operated with coal or not. Coal fired glasshouses usually employed covered crucibles to prevent contamination of the glass melt from the sulphur in the fuel (Crossley 1987), and there is no evidence at Sidney Wood to confirm or refute this. If coal were used at Sidney Wood then this would have had a detrimental effect on homogeneity (see Section 2.4.4).

A smaller assemblage was available for sampling compared to Blunden's Wood or Knightons. Three samples of fully formed vessel glass (no window glass was available), three crucible fragments and one furnace fragment were selected for analysis in Chapter 8 and are listed in Table VII:7.

7.3 The Medieval Glass Industry in Staffordshire

The Staffordshire forests were another area of medieval glass production (Welch 1997). Archaeological and documentary evidence suggests that glass was produced in this region from the late 13th century to the end of the 16th and possibly the beginning of the 17th centuries (Crossley 1967, Pape 1933-34, Welch 1997). The industry was concentrated in two areas between the forests of Cannock Chase and Needwood. Fifteen furnace sites were concentrated in Bagot's Park near Abbots Bromley and a smaller number in the Wolseley Estate near Rugeley (Figure 7:7) (Crossley 1972, Welch 1997).

Pape (1933-34) carried out some of the earliest excavations of the Staffordshire glasshouses, such as Bishop's Wood (dated to the 16th century). Recent studies have included work by Crossley (1967) at Bagot's Park and Welch (1997) at Little Birches. Glass production in Staffordshire was on a smaller scale compared to the Weald but there is less excavated evidence. Peak glass production was reached in the mid 16th century and, as in the Weald, this is frequently attributed to the arrival of French immigrant workers. There are also documented links between Wealden and Staffordshire glass making families in this period (Kenyon 1967, Welch 1997).

Silica sources are plentiful in the region of Bagot's Park and include sand and pebble deposits. Larger areas of suitable glassmaking sand are also noted at nearby sites in southern Derbyshire (Crossley 1967). White pebbles have been found in some of the waste glasses and glass in crucible bases from the Staffordshire sites (see Section 2.2.1). However, Crossley (1967) notes that opalescence can also be seen in the glass. This may have been introduced by the use of apatite rich sands (which are known to be prevalent in Derbyshire) or the use of plant ashes (Crossley 1967, 1998). Documentary evidence suggests that the main alkali source for medieval glassmaking in Staffordshire may have been bracken ashes (see Section 2.2.2), but these may have been used in conjunction with fuel ashes (Crossley 1967, Pape 1933-34). The results of Chapters 4-6 have shown that bracken ashes are more likely to form a homogeneous glass than ashes with a lower total alkali content such as beech or oak (see Section 4.3.3.2). The Staffordshire glasses might therefore be expected to contain less inhomogeneities than those from the Weald.

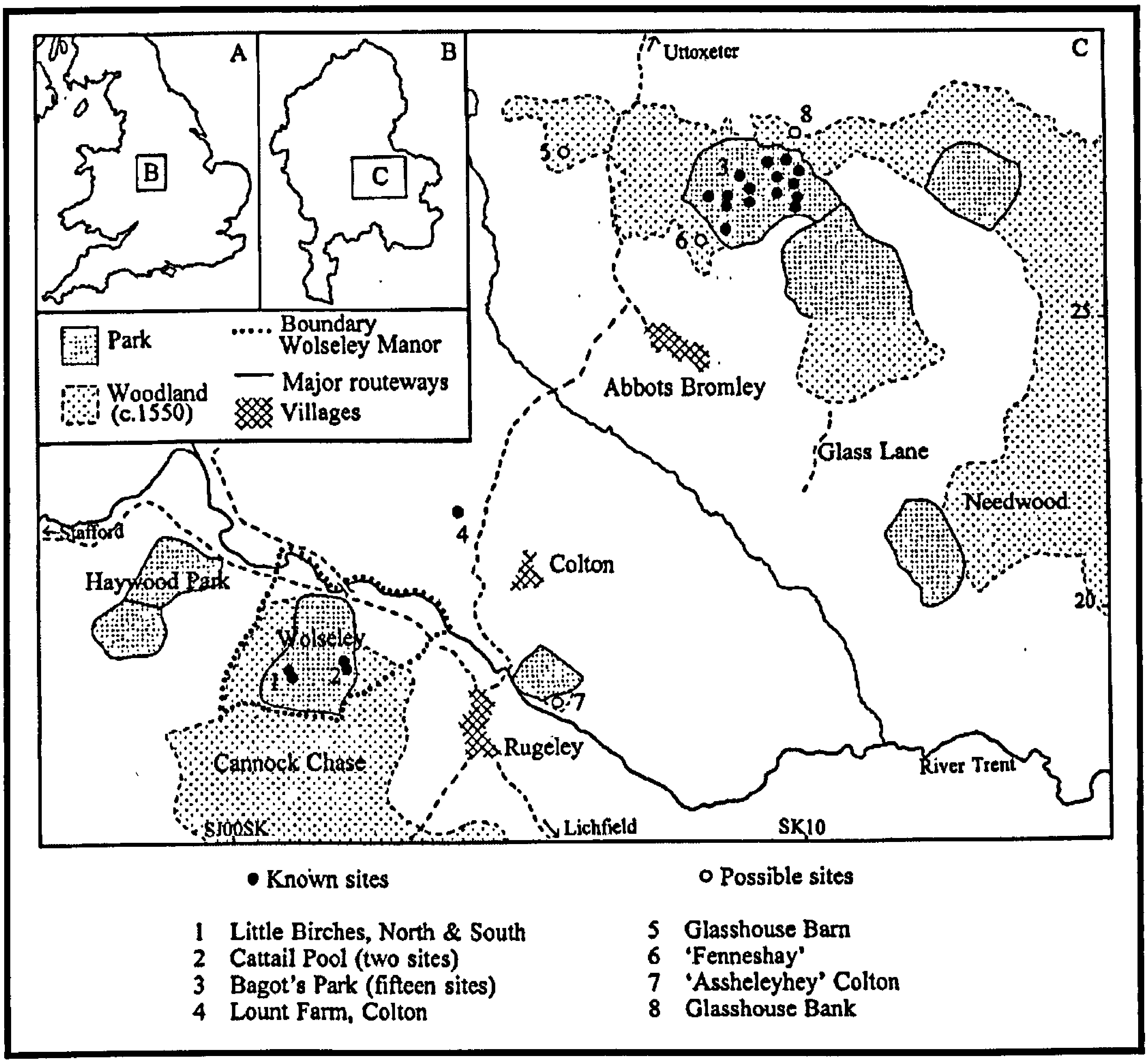


Figure 7:7 Map of Glass Sites in Staffordshire (Welch 1997: Figure 1)

The Staffordshire crucibles are similar in shape and size to those found in the Weald and are made of highly refractive clay (Crossley 1967, Pape 1933-34). In contrast to the Weald the local clay sources appear to have been utilised for crucible production. For example, at Bagot's Park the material appears to have been obtained from the local Cannock fireclay deposits. This clay was then mixed with quartz to increase the strength and reduce the shrinkage of the material for crucible production (Crossley 1967, Doherty 1993). There is documentary evidence dated to *c*1616 that the local Staffordshire clays were so well suited for glassmaking pots that they were exported to Newcastle upon Tyne for this purpose (Kenyon 1967). The glass found associated with the Staffordshire glasshouses is comparable with contemporary material found in the Weald, with the quality and resistance to weathering improving at the later sites (Kenyon 1967) (see Section 7.2).

There is documentary evidence that glassmaking continued in Staffordshire until the mid 1600's, but no archaeological evidence for this has yet been located (Crossley 1967). The Staffordshire glassmaking site selected for this research will be discussed in Section 7.3.1.

7.3.1 Little Birches

The glass site at Little Birches, Wolseley, near Rugley, Staffordshire (SK00809 18909) was excavated in 1991-2, and had two phases of working. The South site, containing three furnaces (Furnaces 1, 2 and 3) and three waste tips (south, west and east tips), is dated to sometime between 1521-1565 and is thought to be almost contemporary with Bagot's Park (see Section 7.3). There is no evidence to suggest that French immigrant workers were associated with the Wolseley area even though they are documented at Bagot's Park. The North site (containing furnace 4 and the north waste tip) cannot be dated so accurately and is thought to have been in use sometime in the 13th and 14th centuries. Figure 7:8 illustrates a plan of Little Birches showing the north and south sites (Welch 1997).

The name Little Birches refers to the wood next to the glass site that was planted in the 1880s, but there is still birch covering much of the surrounding area. Welch (1997: 25, 33) suggests that birch charcoal excavated within the contexts of the furnaces may be an indication that this wood was used as fuel. However, there is no conclusive evidence to confirm or refute whether this was the only species used.

The documentation of glass manufacture in Wolseley is vague until the latter half of the 15th century when it is certain that there was glass production in the area, although these records cannot be attributed directly to the site at Little Birches. A rental document dated to 1479 notes the sale of 'ferns' (see Section 2.2.2) to a glasshouse in the Wolseley area (Welch 1997: 2). The possible use of bracken ash as an alkali source is an important reason why Little Birches was selected for this research. The results of Chapters 4-6 have confirmed that bracken based glasses form more homogeneous glasses than those made from beech. The Little Birches glass samples are therefore expected to be more homogeneous than those from the Wealden sites (see Section 7.2). However, other factors that effect homogeneity, such as melting temperatures must be considered and these will be discussed for the North site in Sections 7.3.1.1 and the South site in Section 7.3.1.2.

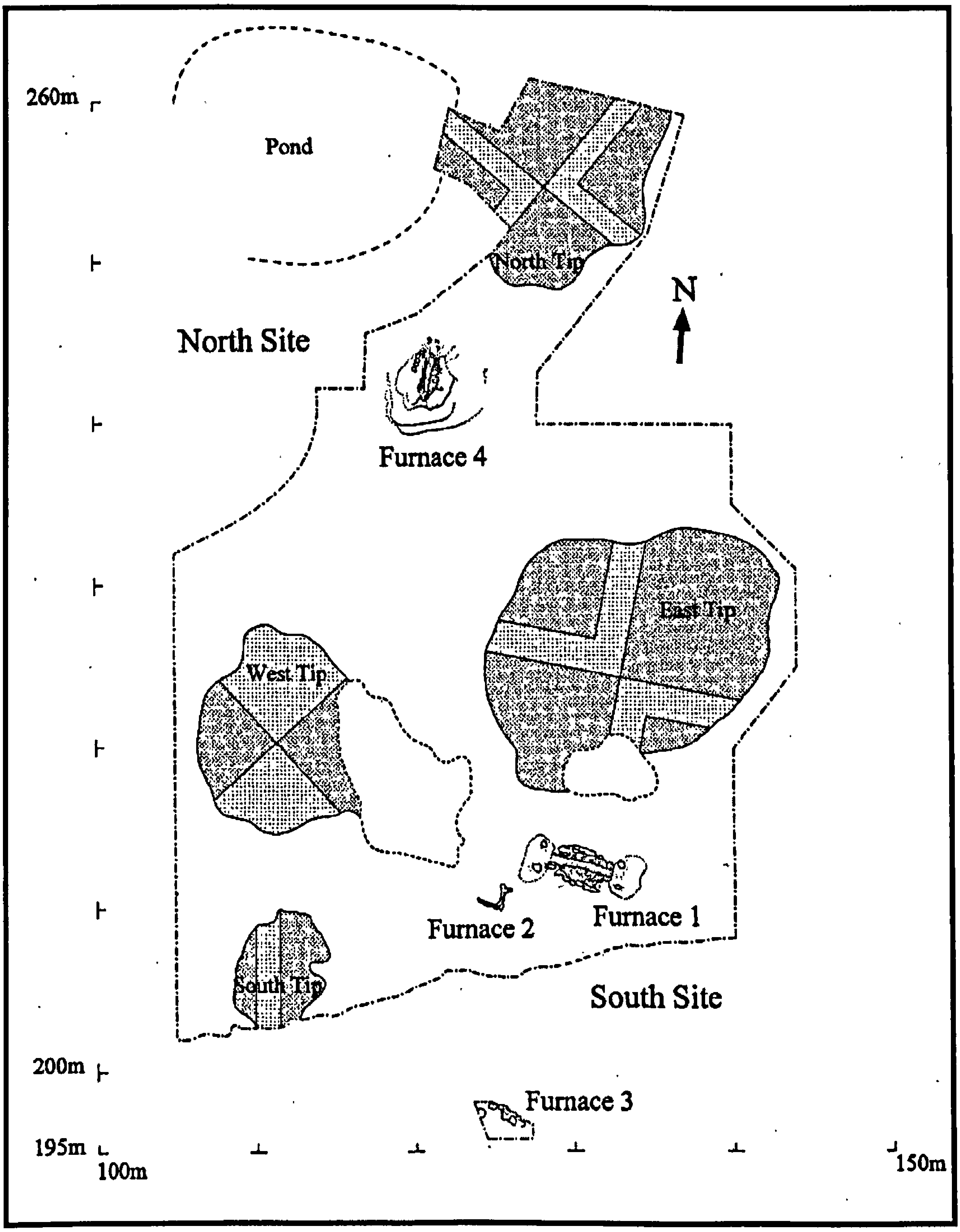


Figure 7:8 Little Birches site plan (Welch 1997: Figure 3)

7.3.1.1 The North Site (13th-14th centuries)

There is less excavated evidence for medieval glassmaking on the North site compared to the South site (see Section 7.3.1.2). The only furnace to be uncovered was furnace 4 (Figure 7:8, Plate 7:4), which was rectangular with a central fire trench blocked with waste material. Although of similar design it was smaller in size than furnace 1 on the South site (see Section 7.3.1.2), the trench being 2.6m compared to 4.3m long (Welch 1997: 15). The estimated maximum firing temperatures for furnace 4 (based on refiring experiments) are 1398-1430°C, but the real temperatures achieved are likely to be lower than this (White in Welch (1997: Table 7)). The results from Chapters 4-6 have shown that the combination of bracken as an alkali source and high furnace temperatures will facilitate homogeneity. These results suggest that the North site glass would be homogeneous. However, homogeneity will also be affected by other variables such as melt size, crucible fabric, and therefore these must also be considered.

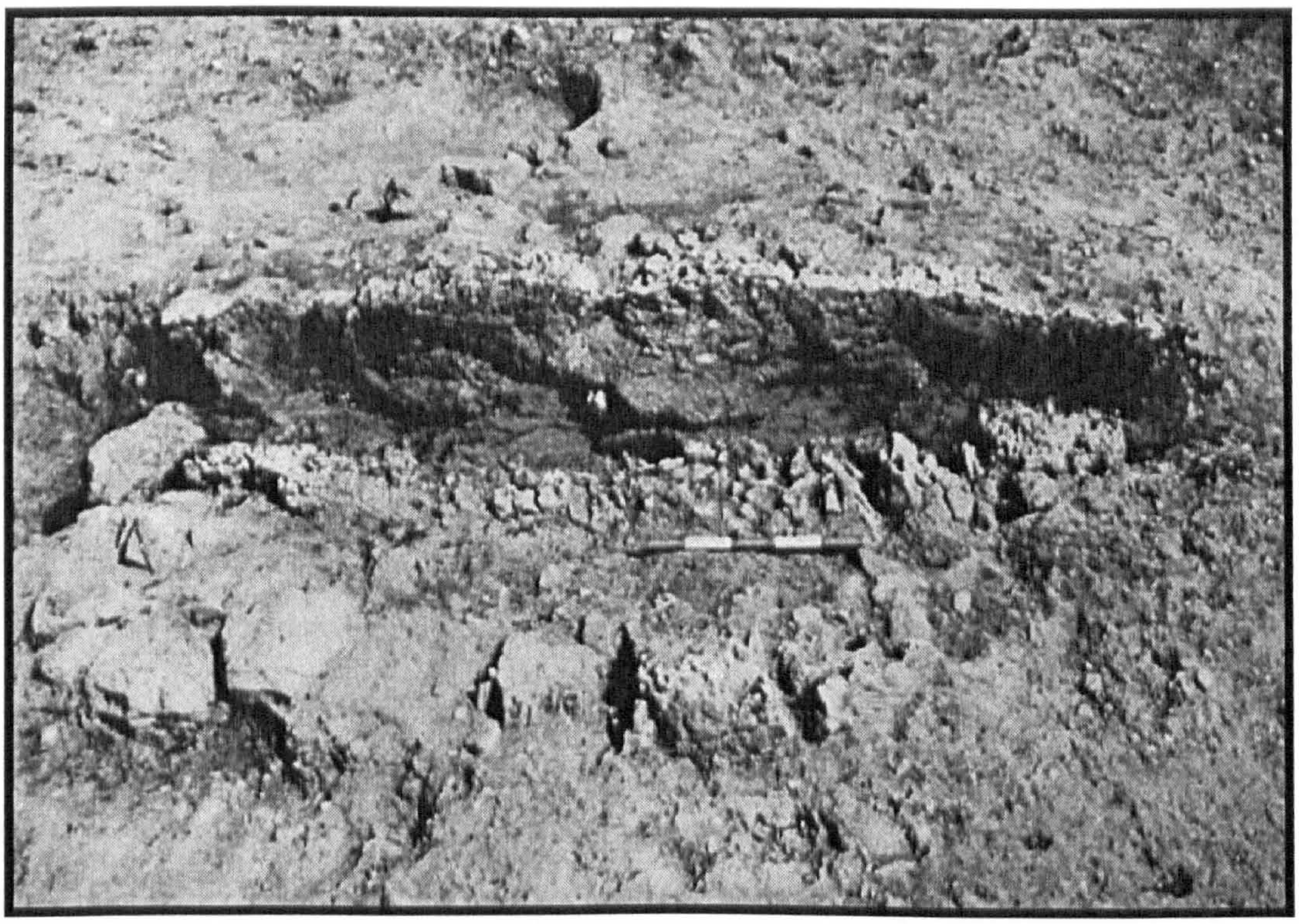


Plate 7:4 Furnace 4, North Site, Little Birches (Welch 1997: Figure 12)

A majority of crucible fragments excavated from Little Birches were from the North site. They featured bucket and barrel shapes (see Section 7.2) as well as a 'goldfish bowl' type. The estimated dimensions obtained from the assembly of two crucibles were 280mm internal rim diameter, basal diameter 300mm and overall height of 360mm. Many of the crucible fragments were obtained from deposit 116 that lay just to the west and south sides of furnace 4 (Welch 1997: 15). The North site crucibles are made of a similar high refractory fabric and have comparable dimensions to those excavated at Blunden's Wood (Section 7.2.1). Therefore the effects on homogeneity of melt size, the thermal conductivity of the crucible fabric and refractory corrosion will be similar (Section 7.2.1).

The North site only yielded nine fragments of heavily weathered, thin, milky green, Early type (see Section 7.2) glass. The north tip (Figure 7:8) contained a small amount of glass waste but this was predominantly made up of crucible and stone fragments (Welch 1997). The composition of samples of this glass can be seen in Table VII:8 (Welch 1997: 41). The glass has a slightly wider range of total alkali (11.0-20.7Wt.%) concentrations and similar levels of lime (16.6-17.4Wt.%) as the contemporary Blunden's Wood glass (see Section 7.2.1). A two component silica and bracken ash batch would not impart these high levels of calcium to the glass (see Section 2.2.2). To achieve this it would therefore appear that lime must have been being added from another source. The function of lime in glasses was not fully understood until the 18th century and therefore it is not thought that this inclusion is deliberate. The two possible sources for the lime are from calcium rich plant ashes (for example oak and beech trees) or limestone. However, in comparison to the Weald (see Section 7.2.3) there is no lime industry associated with the Little Birches area (Crossley 1998). Therefore, although there are compositional similarities between the material from the North site and Blunden's Wood (see Section 7.2.1), the Little Birches glass will probably be more homogeneous due to the combination of higher melting temperatures and the use of bracken ashes as an alkali source.

A selection of waste and crucible glass was chosen for analysis. The North site glass is likely to be more homogeneous for the reasons described above and therefore the analysis of waste products is beneficial as they are more likely to show inhomogeneities than the finished product. The 7 samples selected are listed in Table VII:9.

7.3.1.2 The South Site (16th century)

The main melting furnace on the South site was furnace 1 (Figure 7:8, Figure 7:9), which was rectangular with a central fire trench and parallel sieges containing impressions of crucibles (Welch 1997). Welch (1997) suggests that three crucibles would probably have fitted on either side of furnace 1. Furnace 2 (Figure 7:8) was square in shape and probably for a different purpose other than glass melting. Furnace 3 (Figure 7:8) was significantly destroyed but appeared to have been similar to and probably contemporary with furnace 1. Both of the furnaces had post pits associated with them and these may have been evidence for some sort of roofed structure (Welch 1997). This may have helped to keep the raw materials dry and the importance of this to homogeneity has been discussed in Section 7.2.2.

Refiring of clay fabric from the melting furnace by White in Welch (1997: Table 7) has suggested a maximum operating temperature of 1512-1541°C. Although White in Welch (1997: 51) suggests that this is probably higher than the real temperatures achieved it is still higher than those achieved at the North site (see Section 7.3.1.1). As homogeneity improves with increasing furnace temperature (see Section 2.4.2) the glass from the South site is likely to be more homogeneous than that from the North site.

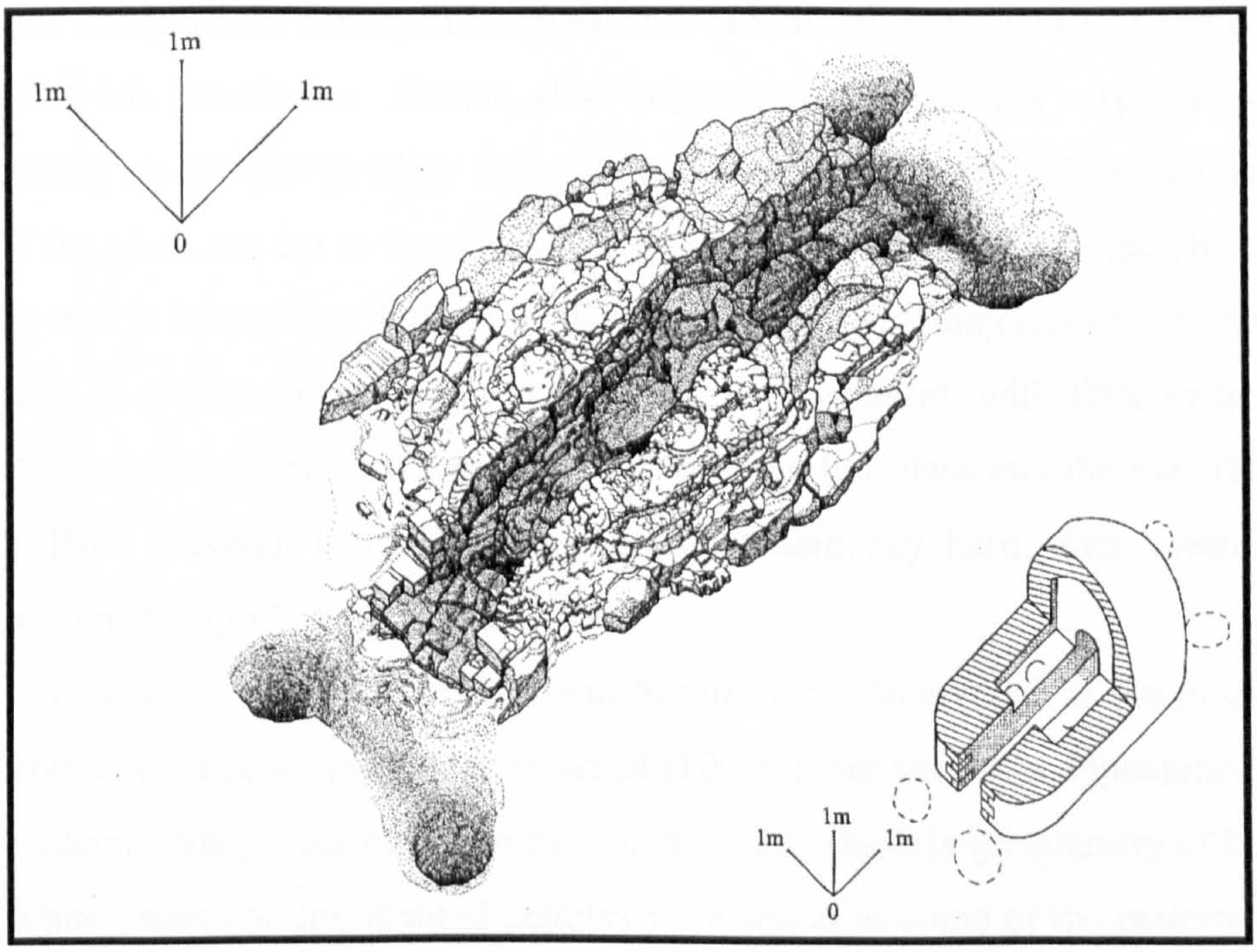


Figure 7:9 Furnace 1, Little Birches with a speculative reconstruction (Welch 1997: Figure 6)

The crucibles associated with the South site were thicker and larger than those from the North Site (see Section 7.3.1.1). Barrel and bucket shaped crucibles (see Section 7.2) were excavated with an approximate internal rim diameter of 300-350mm (Welch 1997). The South site crucibles were comparable with the nearby contemporary site of Bagot's Park but not with Knightons (see Section 7.2.2). Larger crucibles would mean that larger melt sizes might have been used. These would have then required longer melt times and higher melt temperatures to form a homogeneous glass (see Section 2.4.5.2).

Refiring experiments by White in Welch (1997: Table 7) suggest that the South site crucibles were subjected to temperatures in the region of 1140-1210°C, and that the maximum operating temperatures for the melting furnace was 1512-1541°C. In addition to the ceramic analyses, the liquidus temperature for a piece of South site glass was determined to be greater than 1320°C (White in Welch (1997: 49)). These findings suggest that the temperatures achieved at the South site were greater than at the North site and therefore this would have had an effect on the raw materials that could be utilised and the quality and homogeneity of the glass produced.

A large volume of vessel, window and glass production waste was excavated from the South site. The large number of 'bulls eyes' and proportions of other glass fragments found at the South site suggest that crown window glass was the primary product of this glasshouse. Crown glass is produced by blowing a sphere of glass and opening up the end to allow the glass to be spun into a disk. The thinner outer parts of the glass are cut to form window glass and the thickest part attached to the blowing iron is termed the 'bulls eye' (Kenyon 1967). The majority of the glass was pale green in colour and usually translucent and transparent, with little evidence of opacity. There was a marked similarity between the flat glass and the material from Bagot's Park although Little Birches did not contain any hard, dark green (Late) glass as seen at Bagot's Park (Welch 1997).

Three waste tips (East, West and South) were uncovered at the South site. These contained a large amount of material (100m^3) that varied in appearance, some being predominantly clear glass lumps, others containing a large quantity of bubbles. Small white chips and fragmented pebbles were found in some of the material and it appeared that some of the glass had cooled whilst in contact with the ground. A large waste pit (101) was excavated just to the north of furnace 1 and contained a large amount of vessel glass in addition to most of the coloured glass found at the site. The East tip adjoined deposit 101 although it was not certain if the two features were linked. South of furnace 1 was deposit 90, which contained a large amount of worked glass fragments. However, the material was different in nature to that found in 101. It appears that different waste tips were used for housing different types of cullet, which may suggest a deliberate selection procedure. It is not thought that the vessel glass found was produced on site and could have been collected for remelting.

A selection of analyses of the South site glass carried out by Mortimer (Welch 1997: Table 1) are listed in Table VII:10. The total alkali content ranges from 10.5-17.6Wt.% and the lime levels from 11.3-18.6Wt.%, and as at the North site (see Section 7.3.1.1), these compositions suggest that another component was being added to the batch that gives a higher lime concentration than the bracken ash alone. Although higher temperatures would have been required to produce a homogeneous glass, the evidence above suggests that at the South site these may have been attained and were greater than those achieved at the North site. Although the crucibles were larger and the melt size may have been increased, the furnace temperature may have been the dominating factor. The South site glass is therefore likely to be more homogeneous than comparative material from the earlier North site.

No fully formed glass was available for analysis and therefore the material selected from the South site was waste and crucible glass, which is comparable with the material selected from the North site (see Section 7.3.1.1). The 9 samples are recorded in Table VII:11.

7.4 The Medieval Glass Industry in Hils

The Hils region, near Grünenplan, northern Germany was a major area of medieval glass production in northern Europe (Leiber 1990/1991). Evidence for eighteen medieval, and fourteen early modern glasshouses has been excavated and the relative location of the medieval sites (A2-A18) is illustrated in Figure 7:10 (for key to sites see Table VII:12) (Six 1976).

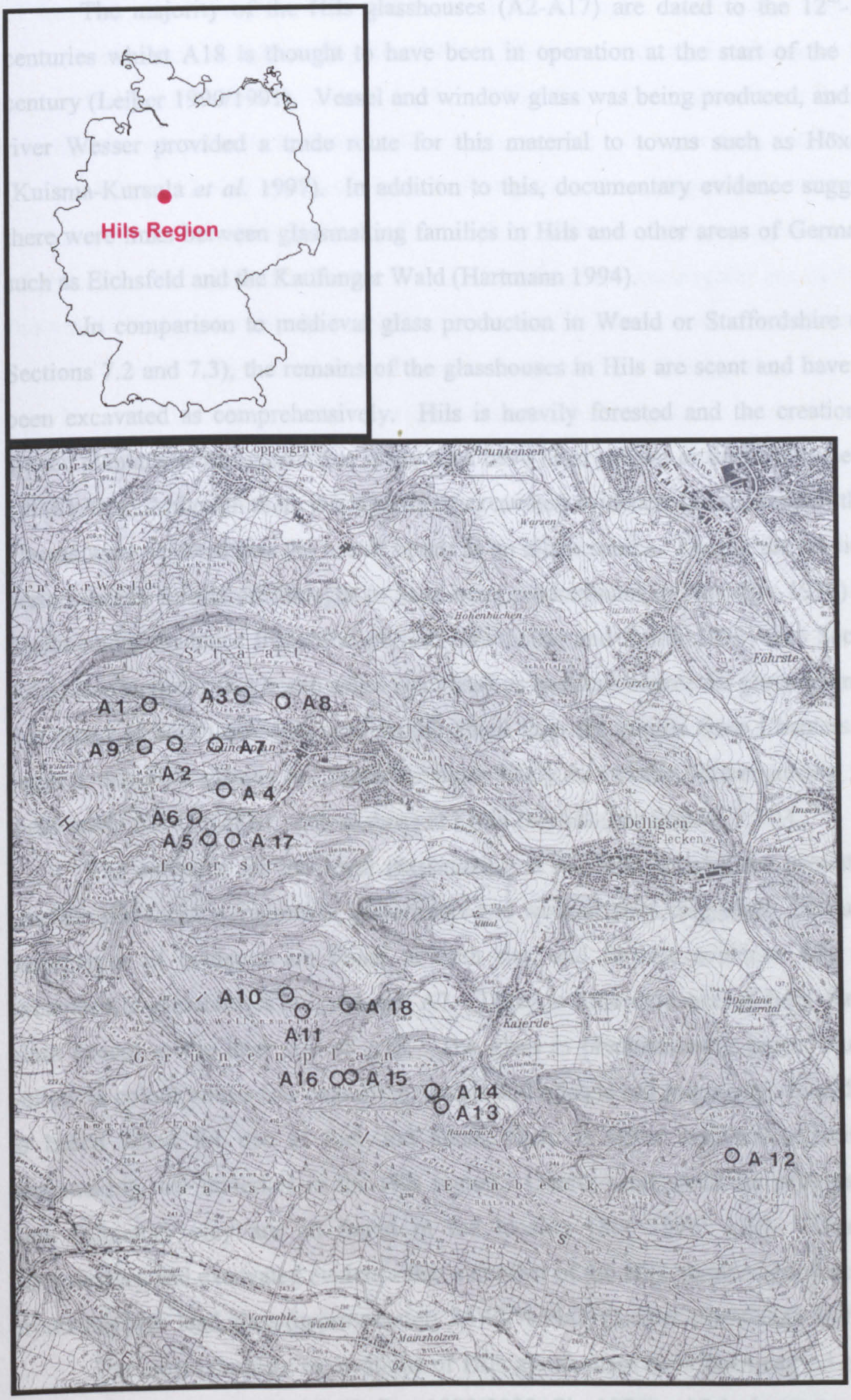


Figure 7:10 **The Location of Glasshouses A2-A18 in the Hils Region, near Grünenplan, Germany (Leiber 1999/2000: Figure 1) (Scale 1:75000) (Key to Site Numbers in Table VII:12)**

The majority of the Hils glasshouses (A2-A17) are dated to the 12th-13th centuries whilst A18 is thought to have been in operation at the start of the 15th century (Leiber 1990/1991). Vessel and window glass was being produced, and the river Wesser provided a trade route for this material to towns such as Höxeter (Kuisma-Kursula *et al.* 1997). In addition to this, documentary evidence suggests there were links between glassmaking families in Hils and other areas of Germany, such as Eichsfeld and the Kaufunger Wald (Hartmann 1994).

In comparison to medieval glass production in Weald or Staffordshire (see Sections 7.2 and 7.3), the remains of the glasshouses in Hils are scant and have not been excavated as comprehensively. Hils is heavily forested and the creation of spruce plantations has meant that many sites have been robbed or destroyed (Leiber 1990/1991). Although there is a paucity of excavated evidence, the reason that these glasses were selected was the use of beech as an alkali source. During the medieval period, beech forests are thought to have been predominant in Hils (Six 1976) and documentary evidence from Theophilus (Hawthorne and Smith 1979) (see Section 2.2.2) also suggests that beech ashes were used as an alkali source for glassmaking in this area. If beech ash was used as the alkali then the results from Chapters 4-6 suggest that Hils glasses are therefore more likely to exhibit inhomogeneity than those made from bracken, such as those at Little Birches (see Section 7.3.1).

The evidence for medieval glassmaking at the Hils glasshouses consists of crucible and furnace fragments, glass waste and worked glass fragments. Not all of these types of evidence are found at each site, and furnace evidence was only excavated at glasshouses A2, A4 and A7. There is little evidence of fully formed glass except at the later site of A18. The glass is predominantly green, blue or yellow in colour with a few colourless, purple and opaque red fragments. In addition to beech wood for use as fuel and alkali, there is other evidence of suitable glassmaking raw materials in the Hils region. Quartz sand, quartzite pebbles and high refractory clay are all found in the locality (Six 1976: 129). There is documentary and excavated evidence that a number of the Hils glasshouses were also producing high lead glass (approximately 25Wt.% PbO) (Leiber 1999/2000: 548).

The most complete excavations of Hils glasshouses have been carried out at sites A2 and A4 (Figure 7:10) (Leiber 1999/2000, Six 1976). A2 had a rectangular 'northern' style (see Section 2.4.1) main melting furnace and three smaller furnaces, which have been suggested by Six (1976: 136) to be for fritting and annealing. Two of these were rectangular and approximately 1.5m in length, and one was oval and connected to what is suggested by Six (1976: 136) to be a rectangular chimney. The glasshouse at A4 had three furnaces (Leiber 1999/2000). The main melting furnace was again northern style and rectangular in shape with a 2 metre long central fire trench. Furnace 2 was associated with molten glass and melting crucibles but was horseshoe in shape with a 1.5m long fire trench. The rounded shape suggests a more southern type of design (see Section 2.4.1). Furnace 3 was rectangular and had two fire trenches of approximately 1.5m. The remains of this furnace are scant but it had not been fired to such as high temperature as furnaces 1 and 2, suggesting that may have been used for a lower temperature process such as fritting or annealing.

Unfortunately, there are no analyses of furnace or crucible fabric from the Hils glasshouses to provide estimates of the melting temperatures used to produce these glasses. Thus it is difficult to assess how homogeneity will be affected, but it was noted in Chapter 5 that to form a homogeneous beech glass under laboratory conditions, temperatures in excess of 1300°C were required. However, other factors, such as crucible dimensions and melt size (see Section 2.4.5.2) will affect homogeneity. The dimensions of the crucibles from the Hils glasshouses appear to have been uniform and fall into two main types that are illustrated in Figure 7:11 (Leiber 1999/2000: 527).

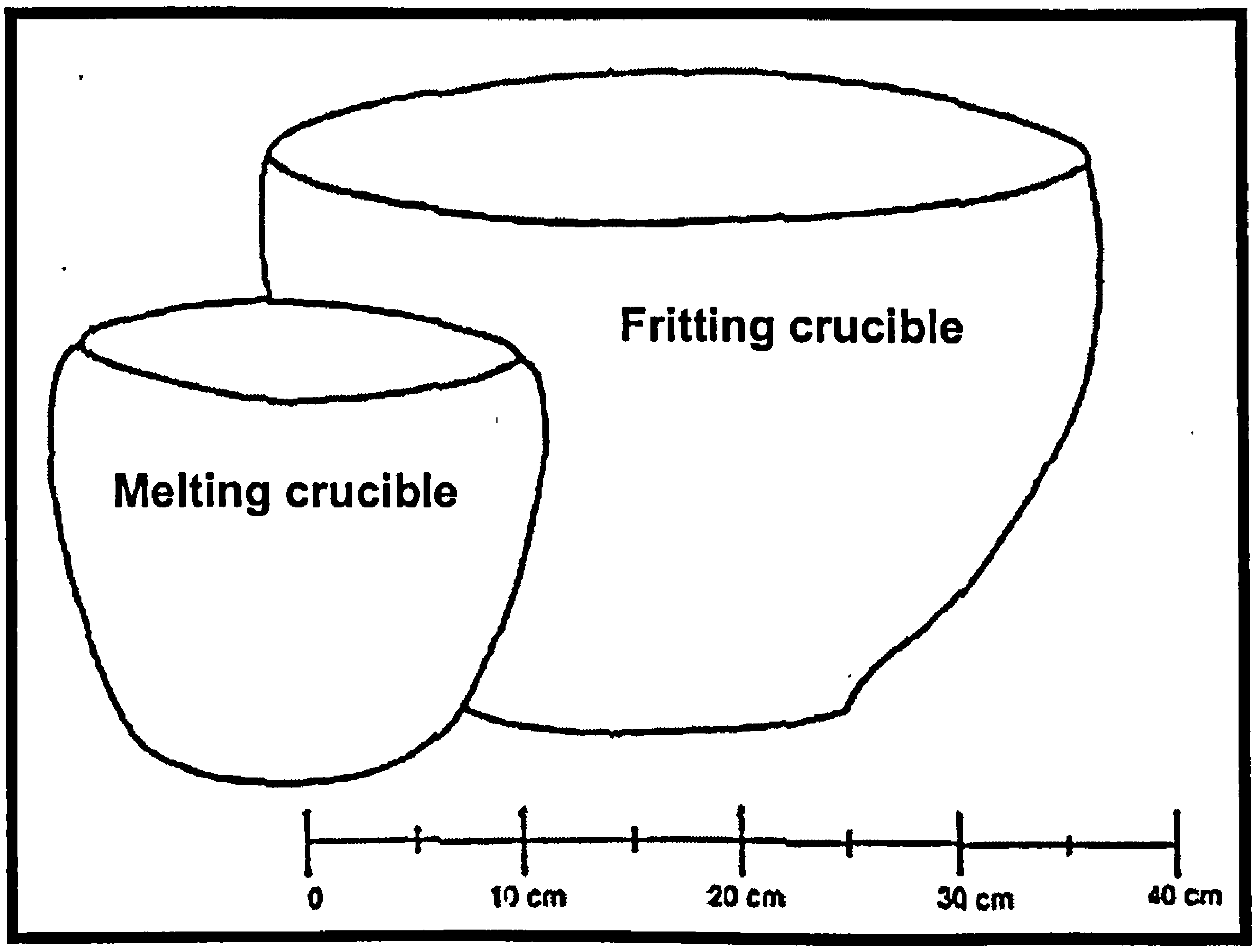


Figure 7:11 Reconstruction of Crucibles from Hils Glasshouse A7 (after Six 1976: Figure 5)

The large crucibles are approximately 16cm base and 40cm rim diameter, and 30cm in height. Six (1976: 137) has suggested that these were for fritting but there is no evidence to confirm or refute this. The use of fritting crucibles contrasts with fritting on the furnace floor, which may have been used at the Wealden and Staffordshire sites discussed in Sections 7.2 and 7.3. The use of a crucible will therefore have different effects on homogeneity (see Section 2.3.4), and it has been seen in Chapter 5 that fritting temperature and time have to be adjusted depending on the surface area and volume ratio of the fritting vessel.

The melting crucibles have curved in rims and are similar to those described by Theophilus (Hawthorne and Smith 1979). Based on the reconstruction of crucibles from glasshouses A2 and A7 (Figure 7:10), the dimensions of the melting crucibles (Figure 7:11) are estimated to range from 10-12cm base diameter, 25cm rim diameter, and to be 20-26cm in height. Leiber (1999/2000: 528) suggests that these would have held 5-6litres of glass. These are smaller than the Wealden and Staffordshire crucibles (see Sections 7.2 and 7.3). In isolation, a smaller melt size and crucible dimensions would have facilitated homogeneity (see Section 2.4.5.2) but this has to be balanced against the effects of other variables such as melting temperature and alkali composition. The crucibles are made from low iron, high refractory clay from the clay beds just to the north and north east of Hils but it is not know how this data was determined (Leiber 1999/2000: 528). The use of this type of clay would have also facilitated homogeneity by resisting refractory corrosion (see Section 2.4.5.1).

Analyses of Hils glass can be seen in Table VII:13 (Kuisma-Kursula *et al.* 1997 66, Sellner *et al.* 1979, Six and Madder 1989). The 12th and 13th century glass (Samples 3-7) contains a wide range of total alkali (12.8-18.9Wt.%) and lime (3.1-21.2) levels. The compositional variability within single pieces of Hils glass was noted by Wedepohl (1997: 251). He has suggested that this is due to the glass being from failed melts and that therefore these compositions are not indicative of the glass used to produce objects. The variability is important as it suggests that inhomogeneity is present in some of the Hils glasses. The later glass samples (1 and 2) contain lower total alkali (8.4-9.5Wt.%) and increased lime levels (21.6-22.2Wt.%). The change in composition suggests that lime may have been added from another source other than beech ashes (see Section 2.2.2.1). Although, higher lime levels increase inhomogeneity, higher furnace temperatures are required to melt this type of glass and these facilitate homogeneity. Therefore, as suggested at Sidney Wood (see Section 7.2.3) the later Hils glass may be more homogeneous than the earlier material.

A small assemblage of Hils glass samples was available for sampling and the majority of pieces were trails and drops from glass working, or test pulls (see Section 2.4.3) from the 12th-13th century glasshouses. Two pieces of vessel glass and a glass drop were available from the later glasshouse (1400) A18. The vessel glass is important, as it will enable a comparison between the homogeneity of the finished and waste glass. The twenty seven samples selected are listed in Table VII:14.

7.5 Summary and Conclusions

It can be seen that it is not always possible to infer all of the factors that will affect homogeneity from the remains and documentary evidence associated with medieval glassmaking sites. Certain parameters such as melting times and fritting procedures are more difficult to assess than others such as melt size or possible furnace temperatures. However, some general conclusions about the homogeneity of the glass selected for analysis in Chapter 8 can be suggested from the evidence discussed above and are summarised below. These predictions are based on isolated factors and glassmaking practices thought to have been used at each site. It should also be noted that many of these factors might be overridden if higher melting temperatures were used (see Sections 2.4.2 and 5.5.6.5).

- The Little Birches glass (see Section 7.3.1) is the most likely to be homogeneous due to the suggested use of bracken as an alkali source.
- The higher furnace temperatures achieved at Little Birches, South site (see Section 7.3.1.2) suggest that this glass is likely to be more homogeneous than the material from the North site (see Section 7.3.1.1).
- The Wealden glass from Blunden's Wood (see Section 7.2.1), Knightons (see Section 7.2.2) and Sidney Wood (see Section 7.2.3) is likely to contain inhomogeneities due to the use of oak as an alkali source.
- The Blunden's Wood glass is likely to be more inhomogeneous than the Knightons and Sidney Wood material due to the use of lower furnace temperatures.

- The Knightons glass covers the transitional period in Wealden glass production. It is therefore likely to be less inhomogeneous than the material from Blunden's Wood but possibly more inhomogeneous than the glass from Sidney Wood.
- The Sidney Wood glass is likely to be the most homogeneous out of all the Wealden glass analysed.
- The Hils glass is likely to be inhomogeneous due to the use of beech as an alkali source.
- The earlier Hils glasses (12th-13th centuries) are likely to be more inhomogeneous than the later material (15th century) due to increasing lime levels that require increased furnace temperatures.

The glass selected in this chapter (Table VII:3, Table VII:5, Table VII:7, Table VII:9, Table VII:11 and Table VII:14) will now be examined for inhomogeneity using SEM and EPMA as described in Section 3.3.

CHAPTER 8

Analysis of Archaeological Material

8.1 Introduction

The significance of inhomogeneity to the compositional study of archaeological glasses was discussed in Section 1.3. It was noted that the fundamental assumption behind these studies is that the glass analysed is compositionally homogeneous. However, the results of Chapters 4-6 have shown although many of the experimental glasses appeared to be visually homogeneous a significant number contained inhomogeneities that could only be located by backscattered SEM imaging. If inhomogeneities are present in archaeological glasses they may therefore exert a significant bias on the compositional results obtained (see Section 1.5).

The aim of this Chapter is to determine to what extent inhomogeneity is present in the medieval glasses selected in Chapter 7. These samples were chosen to represent glasses produced from different ash types because the results of Chapters 4-6 determined that certain variables in the medieval glassmaking process are more likely to have a significant effect on inhomogeneity than others. For example, bracken batches form more homogeneous glasses than beech batches in this experimental work (see Sections 7.3 and 7.4). However, the effects of other key variables such as furnace temperature and crucible dimensions were also considered, but it should be noted that it is difficult to determine these effects in archaeological samples (see Chapter 7).

The archaeological material analysed from Blunden's Wood (Table VII:3), Knightons (Table VII:5), Sidney Wood (Table VII:7), Little Birches (Table VII:9 and Table VII:11) and Hils (Table VII:14) was prepared for SEM and EPMA analysis as described in Section 3.3.2.2. The SEM backscattered imaging results are described in Section 8.2 and these results are then used to plan the EPMA analysis in Section 8.3. Both sets of results are discussed in Section 8.4.

8.2 Backscattered SEM Imaging

8.2.1 Wealden Glassmaking Sites

Glass from the Wealden, glassmaking sites of Blunden's Wood, Knightons and Sidney Wood was selected for analysis (see Section 7.2). It has been seen that glass from these sites is likely to contain inhomogeneities based on the assumption that oak was used as an alkali source (see Section 7.2). In addition to this, due to factors such as higher furnace temperatures (see Section 7.2.1), it is thought that the material from Blunden's Wood is likely to be the most inhomogeneous, Sidney Wood the least inhomogeneous, with the material from Knightons falling in the middle. Sections 8.2.1.1-8.2.1.3 will examine glass from these sites to determine whether the predicted results made in Section 7.5 can be observed.

8.2.1.1 Blunden's Wood

The results of the backscattered imaging of the Blunden's Wood glass samples (see Section 7.2.1, Table VII:3) are recorded in Table VIII:1. The samples of bottle glass (BW1) and waste glass/cullet (BW2 and 3) (Plate 8:1) were visually and microscopically **homogeneous**. However, one sample of waste glass or cullet (BW4) contained visual opacity and medium levels of **inhomogeneity** (Plate 8:2).

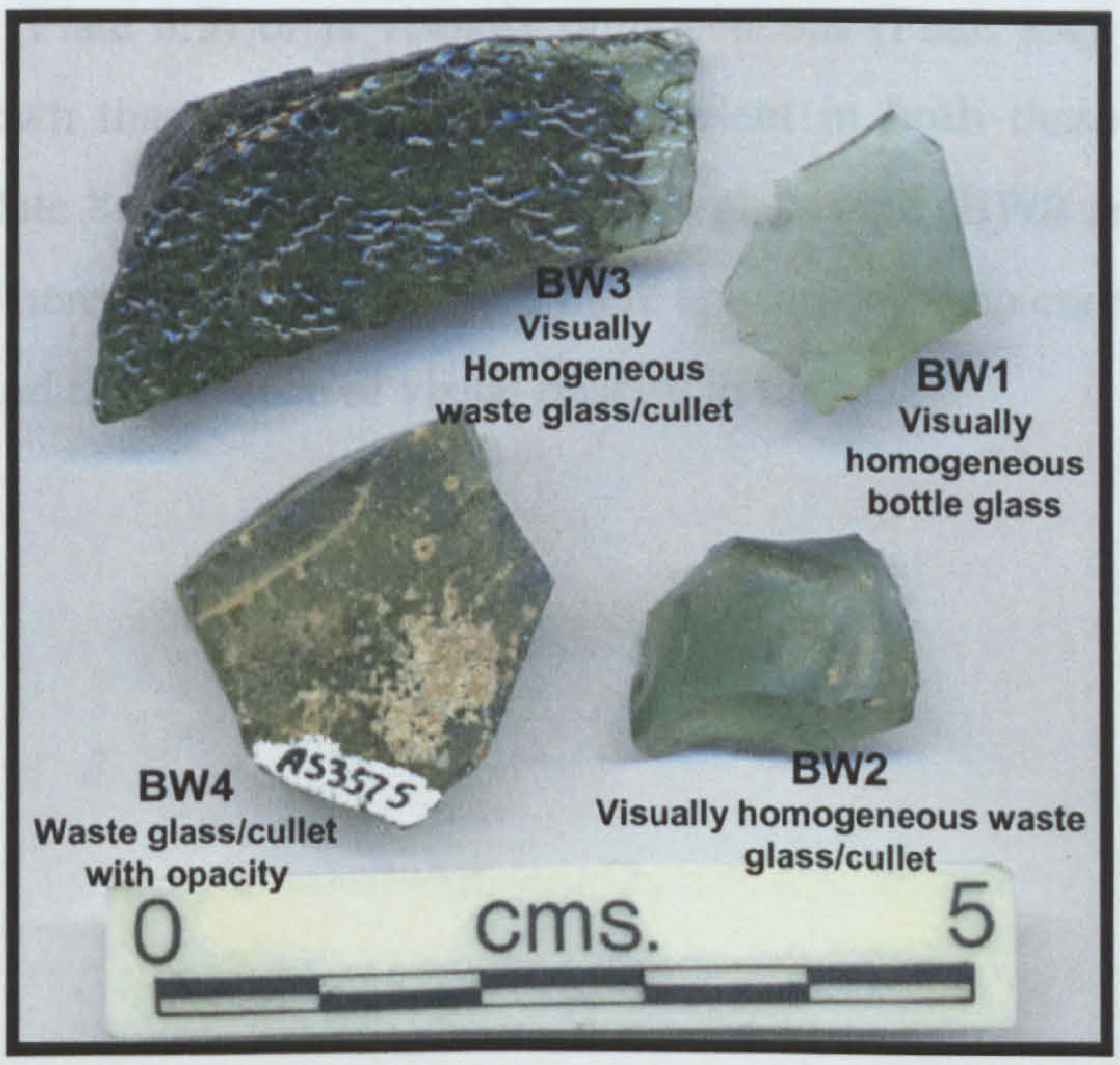


Plate 8:1 Bottle glass and waste glass/cullet from Blunden's Wood (BW1-4, Table VII:3)

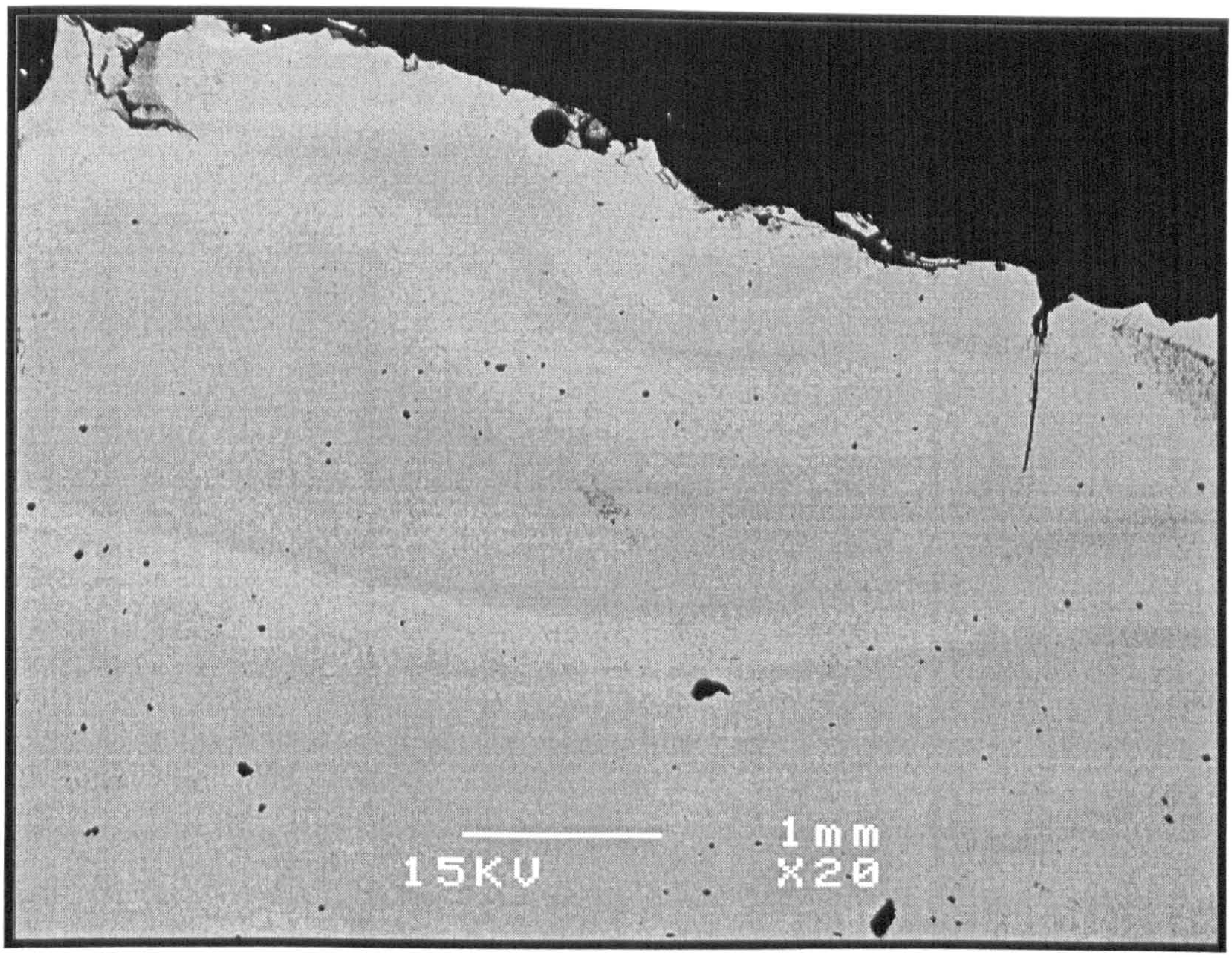
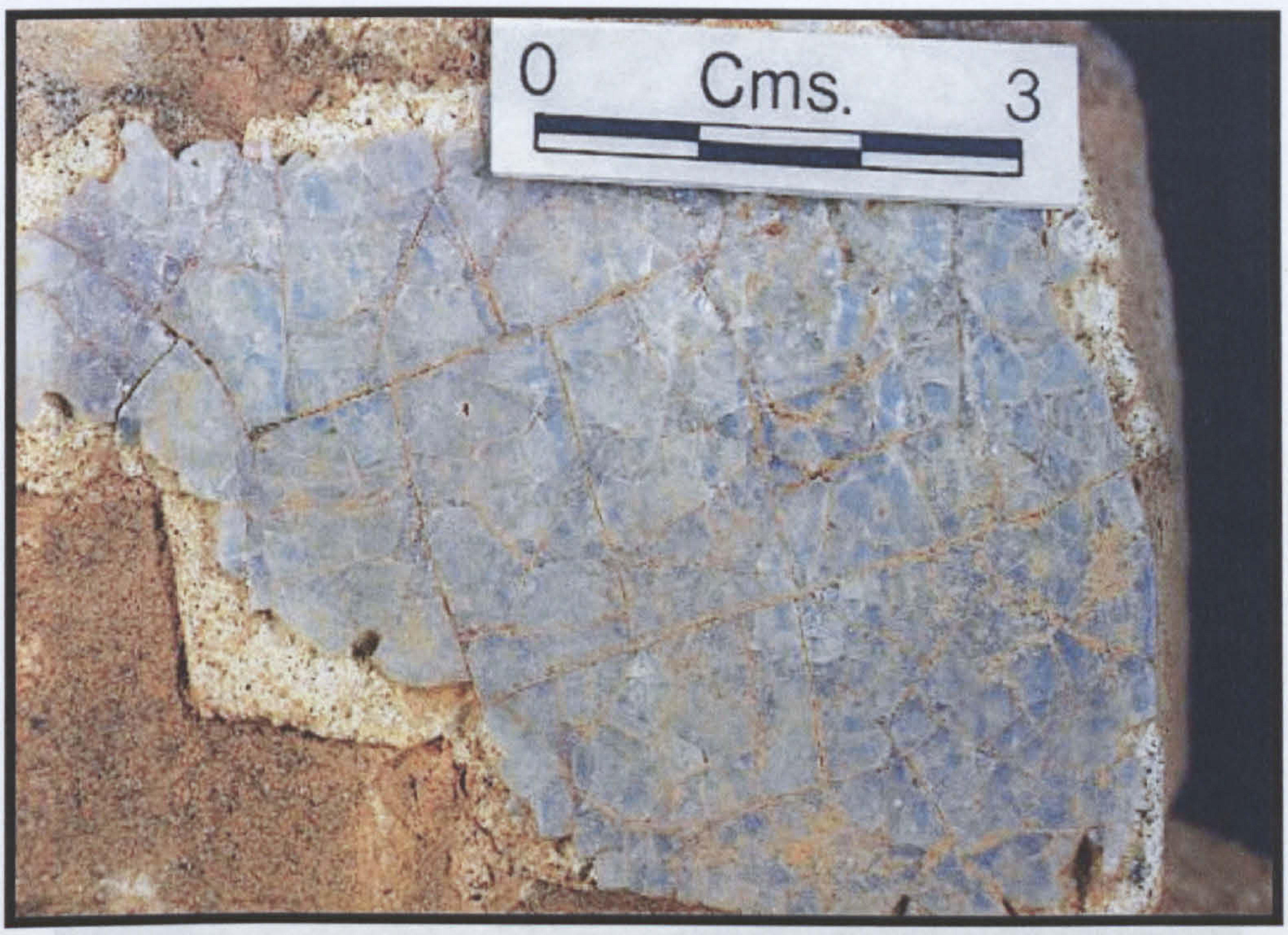
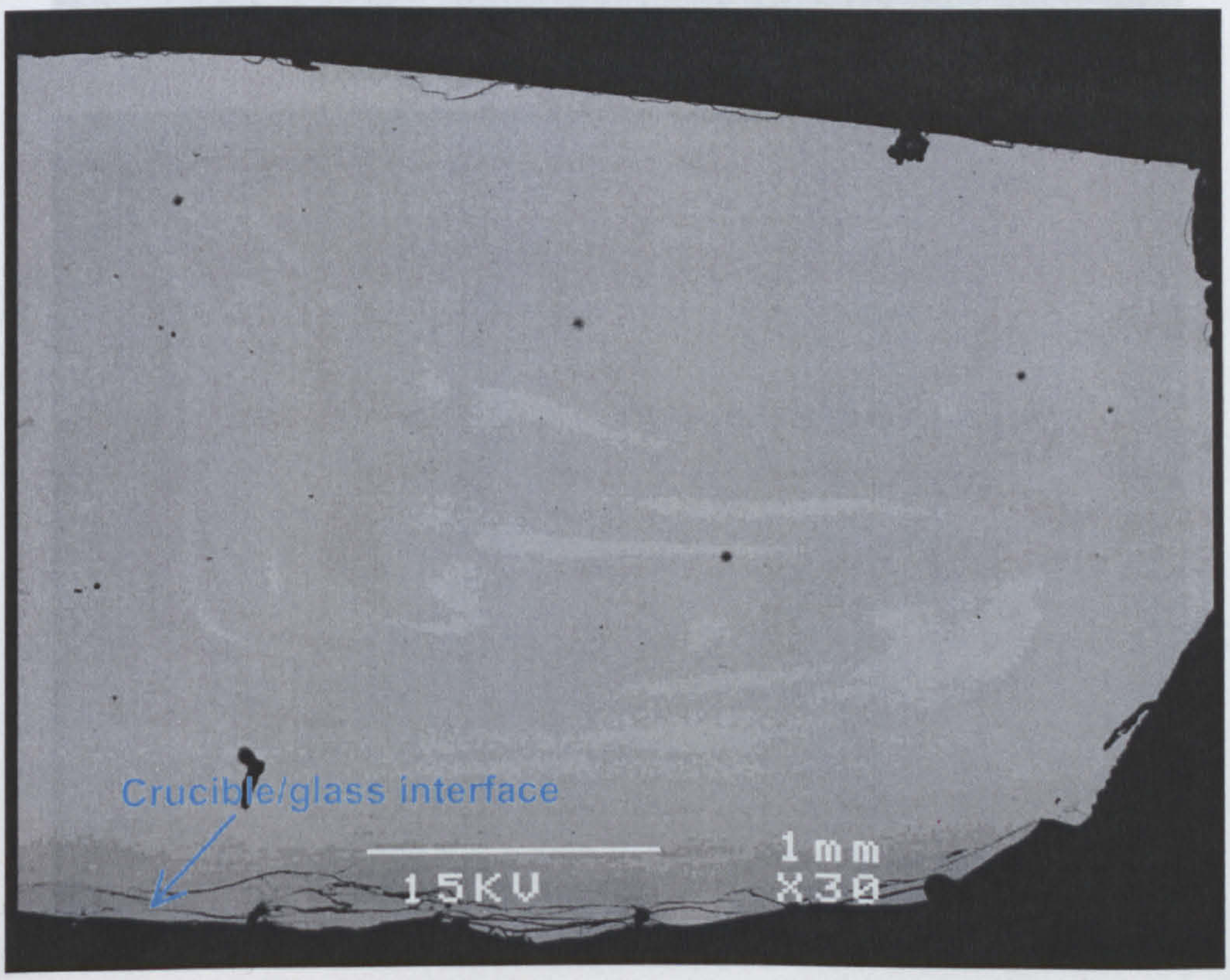


Plate 8:2 **Backscattered SEM image of a sample of waste glass/cullet (BW4) from Blunden's Wood with medium levels of inhomogeneity (Table VIII:1)**

The crucibles from Blunden's Wood (BW5-10) either contain glass that exhibits opacity (Plate 8:3) or is visually homogeneous (Plate 8:4). Backscattered imaging has shown that inhomogeneity was present in **both** these types of glass (Plate 8:3 and Plate 8:4), but one sample of each glass type (BW8 and 9) was also homogeneous. Therefore in these samples there appears to be no correlation between inhomogeneity and the presence of visual opacity in the glass.

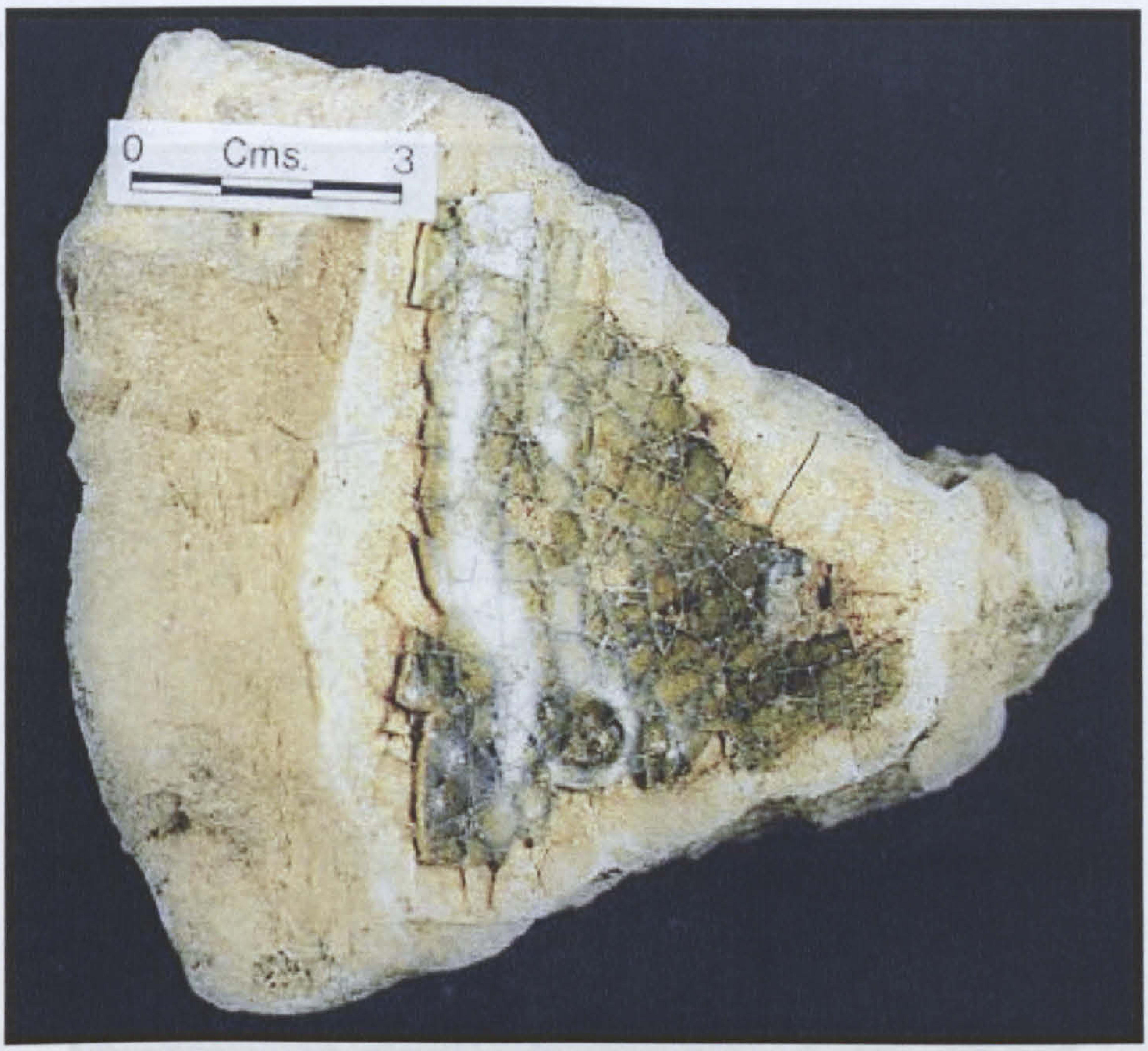


Crucible glass with opacity BW6

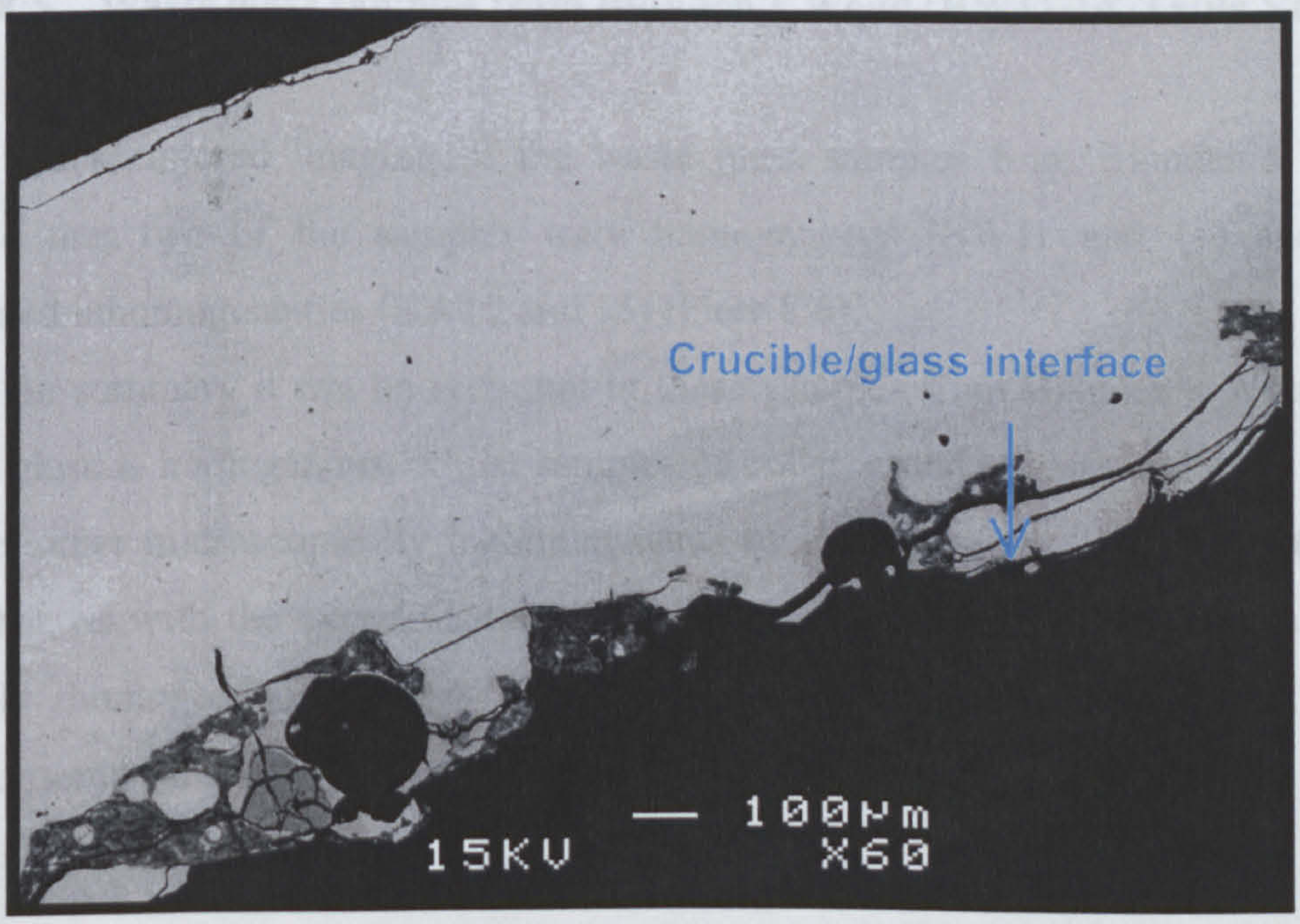


Backscattered SEM image of BW6

Plate 8:3 Crucible glass with opacity from Blunden's Wood (BW6, Table VII:3) and the comparative backscattered SEM image of a sample of the glass showing medium levels of inhomogeneity (Table VIII:1)



Visually homogeneous crucible glass BW5



Backscattered SEM image of BW5

Plate 8:4 Visually homogeneous crucible glass from Blunden's Wood (BW5, Table VII:3) and the comparative backscattered SEM image of a sample of the glass, showing medium levels of inhomogeneity (Table VIII:1)

The samples of glass waste from Blunden's Wood (BW11-14) are illustrated in (Plate 8:5).

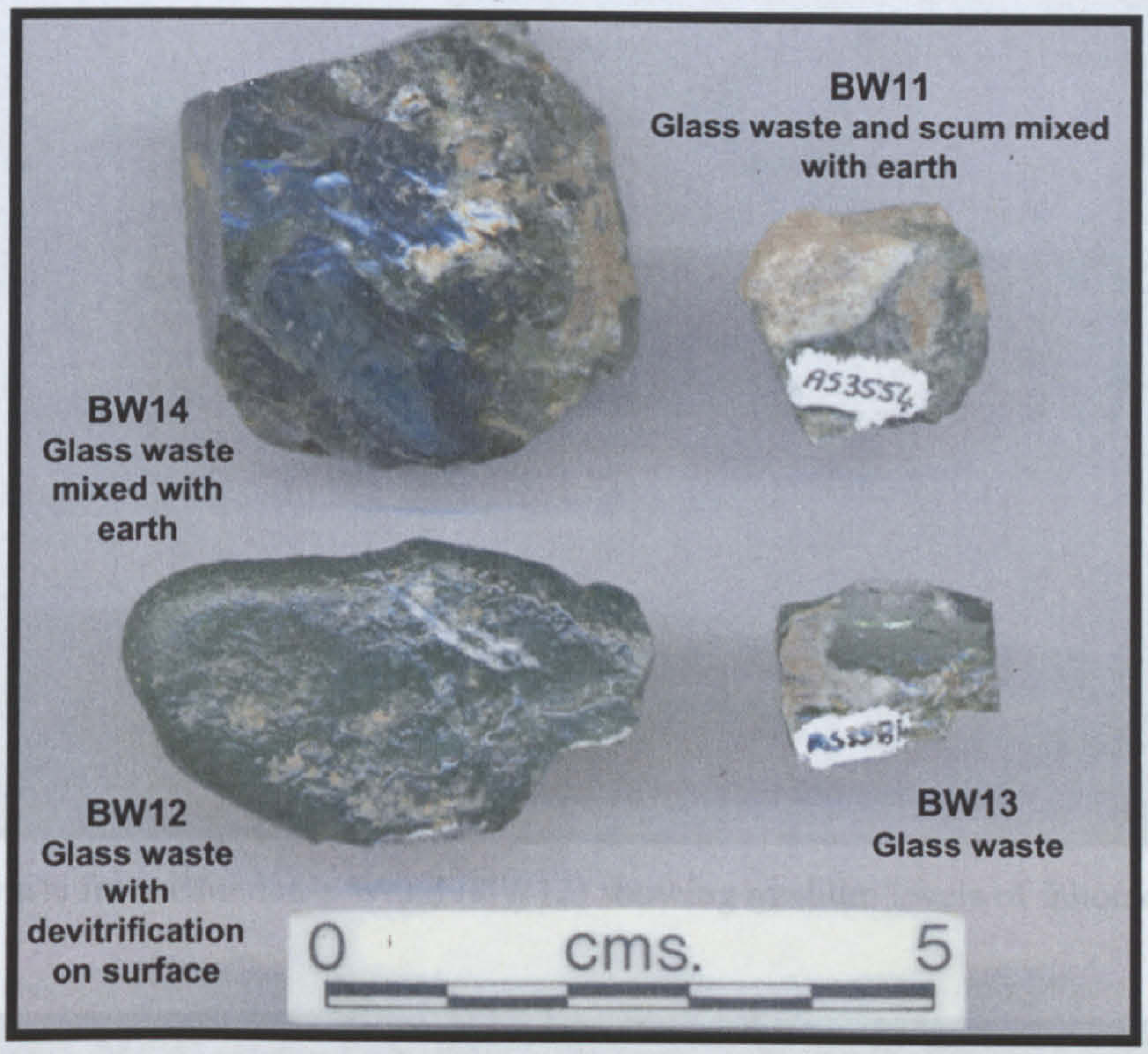
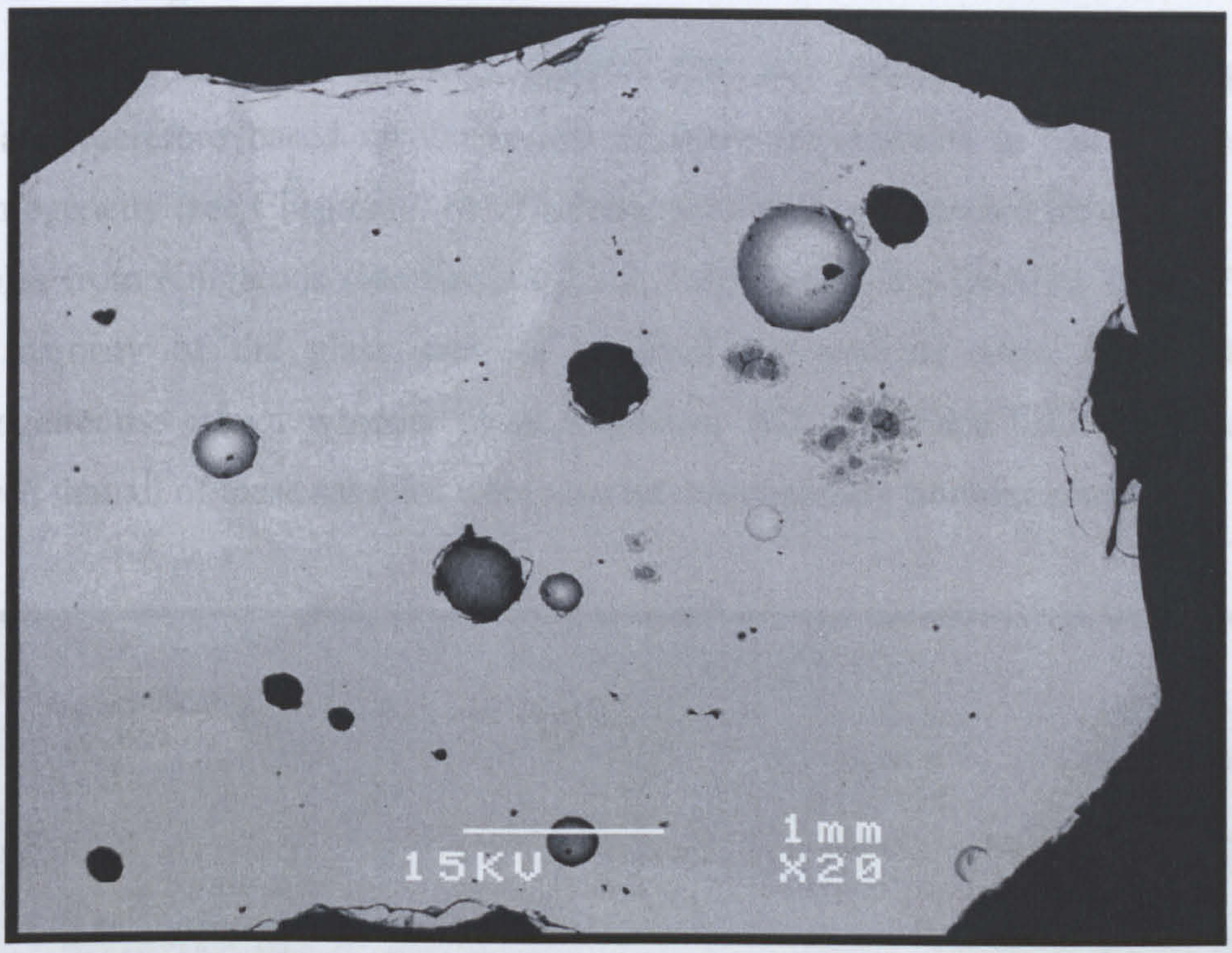


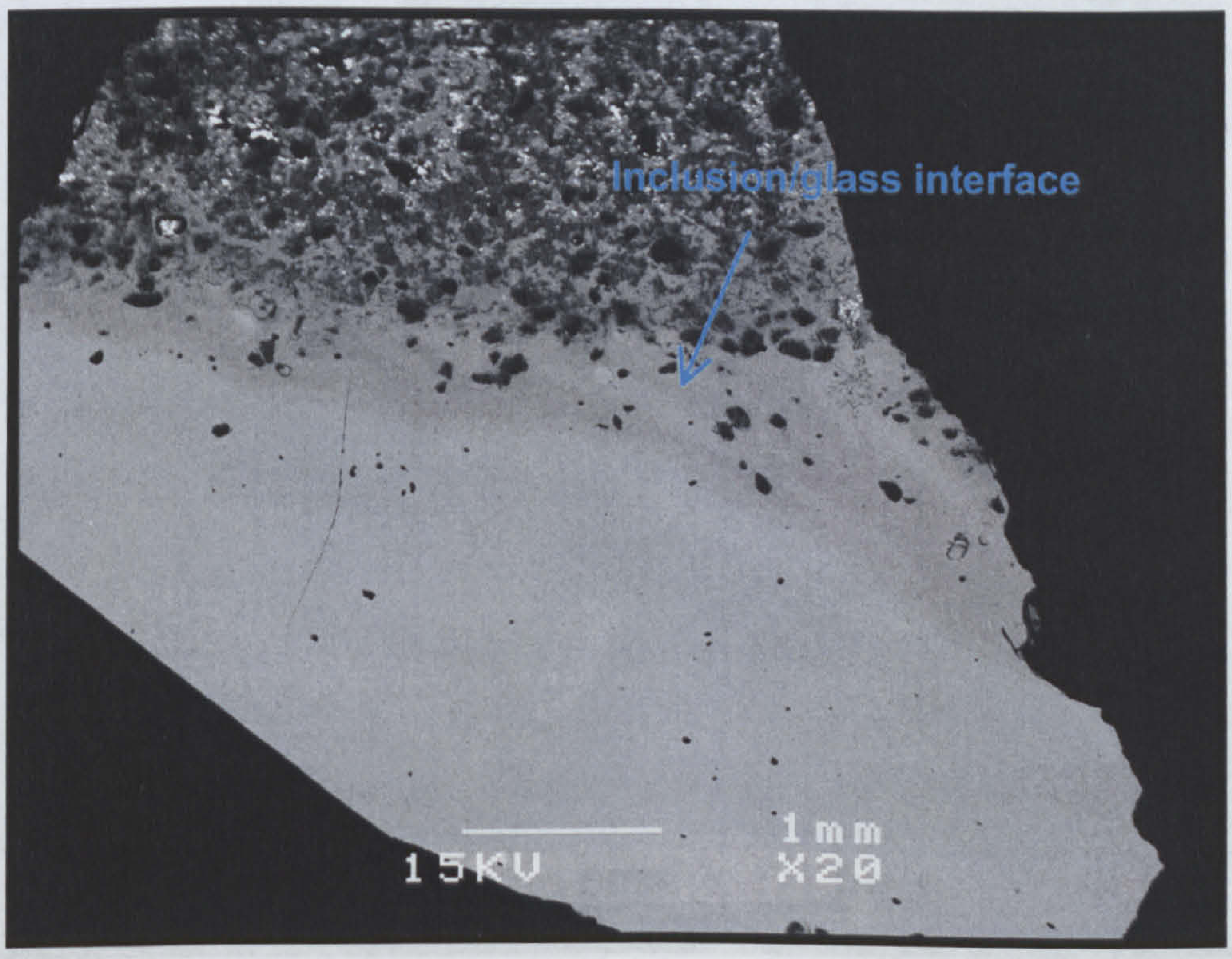
Plate 8:5 Waste glass samples from Blunden's Wood (BW11-14, Table VII:3)

Backscattered imaging of the waste glass samples from Blunden's Wood showed that two of the samples were homogeneous (BW11 and 14) and two contained inhomogeneities (BW12 and 13) (Plate 8:6).

In summary it can be seen that in these samples from Blunden's Wood, the vessel glass is homogenous, whilst samples of cullet, crucible glass and glass waste can be either microscopically inhomogeneous **or** homogeneous. It is important to note that, as with the experimental glasses produced in Chapters 4-6, a number of **visually** homogeneous glasses contained **inhomogeneities** only visible using backscattered SEM imaging.



Glass waste from Blunden's Wood (BW12) showing medium levels of inhomogeneity .



Glass waste from Blunden's Wood (BW13) showing low levels of inhomogeneity at the inclusion/glass interface

Plate 8:6 Backscattered SEM images of glass waste from Blunden's Wood showing medium (BW12), and low (BW13) levels of inhomogeneity (Table VIII:1)

8.2.1.2 Knightons

Section 7.2 noted that the Knightons glass was probably produced using oak ash, and therefore based on the results of these experiments is likely to exhibit inhomogeneity (see Chapters 4-6). The results of the backscattered imaging of glass samples from Knightons (see Section 7.2.2, Table VII:5) are listed in Table VIII:2. The majority of the glass samples obtained for analysis were from **visually homogeneous**, crown window glass fragments (K1-11) (Plate 8:7). The results showed that all of these samples were also **microscopically homogeneous**.

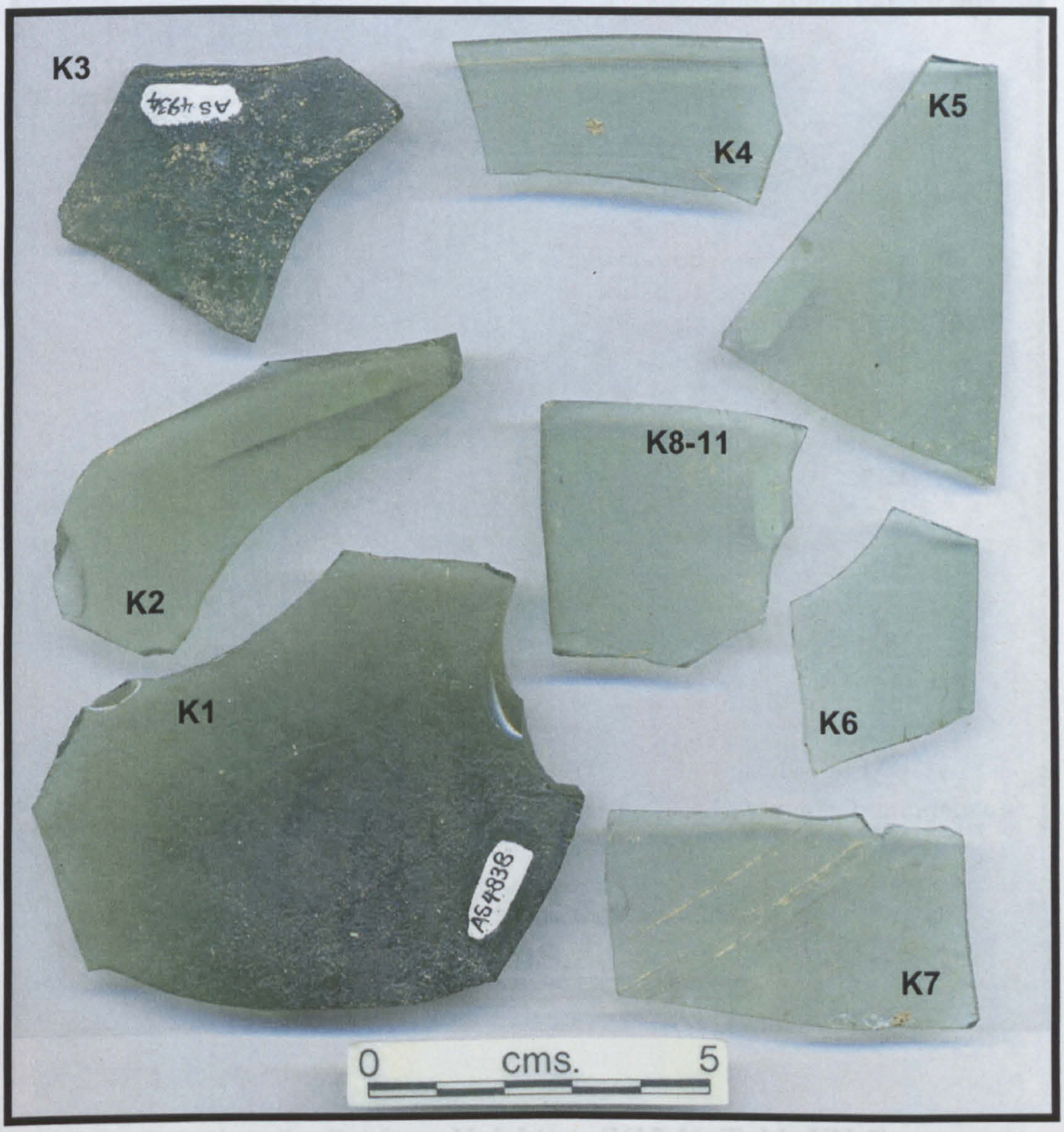


Plate 8:7 Visually homogeneous crown glass from Knightons (K1-11, Table VII:5)

The samples of local cullet selected from Knightons (K12-16) (see Section 7.2.2) are illustrated in Plate 8:8. The samples taken from strike offs (K12-14) were all visually and microscopically **homogeneous**. Samples K15 and 16 were removed from larger lumps of glass cullet. K15 was visually homogeneous and K16 contained opacity but both were found to be microscopically **inhomogeneous** (Plate 8:9). The backscattered images in Plate 8:9 show that K15 contains lower levels of inhomogeneity than K16, and that K16 also contains devitrification.

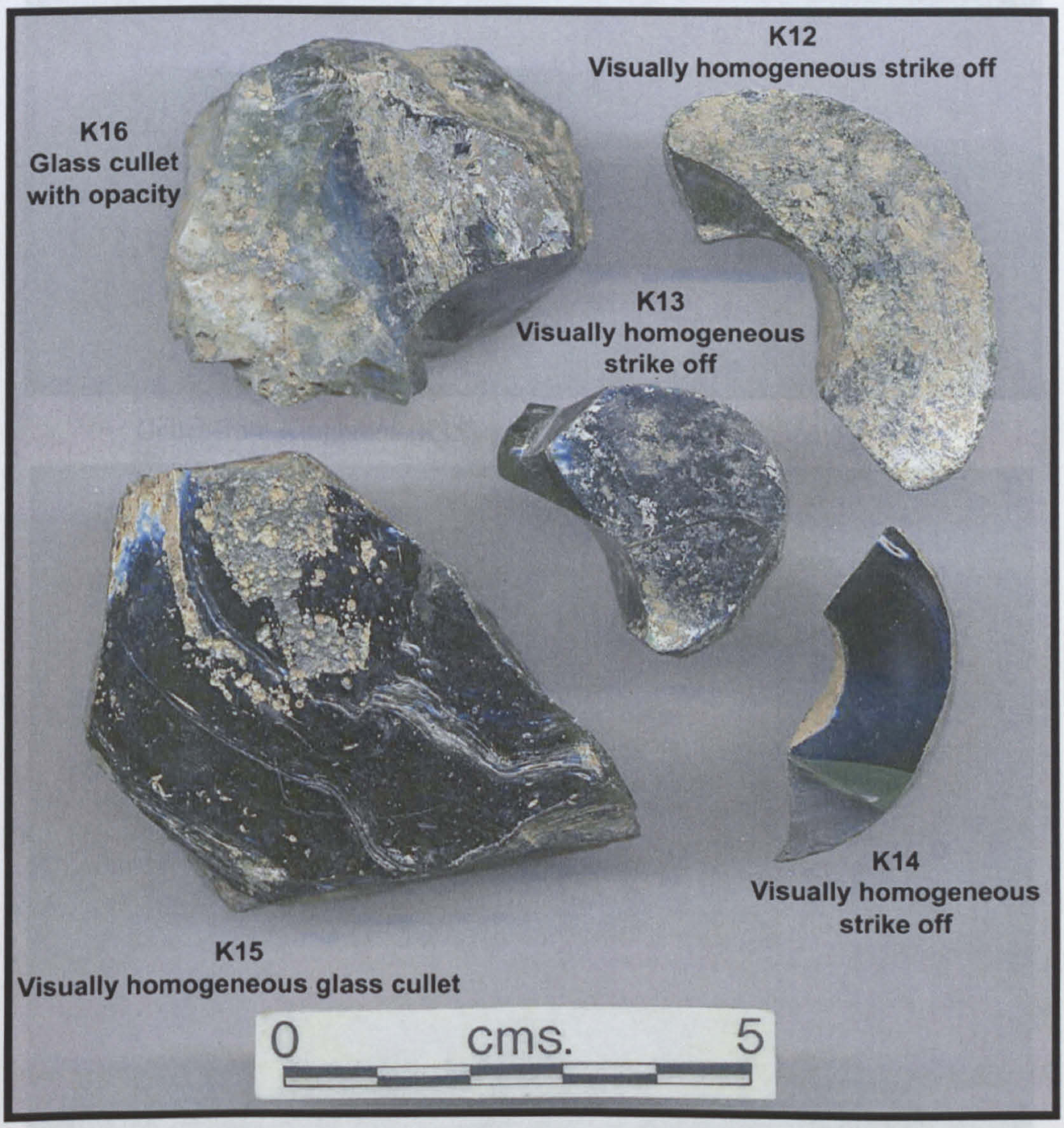
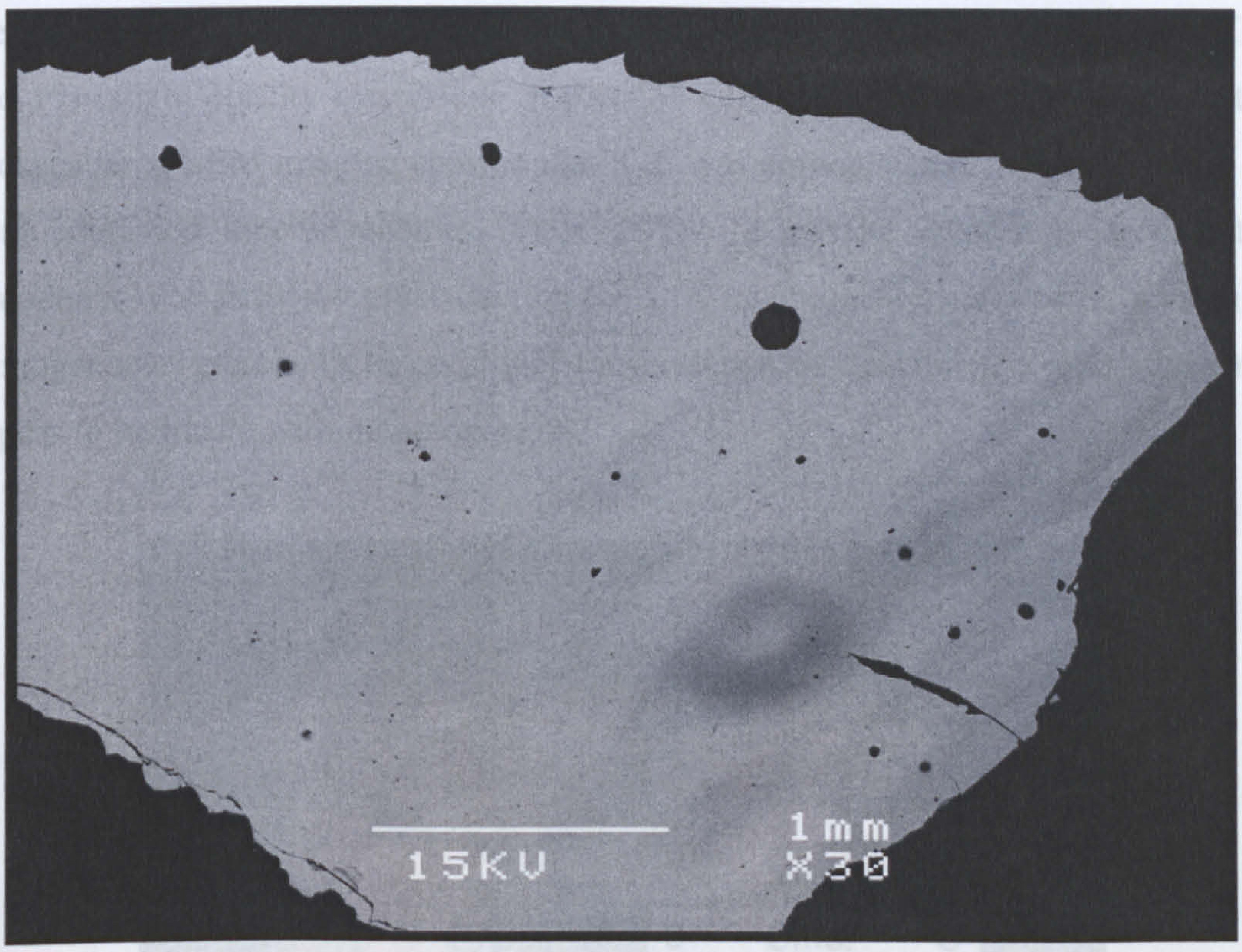
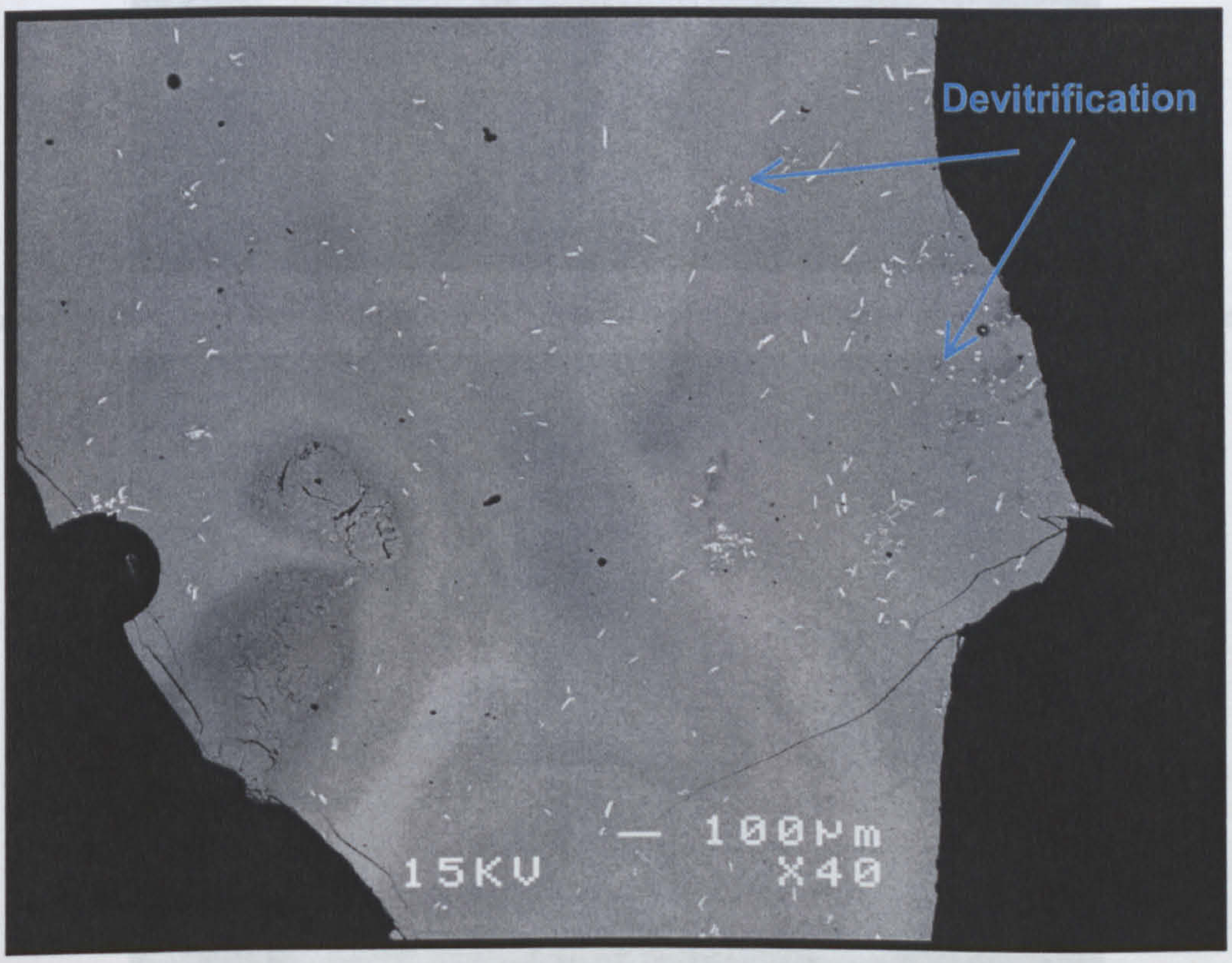


Plate 8:8 Samples of cullet from Knightons (K12-16, Table VII:5)



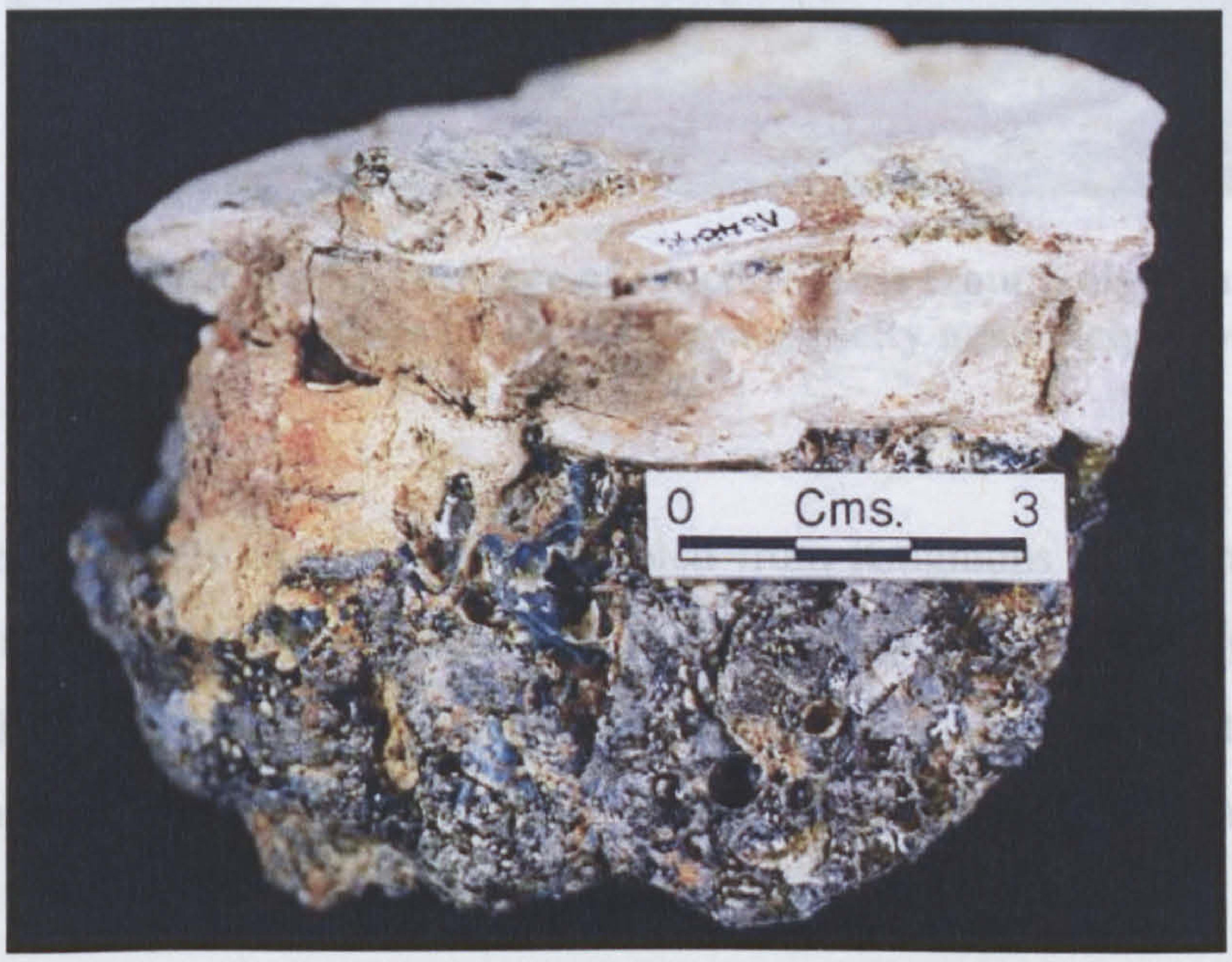
Cullet from Knightons (K15) with medium levels of inhomogeneity



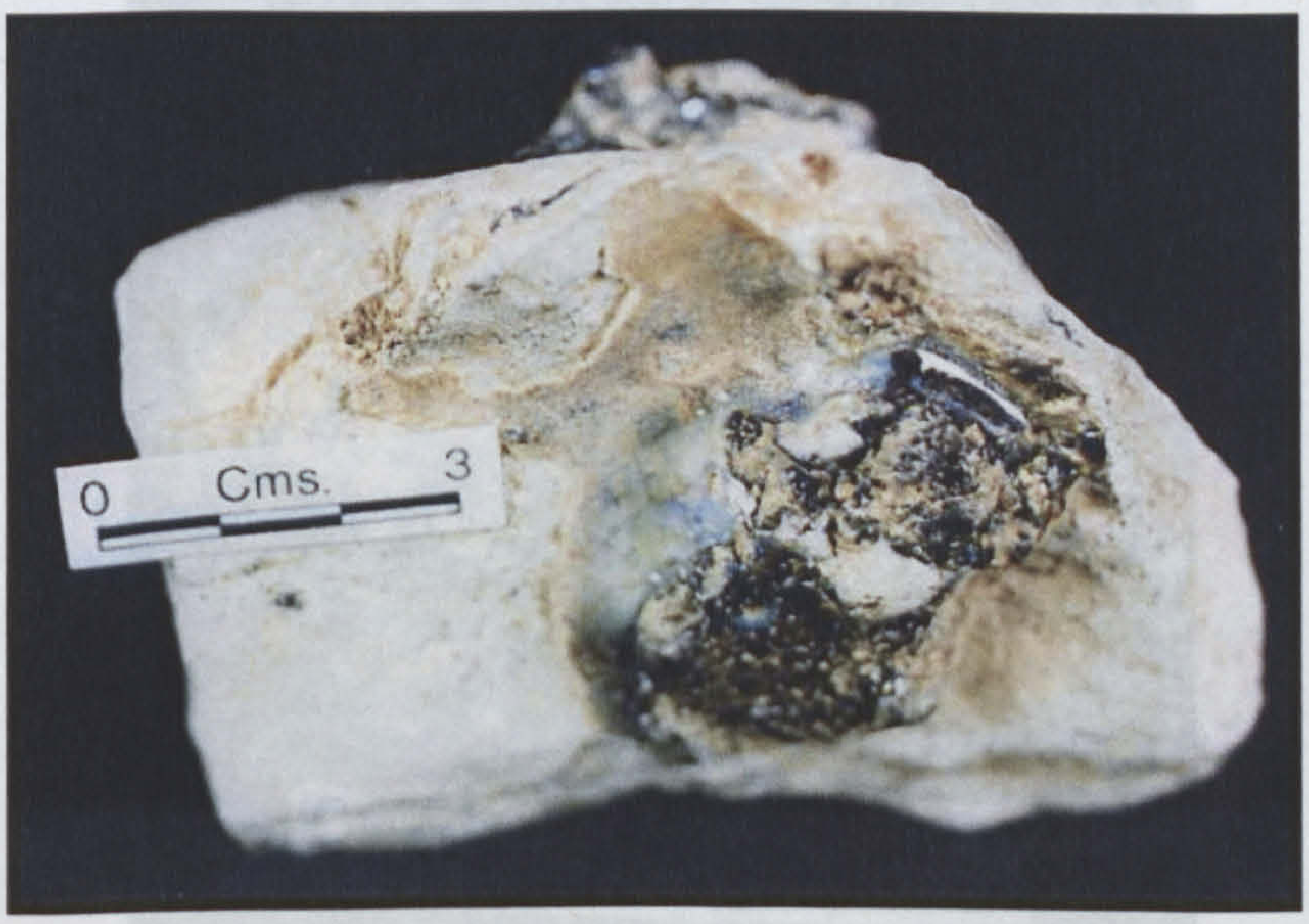
Cullet from Knightons (K16) with devitrification, and high levels of inhomogeneity

Plate 8:9 Backscattered SEM images of cullet from Knightons with medium (K15) and high (K16) levels of inhomogeneity (Table VIII:2)

The crucible fragments from Knightons contained either a mixture of heavily weathered glass and scum (K17), or visually homogeneous dark green glass (K18 and 19) (slight opacity was visible in parts of K18) (Plate 8:10). The results of the backscattered SEM imaging showed that K18 was homogeneous, whilst K17 and 19 both contained inhomogeneities (Plate 8:11). It can be seen that, as with the Blunden's Wood crucibles (see Section 8.2.1.1), inhomogeneity is present in visually homogeneous glasses (K19) and that the presence of opacity in a glass does not appear to be linked with inhomogeneity.



Crucible fragment from Knightons (K17) with heavily weathered glass and scum attached



Crucible fragment from Knightons (K18) with glass containing some opacity

Plate 8:10 Crucible fragments from Knightons (K17 and 18, Table VII:5)

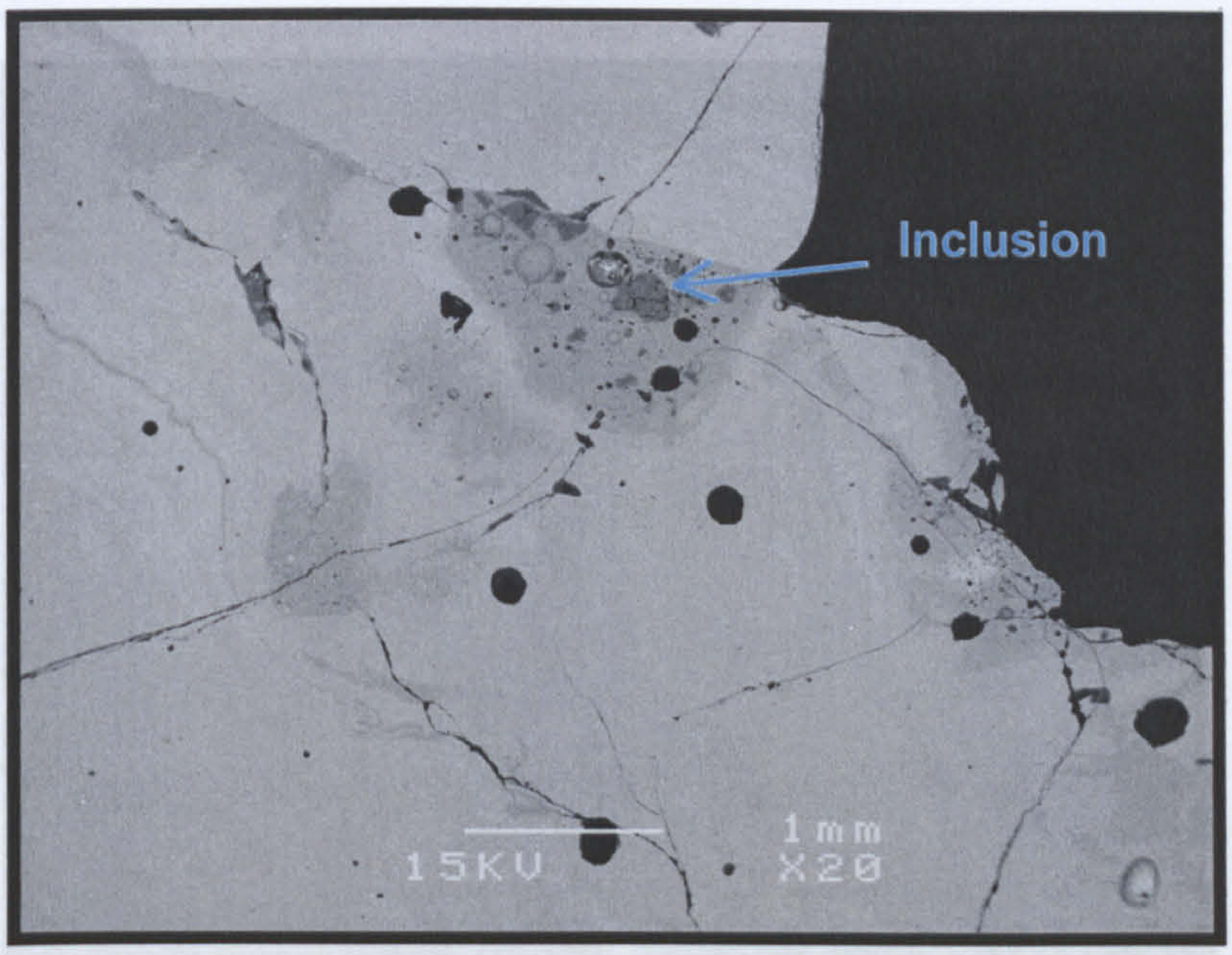


Plate 8:11 Backscattered SEM image of crucible glass from Knightons (K17) with low to medium levels of inhomogeneity near inclusions (Table VIII:2)

The fragments of glass waste sampled from Knightons (K20 and 21) both contained a mixture of transparent dark green, and opaque pale blue/green glass (Plate 8:12). Examination of samples of these glasses using backscattered SEM imaging showed, unsurprisingly, that both contained inhomogeneities (Plate 8:13).

Plate 8:12 Waste glass from Knightons (K20, Table VII:5)

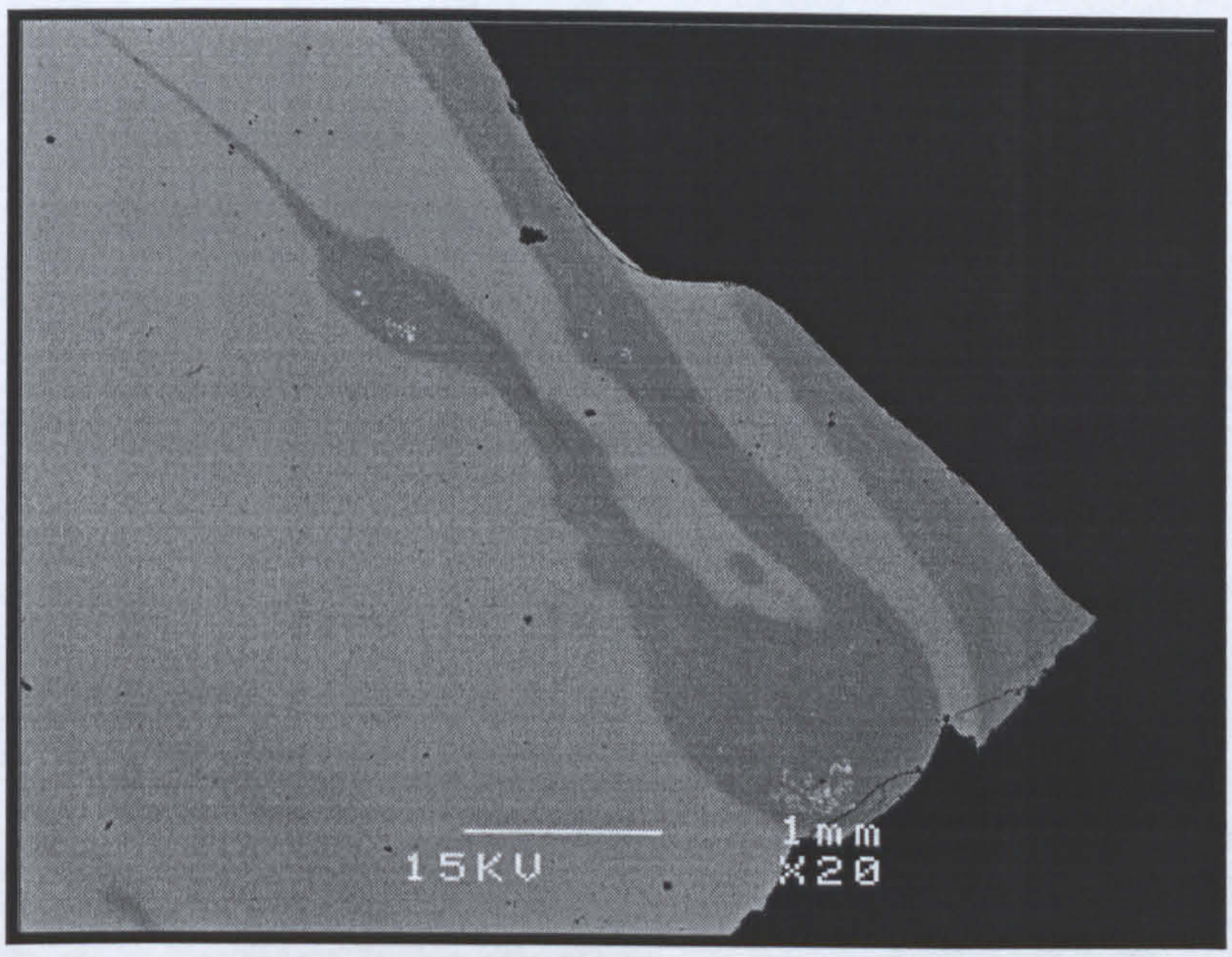


Plate 8:13 Backscattered SEM image of glass waste from Knightons (K20) with high levels of inhomogeneity (Table VIII:2)

It can be seen that the results of the Knightons glass are similar to those obtained from the Blunden's Wood material (see Section 8.2.1.1). All of the fully formed (crown) glass is homogeneous, but inhomogeneity is present in a number of fragments of cullet, crucible glass and glass waste. Inhomogeneity can also be detected in **visually** homogeneous glasses, but again there appears to be no link between the presence of opacity and microscopic inhomogeneities.

8.2.1.3 Sidney Wood

The results of backscattered SEM imaging of the Sidney Wood glass (see Section 8.2.1.3, Table VII:7) are recorded in Table VIII:3. The blue/green vessel glass samples (SW1-3) were both visually (Plate 8:14) and microscopically homogeneous. The Sidney Wood crucible glass was dark green, and was either visually homogeneous (SW4) (Plate 8:15), or contained extensive blue/green opacity (SW5 and 6). However, **all** of the crucible glass samples (SW4-6) contained inhomogeneities that were visible using backscattered SEM imaging (Plate 8:16). The thin fragment of purple furnace glass (SW7) (Plate 8:17) appeared to be visually homogeneous but was also found to contain inhomogeneities when examined under the SEM. (Plate 8:18)

Plate 8:14 Visually homogeneous vessel glass (SW1-3) from Sidney Wood (Table VII:7)

Plate 8:15 Crucible fragments (SW4) from Sidney Wood containing visually homogeneous dark green glass (Table VII:7)

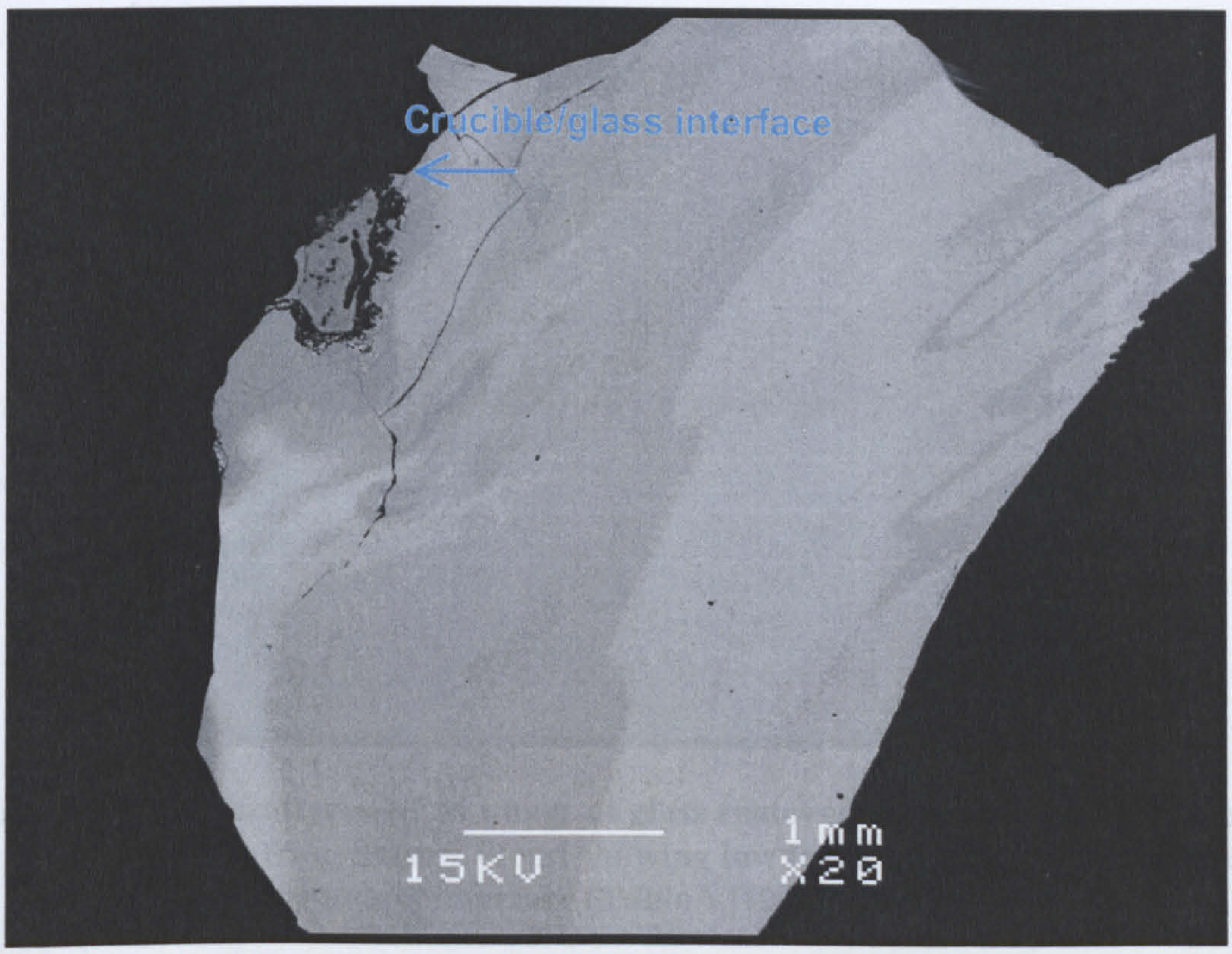


Plate 8:16 **Backscattered SEM image of crucible glass (SW4) from Sidney Wood showing a high level of inhomogeneity (Table VIII:3)**

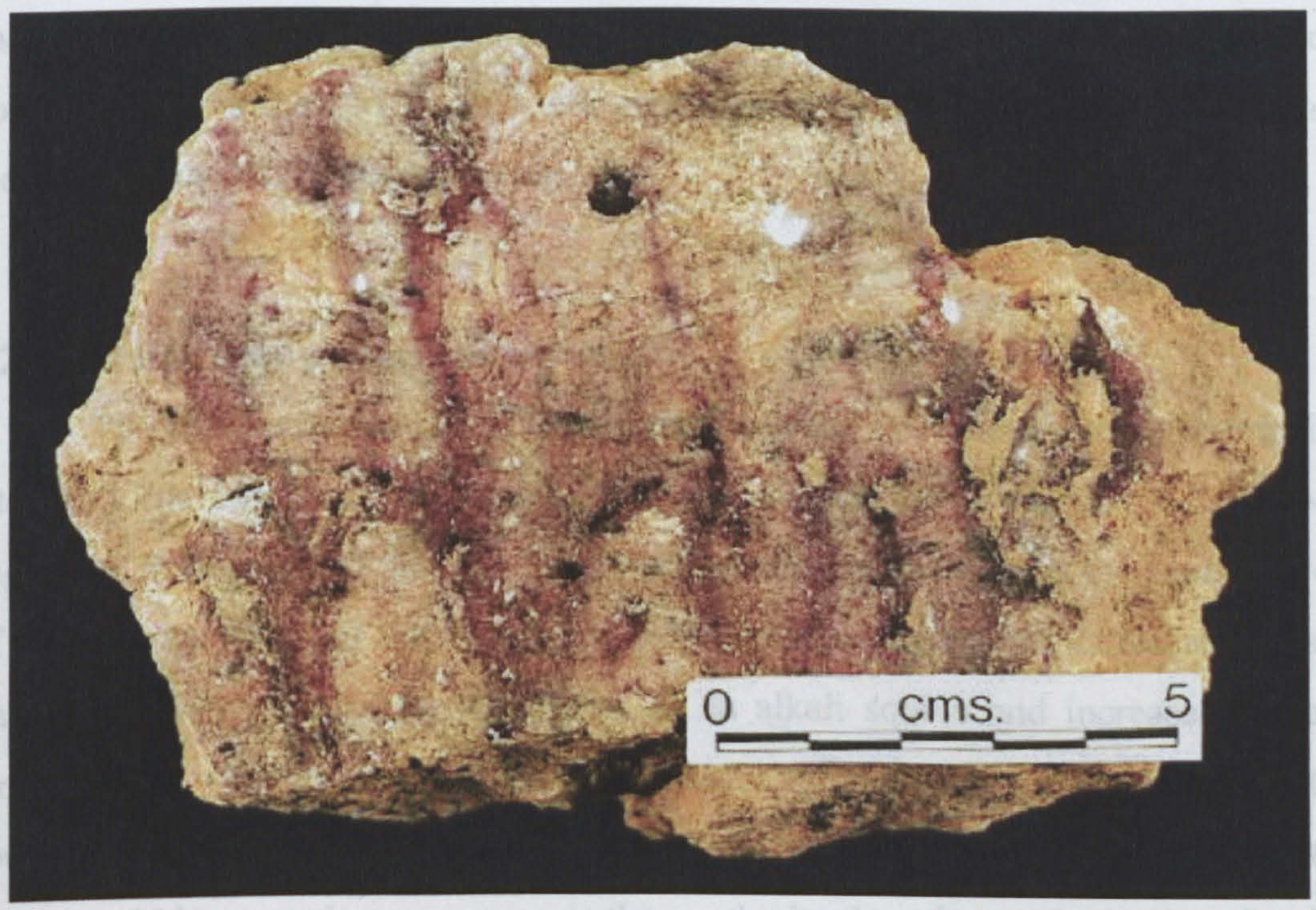


Plate 8:17 **Visually homogeneous, purple glass (SW7) on a furnace fragment from Sidney Wood (Table VII:7)**

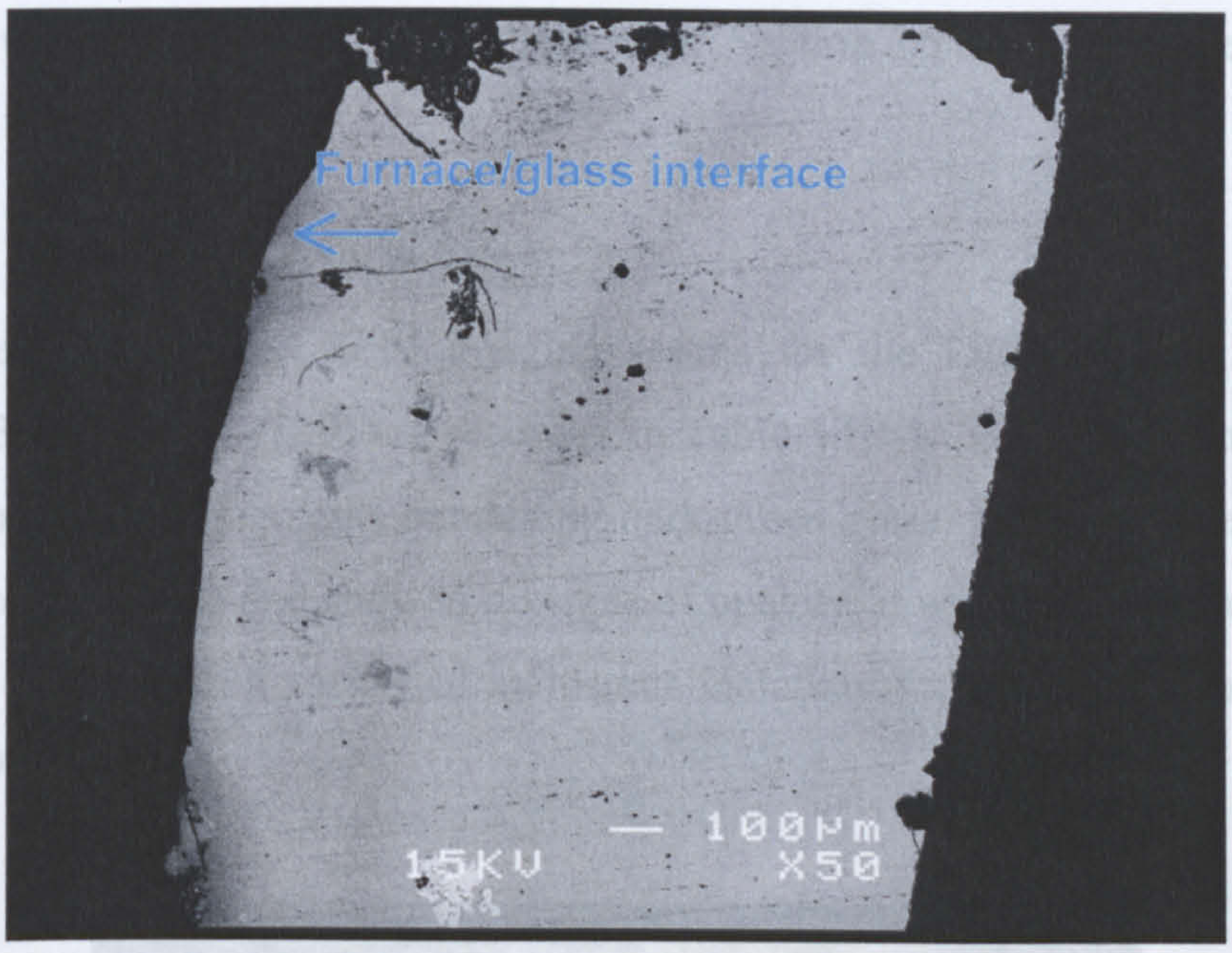


Plate 8:18 Backscattered SEM image of glass removed from a furnace fragment (SW7) from Sidney Wood showing low levels of inhomogeneity near the furnace/glass interface (Table VIII:3)

Although a smaller number of samples were analysed from Sidney Wood compared to Blunden's Wood or Knightons (see Sections 8.2.1.1 and 8.2.1.2) it can be seen that the results from the three sites are very similar. As at Blunden's Wood and Knightons, all of the Sidney Wood vessel glass samples examined were homogeneous, and all of the crucible glass contained **inhomogeneities** even when the glass was **visually homogeneous.**

8.2.2 Staffordshire Glassmaking Sites

The reasons why glass was selected from the north and south glassmaking sites at Little Birches, Staffordshire have been discussed in Section 7.3. It was suggested in Section 7.5 that the Little Birches glass would exhibit the lowest levels of inhomogeneity of all the archaeological material analysed in this research based on the suggested use of bracken ashes as an alkali source and increased furnace temperatures. The evidence that higher furnace temperatures were achieved at the south site compared to the earlier dated north site was also thought to suggest that the glass would be more homogeneous at the south site than the north site (see Section

7.3.1). Sections 8.2.2.1-8.2.2.2 will examine glass from both of these sites to determine whether the predicted results made in Section 7.5 can be observed.

8.2.2.1 Little Birches North Site

The backscattered SEM imaging results for the Little Birches glass (see Section 7.3.1.1, Table VII:9) are recorded in Table VIII:4. All of the samples were taken from crucible fragments containing dark green glass. Although the glass was visually homogeneous and showed no signs of opacity, it was heavily weathered and frequently mixed with a variety of inclusions including fragments of quartz pebbles (Plate 8:19).

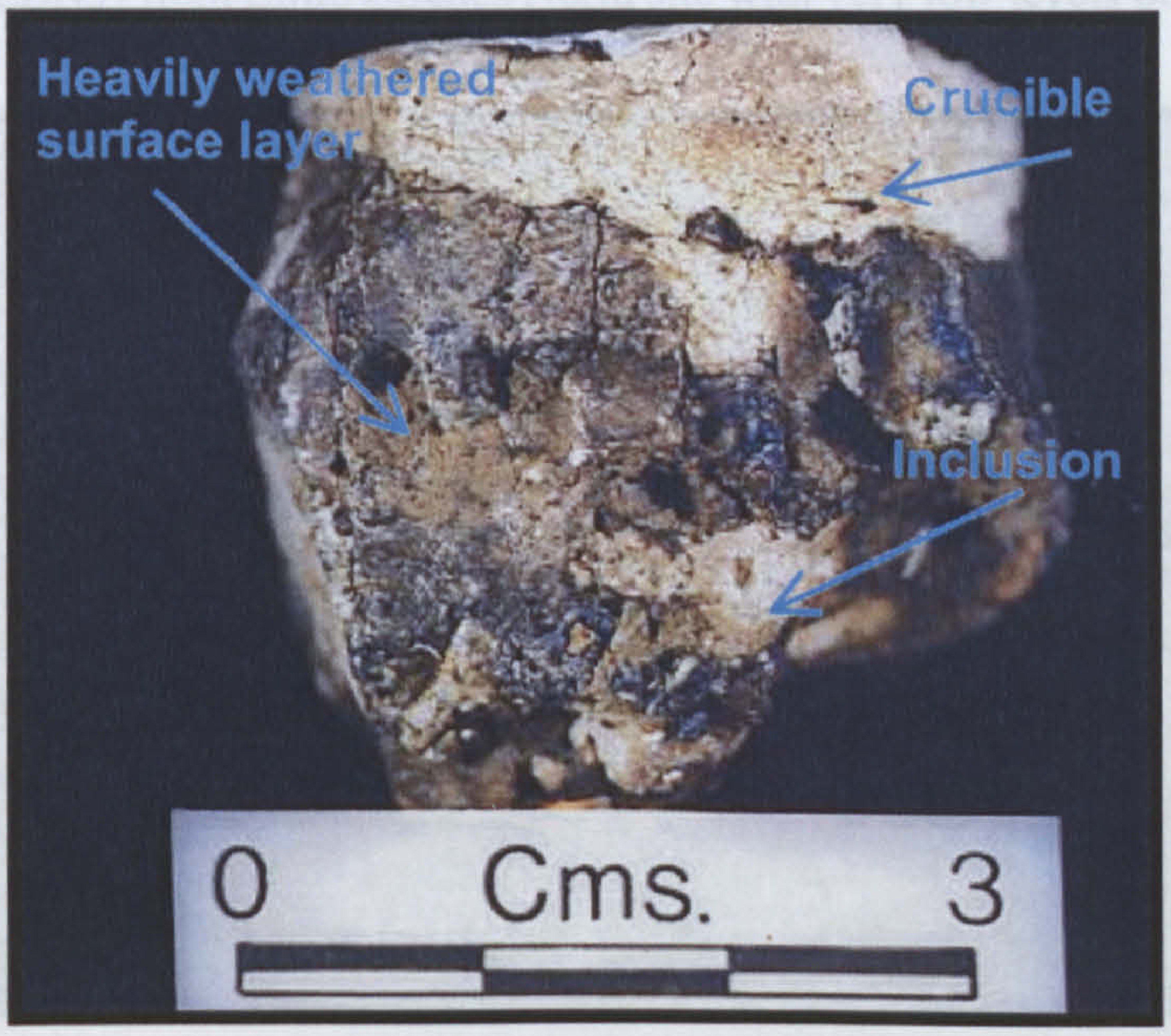
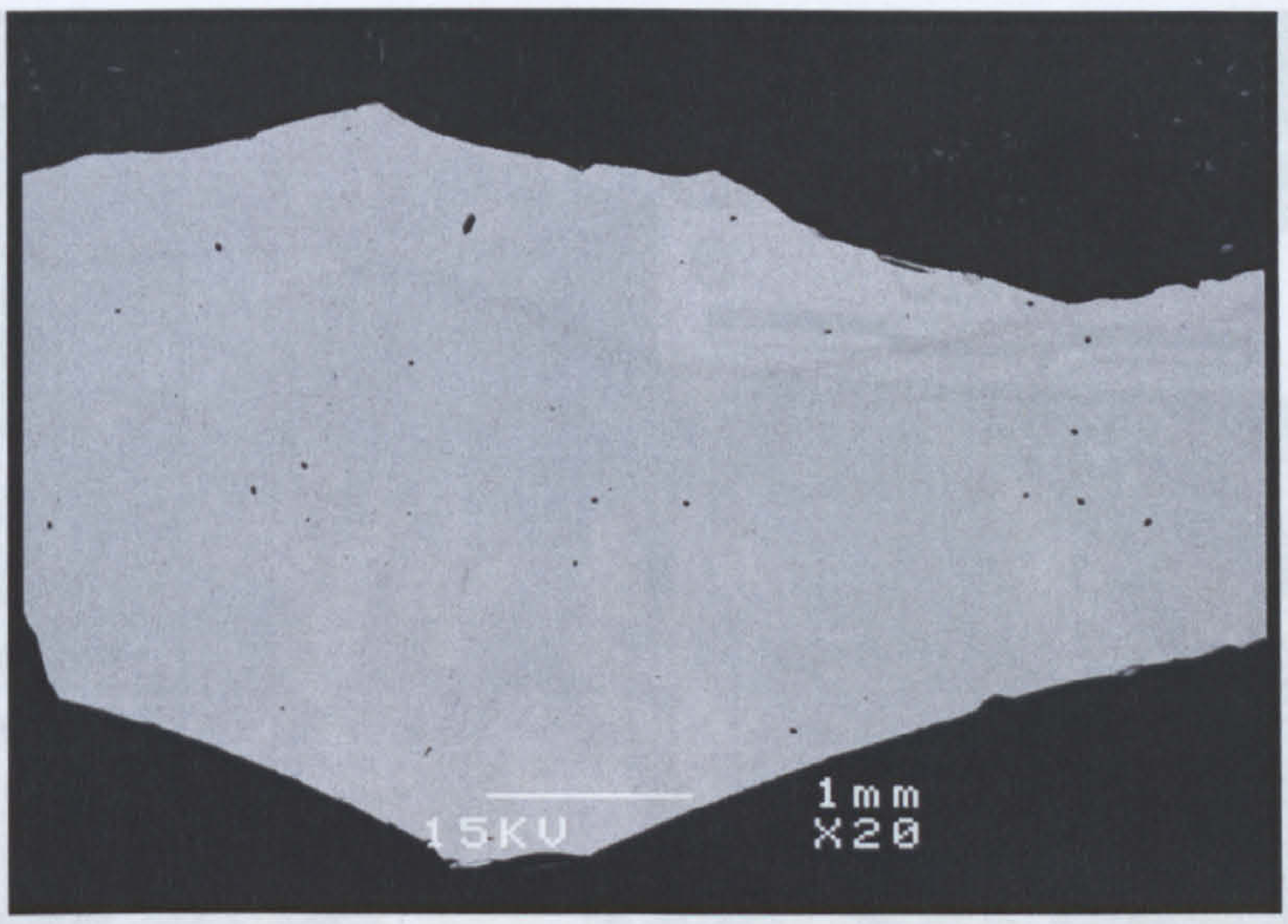
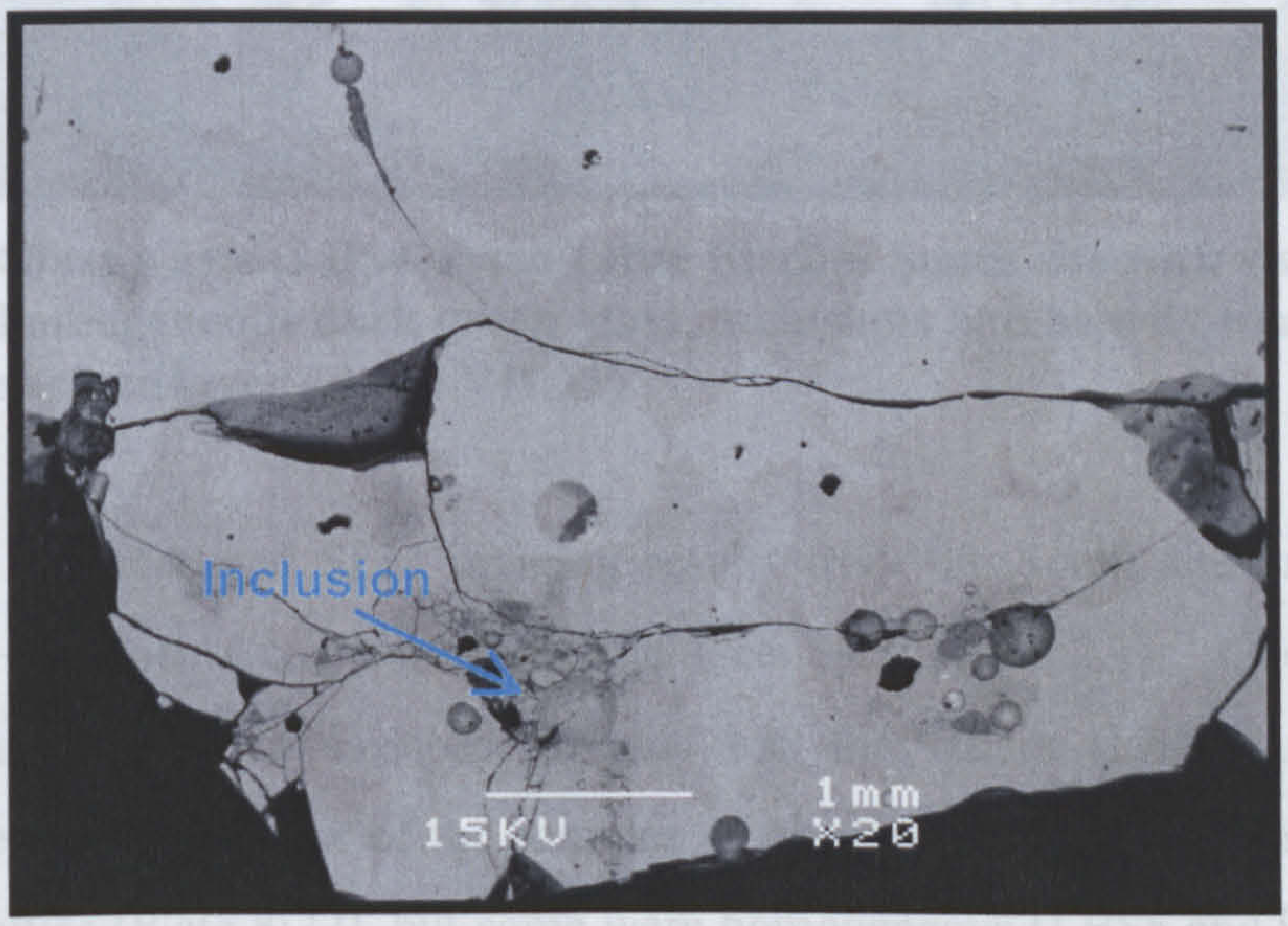


Plate 8:19 Crucible fragment (LBN5) from Little Birches North site (Table VII:9)

Backscattered imaging determined that although the glass was visually homogeneous in some cases inhomogeneity was present. For example, samples LBN2, 4, 6 and7 were **homogeneous** but LBN1, 3 and 5 were **inhomogeneous**. Inhomogeneities are predominantly associated with the presence of inclusions in the glass (Plate 8:20). In comparison to the Wealden material (see Section 8.2), the levels of inhomogeneity observed in the North site glass are extremely low, and in some cases very difficult to detect on the backscattered image.



Crucible glass (LBN3) from Little Birches North site with very low levels of inhomogeneity



Crucible glass (LBN5) from North site with medium levels of inhomogeneity around inclusions

Plate 8:20 Backscattered SEM images of crucible glass (LBN3 and 5) from Little Birches North site showing low levels of inhomogeneity (Table VIII:4)

8.2.2.2 Little Birches South Site

The results of the backscattered SEM imaging of the Little Birches, South site glass (see Section 7.3.1.2, Table VII:11) is recorded in Table VIII:5. The material is a mixture of crucible glass (LBS1-3) and glass waste (LBS4-9) (Plate 8:21), and is very similar in appearance to the material from the North site (Plate 8:19).

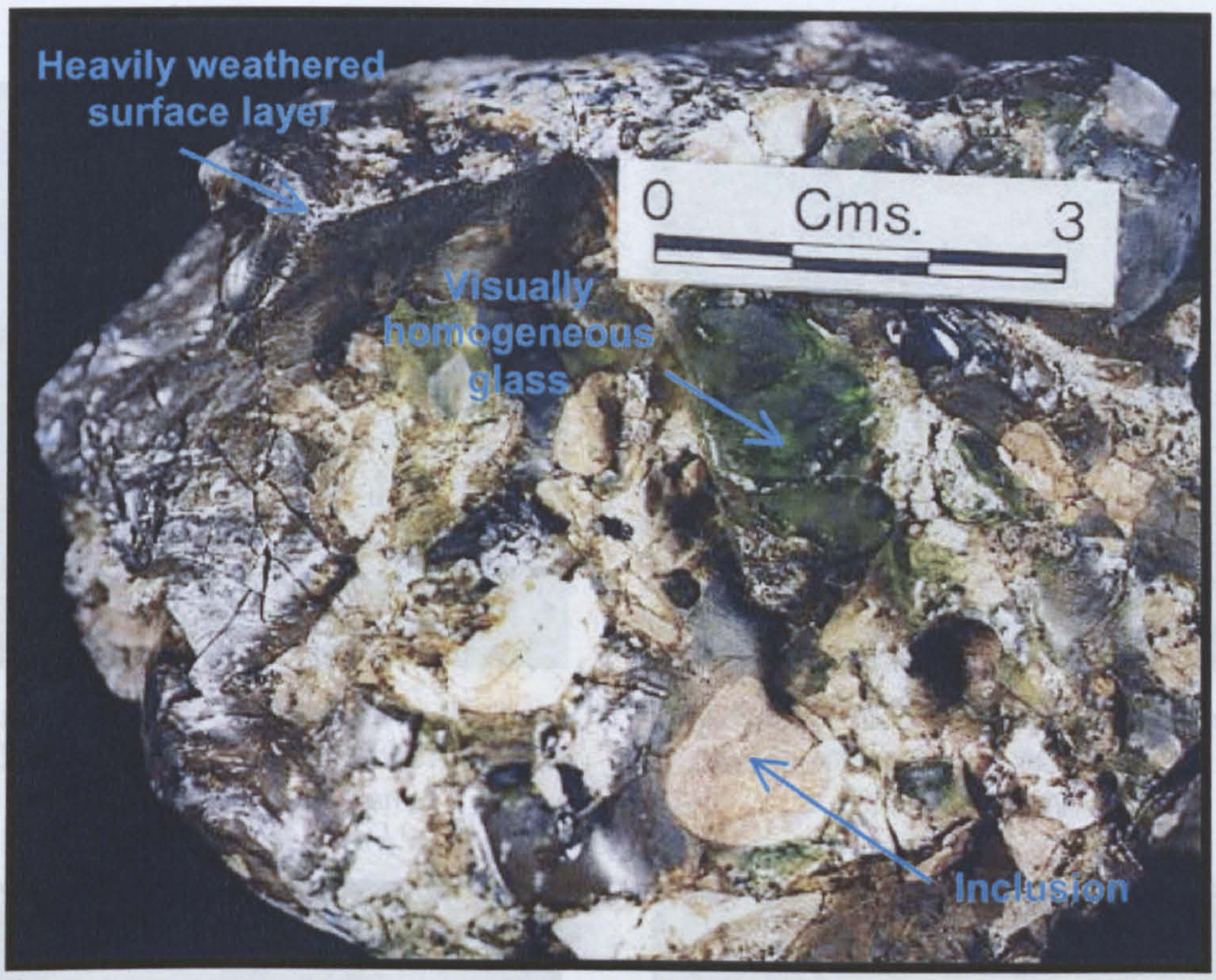
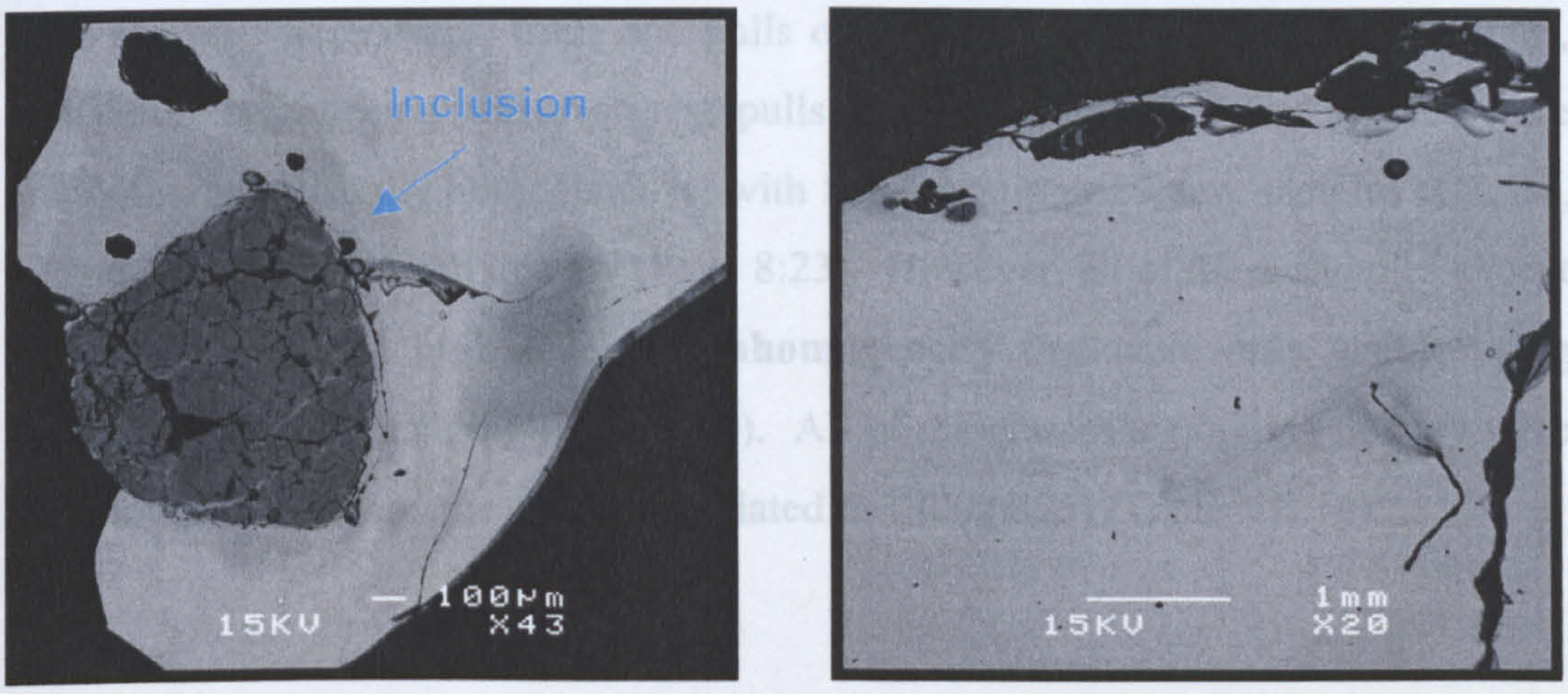


Plate 8:21 Glass waste (LBS4) from Little Birches South site with visually homogeneous dark green glass, inclusions and heavily weathered surface layer (Table VII:11)

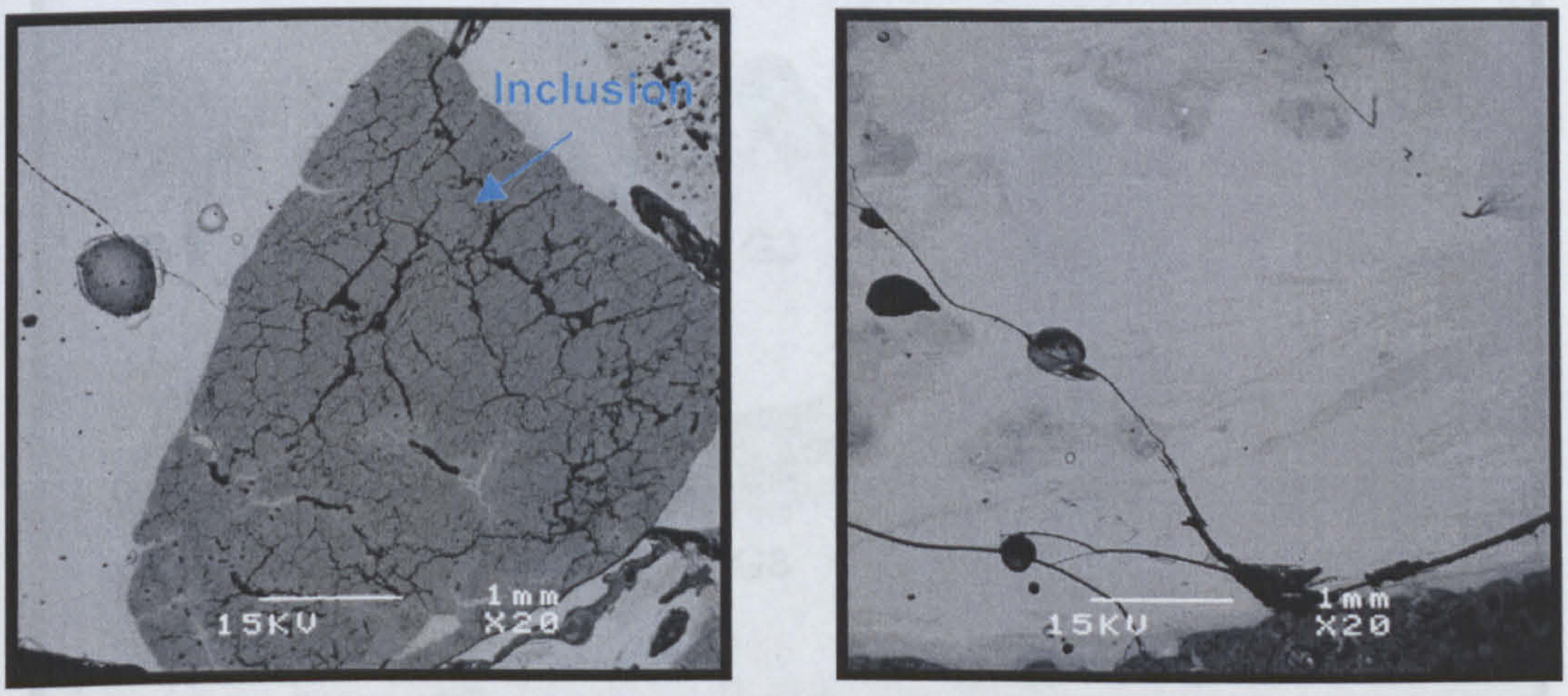
The backscattered SEM imaging results from the South site material were comparable to those from the North site (see Section 8.2.2.1). One sample of crucible glass (LBS1) was inhomogeneous but the others (LBS2 and 3) were homogeneous. A number of the samples of glass waste (LBS4-7) also contained inhomogeneities (Plate 8:22), but some were homogeneous (LBS8 and 9). It can be seen from Plate 8:22 that inhomogeneities are associated with the presence of inclusions.

It can be seen from the results of the glass from both the North and South sites at Little Birches, that the levels of inhomogeneity in crucible glass and glass waste are much **lower** that that observed in the Wealden glass in Section 8.2. The reasons for this will be discussed in Section 8.4.



Glass waste (LBS4) from Little Birches South site with low levels of inhomogeneity around an inclusion

Glass waste (LBS5) from Little Birches South site with very low levels of inhomogeneity



Glass waste (LBS6) from Little Birches South site with very low levels of inhomogeneity around an inclusion

Glass waste (LBS7) from Little Birches South site with low levels of inhomogeneity

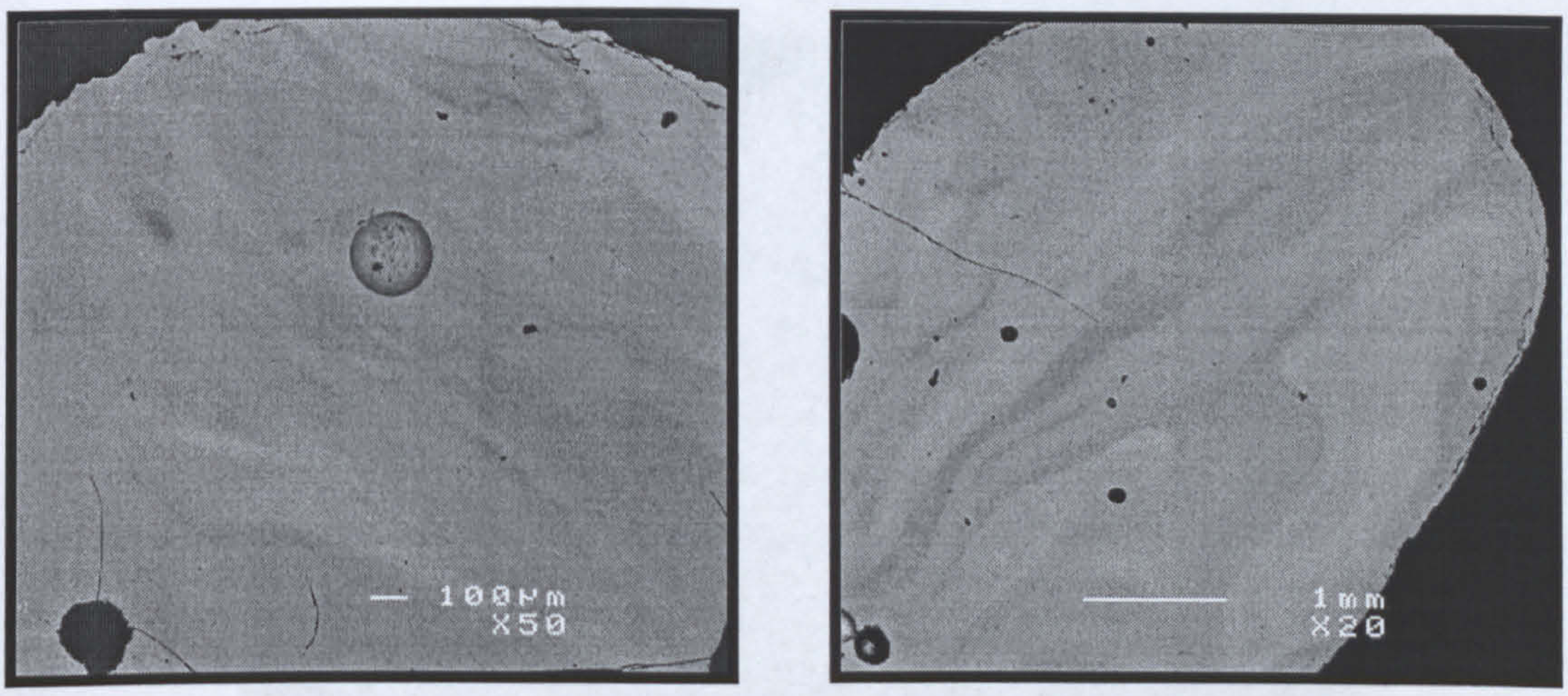
Plate 8:22 Backscattered SEM images of inhomogeneous glass waste from Little Birches South site (Table VIII:5)

8.2.3 Hils Glasshouses

Section 7.4 discussed the reasons for selecting glass from the medieval glassmaking sites in Hils for this research. It is though that these glasses will be the most likely of all the archaeological glass examined in this research to exhibit inhomogeneity due to the use of beech ashes as an alkali source and the results of the experimental beech ash glasses in Chapters 4-6 (see Section 7.5).

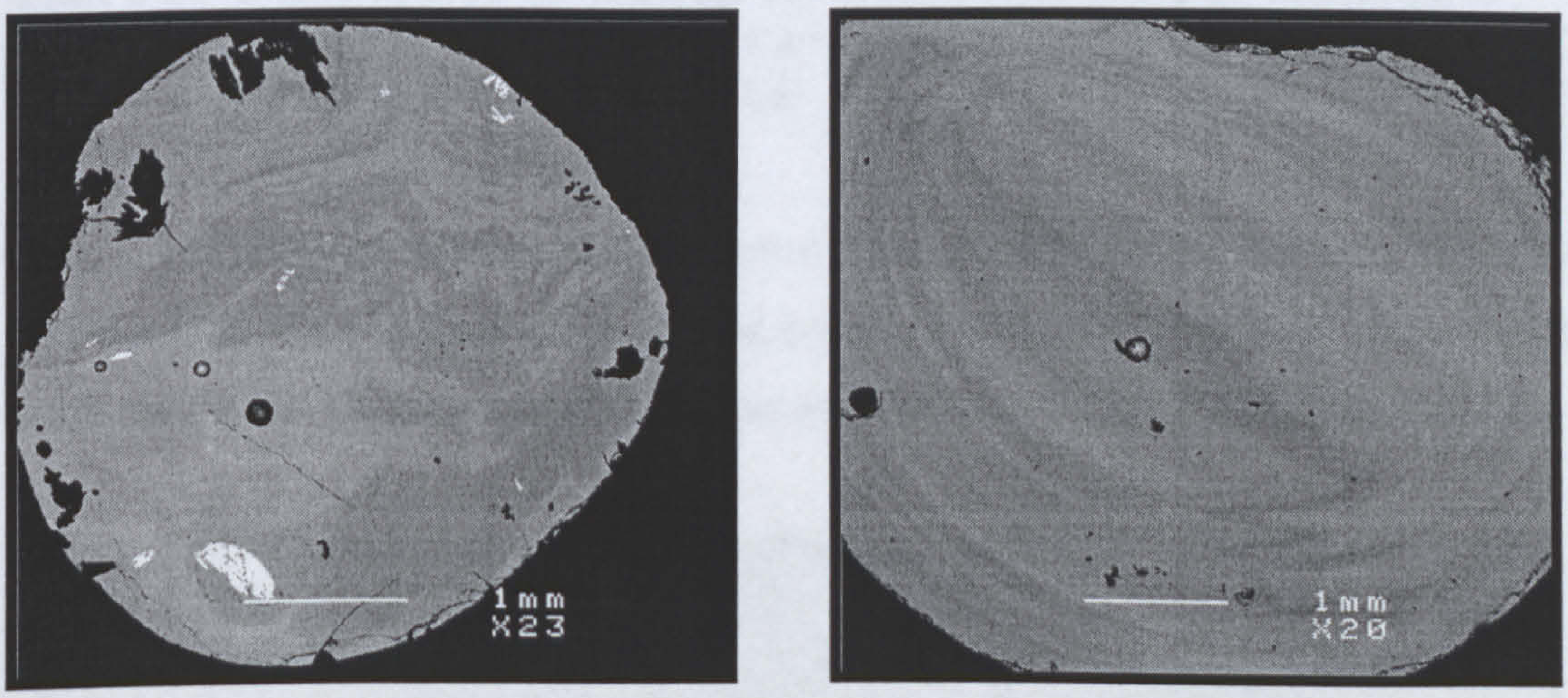
The backscattered SEM imaging results from the Hils glass samples (see Section 7.4, Table VII:14) are recorded in Table VIII:6. The majority of the Hils glass samples were drops, trails and pulls of glass in a variety of colours (G1-18), that could be working waste or test pulls (see Section 7.4). The glasses were predominantly visually homogeneous, with the exception of a few samples (G1, 10, 12 and 16) that contained opacity (Plate 8:23). However, all of these samples except G2 and 6 exhibited **high** levels of **inhomogeneity** that were only visible using backscattered SEM imaging (Plate 8:24). All of the glasses containing opacity were inhomogeneous as was the one sample dated to 1400 (G25) (Table VII:14).

Plate 8:23 Visually homogeneous glass (G1-11, 13-15, and window glass (G19 and 20) selected from Hils for analysis (Table VII:14)



Visually homogeneous glass drop (G9) from glasshouse A11 (12th/13th centuries) with high levels of inhomogeneity

Visually homogeneous glass drop (G11) from glasshouse A12 (12th/13th centuries) with high levels of inhomogeneity



Visually homogeneous glass drop (G14) from glasshouse A13 (12th/13th centuries) with devitrification and high levels of inhomogeneity

Visually homogeneous glass drop (G18) from glasshouse A18 (1400AD) with high levels of inhomogeneity

Plate 8:24 Backscattered SEM images of inhomogeneous glass drops from Hils glasshouses A11-13 and A18 (Table VIII:6)

The two samples of window glass (G19 and 20) were visually homogeneous but had a heavily weathered surface layer (Plate 8:23). Examination using backscattered SEM imaging showed that G19 was homogeneous but G20 contained high levels of inhomogeneity (Plate 8:25).

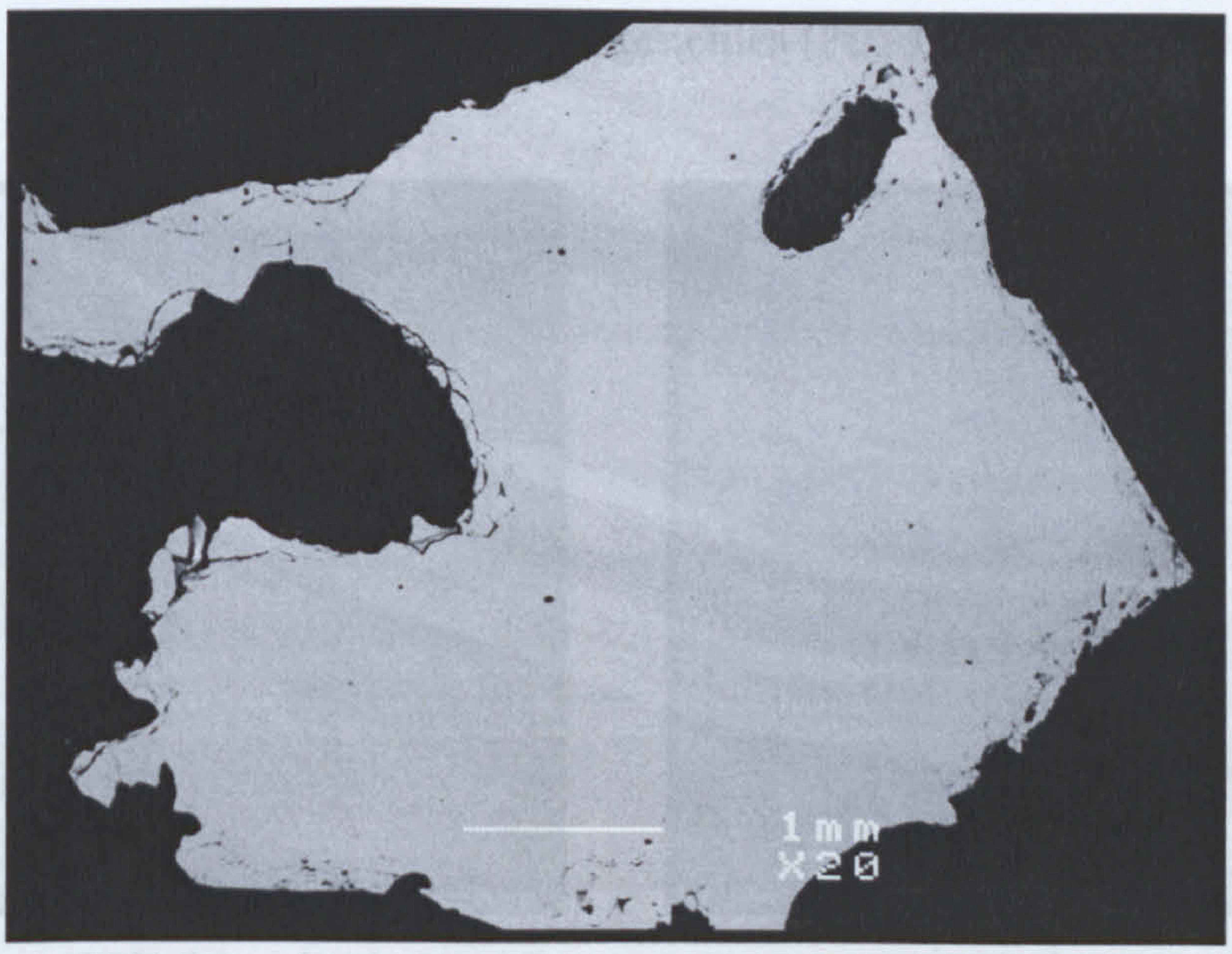


Plate 8:25 **Backscattered SEM image of visually homogeneous window glass (G20) from Hils glasshouse A18 (1400AD) with high levels of inhomogeneity (Table VIII:6)**

The samples of glass waste selected from the Hils glasshouses are illustrated in Plate 8:26. The glass is green or blue and the majority of samples are mixed with earth and scum. Opacity was also present in a number of samples (G22 and 25-27).

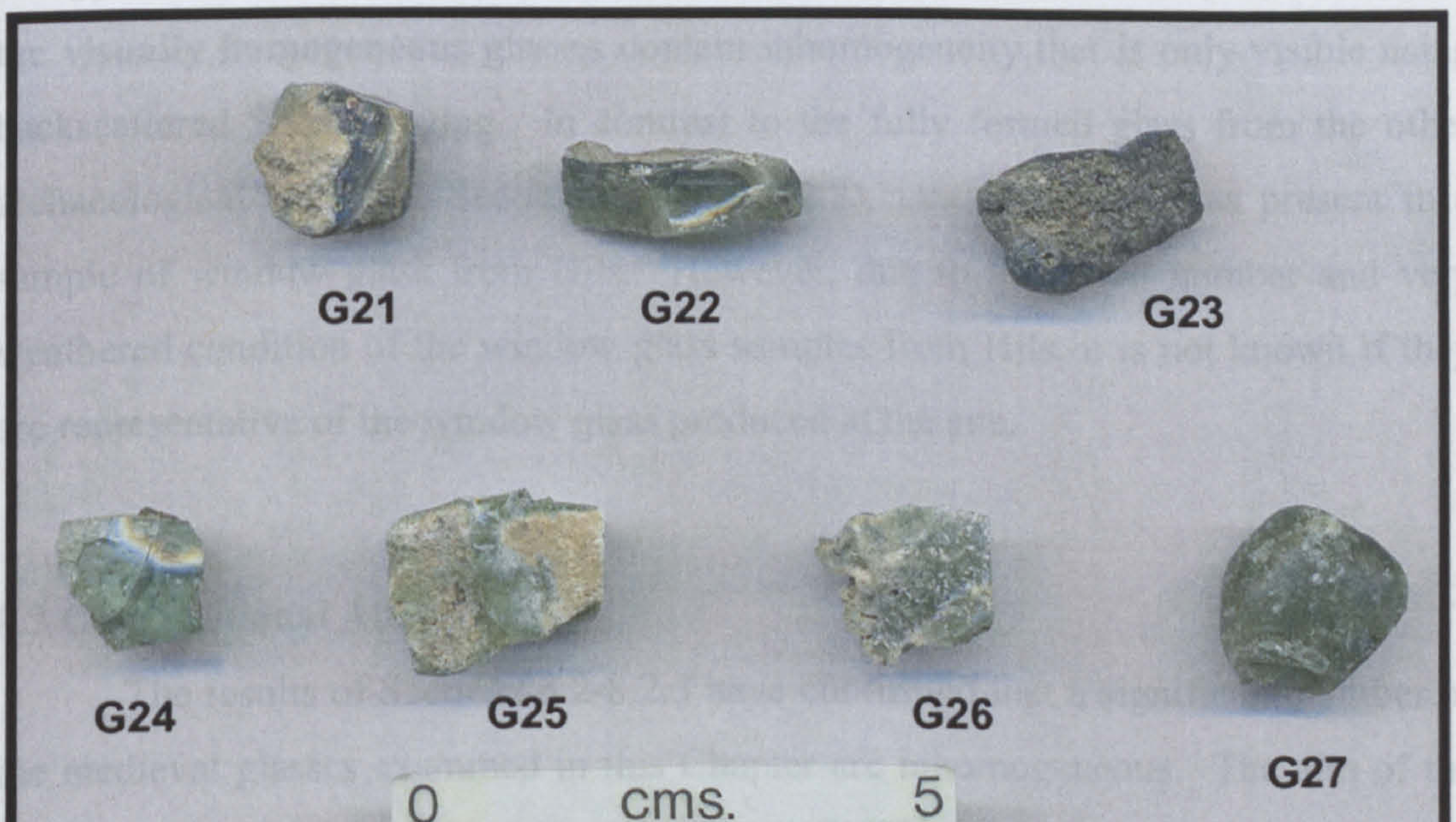
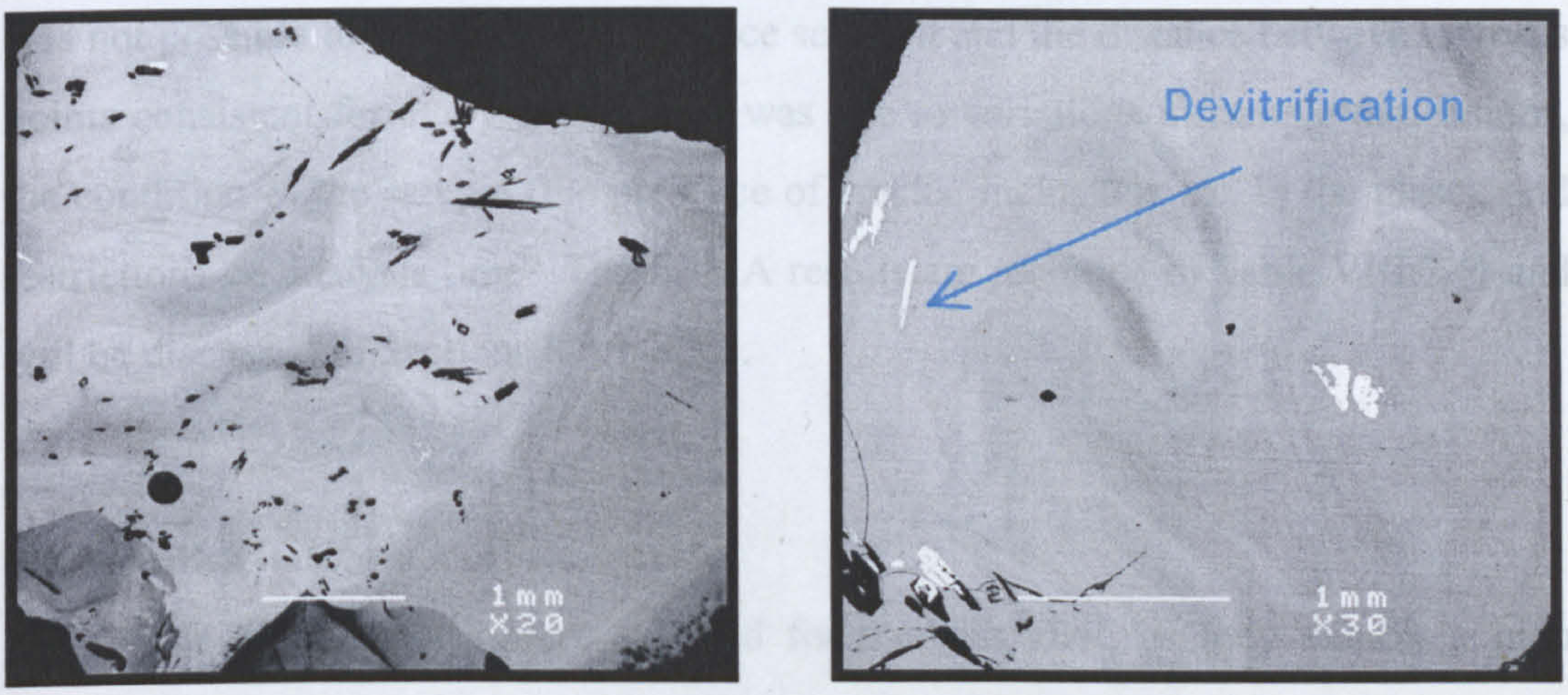


Plate 8:26 **Glass waste (G21-27) selected from Hils glasshouses for analysis (Table VII:14)**

Examination of the waste glass samples using backscattered SEM imaging determined that they all contained inhomogeneities (Plate 8:27).



Glass waste (G22) from glasshouse A5 ($12^{th}/13^{th}$ centuries) with high levels of inhomogeneity

Glass waste (G27) from glasshouse A16 ($12^{th}/13^{th}$ centuries) with devitrification and high levels of inhomogeneity

Plate 8:27 Backscattered SEM images of glass waste from Hils glasshouses A5 and 16 (12^{th}-13^{th} centuries) (Table VIII:6)

It can be seen that the Hils glass samples exhibit the highest levels of inhomogeneity of all the archaeological glasses examined in this research. There is no apparent link between the presence of opacity and inhomogeneity, and many of the **visually homogeneous** glasses contain inhomogeneity that is only visible using backscattered SEM imaging. In contrast to the fully formed glass from the other archaeological sites (see Sections 8.2 and 8.2.2), inhomogeneity **was** present in a sample of window glass from Hils. However, due to the small number and very weathered condition of the window glass samples from Hils, it is not known if they are representative of the window glass produced at the site.

8.3 Compositional Analysis

The results of Sections 8.2-8.2.3 have confirmed that a significant number of the medieval glasses examined in this Chapter are inhomogeneous. The aim of the following sections is to quantify these inhomogeneities using EPMA (see Section 3.3.2.5) and compare the results to data obtained from the comparative homogeneous glasses in this Chapter. This will enable the effect of inhomogeneity on compositional analyses of medieval glasses to be assessed (see Section 1.3).

The backscattered images obtained in Sections 8.2-8.2.3 were used as a guide for the position of analyses, a combination of elemental mapping, line scans and point analyses were used (see Section 3.3.2.5). Where line scans were carried out, it was not possible to keep the total distance scanned and the distance between analysis points consistent for every glass. This was due to variations in sample dimensions, the condition of the sample (the presence of cracks, inclusions etc. in the glass), and restrictions on analysis time. The EPMA results are recorded in Table VIII:7-31 and will be discussed in Sections 8.3.1-8.3.3.

8.3.1 Hils Glasses

The Hils samples were selected for analysis first, as they exhibit a high degree of inhomogeneity and therefore any changes in composition will be more apparent (see Section 8.2.3). Elemental mapping was used initially to provide an overall picture of the compositional changes occurring over a set area of glass. Due to the time taken to carry out this type of analysis it was only possible to use this method for one sample. The backscattered SEM image in Plate 8:28 is taken from a fragment of worked glass (G13) from glasshouse A13 (Table VIII:6). The red box represents the area analysed (approximately 1mm^2), and the elemental maps produced are illustrated in Plate 8:29-Plate 8:32. The colour differences on the maps refer to the intensity of the element being measured present, (red high, blue low).

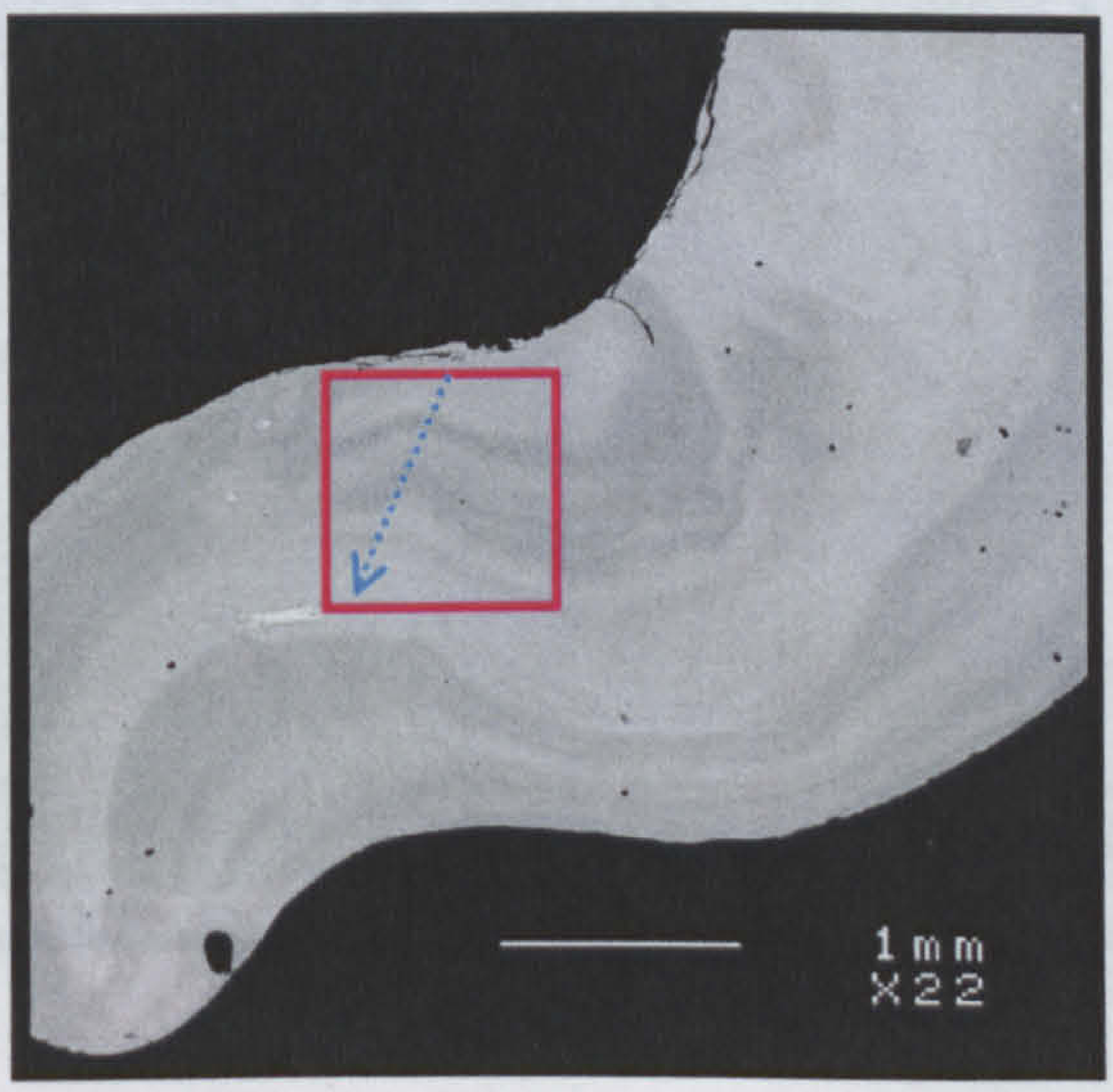
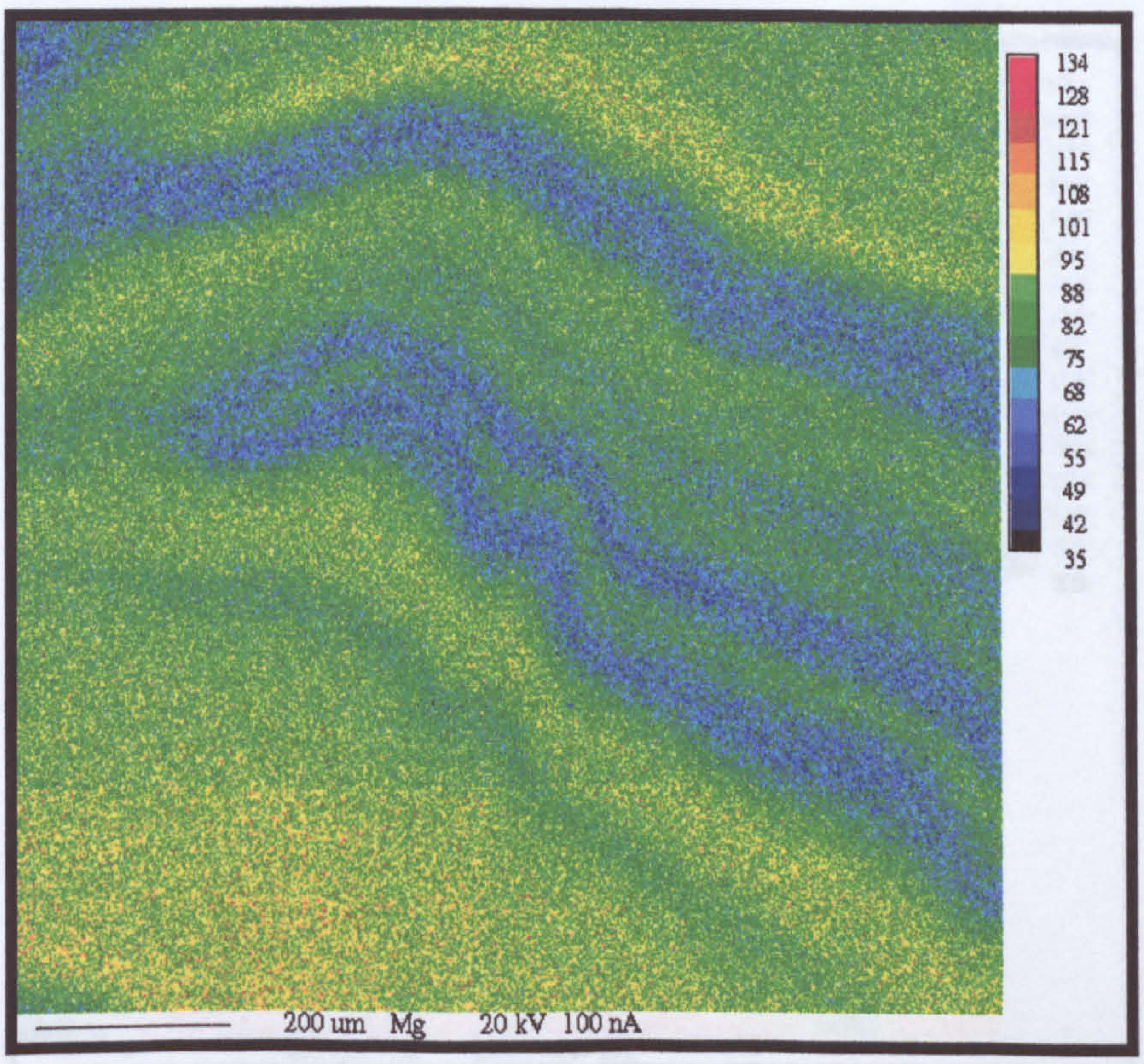
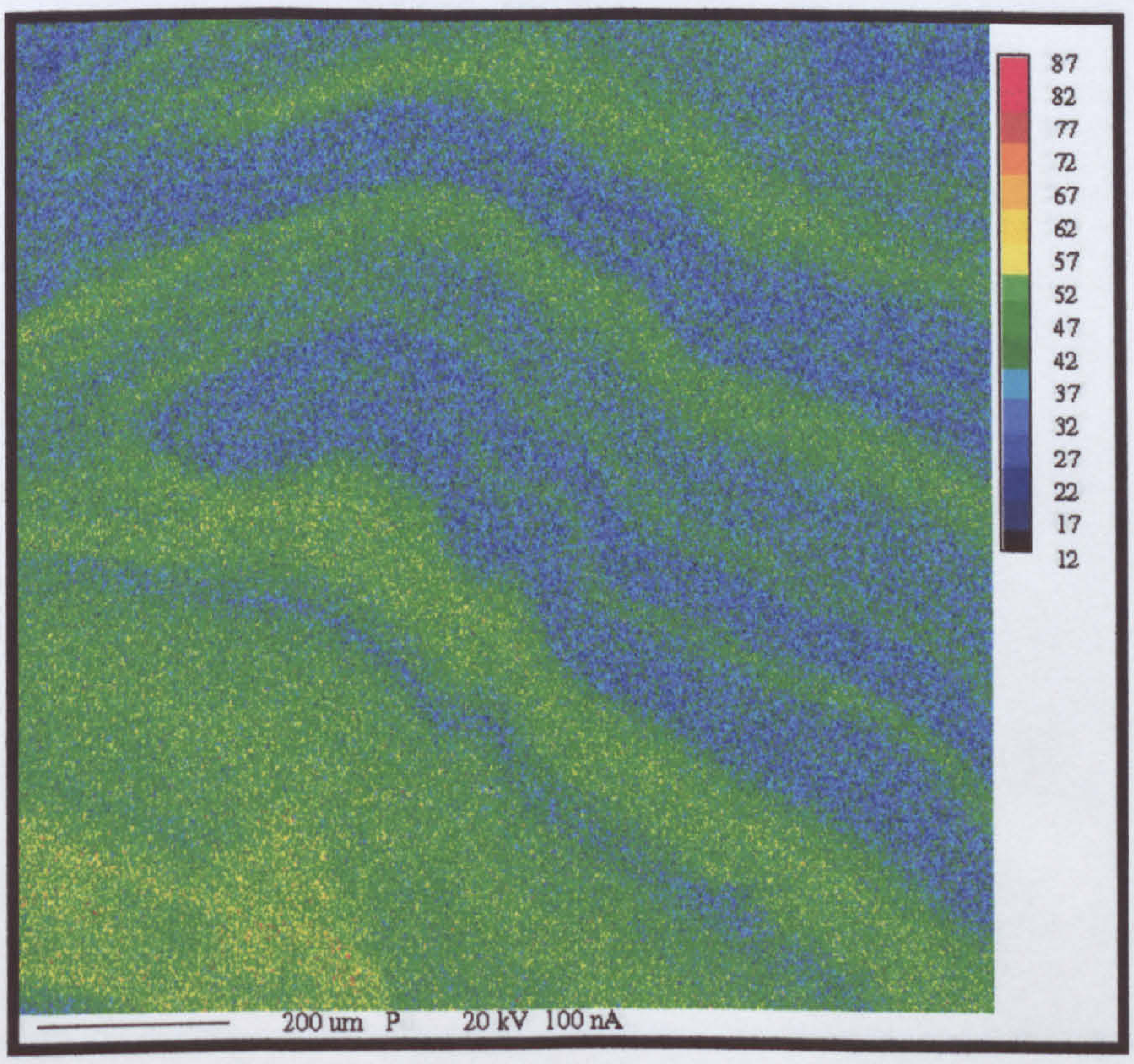


Plate 8:28 Backscattered SEM image of G13 (Table VIII:6), the boxed area represents the area selected for elemental mapping, and the arrow the direction of the line scan

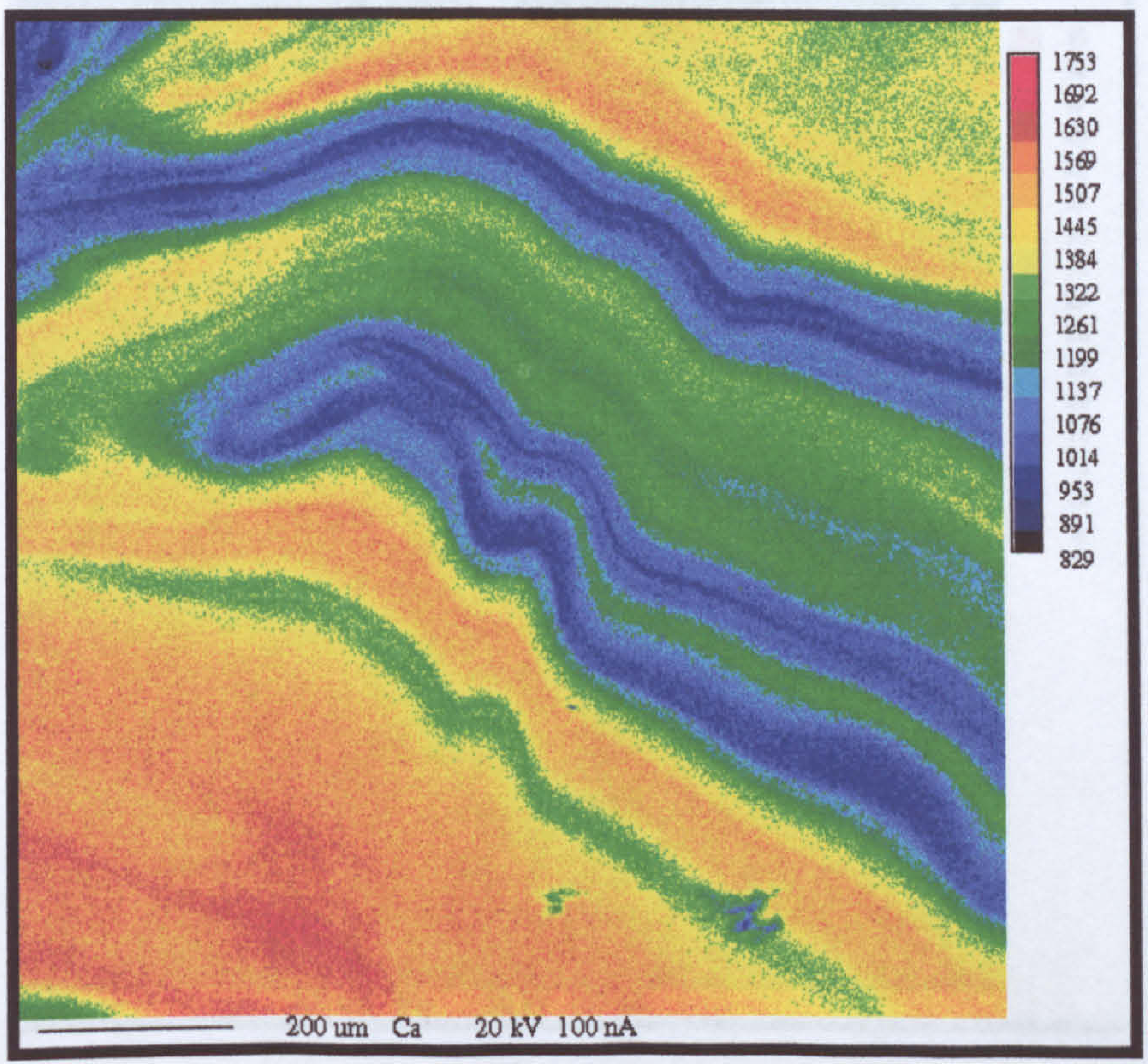


Magnesium

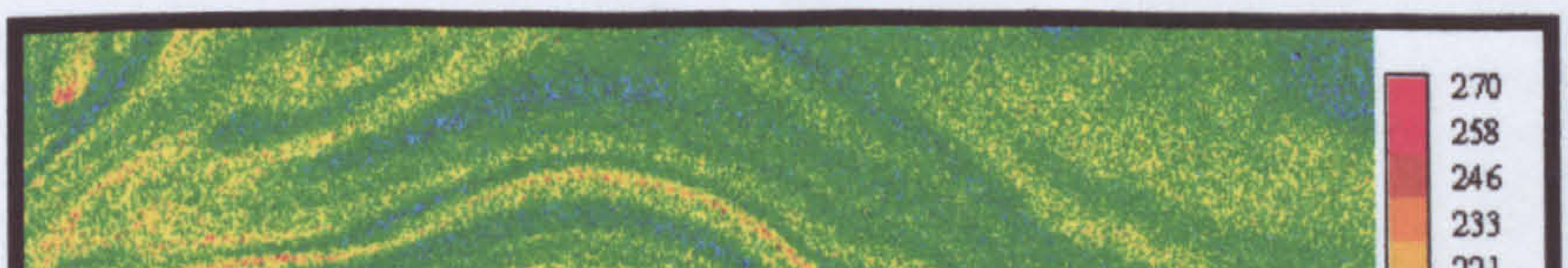


Phosphorus

Plate 8:29 Elemental maps illustrating the relative concentrations of magnesium and phosphorus in the boxed area of G13 (Table VIII:6, see Plate 8:28)

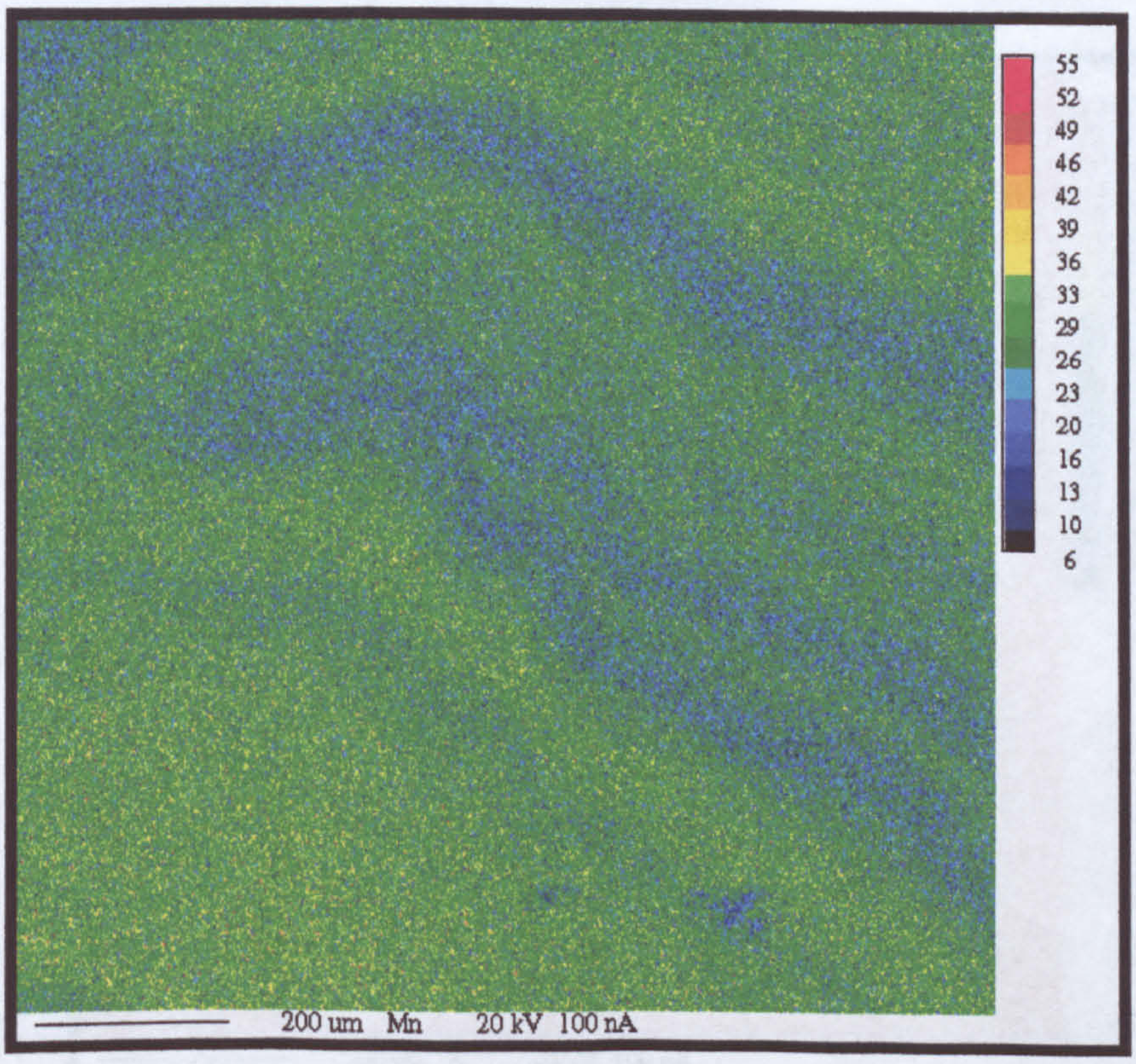


Calcium

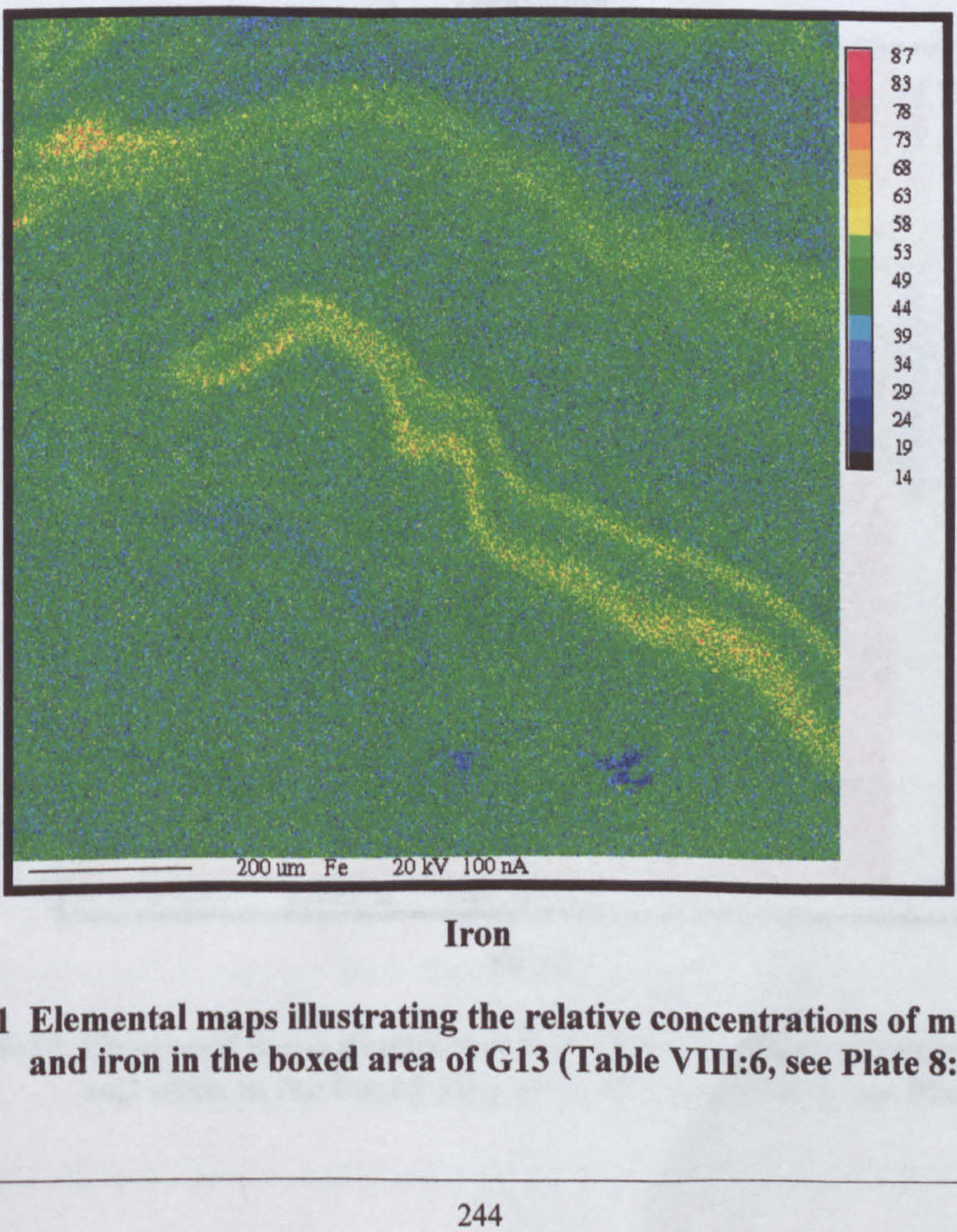


Aluminium

Plate 8:30 Elemental maps illustrating the relative concentrations of calcium and aluminium in the boxed area of G13 (Table VIII:6, see Plate 8:28)

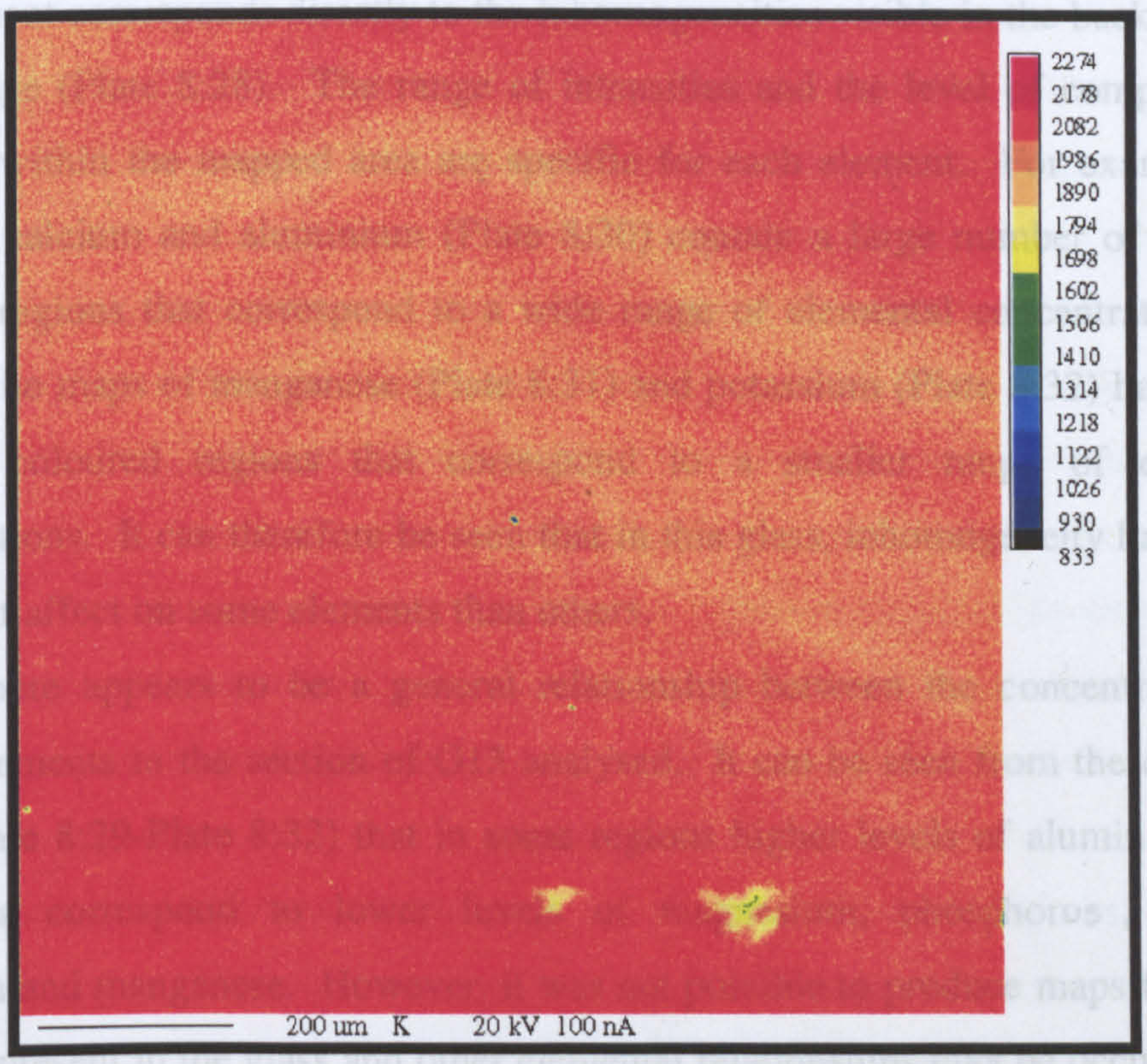


Manganese

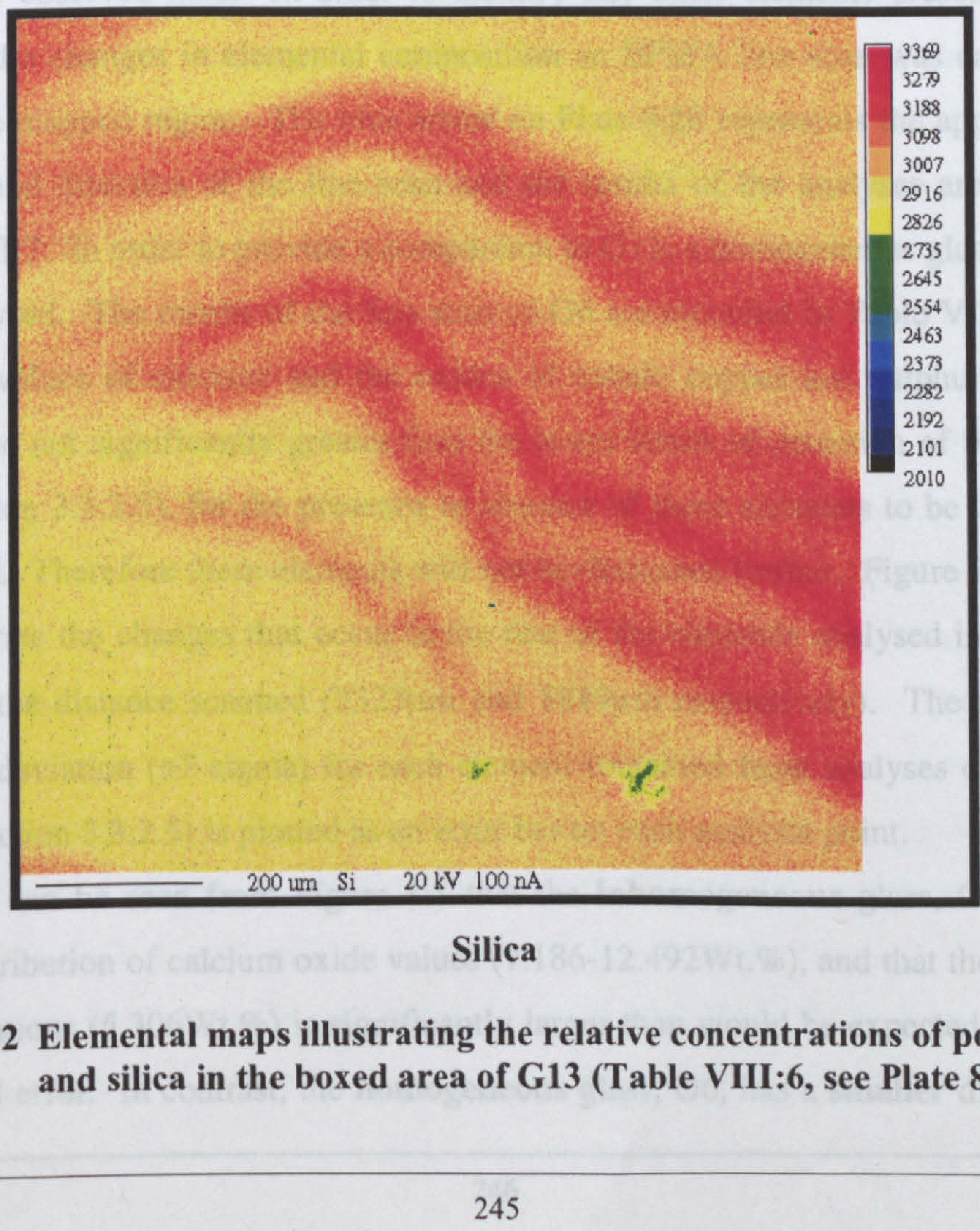


Iron

Plate 8:31 Elemental maps illustrating the relative concentrations of manganese and iron in the boxed area of G13 (Table VIII:6, see Plate 8:28)



Potassium



Silica

Plate 8:32 Elemental maps illustrating the relative concentrations of potassium and silica in the boxed area of G13 (Table VIII:6, see Plate 8:28)

The results from the elemental mapping show that the pattern of variation for each element corresponds directly to the inhomogeneities visible in the backscattered SEM image (Plate 8:28). The range of intensities and the level of compositional variation within the mapped area are specific for each element. For example, the maps for calcium and aluminium (Plate 8:30) contain a large number of different coloured regions that correspond to a wide range of elemental concentrations. In contrast, the maps of manganese (Plate 8:31) and potassium (Plate 8:32) have fewer different coloured regions that correspond to a smaller range of elemental concentrations. It can therefore be seen that in this glass, inhomogeneity has a more significant affect on some elements than others.

There appears to be a general relationship between the concentrations of certain elements in the section of G13 analysed. It can be seen from the elemental maps (Plate 8:29-Plate 8:32) that in some regions higher levels of aluminium, iron and silica correspond to lower levels of magnesium, phosphorus, calcium, potassium and manganese. However, it was not possible to produce maps for all the elements present in the glass and other elemental relationships may be occurring that cannot be observed here. In order to identify any other elements present, and to quantify the changes in elemental composition an EPMA line scan was carried out across the mapped region. The blue arrow on Plate 8:28 represents the approximate position and direction of the line scan and the results of the analyses are listed in Table VIII:7. In order to provide a comparison to G13, a homogeneous glass G6 was also analysed. The results of the line scan of G6 are recorded in Table VIII:8. The reported values of chlorine and the oxides of cobalt, copper and sulphur for both glasses are not significantly greater than the lower limits of detection of the EPMA (see Section 3.3.2.5), for the presence or absence of these elements to be confirmed or refuted. Therefore these elements will not be discussed further. Figure 8:1-Figure 8:6 illustrate the changes that occur in the rest of the elements analysed in G13 and G6 over the distance scanned (2323µm and 1819µm respectively). The respective standard deviation (±2 sigma) for each element (obtained from analyses of Corning D, see Section 3.3.2.5) is plotted as an error bar on each analysis point.

It can be seen from Figure 8:1 that the **inhomogeneous** glass, G13, has a **wide** distribution of calcium oxide values (7.186-12.492Wt.%), and that the range of concentrations (5.306Wt.%) is significantly larger than would be expected from any analytical error. In contrast, the **homogeneous** glass, G6, has a **smaller** distribution of calcium oxide concentrations (14.933-15.692Wt.%), a range of just 0.759Wt.%. It can be seen that for G6, when the standard deviation of the analyses is considered, at a 96% confidence level the majority of the data points fall within the same range.

Figure 8:2 illustrates the range of potassium oxide concentrations obtained for G13 and G6. Although there is a greater proportion of potassium than calcium present in both glasses, the variation in the potassium oxide values is less (G13 14.734-16.509Wt.% and G6 14.866-15.279Wt.%), giving a much smaller range of results (G13 1.775Wt.% and G6 0.413 Wt.%). However, the range of values for G13 is significantly greater than would be expected from experimental error whilst the majority of the values from G6 are within the expected standard deviation of the data. These results also confirm the observations made from the elemental maps of G13, where it was seen that inhomogeneity has a more significant affect on calcium compared to potassium.

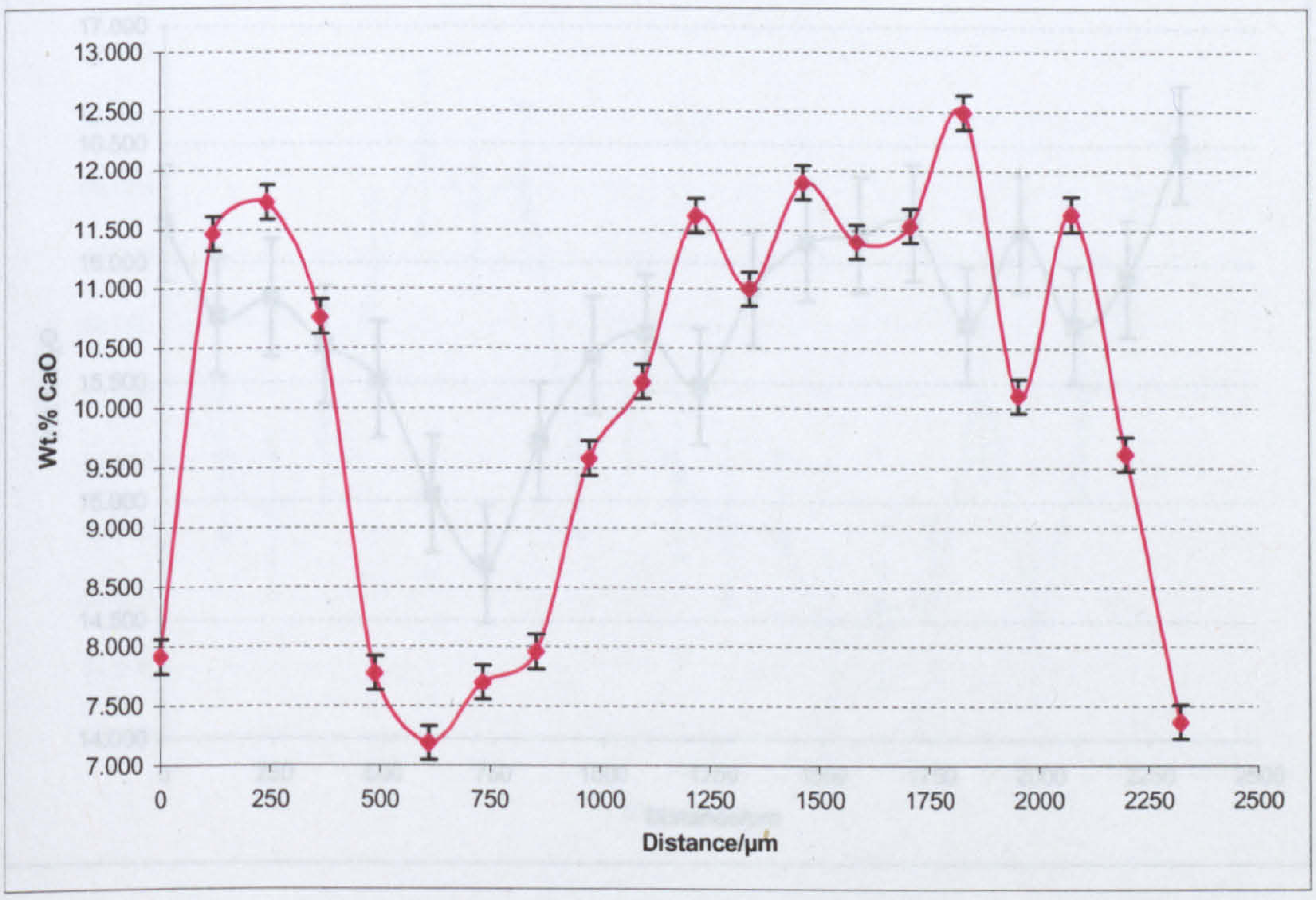
Figure 8:3 illustrates the variation in silica (61.336-68.510Wt.% SiO_2) over the line scanned on G13, and it can be seen that a wide range of concentrations occur over a small area and these are greater than would be expected from experimental error. In addition to this, Figure 8:4 and Figure 8:5 show that there is also a significant range of magnesium oxide (1.549-2.437Wt.%) and aluminium oxide (2.382-3.842Wt.%) concentrations in G13. In contrast, the distribution of silica (59.579-60.818Wt.% SiO_2), magnesium (2.579-2.740Wt.% MgO), and aluminium (2.863-3.323Wt.% Al_2O_3) values for G6 is much smaller (Figure 8:3-Figure 8:5). The analyses of silica and magnesium oxide for G6 fall within the expected standard deviation of the results but the distribution of alumina values fall outside this. This is interesting, as G6 was observed to be homogeneous using backscattered SEM imaging.

Although it can be seen in Figure 8:6 that the range of phosphorus values is greater in the inhomogeneous glass G13 (0.388-0.778Wt.% P_2O_5) than the homogeneous glass G6 (0.571-0.681Wt.% P_2O_5), the low level of precision for phosphorus (see Section 3.3.2.5) means that in each glass all the data points are within the standard deviation obtained from the comparative Corning D analyses. The distribution of iron (0.406-0.790Wt.% FeO, Figure 8:7), manganese (0.303-0.505Wt.% MnO, Figure 8:7), and sodium (0.307-0.565Wt.% Na_2O, Figure 8:8) concentrations in G13 are all greater than the calculated limits of experimental error. In contrast to this, the same elements in G6 do not show such a large variation

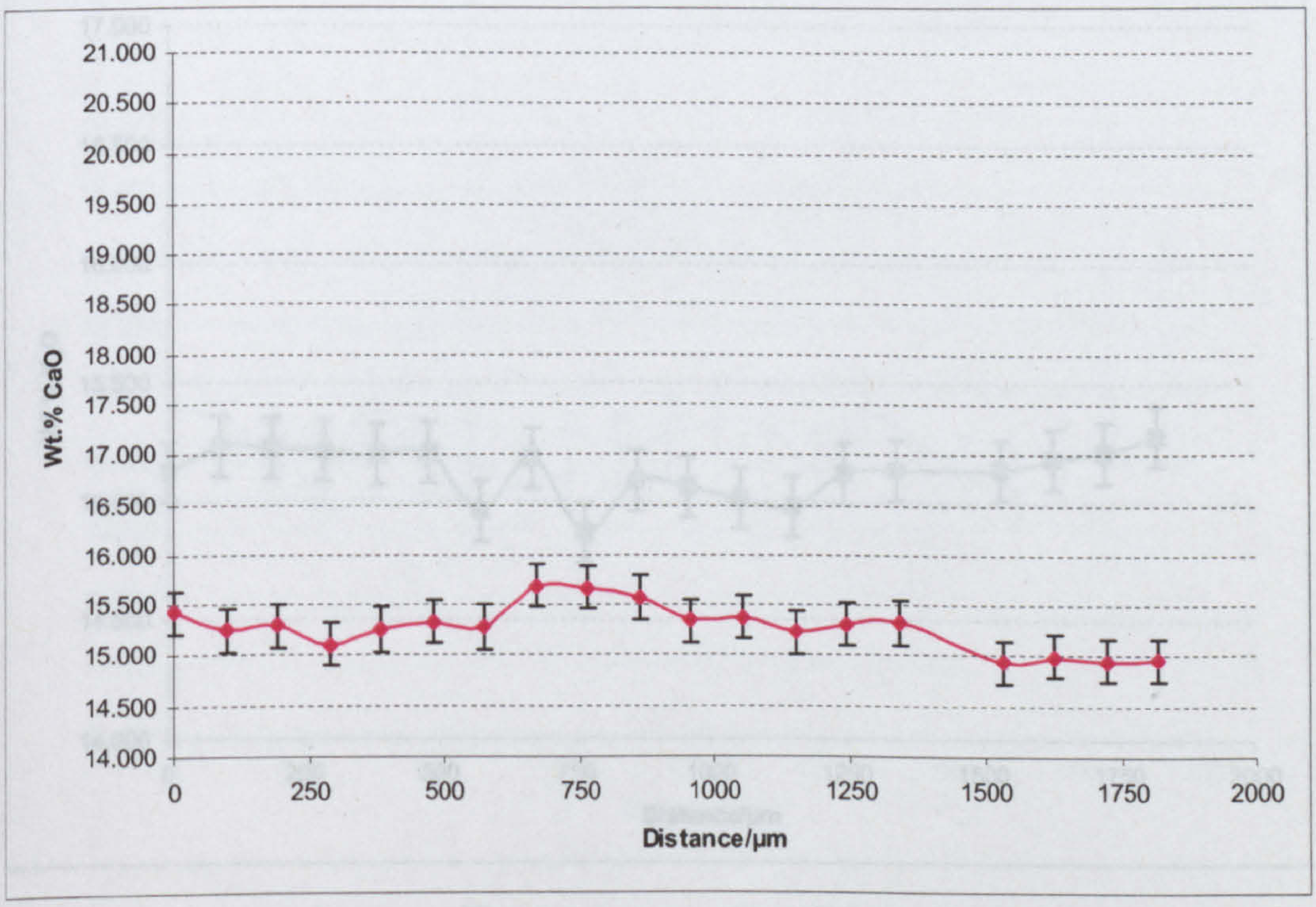
(0.331-0.459Wt.% FeO, 0.807-0.929Wt.% MnO, and 0.404-0.574Wt.% Na_2O) and are all within the expected standard deviation of the data. The only element where the concentrations and ranges are virtually identical for both glasses is titanium (G13, 0.190-0.275Wt.% TiO_2 and G6, 0.170-0.264Wt.% TiO_2), and it can be seen in Figure 8:8 that the majority of the titanium values for both glasses fall within a range expected from experimental error.

A number of inter-elemental relationships were observed from the results of the elemental mapping of G13. The results of the line scans have shown that calcium (Figure 8:1), magnesium (Figure 8:4) and silica (Figure 8:3) appear to be directly related and have extremely similar shaped plots, calcium and magnesium increasing and decreasing together whilst silica mirrors these effects. However, the relationships between the other elements analysed are much more complex and vary depending on the part of the glass analysed. For example, it can be seen in Figure 8:1 and Figure 8:2 that for G13 the calcium and potassium concentrations rise and fall together between 122-1100μm but are opposed between 1711 and 2323μm. It would appear from these results that G13 is made up of **many combinations** of different glass compositions. In comparison to G13 there do not appear to be any inter elemental relationships in the analyses from G6.

In summary it can be seen that for the majority of elements, the data from the **inhomogeneous** glass (G13) contains significantly **larger** ranges of elemental concentrations than the analyses from the homogeneous glass (G6). To confirm whether the same trend in results was observed in G13 as above, a repeat line scan of the sample was carried out in the same area as before. The results are recorded in Table VIII:9 and although the distance scanned was reduced it can be seen that the elemental ranges of the two sets of data from G13 are comparable. For example the values of calcium vary from 8.090-12.736Wt.% CaO, a range of 4.646Wt.% CaO, whilst the distribution of potassium values is 14.727-16.608Wt.% K_2O, a range of 1.882Wt.% K_2O. The inhomogeneous nature of G13 means that the range of elemental concentrations obtained from different line scans in the same area is likely to be slightly variable, as the results will depend on the specific areas of inhomogeneity that the scan crosses.

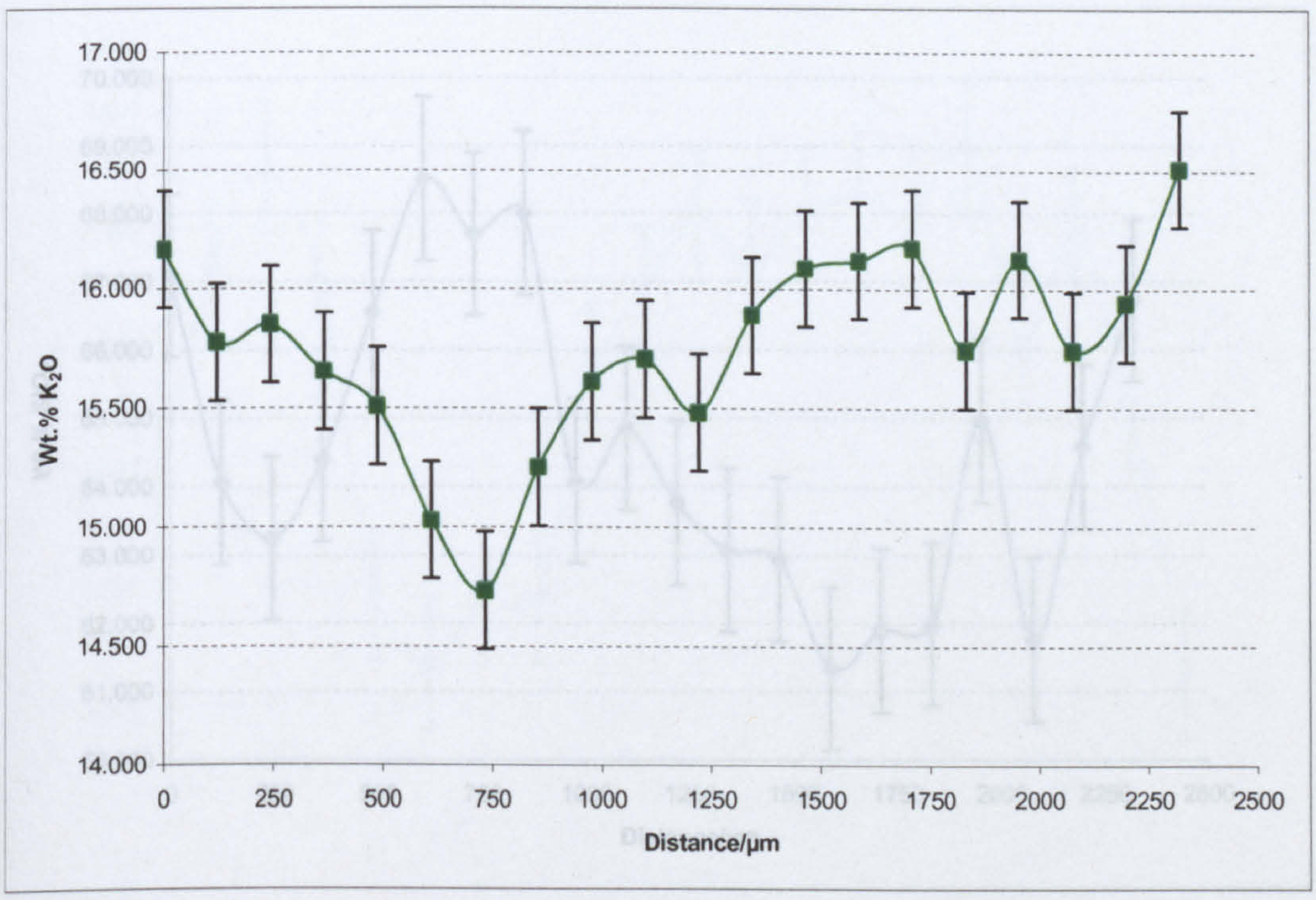


Inhomogeneous glass G13

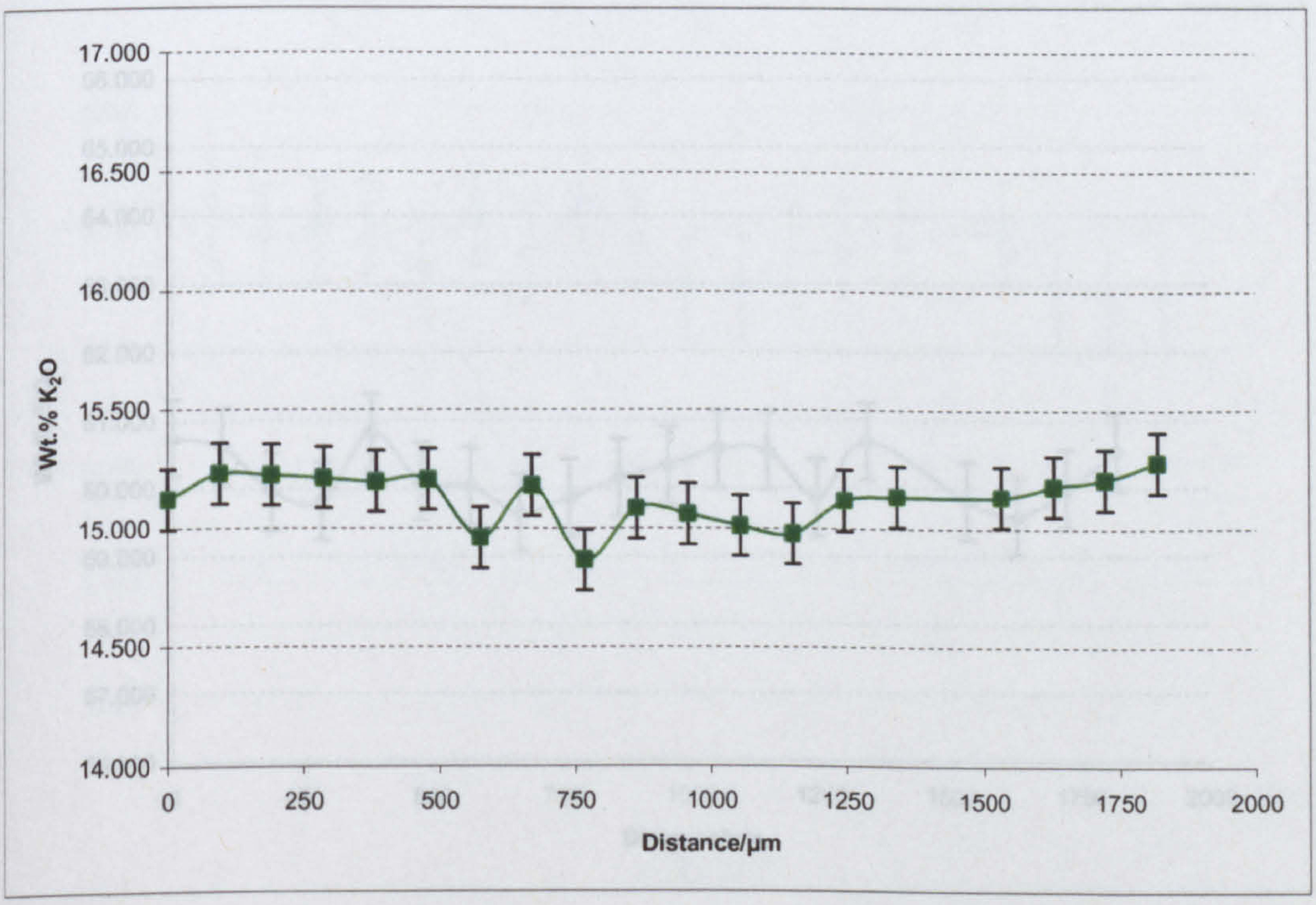


Homogeneous glass G6

Figure 8:1 Graph of EPMA line scan data illustrating the change in CaO concentration over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)

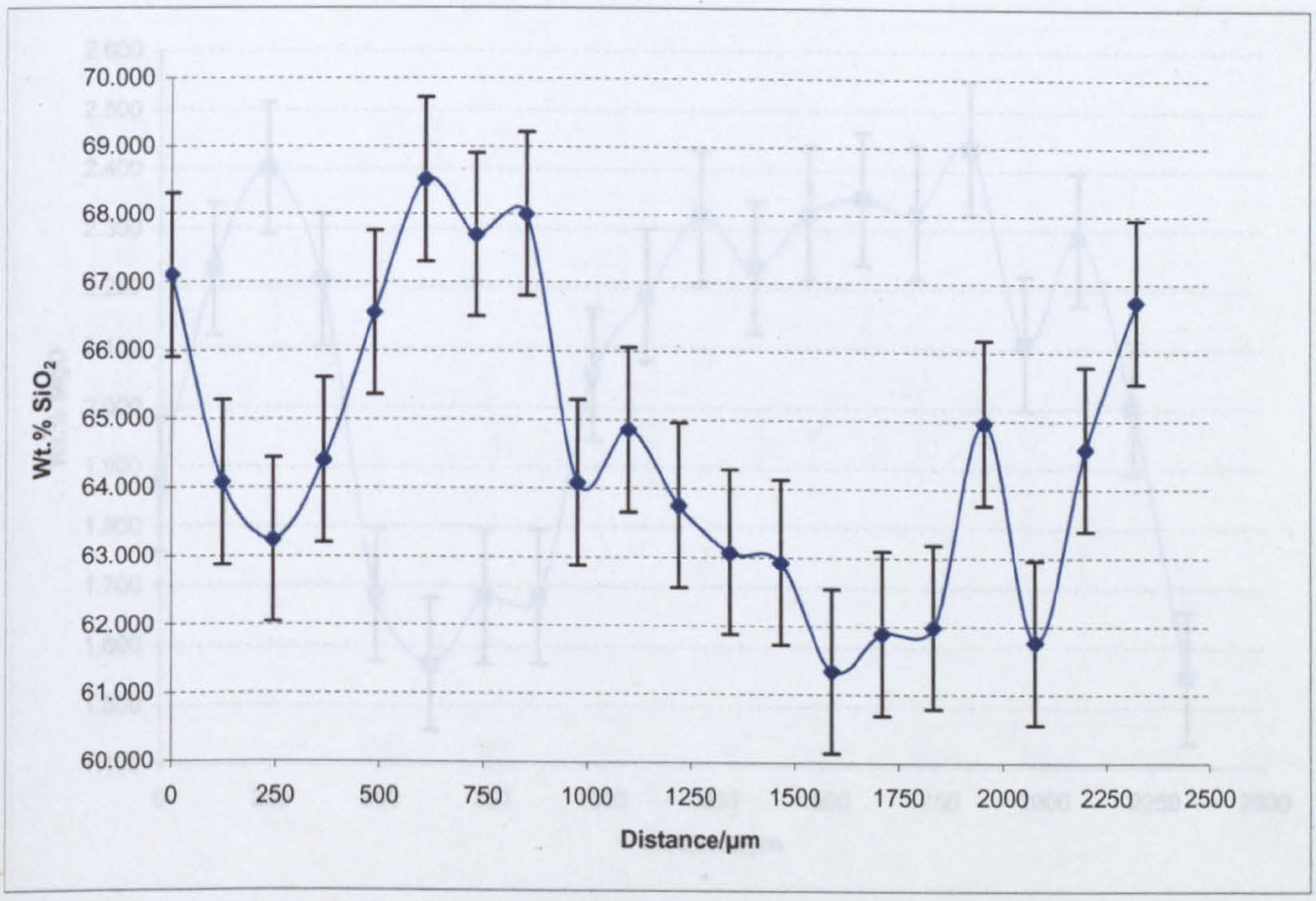


Inhomogeneous glass G13

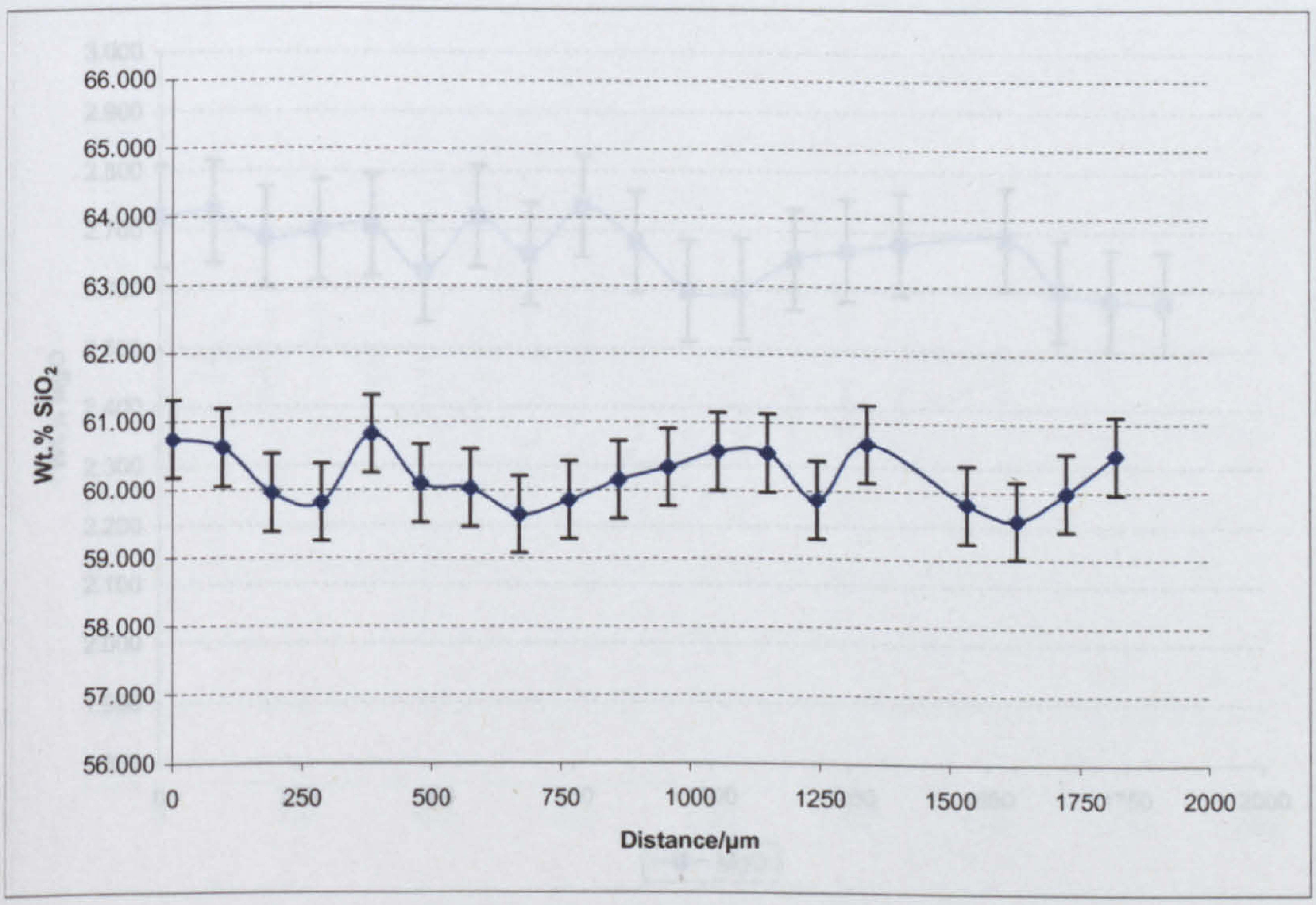


Homogeneous glass G6

Figure 8:2 Graph of EPMA line scan data illustrating the change in K_2O concentration over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)

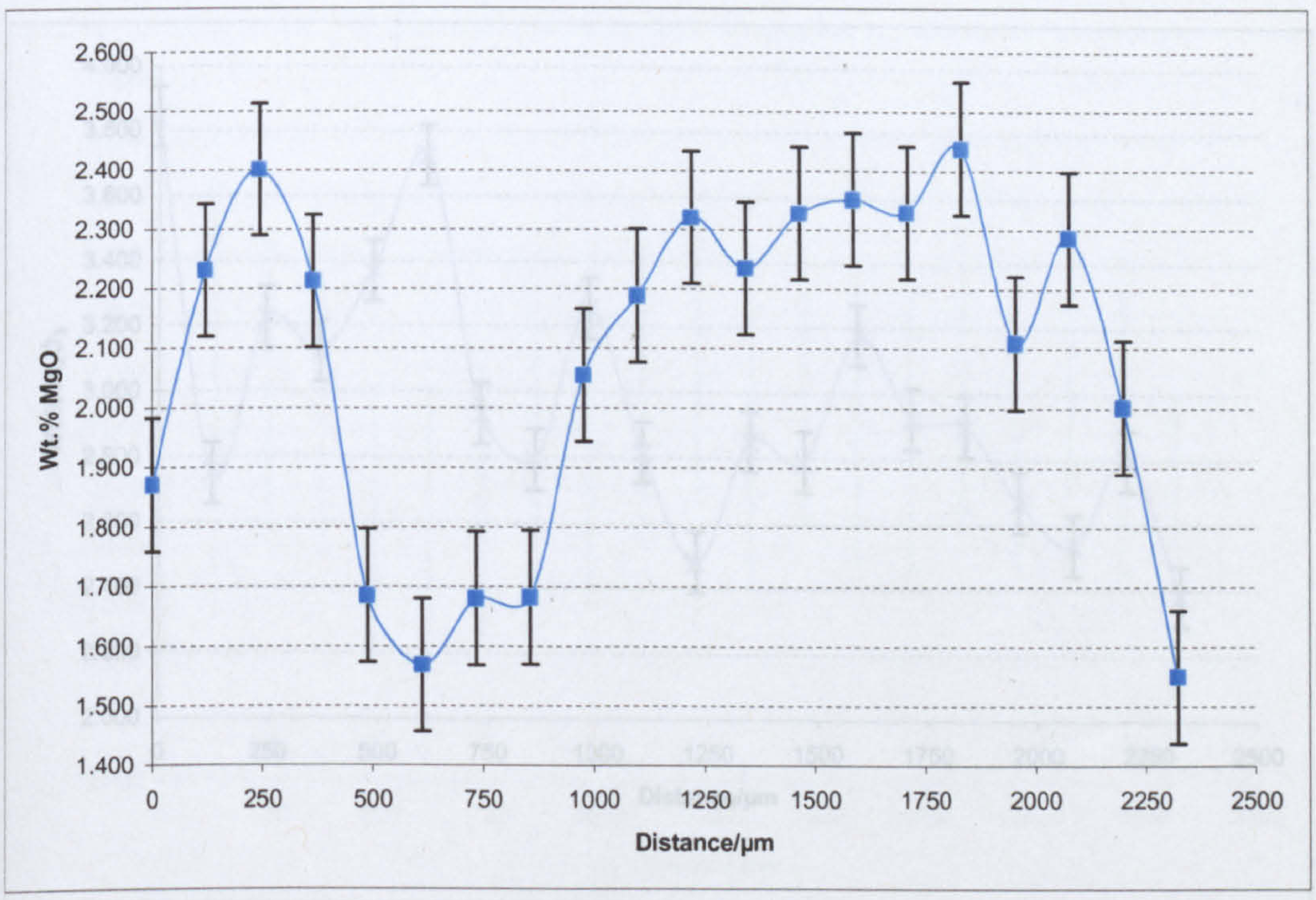


Inhomogeneous glass G13

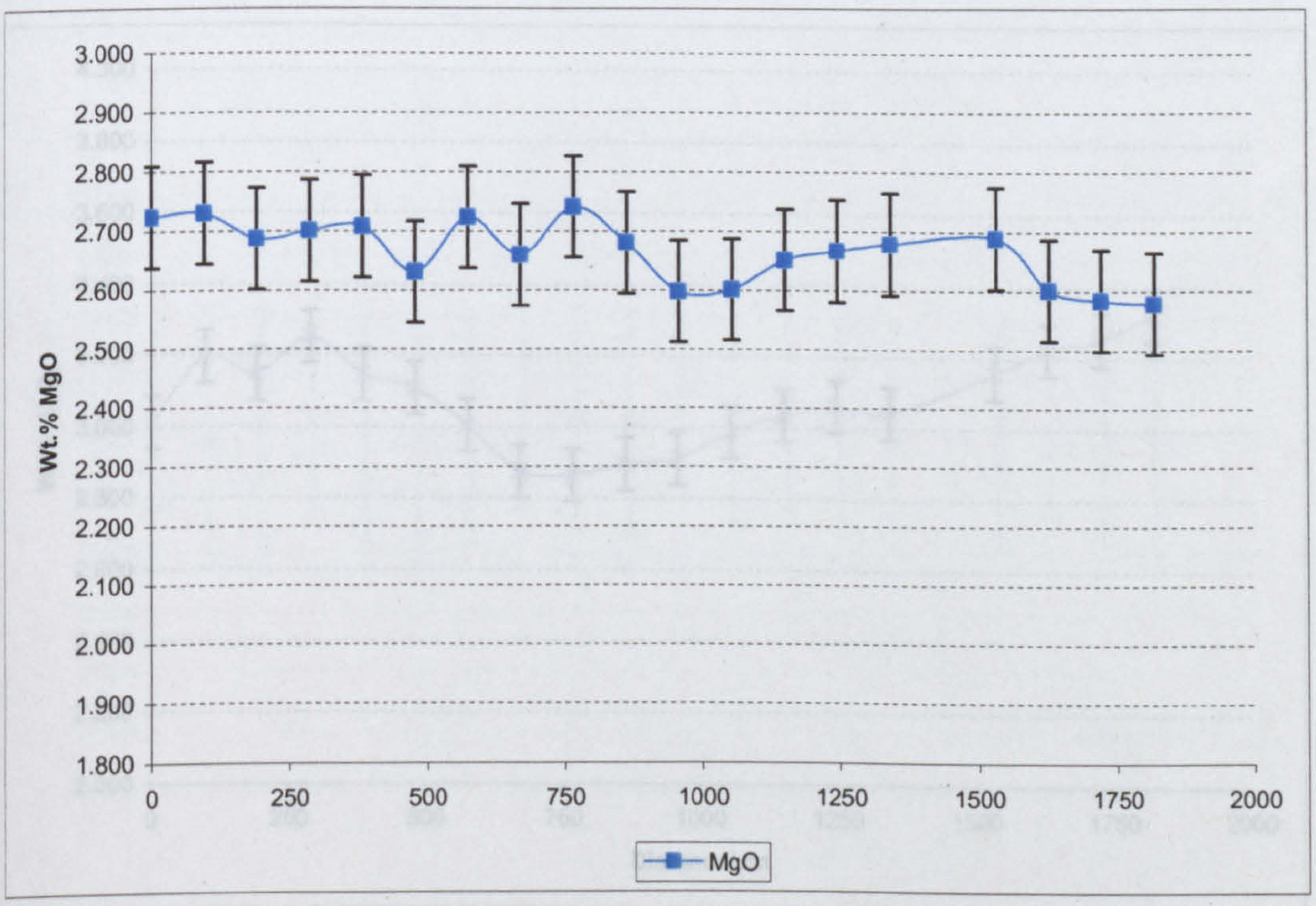


Homogeneous glass G6

Figure 8:3 **Graph of EPMA line scan data illustrating the change in SiO_2 concentration over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)**

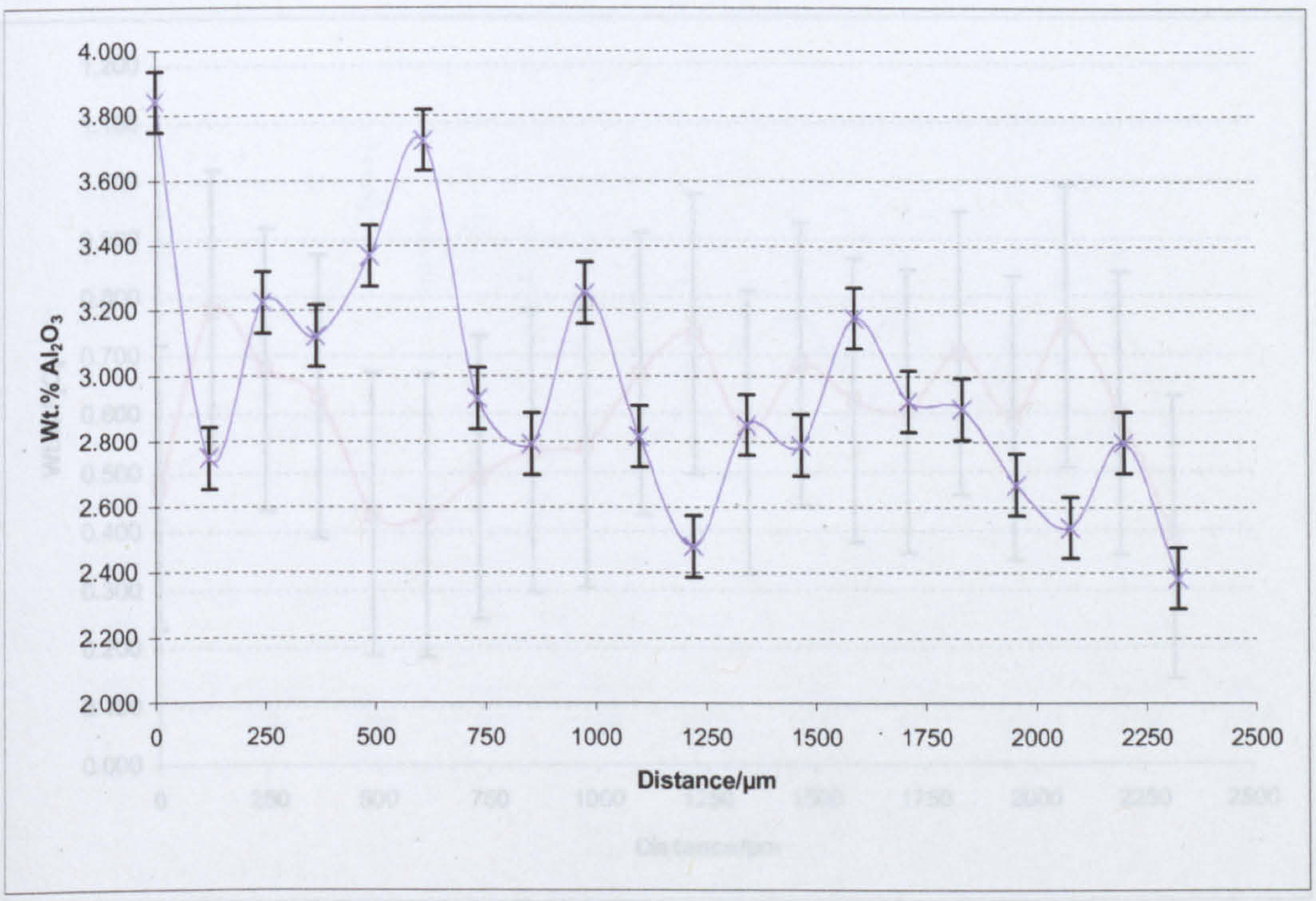


Inhomogeneous glass G13

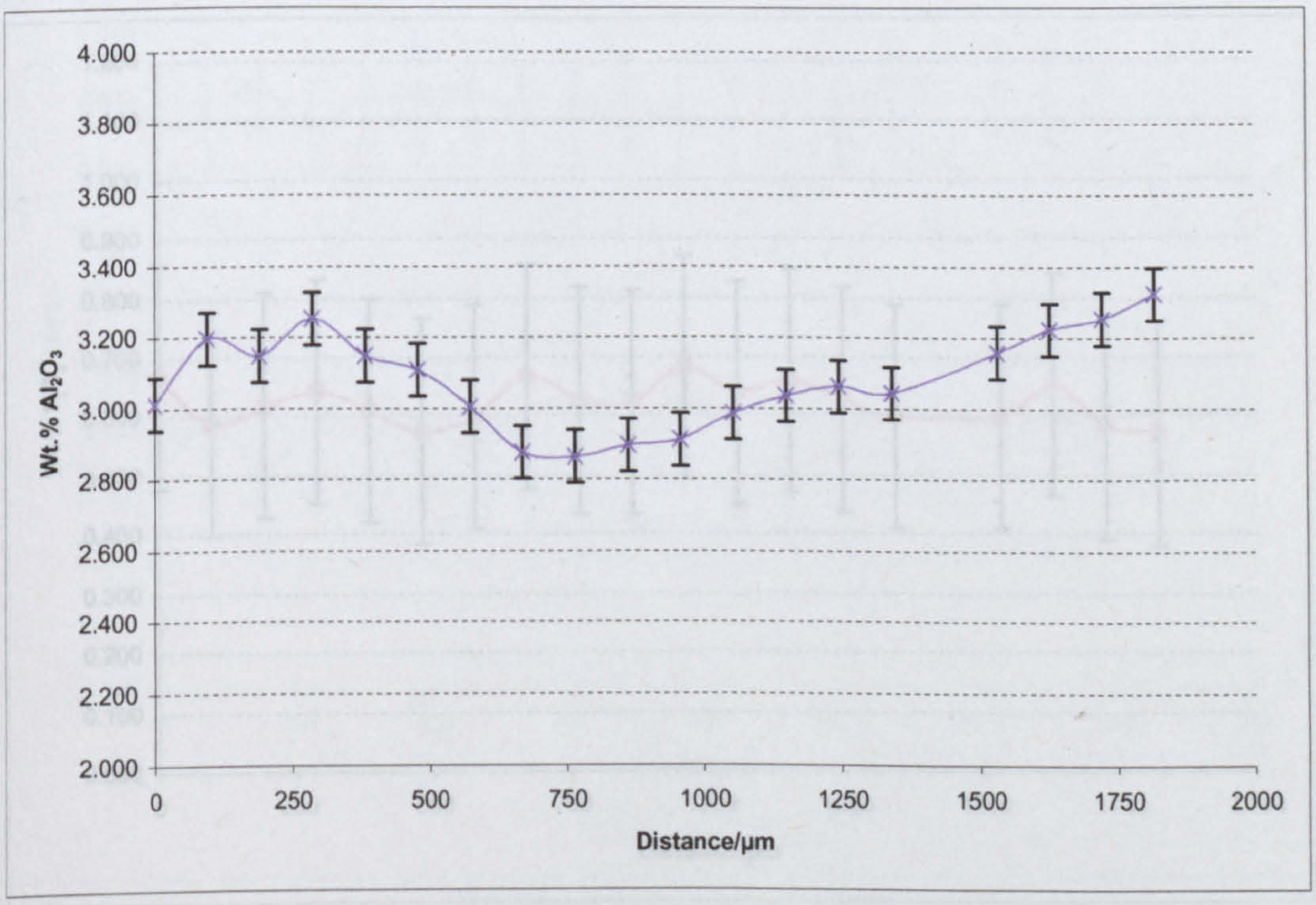


Homogeneous glass G6

Figure 8:4 Graph of EPMA line scan data illustrating the change in MgO concentrations over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)

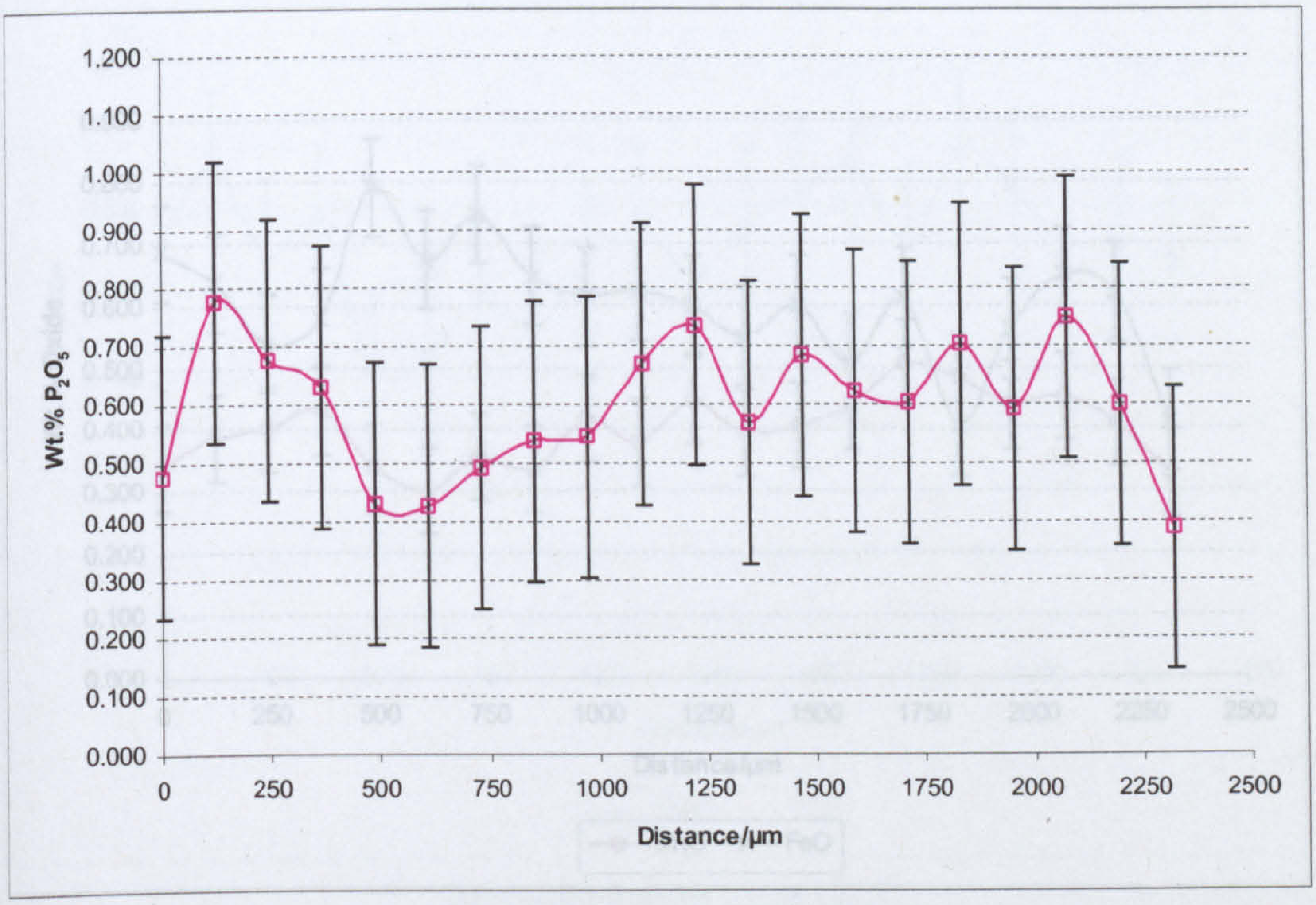


Inhomogeneous glass G13

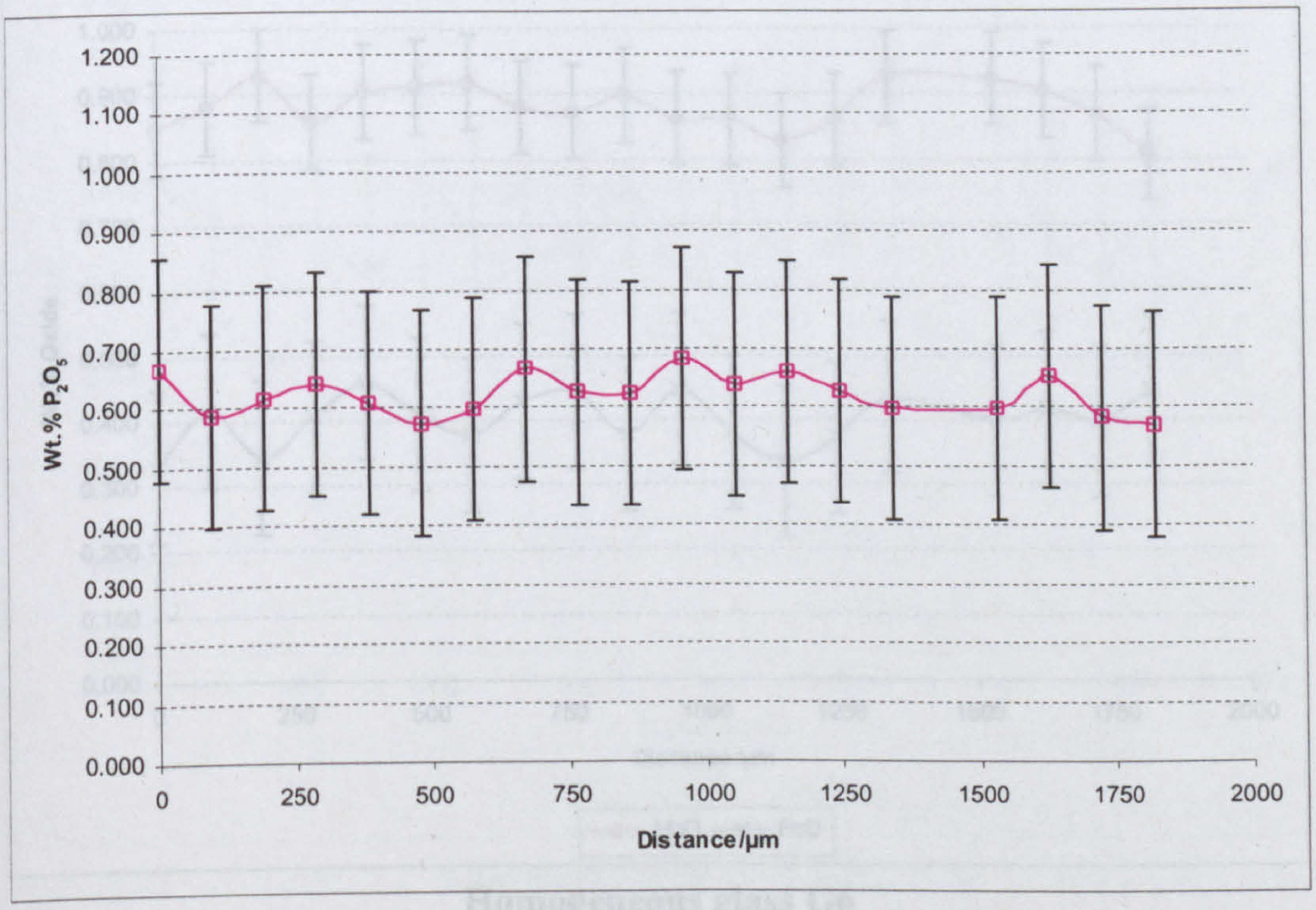


Homogeneous glass G6

Figure 8:5 Graph of EPMA line scan data illustrating the change in Al_2O_3 concentrations over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)

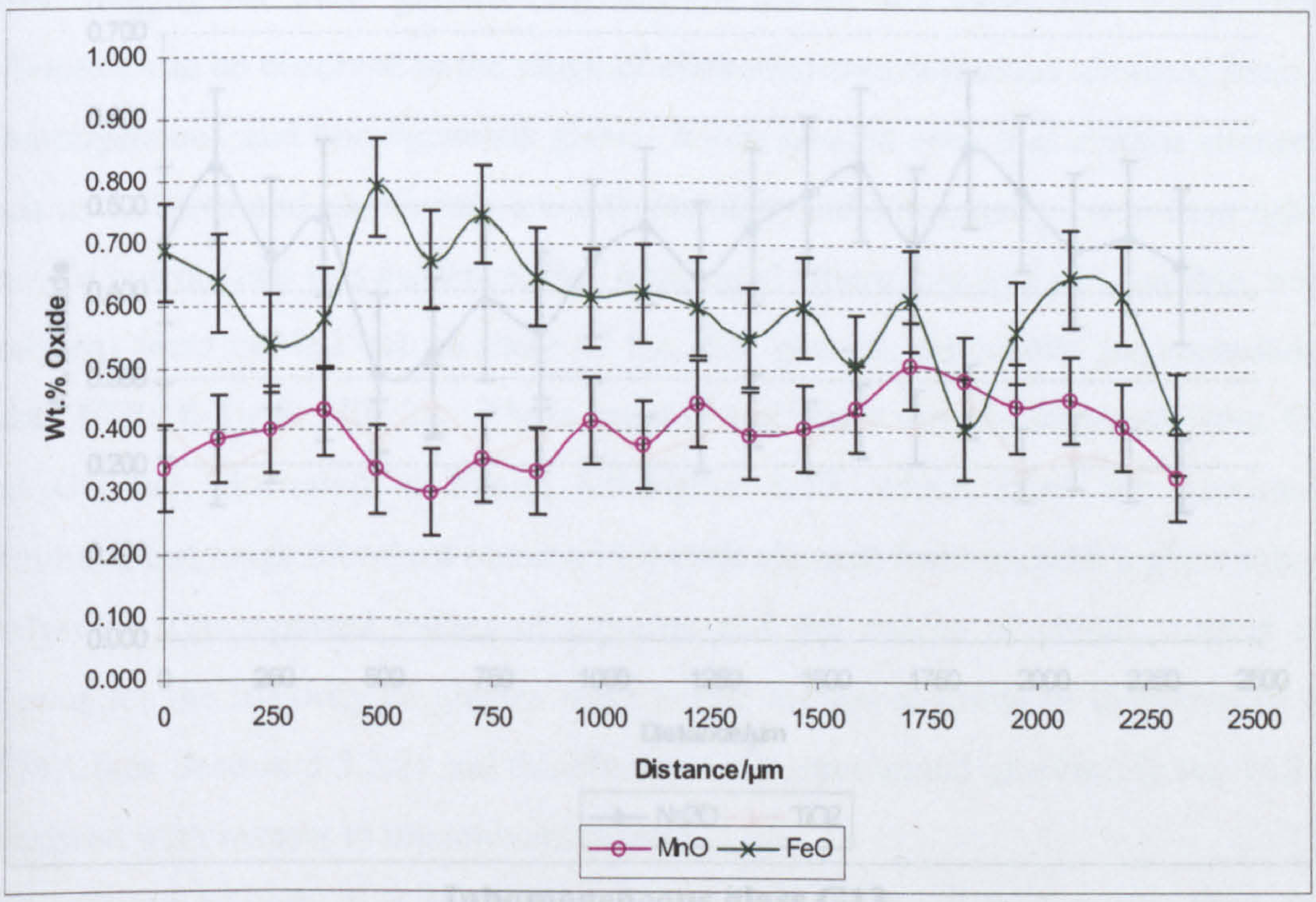


Inhomogeneous glass G13

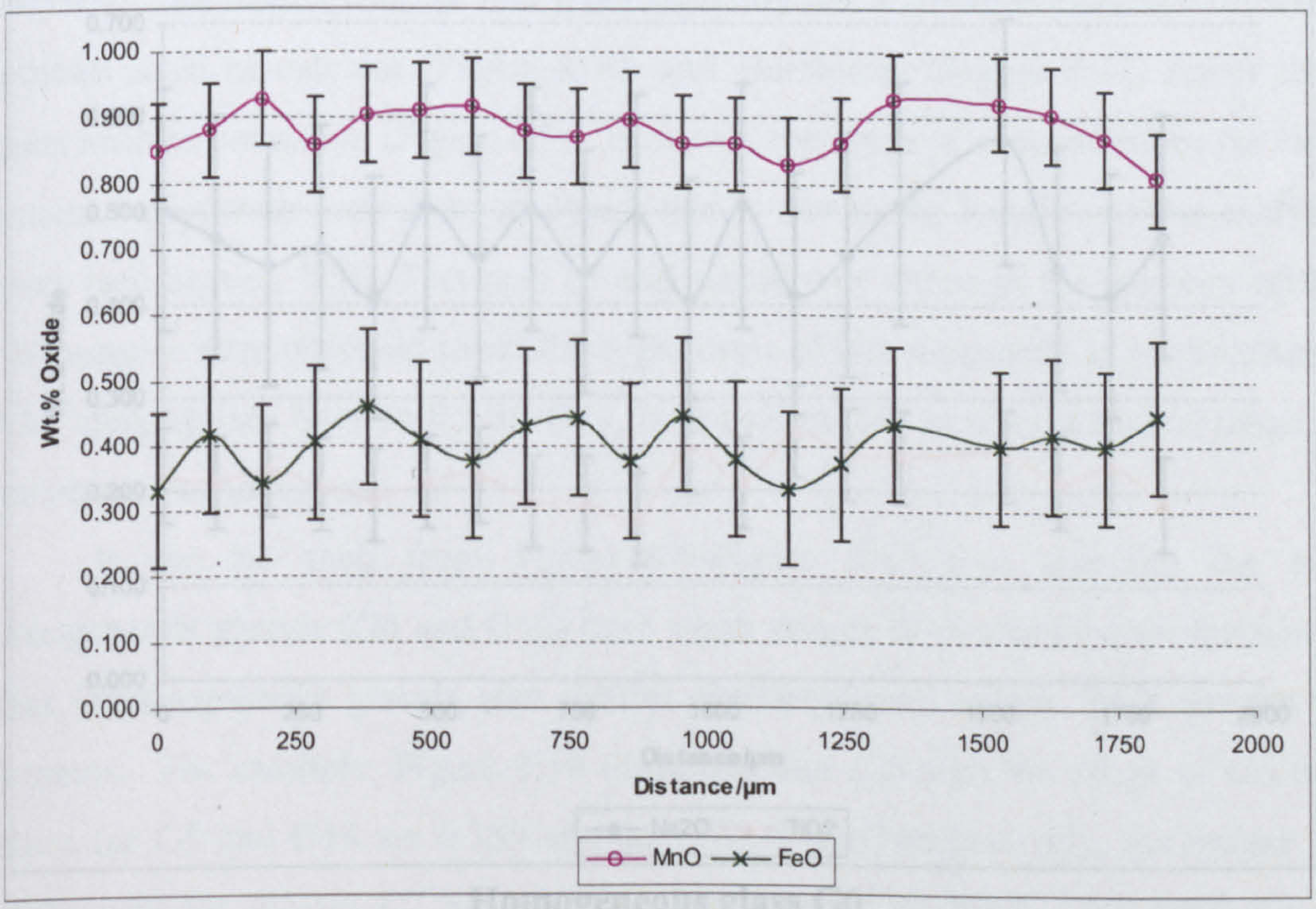


Homogeneous glass G6

Figure 8:6 **Graph of EPMA line scan data illustrating the change in P_2O_5 concentrations over distance for inhomogeneous Hils glass sample G13 (Table VIII:7) and homogeneous Hils glass sample G6 (Table VIII:8)**

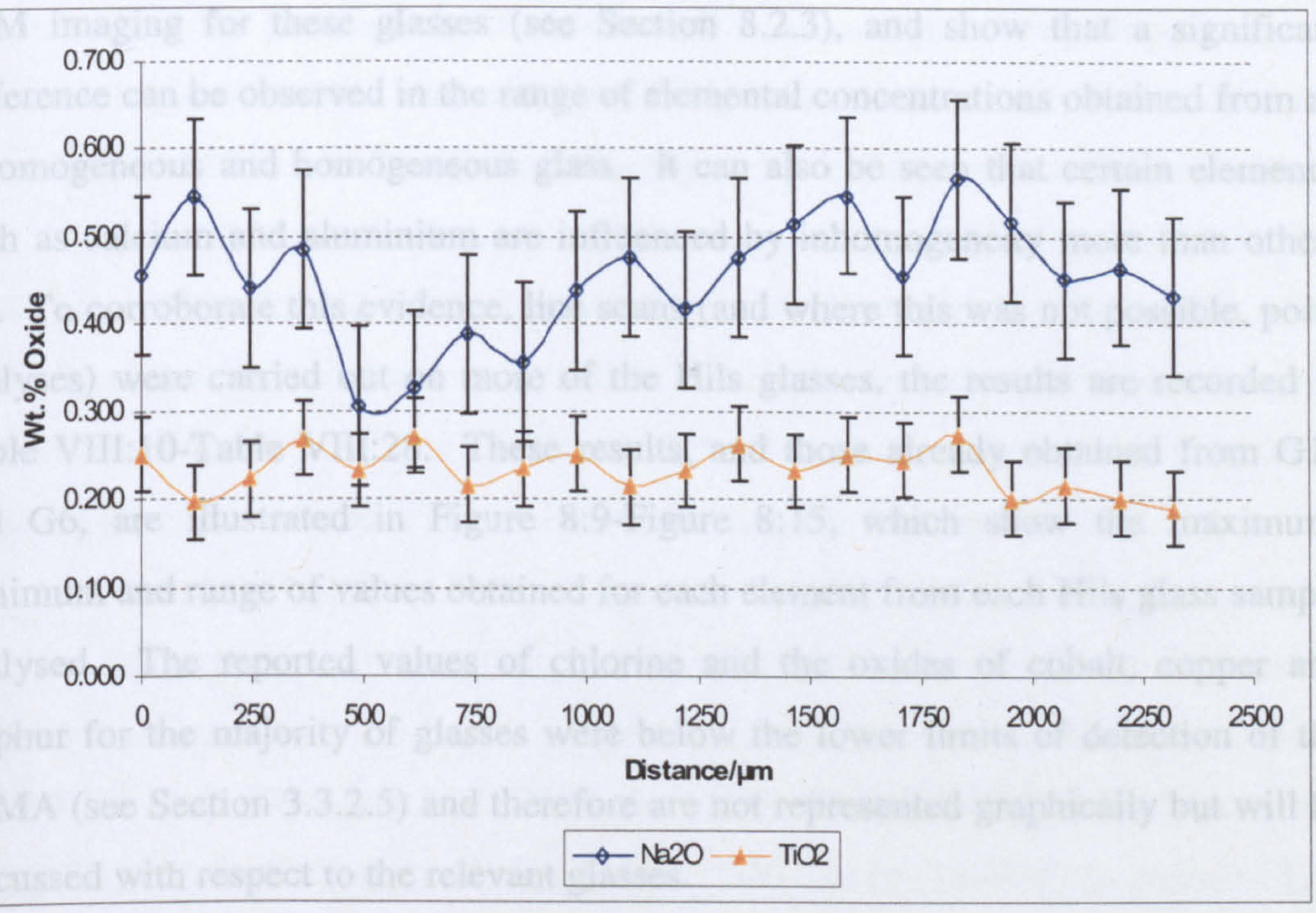


Inhomogeneous glass G13

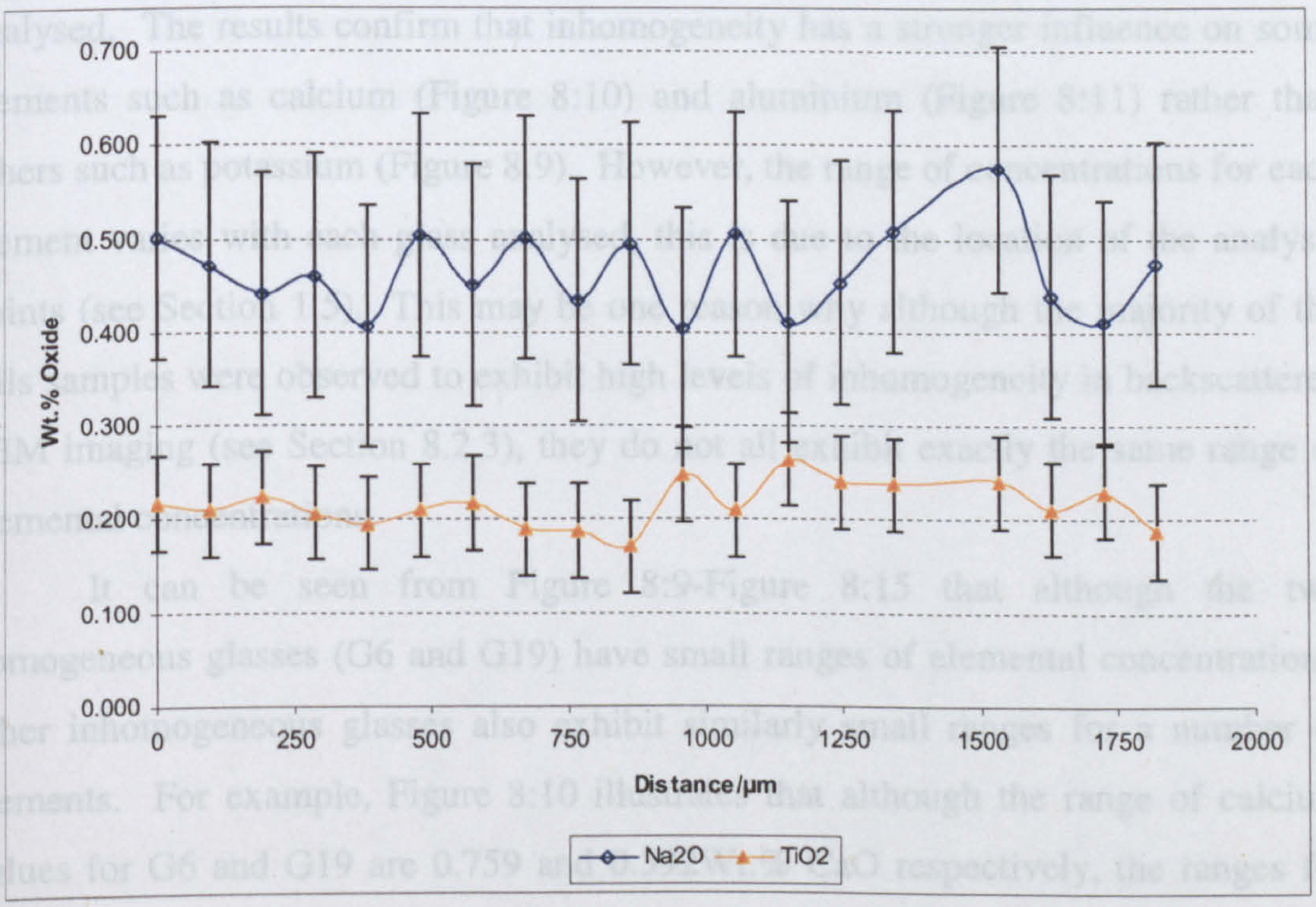


Homogeneous glass G6

Figure 8:7 Graph of EPMA line scan data illustrating the change in FeO and MnO concentrations over distance for inhomogeneous Hils glass sample G13 (Table VIII:8) and homogeneous Hils glass sample G6 (Table VIII:8)



Inhomogeneous glass G13



Homogeneous glass G6

Figure 8:8 Graph of EPMA line scan data illustrating the change in Na_2O, and TiO_2 concentrations over distance for inhomogeneous Hils glass sample G13 (Table VIII:8) and homogeneous Hils glass sample G6 (Table VIII:8)

The EPMA results from G13 and G6 confirm the results of the backscattered SEM imaging for these glasses (see Section 8.2.3), and show that a significant difference can be observed in the range of elemental concentrations obtained from an inhomogeneous and homogeneous glass. It can also be seen that certain elements, such as calcium and aluminium are influenced by inhomogeneity more than others are. To corroborate this evidence, line scans (and where this was not possible, point analyses) were carried out on more of the Hils glasses, the results are recorded in Table VIII:10-Table VIII:28. These results, and those already obtained from G13 and G6, are illustrated in Figure 8:9-Figure 8:15, which show the maximum, minimum and range of values obtained for each element from each Hils glass sample analysed. The reported values of chlorine and the oxides of cobalt, copper and sulphur for the majority of glasses were below the lower limits of detection of the EPMA (see Section 3.3.2.5) and therefore are not represented graphically but will be discussed with respect to the relevant glasses.

It can be seen from Figure 8:9-Figure 8:15 that the EPMA results from each Hils glass exhibit different levels of compositional homogeneity for each element analysed. The results confirm that inhomogeneity has a stronger influence on some elements such as calcium (Figure 8:10) and aluminium (Figure 8:11) rather than others such as potassium (Figure 8:9). However, the range of concentrations for each element varies with each glass analysed, this is due to the location of the analysis points (see Section 1.5). This may be one reason why although the majority of the Hils samples were observed to exhibit high levels of inhomogeneity in backscattered SEM imaging (see Section 8.2.3), they do not all exhibit exactly the same range of elemental concentrations.

It can be seen from Figure 8:9-Figure 8:15 that although the two homogeneous glasses (G6 and G19) have small ranges of elemental concentrations, other inhomogeneous glasses also exhibit similarly small ranges for a number of elements. For example, Figure 8:10 illustrates that although the range of calcium values for G6 and G19 are 0.759 and 0.392Wt.% CaO respectively, the ranges for inhomogeneous glasses G7 and G24 are 0.619 and 0.501Wt.% CaO respectively. Therefore, in this case the **inhomogeneous** glasses exhibit a smaller range of calcium values than the **homogeneous** glass G19. It is important to note that using backscattered SEM imaging G7 and G24 were classified as having high and low levels of inhomogeneity respectively (see Section 3.3.2.3). Figure 8:9-Figure 8:15

illustrate that although both these glasses exhibit similar ranges of elemental concentrations for the majority of elements, G24 has a significantly larger range of aluminium concentrations than G7. It is important to note that in this case the backscattered SEM classification for inhomogeneity could be potentially misleading.

Figure 8:9-Figure 8:15 shows that the range of inhomogeneity observed in the waste glass (G21-24 and 27) and glass drops (G1, 5-14 and 16-18) appears to be similarly varied. In addition to this there is no correlation between the samples from each different glasshouse, although this is difficult to confirm, as there are only small number of samples available for analysis from each site (see Section 7.4).

Figure 8:9-Figure 8:15 show that the majority of the Hils glass samples analysed have different compositions to each other. For example, Figure 8:10 shows that the maximum calcium levels recorded for each glass are distributed between 2.773Wt.% CaO (G24) to 15.692Wt.% CaO (G6) for the 12/13th century glass and 13.313Wt.% CaO (G18) to 24.876Wt.% CaO (G20) for the 1400AD fragments. This wide variation in chemical compositions between different samples has also been noted in published analyses of Hils glass (see Section 7.4). However, it is difficult to determine whether there is any relationship between the glass composition and the level of inhomogeneity observed due to the limited number of samples.

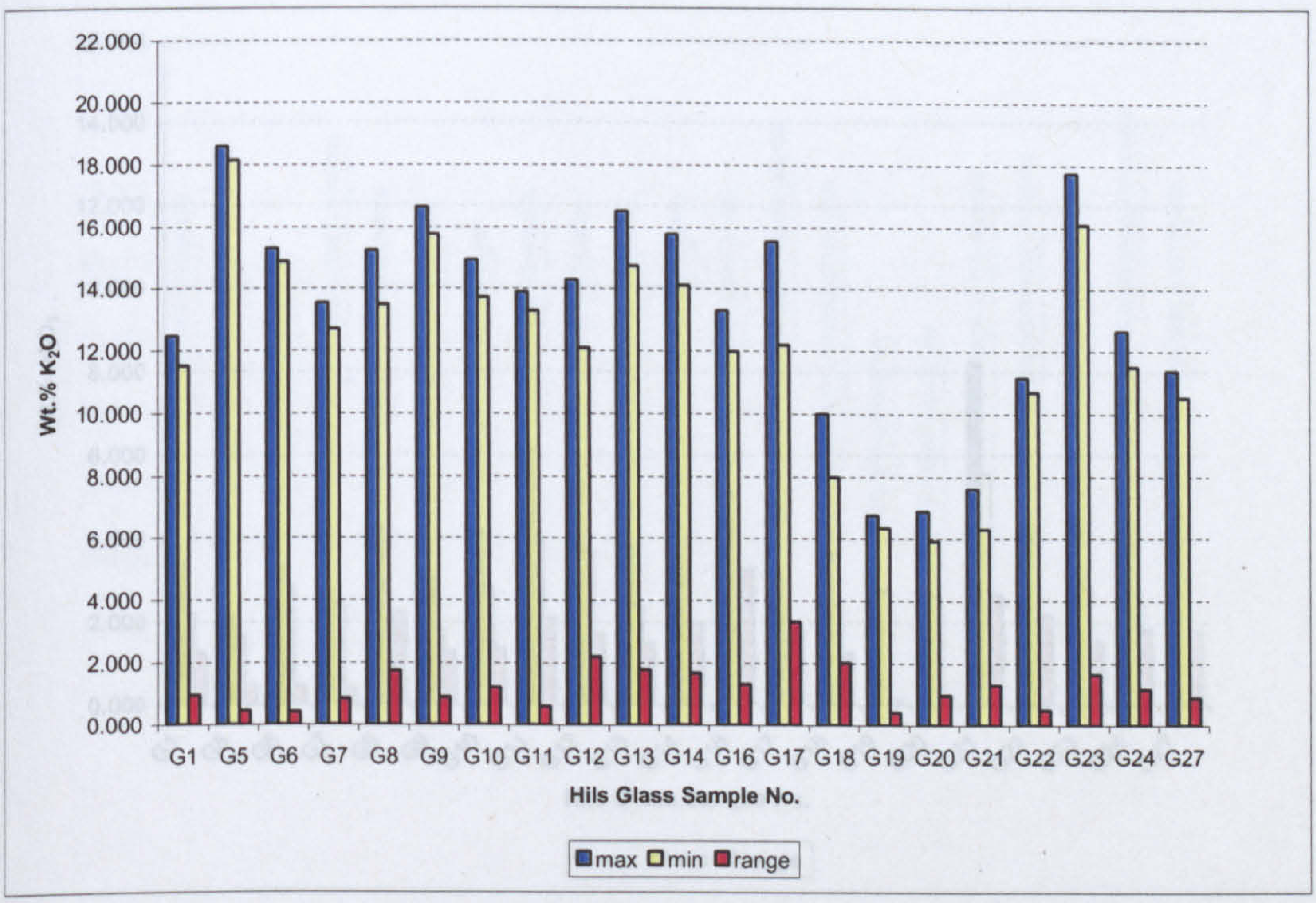


Figure 8:9 A comparison of the maximum, minimum and range of values obtained for K_2O for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

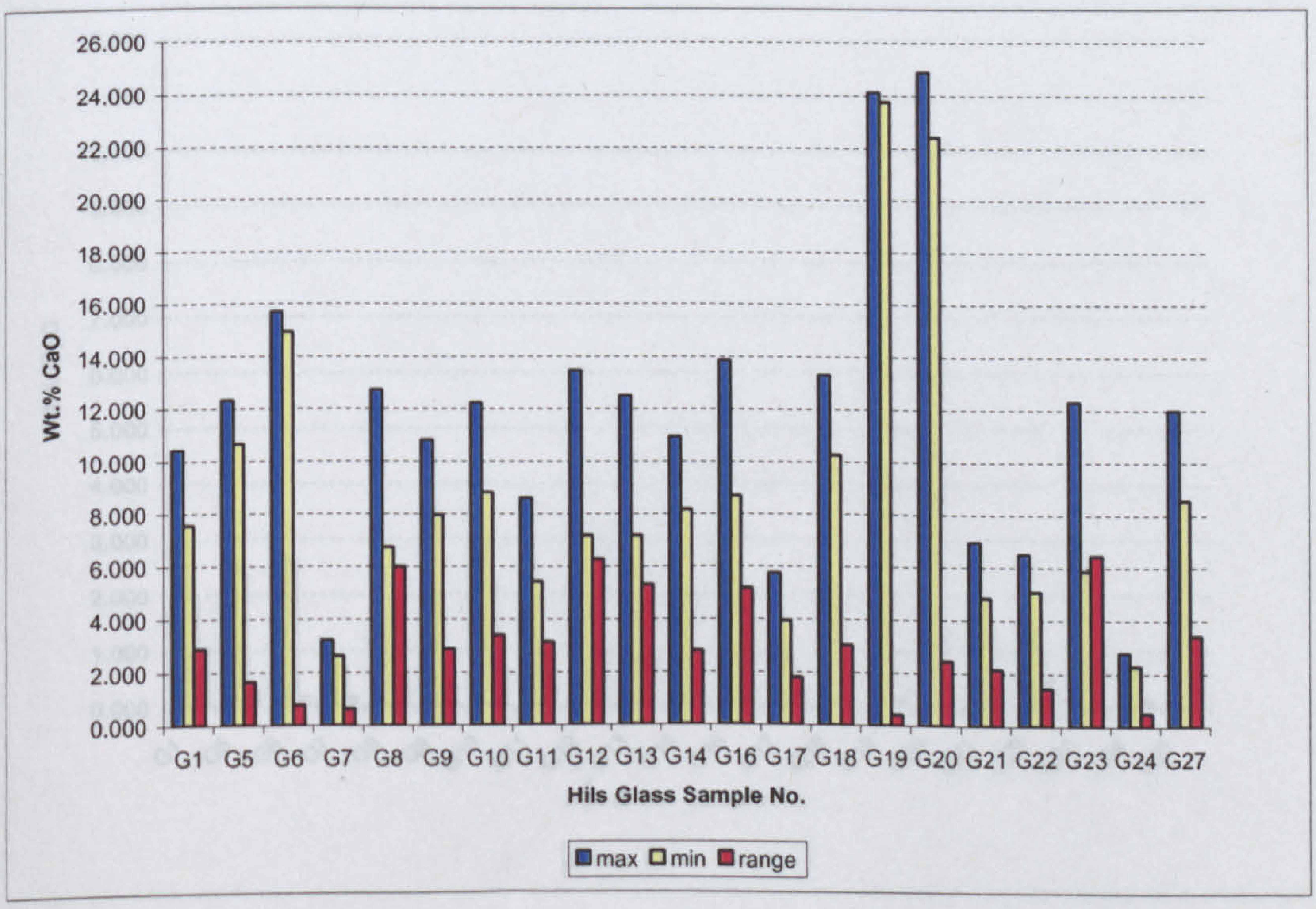


Figure 8:10 A comparison of the maximum, minimum and range of values obtained for CaO for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

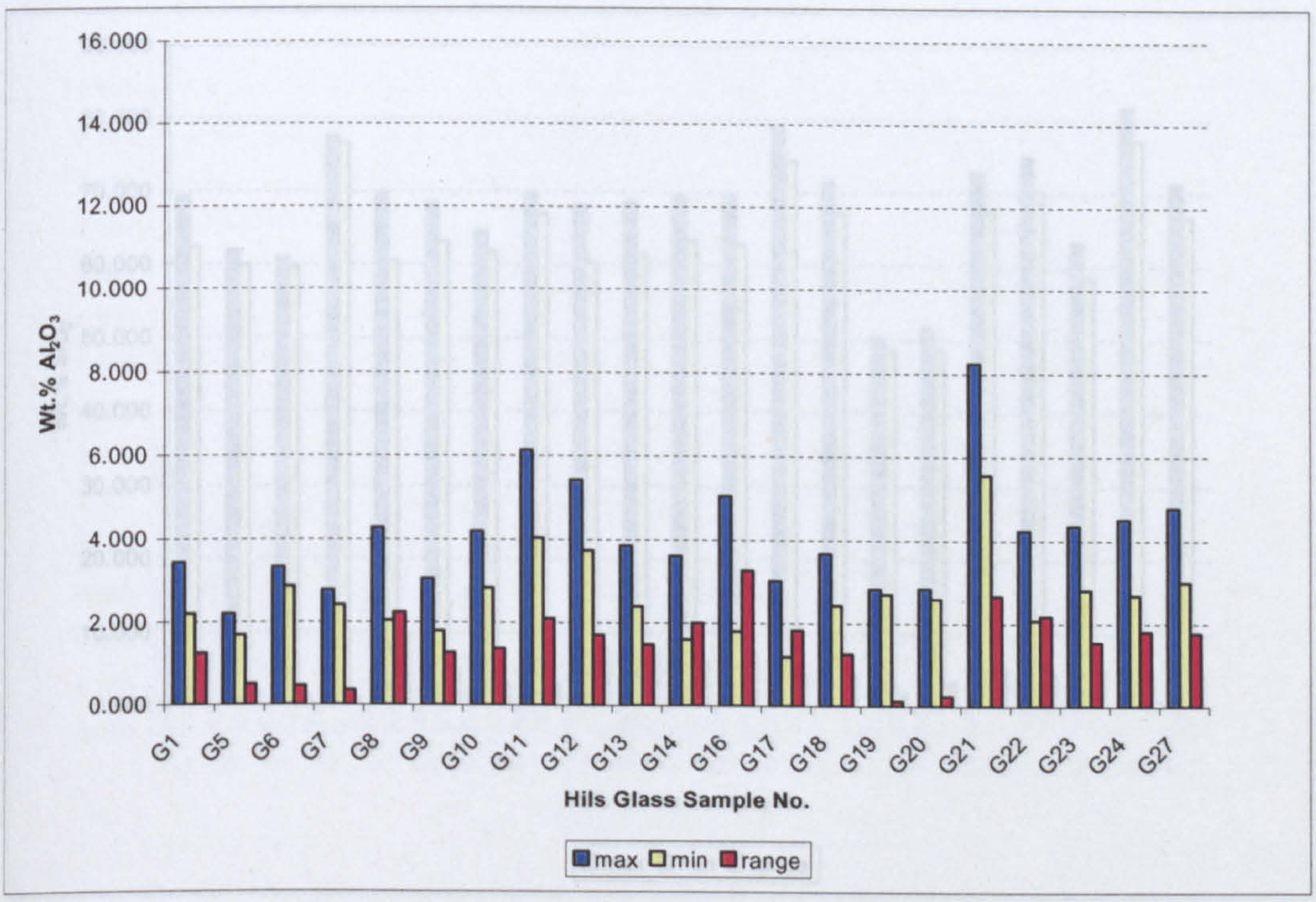


Figure 8:11 A comparison of the maximum, minimum and range of values obtained for Al_2O_3 for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

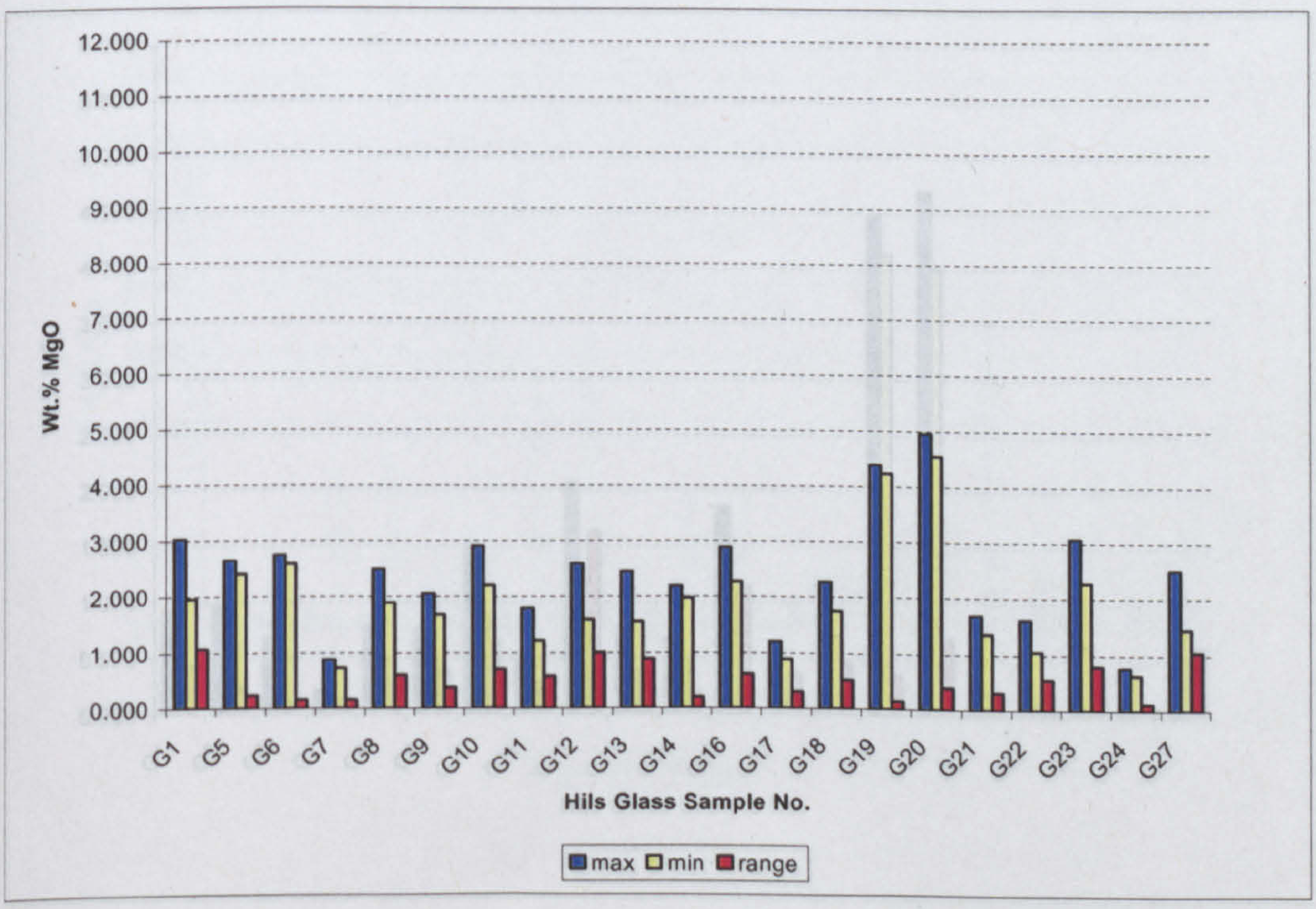


Figure 8:12 A comparison of the maximum, minimum and range of values obtained for MgO for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

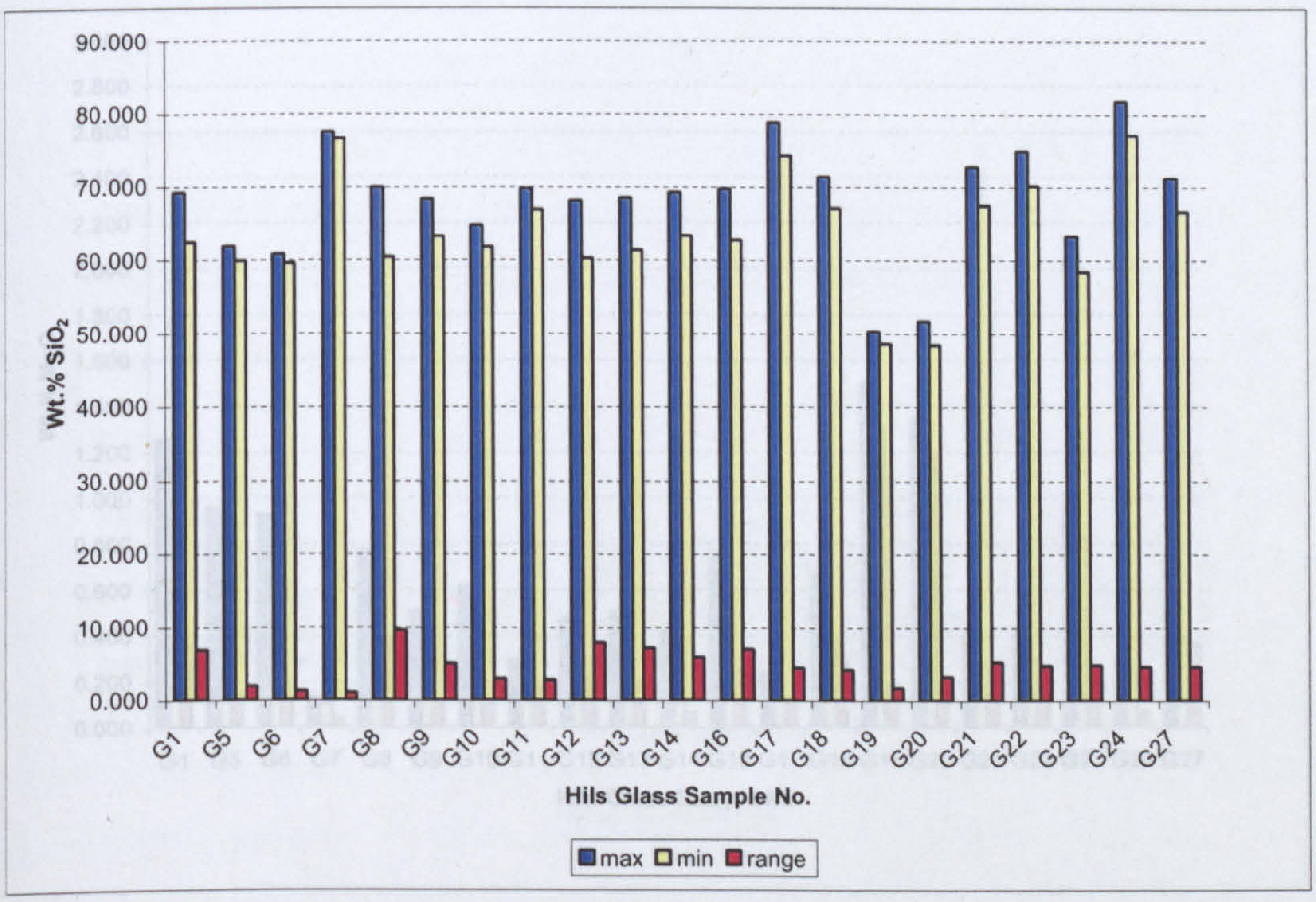


Figure 8:13 A comparison of the maximum, minimum and range of values obtained for SiO_2 for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

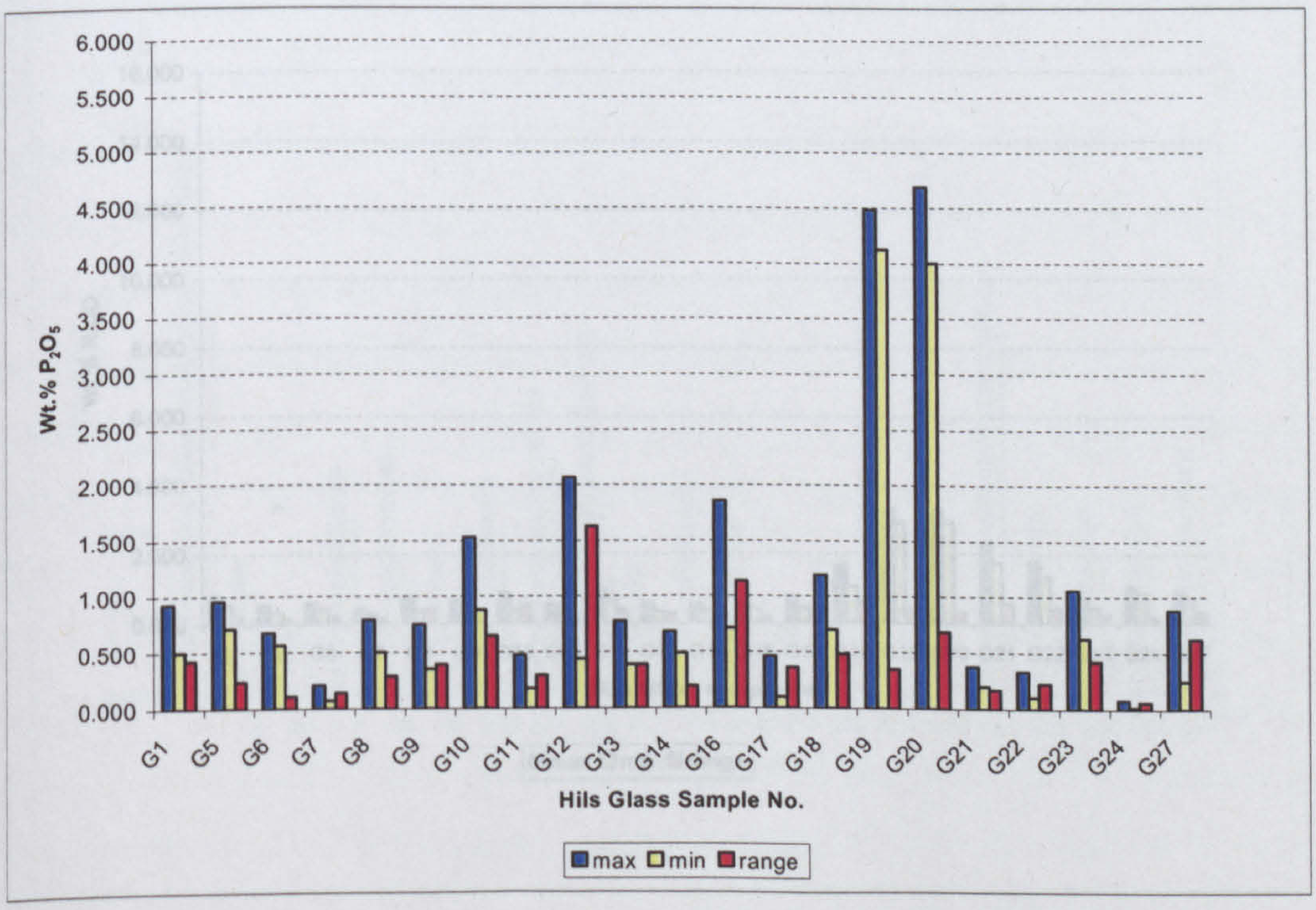


Figure 8:14 A comparison of the maximum, minimum and range of values obtained for P_2O_5 for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

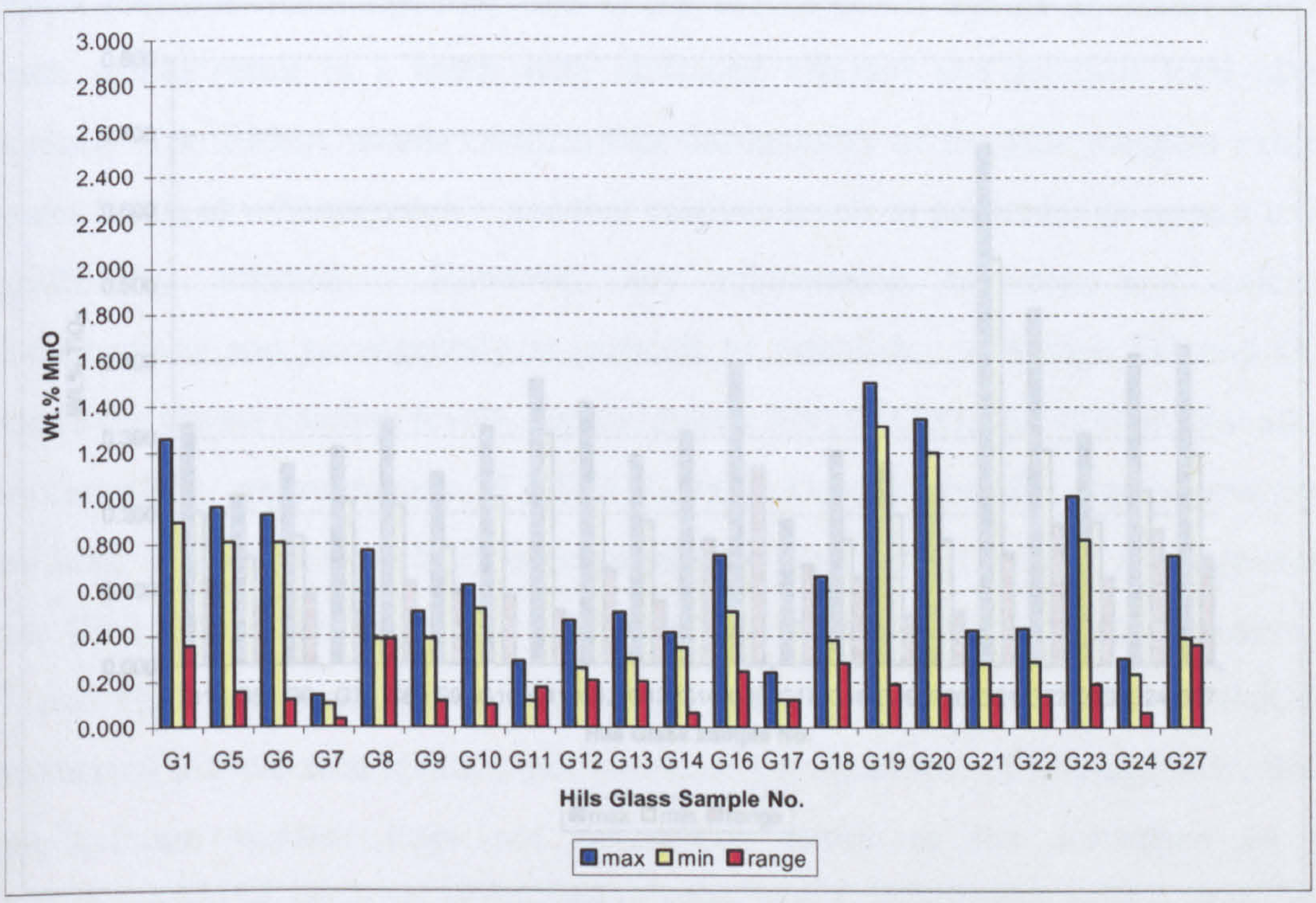


Figure 8:15 A comparison of the maximum, minimum and range of values obtained for MnO for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

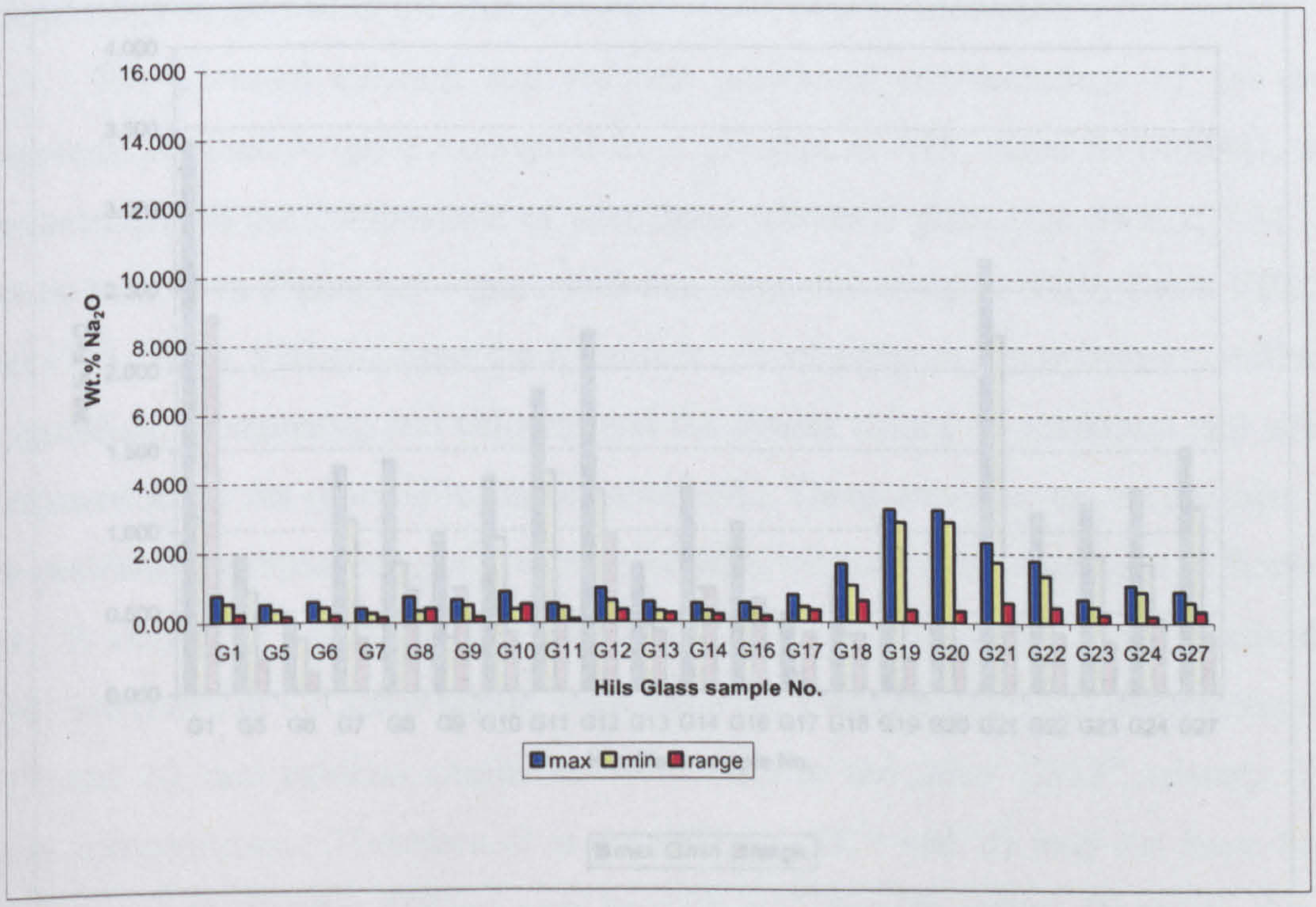


Figure 8:16 A comparison of the maximum, minimum and range of values obtained for Na_2O for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

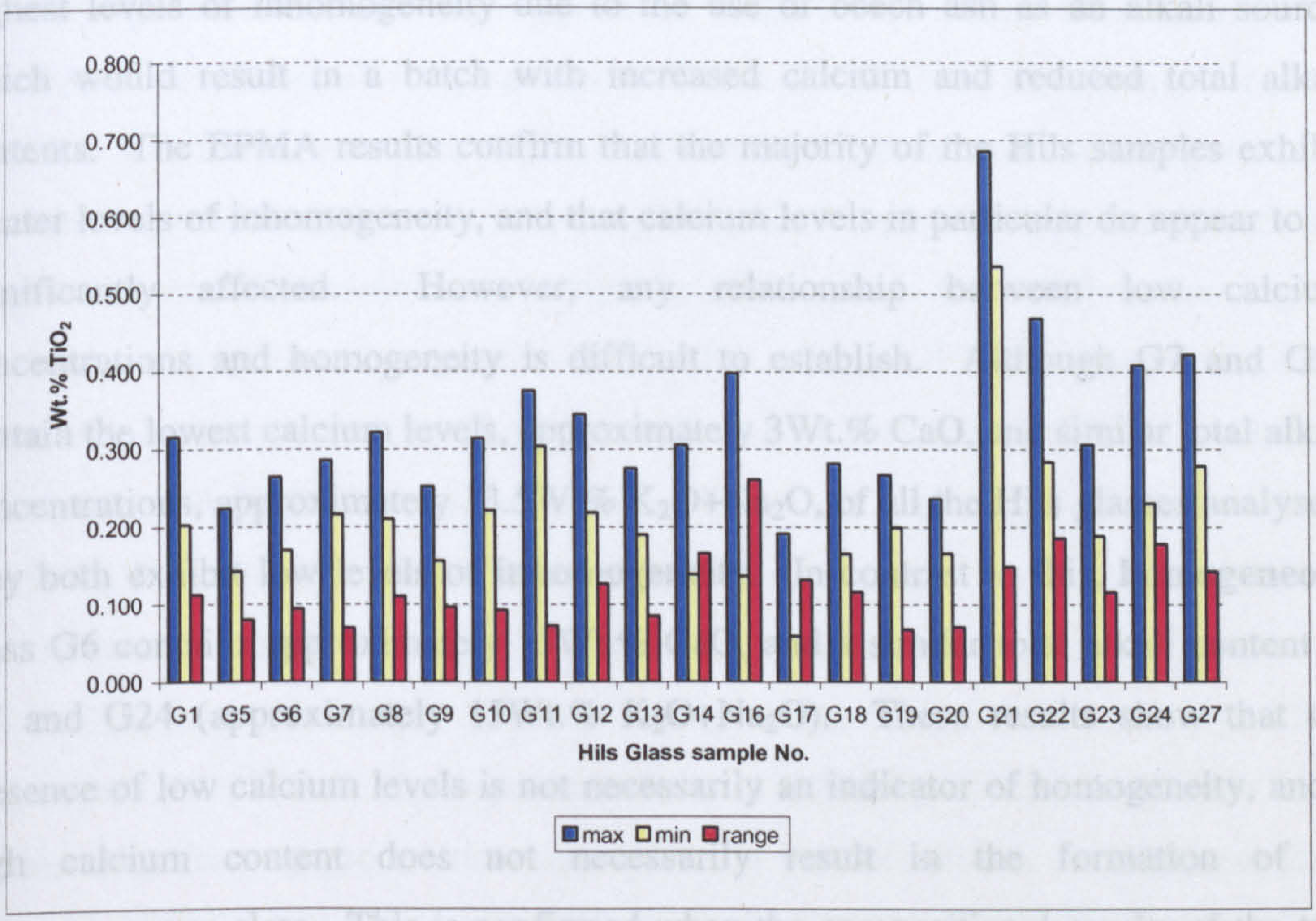


Figure 8:17 A comparison of the maximum, minimum and range of values obtained for TiO_2 for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

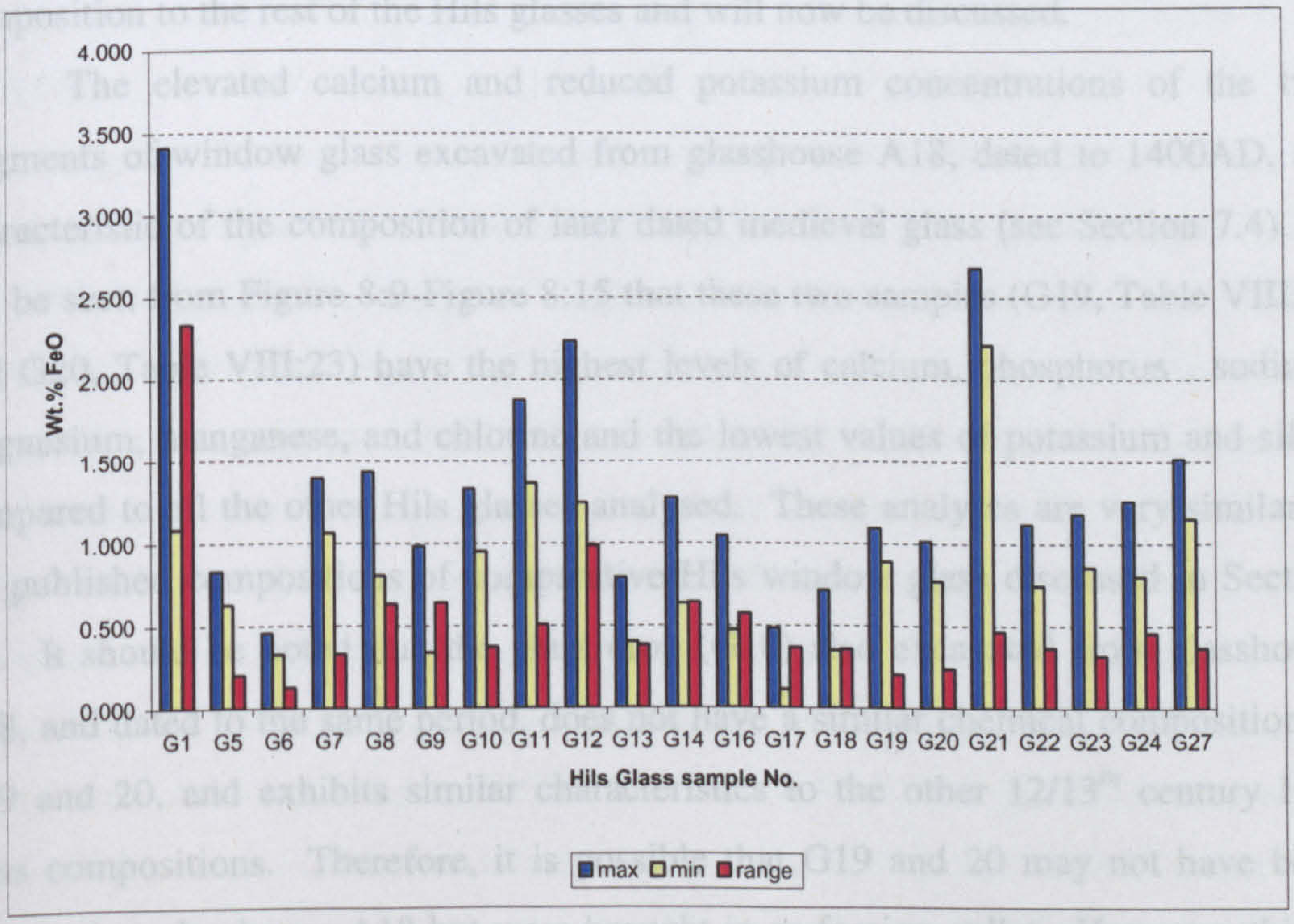


Figure 8:18 A comparison of the maximum, minimum and range of values obtained for FeO for Hils glass samples using EPMA (Table VIII:7-Table VIII:28)

It was noted in Section 7.5 that the Hils glasses were likely to exhibit the highest levels of inhomogeneity due to the use of beech ash as an alkali source, which would result in a batch with increased calcium and reduced total alkali contents. The EPMA results confirm that the majority of the Hils samples exhibit greater levels of inhomogeneity, and that calcium levels in particular do appear to be significantly affected. However, any relationship between low calcium concentrations and homogeneity is difficult to establish. Although G7 and G24 contain the lowest calcium levels, approximately 3Wt.% CaO, and similar total alkali concentrations, approximately 13.5Wt% K_2O+Na_2O, of all the Hils glasses analysed, they both exhibit low levels of **inhomogeneity**. In contrast to this, **homogeneous** glass G6 contains approximately 15Wt.% CaO, and a similar total alkali content to G7 and G24 (approximately 15Wt.% K_2O+Na_2O). These results show that the presence of low calcium levels is not necessarily an indicator of homogeneity, and a high calcium content does not necessarily result in the formation of an inhomogeneous glass. This is confirmed when the compositional results of the two fragments of Hils window glass (G19 and 20) are examined. Although G19 and 20 contain the highest calcium levels out of all the Hils glass, G19 has a very low range of elemental compositions. These two glasses are significantly different in composition to the rest of the Hils glasses and will now be discussed.

The elevated calcium and reduced potassium concentrations of the two fragments of window glass excavated from glasshouse A18, dated to 1400AD, are characteristic of the composition of later dated medieval glass (see Section 7.4). It can be seen from Figure 8:9-Figure 8:15 that these two samples (G19, Table VIII:22 and G20, Table VIII:23) have the highest levels of calcium, phosphorus, sodium, magnesium, manganese, and chlorine and the lowest values of potassium and silica compared to all the other Hils glasses analysed. These analyses are very similar to the published compositions of comparative Hils window glass discussed in Section 7.4. It should be noted that the glass drop (G18) also excavated from glasshouse A18, and dated to the same period, does not have a similar chemical composition to G19 and 20, and exhibits similar characteristics to the other 12/13th century Hils glass compositions. Therefore, it is possible that G19 and 20 may not have been produced at glasshouse A18 but were brought in as foreign cullet. However, this is difficult to determine due to the small number of samples available for analysis and the paucity of excavated evidence at Hils (see Section 7.4).

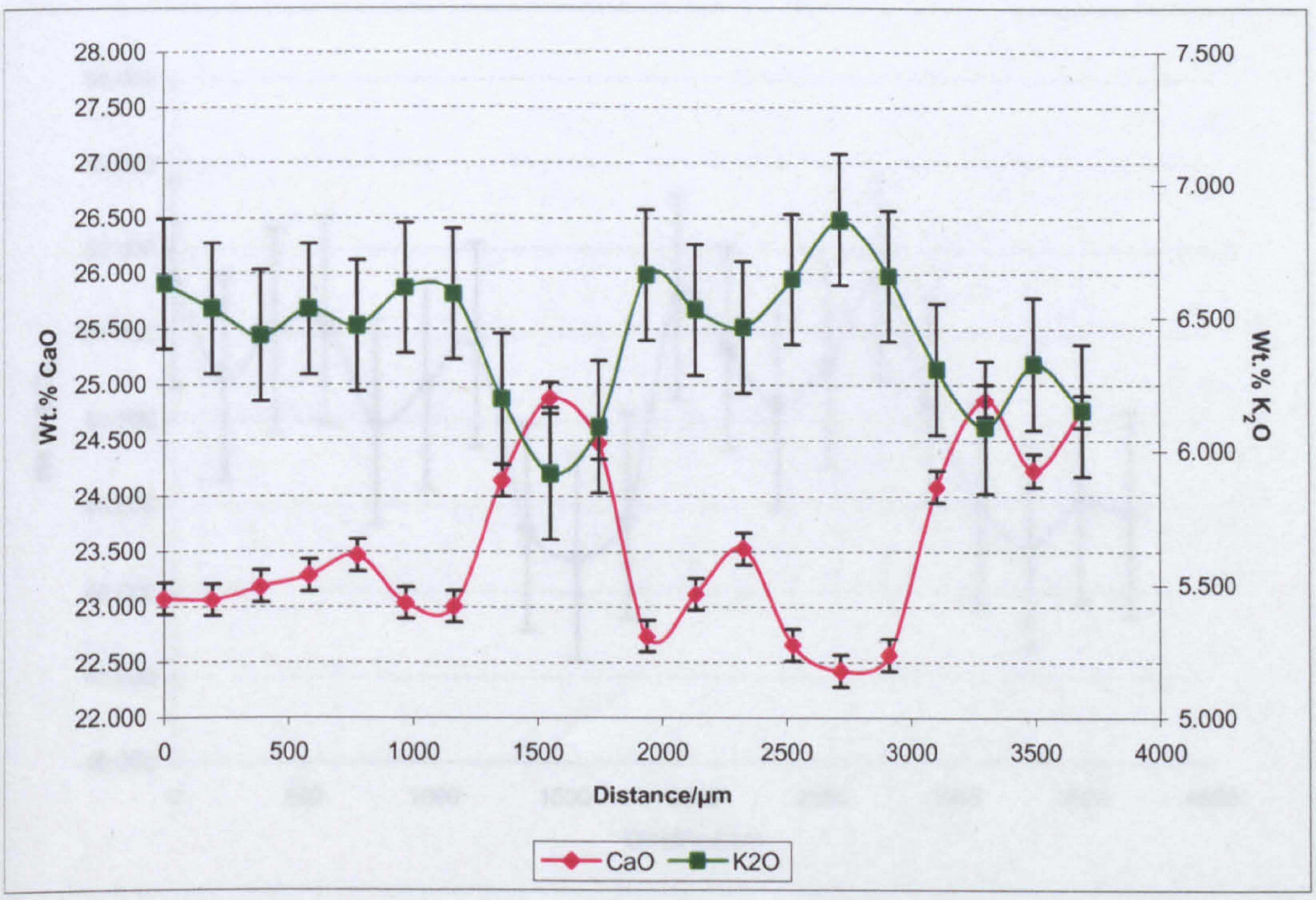
The results of backscattered imaging in Section 8.2.3 determined that G19 was homogeneous and G20 inhomogeneous. Figure 8:19-Figure 8:22 illustrate the distribution of elemental compositions in G19 and G20 over the distance scanned (4149μm and 3687μm respectively). It can be seen that as with the comparison of the inhomogeneous and homogeneous glasses G13 and G6 discussed above, the range of elemental concentrations is significantly larger in the inhomogeneous glass G20 compared to the homogeneous glass G19. Figure 8:19 illustrates that G20, contains a broad distribution of calcium (22.424-24.876Wt.% CaO) and potassium (5.916-6.869Wt.% K_2O) concentrations. However, the range of these values (2.453Wt.% CaO and 0.954Wt.% K_2O) is not as large as observed in many of the inhomogeneous 12/13th century Hils glasses discussed above.

The range of silica (3.272Wt.% SiO_2), aluminium (0.255Wt.% Al_2O_3) and magnesium (0.397Wt.% MgO) concentrations in G20 (Figure 8:20 and Figure 8:21) are also significantly greater than any spread in the data due to experimental error but, as can be seen in Figure 8:9-Figure 8:18, less than a number of the other inhomogeneous glasses analysed. Figure 8:19 illustrates that in the homogeneous glass, G19, the distribution of all the potassium and the majority of the calcium values are within the limits expected due to experimental error, this is also the case for the analyses of silica (Figure 8:20), magnesium and aluminium (Figure 8:21) from G19.

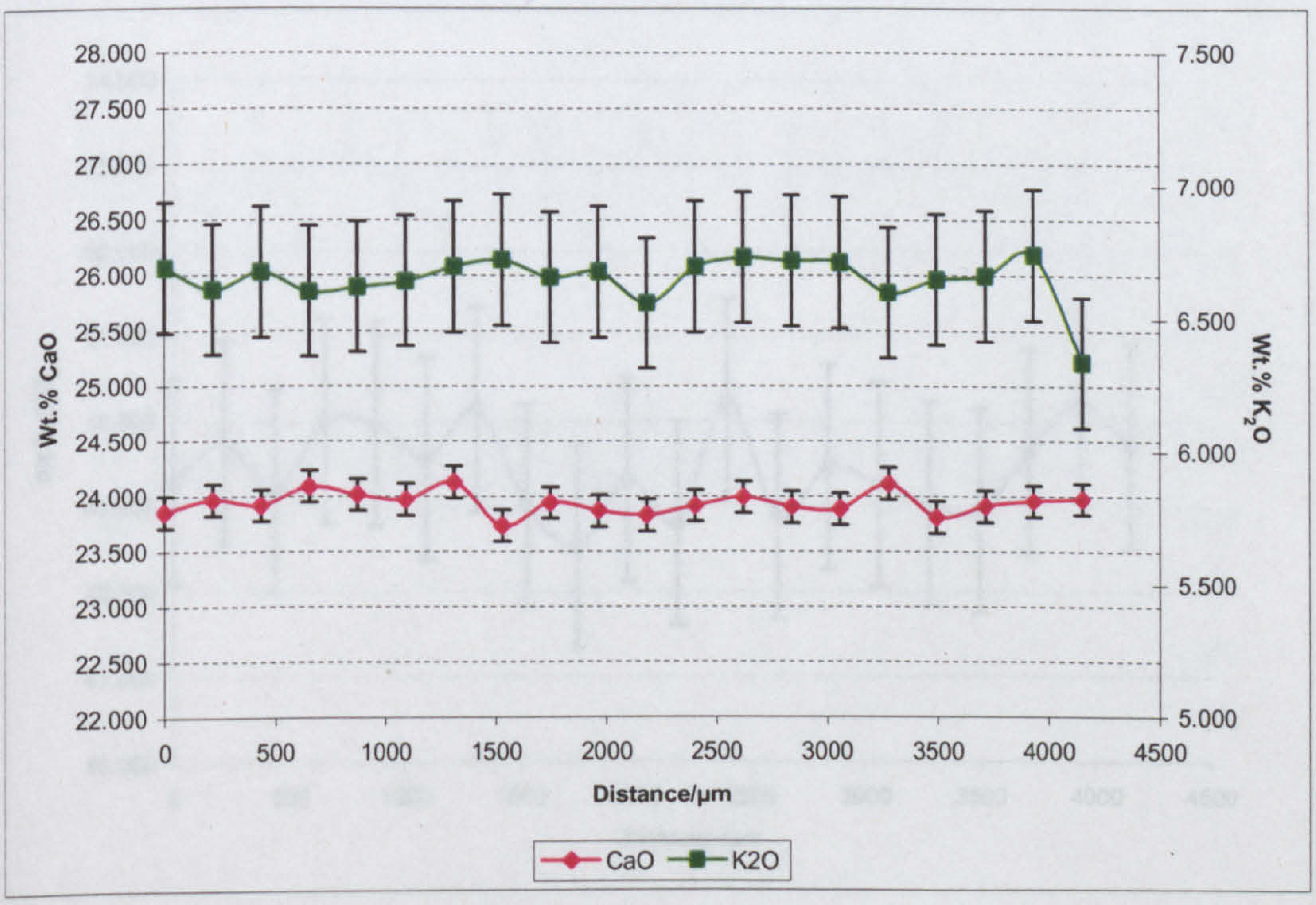
Figure 8:22 shows the distribution of phosphorus concentrations is larger for inhomogeneous glass G20 (0.689Wt.% P_2O_5) than homogeneous glass G19 (0.353Wt.% P_2O_5). The range of sodium values is smaller for G20 (0.338Wt.% Na_2O) than G19 (0.358Wt.% Na_2O), but when the data is examined it can be seen that there is a more varied distribution of values for G20 than G19. The range of concentrations of iron, manganese and titanium are similar for both G19 and 20 (Figure 8:23), and the majority of the data for all the elements is distributed within the spread of data expected due to experimental error. G19 and 20 are the only Hils glasses that contain chlorine concentrations that are significantly greater than the lowest limit of detection for the EPMA (see Section 3.3.2.5). Figure 8:24 shows that although the range of chlorine values is greater for G20 (0.281Wt.% Cl) than G19 (0.174Wt.% Cl), the level of precision for this element means that all the majority of the data points for both glasses are within the spread expected from experimental error. G20 also contains sulphur concentrations that are greater than the lower limit of detection of the EPMA, but poor precision (see Section 3.3.2.5) means that it is difficult to confirm whether the range of values obtained (0.311Wt.% SO_2) is due to inhomogeneity or instrumental error. The EPMA results also confirm that the deep blue colour of G19 (Plate 8:23) is due to the presence of cobalt in the glass (Weyl 1951: 168). However, it is only present in very small quantities, close to the lower limit of detection of the EPMA.

It can be seen from Figure 8:19-Figure 8:22 that G20 contains some distinct inter elemental relationships, magnesium, aluminium, phosphorus and calcium all appear to increase as potassium and silica decrease. The relationship between calcium and potassium is illustrated well in Figure 8:19. In comparison to the spread of different compositions in G13, G20 appears to contain a smaller number of distinct glass compositions. It is important to note that G19 and 20 were heavily weathered (see Section 7.4), and therefore any compositional changes may be due to corrosion.

In summary it can be seen that the majority of the Hils glasses did exhibit high levels of inhomogeneity as expected from the results of the backscattered SEM imaging (see Section 8.2.3) and elemental mapping (see above). The majority of the elemental variations observed in these inhomogeneous glasses were also greater than those expected due to experimental error. It is important to note that significant levels of elemental variation were also observed for aluminium in glass sample G6 that had appeared homogeneous under backscattered SEM imaging. Specific elements were found to be more significantly affected by inhomogeneity than others, in particular calcium, aluminium, magnesium, and phosphorus . A number of elemental relationships were also observed, and a number of the samples analysed exhibited a combination of many different compositions.

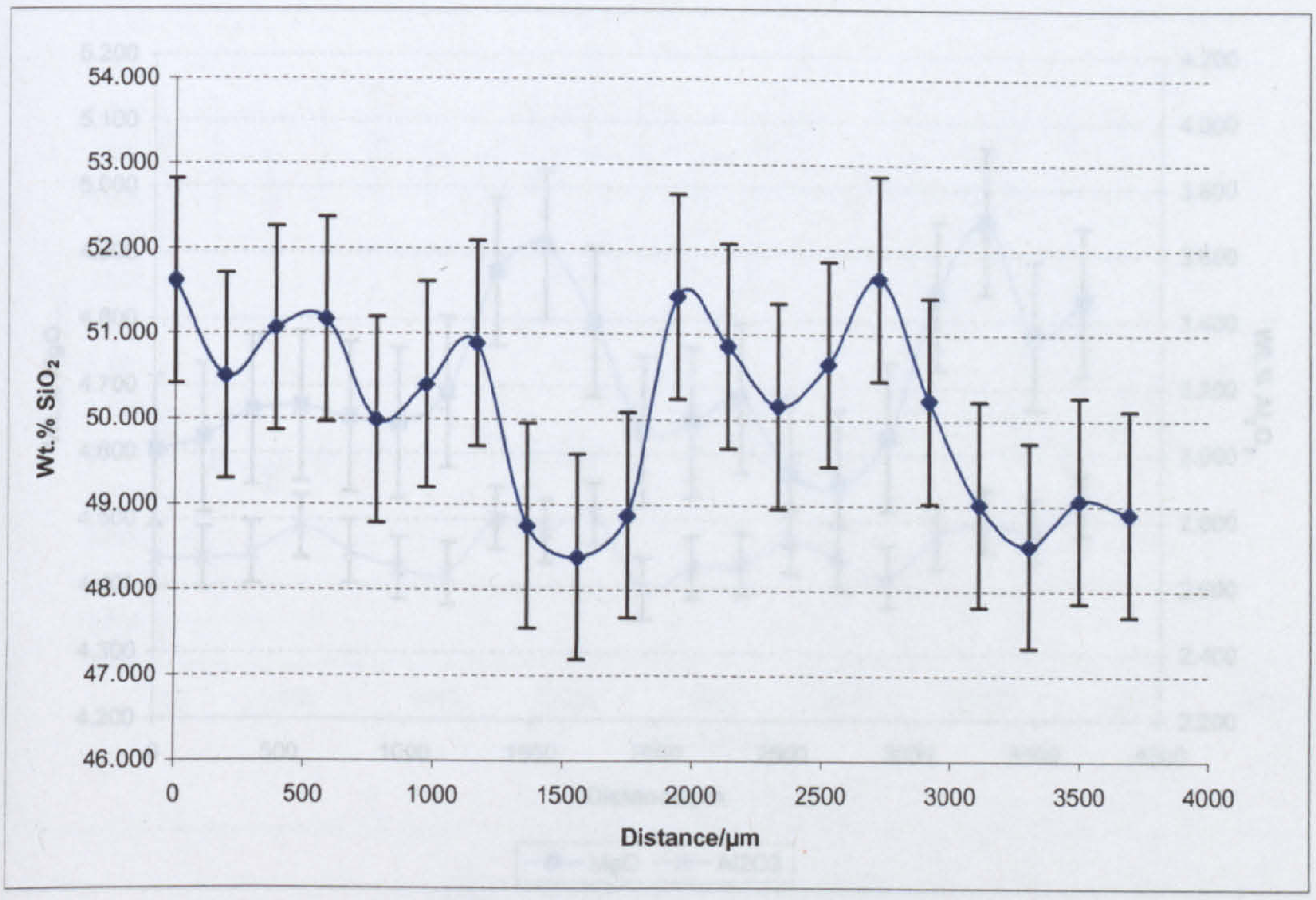


Inhomogeneous glass G20

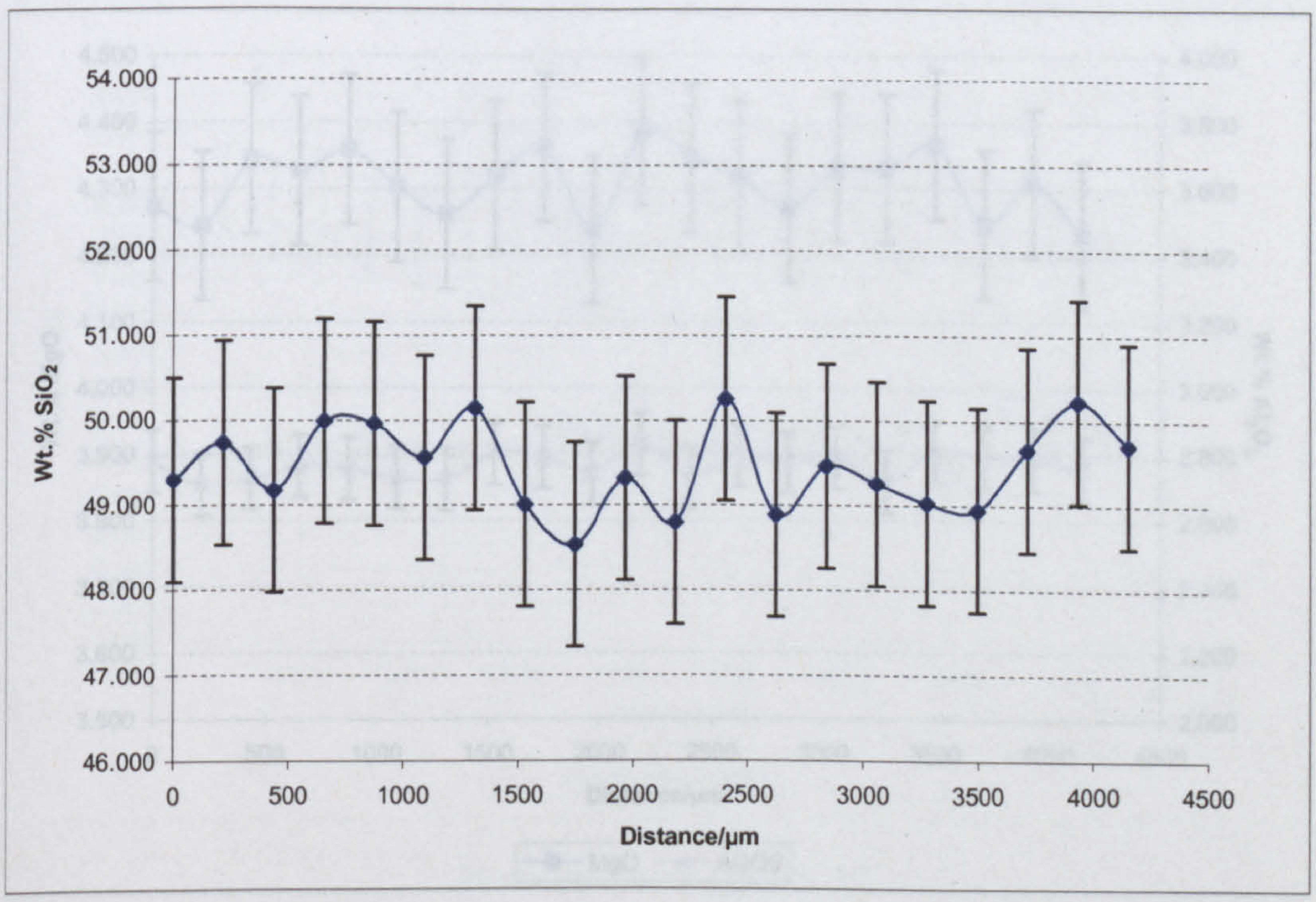


Homogeneous glass G19

Figure 8:19 Graph of EPMA line scan data illustrating the change in CaO and K_2O concentrations over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and homogeneous Hils glass sample G19 (Table VIII:22)

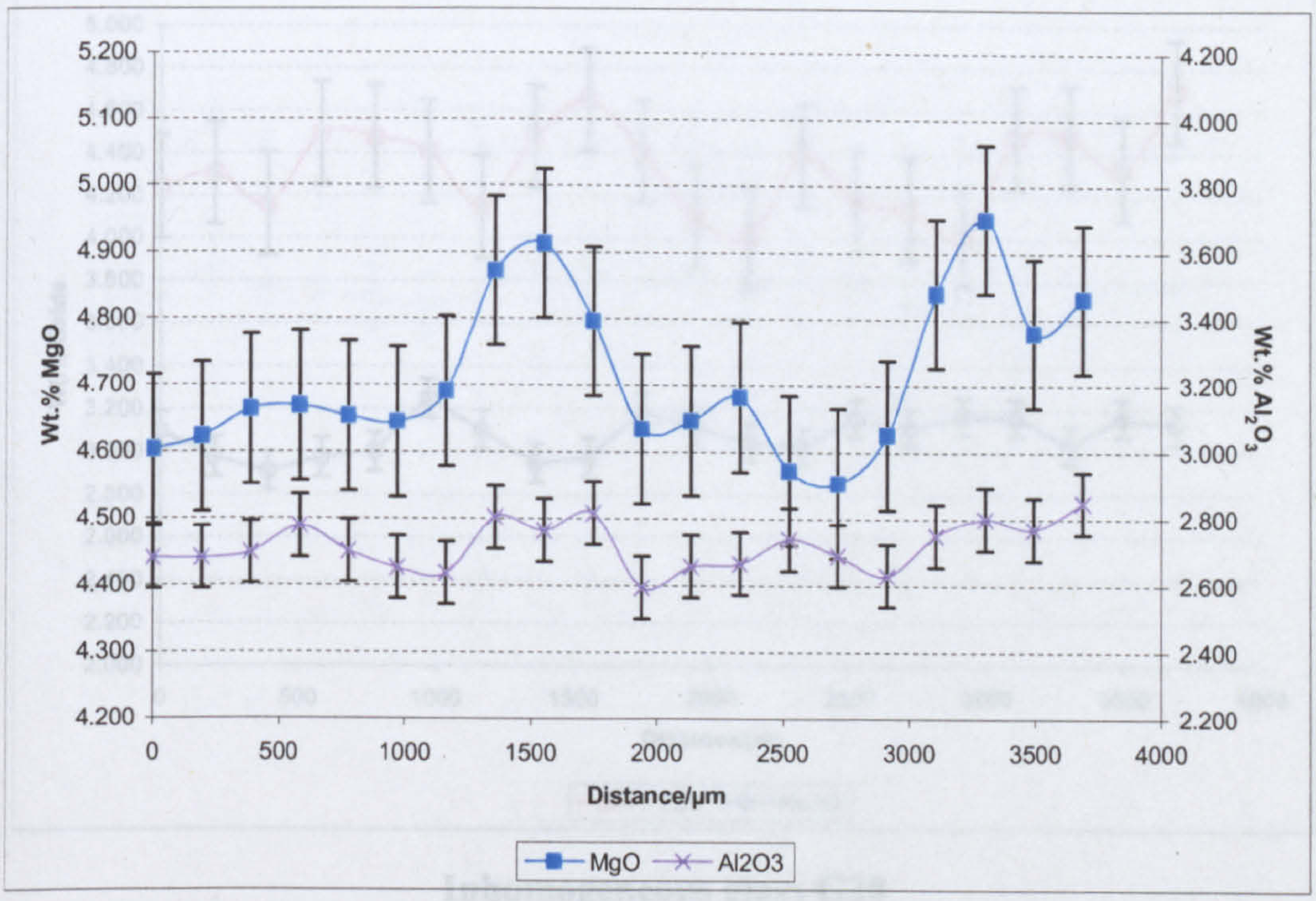


Inhomogeneous glass G20

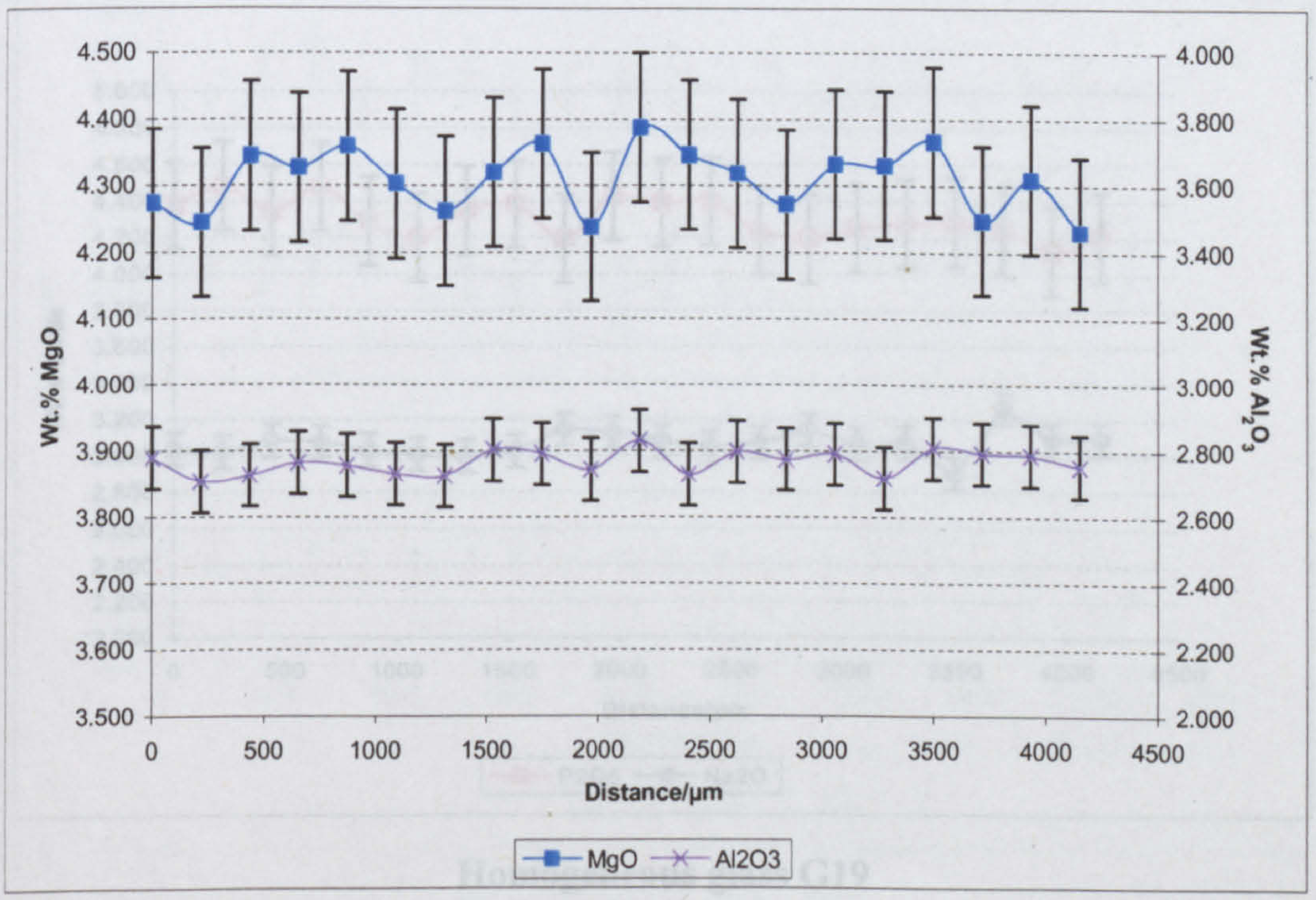


Homogeneous glass G19

Figure 8:20 Graph of EPMA line scan data illustrating the change in SiO_2 concentration over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and homogeneous Hils glass sample G19 (Table VIII:22)

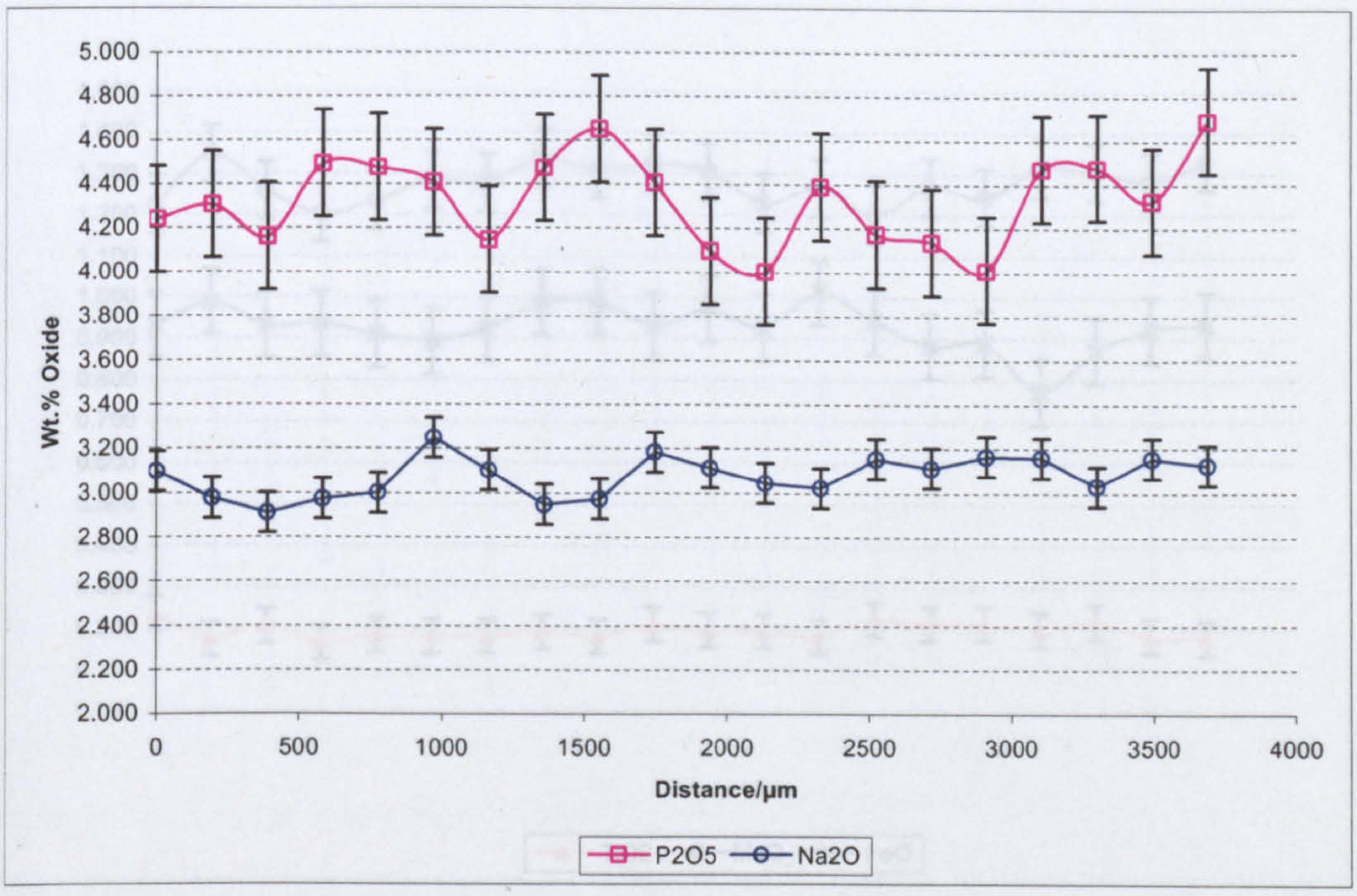


Inhomogeneous glass G20

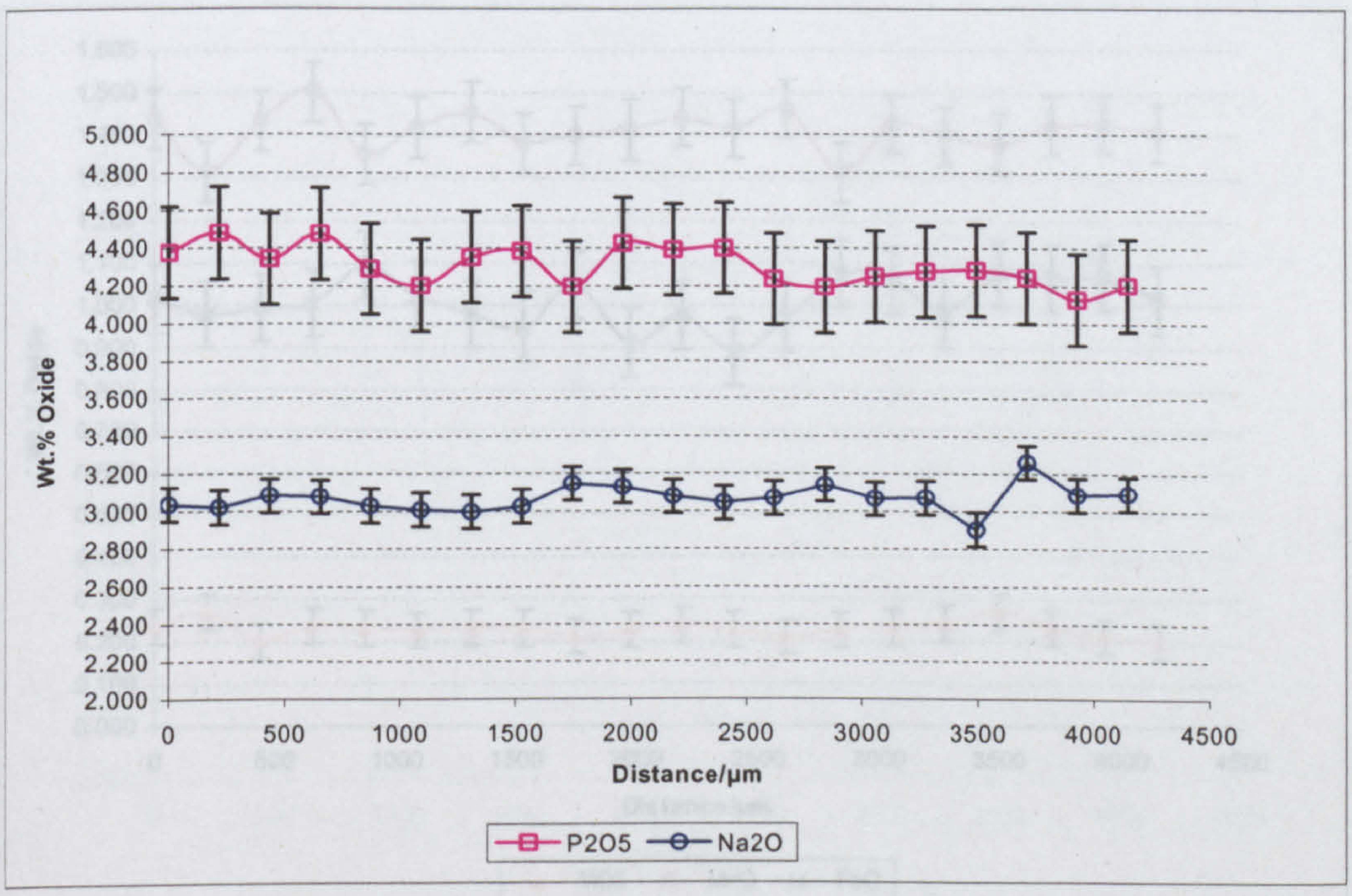


Homogeneous glass G19

Figure 8:21 Graph of EPMA line scan data illustrating the change in MgO and Al_2O_3 concentrations over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and homogeneous Hils glass sample G19 (Table VIII:22)

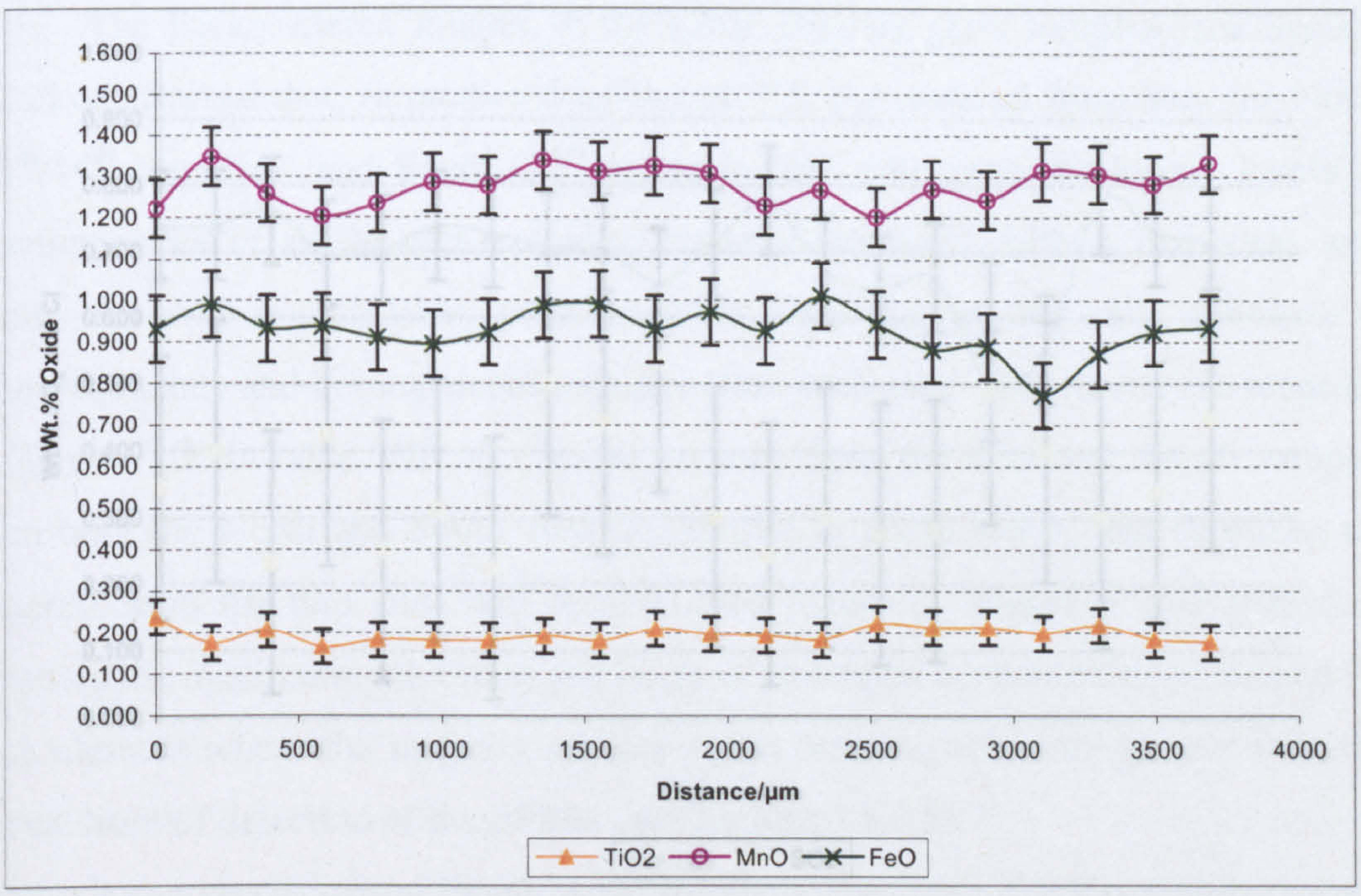


Inhomogeneous glass G20

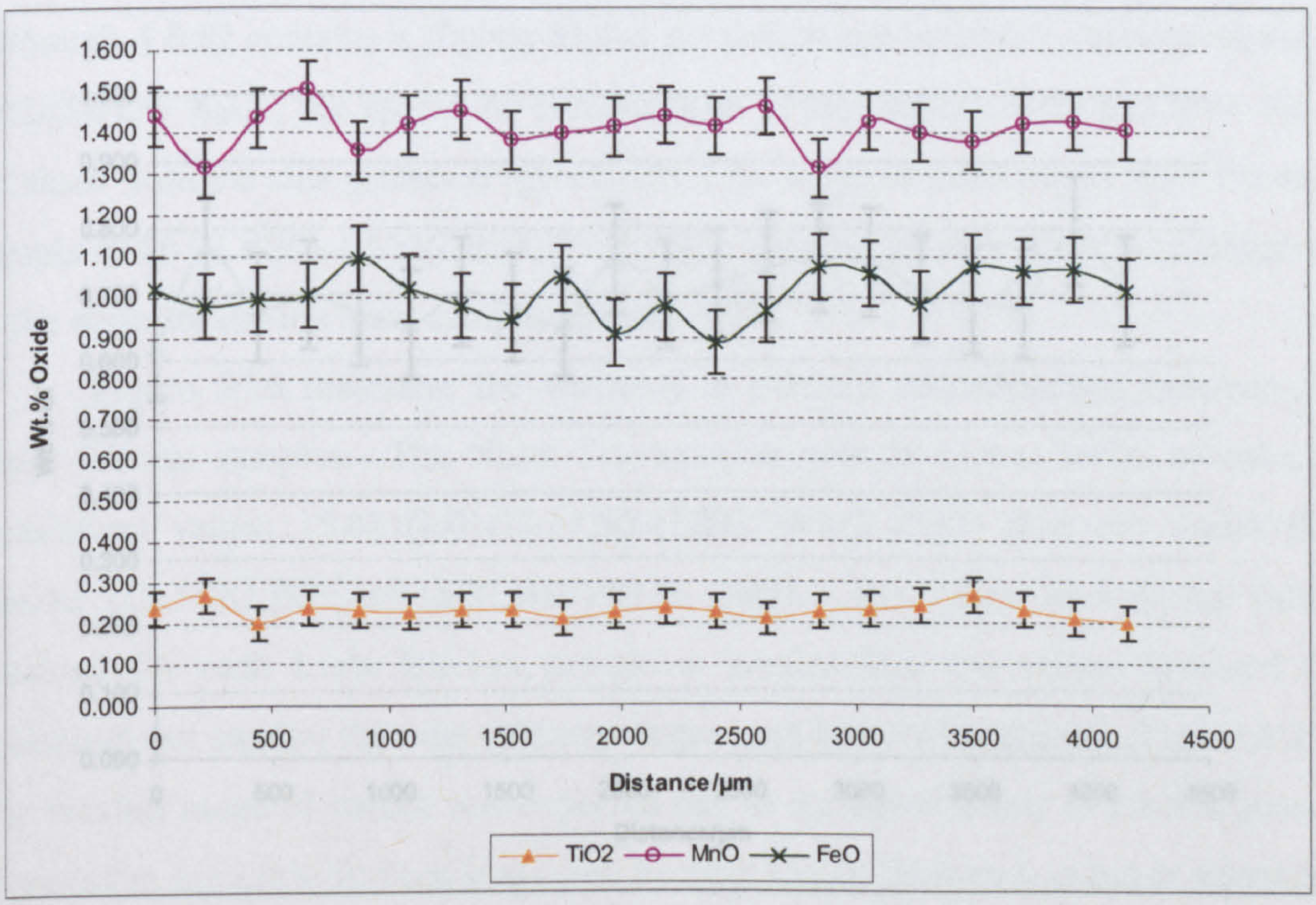


Homogeneous glass G19

Figure 8:22 **Graph of EPMA line scan data illustrating the change in Na_2O and P_2O_5 concentrations over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and homogeneous Hils glass sample G19 (Table VIII:22)**

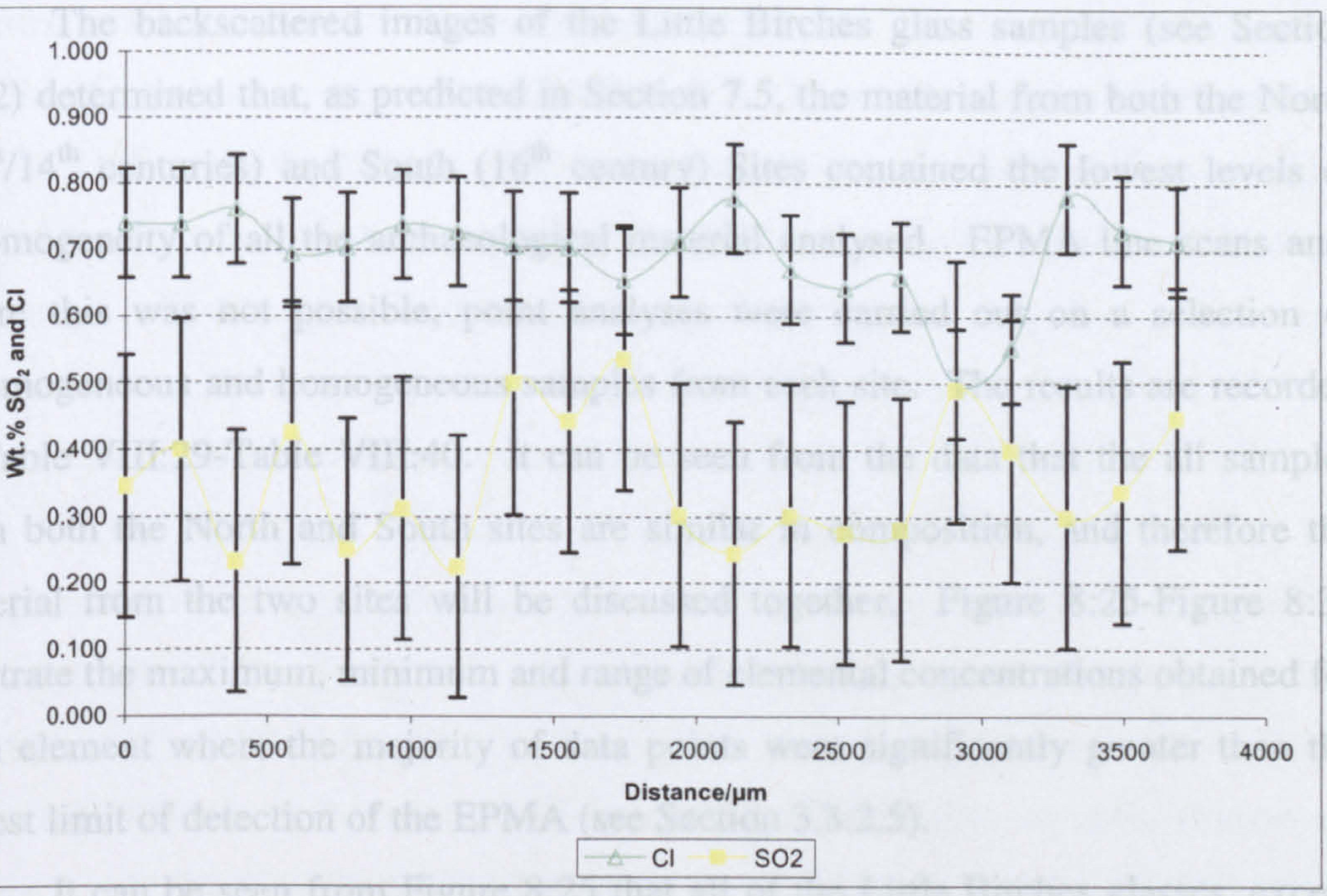


Inhomogeneous glass G20

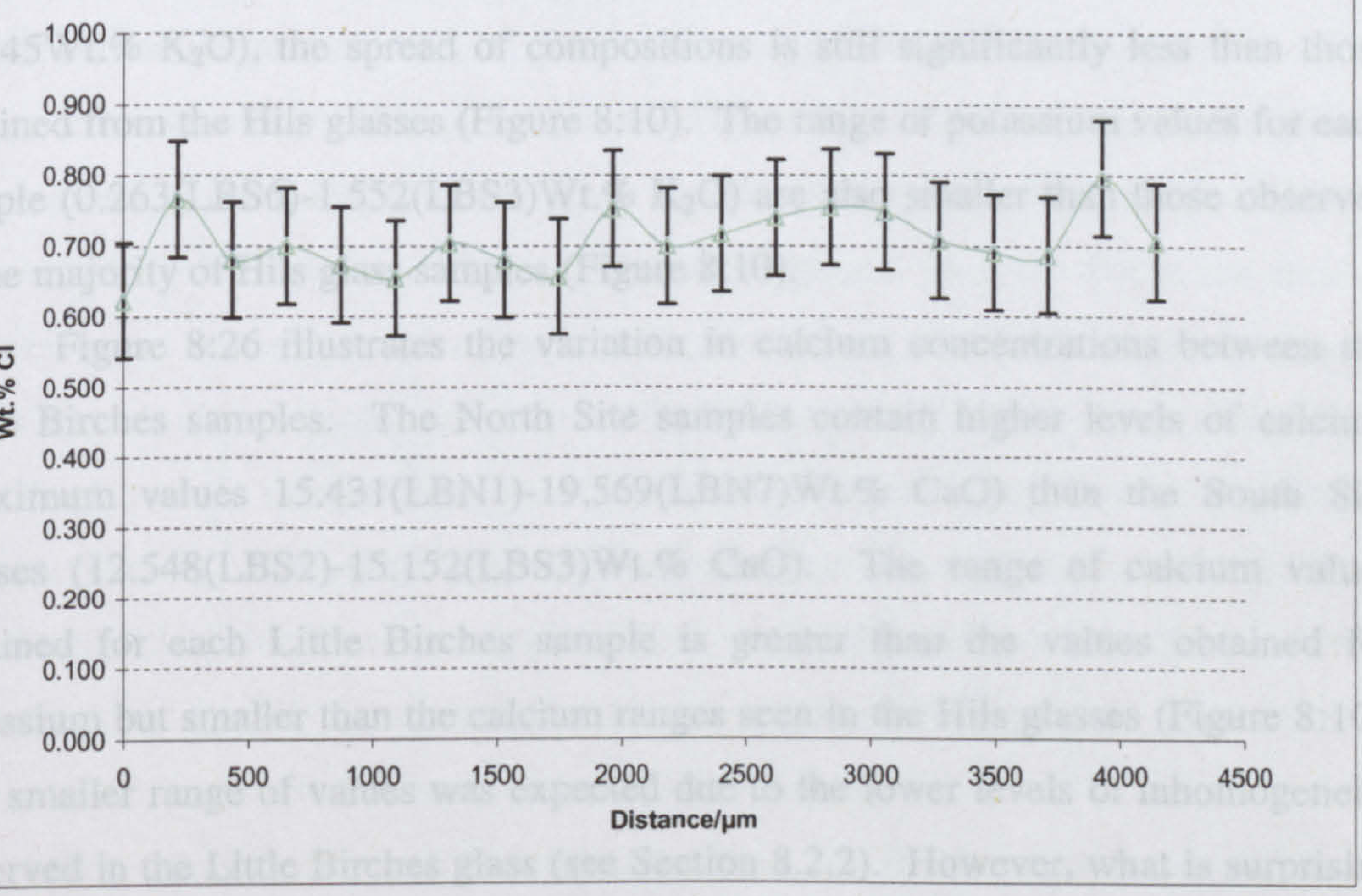


Homogeneous glass G19

Figure 8:23 Graph of EPMA line scan data illustrating the change in TiO_2 MnO and FeO concentrations over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and homogeneous Hils glass sample G19 (Table VIII:22)



Inhomogeneous glass G20



Homogeneous glass G19

Figure 8:24 Graph of EPMA line scan data illustrating the change in SO$_2$ and Cl concentrations over distance for inhomogeneous Hils glass sample G20 (Table VIII:23) and the change in Cl concentration over distance for homogeneous Hils glass sample G19 (Table VIII:22)

8.3.2 Little Birches

The backscattered images of the Little Birches glass samples (see Section 8.2.2) determined that, as predicted in Section 7.5, the material from both the North (13th/14th centuries) and South (16th century) Sites contained the lowest levels of inhomogeneity of all the archaeological material analysed. EPMA line scans and, where this was not possible, point analyses were carried out on a selection of inhomogeneous and homogeneous samples from each site. The results are recorded in Table VIII:29-Table VIII:40. It can be seen from the data that the all samples from both the North and South sites are similar in composition, and therefore the material from the two sites will be discussed together. Figure 8:25-Figure 8:35 illustrate the maximum, minimum and range of elemental concentrations obtained for each element where the majority of data points were significantly greater than the lowest limit of detection of the EPMA (see Section 3.3.2.5).

It can be seen from Figure 8:25 that all of the Little Birches glasses, except for one sample of glass waste (LBS2), contain similar potassium concentrations, the maximum values ranging between 12.691(LBN7)-14.474(LBS3)Wt.% K_2O. Although, LBS2 contains a slightly higher potassium concentration (maximum value 17.245Wt.% K_2O), the spread of compositions is still significantly less than those obtained from the Hils glasses (Figure 8:10). The range of potassium values for each sample (0.263(LBS6)-1.552(LBS3)Wt.% K_2O) are also smaller than those observed in the majority of Hils glass samples (Figure 8:10).

Figure 8:26 illustrates the variation in calcium concentrations between the Little Birches samples. The North Site samples contain higher levels of calcium (maximum values 15.431(LBN1)-19.569(LBN7)Wt.% CaO) than the South Site glasses (12.548(LBS2)-15.152(LBS3)Wt.% CaO). The range of calcium values obtained for each Little Birches sample is greater than the values obtained for potassium but smaller than the calcium ranges seen in the Hils glasses (Figure 8:10). The smaller range of values was expected due to the lower levels of inhomogeneity observed in the Little Birches glass (see Section 8.2.2). However, what is surprising is that the majority of **homogeneous** Little Birches samples (LBN4 and 7, and LBS2, 3, 8 and 9) contain **larger** ranges of potassium and calcium than the **inhomogeneous** samples (LBN1 and 3, and LBS4-7).

The Little Birches data for aluminium and magnesium is represented in Figure 8:27 and Figure 8:28 respectively. It can be seen that the glasses from both the North and South Sites contain similar levels of both these elements (approximately 1.5-2.5Wt% Al_2O_3 and 7-8Wt.% MgO). The exception to this, is one sample of glass waste from the North Site (LBN7), which contains approximately 3Wt.% Al_2O_3 and 6Wt.% MgO. The Little Birches glasses therefore contain higher levels of magnesium and lower levels of aluminium than the Hils glasses. Although, the ranges of aluminium and magnesium concentrations vary for each sample analysed, there does not appear to be a relationship between the extent of these elemental variations and the presence of inhomogeneity observed under the SEM.

Figure 8:29 and Figure 8:30 illustrate the differences in silica and phosphorous concentrations for each of the Little Birches glasses. It can be seen that the majority of the South Site glass contains **higher** silica (maximum values 52.212(LBS5)-60.874(LBS2)Wt.% SiO_2) and **lower** phosphorus (2.759(LBS9)-3.836(LBS9)Wt.% P_2O_5) concentrations than the North Site samples (maximum values 51.361(LBN7)-52.087(LBN4)Wt.% SiO_2 and 3.771(LBN4)-3.838(LBN7)Wt.% P_2O_5). The range of silica values obtained from each of the Little Birches glasses is significantly less than seen in the majority of the Hils samples. In comparison, the ranges of phosphorus values obtained from each Little Birches sample are similar to those seen in the majority of the Hils glasses analysed.

It can be seen from Figure 8:16 and Figure 8:17 that the levels of manganese and sodium in the Little Birches glass samples are greater than observed in the majority of the Hils glasses. The majority of the glasses from the South site contain slightly lower concentrations of both elements. The Little Birches glasses contain lower concentrations (approximately 0.1Wt.% TiO_2 and 0.5Wt.% FeO) and smaller spreads of data for titanium (Figure 8:33) and iron (Figure 8:34) than the majority of the Hils glasses. The values for both these elements are similar for both the North and South Site Little Birches samples. The range of concentrations obtained from each analysis for all these elements do not appear to be linked to the extent of inhomogeneity observed in backscattered SEM imaging.

The chlorine (Figure 8:35) values for the Little Birches glasses are varied but for this element the range of values obtained for each analysis does appear to be greater for glasses that were deemed to be homogeneous using backscattered SEM imaging.

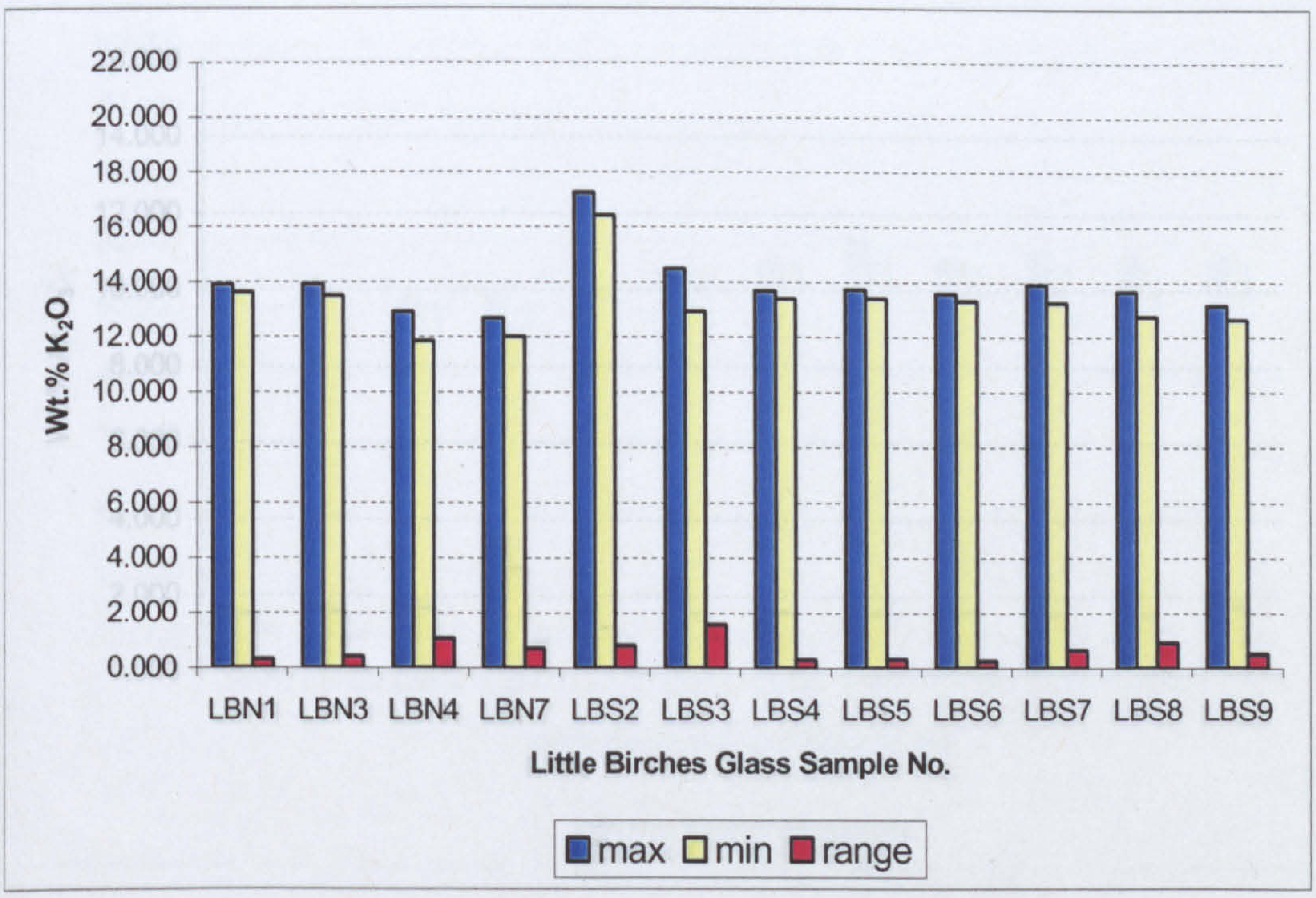


Figure 8:25 A comparison of the maximum, minimum and range of values obtained for K_2O for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

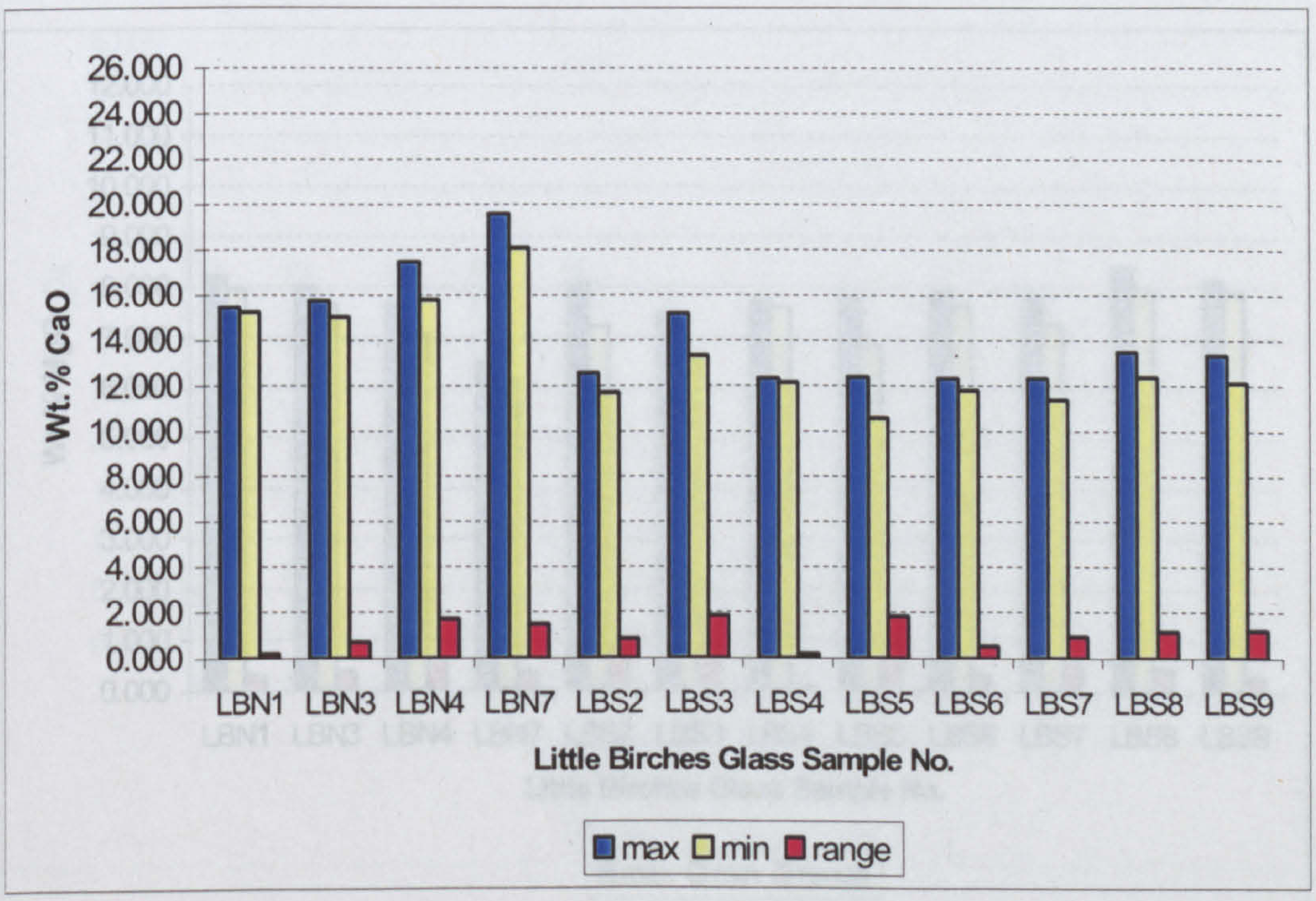


Figure 8:26 A comparison of the maximum, minimum and range of values obtained for CaO for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

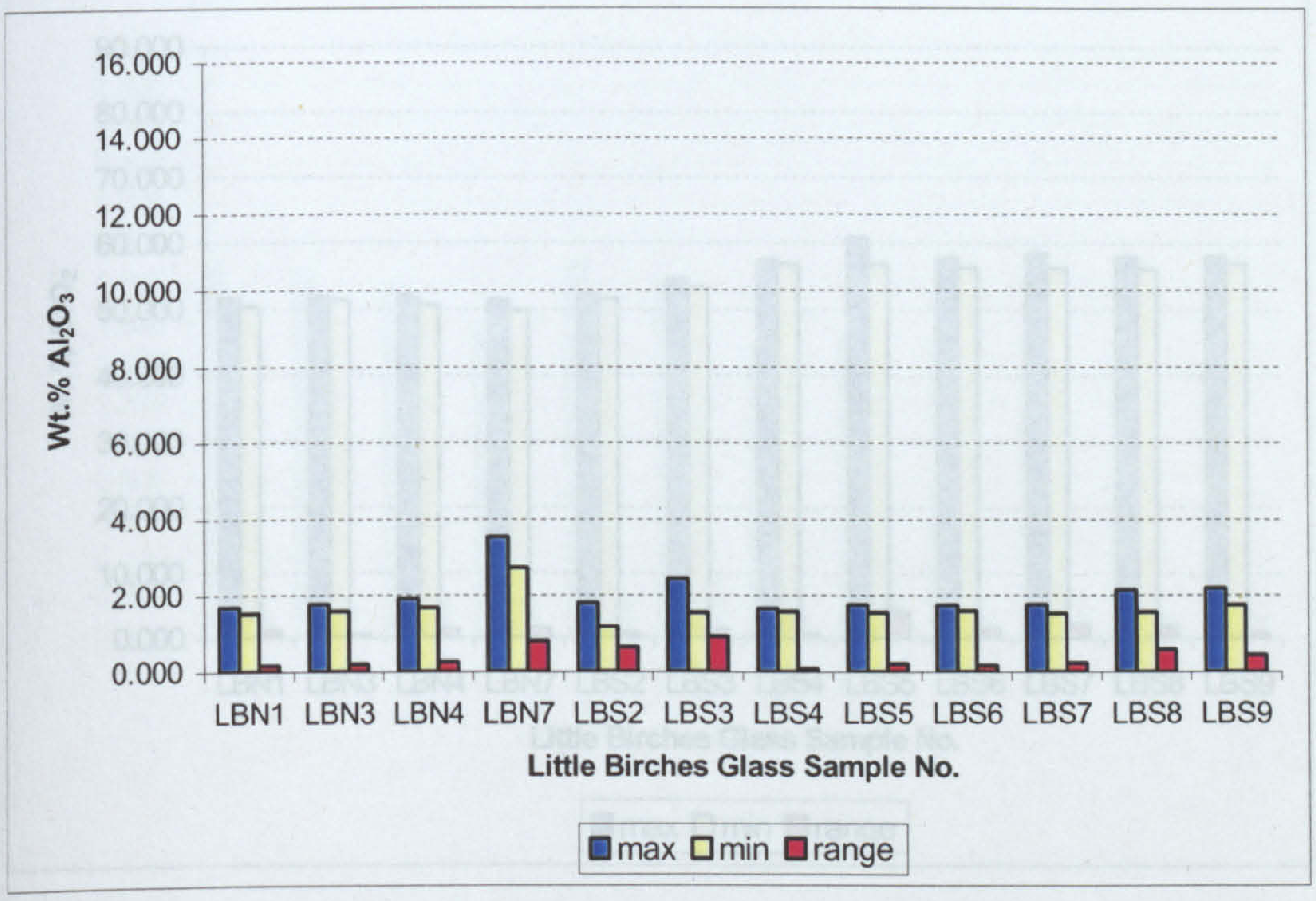


Figure 8:27 A comparison of the maximum, minimum and range of values obtained for Al_2O_3 for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

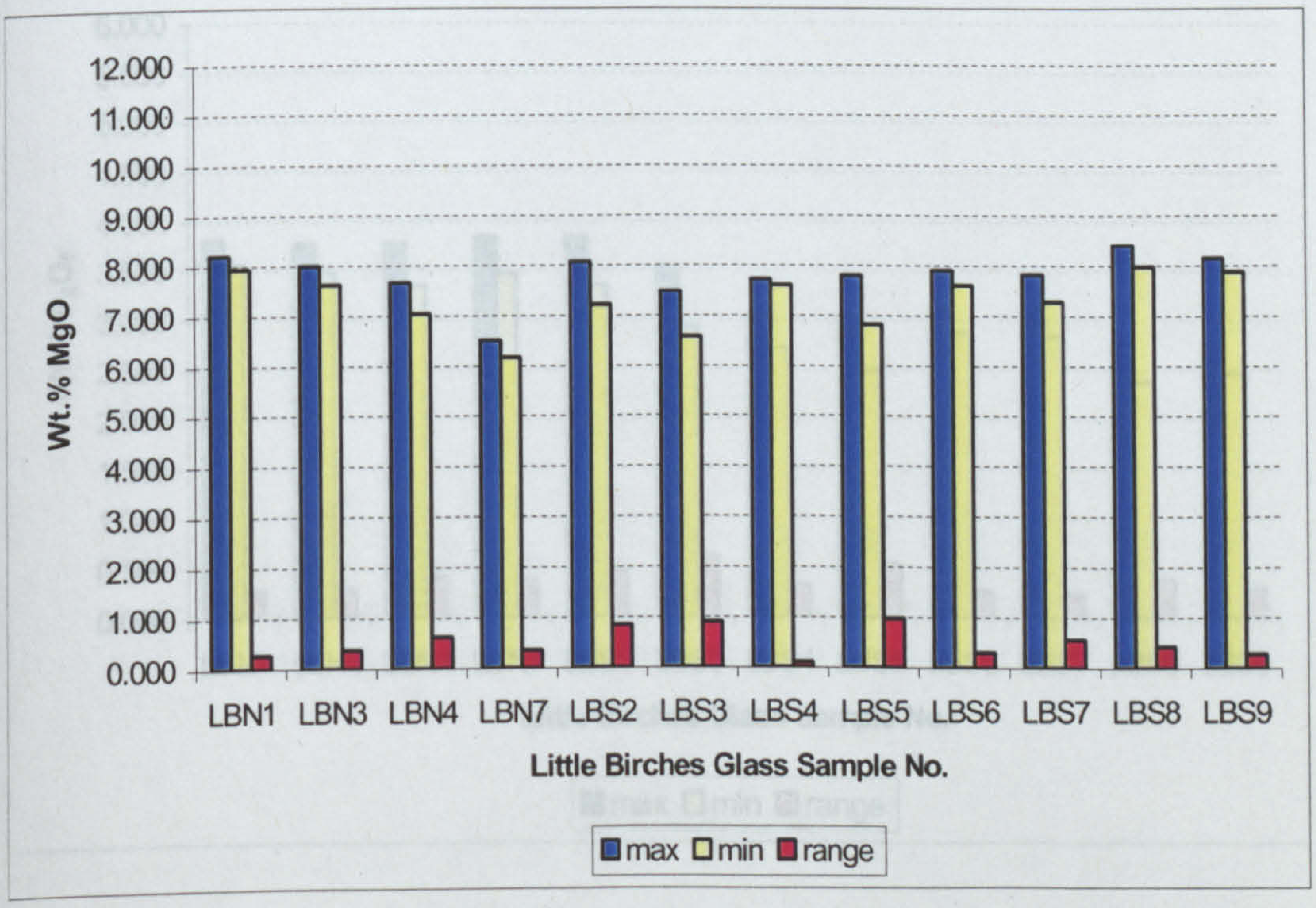


Figure 8:28 A comparison of the maximum, minimum and range of values obtained for MgO for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

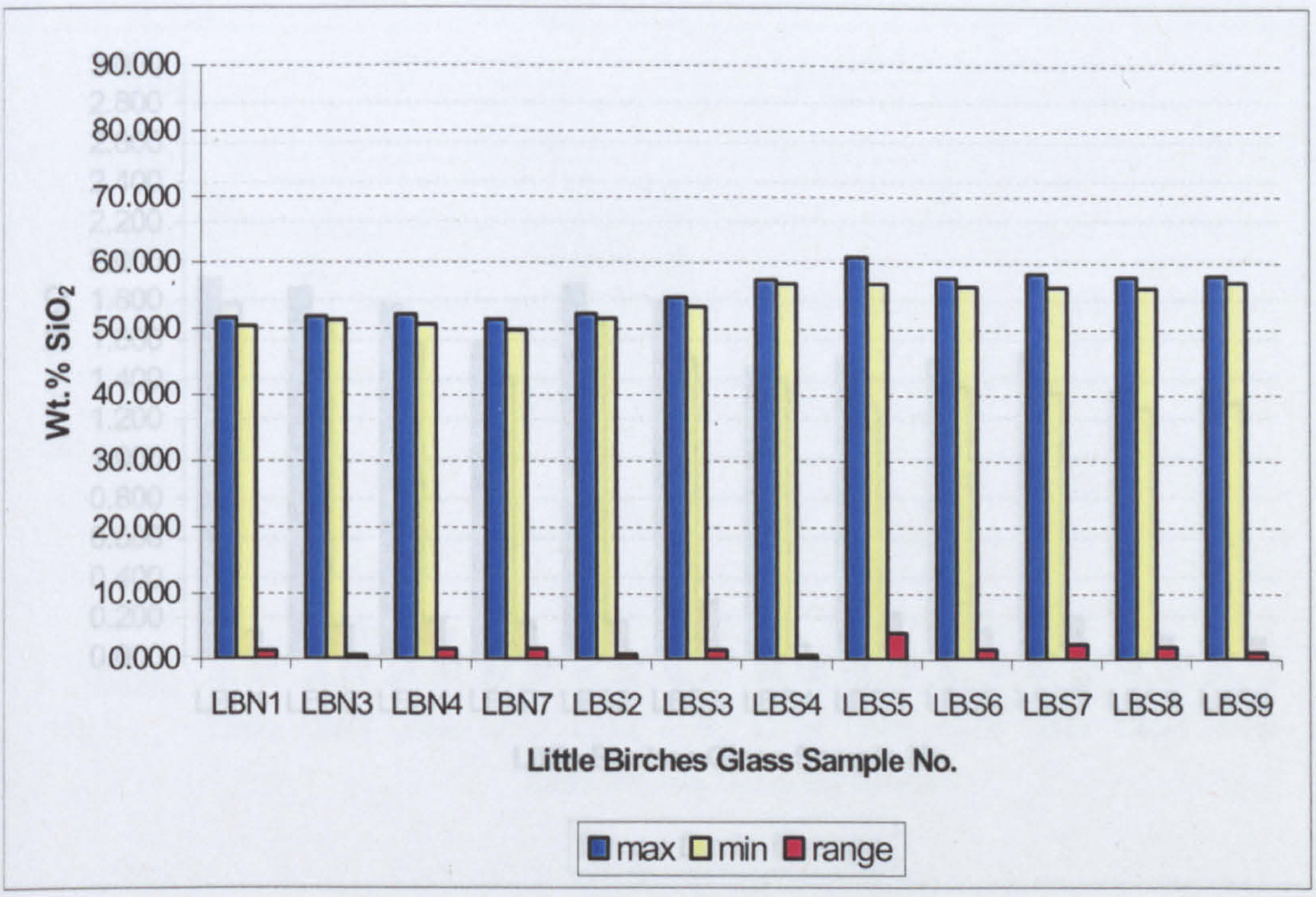


Figure 8:29 A comparison of the maximum, minimum and range of values obtained for SiO_2 for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

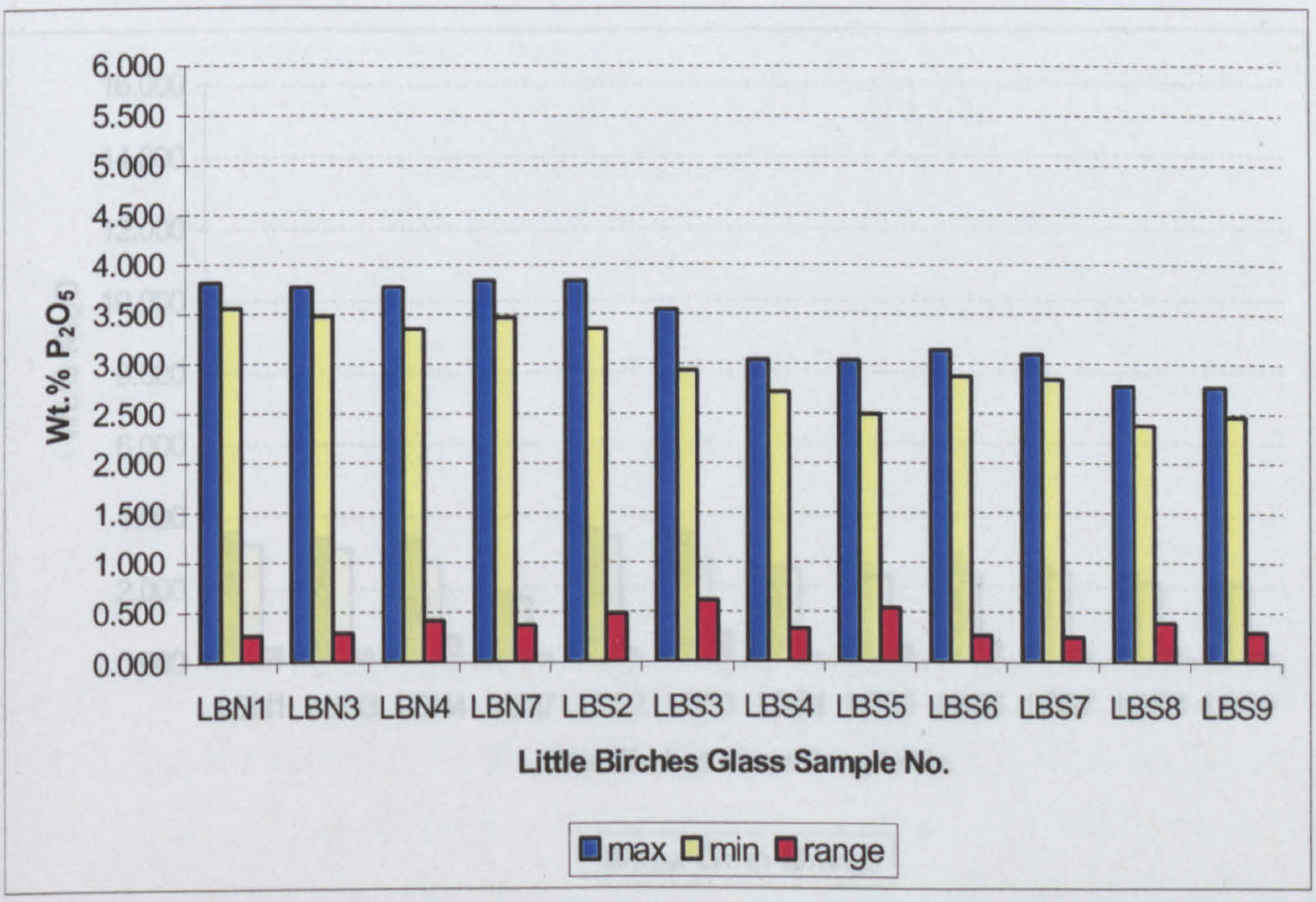


Figure 8:30 A comparison of the maximum, minimum and range of values obtained for P_2O_5 for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

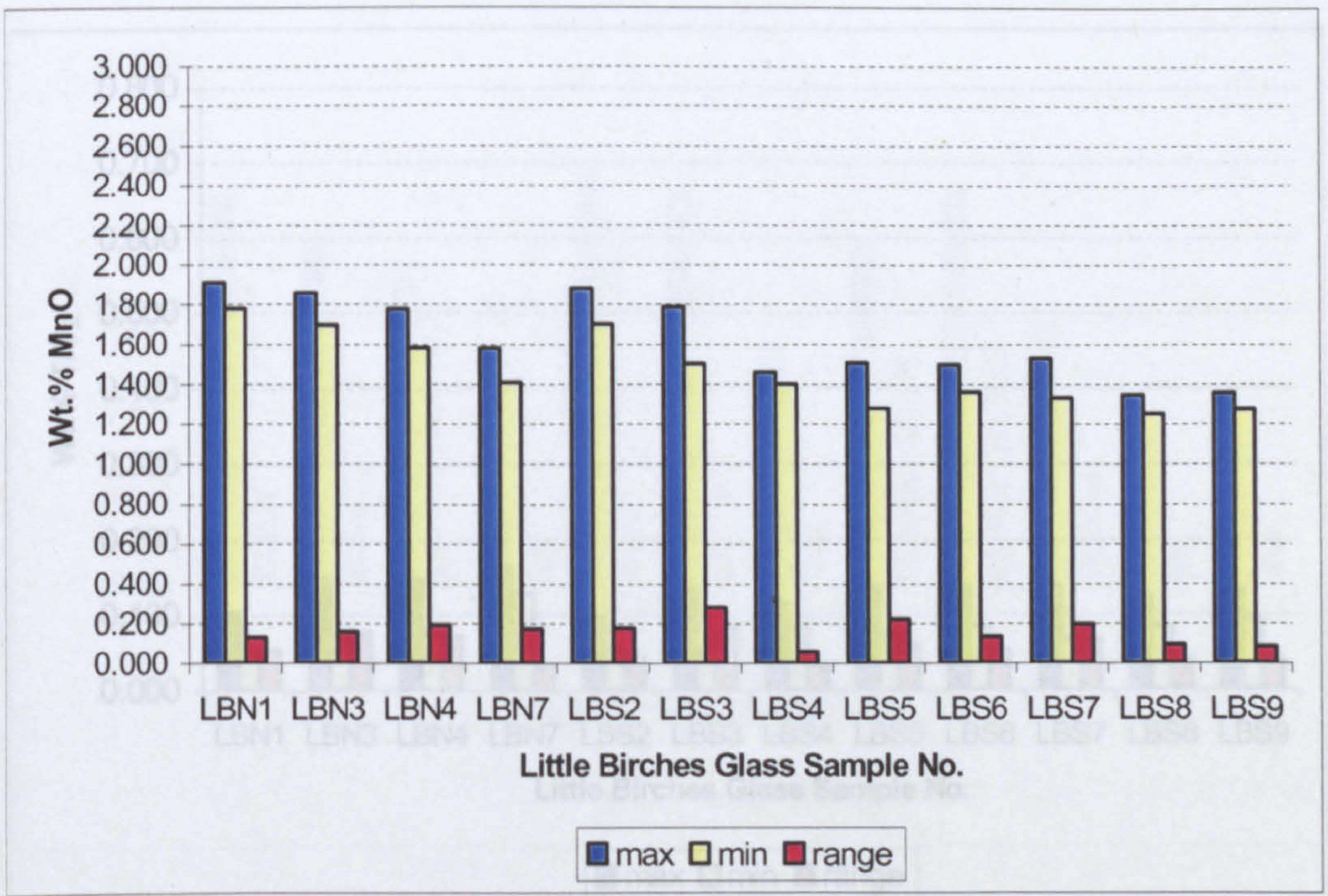


Figure 8:31 A comparison of the maximum, minimum and range of values obtained for MnO for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

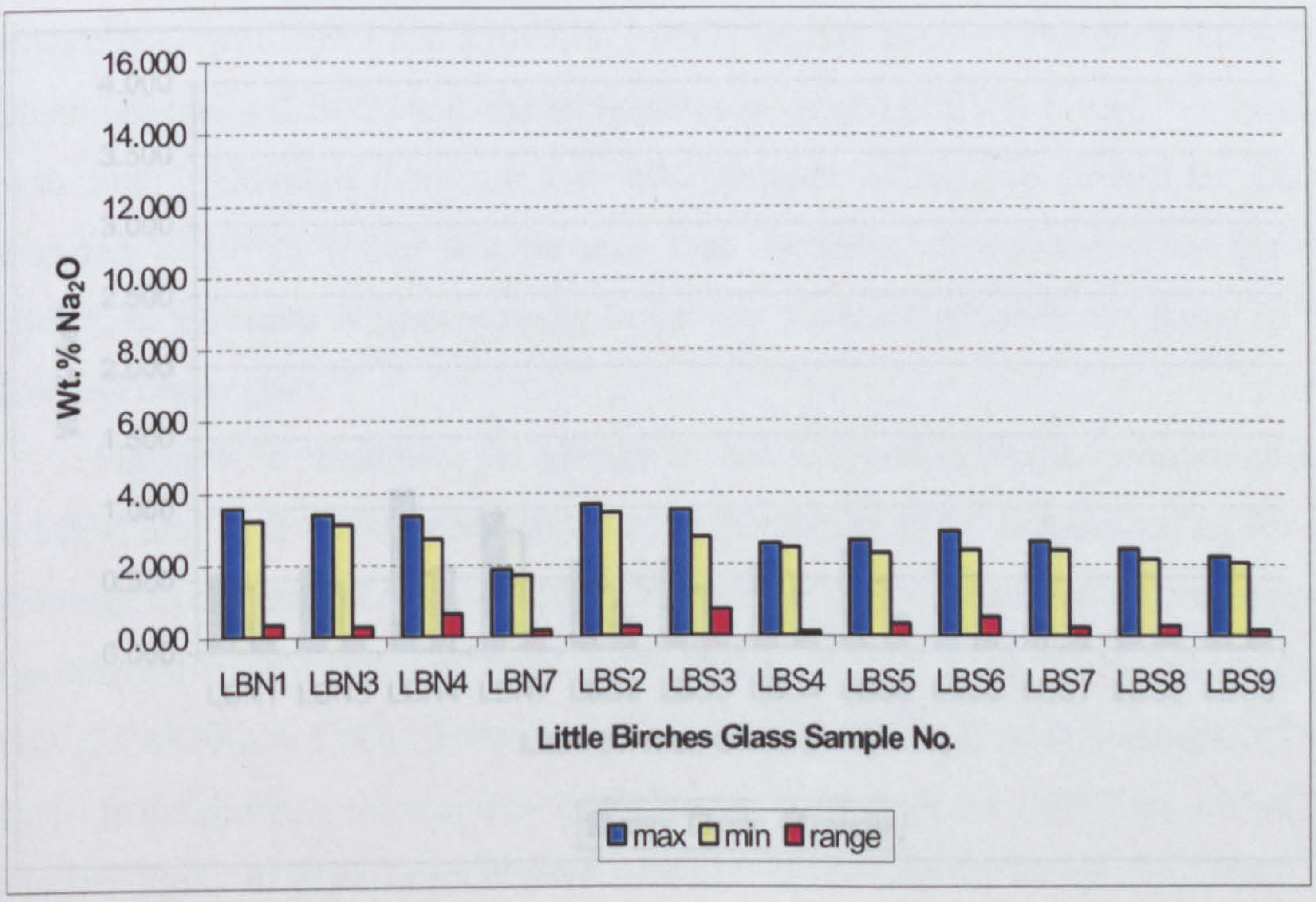


Figure 8:32 A comparison of the maximum, minimum and range of values obtained for Na_2O for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

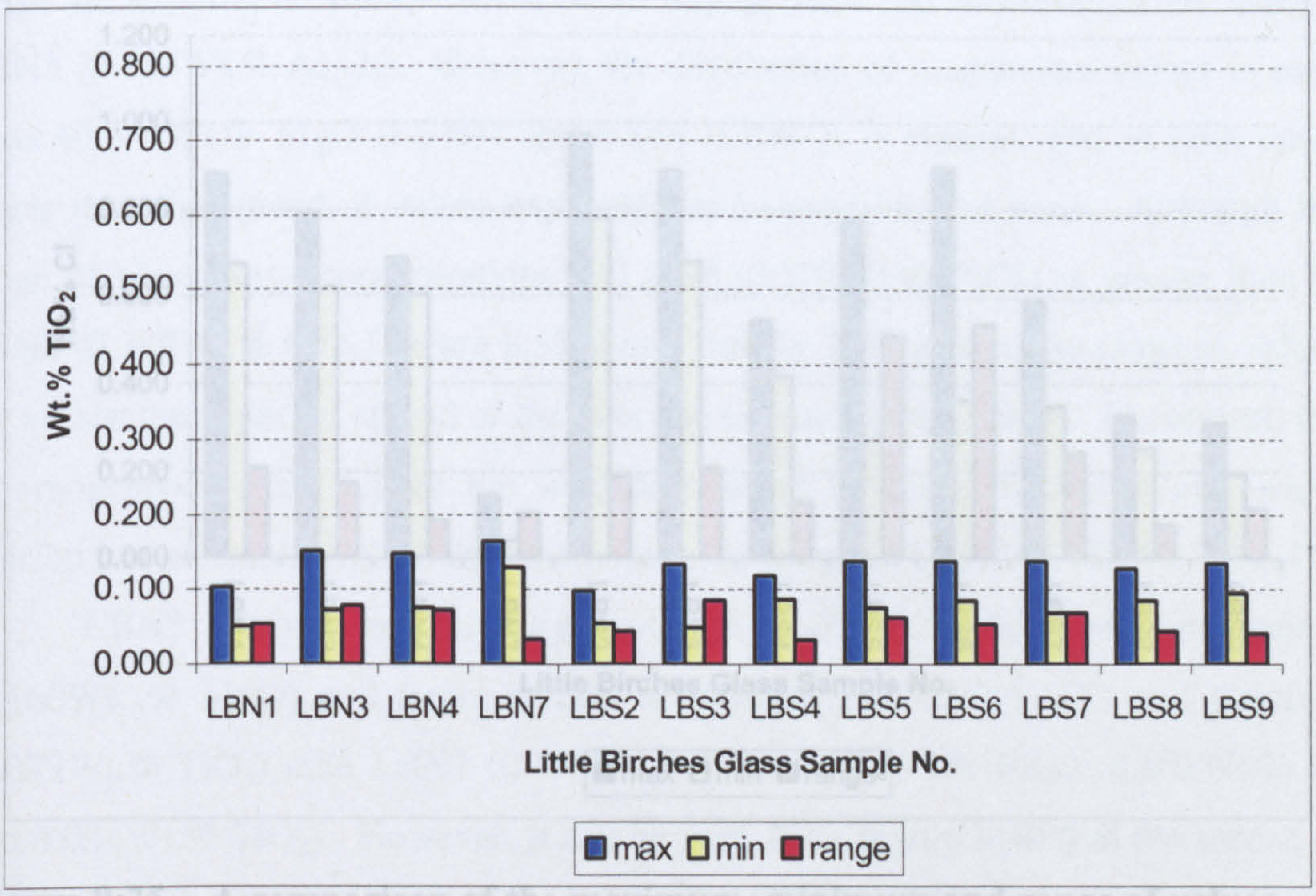


Figure 8:33 **A comparison of the maximum, minimum and range of values obtained for TiO_2 for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)**

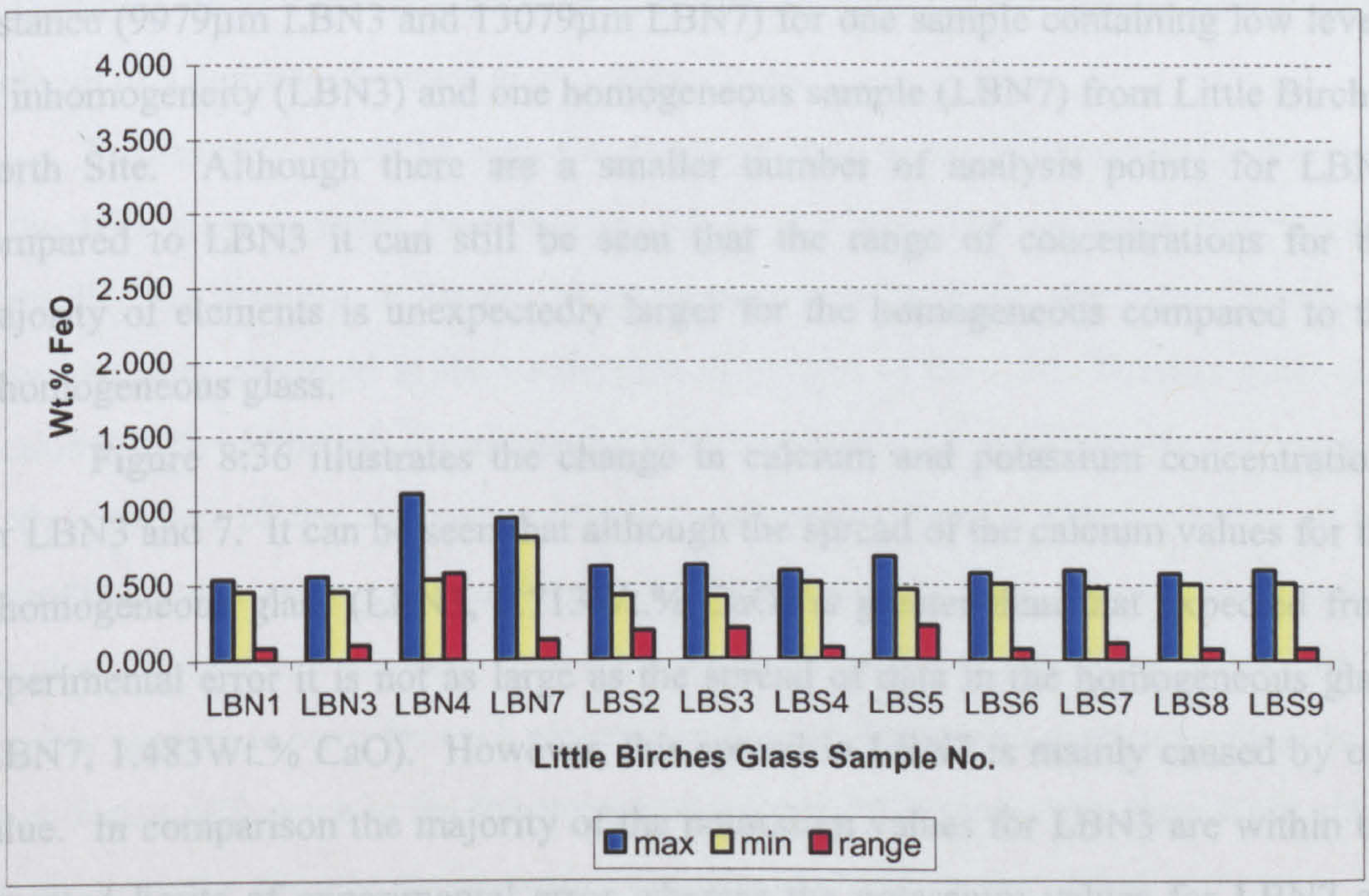


Figure 8:34 **A comparison of the maximum, minimum and range of values obtained for FeO for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)**

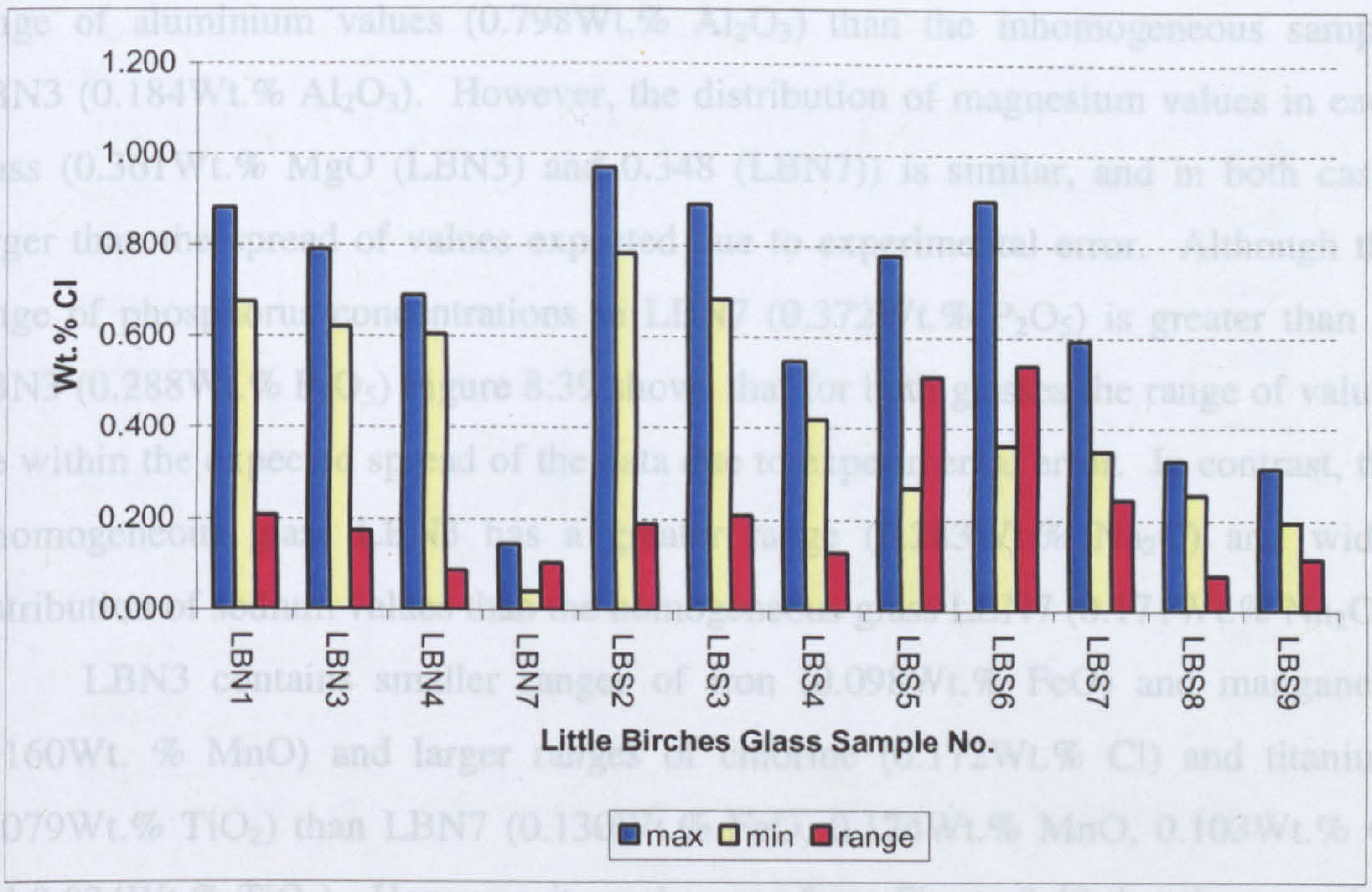


Figure 8:35 A comparison of the maximum, minimum and range of values obtained for Cl for Little Birches glass samples using EPMA (Table VIII:29-Table VIII:40)

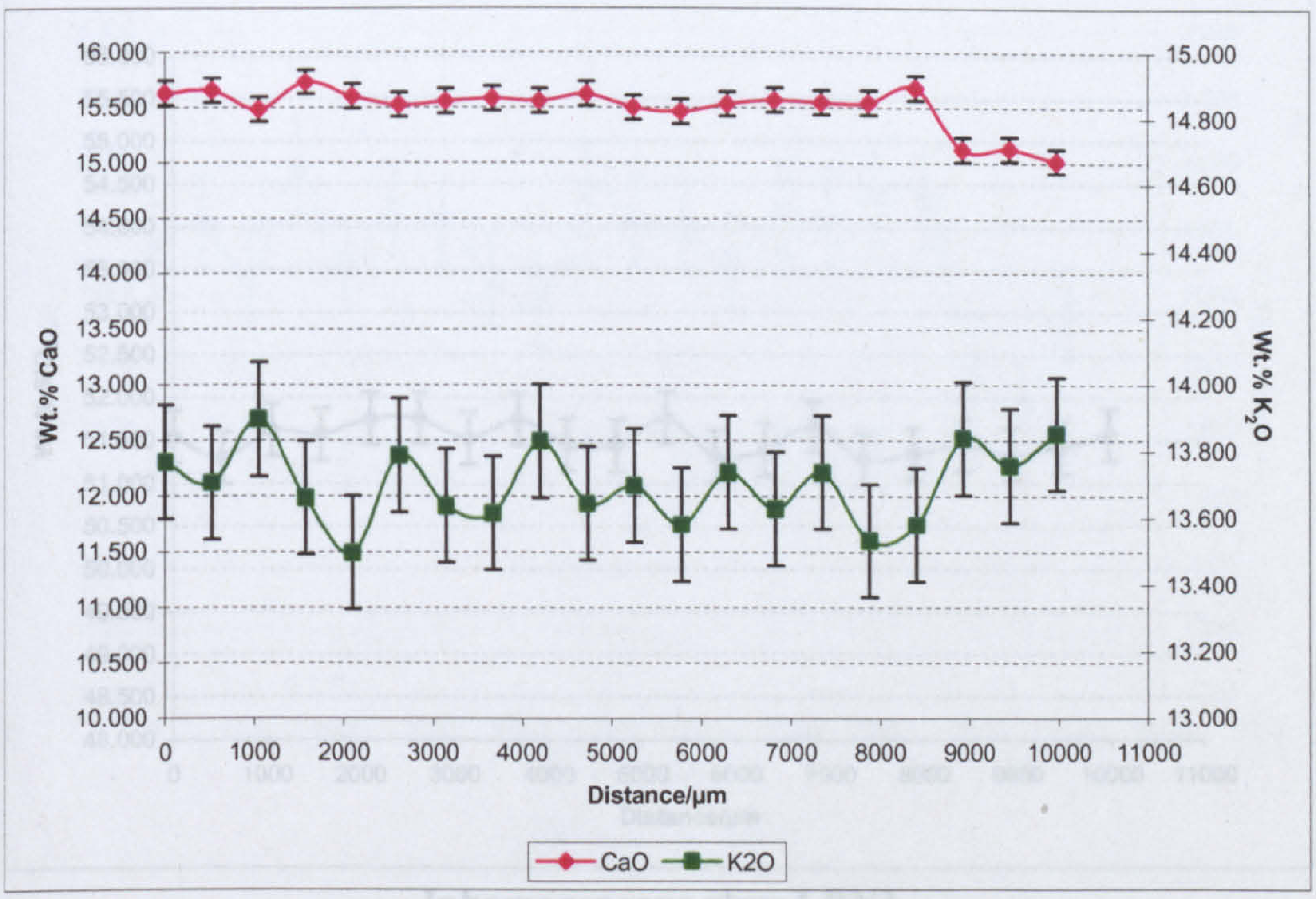
Figure 8:36-Figure 8:39 illustrate the change in elemental composition over distance (9979µm LBN3 and 13079µm LBN7) for one sample containing low levels of inhomogeneity (LBN3) and one homogeneous sample (LBN7) from Little Birches North Site. Although there are a smaller number of analysis points for LBN7 compared to LBN3 it can still be seen that the range of concentrations for the majority of elements is unexpectedly larger for the homogeneous compared to the inhomogeneous glass.

Figure 8:36 illustrates the change in calcium and potassium concentrations for LBN3 and 7. It can be seen that although the spread of the calcium values for the inhomogeneous glass (LBN3, 0.713Wt.% CaO) is greater than that expected from experimental error it is not as large as the spread of data in the homogeneous glass (LBN7, 1.483Wt.% CaO). However, this spread in LBN7 is mainly caused by one value. In comparison the majority of the potassium values for LBN3 are within the expected limits of experimental error whereas the potassium values for LBN7 are not. This is also seen in the comparison of the distribution of silica values for each glass sample (Figure 8:37).

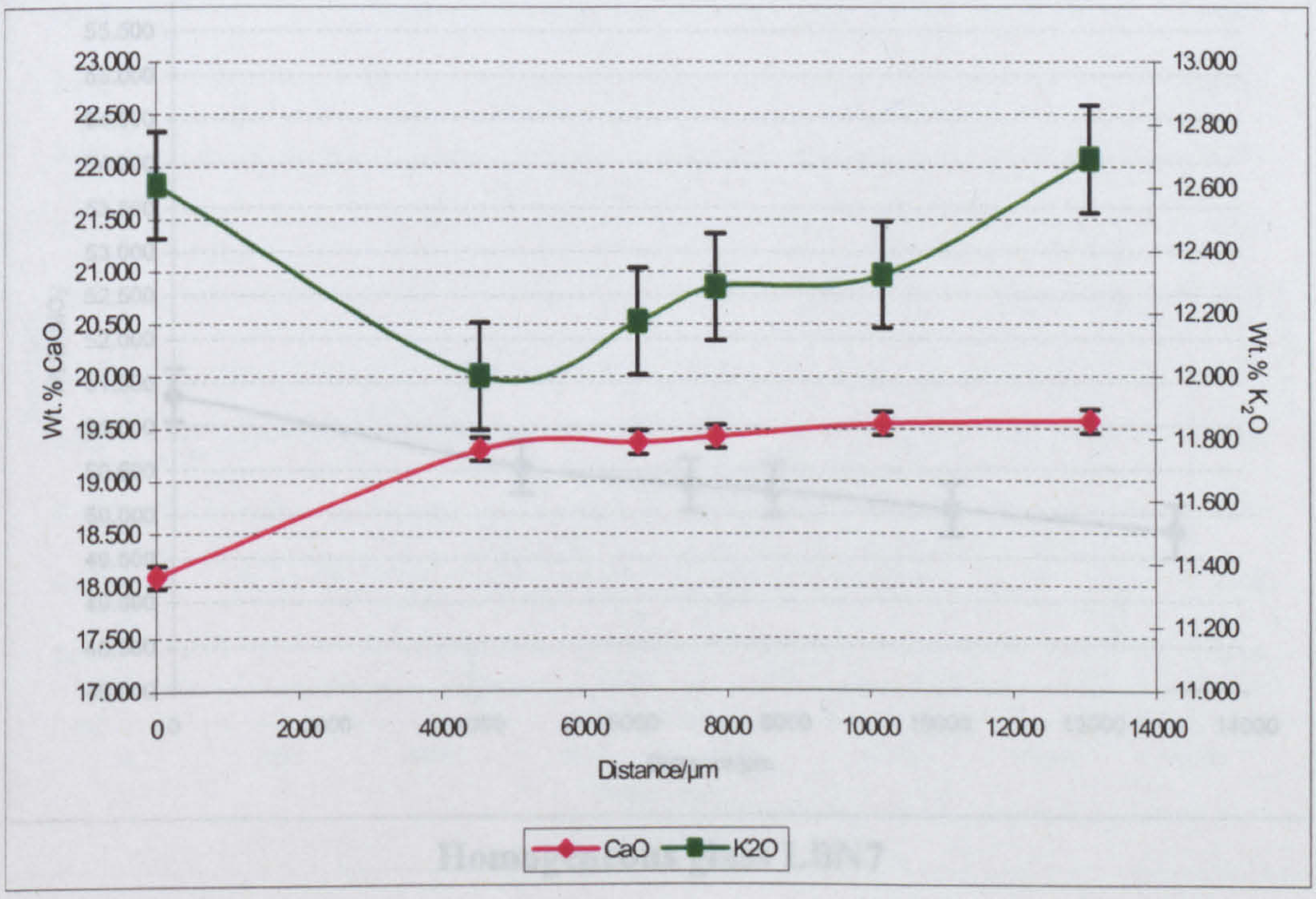
Figure 8:38 illustrates that the homogeneous sample LBN7 contains a wider range of aluminium values (0.798Wt.% Al_2O_3) than the inhomogeneous sample LBN3 (0.184Wt.% Al_2O_3). However, the distribution of magnesium values in each glass (0.361Wt.% MgO (LBN3) and 0.348 (LBN7)) is similar, and in both cases larger than the spread of values expected due to experimental error. Although the range of phosphorus concentrations in LBN7 (0.372Wt.% P_2O_5) is greater than in LBN3 (0.288Wt.% P_2O_5) Figure 8:39 shows that for both glasses the range of values are within the expected spread of the data due to experimental error. In contrast, the inhomogeneous glass LBN3 has a greater range (0.283Wt.% Na_2O) and wider distribution of sodium values than the homogeneous glass LBN7 (0.171Wt.% Na_2O).

LBN3 contains smaller ranges of iron (0.098Wt.% FeO) and manganese (0.160Wt. % MnO) and larger ranges of chlorine (0.172Wt.% Cl) and titanium (0.079Wt.% TiO_2) than LBN7 (0.130Wt.% FeO, 0.174Wt.% MnO, 0.103Wt.% Cl and 0.034Wt.% TiO_2). However, it can be seen from Figure 8:40 that the spread of manganese, iron and chlorine concentrations for LBN3 and LBN7 are slightly greater than any spread due to experimental error in the samples. The values of titanium for both glasses are within the spread due to error expected from the analyses. Although it is difficult to determine any distinct elemental relationships in LBN3 and 7, it can be seen that, as in the Hils glass G13 (see Section 8.3.1), these glasses appear to be made up of a number of varied glass compositions.

In summary, it can be seen that in comparison to the inhomogeneity observed in the Hils glass samples (see Section 8.3.1), the elemental variation within each Little Birches sample is small. This corresponds well to the lower levels of inhomogeneity observed in the backscattered images of the Little Birches glass (see Section 8.2.2). Although the elemental ranges obtained for each sample will depend on the position of the analysis points, it is important to note that a number of the **homogeneous** glasses contain **larger** elemental ranges than the inhomogeneous samples. However, it has been seen from the descriptions of LBN3 and LBN7 above that this appears to vary for each element analysed. There also does not appear to be a significant difference in the inhomogeneity observed between the glass from either site although the average concentrations of certain elements are varied.

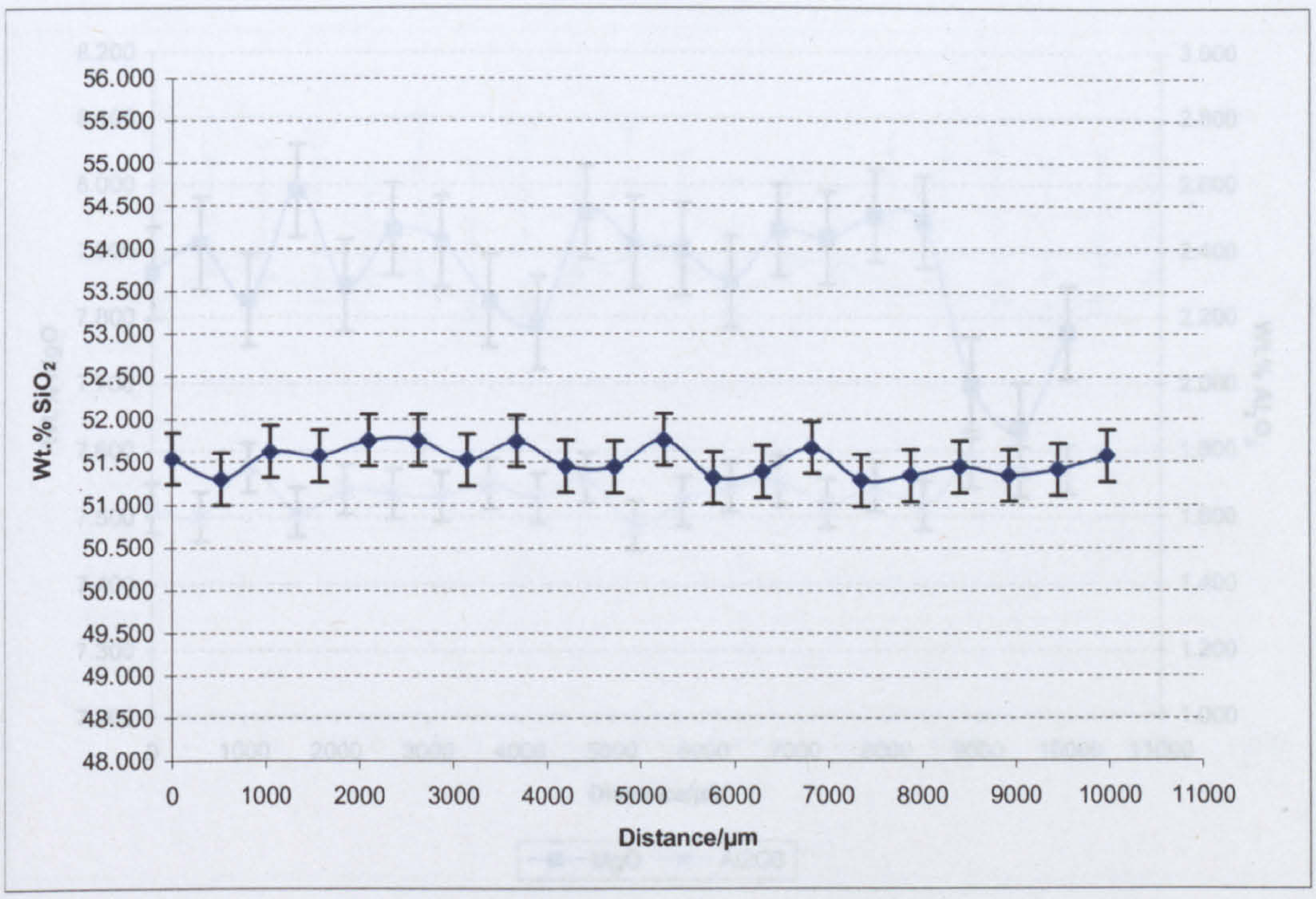


Inhomogeneous glass LBN3

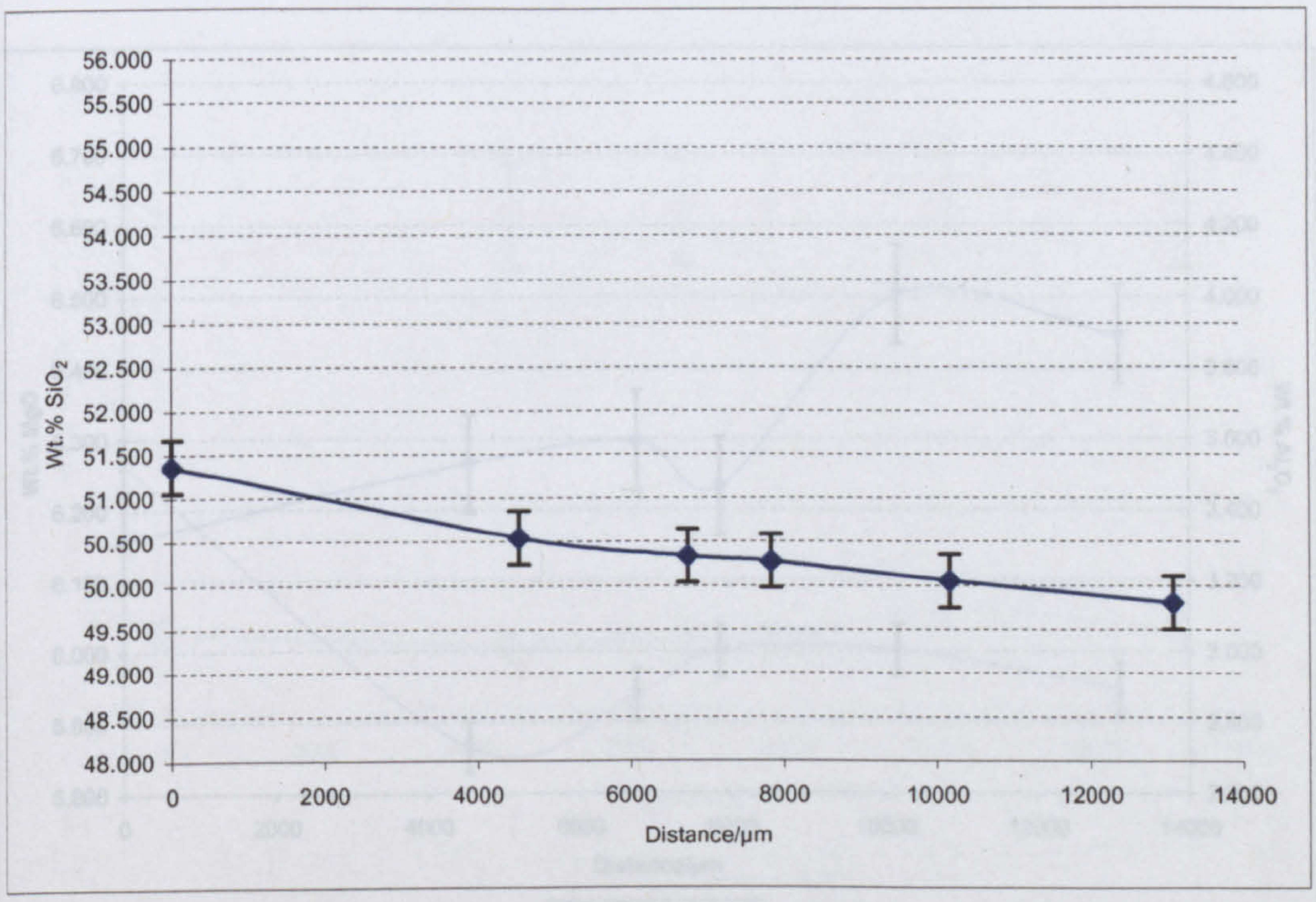


Homogeneous glass LBN7

Figure 8:36 Graph of EPMA line scan data illustrating the change in CaO and K_2O concentrations over distance for North Site inhomogeneous glass sample LBN3 (Table VIII:30) and homogeneous glass sample LBN7 (Table VIII:32)

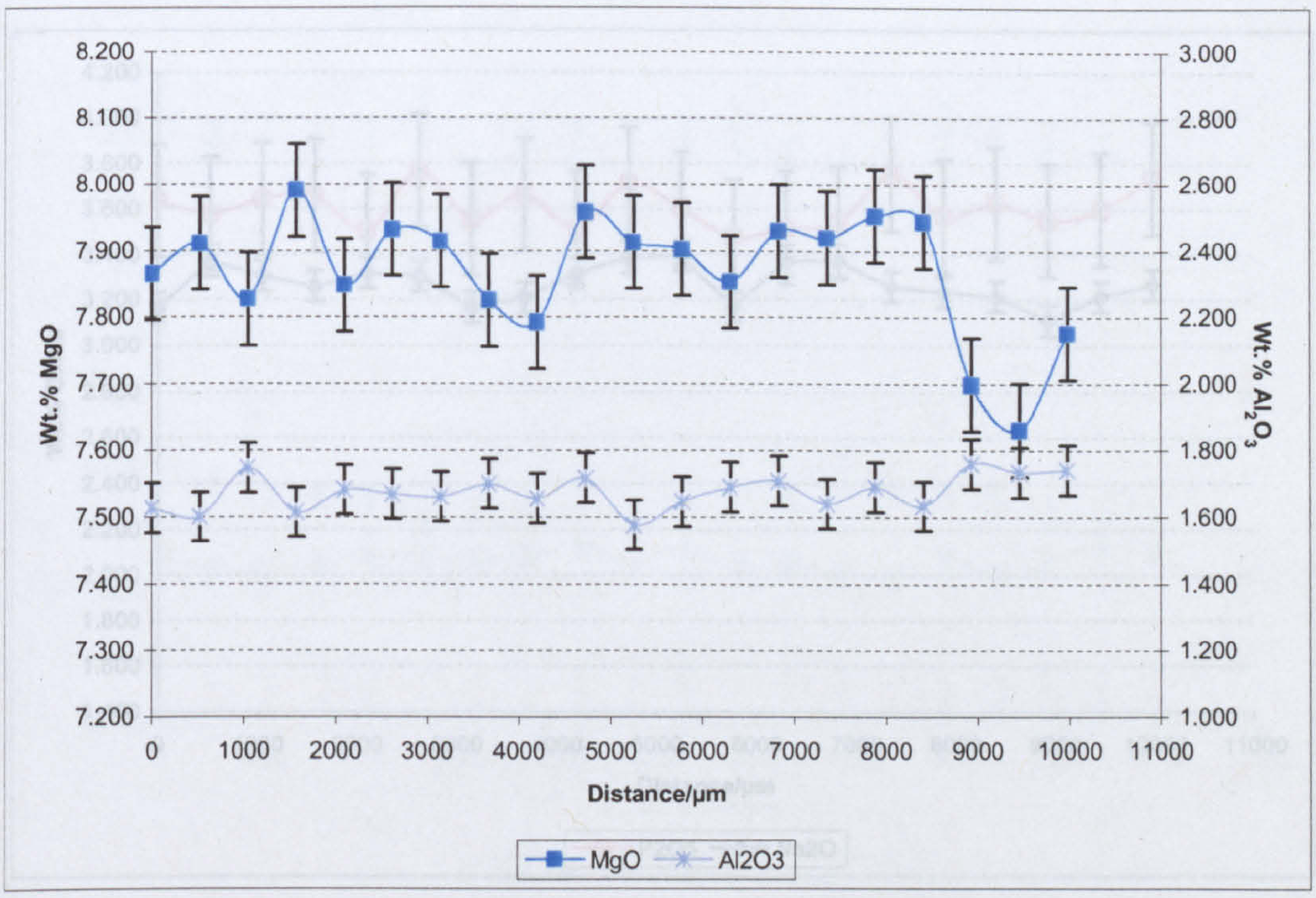


Inhomogeneous glass LBN3

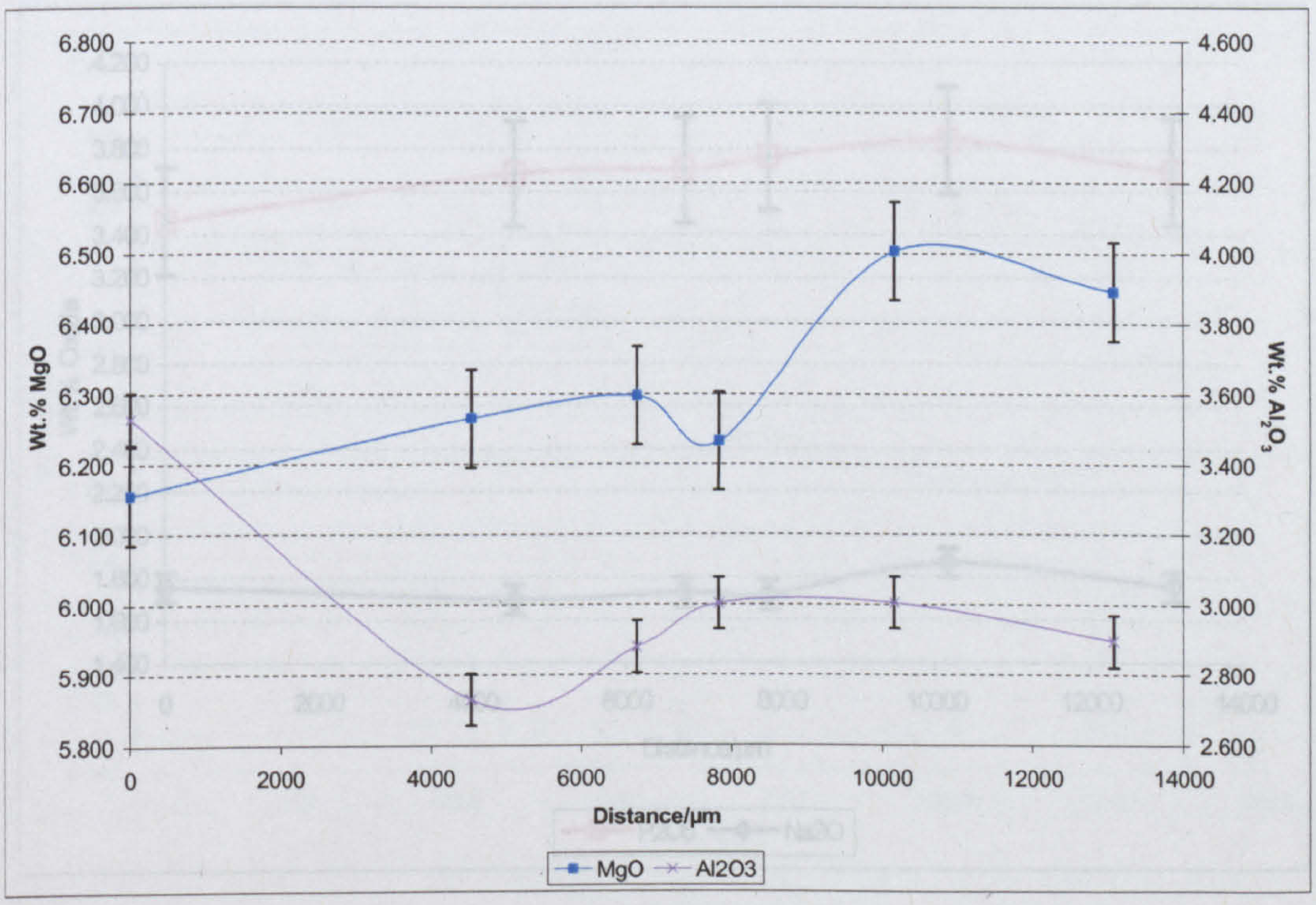


Homogeneous glass LBN7

Figure 8:37 **Graph of EPMA line scan data illustrating the change in SiO_2 concentrations over distance for North Site glass sample LBN3 (Table VIII:30) and homogeneous glass sample LBN7 (Table VIII:32)**

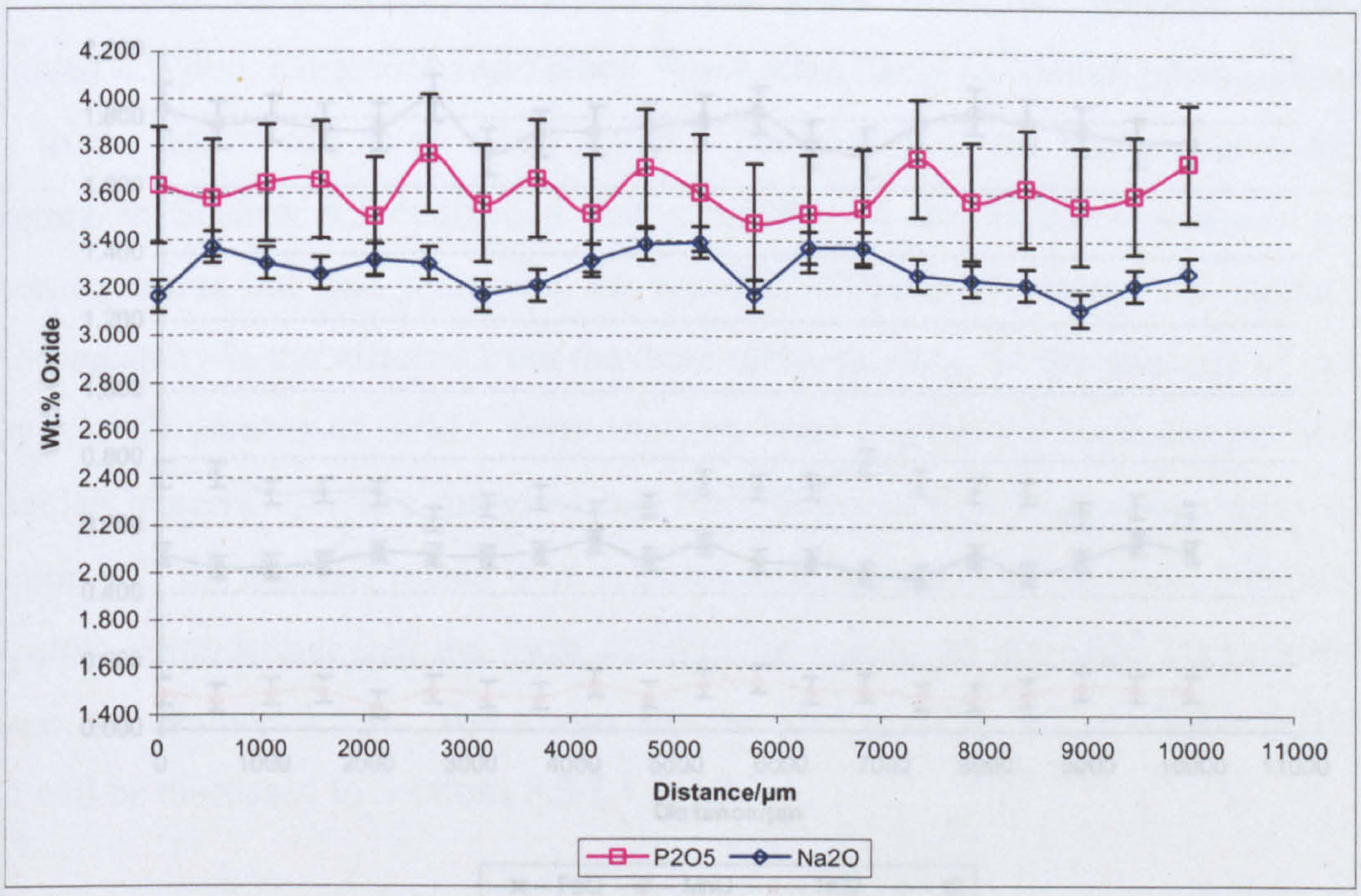


Inhomogeneous glass sample LBN3

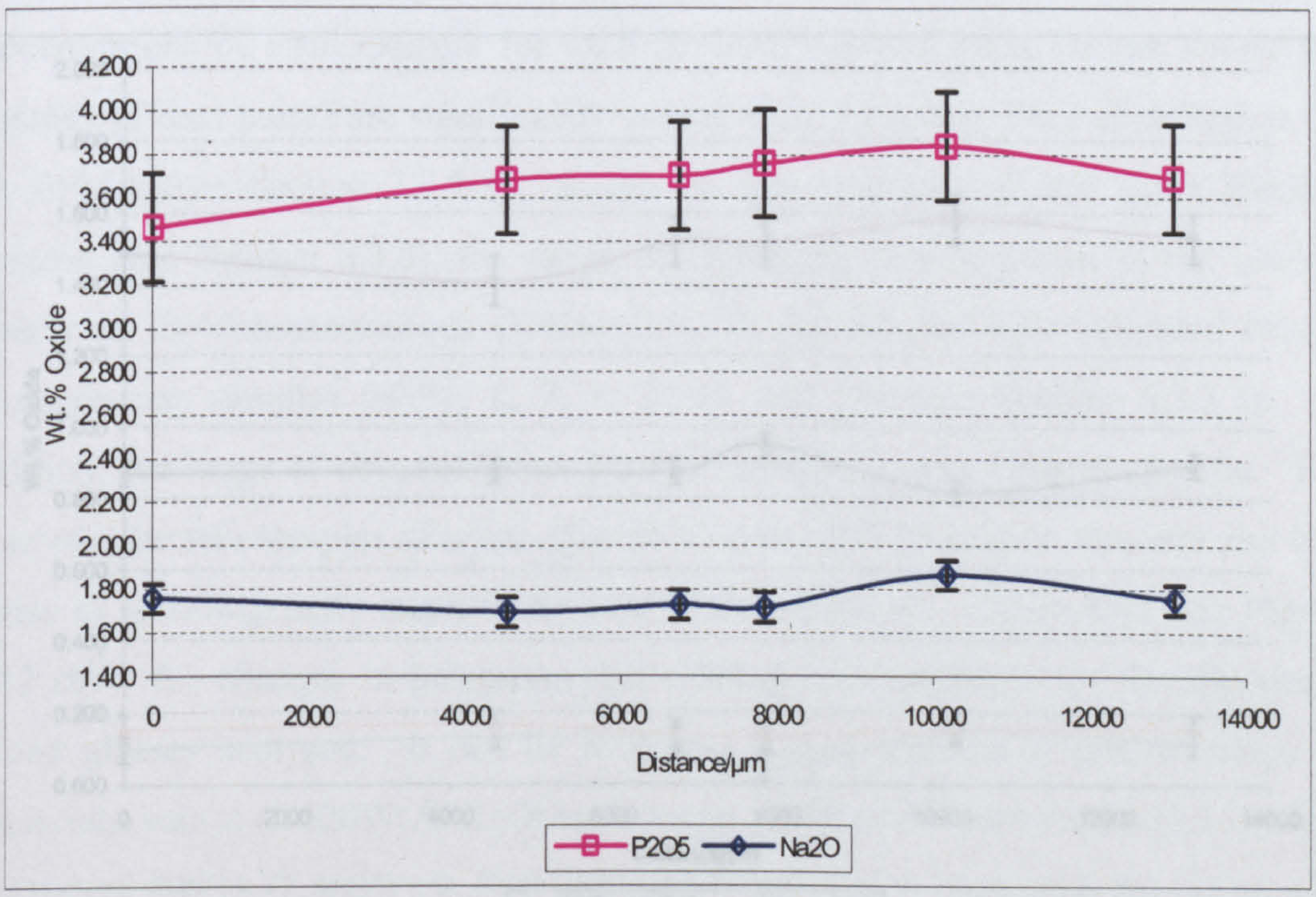


Homogeneous glass sample LBN7

Figure 8:38 **Graph of EPMA line scan data illustrating the change in MgO and Al_2O_3 concentrations over distance for North Site glass sample LBN3 (Table VIII:30) and homogeneous glass sample LBN7 (Table VIII:32)**

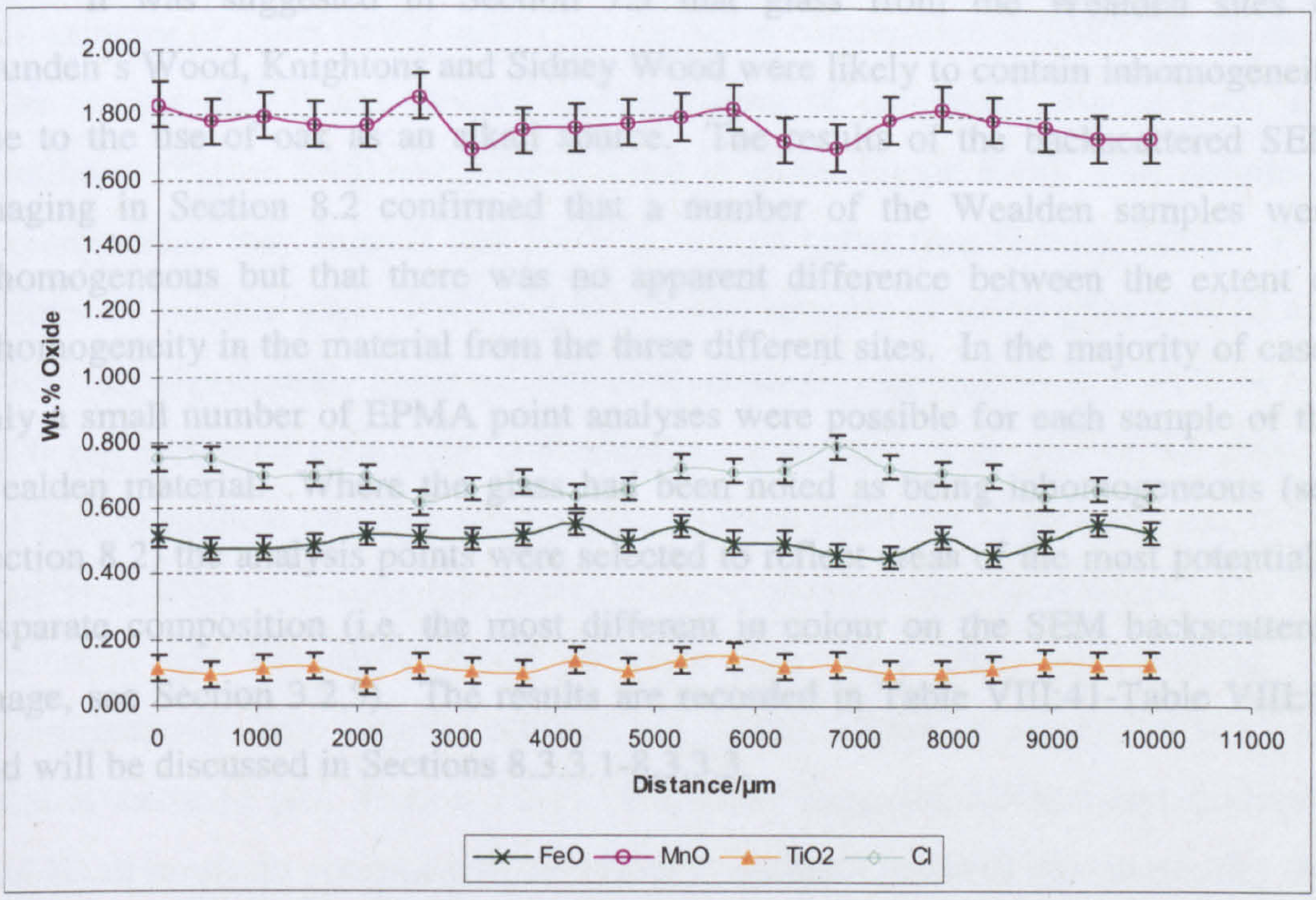


Inhomogeneous glass sample LBN3

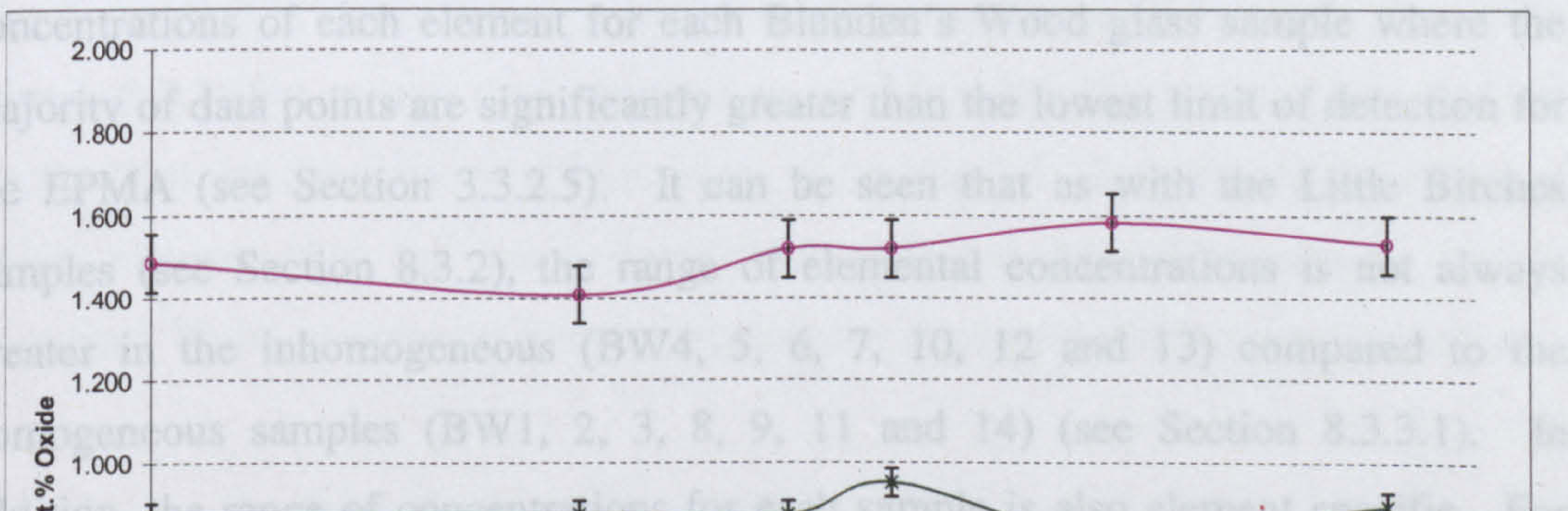


Homogeneous glass sample LBN7

Figure 8:39 Graph of EPMA line scan data illustrating the change in Na_2O and P_2O_5 concentrations over distance for North Site glass sample LBN3 (Table VIII:30) homogeneous glass sample LBN7 (Table VIII:32)



Inhomogeneous glass sample LBN3



Homogeneous glass sample LBN7

Figure 8:40 Graph of EPMA line scan data illustrating the change in MnO, FeO, TiO_2 and Cl concentrations over distance for North Site glass sample LBN3 (Table VIII:30) homogeneous glass sample LBN7 (Table VIII:32)

8.3.3 Wealden Glasses

It was suggested in Section 7.5 that glass from the Wealden sites of Blunden's Wood, Knightons and Sidney Wood were likely to contain inhomogeneity due to the use of oak as an alkali source. The results of the backscattered SEM imaging in Section 8.2 confirmed that a number of the Wealden samples were inhomogeneous but that there was no apparent difference between the extent of inhomogeneity in the material from the three different sites. In the majority of cases only a small number of EPMA point analyses were possible for each sample of the Wealden material. Where the glass had been noted as being inhomogeneous (see Section 8.2) the analysis points were selected to reflect areas of the most potentially disparate composition (i.e. the most different in colour on the SEM backscattered image, see Section 3.2.5). The results are recorded in Table VIII:41-Table VIII:81 and will be discussed in Sections 8.3.3.1-8.3.3.3.

8.3.3.1 Blunden's Wood

Figure 8:41-Figure 8:50 illustrate the maximum, minimum and range of concentrations of each element for each Blunden's Wood glass sample where the majority of data points are significantly greater than the lowest limit of detection for the EPMA (see Section 3.3.2.5). It can be seen that as with the Little Birches samples (see Section 8.3.2), the range of elemental concentrations is not always greater in the inhomogeneous (BW4, 5, 6, 7, 10, 12 and 13) compared to the homogeneous samples (BW1, 2, 3, 8, 9, 11 and 14) (see Section 8.3.3.1). In addition, the range of concentrations for each sample is also element specific. For example, the two samples of waste glass BW12 and BW13 contain medium and low levels of inhomogeneity respectively (see Section 8.2.1.1). Figure 8:41 and Figure 8:42 show the changes in potassium and calcium concentrations for the Blunden's Wood glasses analysed. It can be seen that BW12 contains a smaller range of potassium values (1.620Wt.% K_2O) but a larger range of calcium values (3.151Wt.% CaO) than BW13 (2.608Wt.% K_2O and 1.026Wt.% CaO). Although the position of the analysis points will affect the range of values obtained, it can be seen that it is also difficult to relate the extent of inhomogeneity viewed under the SEM to the differences observed in the analytical data.

The composition of the vessel glass (BW1) corresponds well with the published analyses of comparative Blunden's Wood material (see Section 7.2.1). Two samples of cullet (BW2 and 4) are similar in composition to BW1 but the third cullet sample (BW3) has elevated concentrations of potassium (Figure 8:42) and phosphorus (Figure 8:46) and reduced levels of silica (Figure 8:45). This difference in composition may suggest that BW3 is foreign cullet (see Section 2.2.5). Two samples of crucible glass (BW7 and 8) and two samples of waste glass (BW12 and 13) contain significantly lower calcium concentrations (approximately 5Wt.% or less CaO) and increased aluminium concentrations compared to the rest of the glasses. The change in these two elements suggests that the difference is probably due to the analysis of areas containing refractory corrosion products (see Section 2.4.5.1). The data from the Blunden's Wood material does show that, as expected, the inhomogeneous waste material contains the greatest elemental ranges out of all the material analysed (see Section 7.2.1). However, increased calcium and decreased total alkali levels do not appear to be related to different levels of inhomogeneity (see Section 2.2.2.1).

The range of elemental compositions observed in each of the Blunden's Wood samples is predominantly less than those measured in the Hils glass (see Section 8.3.1) but greater than observed in the Little Birches material (see Section 8.3.2). This confirms the prediction made in Section 7.5. It is difficult to ascertain which elements are the most significantly affected by inhomogeneity in the Blunden's Wood samples, as it would appear that in general this is sample specific.

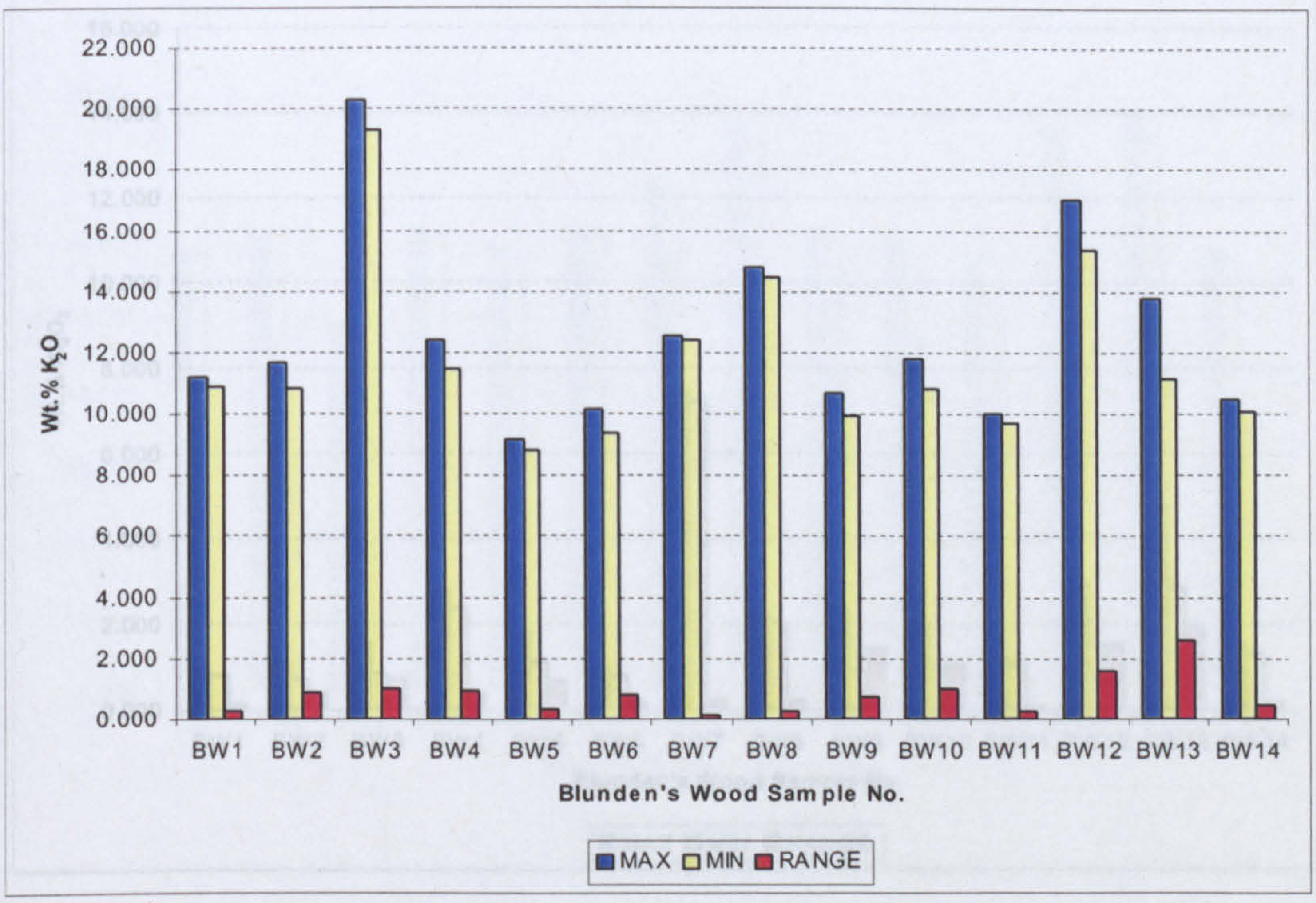


Figure 8:41 A comparison of the maximum, minimum and range of values obtained for K_2O for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

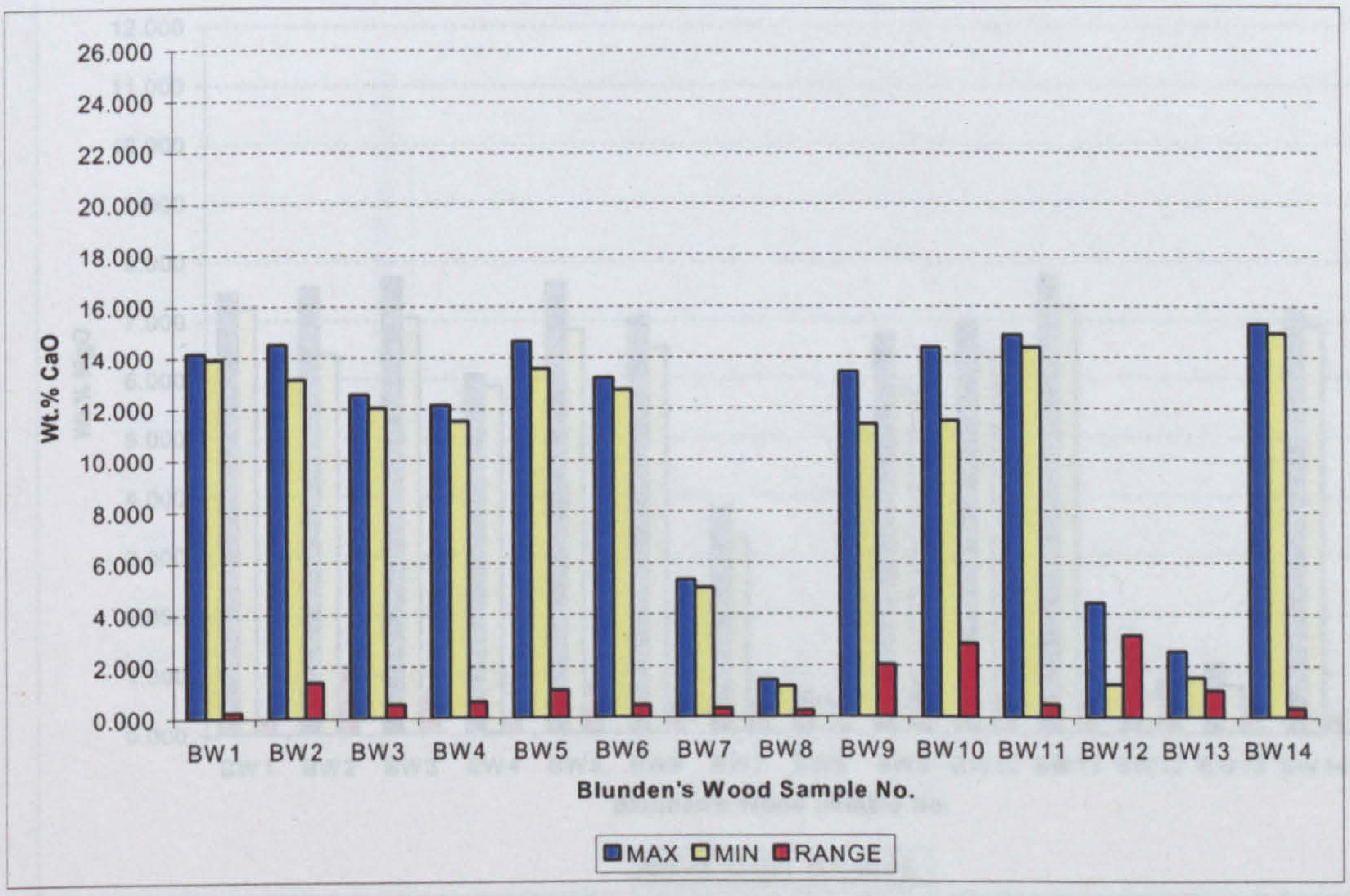


Figure 8:42 A comparison of the maximum, minimum and range of values obtained for CaO for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

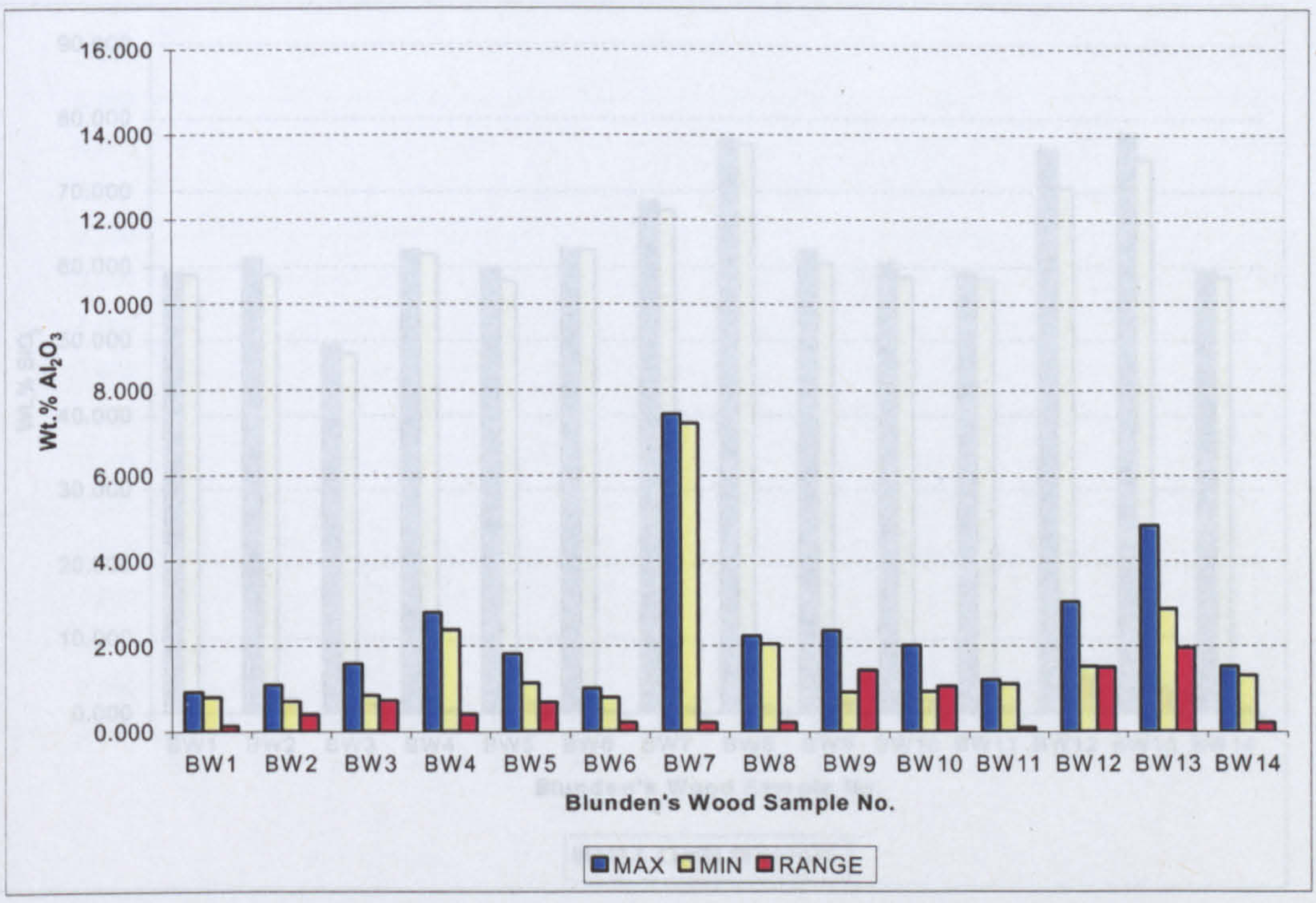


Figure 8:43 **A comparison of the maximum, minimum and range of values obtained for Al_2O_3 for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)**

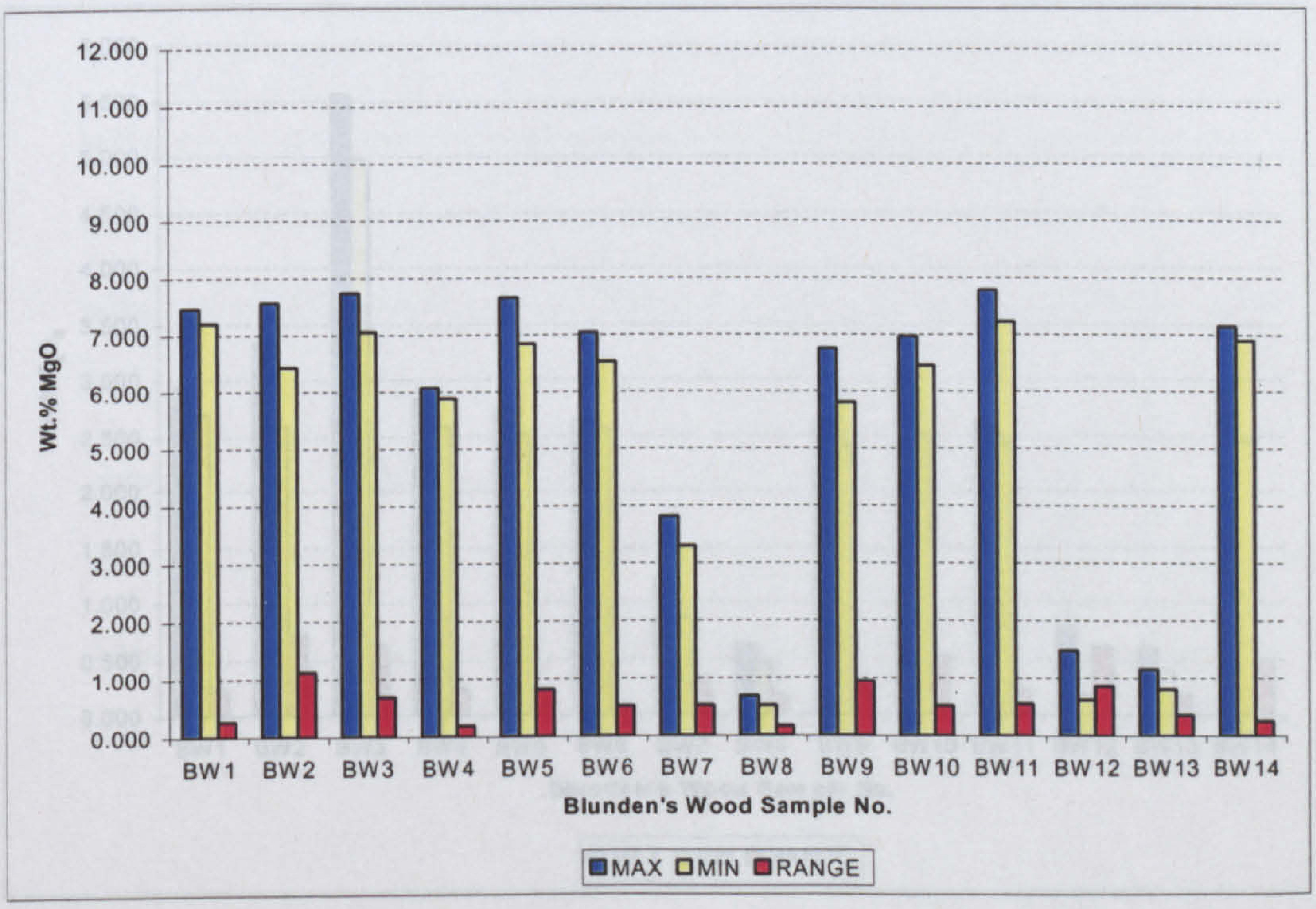


Figure 8:44 **A comparison of the maximum, minimum and range of values obtained for MgO for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)**

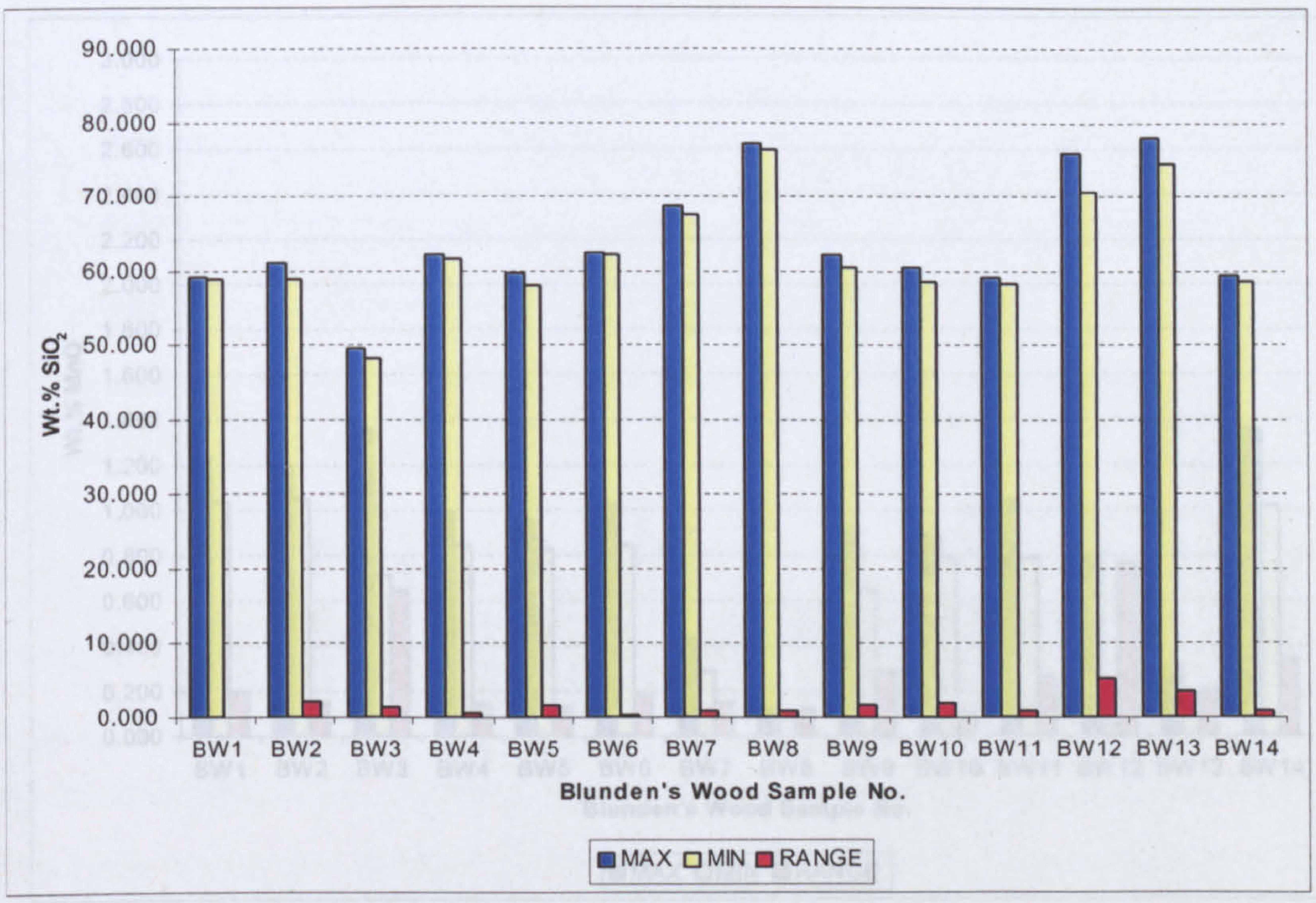


Figure 8:45 A comparison of the maximum, minimum and range of values obtained for SiO_2 for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

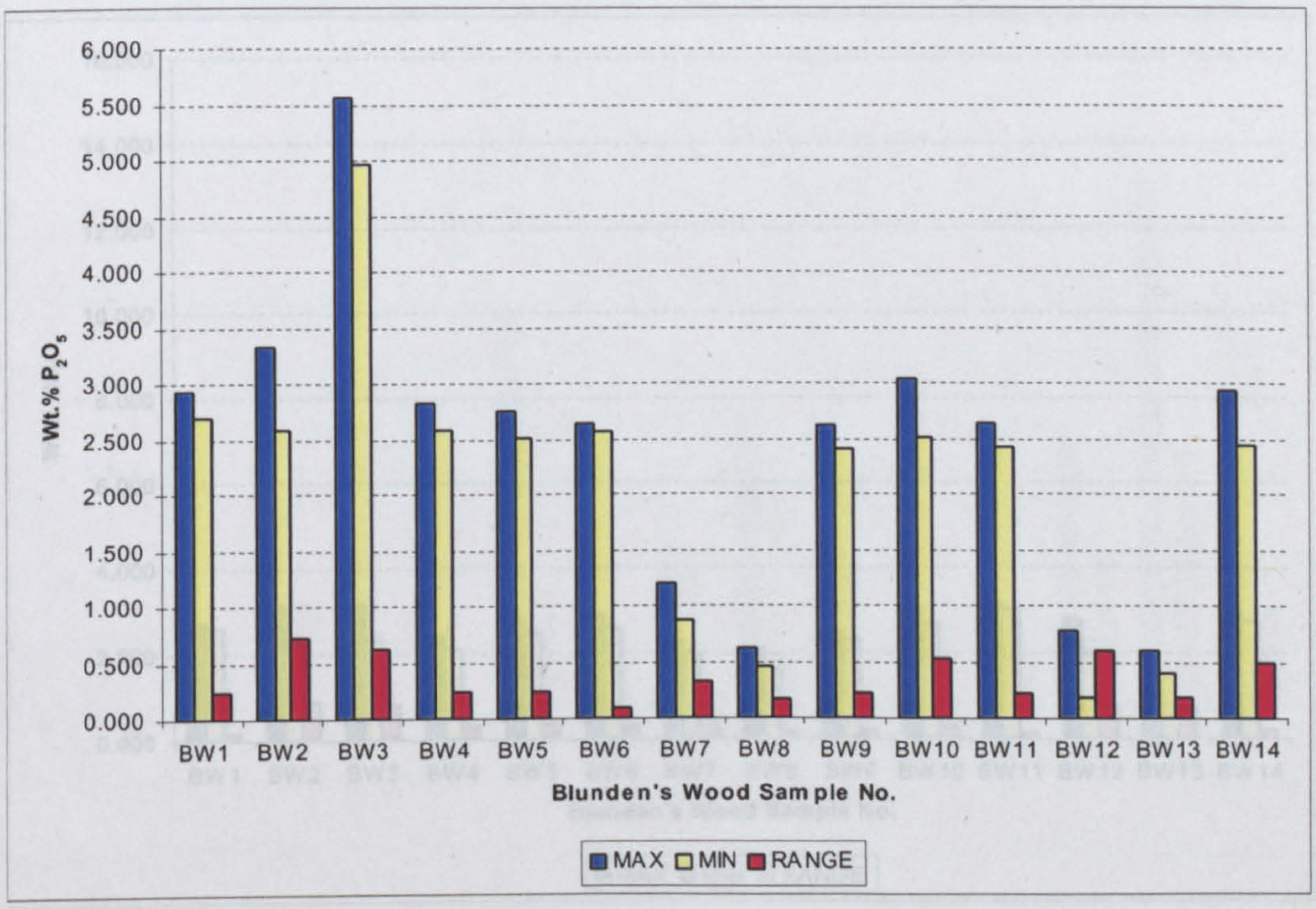


Figure 8:46 A comparison of the maximum, minimum and range of values obtained for P_2O_5 for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

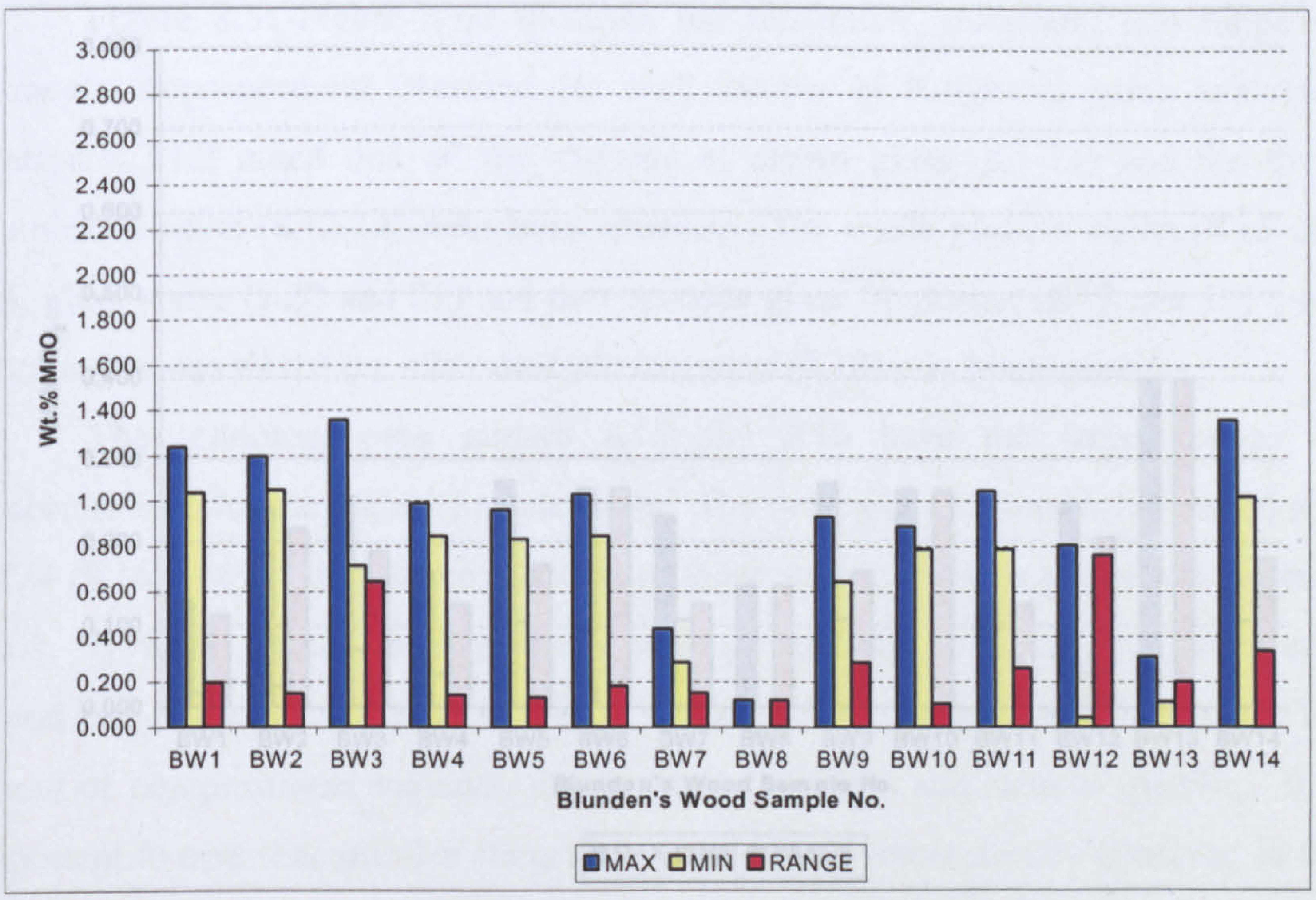


Figure 8:47 A comparison of the maximum, minimum and range of values obtained for MnO for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

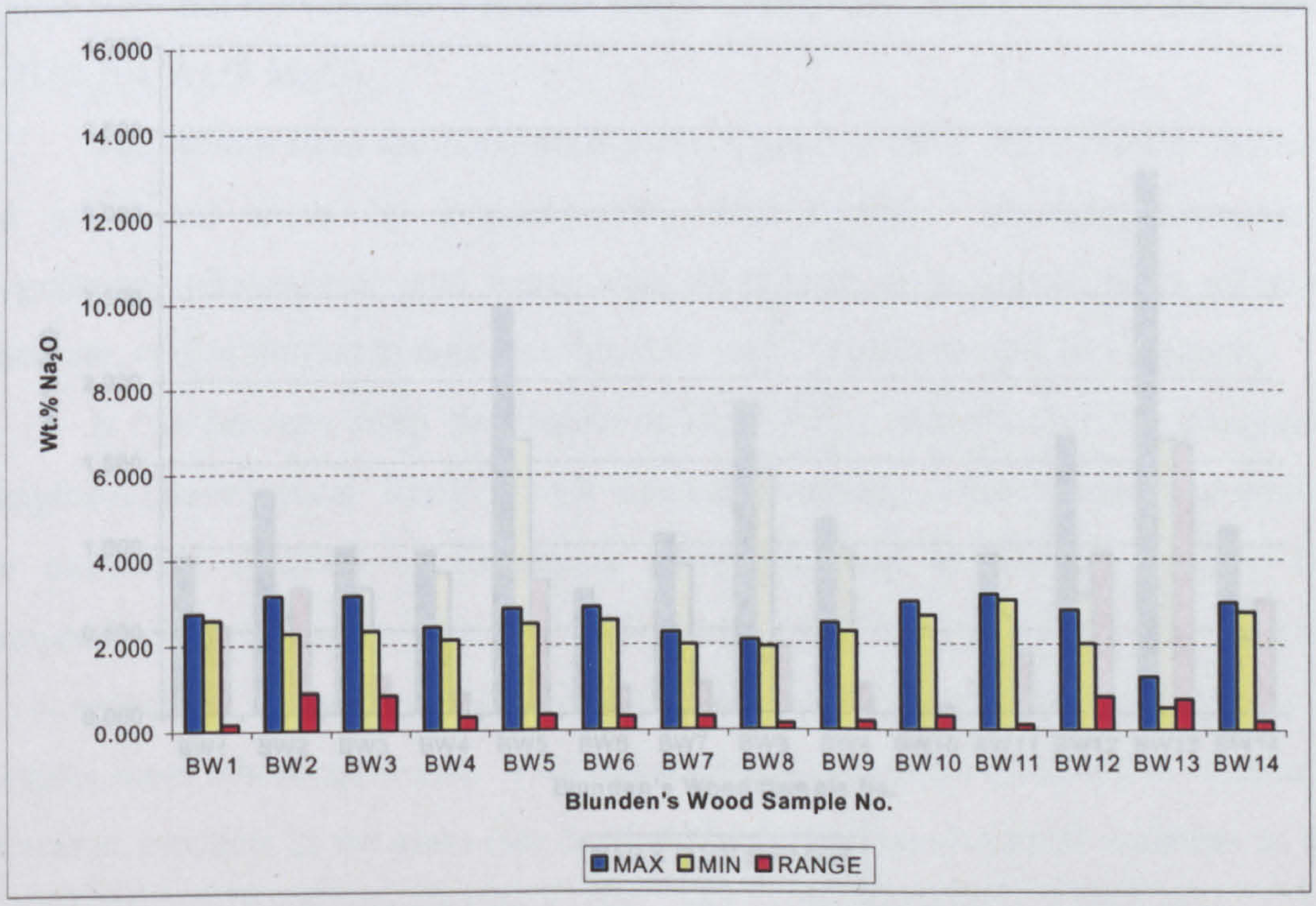


Figure 8:48 A comparison of the maximum, minimum and range of values obtained for Na_2O for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

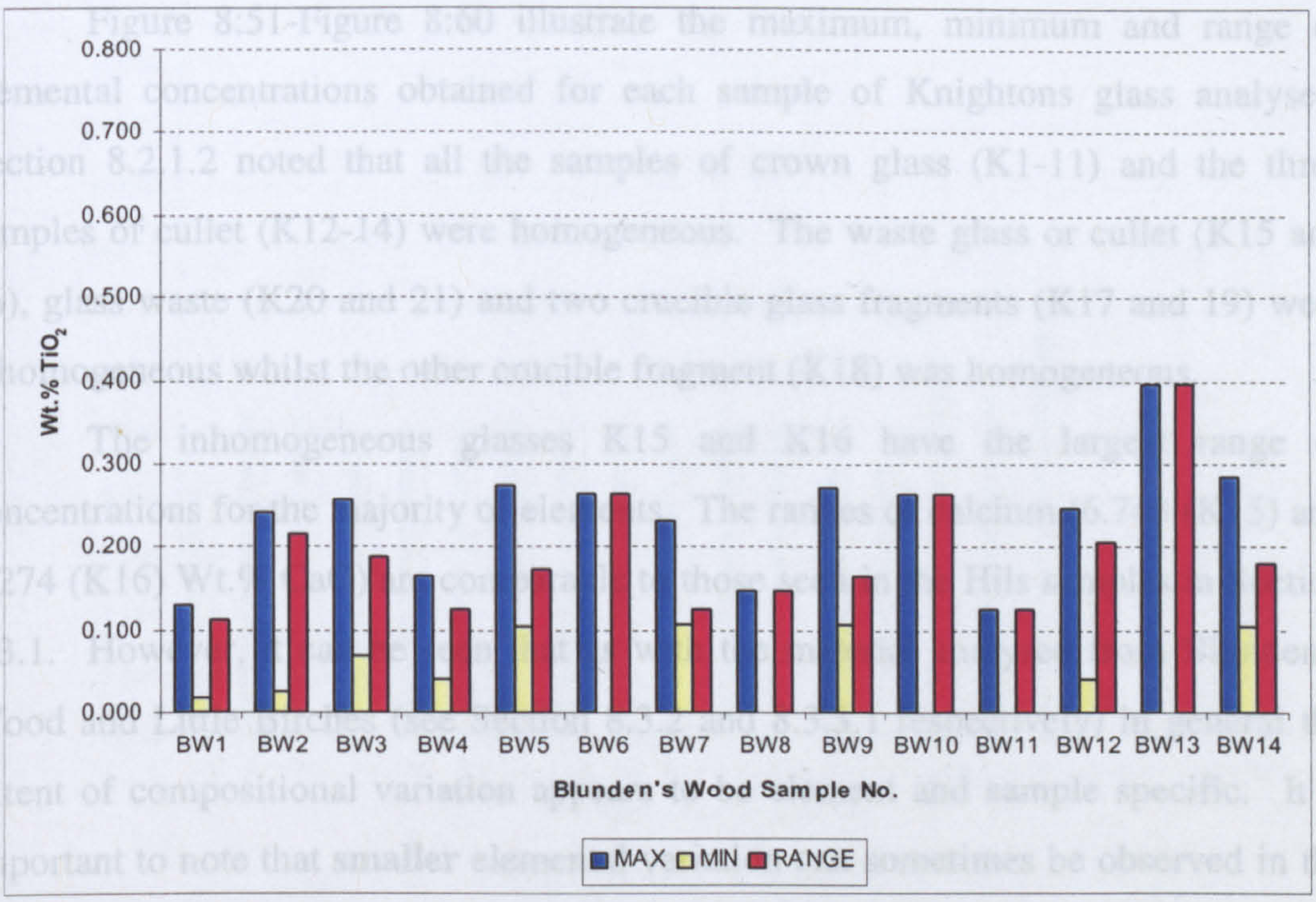


Figure 8:49 A comparison of the maximum, minimum and range of values obtained for TiO_2 for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

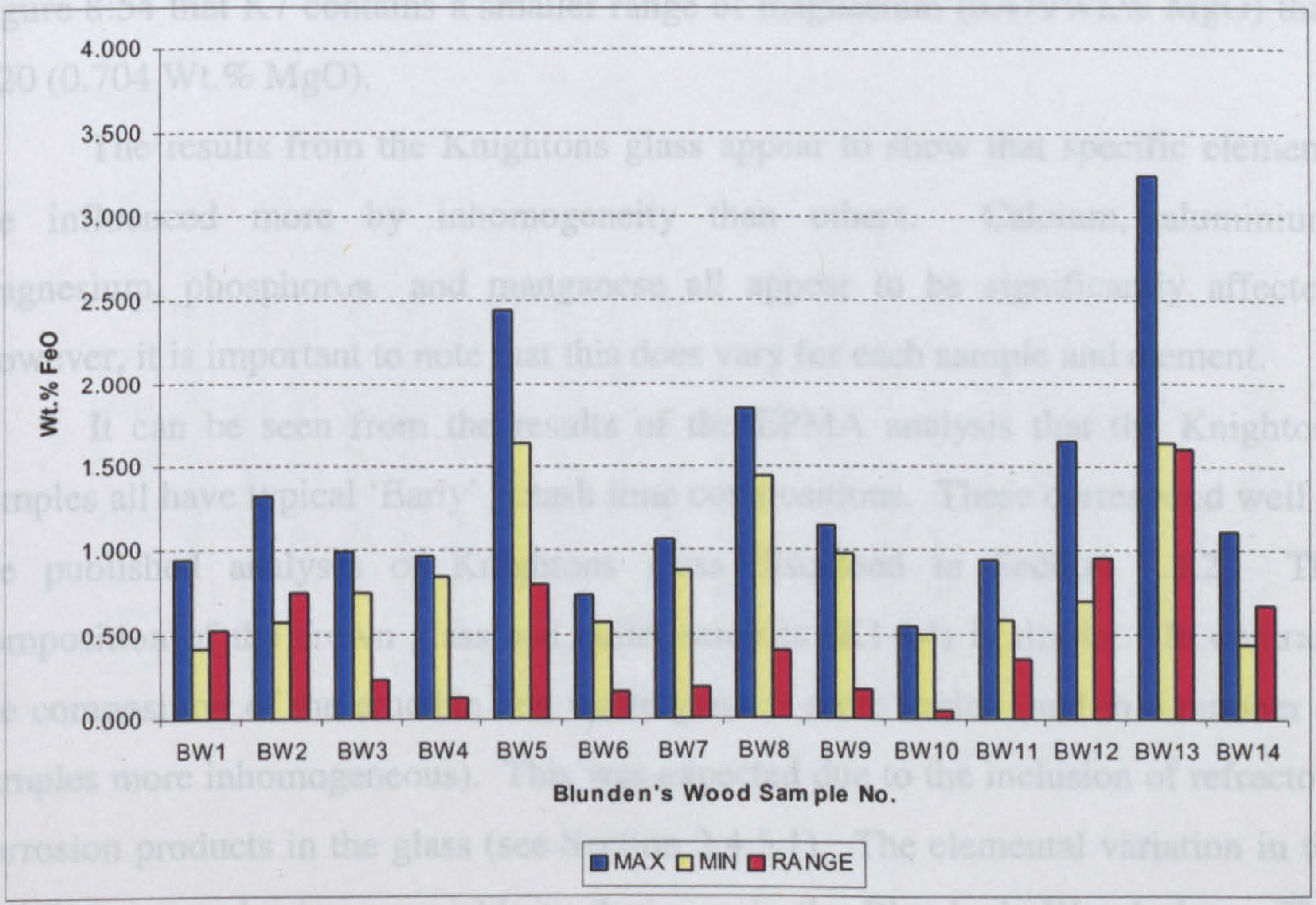


Figure 8:50 A comparison of the maximum, minimum and range of values obtained for FeO for Blunden's Wood glass samples using EPMA (Table VIII:41-Table VIII:54)

8.3.3.2 Knightons

Figure 8:51-Figure 8:60 illustrate the maximum, minimum and range of elemental concentrations obtained for each sample of Knightons glass analysed. Section 8.2.1.2 noted that all the samples of crown glass (K1-11) and the three samples of cullet (K12-14) were homogeneous. The waste glass or cullet (K15 and 16), glass waste (K20 and 21) and two crucible glass fragments (K17 and 19) were inhomogeneous whilst the other crucible fragment (K18) was homogeneous.

The inhomogeneous glasses K15 and K16 have the largest range of concentrations for the majority of elements. The ranges of calcium (6.743 (K15) and 3.274 (K16) Wt.% CaO) are comparable to those seen in the Hils samples in Section 8.3.1. However, it can be seen that as with the material analysed from Blunden's Wood and Little Birches (see Section 8.3.2 and 8.3.3.1 respectively) in general the extent of compositional variation appears to be element and sample specific. It is important to note that **smaller** elemental variation can sometimes be observed in the results from **inhomogeneous** rather than homogeneous glasses. For example, it can be seen from Figure 8:53 that the range of aluminium values in a sample of homogeneous glass K7 (0.304 Wt.% Al_2O_3) is greater than observed in the inhomogeneous glass K20 (0.131Wt.% Al_2O_3). In addition, it can be seen from Figure 8:54 that K7 contains a smaller range of magnesium (0.479Wt.% MgO) than K20 (0.704 Wt.% MgO).

The results from the Knightons glass appear to show that specific elements are influenced more by inhomogeneity than others. Calcium, aluminium, magnesium, phosphorus and manganese all appear to be significantly affected. However, it is important to note that this does vary for each sample and element.

It can be seen from the results of the EPMA analysis that the Knightons samples all have typical 'Early' potash lime compositions. These correspond well to the published analyses of Knightons glass discussed in Section 7.2.2. The composition of the crown glass and cullet samples (K1-14) is similar. In contrast, the composition of the crucible and waste glass is more varied (and in a number of samples more inhomogeneous). This was expected due to the inclusion of refractory corrosion products in the glass (see Section 2.4.5.1). The elemental variation in the Knightons samples is comparable to that seen in the Blunden's Wood glass. This confirms the observations made using the SEM in Sections 8.2.1.1 and 8.2.1.2.

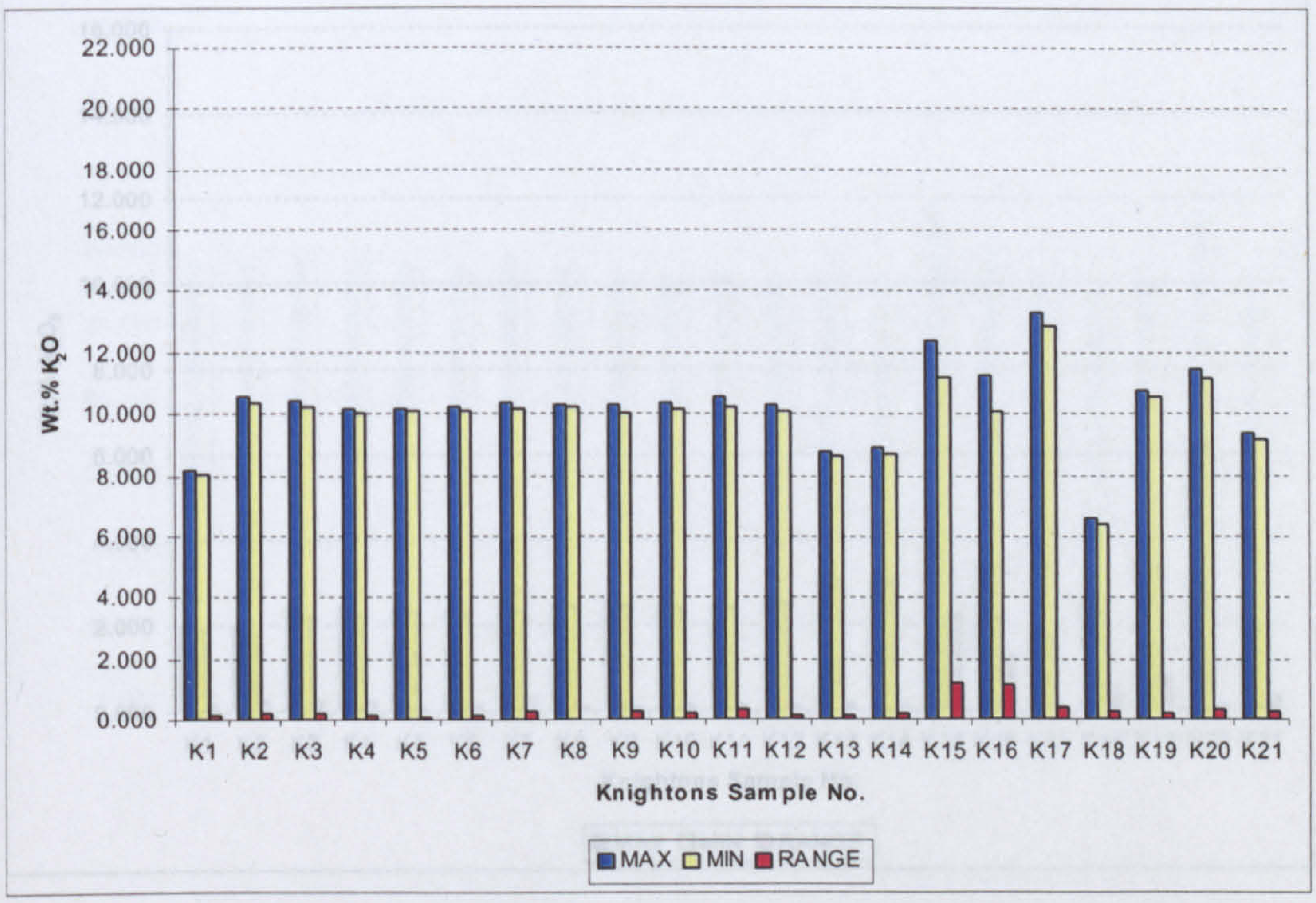


Figure 8:51 A comparison of the maximum, minimum and range of values obtained for K_2O for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

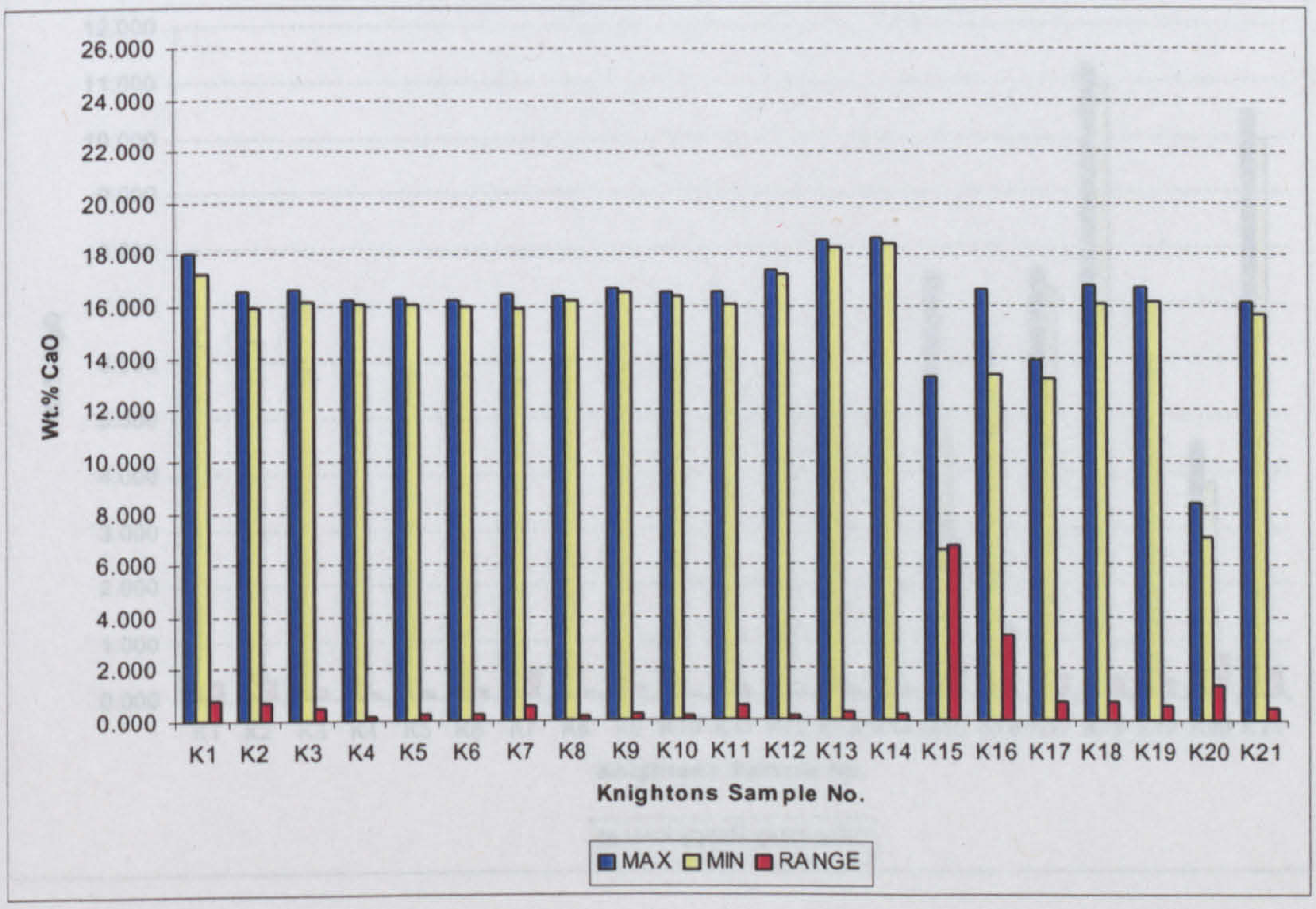


Figure 8:52 A comparison of the maximum, minimum and range of values obtained for CaO for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

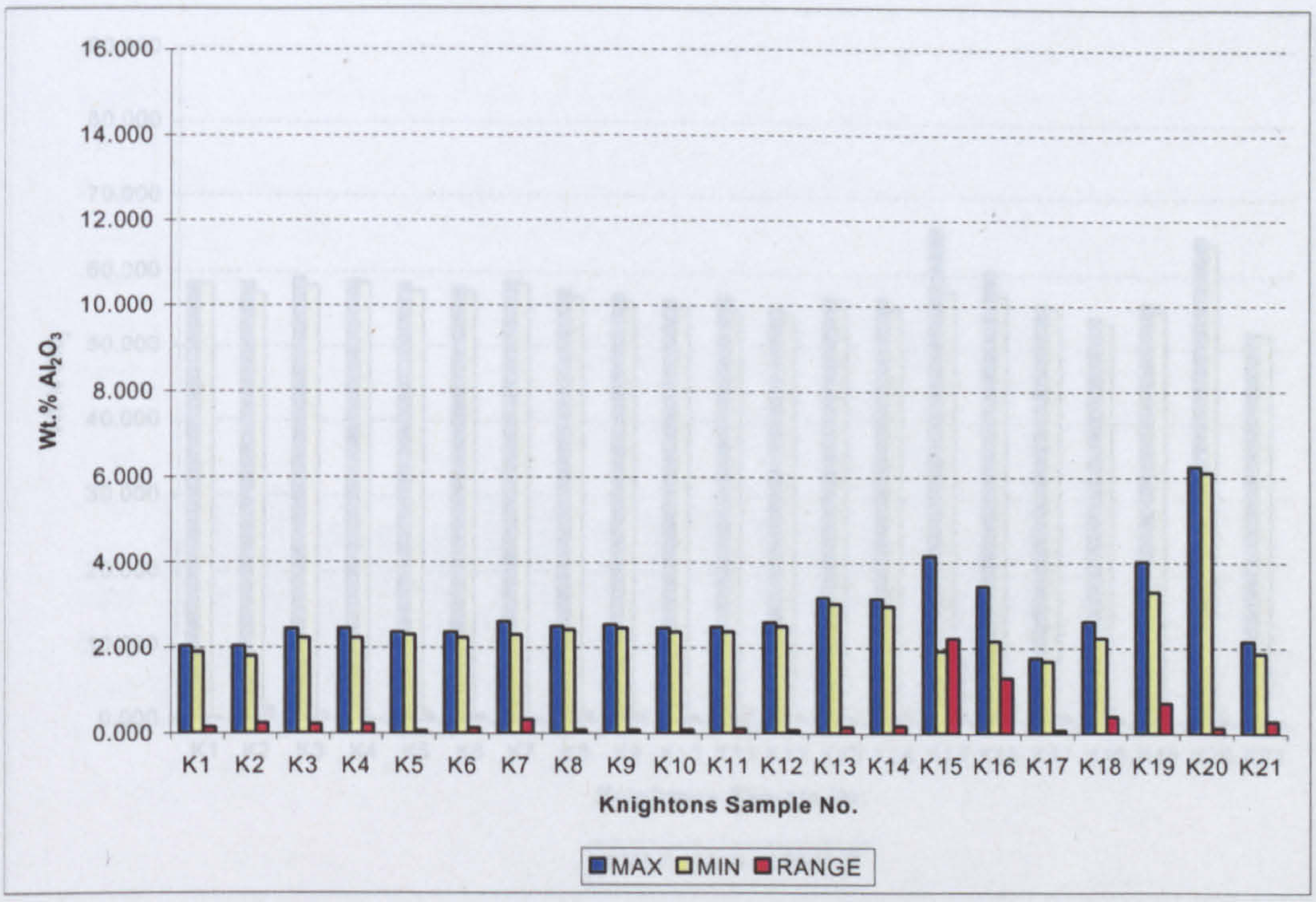


Figure 8:53 **A comparison of the maximum, minimum and range of values obtained for Al_2O_3 for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)**

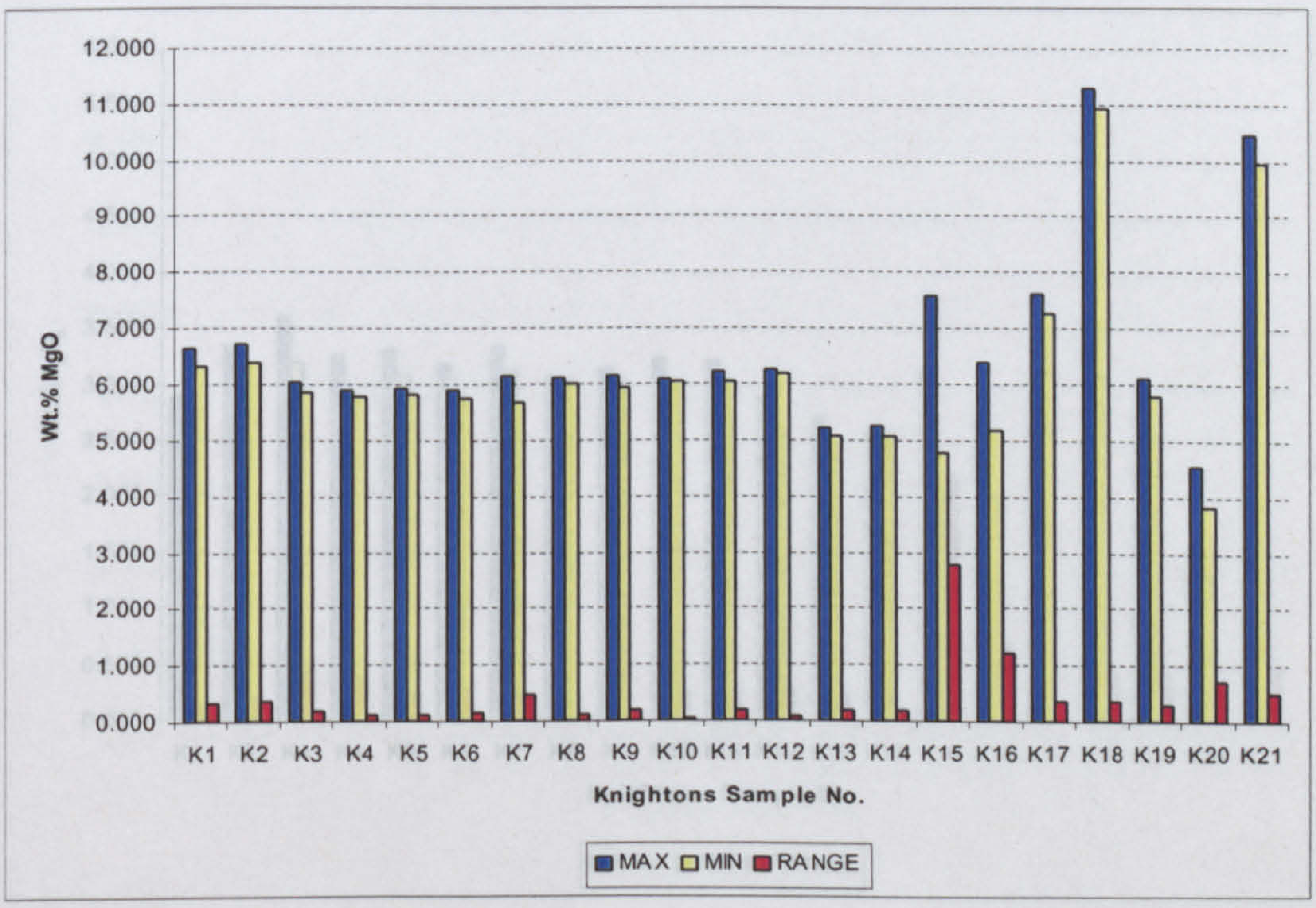


Figure 8:54 **A comparison of the maximum, minimum and range of values obtained for MgO for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)**

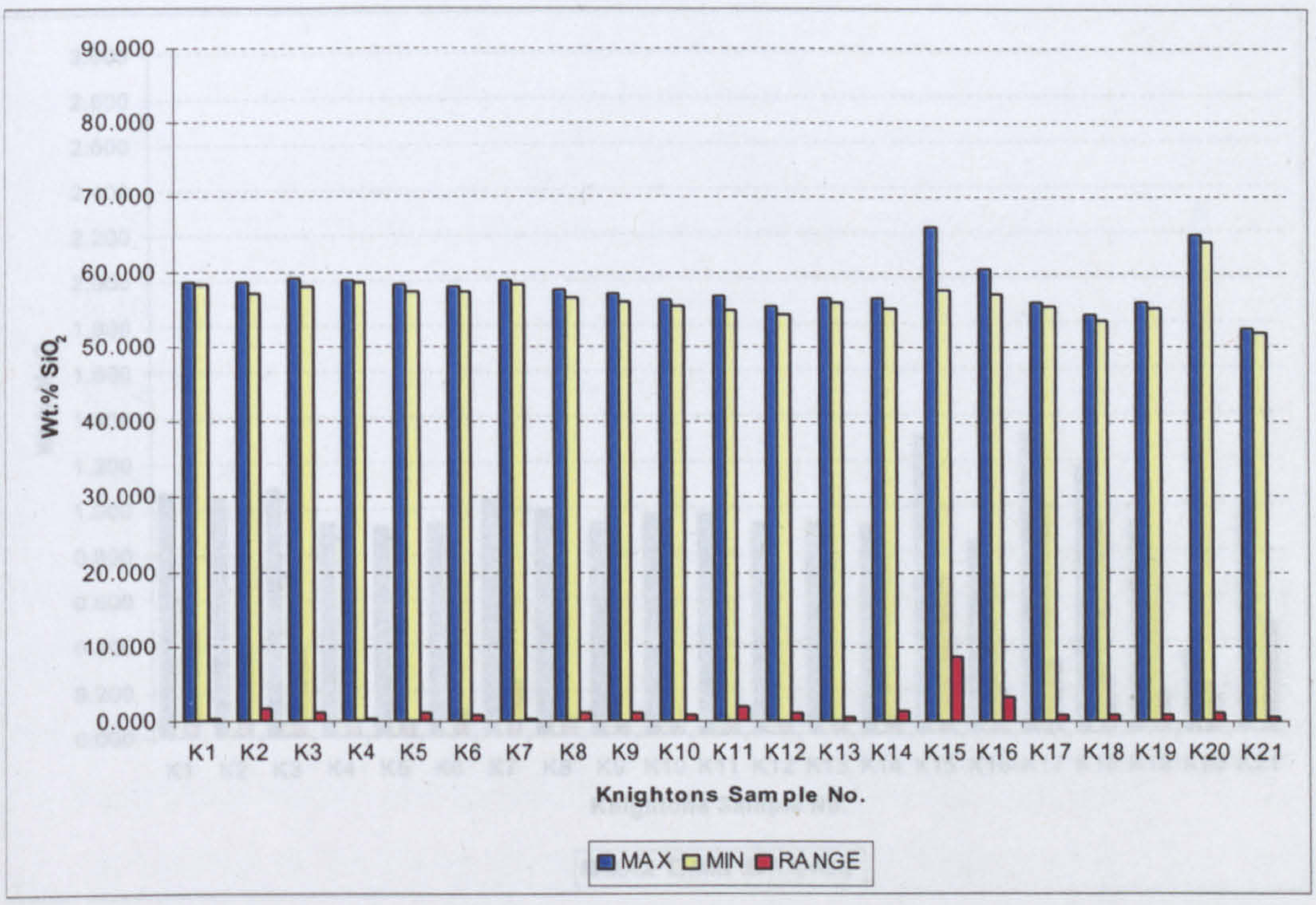


Figure 8:55 A comparison of the maximum, minimum and range of values obtained for SiO_2 for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

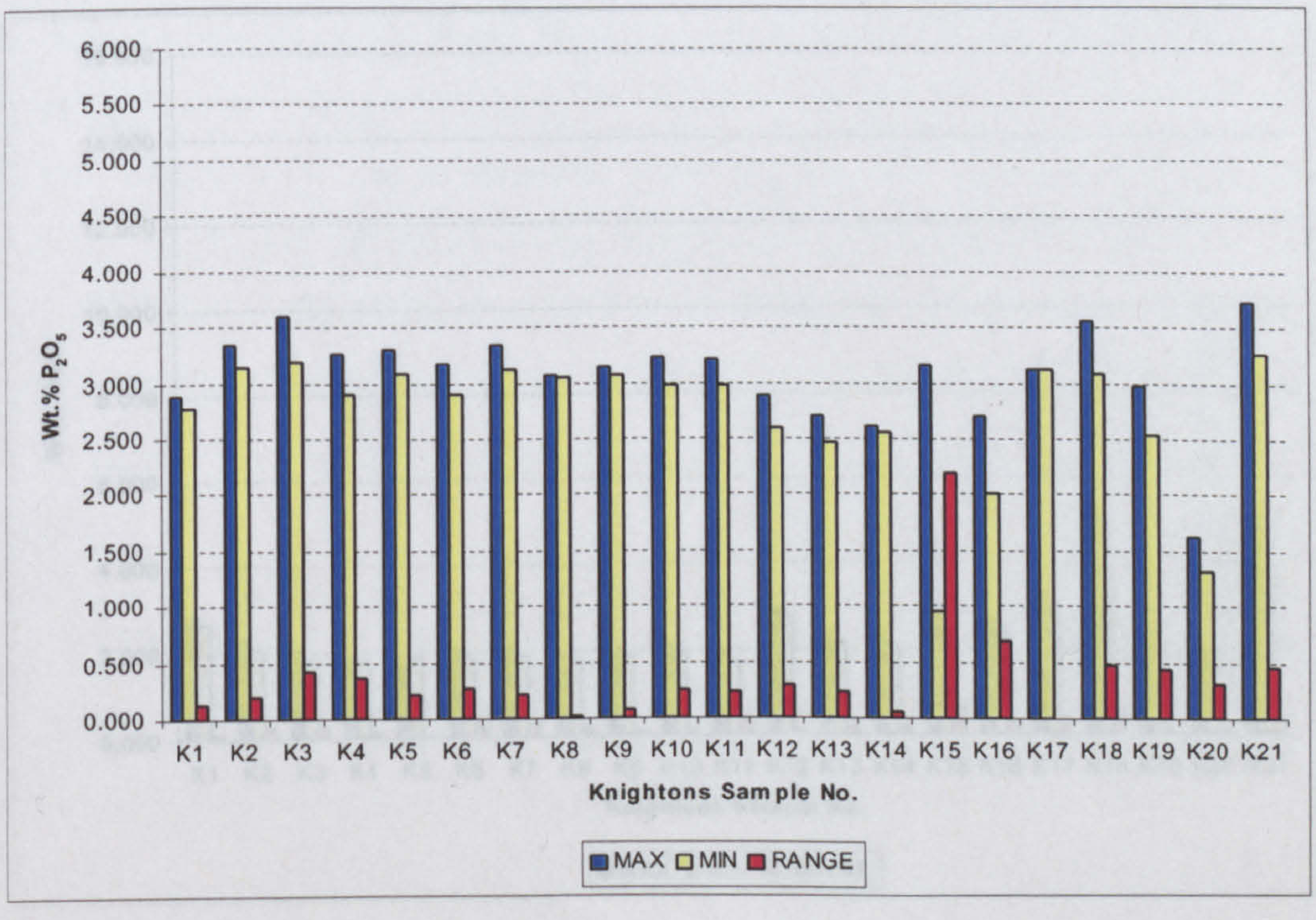


Figure 8:56 A comparison of the maximum, minimum and range of values obtained for P_2O_5 for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

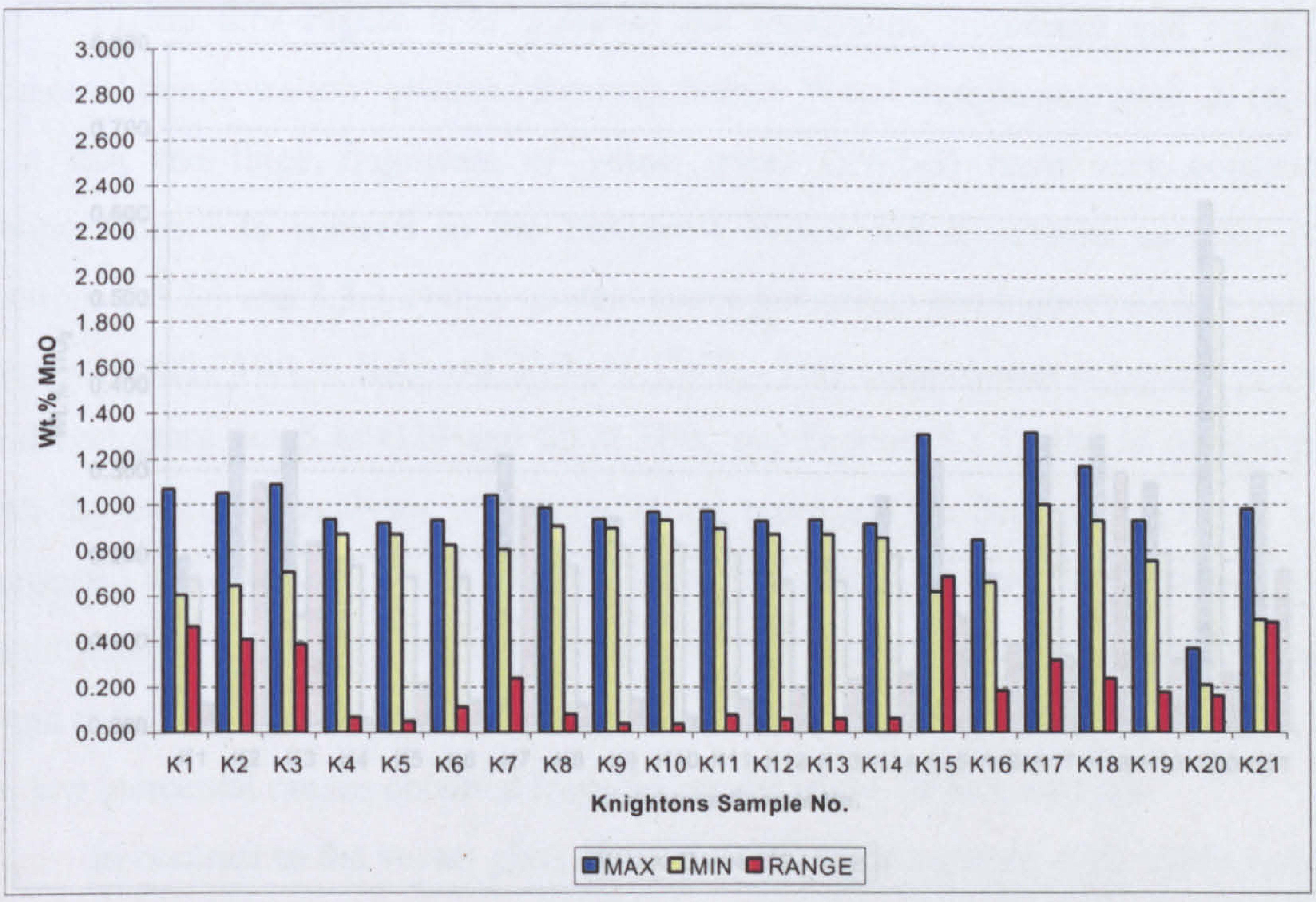


Figure 8:57 A comparison of the maximum, minimum and range of values obtained for MnO for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

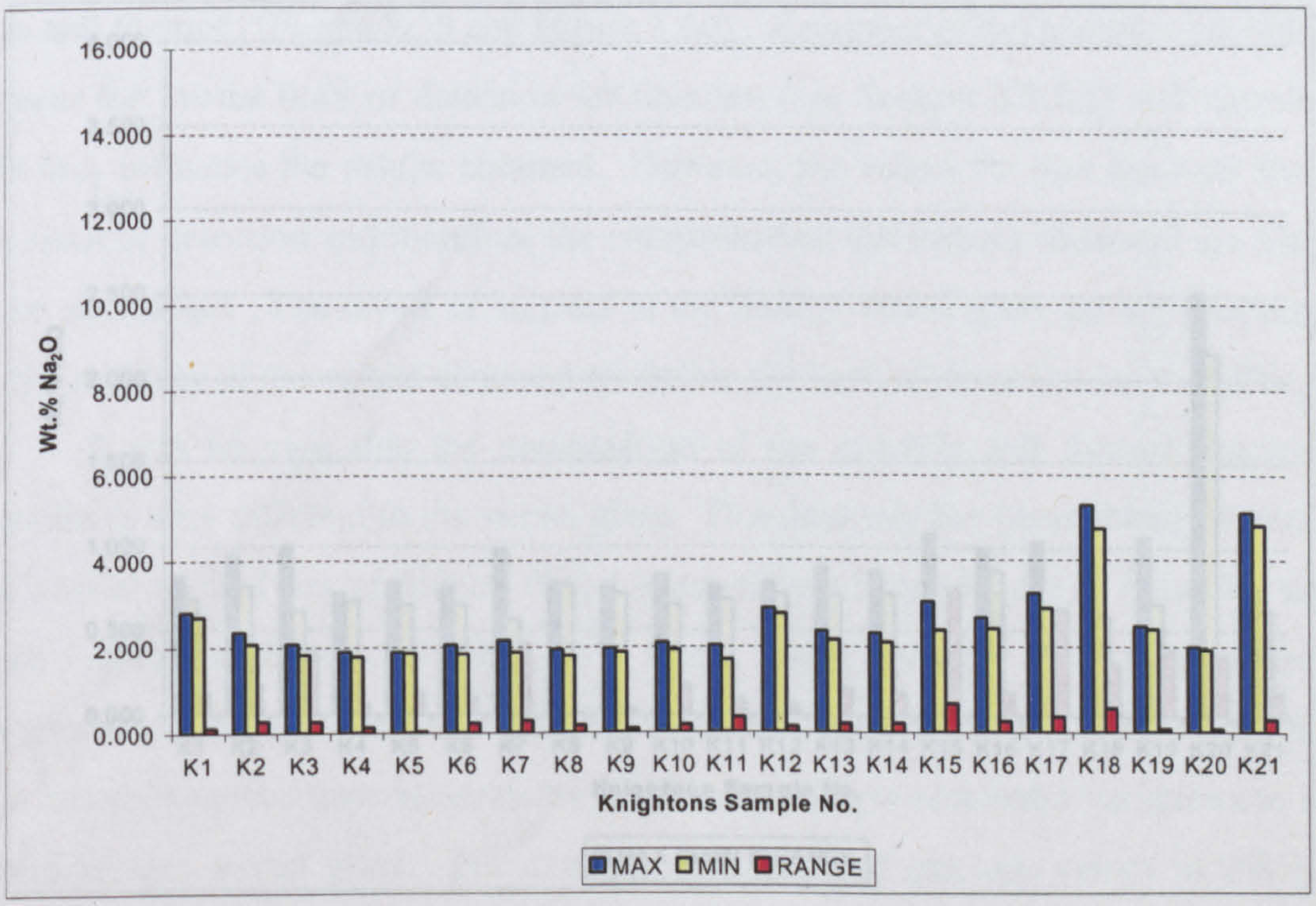


Figure 8:58 A comparison of the maximum, minimum and range of values obtained for Na_2O for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)

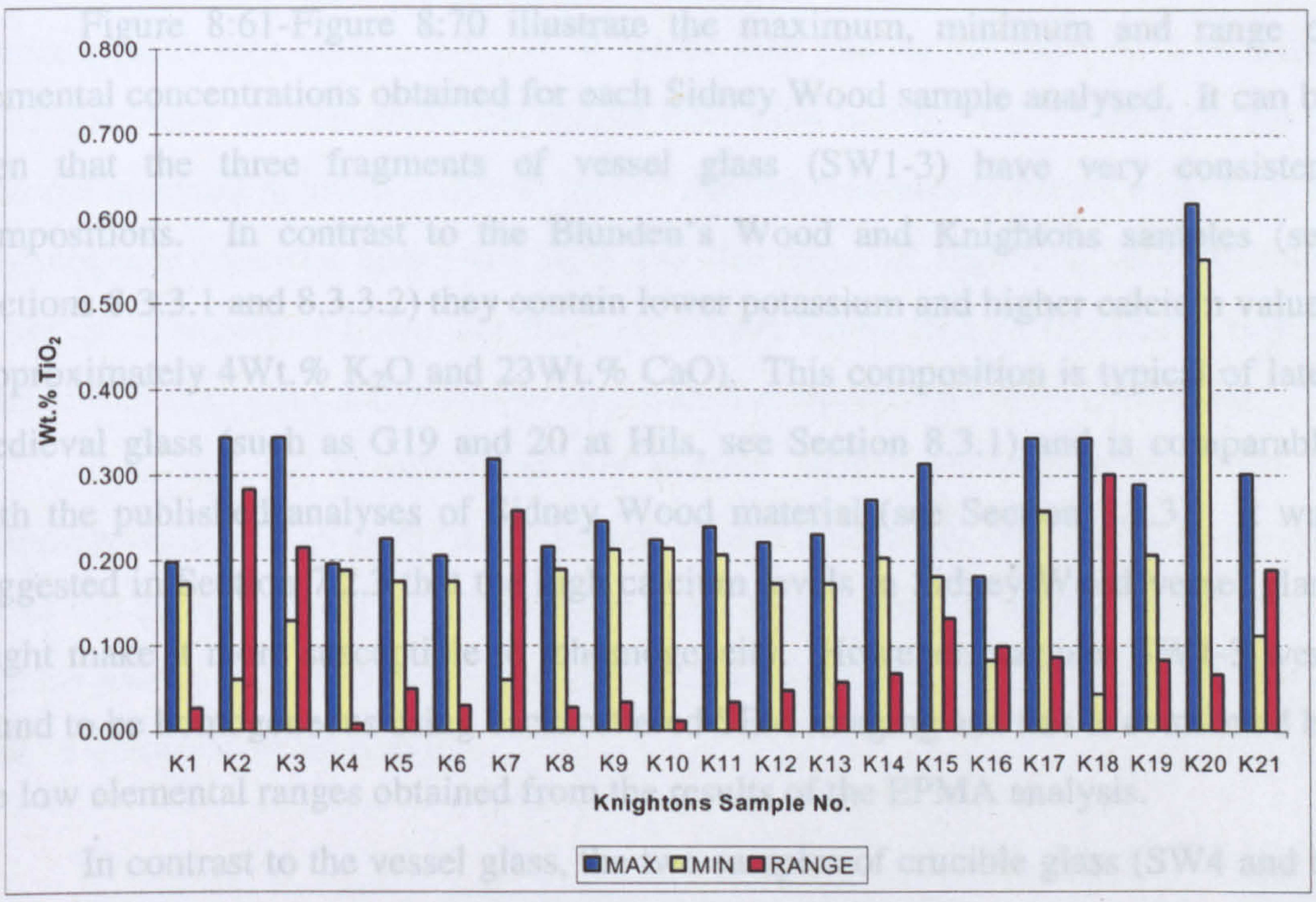


Figure 8:59 **A comparison of the maximum, minimum and range of values obtained for TiO_2 for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)**

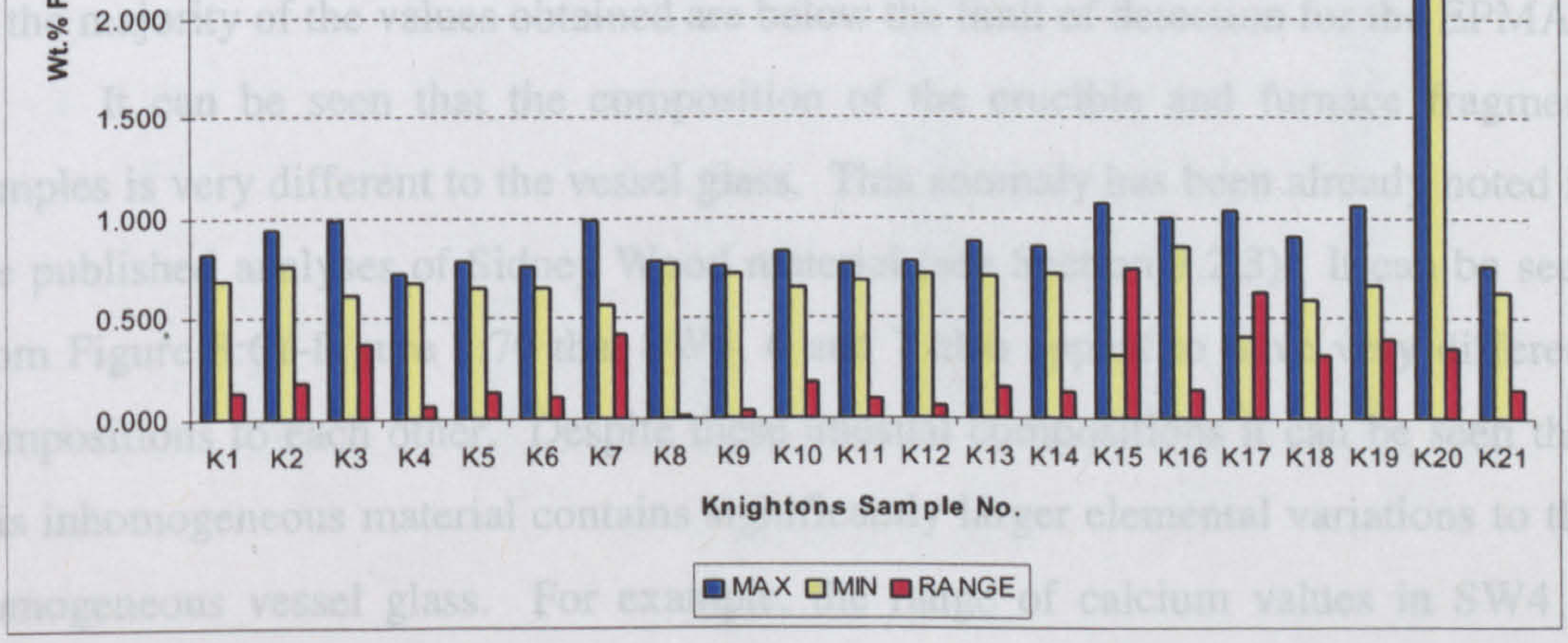


Figure 8:60 **A comparison of the maximum, minimum and range of values obtained for FeO for Knightons glass samples using EPMA (Table VIII:55-Table VIII:75)**

8.3.3.3 Sidney Wood

Figure 8:61-Figure 8:70 illustrate the maximum, minimum and range of elemental concentrations obtained for each Sidney Wood sample analysed. It can be seen that the three fragments of vessel glass (SW1-3) have very consistent compositions. In contrast to the Blunden's Wood and Knightons samples (see Sections 8.3.3.1 and 8.3.3.2) they contain lower potassium and higher calcium values (approximately 4Wt.% K_2O and 23Wt.% CaO). This composition is typical of later medieval glass (such as G19 and 20 at Hils, see Section 8.3.1) and is comparable with the published analyses of Sidney Wood material (see Section 7.2.3). It was suggested in Section 7.2.3 that the high calcium levels in Sidney Wood vessel glass might make it more susceptible to inhomogeneity. However, samples SW1-3 were found to be homogeneous using backscattered SEM imaging and this is confirmed by the low elemental ranges obtained from the results of the EPMA analysis.

In contrast to the vessel glass, the two samples of crucible glass (SW4 and 6) and the furnace fragment (SW7) exhibited inhomogeneity in backscattered SEM imaging (see Section 8.2.1.3). The EPMA results confirm that for the majority of elements, these glasses contain larger elemental ranges than the homogeneous vessel glasses (Figure 8:61-Figure 8:70). The exceptions to this are the values obtained for iron and titanium (Figure 8:59 and Figure 8:60). A number of the analyses are below or near the lowest limit of detection for titanium (see Section 3.3.2.5) and therefore this may influence the results obtained. However, the values for iron are well above the limit of detection and therefore the compositional differences observed are likely to be significant. The levels of sulphur in the Sidney Wood glass are not illustrated as the majority of the values obtained are below the limit of detection for the EPMA.

It can be seen that the composition of the crucible and furnace fragment samples is very different to the vessel glass. This anomaly has been already noted in the published analyses of Sidney Wood material (see Section 7.2.3). It can be seen from Figure 8:61-Figure 8:70 that SW4, 6 and 7 also appear to have very different compositions to each other. Despite these unusual compositions it can be seen that this inhomogeneous material contains significantly larger elemental variations to the homogeneous vessel glass. For example, the range of calcium values in SW4 is 4.095Wt. % CaO, whilst the homogeneous sample SW1 has a range of just 0.677Wt.% CaO (Figure 8:52).

SW7 was classified as having low levels, and SW4 and 6 high levels of inhomogeneity (see Section 8.2.1.3). It can be seen that for the majority of elements SW7 does have smaller elemental ranges than SW4 and 6. This is the only set of material analysed in this research to show a distinct relationship between the level of inhomogeneity viewed under the SEM and the range of analytical data obtained. However, it should be noted that these results are based on a small number of data points from each glass and therefore may alter if more analyses were carried out.

It is difficult to determine any distinct difference between the level of inhomogeneity seen in all of the Wealden glasses analysed. The EPMA results for all of the glass analysed in this Chapter have shown that the relationship between inhomogeneity and composition is complex and varied. The EPMA and SEM results will be discussed in Section 8.4.

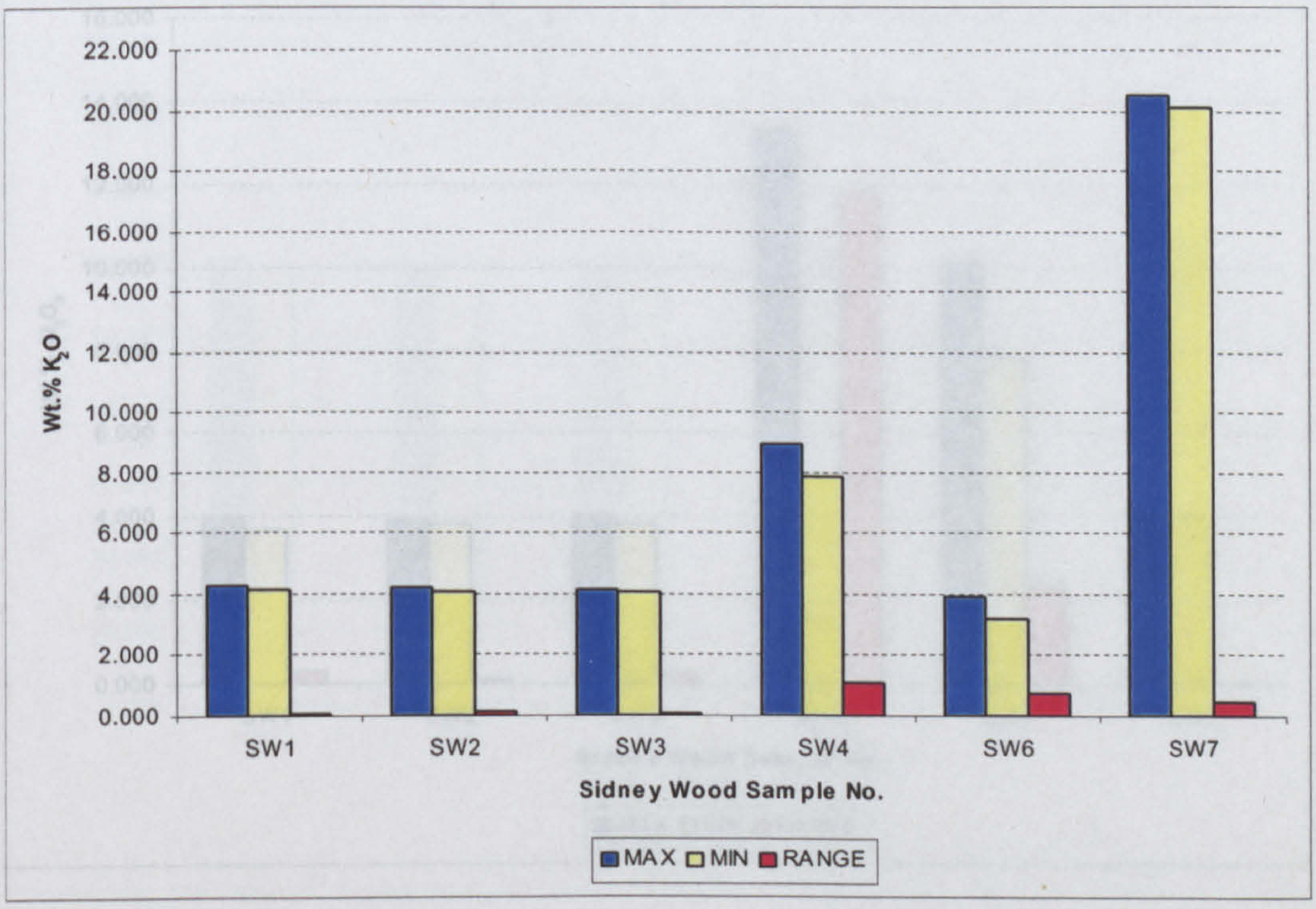


Figure 8:61 A comparison of the maximum, minimum and range of values obtained for K_2O for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

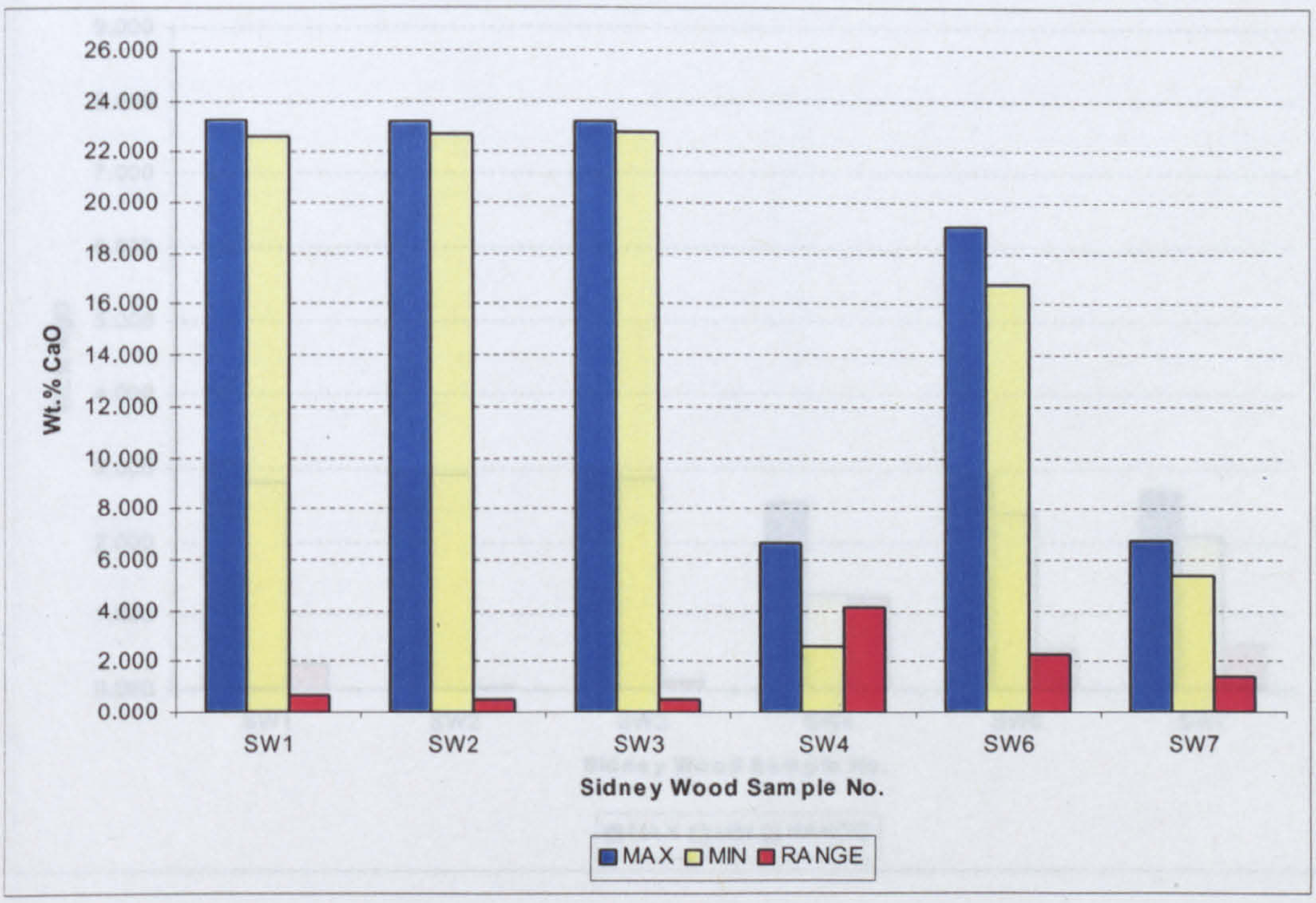


Figure 8:62 A comparison of the maximum, minimum and range of values obtained for CaO for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

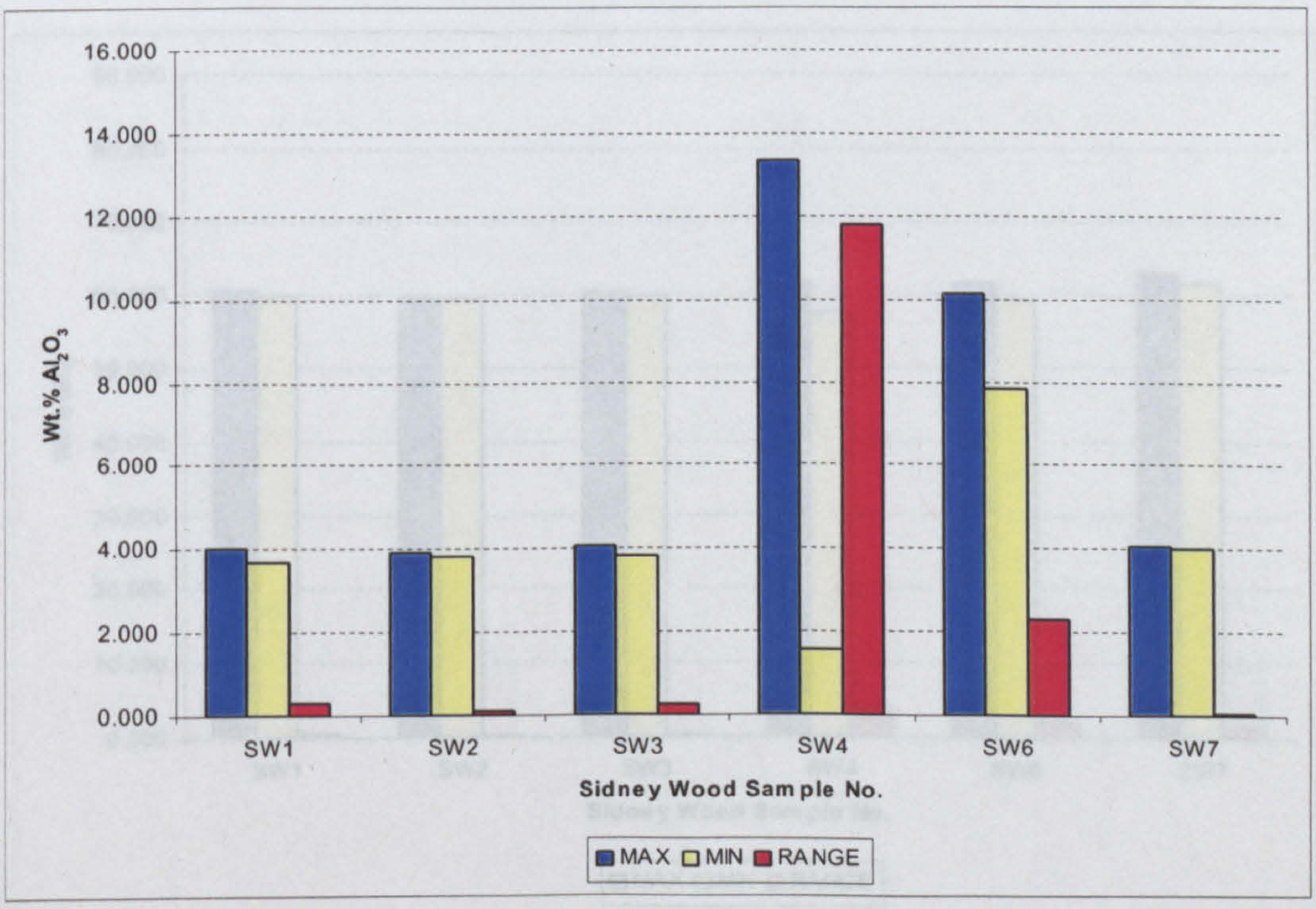


Figure 8:63 A comparison of the maximum, minimum and range of values obtained for Al_2O_3 for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

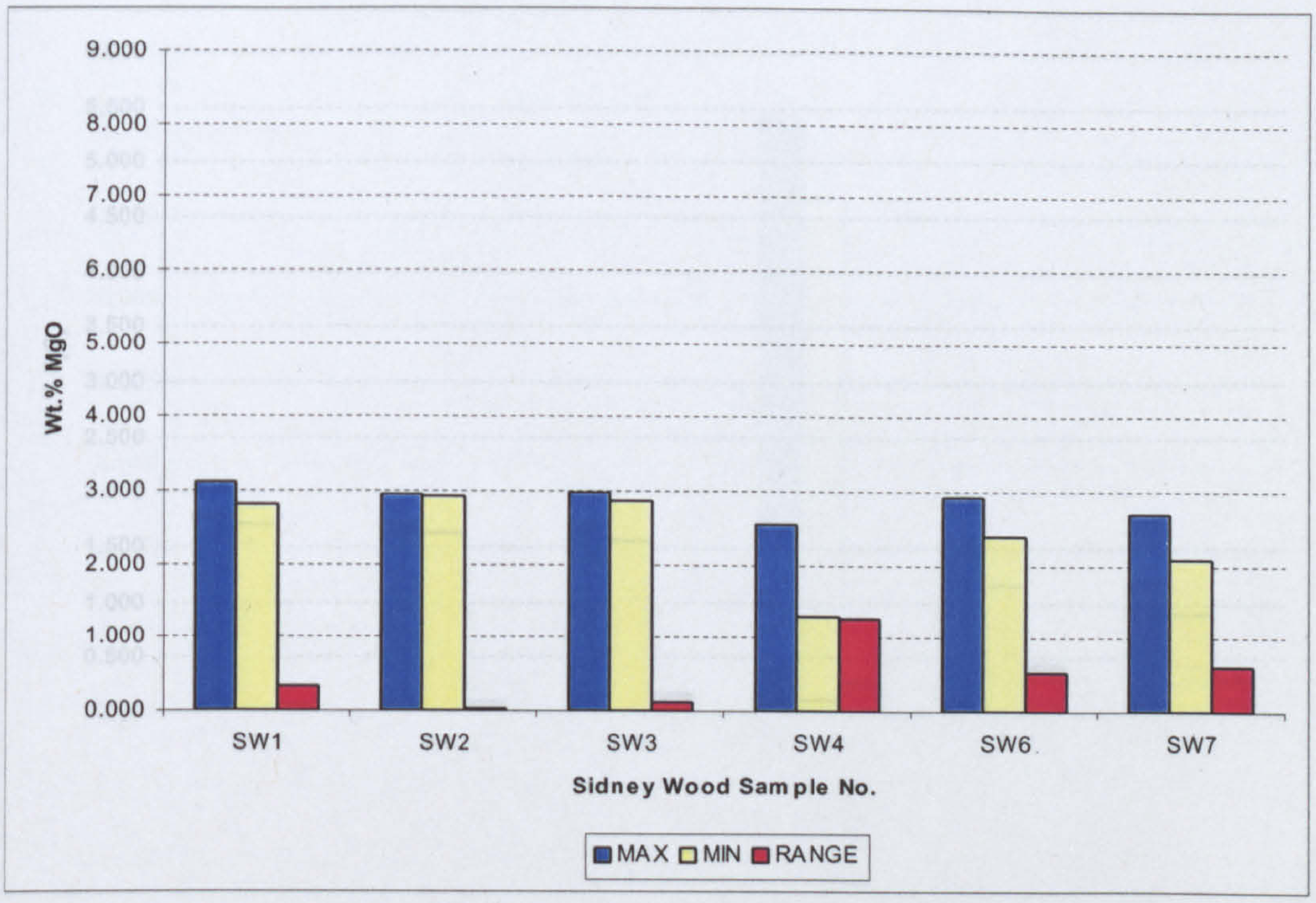


Figure 8:64 A comparison of the maximum, minimum and range of values obtained for MgO for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

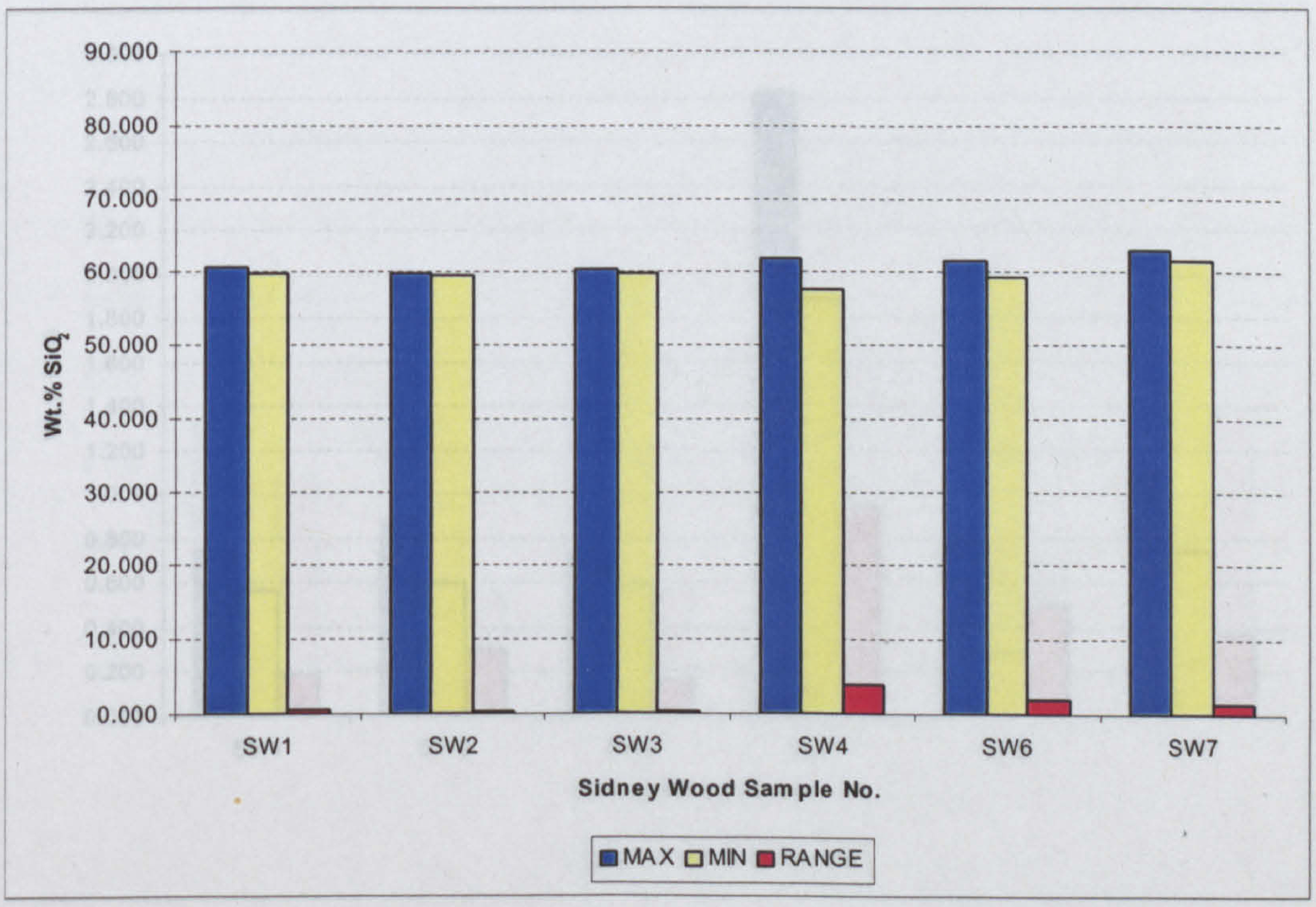


Figure 8:65 A comparison of the maximum, minimum and range of values obtained for SiO_2 for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

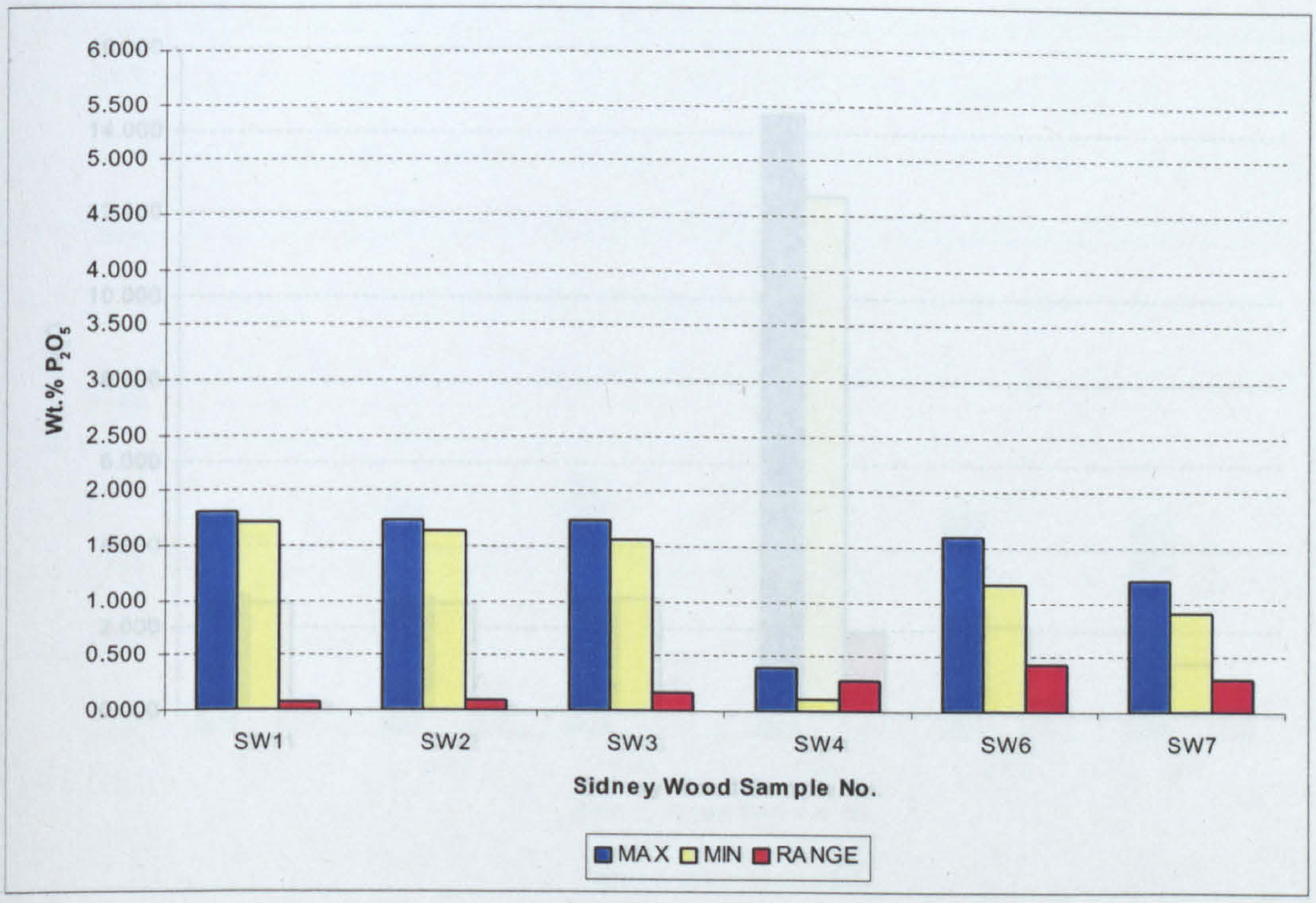


Figure 8:66 A comparison of the maximum, minimum and range of values obtained for P_2O_5 for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

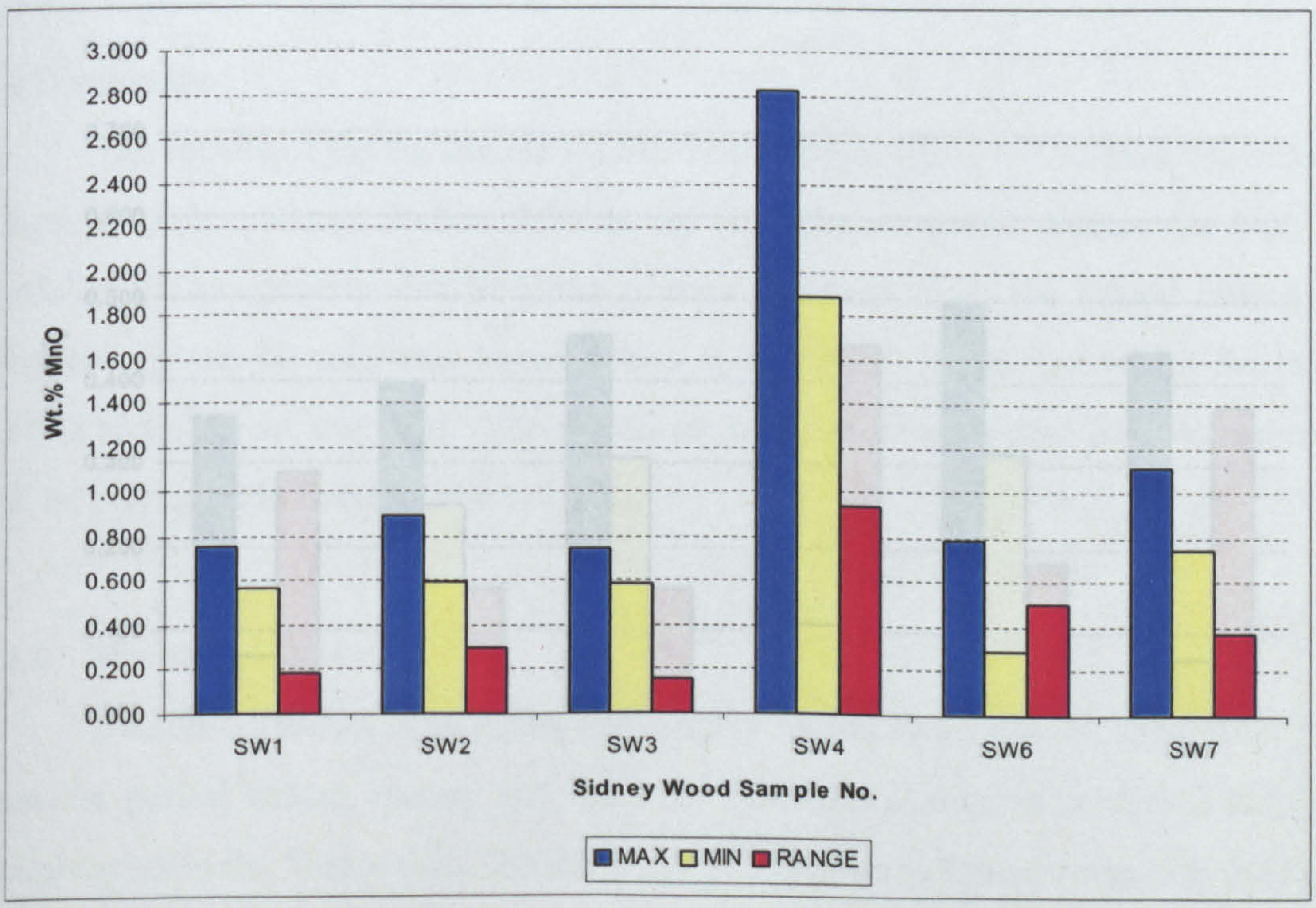


Figure 8:67 A comparison of the maximum, minimum and range of values obtained for MnO for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

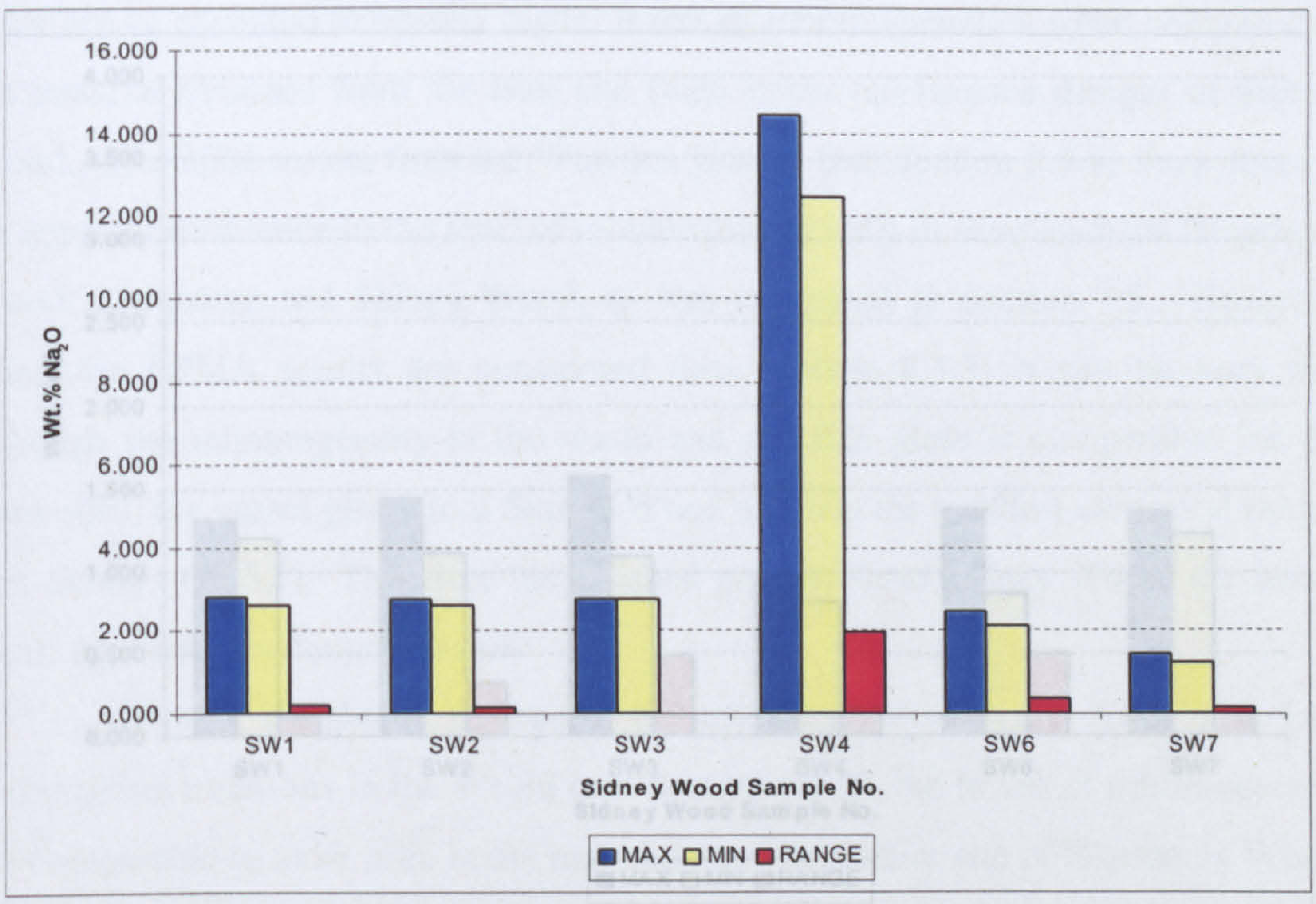


Figure 8:68 **A comparison of the maximum, minimum and range of values obtained for Na_2O for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)**

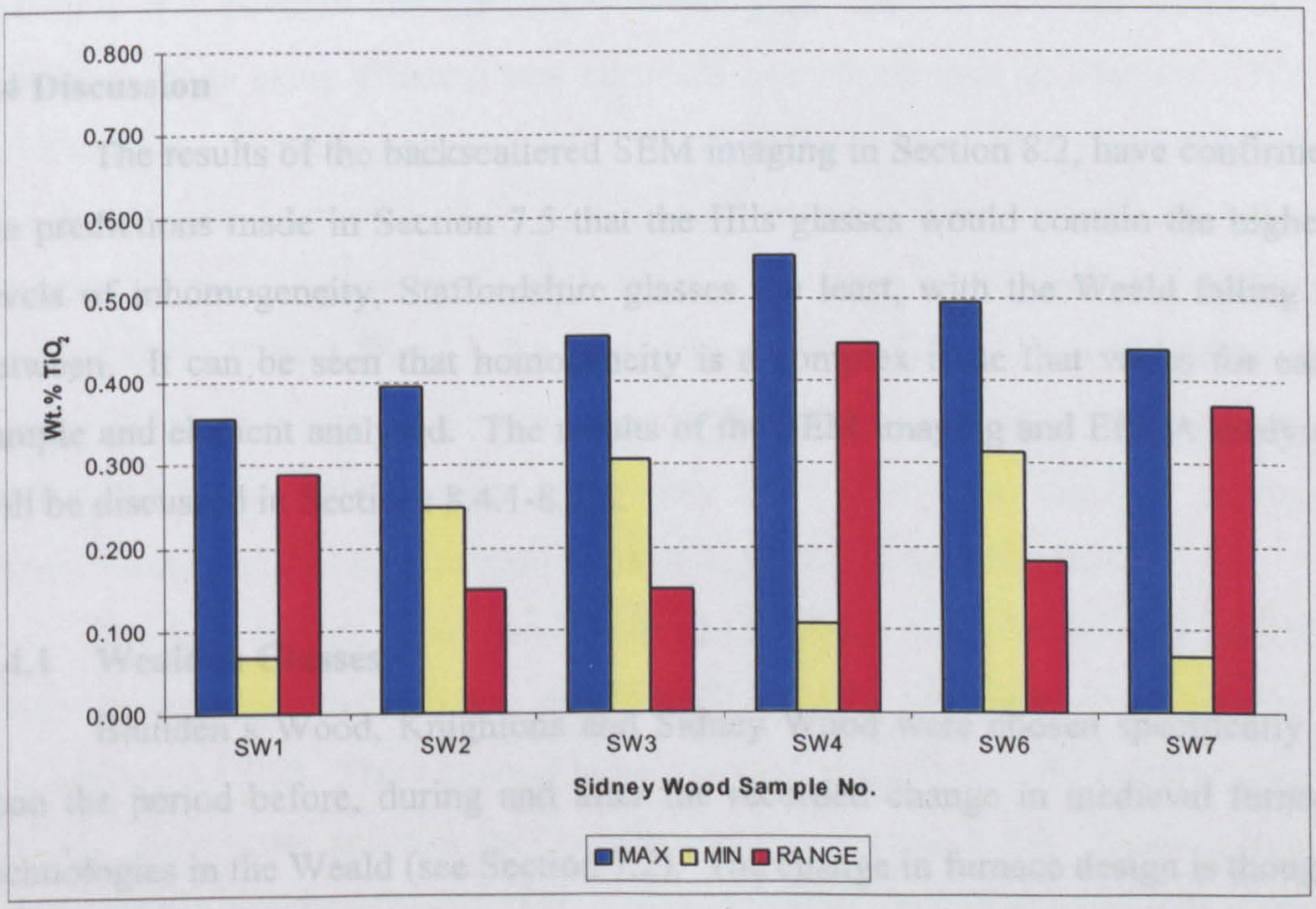


Figure 8:69 **A comparison of the maximum, minimum and range of values obtained for TiO_2 for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)**

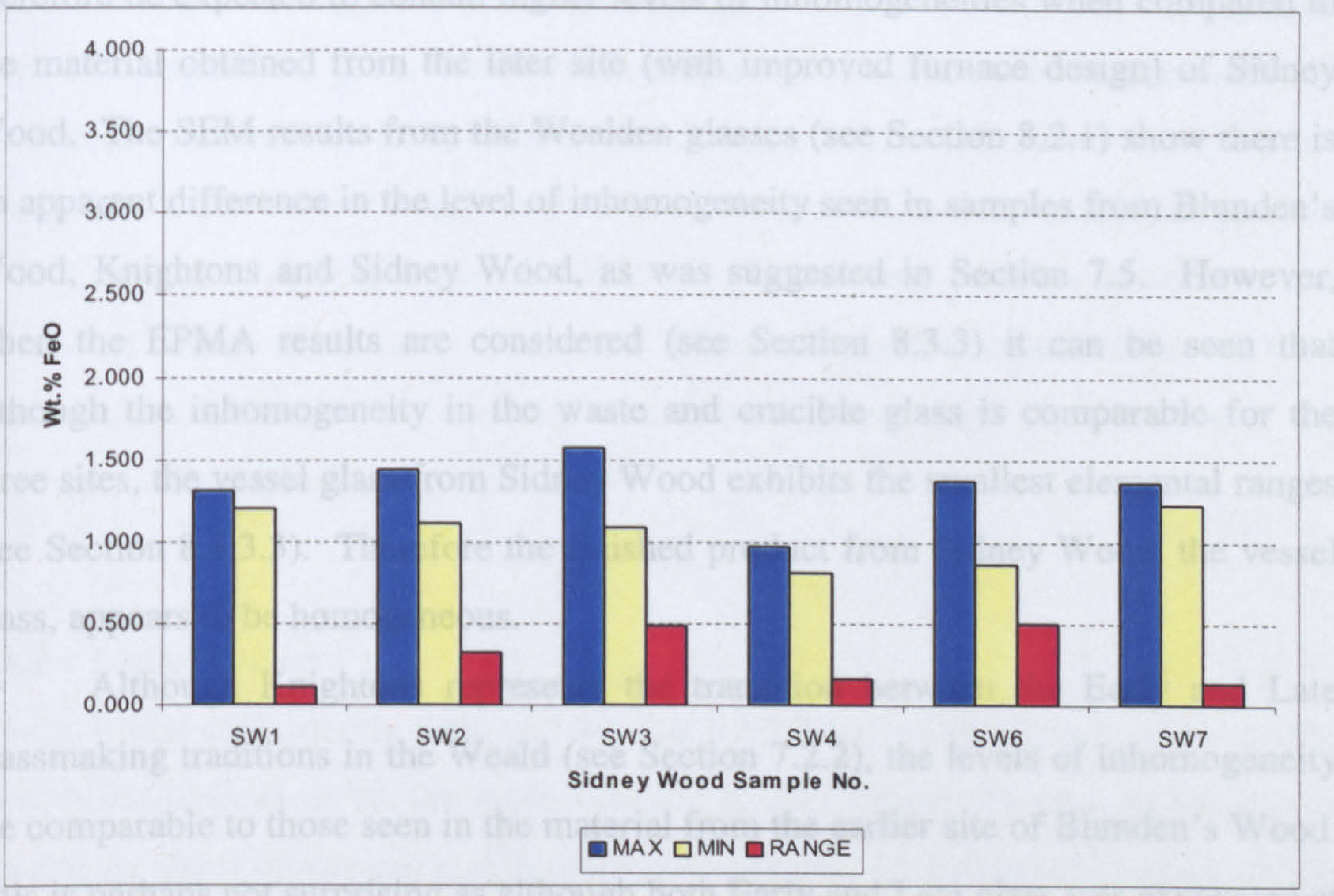


Figure 8:70 A comparison of the maximum, minimum and range of values obtained for FeO for Sidney Wood glass samples using EPMA (Table VIII:76-Table VIII:81)

8.4 Discussion

The results of the backscattered SEM imaging in Section 8.2, have confirmed the predictions made in Section 7.5 that the Hils glasses would contain the highest levels of inhomogeneity, Staffordshire glasses the least, with the Weald falling in between. It can be seen that homogeneity is a complex issue that varies for each sample and element analysed. The results of the SEM imaging and EPMA analyses will be discussed in Sections 8.4.1-8.4.8.

8.4.1 Wealden Glasses

Blunden's Wood, Knightons and Sidney Wood were chosen specifically to span the period before, during and after the recorded change in medieval furnace technologies in the Weald (see Section 7.2). The change in furnace design is thought to have increased the melting temperatures attainable, and from the information in Chapter 2 and the conclusions from the experimental glass in Chapter 5, it can be seen that this variable has a significant effect on the formation of a more homogeneous glass. The earlier glass from Blunden's Wood or Knightons might therefore be expected to contain higher levels of inhomogeneities when compared to the material obtained from the later site (with improved furnace design) of Sidney Wood. The SEM results from the Wealden glasses (see Section 8.2.1) show there is no apparent difference in the level of inhomogeneity seen in samples from Blunden's Wood, Knightons and Sidney Wood, as was suggested in Section 7.5. However, when the EPMA results are considered (see Section 8.3.3) it can be seen that although the inhomogeneity in the waste and crucible glass is comparable for the three sites, the vessel glass from Sidney Wood exhibits the smallest elemental ranges (see Section 8.3.3.3). Therefore the finished product from Sidney Wood, the vessel glass, appears to be homogeneous.

Although Knightons represents the transition between the Early and Late glassmaking traditions in the Weald (see Section 7.2.2), the levels of inhomogeneity are comparable to those seen in the material from the earlier site of Blunden's Wood. This is perhaps not surprising as although both Early and Late glass was excavated at Knightons, all the samples analysed here were of the Early type.

The vessel glass from Sidney Wood is of extremely high quality visually, and has a different chemical composition to the Blunden's Wood and Knightons material. Therefore it is possible that the Sidney Wood glass samples analysed are likely to have been made using different raw materials from those used at Blunden's Wood and Knightons. Even though the Sidney Wood glass has lower total alkali and higher lime levels (see Section 8.3.3.3), it is homogeneous. These factors suggest that increased furnace temperatures and times *may* have been used by medieval glassmakers at Sidney Wood. The composition of the Sidney Wood crucibles and furnace fragment is significantly different to the fully formed glass. It was seen in Section 7.2.3 that there is some uncertainty to whether these crucibles are from Sidney Wood, and this may provide an explanation for these differences.

The fully formed glass (vessel and window) from the Wealden sites exhibited greater homogeneity than the majority of crucible, cullet and waste glass as expected (see Section 2.4.5.2). There appears to be a distinct difference in the homogeneity of different glass types and this will be discussed in Section 8.4.4. It was noted in Section 2.2.2.1 that Wealden oak ash contained similar total alkali and calcium levels to beech ash. The results of the experimental glasses in Chapters 4-6 have shown that small beech ash melts require melting temperatures of 1300°C to produce a homogeneous glass. If the oak ash batches behave in a similar way to beech ash batches it might be suggested that similar melting temperatures would be required to form a homogeneous glass. The furnace temperatures achieved at Blunden's Wood have been estimated at 1200-1300°C (see Section 7.2.1). Therefore based on the results of Chapters 4-6 it might be assumed that to achieve a homogeneous product 1300°C would have been required. However, it was only possible to analyse one sample of vessel glass from Blunden's Wood and further examination of fully formed glass from this site is needed to determine whether this is indicative of the finished products produced at the site.

8.4.2 Little Birches

It was suggested in Section 7.3.1 that the Little Birches glasses would be the most homogeneous of all the archaeological glasses analysed based on the use of ferns as an alkali source and high furnace temperatures. The SEM and EPMA results confirmed that overall, the Little Birches glasses did contain the lowest levels of inhomogeneity. It was expected from the results of the experimental work (see Chapters 4-6) that the glass from the Little Birches South Site might contain the lowest levels of inhomogeneity due to the use of higher furnace temperatures (see Section 7.3.1.2). However, it was not possible to see any apparent differences between the glass from either site. These observations are only based on the examination of a small number of waste glasses and further examination of a wider range of material would be required to confirm this.

The glass obtained from Little Birches was all found in tips near the furnaces (see Section 7.3.1). It might therefore be that the medieval glassmakers were deliberately discarding this glass because it was unsuitable for further working. The results of this Chapter (see Section 8.2) have shown that samples of fully formed glass appear to contain less inhomogeneity than waste glass from the same site. At Little Birches, the low levels of inhomogeneity in the waste glass would suggest that any fully formed glass would contain no or only very low levels of inhomogeneity.

It was seen in Section 8.3.2 that the majority of the homogeneous Little Birches samples contained larger elemental ranges than the inhomogeneous ones. This apparent anomaly in the EPMA results is difficult to explain. However, the very low levels of inhomogeneities present in the Little Birches glasses are not always easy to identify on the backscattered SEM image of the sample (see Section 8.2.2). Therefore it is possible that a number of the EPMA scans of 'homogeneous' Little Birches samples covered areas that contained extremely low levels of inhomogeneity that were not identified on the backscattered SEM image.

8.4.3 Hils

It was suggested in Section 7.5 that the Hils glasses would contain the highest levels of inhomogeneity, and this has been confirmed by the results of the SEM and EPMA analyses in this Chapter. The high levels of inhomogeneity in the Hils glasses were expected, as it was thought that beech ashes were used as the alkali source in these glasses (see Section 7.4). It is interesting to note that the samples from both the 12th/13th and 15th centuries contain inhomogeneities. However, only three 15th century samples were available for analysis. This combined with the paucity of excavated evidence from the glassmaking sites at Hils (see Section 7.4) means that is difficult to assess whether the extent of homogeneity is related to the period of production or the glasshouse where the sample originated.

The majority of the Hils samples are drops and trails of glass and glass waste. The inhomogeneity seen in the glass waste samples is not unexpected (see Section 8.4.4). However, it would be interesting to know which part of the glassmaking process the inhomogeneous glass drops come from. If these are the by-products of glass working (for example the ends of decorative trails, or working waste from the manufacture of vessel and windows), then this may mean that the fully formed glass they relate to contains substantial inhomogeneity as well. Unfortunately there was no comparative material to test this against. The drops may also be test pulls used to determine whether the glass melt was suitable for working (see Section 2.4.3), in which case the high levels of inhomogeneity are therefore not unexpected.

The images and EPMA analyses obtained from the Hils samples show that the majority of the glasses investigated exhibit a significant degree of inhomogeneity (see Sections 8.2.3 and 8.3.1). In most cases the inhomogeneities are present throughout the whole cross section of the glass and in some samples they appear to have been stretched out in the direction that the glass was being worked (G15 and G19). The orientation of inhomogeneities must be considered and will be discussed in Section 8.4.5.

Although there was a distinct difference in the results of glass from the Weald, Little Birches and Hils, it can be seen that in general, crucible or waste glass is more prone to inhomogeneity than fully formed glass. This will be discussed in Section 8.4.4.

8.4.4 Glass Artefact Type and Inhomogeneity

The results of this Chapter have shown that inhomogeneity is more common in crucible or waste glass fragments than in window or vessel glass. It is perhaps not surprising that the fully formed glass is predominately homogeneous, as the presence of major inhomogeneities might prevent successful working and annealing (see Sections 2.5 and 2.6). Artefacts that broke in the annealing process would probably have been recycled as cullet and therefore may be less likely to be found in the archaeological record. The results of the Knightons material show that the moil fragments analysed (K12-14), are more homogeneous than other samples of cullet (such as unidentified lumps of glass). However, only a comparatively small amount of cullet was analysed and therefore the difference in homogeneity may be due to a sampling bias.

It was seen in Chapter 7 that high refractory fabrics were used to produce glassmaking crucibles at all of the sites selected for this research. The use of crucibles with good refractory properties will reduce the level of inhomogeneity caused by ceramic corrosion. However, molten glass is extremely corrosive (see Section 2.4.5.1) and therefore the majority of the crucible glasses analysed in Section 8.2 contain a number of inhomogeneities that occur at the glass/crucible interface (for example BW5 (Plate 8:4) and SW4 (Plate 8:16)). In a number of samples these inhomogeneities can be observed to extend outwards into the bulk of the glass (for example BW6 and 8).

Thermal and diffusion currents will distribute any inhomogeneities formed by ceramic dissolution throughout the glass melt. The rate at which this homogenisation occurs will depend on many factors such as the position of the heat source, melt temperature and time, glass composition and the heat transfer properties of the crucible fabric (see Section 2.4.5.1). The relatively large melt sizes of the glass analysed (see Sections 7.2-7.4) may mean that it is unlikely that crucible dissolution will significantly alter the bulk composition of the glass. However, if extended melting times were used, this may be difficult to ascertain.

It is therefore likely that the incidence of inhomogeneities will increase in glass removed from nearer the bottom of the melt. However, it has been seen that the majority of the fully formed glass is homogeneous. One reason for this may be that the glass at the bottom of the crucible was never utilised. For example, Crossley (1972: 432) suggests that the medieval glassmaker is likely to have deliberately avoided glass at the bottom of the crucible in order to avoid contamination with unwanted inclusions that would impair the quality of the glass.

Although the glass at the bottom of the crucible may have been avoided in medieval glassmaking (see Section 2.4.5.2), the majority of excavated crucible fragments only contain a thin (approximately 1cm or less) layer of glass. This is apparent in the crucible glass samples from this Chapter. Although this glass is unlikely to be representative of the bulk of the glass originally in the crucible (Mortimer in Welch (1997: 38)), the high incidence of inhomogeneity in this type of samples should still be noted as it will influence compositional analysis in glass from crucibles.

In comparison to the crucible fragments, the inhomogeneities in waste glass samples tend to be distributed more evenly throughout the whole of the glass. However, it can be seen that where there are inclusions within the glass sample, as in BW14, the level of inhomogeneity will be higher in that area. Depending on the source of the glass waste these inclusions may have been picked up from a variety of places, such as rocks or earth picked up from around the glass site, glass scum or waste crucible and furnace fragments. The inhomogeneity around the inclusion is caused by the corrosive nature of molten glass, which will attack these features altering the composition of the glass (see Section 2.4.5.1). In addition to these observations, it should be noted that the visual appearance of the glass samples does not appear to relate to the levels of homogeneity observed and the presence of opaque regions in the glass cannot be directly related to inhomogeneity.

8.4.5 Orientation of Inhomogeneities

It was suggested in Section 1.5 that inhomogeneities are likely to align in parallel with the glass surface and that this can have a significant effect on compositional analysis. The backscattered SEM imaging of the medieval glasses in Section 8.2 has shown that the majority of the crucible glass samples have inhomogeneities that are aligned with the glass surface and crucible wall. This is perhaps not surprising due to the refractory dissolution occurring at the crucible/glass interface (see Section 8.4.4). In contrast, the waste glass samples contain randomly orientated inhomogeneities and the glass drops from Hils exhibit inhomogeneity in both parallel and random orientations to the glass surface. The only sample of fully formed glass containing inhomogeneity visible under the SEM was G20 (see Section 8.2.3). Although Plate 8:25 shows that the inhomogeneities present are in parallel alignment, G20 was too thin to be mounted in cross section. The surface visible in Plate 8:25 represents a plane section of the glass. Therefore, in this sample, the inhomogeneities are not aligned in parallel to the glass surface. However, the lack of inhomogeneous window or vessel glass fragments in the samples analysed here, means that it is difficult to assess whether this is a general or unusual occurrence.

The results from this Chapter have confirmed that when using analytical techniques that require polished sections of samples (such as EPMA, see Section 1.5) care must be exercised when examining glass that is prone to the parallel alignment of inhomogeneities (such as crucible glass). However, it was seen in Section 1.5 that as well as the orientation, the size of inhomogeneities will also significantly affect compositional analysis. This will be discussed in Section 8.4.6.

8.4.6 Size of Inhomogeneities

The results of the backscattered SEM imaging of the medieval glasses in Section 8.2 show that the size of the inhomogeneities can vary from approximately a millimetre in width (for example K20, Plate 8:13), to 10s of microns (for example G9, Plate 8:24). However, the majority of samples contain a mixture of a wide range of sizes (for example G14, Plate 8:24). It was seen in Section 1.5 that the size of inhomogeneities must be considered to ensure that the area analysed is representative of the whole glass. It was also noted that different analytical techniques require different sample sizes and analysis areas, and that some of the most common techniques used to study archaeological glasses require only millimetre sized samples.

The EPMA line scans in Section 8.3 have shown that glass composition can alter significantly over a small sample area (for example less than 1mm^2, see Section 8.3.1). Therefore, in cases where large inhomogeneities are present, a small sample would probably **not** to be representative of the whole glass (see Section 1.5). It is possible to see this effect by examining the backscattered SEM images obtained in Section 8.2. For example, the backscattered SEM image of G14, a visually homogeneous glass drop containing high levels of inhomogeneity is illustrated in Plate 8:33. Each blue box represents a different possible position for a 1mm^2 sampling area. The lighter and darker areas on the image represent areas of different mean atomic number (see Section 3.2.5). The large range of EPMA results obtained from this glass also confirms this (see Section 8.3.1).

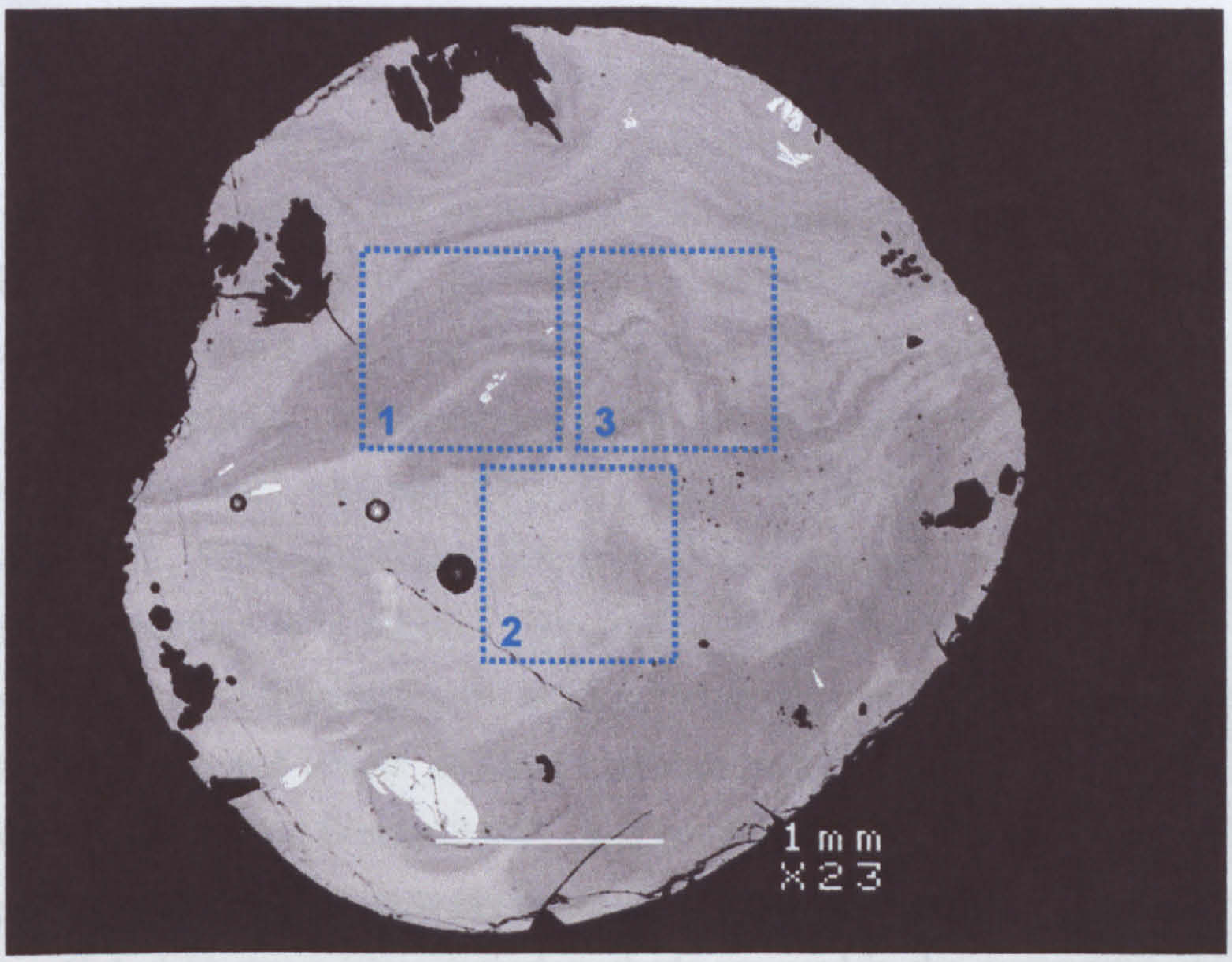


Plate 8:33 Backscattered SEM image of an inhomogeneous glass drop (G14, Table VIII:6) showing how different sampling positions and sizes will contain glass with different compositions

It can be seen that Box 1 is predominantly made up of much darker material, Box 2 of lighter glass and Box 3 is a mixture of the two. Therefore, although they are all from the **same** glass sample, these three regions will have **different** compositions. Depending on the extent of the compositional differences these affects might be cancelled out by using a larger sampling area. However, what is important to remember is that the area **sampled** may be significantly larger than the area actually **analysed** (in many cases only a few microns, see Section 1.5). Therefore a larger sampling area does not necessarily mean that the affects of inhomogeneity will be removed.

What is also important to remember, is that these glasses are **visually** homogeneous and therefore inhomogeneities can **only** be seen using backscattered SEM imaging. Therefore when removing samples for analysis it may be difficult to determine whether the area removed is representative of the whole glass. The effects of this, with respect to different analytical techniques will be discussed in Section 8.4.7.

8.4.7 The Choice of Analytical Technique and the Effects of Inhomogeneity

It was noted in Section 1.5 that the degree to which inhomogeneity influences compositional analysis will be influenced by the analytical technique used to obtain the data. It was seen that this was due to the differences in parameters including sample size, analysis area, and the resolution, sensitivity and precision of different analytical methods. It was suggested that analytical methods that use small sample sizes (a few mm^2), and analysis areas (10's of microns) (such as EPMA, LA-ICP-MS, PIXE, SEM-EDS/WDS, and XRF) would be more prone to the effects of inhomogeneities than others. The results of this research have shown that, if millimetre sized fragments were removed for analysis from an inhomogeneous glass, the compositional results obtained could be subject to a significant bias due to inhomogeneity (see Section 8.4.6). It is possible that different areas from the same glass fragment could potentially be classified as different glasses. Therefore the way in which these types of analytical methods are used in the compositional study of archaeological glass should be carefully considered. Analytical techniques that use a larger glass sample (such as AAS, ICP-AES, ICP-MS, and NAA) may therefore be less influenced by inhomogeneity. However, it has been seen that in many of the glasses analysed in Chapter 8, the size of the inhomogeneities can be relatively large (a few mm or more).

If the sample size is increased to reduce the effects of inhomogeneity, it is still important to consider the size of the area of glass actually analysed. Analytical techniques such as EPMA use analysis areas in the range of 10's of microns across (see Section 1.5). However, as the results from this research have shown, if larger samples are prepared for analysis, and a number of repeat analyses are taken for each sample over the whole sample area, the chances of hitting inhomogeneous regions are increased. Therefore if inhomogeneities were present in the sample, it may be possible to observe this as elemental variation that is larger than expected due to experimental error.

What is not known however, is how large the sample has to be to be representative of the glass. It has been seen in Section 8.4.6 that the size and position of inhomogeneities can vary from sample to sample. Therefore the sample size required will be different for each glass (see Sections 8.2 and 8.3). It was noted that in the archaeological glass analysed the size of inhomogeneities varied from 10's of microns to a few millimetres in size, and that a range of sizes of inhomogeneities could also exist within one sample. Further work is therefore required to determine how wide spread inhomogeneities are in archaeological glass samples, how they can be easily identified (see Section 8.4.8), and whether multi-sampling of material will help reduce the effects of inhomogeneity.

Thus, the orientation of inhomogeneities is particularly important in techniques that look at one surface of the glass, such as analytical SEM and EPMA (see Section 1.5). It has been seen that these techniques are being used increasingly to obtain compositional data from archaeological glasses. A careful sampling strategy is therefore required for fragments of crucible and waste glass, and further work is required to determine whether inhomogeneity forms in a specific orientation in samples of fully formed glass.

8.4.8 The Determination of Inhomogeneity

It can be seen that the backscattered SEM images in Sections 8.2-8.2.3 provide a quick and easy technique to allow the position and occurrence of inhomogeneities to be ascertained. The difference in colour contrast on the image is also a good indicator of the extent of compositional variation within the sample. This is illustrated well in the samples of highly inhomogeneous Hils glass. However, the EPMA results in Section 8.3 have shown that it is not always possible to directly relate the extent of inhomogeneity seen on an SEM image to the extent of compositional variation in the glass. This appears to be a more significant problem in samples that appear to be homogeneous or contain lower levels of inhomogeneity.

For example, the majority of the Hils glasses were observed to be very inhomogeneous using backscattered SEM (see Section 8.2.3). The EPMA analyses of these samples also showed that they contained the largest elemental ranges, as expected (see Section 8.3.1). In contrast, the Little Birches glasses were seen to contain low levels of inhomogeneity or to be homogeneous using backscattered SEM. However, the elemental variation within each of these samples obtained from EPMA analysis did not appear to be related to the extent of homogeneity seen under the SEM (see Section 8.4.2). This is important, as a sample with a 'homogeneous' backscattered SEM image might still contain significant compositional variations. It should be noted that these differences might be caused by a bias in the EPMA results due to the number and position of the analysis points (see Section 8.4.6). It can be seen from Section 8.3.1 that the position of the analysis is paramount, and moving a distance of less than 50μm away from this may cause a significant change in the composition obtained.

The EPMA results have also shown that **many different** glass compositions can exist within a small area in the same glass sample (see Section 8.3.1). This may be one reason why although elemental relationships do occur in a number of inhomogeneous glass samples, they appear to vary depending on the sample and the position of analysis. Section 8.4.4 noted that the presence of inhomogeneity in crucible and waste glasses is common due to the inclusion of refractory corrosion products. It has been seen that the elements that will be most affected at the glass/refractory interface are calcium, aluminium, magnesium and iron. However, the EPMA results show that not all of the samples contain inhomogeneity, and that in some cases the difference in composition is similar to that seen in a homogeneous glass.

The results from the experimental glasses made in Chapters 4-6 suggested that glasses made from alkalis with a higher total alkali and lower calcium content (such as bracken) would be more homogeneous. Glasses made from alkali sources with higher calcium and lower total alkali contents (such as beech and oak) would be more likely to contain inhomogeneities. It was seen that the extent of inhomogeneity observed in the Hils (beech), The Weald (oak), and Little Birches (bracken) glasses is comparable with the expected results predicted from the alkali source. However, the EPMA results show that there does not appear to be a significant difference in the total alkali and calcium levels in the majority of the archaeological glasses analysed in this Chapter. In addition, it is very difficult to relate glass composition to the raw materials used. However, this similarity in composition may suggest that other factors, such as furnace temperatures, are more significant in the formation of a homogeneous glass than the alkali source.

The increased homogeneity seen in the samples of later medieval glass analysed in this Chapter may also be due to a significant increase in furnace temperatures. However, the EPMA results, particularly of the Hils glasses, do suggest that calcium may be more significantly affected by inhomogeneity than other elements. It was observed in Section 1.3 that specific elements, in particular calcium and potassium, are used to group medieval glasses in order to answer a variety of archaeological questions. It can be seen that in the Hils glasses, significantly different calcium values would be obtained depending on the area analysed (see Section 8.3.1). The wide range and distribution of different calcium concentrations mean that if this element was used to discriminate between different sets of glasses it may be possible that samples from the **same** glass would fall into **different** groups. The significance of these elemental variations therefore depends on the compositional tolerances used to differentiate between each group of glasses.

The results of the EPMA analysis in this Chapter has also confirmed that colourants such as cobalt and copper with high atomic numbers are not responsible for the inhomogeneities seen in the backscattered SEM imaging. The results have shown that in general it appears that the extent to which different elements are influenced by inhomogeneity more than others depends on the position and size of the sample, and the area of the sample analysed. The significance of this to compositional studies of archaeological glasses will be discussed further in Chapter 9.

8.5 Overall Summary and Conclusions

The results of the medieval glasses analysed in this chapter can be summarised in the following points:

- A number of medieval glasses contain inhomogeneity that is only visible using backscattered SEM imaging.
- The presence of inhomogeneity in medieval glasses has a significant effect on the elemental composition of the glass.
- Specific glass artefact types such as crucible and waste glass are more likely to exhibit inhomogeneity than fully formed glass. Therefore specific sampling techniques are required for different types of glass artefact.
- The compositional variations observed using EPMA analysis are element and sample specific.
- The size of inhomogeneity is varied and could potentially be greater than the sample size required for analysis. Therefore sample size may significantly alter the composition obtained.
- The position and size of the analysis points will significantly affect the composition obtained.
- Inhomogeneous glasses may contain many different glass compositions within a small area.
- The use of analytical techniques that analyse a minute sample of material, such as XRF, SEM-EDS/WDS, and EPMA may be more prone to the effects of inhomogeneity.
- The identification of the scale and location of inhomogeneities in a glass sample is difficult.
- The use of larger sample sizes, and multi-sampling may reduce the effects of inhomogeneity, and further work is required to determine this.
- Colourants such as copper and cobalt do not appear to be responsible for the presence of inhomogeneity.
- Increased furnace temperature appears to improve homogeneity.

CHAPTER 9

The Effect of Inhomogeneity on Compositional Studies of Archaeological Glass

9.1 Introduction

The significance of inhomogeneity on the compositional analysis of archaeological glass was discussed in Section 1.3. It was established that if inhomogeneities were present in the samples analysed, they may have a significant influence on any compositional groupings formed from the material, and therefore any archaeological inferences made from these groups. The results from Chapter 8 confirmed that inhomogeneity is present in a large number of the medieval glasses analysed in this research. It was seen that there was a significant variation in the elemental differences of these inhomogeneities (see Section 8.3). This Chapter discusses the influence of inhomogeneity on the grouping of data from Chapter 8 (see Section 9.2). These results will then be considered with respect to the compositional study of medieval glass using a number of case studies (see Section 9.3). The broader implications of inhomogeneity with respect to the use of compositional analysis in studies of medieval glass will also be discussed.

9.2 The Effect of Inhomogeneity on the Grouping of Data from Chapter 8

The aim of this Section is to demonstrate the potential influence of inhomogeneity if glass samples are formed into groups based exclusively on similarities in composition. A variety of elements are used as grouping tools in compositional studies of medieval glasses (see Section 1.4). However, the use of alkali ratios (in particular $CaO/(CaO+K_2O)$) is common, as these are the main elements found in plant ash alkalis (see Section 2.2.2.1). Examples of medieval glass studies that use such ratios include Barrera and Velde (1989), Marquis *et al.* (2000), Velde and Barrera (1986), and Mortimer in Welch (1997). The potassium and calcium ratios are usually plotted against the sodium concentration of the glass, and the resulting graph used to group the glass samples analysed. The relationship between magnesium and sodium is also frequently used in conjunction with initial groupings made from the CaO and K_2O ratios. The results from Chapter 8 suggest that magnesium is another element significantly influenced by inhomogeneity. Therefore, the results of the archaeological glasses from Chapter 8 will be considered with respect to calcium, potassium, sodium, and magnesium.

The Hils glasses will be examined first, as they contain the samples with the greatest inhomogeneity and therefore exhibit the largest variations in elemental concentrations (see Section 8.3.1). The ratios of $CaO/(CaO+K_2O)$ for the samples from the Hils glass production sites analysed in Section 8.3.1 are recorded in Table IX:1 and Table IX:2. Figure 9:1 and Figure 9:2 illustrate the spread of compositional data obtained for each of the Hils glass samples when the ratios of $CaO/(CaO+K_2O)$ are plotted against their respective sodium concentrations for each analysis point. The large quantity of data from the Hils glasses means that it is difficult to view all the data on one graph and therefore the samples are split between Figure 9:1 and Figure 9:2.

It can be seen from Figure 9:1 and Figure 9:2, that the two homogeneous glass samples from Hils (G6 and G19) have tightly grouped data points. However, the majority of the Hils glasses exhibit a much wider spread of data, as expected (see Section 8.3.1). Figure 9:2 illustrates most clearly that in a number of the inhomogeneous Hils glasses it is possible to place the data into more than one group. For example, the data for the inhomogeneous glass G13 is clustered into two main areas, highlighted by the red and blue circles in Figure 9:2. If the data in the blue circle is considered, it would appear that on Figure 9:2, G13 has a different composition to the other glasses illustrated. However, if the data in the red circle is considered instead, G13 appears to have a similar composition to G14, G16 and G23. The situation is made more complex as it can also be seen that a number of the data points for G16 group in a separate cluster outside the blue circle, and that one point for G23 is in the middle of a cluster of G17 analyses. It is therefore apparent from these results that it is possible to place a large number of the **inhomogeneous** Hils glass samples into **many different groups** based on their calcium, potassium and sodium contents (see Figure 9:1 and Figure 9:2).

It can also be seen that there are similar difficulties in identifying groups when the magnesium values for the Hils glasses are plotted against their comparative sodium concentrations. The magnesium and sodium values for the Hils glasses are recorded in Table VIII:7-Table VIII:28, and illustrated in Figure 9:3-Figure 9:4.

Figure 9:3-Figure 9:4 illustrate that a number of the inhomogeneous Hils glasses have magnesium values that spread over approximately 1Wt% MgO. The data from the homogeneous samples (G6 and G19) is again in comparatively tight clusters. Therefore, it would also be possible to classify a number of the inhomogeneous Hils glass samples into many different groupings based on their magnesium concentrations.

The ratios of $CaO/(CaO+K_2O)$ for the Little Birches (North and South Site) glass samples analysed in Section 8.3.2 are recorded in Table IX:3. In contrast to the very inhomogeneous Hils glass samples, the results from Chapter 8 determined that the Little Birches glass contained the lowest levels of inhomogeneity of all the archaeological glass analysed. Figure 9:5 illustrates the spread of compositional data obtained for each of the Little Birches glass samples when the ratios of $CaO/(CaO+K_2O)$ are plotted against their respective sodium concentrations for each analysis point. If the graphs of the Hils (Figure 9:1 and Figure 9:2) and Little Birches (Figure 9:5) data are compared, it can be seen that the spread of the data points for the majority of the Little Birches glass samples is **significantly smaller** than those observed in the inhomogeneous Hils glasses. However, a few of the samples (such as LBS4 and 5) have one data point that is an outlier from the main group of analyses, and this is probably therefore not indicative of inhomogeneity.

Figure 9:6 illustrates that the majority of the Little Birches glass samples also contain a smaller spread of magnesium values (Table VIII:29-Table VIII:40), as was expected due to their greater homogeneity. However, LBS2 and 3 also exhibit similar magnesium ranges compared to the inhomogeneous Hils samples. The larger spread of data in LBS3 and the other homogeneous Little Birches glasses compared to the inhomogeneous samples from the same sites is also apparent from Figure 9:5 and Figure 9:6. This result was unexpected and the possible reasons for this anomaly have been discussed in Section 8.4.2.

The ratios of $CaO/(CaO+K_2O)$ for the Wealden glass samples from Blunden's Wood, Knightons and Sidney Wood analysed in Section 8.3.3, are recorded in Table IX:4-Table IX:7. Figure 9:7-Figure 9:9 illustrate the relationship between $CaO/(CaO+K_2O)$ and sodium for these samples. It was noted in Section 8.3.3 that the degree of inhomogeneity observed in many of the Wealden samples is less than that observed in the Hils glasses, but greater than that seen in the Little Birches material. The results illustrated in Figure 9:7-Figure 9:9 confirm this observation. It can also be seen that the analysis points for the homogeneous fully formed glass samples (BW1, K1-11, and SW1-3) are in tighter clusters than the majority of the inhomogeneous cullet, crucible and waste samples.

Figure 9:10-Figure 9:12 illustrate the distribution of magnesium concentrations for the Wealden glass samples plotted against their comparative sodium values (Table VIII:41-Table VIII:81). The results confirm that the majority of the Blunden's Wood and a number of the Knightons and Sidney Wood samples also exhibit a large variation in elemental concentrations for magnesium.

It was noted in Section 8.3.3 that there were a smaller number of analysis points available for the Wealden glass samples. This means that it is more difficult to confirm the differences in composition observed in the samples in comparison to the data from Hils and Little Birches. However, it can be seen that on the basis of the data recorded from a number of medieval glasses analysed in this research, it is possible to place the same sample into more than one compositional group depending on which analysis point is chosen (see Figure 9:1-Figure 9:12). The results from Chapter 8 have also confirmed that this is observed for a number of elements.

It is important to note that in this case the samples are from known archaeological contexts (see Chapter 7), and the presence or absence of inhomogeneity has also been identified (see Section 8.2). However, what has to be considered is how the groupings would be influenced if these factors were not known. Therefore what will be considered in the next section is the way in which compositional data is applied in studies of medieval glass and how the presence of inhomogeneity will affect this.

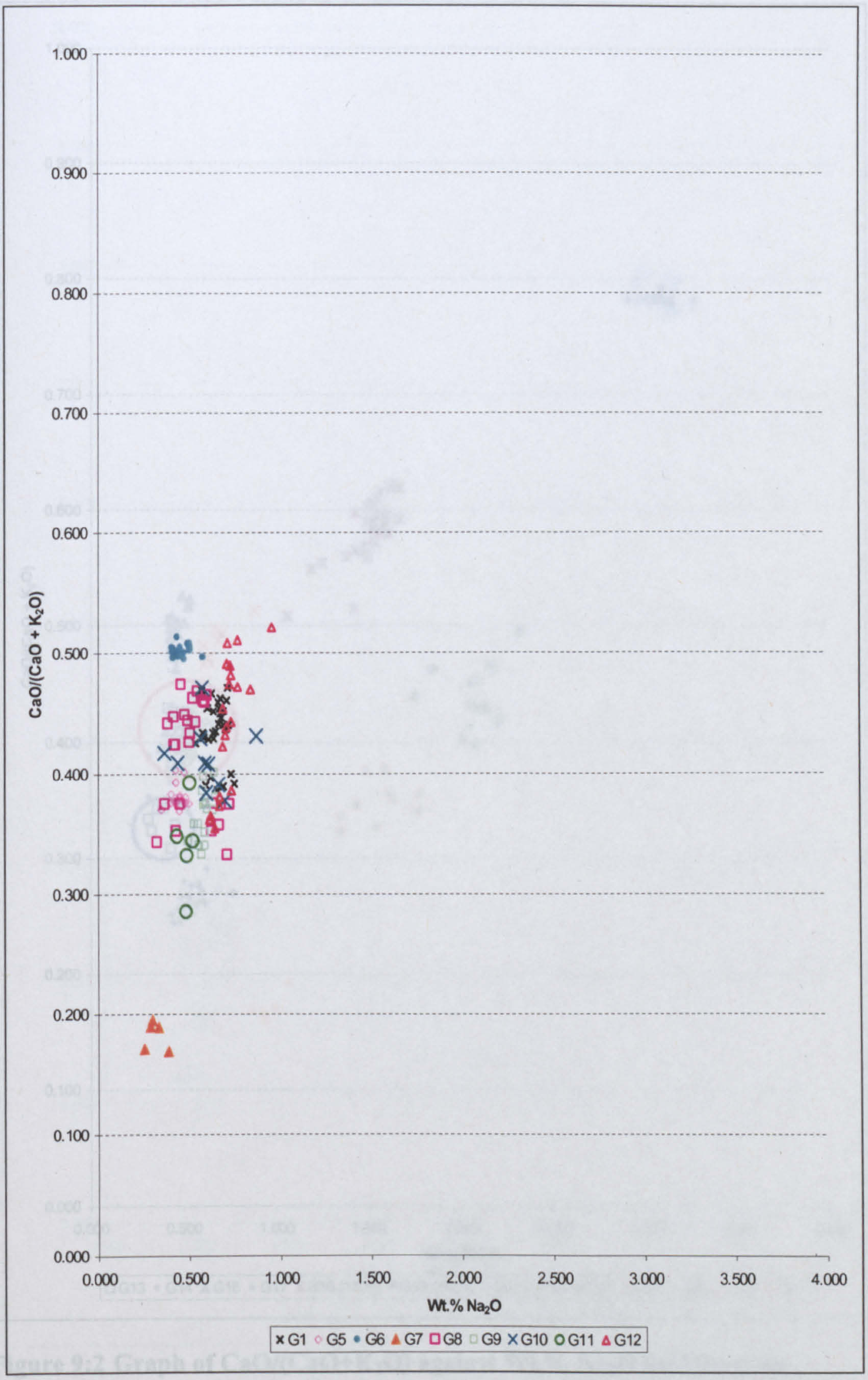


Figure 9:1 Graph of CaO/(CaO+K$_2$O) against Wt.% Na$_2$O for Hils glass samples G1 and G5-12 (Table IX:1)

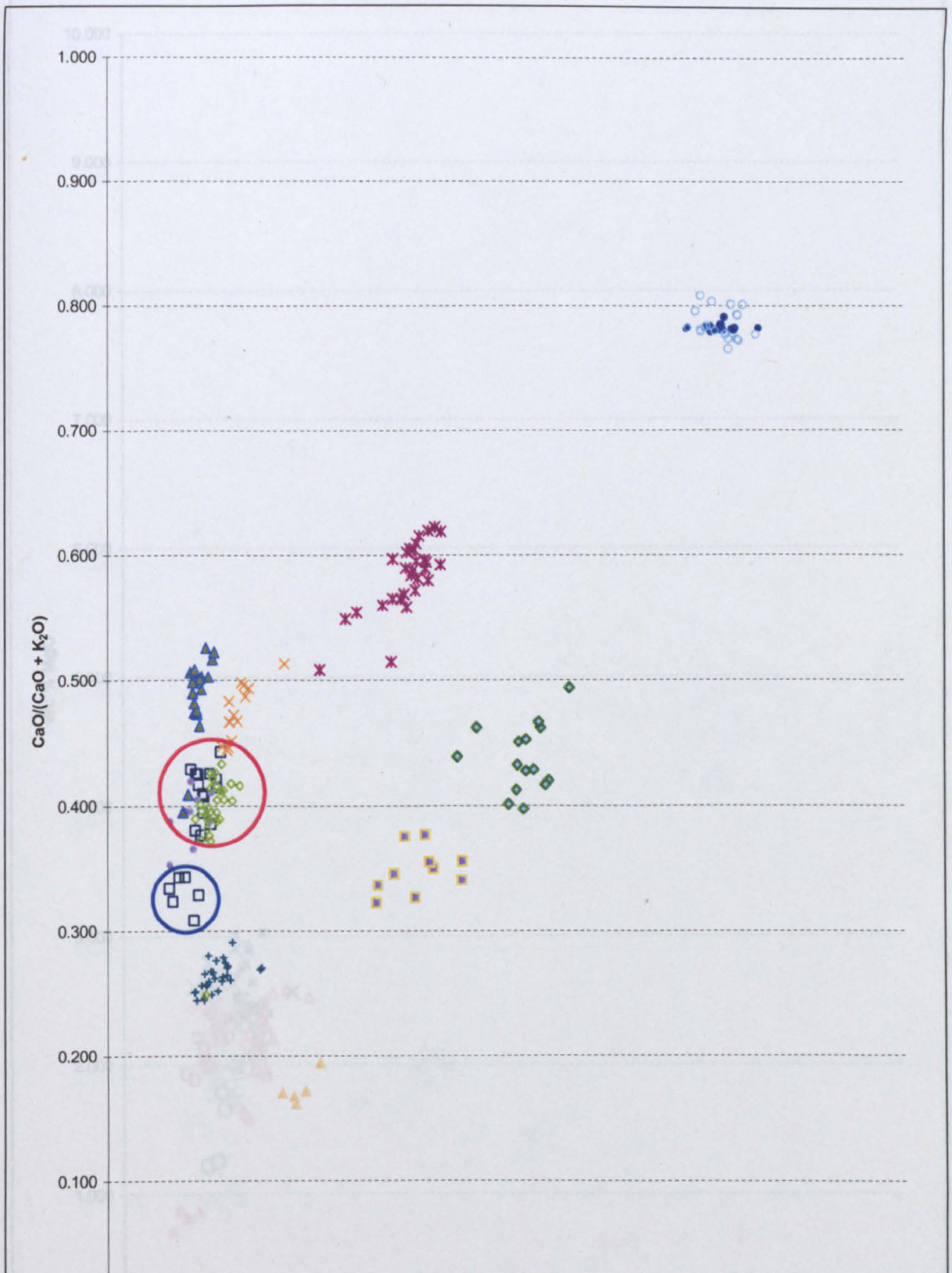


Figure 9:2 **Graph of CaO/(CaO+K$_2$O) against Wt.% Na$_2$O for Hils glass samples G13-14, G16-24 and G27 (Table IX:2). The red and blue circles illustrate the two different groupings that could be made from the G13 data**

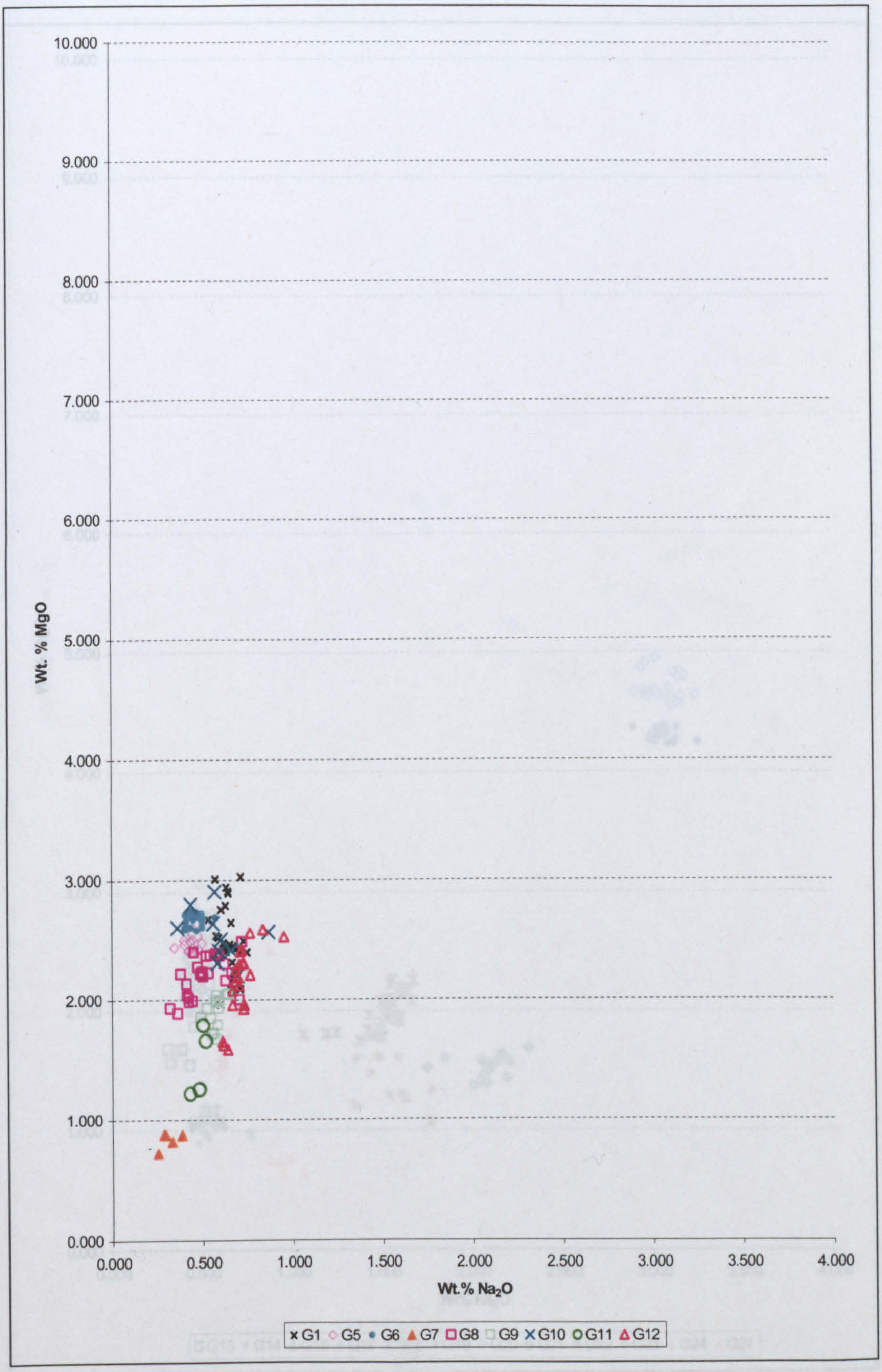


Figure 9:3 **Graph of Wt.% MgO against Wt.% Na_2O for Hils glass samples G1 and G5-12 (Table VIII:8 and Table VIII:10-Table VIII:17)**

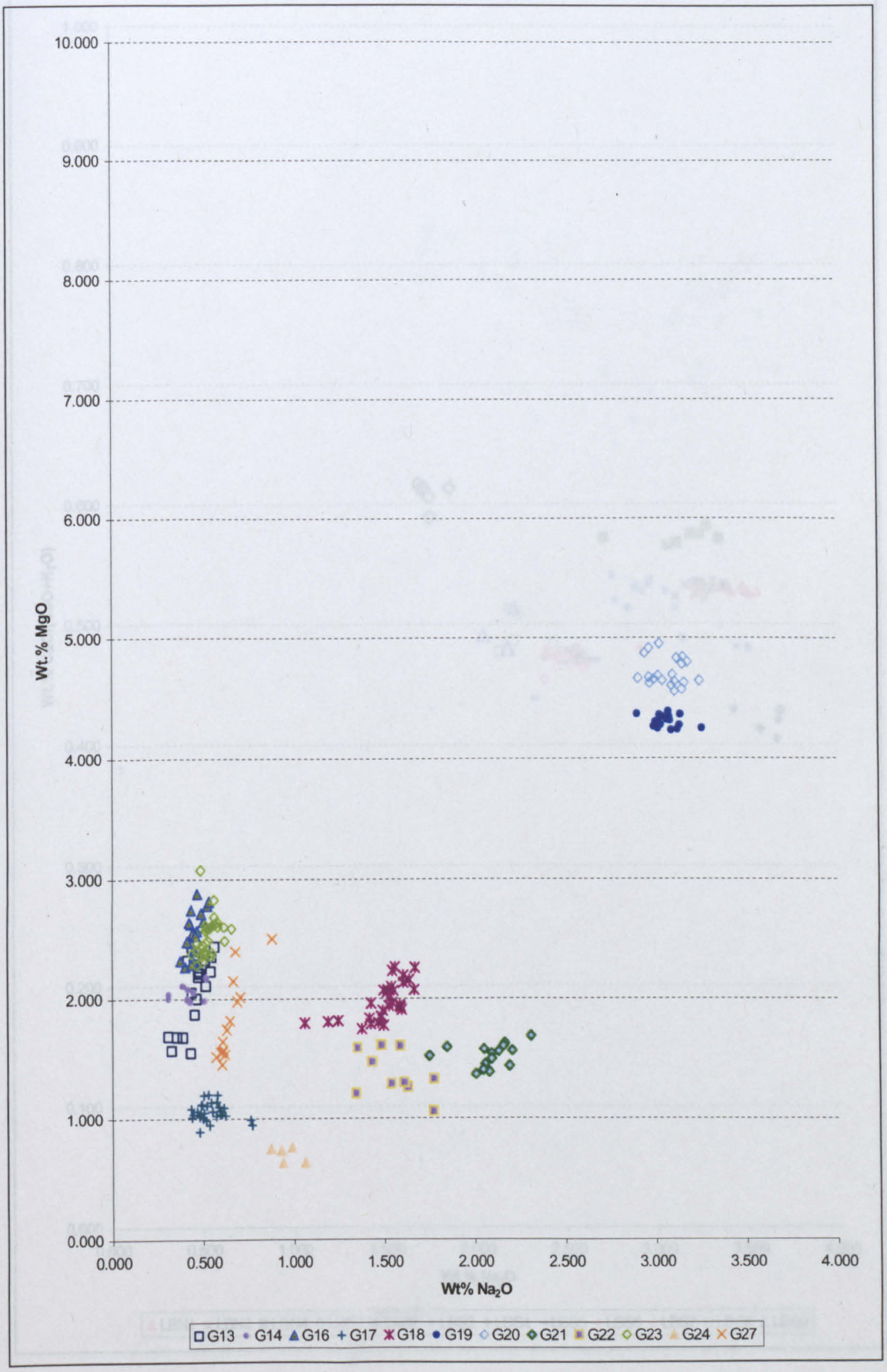


Figure 9:4 Graph of Wt.% MgO against Wt.% Na_2O for Hils glass samples G13-14, G16-24 and G27 (Table VIII:7, Table VIII:18, and Table VIII:28)

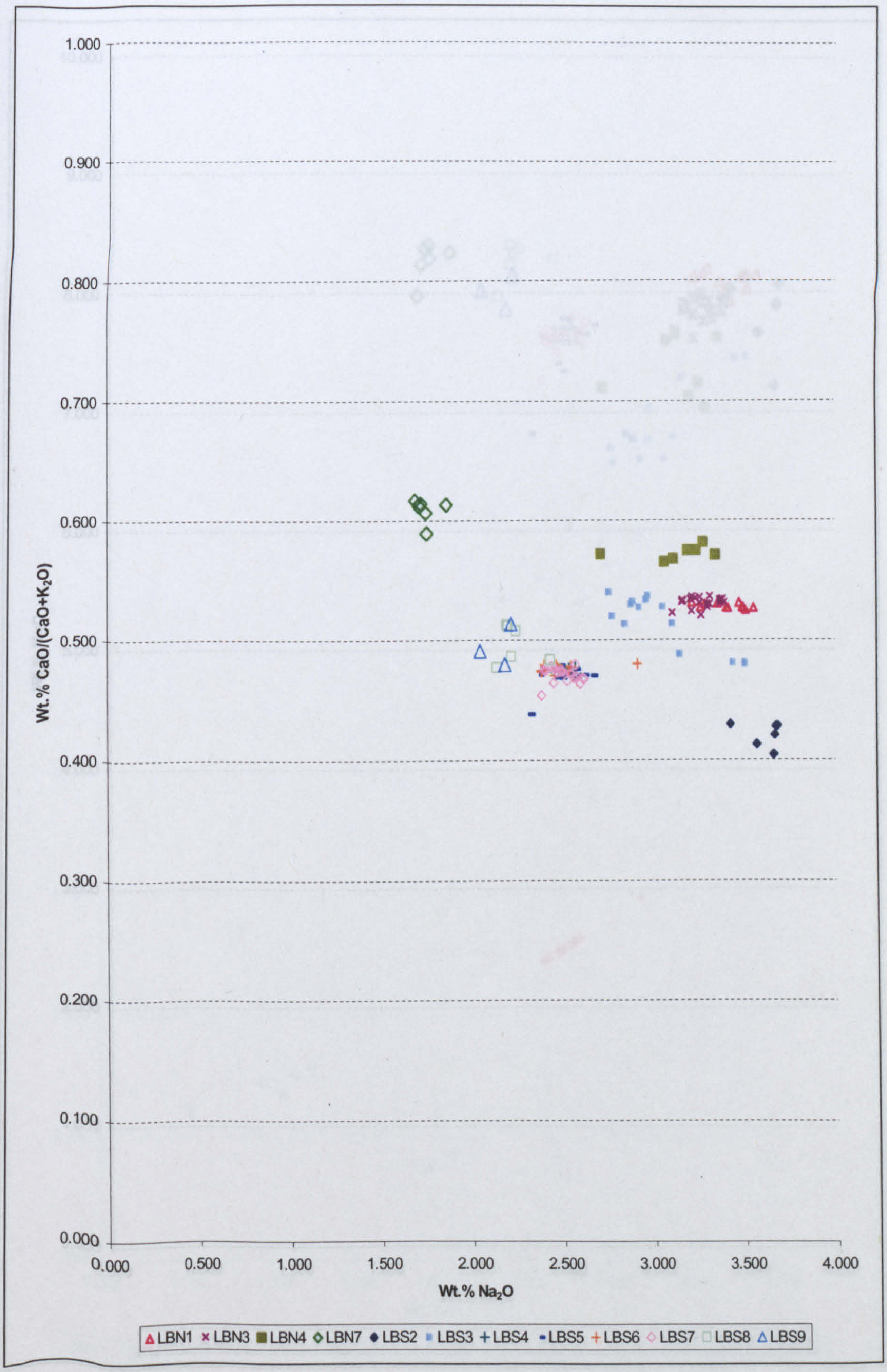


Figure 9:5 Graph of $CaO/(CaO+K_2O)$ against Wt.% Na_2O for Little Birches (North and South Site) glass samples LBN1, 3, 4, and 7 and LBS2-9 (Table IX:3)

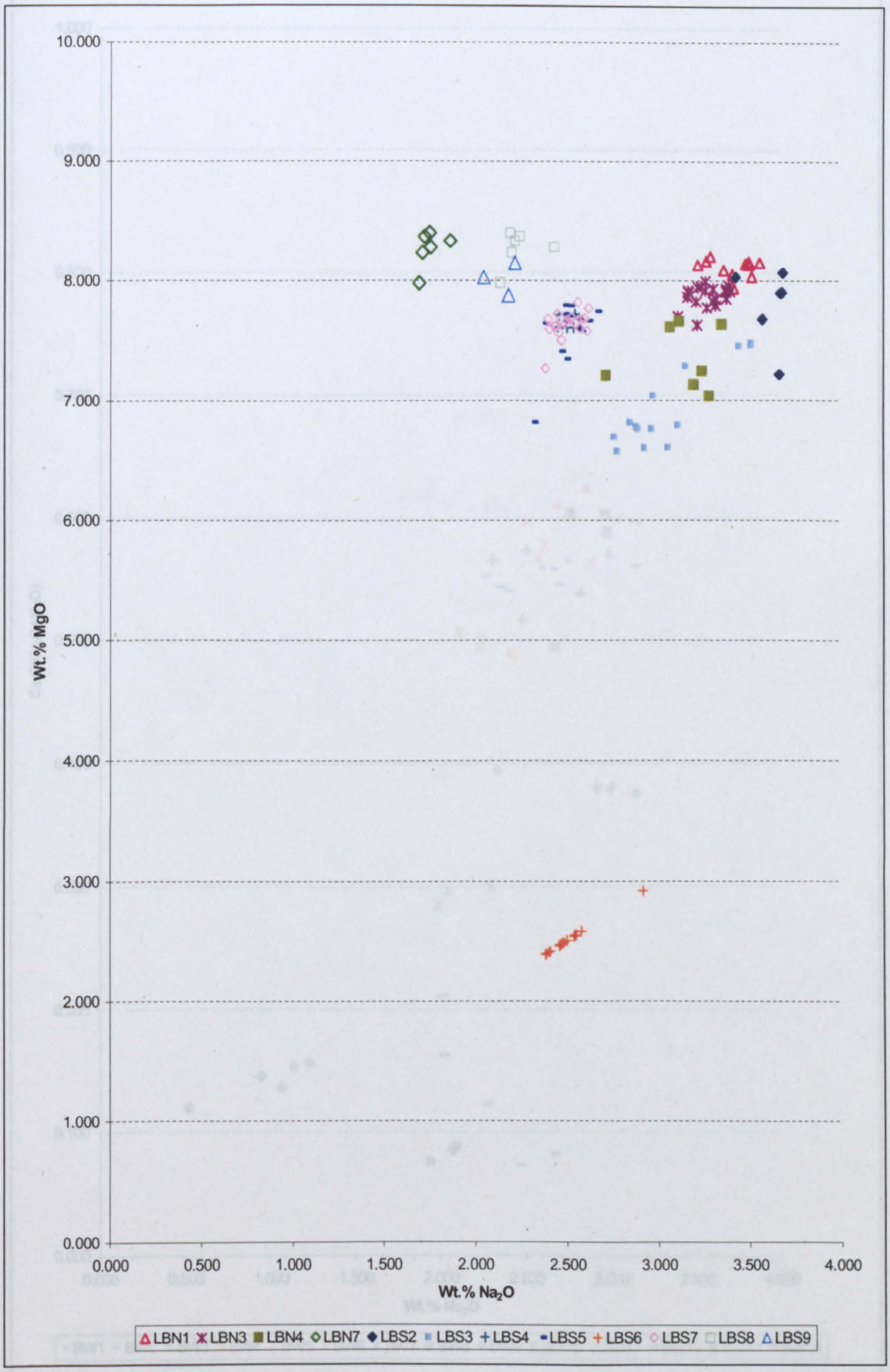


Figure 9:6 Graph of Wt.% MgO against Wt.% Na_2O for Little Birches (North and South Site) glass samples LBN1, 3, 4, and 7 and LBS2-9 (Table VIII:29-Table VIII:40)

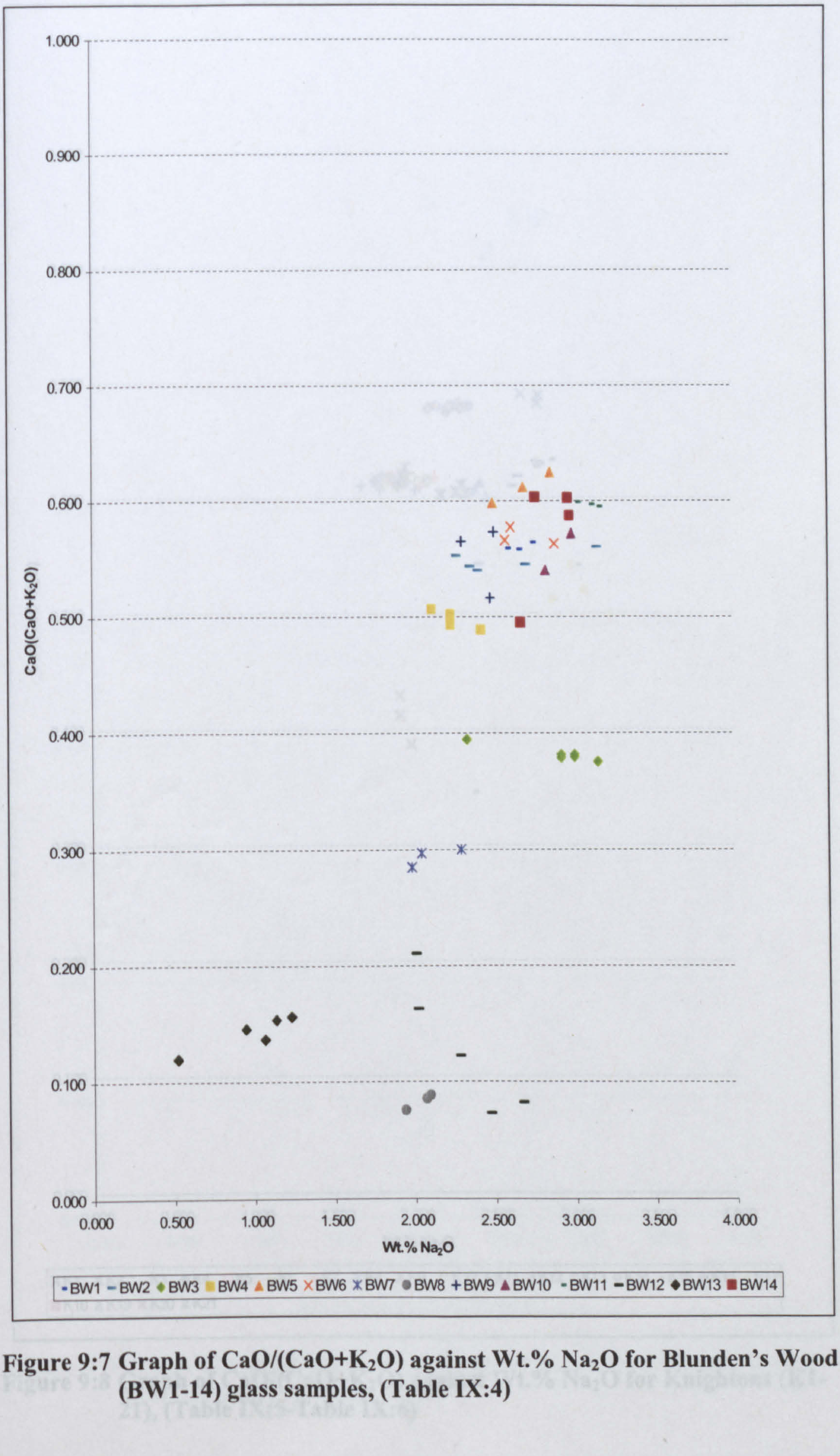


Figure 9:7 Graph of $CaO/(CaO+K_2O)$ against Wt.% Na_2O for Blunden's Wood (BW1-14) glass samples, (Table IX:4)

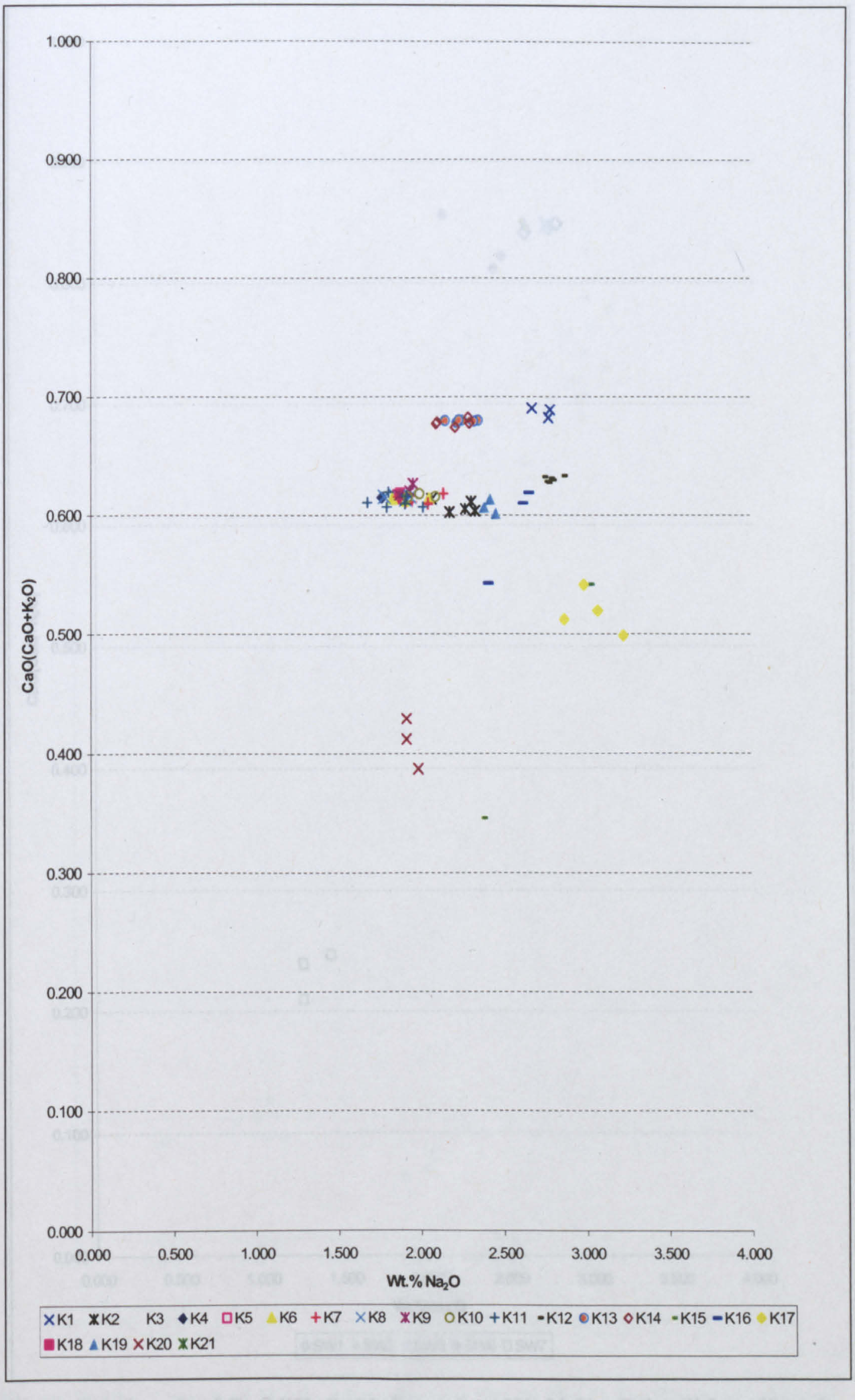


Figure 9:8 Graph of CaO/(CaO+K$_2$O) against Wt.% Na$_2$O for Knightons (K1-21), (Table IX:5-Table IX:6)

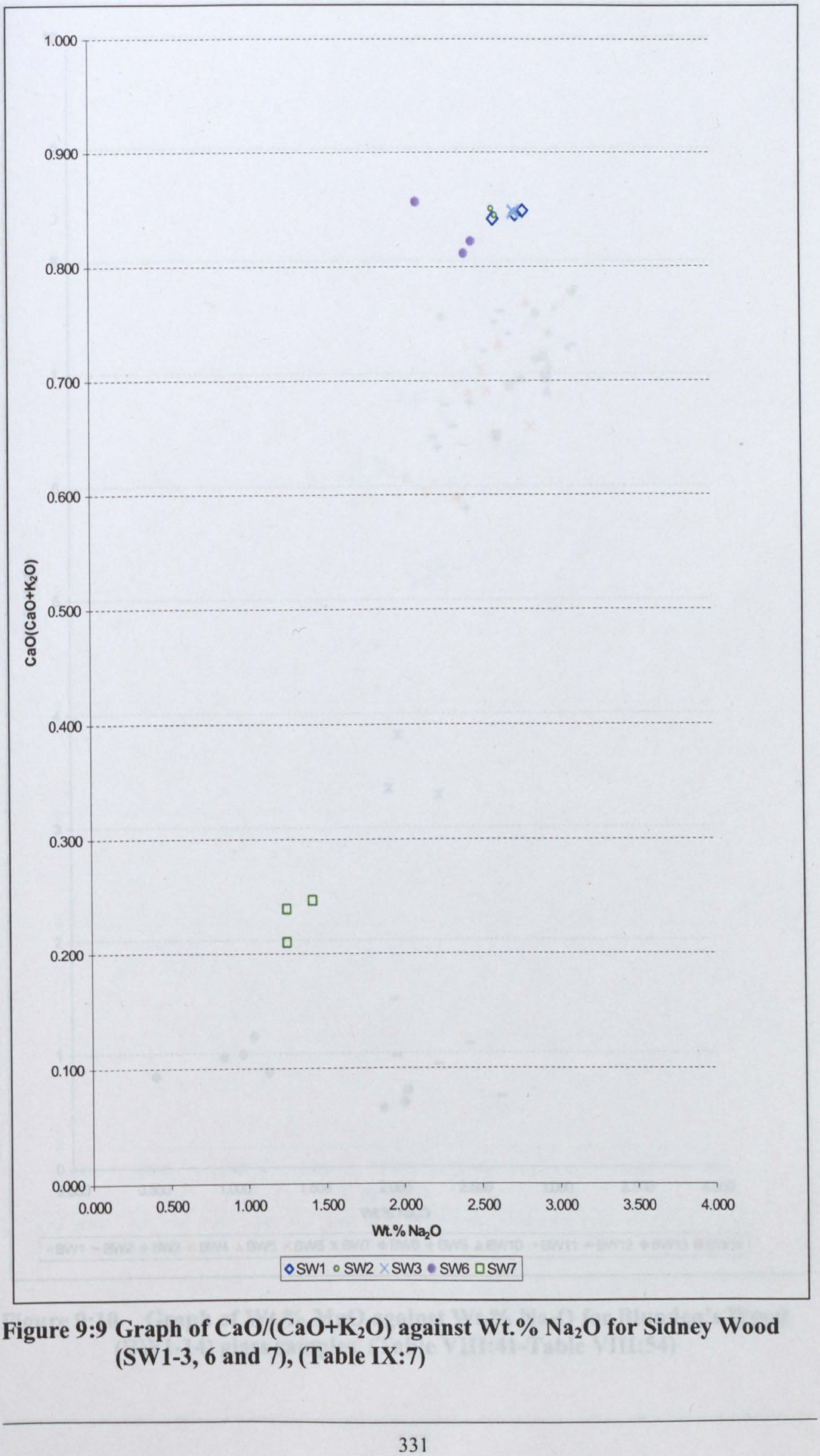


Figure 9:9 Graph of CaO/(CaO+K_2O) against Wt.% Na_2O for Sidney Wood (SW1-3, 6 and 7), (Table IX:7)

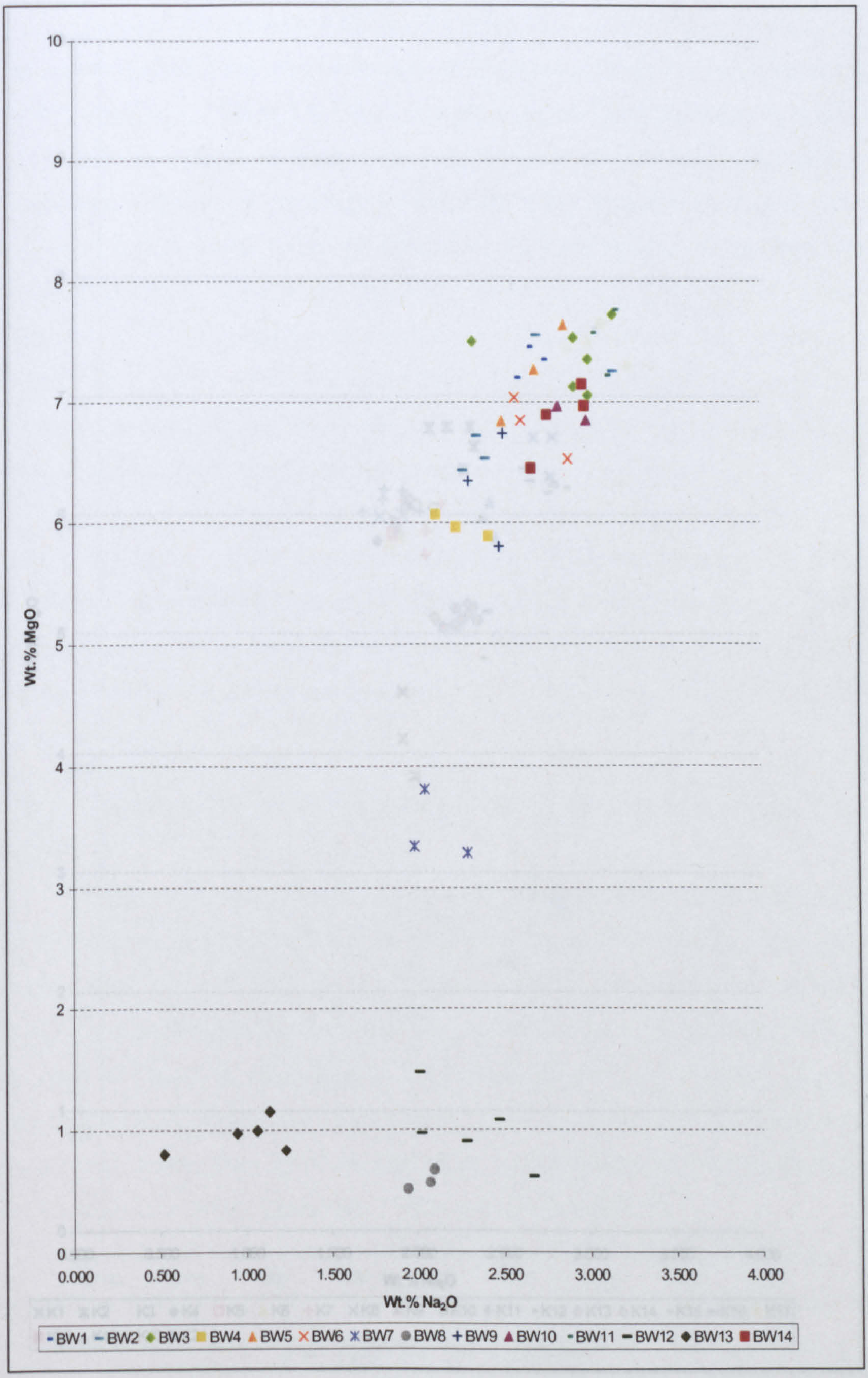


Figure 9:10 **Graph of Wt.% MgO against Wt.% Na_2O for Blunden's Wood (BW1-14) glass samples, (Table VIII:41-Table VIII:54)**

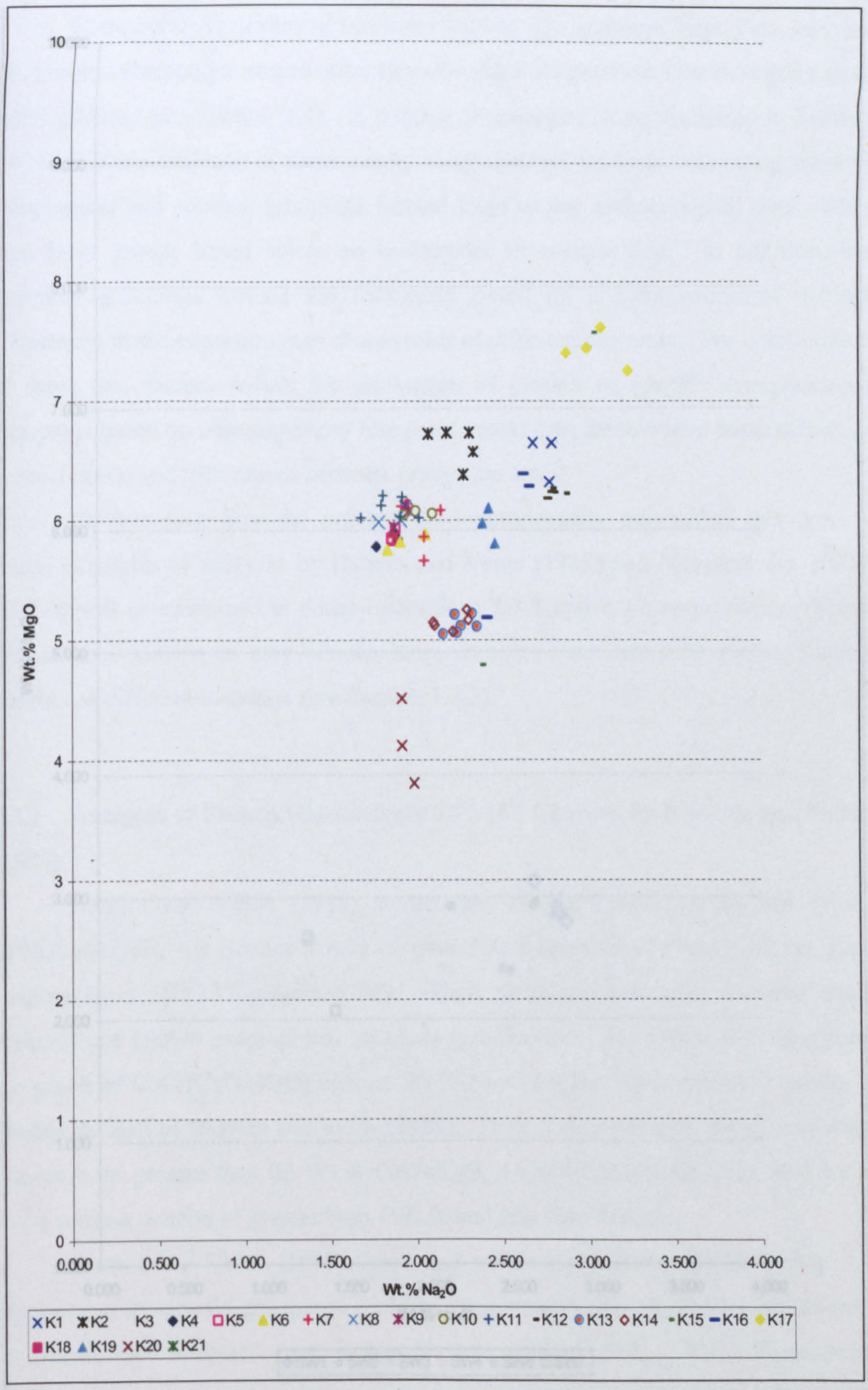


Figure 9:11 Graph of Wt.% MgO against Wt.% Na$_2$O for Knightons (K1-21), (Table VIII:55-Table VIII:75)

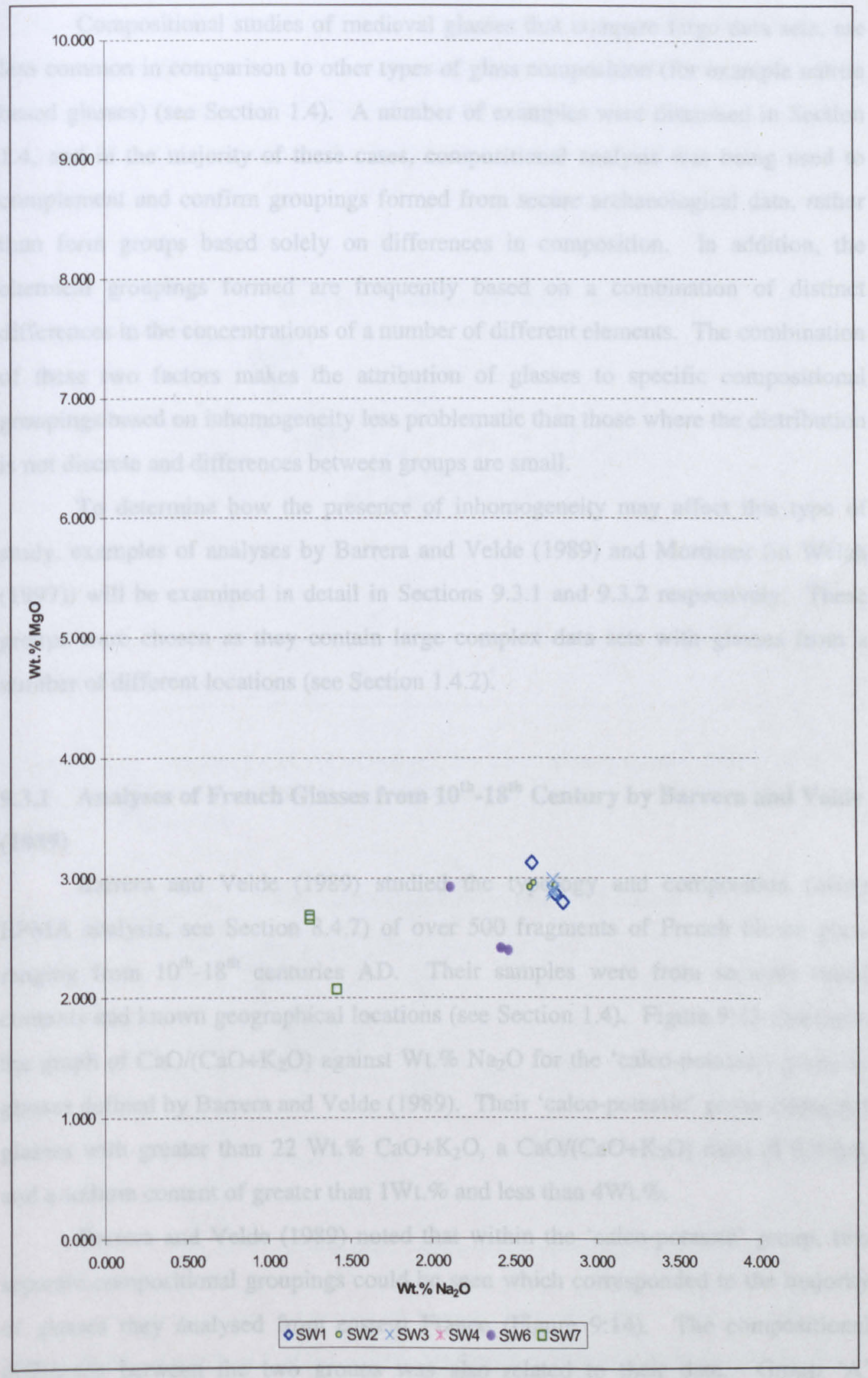


Figure 9:12 Graph of Wt.% MgO against Wt.% Na_2O for Sidney Wood (SW1-4, 6 and 7), (Table VIII:76-Table VIII:81)

9.3 Compositional Studies of Medieval Glass

Compositional studies of medieval glasses that compare large data sets, are less common in comparison to other types of glass composition (for example natron based glasses) (see Section 1.4). A number of examples were discussed in Section 1.4, and in the majority of these cases, compositional analysis was being used to complement and confirm groupings formed from secure archaeological data, rather than form groups based solely on differences in composition. In addition, the chemical groupings formed are frequently based on a combination of distinct differences in the concentrations of a number of different elements. The combination of these two factors makes the attribution of glasses to specific compositional groupings based on inhomogeneity less problematic than those where the distribution is not discrete and differences between groups are small.

To determine how the presence of inhomogeneity may affect this type of study, examples of analyses by Barrera and Velde (1989) and Mortimer (in Welch (1997)) will be examined in detail in Sections 9.3.1 and 9.3.2 respectively. These groups were chosen as they contain large complex data sets with glasses from a number of different locations (see Section 1.4.2).

9.3.1 Analyses of French Glasses from 10th-18th Century by Barrera and Velde (1989)

Barrera and Velde (1989) studied the typology and composition (using EPMA analysis, see Section 8.4.7) of over 500 fragments of French blown glass ranging from 10th-18th centuries AD. Their samples were from securely dated contexts and known geographical locations (see Section 1.4). Figure 9:13 illustrates the graph of $CaO/(CaO+K_2O)$ against Wt.% Na_2O for the 'calco-potassic' group of glasses defined by Barrera and Velde (1989). Their 'calco-potassic' group contained glasses with greater than 22 Wt.% $CaO+K_2O$, a $CaO/(CaO+K_2O)$ ratio of 0.4-0.6, and a sodium content of greater than 1Wt.% and less than 4Wt.%.

Barrera and Velde (1989) noted that within the 'calco-potassic' group, two separate compositional groupings could be seen which corresponded to the majority of glasses they analysed from eastern France (Figure 9:14). The compositional difference between the two groups was also related to their date. Group 'A' corresponding to samples dating from the end of 15th to the end of 16th century, and group 'B' to earlier dated glass (13th to the first half of the 15th century) (Figure 9:14). It can be seen from Figure 9:14 that in these groupings, the smallest cluster, Group 'A', ranges over an area of approximately 0.1CaO/(CaO+K_2O) and 0.5Wt.% Na_2O. The difference in CaO/(CaO+K_2O) ratios between the group 'A' and 'B' is less than 0.1, and the sodium the levels overlap slightly for the two groups (see Figure 9:14).

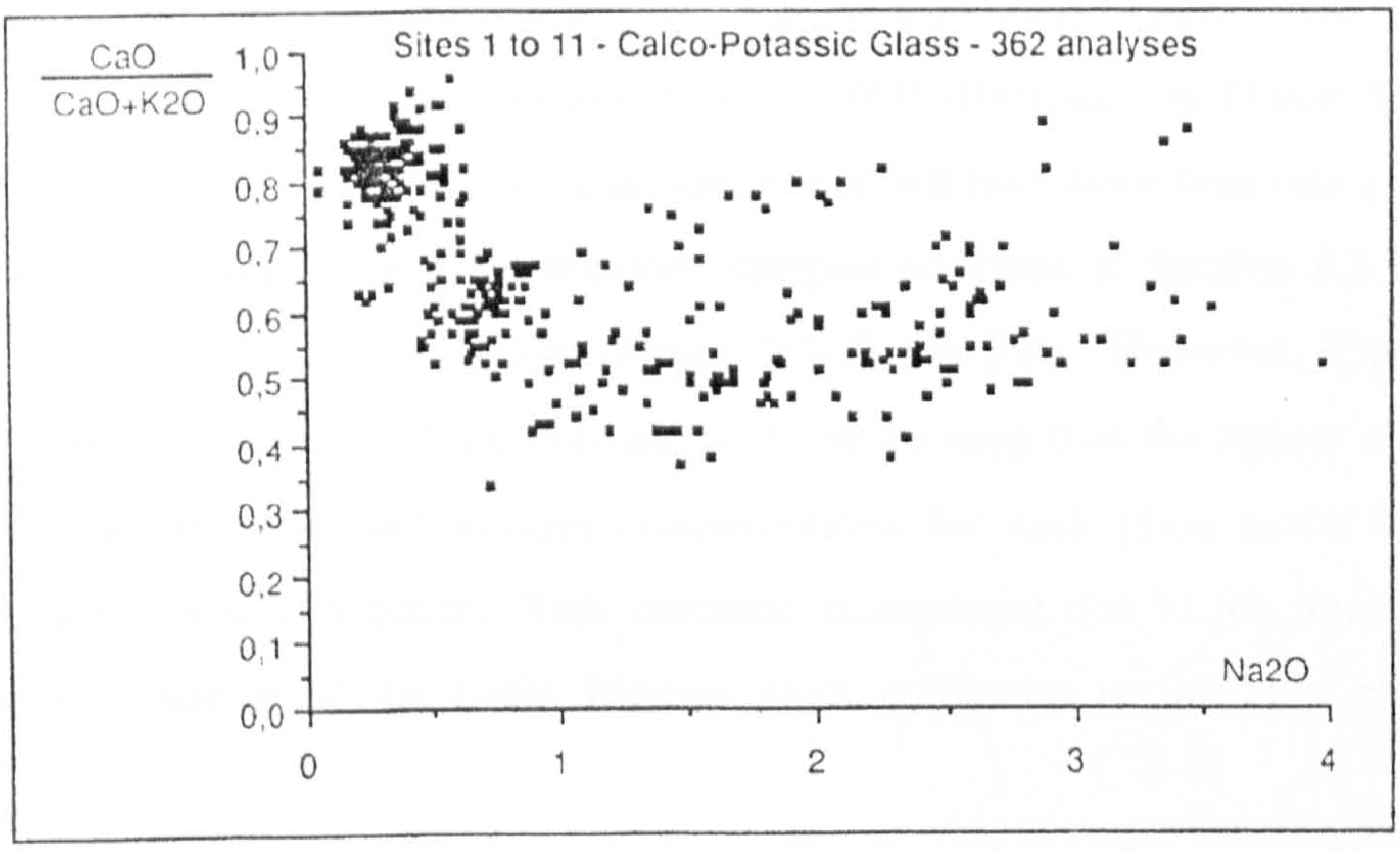


Figure 9:13 Graph of CaO/(CaO+K_2O) for the 'calco-potassic' group of 10th-18th century French glass analysed by Barrera and Velde (1989: Figure 10)

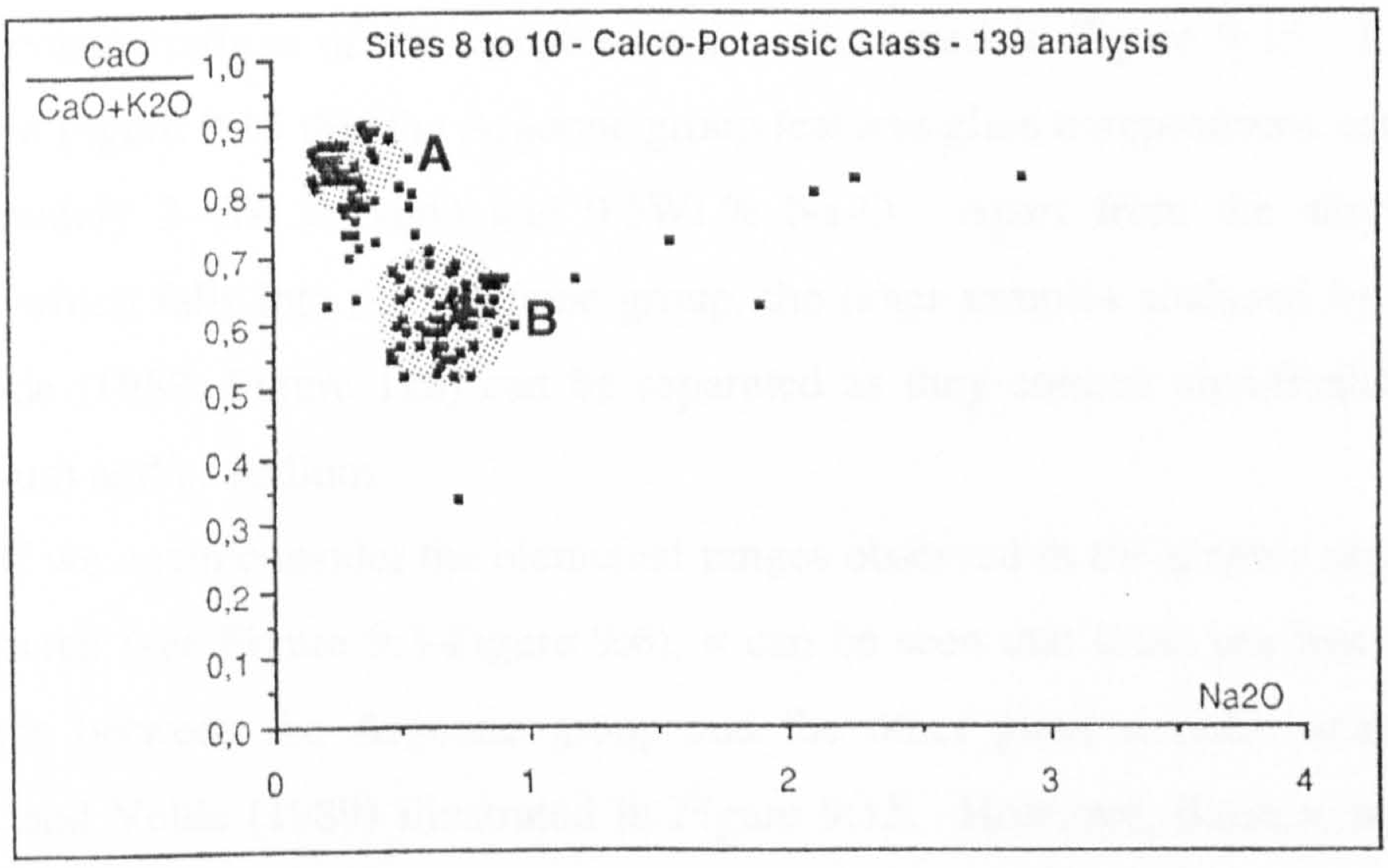


Figure 9:14 Graph of CaO/(CaO+K_2O) for glass from eastern France in the 'calco-potassic' group, after Barrera and Velde (1989: Figure 11)

If we consider the results of the archaeological glass analysed in this research (see Section 8.3). It was seen that a number of the inhomogeneous Hils glasses exhibited a spread of CaO/(CaO+K_2O) ratios of greater than 0.1 **within** the same sample (see Section 9.2). For example, the maximum and minimum CaO/(CaO+K_2O) values for G13 are 0.442 and 0.309 respectively (Figure 9:2, Table IX:2). A number of Hils samples also exhibit large variations in sodium contents (see Section 8.3.1). Therefore, if the Hils glasses analysed in this research were classified using a similar spread of CaO/(CaO+K_2O) ratios and sodium concentrations as those in Barrera and Velde (1989) illustrated in Figure 9:13 and Figure 9:14, it is possible that glass samples would fall into more than one grouping. A number of the inhomogeneous Wealden samples analysed in Section 8.3.3 would also be subject to the same problem (Figure 9:7-Figure 9:9). However, if the Little Birches glasses in Figure 9:5 are considered it can be seen that the tighter cluster of CaO/(CaO+K_2O) ratios and sodium concentrations for each glass mean that it is unlikely that this would occur. This outcome is expected due to the overall more homogeneous nature of the Little Birches glass compared to the Hils glass (see Section 8.4).

Barrera and Velde (1989) (see above, Figure 9:13 and Figure 9:14) note that the composition of samples from a glasshouse in Argonne can be distinguished from the other 'calco-potassic' French material they analysed from the 13th to the first half of 15th century. This is done on the basis of differences in the magnesium and sodium concentrations of the samples, and is illustrated in Figure 9:15. It can be seen from Figure 9:15 that the Argonne group features glass compositions containing approximately 3-4Wt.% MgO and 0.5Wt.% Na_2O. Apart from the single glass sample, which falls into the Argonne group, the other samples analysed by Barrera and Velde (1989: Figure 12a) can be separated as they contain significantly more magnesium and/or sodium.

If we again consider the elemental ranges observed in the glasses analysed in this research (see Figure 9:3-Figure 9:6), it can be seen that these are less than the difference between the Argonne group and the other glass samples analysed by Barrera and Velde (1989) illustrated in Figure 9:15. However, Barrera and Velde (1989) also found that the samples of later (end of 15th to end of 16th centuries) Argonne glass they analysed formed a specific group within other samples of French glass from the same period (Figure 9:16). It can be seen from this graph that the spread of glass analyses is much wider and that there are samples that fall in close proximity to the Argonne group. Therefore in this case, the elemental variations in the magnesium values, observed in the Hils, Wealden, and Little Birches samples (Figure 9:3-Figure 9:6), might place these glasses either within or outside the Argonne group.

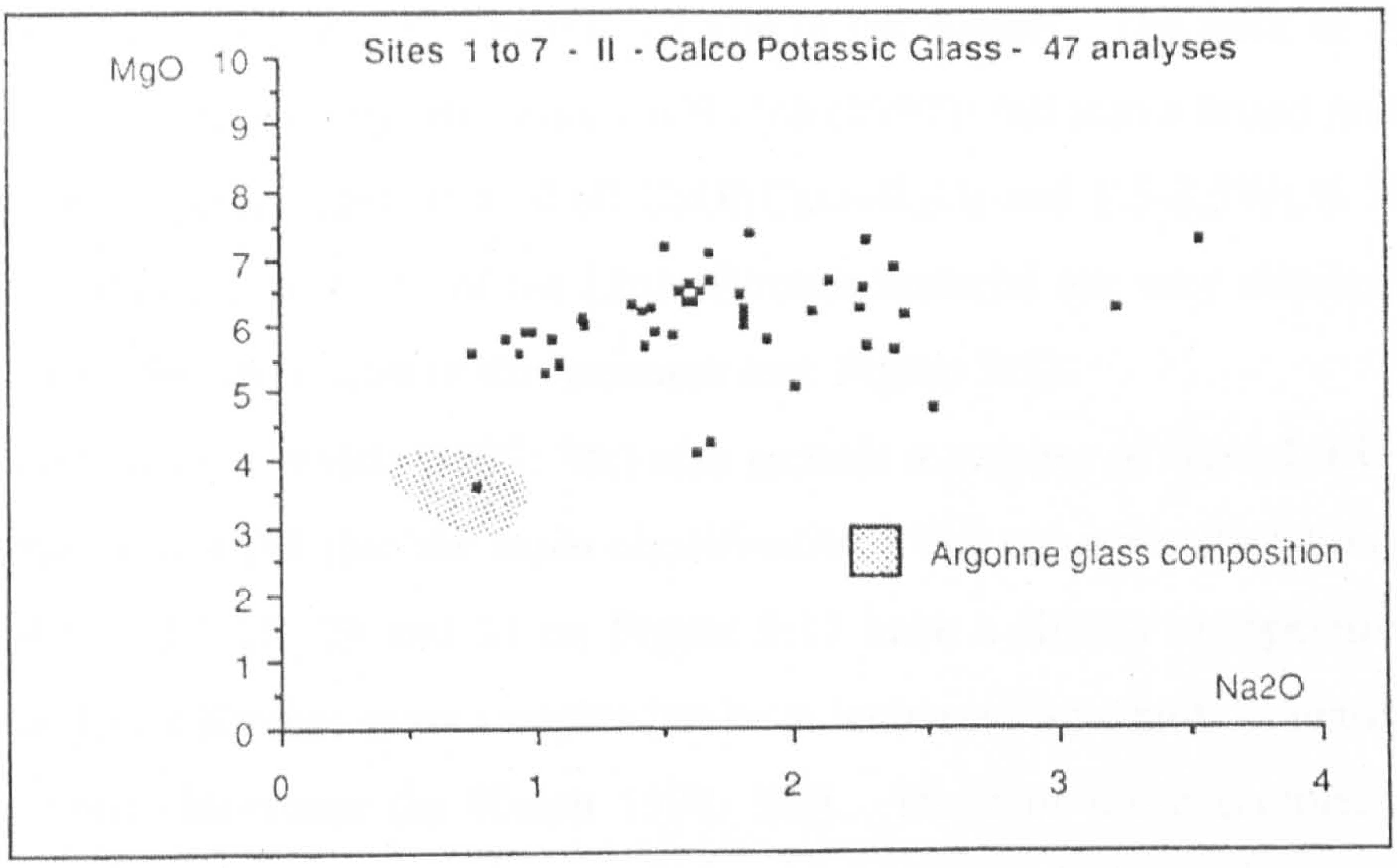


Figure 9:15 Graph of Wt.% MgO against Wt.% Na_2O for French medieval glasses from 13th to mid 15th century in the 'calco-potassic' group, after (Barrera and Velde 1989: Figure 12a)

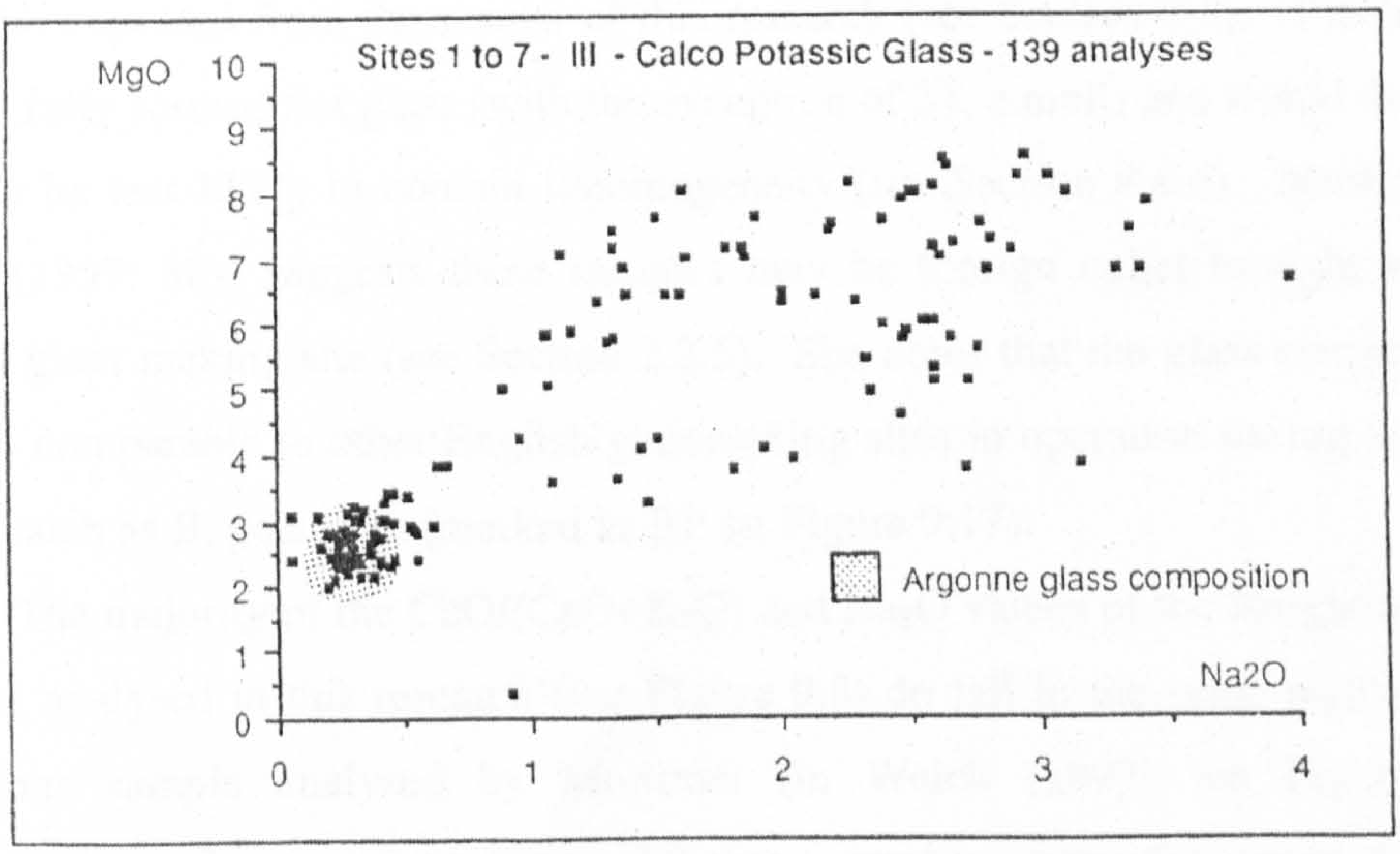


Figure 9:16 Graph of Wt.% MgO against Wt.% Na_2O for French medieval glasses in the 'calco-potassic' group dated between the end of 13th to the end of 15th century (Barrera and Velde 1989: Figure 12b)

9.3.2 Analyses of Glass from English Medieval Glassmaking Sites by Mortimer (in Welch (1997))

Mortimer (in Welch (1997: Figure 18)) analysed glass samples from Little Birches and other comparative English glassmaking sites, including Knightons (see Section 1.4). She used a plot of $CaO/(CaO+K_2O)$ against Wt.% Na_2O to attempt to highlight any compositional relationships between glass samples from known production sites. Figure 9:17 illustrates some of her results. The bulk of the Little Birches glasses analysed by Mortimer (in Welch (1997)) fall into a broad main group ranging from approximately 0.45-0.60 $CaO/(CaO+K_2O)$ and 1.5-3.5Wt.% Na_2O. It can be seen that the analyses of the Little Birches material are very similar to those obtained from the same sites in this research (see Figure 9:5).

Mortimer (in Welch (1997: 38)) also records a number of other Little Birches glasses that do not fall into the main classification. For example, the glass samples numbered 9.3, 27, 28, 29 and 31 on Figure 9:17 have a similar composition to the bulk of the Little Birches glass samples but have increased lime and decreased potash concentrations (Mortimer (in Welch 1997: 38)). Three of these samples are also typologically distinct from the rest of the Little Birches glass and have higher aluminium and lower magnesium contents than the bulk of the Little Birches glass analysed. These elemental differences could be due to the presence of inhomogeneity but the difference in concentration is probably rather larger than would be expected from the results of this research (see Section 9.2). The samples are also fully formed flat glass (with the exception of 31, a moil) and would therefore possibly be less likely to contain inhomogeneity (see Section 8.4.4). Mortimer (in Welch (1997: 38)) suggests these samples may be foreign cullet brought in from another glass making site (see Section 2.2.5). She notes that the glass compositions are also comparable to other English glassmaking sites in operation during the same period, such as Bagots Park (marked as BP on Figure 9:17).

The majority of the $CaO/(CaO+K_2O)$ and Na_2O values of the Knightons glass samples analysed in this research (see Figure 9:8) do fall in the same region as the Knightons sample analysed by Mortimer (in Welch (1997)) on Figure 9:17. However, it can be seen from Figure 9:8 that a number of the data points from the Knightons samples fall into the main group of Little Birches analyses marked on Figure 9:17. Therefore, on the basis of differences in potassium, calcium and sodium concentrations, it would be difficult to determine distinct groupings for glass from

Knightons and Little Birches. It is also interesting to note the broad spread of sodium values within Mortimer's (in Welch (1997: 38)) analyses, as this was also noted in the Little Birches samples analysed in this research (see Section 8.3.2 and Figure 9:5).

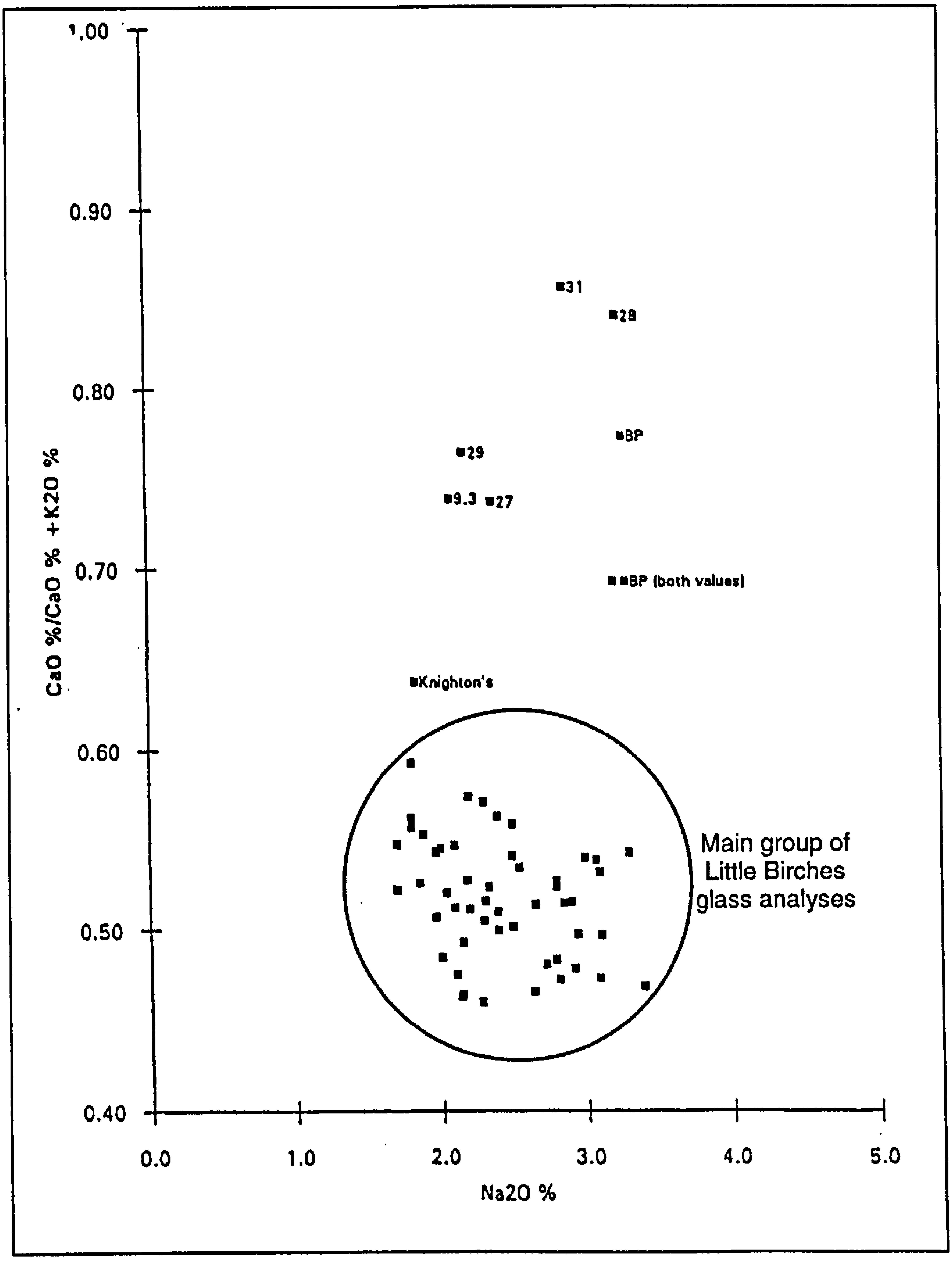


Figure 9:17 **Graph of $CaO/(CaO+K_2O)$ for glass from Little Birches after Mortimer (in (Welch 1997: Figure 18)) (BP=Bagots Park glass, the numbered points refer to possible foreign cullet excavated from Little Birches)**

9.4 Summary and Conclusions

The results of this Chapter have determined that the presence of inhomogeneity can place a significant bias on the analytical data obtained from a glass sample. A number of these elemental differences are significantly larger than those sometimes used to distinguish between published groups of medieval glasses. On the basis of composition alone, it is possible to place an inhomogeneous glass sample into many different compositional groups (see Section 9.2). These results have therefore highlighted the importance of using compositional data obtained from samples with a secure archaeological context. It is also important to note that the results from Chapter 8 determined that a number of other elements exhibited considerable inhomogeneity. This is in addition to the elemental differences seen in the calcium, sodium, potassium, and magnesium values discussed in Sections 9.2 and 9.3. The results of this Chapter can be summarised in the following points:

- Elements that are commonly used as compositional grouping tools for medieval glasses (such as calcium, potassium, sodium and magnesium) are among those significantly influenced by inhomogeneity.
- The presence of inhomogeneity in the medieval glasses analysed in this research can have a significant effect on compositional groupings made from the data.
- The effect of inhomogeneity on compositional studies of archaeological glasses will depend on the elements and elemental variations used to group the samples.
- It is important that compositional groupings of glasses are based on samples from secure archaeological contexts or known typological groups where possible.

It is important to note that this research has focused on potash rich glasses as these were thought to be the most likely to exhibit inhomogeneity (see Section 1.6). However, there are many analytical studies that look at different compositional types of glass, such as mineral alkali or lead based glasses. It is possible that other glass compositions are also influenced by the presence of inhomogeneity. In particular it has been seen that the compositional differences used to distinguish between groupings of sodium based glasses are significantly smaller than those used in potash based glasses (see Section 1.4). Therefore the presence or absence of inhomogeneity in other types of archaeological glass compositions is a subject that needs to be addressed.

The conclusions and further work suggested by the results of this research will be discussed in Chapter 10.

CHAPTER 10

Conclusions and Further Work

10.1 Conclusions

In conclusion, it can be seen that inhomogeneity is a complex issue that has significant implications for the compositional study of archaeological glass. It was seen that each stage of medieval glass production contained a number of variables that would influence homogeneity (see Chapter 2). The laboratory replication of medieval potash based glasses (Chapters 4-6) determined that a number of these variables were dominant factors in the formation of a homogeneous glass. This was also confirmed by the levels of inhomogeneity seen in the comparative medieval glass analysed in this research (see Chapters 7 and 8). The conclusions drawn with respect to inhomogeneity and the medieval glass production process are summarised in Section 10.1.1.

It has been seen that the consideration of the presence of inhomogeneity in medieval glass is of vital importance to compositional studies of this material (see Chapter 9). The conclusions of this research with respect to the compositional study of medieval glass are summarised in Section 10.1.2. Finally, further work suggested by the results of this research will be discussed in Section 10.2.

10.1.1 Inhomogeneity and Medieval Glass Production

The results from the experimental beech and bracken ash glasses produced in Chapters 4-6, have shown that the production of a homogeneous glass is influenced by a complex set of variables. It was seen that altering parameters in batch preparation, fritting and melting does have a significant effect on the compositional homogeneity of the glass produced. However, it was concluded that the dominating factors in the formation of a homogeneous glass, are the use of ash sources with an increased total alkali content, and increased melting temperatures (see Section 6.2). The significant influence of these factors on the homogeneity of medieval glasses were confirmed from the analyses of comparative archaeological material from the Weald and Little Birches, in England, and Hils in Germany (see Chapter 7).

The conclusions relating specifically to each stage of glass production, based on the results of the experimental glasses in Chapters 4-6, are summarised in the following points.

Raw Materials

- Smaller sand grain sizes improve glass formation and therefore homogeneity. However, this has to be balanced against refining time and therefore the quality of the glass desired (see Section 4.6.5.2).
- Mixing the batch will facilitate the production of a more homogeneous glass (see Section 4.6.5.1).
- Batches containing ashes with increased total alkali (sodium + potassium) levels facilitate homogeneity (see Section 6.2).

Fritting

- Lower fritting temperatures and shorter fritting times facilitate homogeneity (see Section 5.5.6.1).
- Mixing the frit prior to melting increases homogeneity (see Section 5.5.6.2).
- Stirring the frit facilitates faster reactions between the raw materials, and facilitates homogeneity (see Section 5.5.6.3).
- Smaller surface area to volume ratio fritting crucible dimensions will increase homogeneity (see Section 5.5.6.4).
- The inclusion of a fritting stage does not always facilitate the production of a homogeneous glass (see Section 6.1.6.4).

Melting

- Increasing melting temperatures will increase homogeneity and will generally cancel out the effects of factors which appear to cause inhomogeneities, such as increased fritting temperatures or times (see Section 5.5.6.5).
- The use of smaller surface area to volume ratio crucibles increases homogeneity (see Section 6.1.6.1).

- Variations in melting crucible dimensions (using CON9, CON7and CYL7 crucibles (see Appendix B)) does not affect homogeneity (see Section 6.1.6.1).
- An increase in melt size within the experimental limits (9-36g total batch weight) does not affect homogeneity (see Section 6.1.6.1).
- Altering the melting crucible fabric (using mullite and alumina) does not affect homogeneity in beech ash glasses (see Section 6.1.6.2).
- Altering the furnace atmosphere does not give a conclusive change in homogeneity (see Section 6.1.6.3).

The results of the experimental glasses produced in Chapters 4-6 also illustrates that different ashes behave in different ways. This suggests that each one (or mixture of several see Section 2.2.2) would require a unique set of fritting and melting parameters. The changes in variables, such as colour, vitrification and batch volume, observed in the production of the experimental glasses, would have all been important indicators to the medieval glassmaker. Without the ability to accurately measure temperatures or control raw materials these factors would have provided an important guide to the reactions occurring.

10.1.2 Inhomogeneity and Compositional Analyses of Medieval Glass

The results of this research have shown that inhomogeneity is present in a number of medieval glass samples and that this will have a significant influence on the way in which it is analysed and the compositional data used. The conclusions made from the analyses of the archaeological glass in this research are summarised below:

- A number of medieval glasses contain inhomogeneity that is only visible using backscattered SEM imaging, including a number of glasses that appear visually homogeneous (see Section 8.2).
- The presence of inhomogeneity in medieval glasses can have a significant effect on the elemental composition of the glass depending on the size of the inhomogeneity and the analytical method used (see Section 8.3).

- Crucible and waste glass samples are more likely to contain inhomogeneity than fully formed glass samples (see Section 8.4.4).
- The presence of inhomogeneities is more likely at a glass/crucible or glass/inclusion interface. Therefore, specific sampling and analytical techniques may be required for different types of glass artefact (see Sections 8.4.4 and 8.4.5).
- The size of inhomogeneity is varied and could be potentially greater than the sample size required for analysis. Therefore sample size may significantly alter the composition obtained (see Section 8.4.6).
- The use of analytical techniques that analyse a minute sample of material, such as EPMA, LA-ICP-MS, PIXE, SEM-EDS/WDS, and XRF may be more prone to the effects of inhomogeneity (see Section 8.4.7).
- The presence of inhomogeneity in the medieval glasses analysed in this research had a significant effect on compositional groupings made from the data (see Section 9.2).
- Elements that are commonly used as compositional grouping tools for medieval glasses (such as calcium, potassium, sodium and magnesium) are among those significantly influenced by inhomogeneity. Therefore, effect of inhomogeneity on compositional studies of archaeological glasses will depend on the elements and elemental variations used to group the samples (see Section 9.3).

The results of this research have shown that the influence of inhomogeneity on the compositional analysis of medieval glasses will depend on the nature of the material analysed, the method of analysis, and the type of analytical data required (see Section 8.4). In conclusion, this research has highlighted the importance of using compositional data from material only with secure archaeological or typological contexts (see Chapter 9).

10.2 Further Work

The experimental beech and bracken glasses produced in this research (see Chapters 4-6) have shown that the formation of a homogeneous glass is a complex process. A number of experimental parameters were constrained by the time and laboratory facilities available. It would be interesting to investigate the effects of these parameters further, in particular, the behaviour of different ash types and the effects of fritting, larger batch sizes, and larger ranges of temperatures and times. Compositional analysis of the experimental glasses produced might also help ascertain the processes occurring in the formation of a homogeneous glass.

It was suggested in Section 8.4.7 that the effects of inhomogeneity might be reduced by the use of larger sample sizes for analysis and multi-sampling. However, further work is required in this area to ascertain the scale and location of inhomogeneities within glass samples. In addition to this, although this research has illustrated that a number of major and minor elements are significantly influenced by inhomogeneity, it is not known how trace elements are affected.

This research has focused on medieval, potash based glasses. The consequences of inhomogeneity in other glass composition types therefore also need to be considered. A number of examples of compositional studies of non-potash based glasses were discussed in Section 1.4. It was seen that the elements used to group these glasses varied depending on the type of archaeological question being asked of the material. What is important to note is that in comparison to the elemental groupings used in medieval glasses (see Sections 1.4 and 9.3), those used to group other types of glasses tend to be appreciably smaller. If inhomogeneity were present in these samples, the effects on compositional groupings would be even more significant. Therefore it is vital that the presence of inhomogeneity is a consideration in compositional studies of archaeological glass.

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