ENGLISH MEDIEVAL GLASS-MAKING TECHNOLGY: SCIENTIFIC ANALYSIS OF THE EVIDENCE

By

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ABSTRACT

This scientific analysis of evidence excavated from glass-making sites, Blunden's Wood (*c.* 1330 AD), Knightons (*c.* 1550 AD) and Sidney Wood (1600 – 1620 AD), has provided further understanding of the technology used to produce 'forest' glass in England between the fourteenth and seventeenth centuries. The influx of immigrant glass-makers into England during this time, especially during the sixteenth century, had a large impact on the English glass industry.

The production of 'forest' glass used ash and sand as the raw ingredients in the glass batch. This work demonstrated that it was possible to determine the correlation between certain components in the glass, and therefore, determine which components entered the batch from the sand, and those that entered from the ash. This work hinted that oak ash was used in preference to beech. In addition to this, it appeared that fritting did take place, from the evidence from Blunden's Wood, at a temperature in the region of 900 °C. This frit was then melted at a temperature that may have been as high as 1300 °C.

The changes in glass technology began to take place during the middle of the sixteenth century, and in the first quarter of the seventeenth century the 'forest' glass industry ceased. The move to coal-fired furnaces, the higher demand for glass and the improvement in quality of glass all contributed to the expansion and migration of the industry that was seen at the start of the seventeenth century.

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CHAPTER ONE

AIMS

The primary aim of this work is to investigate the technology of medieval English glass production. The techniques that the medieval glass-makers were using to produce glass needs to be understood. The techniques have been observed in historical documentary sources, which will be discussed in chapter 2, or from evidence obtained from excavated sites, which will be discussed in chapter 3. The purpose of this work is to attempt to add some substance to the information, in the form of compositional analysis of fragments excavated from a number of sites. The dates chosen for this work are between 1200 and 1620 AD. These dates relate to an era when wood is the source of fuel in the furnaces.

This Medieval period of glass production is dominated by the making of 'forest' glass, a technique that uses plant ash from trees and sand as the main raw ingredients in the production of the glass. The starting date is taken as 1200 AD, which relates to the beginning of a period when glass was being manufactured in the 'forest' glass tradition.

The end date of 1620 AD is generally taken to be post-medieval, so this work deals with the transition from medieval technology into what could nearly be termed pre-industrial.

The region of most importance to 'forest' glass production is the Weald in Surrey and Sussex, which forms the basis for this study. The English manufacture of 'forest' glass is seen to be predominantly in this area, where over forty glass-making sites are thought to have been in operation between 1200 and 1620 AD.

The sites chosen for this work date from the earliest record of an excavated site in the Weald, Blunden's Wood (1330 AD), to one of the latest operational sites, Sidney Wood (1610-1620 AD). A third site, Knightons, fits into these dates, 1550 AD, and has been chosen to represent the time when the influx of immigrant glass-makers may have been taking place. Blunden's Wood and Knightons have been excavated in the last forty years, and the recording of material was extensive. However, Sidney Wood was not investigated to the same standard. Therefore, the reliability of the material from Sidney Wood is harder to guarantee. Having said this, the importance of Sidney Wood, within the context of the manufacture of 'forest' glass cannot be underestimated. It is believed to be one of the last glass-making sites in the Weald that used the techniques of manufacture which were similar to those in 1200 AD.

The archaeologist needs to understand the glass-making technology at a particular time, to compare differences between periods. Technology may progress very slowly before a great advance takes place.

The aim of this work is to ascertain if the technology changes from the beginning of 'forest' glass production in England, to the end.

The possible origin for my observed changes in technology will be discussed. The influx of immigrant glass-makers in the middle of the sixteenth century may be a major cause for changes in methods of glass production. However, this needs to be clarified by comparing the result of the compositions of glasses from the three sites of Blunden's Wood, Knightons and Sidney Wood to other sites. These other sites will be in Lorraine, Normandy or northern Europe, the origin of the immigrant glass-makers. In addition to these comparisons, data from different sources, such as cathedrals and churches will be compared from various regions, again to study similar compositions. This latter comparison may be useful, as the 'forest' glasshouses are seen as the main source of material for ecclesiastical window glass.

Other factors that contribute to the change in glass-making technology will be discussed in chapters 7 and 8. These may include the types of raw materials available, though the location of the exact sources of materials is difficult to determine.

The migration of the glass-makers from the Weald at the beginning of the seventeenth century is to be looked at briefly in chapter 7, by comparing the glass compositions from sites throughout England around this date.

The comparison may highlight the movement of glass-making technology and any differences in the raw materials used to produce the glass. The impact of the change from wood to coal as the source of fuel will be made by comparing glass compositions from different sites.

The quality of the glass will be looked at, firstly subjectively, and secondly by compositional analysis. The quality of the glass is difficult to assess because the material from a particular site may not be representative of the glass which was produced there. Also, the comparisons made between material from glasshouses and windows may only be valid if the material is of similar quality, and if the window glass is from a known source. Reasons for the variability of the quality of the glass will be investigated, and where possible, attempts will be made to show which components enable the formation of a highly durable material.

The material that is to be studied has been taken from collections at The Guildford Museum in Surrey. Samples from the stores were made available, and therefore, may not include the best fragments of glass and crucibles. However, the fragments were chosen on the basis that they best represented the types of glass that were produced on each of the sites. There was a large quantity of glass that had been excavated from Blunden's Wood and Knightons, which allowed for a selection of fragments. As mentioned previously, the recording of samples from Sidney Wood has been more sporadic, and this can be seen in the amount of material available for investigation. A small number of glass fragments were chosen.

Crucible fragments from all three sites were chosen to represent the material from the collection. Where possible crucible fragments with glass adhering to the crucible were chosen.

The glass from Blunden's Wood that is available for analysis consists of fragments of vessel glass. It is unclear where many of the fragments come from in terms of the vessels, as there appears to be no distinctive shape to the fragments. A more detailed description of the glass fragments will be discussed in chapter 4.

The Knightons glass-making site appeared to have been producing window glass, so the fragments of glass from this collection consisted of a number of centres from the 'crown' glass pieces. A more detailed description of the glass fragments will be discussed in chapter 4.

Sidney Wood vessel glass is of great importance to archaeologists, as the quality is superior to most other 'forest' glass. In addition to this the material that is kept in store at Guildford Museum is limited. Therefore, the glass fragments that were taken for study consisted of a few off-cuts of vessel glass, which showed signs of working.

Scientific analysis of glass and crucible fragments from the aforementioned glass-making sites in England will be carried out. The techniques used will include visual inspection, a scanning electron microscope, an electron probe micro-analyser, a x-ray fluorescence spectrometer and a x-ray diffraction spectrometer.

The main tool for compositional identification will be using an energy dispersive spectrometer attached to a scanning electron microscopy, but this form of analysis will be supplemented with the more accurate method of a wavelength dispersive spectrometer within an electron probe micro-analyser. X-ray fluorescence will be used on the glass fragments to determine the composition, which is to confirm the results obtained using both forms of electron microscopy, and to allow the analysis of larger fragments of glass. X-ray diffraction will be used on the crucible materials to identify the phases present in the fired clay, which give an indication of the temperatures wood-fuelled furnaces could reach.

In addition to this a sample of frit from Blunden's Wood will be examined for its phases, partly to determine the validity of the visual identification of frit, but also, to ascertain the fritting temperature.

Scanning electron microscopy will be used to investigate the interaction zone between the glass and the crucible clay, in order to discover the transfer of components from one material to another. This may allow a view of the suitability of the clay for the purpose of glass-making, a prediction of the process temperatures and may enable a greater understanding of the aggressive attack the glass has on the clay. All of this may show the complexity of the medieval glass-making process, and highlight the skill of the glass-makers.

The compositions of glass may allow many details of the medieval glass-making process to be understood better than has previously been seen.

The production of 'forest' glass uses certain raw ingredients, and the analysis of the glass fragments may allow some of the important observations to be made concerning these raw ingredients.

The exact source of the raw materials may be beyond the scope of this study, partly due to the possibility that there may have been a great deal of disturbance and alteration to the ground and vegetation between the date in which the glass-making sites were in operation and today. However, the composition of the glasses from the sites may provide information about the raw ingredients, which will allow the suitability of various sands and ashes to be discussed.

The main aims can be summarised as:

- Investigate the technology of English glass production during the Medieval to Post-medieval Period, defined as 1200 to 1620 AD
- What were the raw materials?
- What temperature was glass melted at?
- Did fritting take place?
- What temperature did fritting take place?
- Can the zone between the glass and the crucible inform us about the transfer of components from one to another?
- What impact did immigrant glass-makers have on the technology?
- Make comparisons with English sites of similar dates
- Make comparisons between various sources of window glass
- Did the change from wood to coal have any impact on the glass?
- Can the quality of the glass be linked to the composition of the glass and/or the technology of glass production?

CHAPTER TWO

GLASS AND ITS RAW MATERIALS

2.1 The nature of glass

The nature of glass causes problems for definition, due to the question of whether it is a super-cooled liquid, or not. Fundamentally, glass is a material that will result from rapidly cooling certain liquids. The crystals are unable to nucleate and grow, therefore an ordered structure is not produced.

One definition shows the unique nature of glass (Brill p129-131, 1962). This definition is;

'glass is a substance in the glassy state, a state in which the molecular units have a disordered arrangement, but sufficient cohesion to produce over-all mechanical rigidity.'

A glass is an amorphous solid, which is lacking a long range, periodic atomic structure. In addition to this a glass exhibits a glass transformation region, where the glass undergoes a time-dependent behaviour over a temperature range (Shelby p3, 1997).

The glass transformation region can be seen when enthalpy is plotted against temperature (fig. 2.1). A liquid can be cooled to a temperature below the melting temperature, T_m. Normally, this would result in a large drop in enthalpy, and the formation of a crystalline material with long range order. However, if the liquid can be super-cooled without crystal formation, and taken below the melting temperature, the atomic structure will continue to rearrange itself as the temperature decreases. Therefore, there will be a gradual reduction in the enthalpy, over the 'glass transformation range', where the rearrangement of the atomic structure will continue until the increase in viscosity fixes the atoms in place, producing a glass material (Shelby p4, 1997).

It is essential to understand the physical properties, the chemical structure, and most importantly, the method of manufacture, of glass before attempting to study the history of its production. It is only when the nature of the glass, and many of its special properties, is understood, that questions concerning the location of glass-making sites, sources of raw materials, and a more detailed analysis of glass production, can be answered.

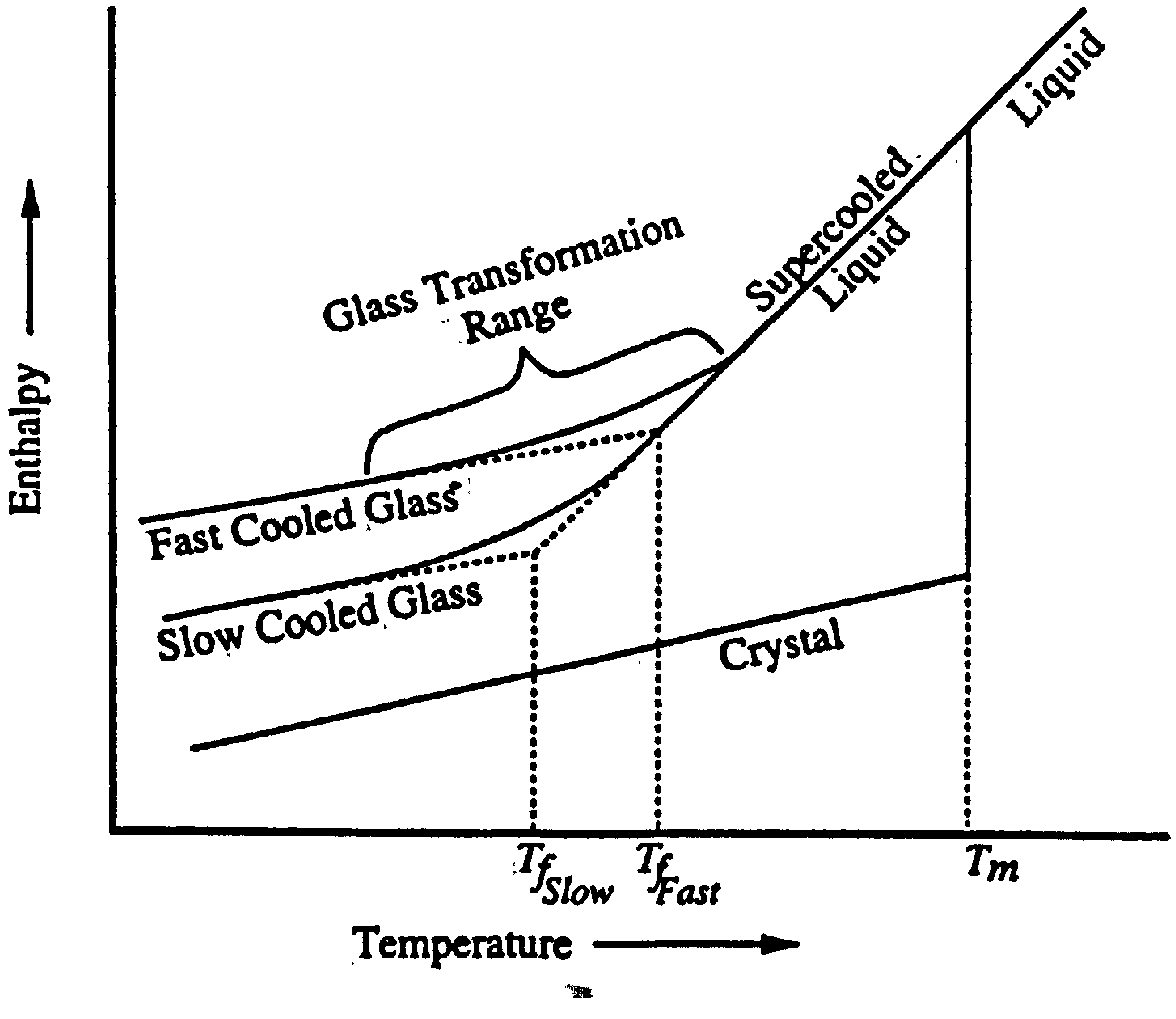

Figure 2.1 – Effect of Temperature on the Enthalpy of a Glassforming Melt (Shelby p4, 1997)

2.1.1 Physical Properties

Glasses exhibit properties, which in many respects are unique. When hot glasses are viscous liquids, but when cold they are brittle and liable to fracture when subject to a sudden change in temperature.

These properties can often be related to the transformation range, where the time-temperature behaviour will affect the final properties of the glass. Glass exhibits a trait where by it can have knowledge of its structure prior to solidification (Hall and Leaver p178-185, 1961).

The Melting Temperature

The melting temperature of silica, in the form of quartz, is 1607 °C (Tennent p85, 1971), a temperature which makes commercial glass production difficult. However, the addition of a material which combines with silica, and one that can lower the melting temperature (fluxing agent), does make silica viable as a material for glass manufacture. Glasses are made by reacting silica with fluxing agents, such as sodium carbonate, or potassium carbonate, and then dissolving the rest of the silica in the melt produced by the reaction. The addition of the fluxing agents can greatly reduce the melting temperature of silica. Depending on the ratio of sand to soda, or potash, the temperature of melting can be in the region of 1100-1200 °C, a more practicable temperature for melting in ancient, wood-fuelled furnaces.

Viscosity

The rigid nature of glass at room temperature is slightly misleading. This is because glass, whilst maintaining the same chemical composition, can behave plastically when heat is applied. Many types of glass may behave as a viscous liquid at temperatures in the region of 900 °C, allowing the glass to be worked into shape.

On cooling, the viscosity will increase. The viscosity is therefore temperature dependent, defined by the Fulcher equation;

$$\log \eta = -A + \frac{(B \times 10^3)}{(T - T_0)}$$

where η is the viscosity, A is a constant, B is a defined variable and T_0 is a temperature well below the glass transformation temperature, T_g.

Viscosity curves can be measured for glasses to determine the various temperatures at which glass can be worked, softened and annealed. The viscosity of the glass during various processes is as follows (Shelby p109, 1997);

working: 1×10^3 N s m^{-2},

softening: 1×10^6 to 1×10^9 N s m^{-2},

annealing: 1×10^{12} N s m^{-2}, and

the strain point: $1 \times 10^{13.5}$ N s m^{-2}.

Optical Properties

The optical properties of glass are most important, and one reason why glass is held in such high regard. The optical properties of glass make it suitable for many objects, from decorative jewellery, to beakers, goblets and windows. Glass can be made transparent (transmission of visible light), coloured or opaque, with relatively small alterations to the internal structure of the base material.

Light is able to pass through transparent glass in the same way as it does in a liquid, without the collisions with crystal boundaries that will scatter the light. One measurement of the optical properties of glass is the refractive index, which for glass lies between 1.48 and 1.96 (Tennent p71, 1971). However, for this work the optical property has been measured as a function of clarity, and included in an assessment of the quality of the glass.

2.1.2 The Structure of Glass

Glass is similar to a liquid, cooled into a solid form without crystals being able to nucleate. The structure of the liquid has no long range order in the atomic structure. A glass can be considered as a material that contains small blocks (with an ordered atomic arrangement) connected together into larger units. Thus, there is a more ordered structure than random connection (Shelby p75, 1997).

If vitreous silica is used as a model for the structure of glass, it is seen that the silica tetrahedra join together in a slightly irregular arrangement (fig. 2.2).

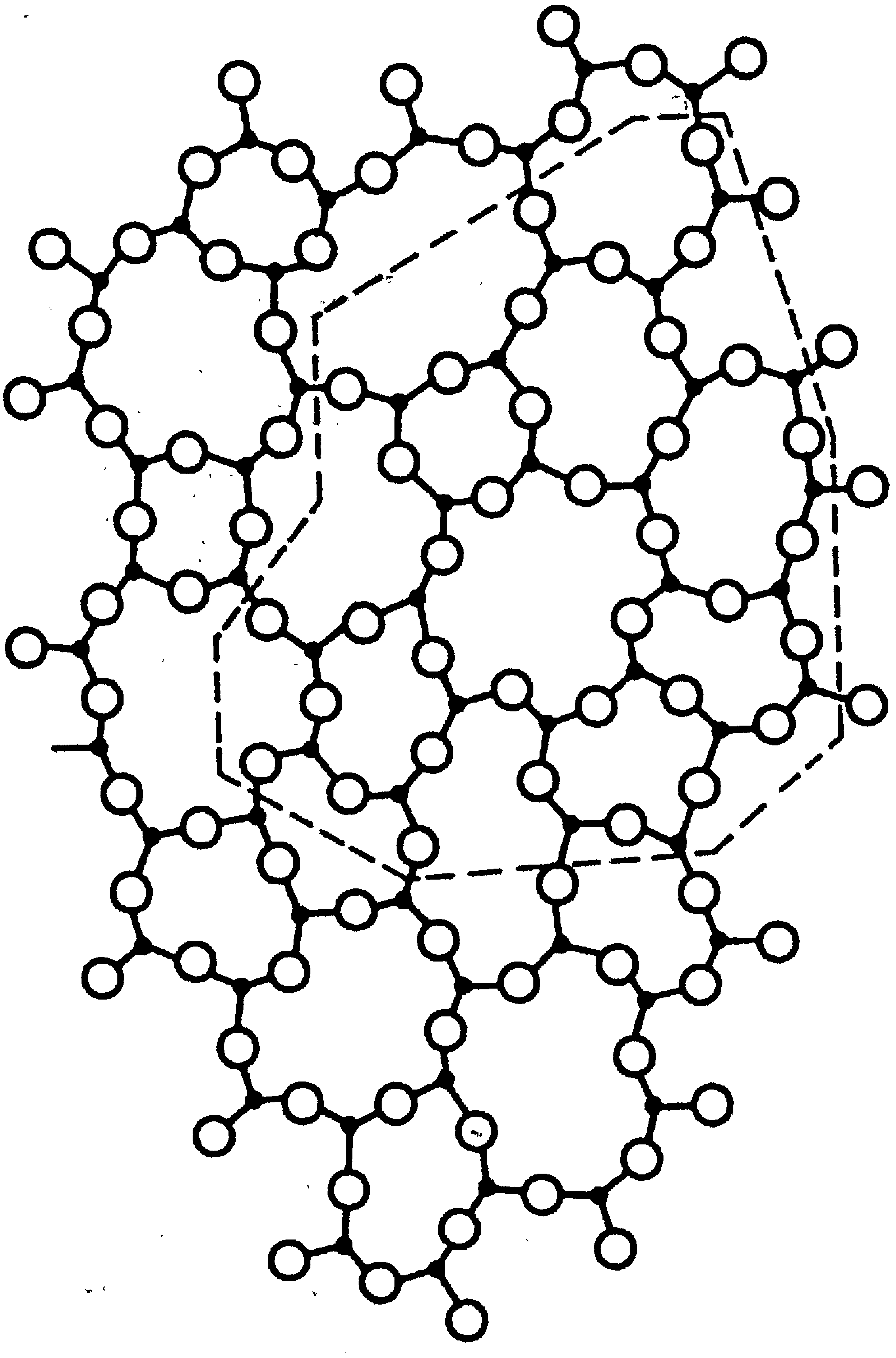

Figure 2.2 – Diagram of Glass Network, based on Silica Tetrahedra

(Newton and Davison p5, 1989 (From model by Zachariasen))

The addition of alkali ions into the glass will result in the interstices sites being filled (fig. 2.3), where sodium and calcium ions can be seen in the network (Shelby p78-81, 1997).

Glasses require a base network, which can be modified when other ions (such as alkali metals) place themselves into the network (fig. 2.3).

Glass networks have three components (Shelby p9, 1997);

1/ formers

2/ modifiers

3/ intermediates

The proportions of these three components are varied to produce the glass of required properties, whether chemical or physical. The network formers are the basic constituents of glass, acting as the base structure. The network former in medieval glass is silica (SiO_2), though other formers exist in modern glasses.

The modifiers sit within the interstices of the glass structure, causing changes in the glass, both physical and chemical, as a result of the disruption. Network modifiers include the alkali oxides of Lithium (Li_2O), sodium (Na_2O), potassium (K_2O), and the alkali earth oxides of calcium (CaO), magnesium (MgO) and barium (BaO).

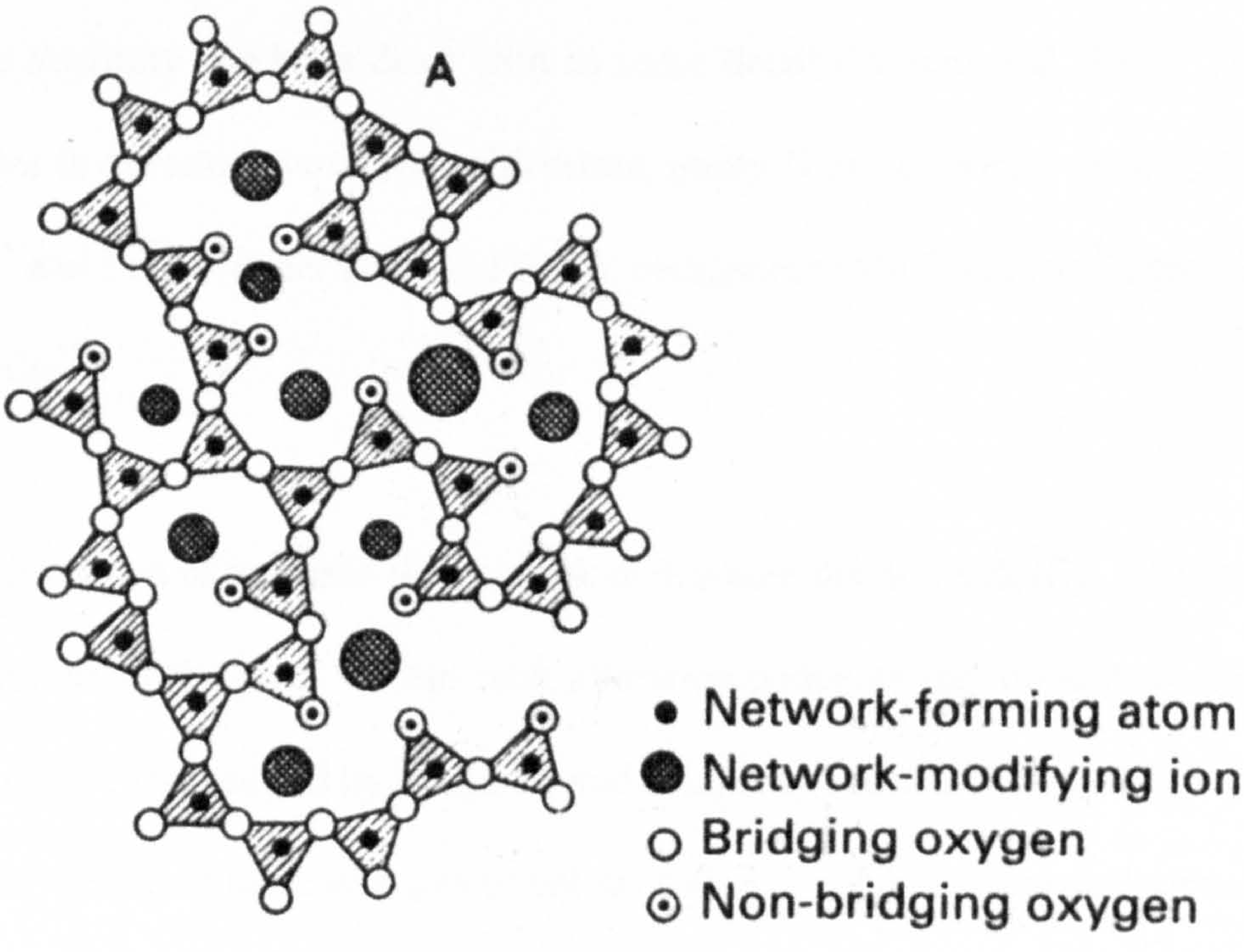

Figure 2.3 – Diagram of Modified Glass Network, based on Silica Tetrahedra

(Newton and Davison p5, 1989 (From model by Zachariasen))

Other ions appear to act as partial replacements for the silicon ion, to produce a network that consists of various tetrahedra. These 'intermediate' ions are predominantly network formers, and include the oxides of titanium (TiO_2), aluminium (Al_2O_3) and zirconium (ZrO_2).

A final category of ion can act as a former or modifier, depending on the circumstance. This group is often associated with the changing of colour of a glass.
A detailed analysis of the contribution of certain ions, and their position within the glass structure has been dealt with in some detail (Pollard and Heron, 1996). The oxides in question are often multi-valent, group D metal oxides, such as those of iron (Fe^{2+} and Fe^{3+}), copper (Cu^{+} and Cu^{2+}), manganese (Mn^{4+} and Mn^{7+}) and cobalt (Co^{2+} and Co^{3+}).

The inclusion of ions into the network or between the network (fig. 2.3), may alter the properties of the glass. One such alteration concerns the amount, or type, of light that can be transmitted by the glass, and thus, may cause a change in the colour of the glass. Some of these changes in colour caused by the incorporated ions can be seen below in Table 2.1.

Metal	**Ion**	**Colour as network former**	**Colour as network modifier**
Chromium	Cr^{3+}	-	Green
Chromium	Cr^{6+}	Yellow	-
Copper	Cu^{2+}	-	Red
Copper	Cu^{+}	Yellow-brown	Blue
Cobalt	Co^{2+}	Blue	Pink
Nickel	Ni^{2+}	Purple	Yellow
Manganese	Mn^{2+}	Colourless	Weak orange
Manganese	Mn^{3+}	Purple	-
Iron	Fe^{3+}	Brown	Weak yellow
Vanadium	V^{3+}	-	Green
Vanadium	V^{4+}	-	Blue
Vanadium	V^{5+}	Colourless-yellow	-

Table 2.1 – Additional Ions that alter the Colour of Glass

2.2 Raw Materials in Medieval Glass

The main ingredients for the production of Medieval 'forest' glass are sand (source of silica) and wood ash (source of alkali oxides and lime), and these are described below (Henderson p62, 1995 and Turner p277, 1956).

2.2.1 Sand

It is difficult to say what type of sand was used by the medieval glass-makers, or whether they were always in search of a local supply. However, there are certain requirements for sand that is to be used in glass production. These requirements state that the sand should ideally consist of 100% silica, in the form of quartz. If there are impurities in the sand, which would often be the case, these must be kept low. Iron oxide must be below 0.1%, which can be a problem as iron oxide is often associated with alumina, and it may be desirable to have an alumina level of 3-4%. The sand should be well graded, and have an average grain diameter between 0,25 and 0.5mm (Boswell, 1917 and West-Oram, 1979). Sand that has been found to be satisfactory for glass-making may have alkali and lime impurities, in addition to 1 to 2% alumina (Gould and Hampton p249, 1930).

Some of the properties of glass-making sand can be seen in Table 2.2 and 2.3, obtained by testing sand from Ashurst Wood, East Grinstead in Surrey. This sand is in a similar location to the area of the Weald under study.

Sand used in the manufacture of ancient glass often may have been obtained from seashores or river beds (Haggar p8-9, 1961).

Component	Weight %
SiO_2	98.77
Al_2O_3	0.73
Fe_2O_3	0.01
CaO	0.14
Loss on Ignition	0.43

Table 2.2 – Major Chemical Components of Ashurst Wood Sand (Boswell, 1917).

Size of Grain, x / mm	Weight %
$x>0.5$	0.0
$0.5> x >0.25$	9.8
$0.25> x >0.1$	85.5
$0.1 > x >0.01$	2.0
$x <0.01$	2.7

Table 2.3 – Grading of Ashurst Wood Sand (Boswell, 1917)

Much work has been carried out on the type of sand in Syria (Turner, p279-283, 1956), but the same sort of study has not been carried out on sands used in medieval 'forest' glass. Inland regions such as Surrey and Norfolk did have a supply of sand for glass, which may have been more refined than many of the sources of sand from seashores (Haggar p8, 1961). Good sources of sand for glass production were known by Christopher Merrett in the seventeenth century, especially in the south-east of England, where deposits of sand were known in Kent, Surrey and Sussex (Turner p210, 1962)

The grading of the sand for medieval glass production is not known, and a reference by Agricola concerning the size of the grain to be used, allows the incorporation of coarse or fine sand into the glass batch (Hoover and Hoover p586, 1950). It has been stated that the sand must be clean, which includes the removal of stones and earth, as well as the washing in water (Hawthorne and Smith p52-53, 1979).

The major component of glass-making sand is silica. Details concerning the structure of the silica are not wholly relevant to this study, but it must be pointed out that silica is polymorphic, and can be found as quartz, cristobalite and tridymite (Worrall p9-11, 1969). This conversion will be discussed in more detail in section 2.3.

2.2.2 Ash

The second major ingredient in medieval glass batches is ash. Ash was the primary source of alkali for the production of glass. The major source of ash in the production of medieval 'forest' glass was made from burning trees. Medieval glass production in England can be distinguished by the reliance on wood ash as the form of fluxing agent. Often this results in a glass having a high potash and low soda content. This contrasts with ancient glass from Egypt where the source of alkali may have been natron, a salt that contains a high level of sodium carbonate (Turner p283-285, 1956).

The ash was prepared by burning cut and dried logs (Hawthorne and Smith p49, 1979). The logs to be burned may have been different from site to site. The preferred wood sources for the production of medieval glass were beech as suggested by Theophilus (Hawthorne and Smith p49, 1979), or oak as suggested by Agricola (Hoover and Hoover p586, 1950). The discovery of records from an early seventeenth glasshouse at Nottingham showed which ashes were best. It stated that 'wiche asse, beanestraw asse or greene fearne asse' were the most suitable ashes for the production of glass. The first of these was probably wich-hazel or witch-elm (Smith p26, 1962).

A major problem can be seen in glasses that use this high potash in relation to soda ash, and this was that the durability of the potash, or 'forest' glass was not as good (Hunter p63, 1985). Therefore, much of the evidence of glasses using potash as the primary source of alkali may be badly weathered.

The weathering of glass is beyond the scope of this work, and detailed discussion can be seen in many sources (including Newton and Davison, 1989, Newton, 1969, Newton, 1971, Cox and Ford, 1993, Cox et al., 1979, El-Shamy, 1973, Gillies and Cox, 1988a and Hench, 1975)

The ashes are added to silica to act as a fluxing agent. Fluxes lower the temperature at which a liquid will form, and as silica melts at a temperature above 1600 °C, it is necessary to combine it with fluxes which firstly melt at a lower temperature, and secondly, will form compounds which can produce glasses. Of such compounds the salts of sodium and potassium are by far the most important ones when discussing medieval glass, where the wood ash may contain a mixture of these alkalis. These fluxing agents and the silica form a eutectic mixture that may reduce the temperature at which liquid forms.

Another constituent of the wood ash is a variety of calcium compounds. As discussed previously, a quantity of lime may have originated from the sand chosen to produce the glass, if a source was located near the sea. However, if the sand was from an inland source, and was much more pure, then it may have been desirable to add lime to the glass batch. In this case the lime present in the wood ash would have been advantageous.

The variability of the chemical composition of the ash, and the variation between each type of vegetation can be seen in Table 2.4. The compositions showed that wood ash glass could be produced with a variety of ashes, and depending which ash was chosen the end composition of the glass would be very different.

Vegetation	SiO_2 /wt%	CaO /wt%	MgO /wt%	Na_2O /wt%	K_2O /wt%	P_2O_5 /wt%
Wheat straw	66.2	6.1	2.5	2.8	11.5	5.4
Heather	35.2	18.8	8.3	5.3	13.3	5.0
Fern	6.1	14.1	7.6	4.6	42.8	9.7
Wheat	1.7	3.3	12.4	3.3	31.1	46.3
Beech, leaves	33.8	44.9	5.9	0.7	5.2	4.7
Beech, trunk	5.4	56.4	10.9	3.6	16.4	5.4
Oak	2.0	72.5	3.9	3.9	9.5	5.8
Apple	2.7	70.9	5.5	1.9	11.8	4.5

Table 2.4 – Chemical Composition of Various Ash Sources (after Turner p289, 1956)

I attempted to reproduce medieval glass using beech ash as suggested by Theophilus. A frit was produced at 800 °C, made from sand (1 part by weight) and beech trunk (2 parts by weight) recovered from Derbyshire. Glass could be produced from this frit, proving that the technology of making glass from beech ash and sand was correct. This has also been done to assess the process of fritting and glass-making (Smedley et al, 1997). However, when this was repeated with beech trunk from Nottingham frit could not be formed until it had been heated to an extremely high temperature of 1250 °C. The glass produced from this frit was not totally satisfactory either, as it required a melting temperature of 1390 °C (compared to 1280 °C for the Derbyshire beech trunk). This showed the complex nature of similar raw materials. The variation of the ash composition was observed in ashes that may have originated from Knightons and Sidney Wood. These samples of beech and oak were ashed and analysed. The results showed that the composition of the certain components with the ash could vary hugely (Sanderson and Hunter p28-29, 1981).

2.3 The Raw Material for the Crucibles and Furnaces

Glass-making sites relied on a supply of raw ingredients to the glass batch. In addition to this a supply of clay would have been needed for the production of the crucibles. The clay would have had to withstand the harsh conditions of the glass-making process. In particular the clay would have had to withstand the high temperature attained in melting the glass. This temperature could be up to 1200 °C, or possibly higher.

Clay minerals are very complex, and have been studied in greater depth (Worrall p16-83, 1969) than is required for this study of glass-making technology. The properties required by the clay, in order to withstand the arduous conditions within the medieval glass furnace, would be similar to the properties required in a modern furnace. However, whereas modern refractory ceramics can be designed for the purpose they are to be used in, the medieval glass-maker would not have had much choice.

The choice of crucible material faced by the medieval glass-maker would have been dictated by the availability of a suitable clay. Theophilus suggested white pottery clay, dried, ground and mixed with water (Hawthorne and Smith p53, 1979). Merrett in 1662 was more specific. He claimed that the pots fired at the high temperatures to produce green glass required fireclay from Worcestershire (probably Stourbridge clay) (Turner p211, 1962). Agricola suggested that the clay used for the building of the furnaces should also be used for the construction of the pots (Hoover and Hoover p590, 1950).

This showed that some thought to the suitability of the clay for the purpose of glass-making pots was made during the medieval period. However, the location of the source of clay may have been determined by the most suitable clay in close proximity to the glass-making site.

In subsequent chapters it will be seen that information about the processes involved in glass-making can be determined by the crystalline structure of the clay crucibles.

Heating clay will result in a transformation, from low temperature phases to those that have high temperature stability. Basic natural clay may contain kaolinite, mica and silica, as well as other impurities (Worrall p45, 1969). Therefore, when the crucibles are analysed it may be of interest to know the transformation of kaolin and silica when subject to the application of heat (Worrall pp26, 1969).

$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$ ....@450 °C......................equation 2.1
Kaolinite "Meta-kaolin"

$3Al_2Si_2O_7 \rightarrow Al_6Si_2O_{13} + 4SiO_2$ ....@925 °C......................equation 2.2
"Meta-kaolin" pseudo-Mullite + Silica

$Al_6Si_2O_{13} \rightarrow Al_6Si_2O_{13}$ ....@1200 °C......................equation 2.3
pseudo-Mullite Mullite

This suggests that the high temperature phase present during the breakdown of kaolin is mullite, and therefore, the observance of mullite crystals within the clay crucibles may indicate that the clay has been heated to 1200 °C.

The other phase within the clay crucibles of interest to this work is silica. Silica has been observed in clays, and silica undergoes a conversion from quartz, as shown below (Worrall p11, 1969).

Quartz → Cristobalite......................@1470 °C......................equation 2.4

Cristobalite ⇌ Tridymite.....................@870 °C....................equation 2.5

This shows that quartz remains the stable form of silica unless it is heated to 1470 °C, when the conversion of quartz to cristobalite will take place. Cristobalite may be converted to tridymite if the former is held above 870 °C for some time.

Clay may have been used in the construction of the furnaces, though it was possible that it may have been used in conjunction with stone materials. Merrett in 1662 suggested that the furnace should be constructed using 'hard stone' from Newcastle (Turner p211, 1962). Theophilus stated that the furnace should be constructed with stones and clay, though the type of material was not mentioned (Hawthorne and Smith p49, 1979). Agricola suggested that the furnaces were made using clay bricks, dried in the sun. These various suggestions to the best materials for use in the construction of glass furnaces indicate that individual preference and an ability to locate a good source of clay and stone were important factors in the choice of ceramic materials.

2.3.1 Wealden Clay

This study centred on a region that had a large supply of clay, Wealden clay. In addition to this an area of sand sits in the middle of the region, Lower Greensand. Walking through the area it is possible to see the outcrops of the clay, typified by the buff colour.

Wealden clay is brick clay (Worrall p76, 1969), which does not require the same tolerance as the refractory, or whiteware clays. The range of compositions is therefore greater, making it possible to use the sedimentary deposits from various geological ages. Brick clays contain kaolinite, chlorite and illite, with small additions of quartz and organic material. Due to the variation of the composition it has been found difficult to characterise the properties of the clays. However, some of the main properties of Wealden clays can be seen in Tables 2.5, 2.6 and 2.7.

Chemical Constituent	Wealden Clay	Range of Brick Clays
SiO_2	68.4	46.2-77.8
Al_2O_3	17.2	11.0-24.0
Fe_2O_3	6.3	0.8-11.4
TiO_2	1.3	0.5-2.2
CaO	1.9	0.2-19.2
MgO	1.2	0.4-12.8
Na_2O	0.5	0.1-1.2
K_2O	2.2	1.5-4.2
SO_3	0.7	0.0-2.3
Loss on ignition	0.3	0.0-1.1

Table 2.5 - Chemical Composition of Wealden clay (Worrall p77, 1969)

	Particle size (smaller than 2 μm diameter)	Working Moisture Content (% dry basis)
Range	15-85%	23.8-42.2%
Average	47%	30.9%

Table 2.6 - Properties of Wealden clay (Worrall p80, 1969)

	Linear Firing Shrinkage	Fired Colour
@850 °C	Not detected	Salmon Pink, light red-brown, buff
@900 °C	0-3.4%	Not detected
@1100 °C	2.5-8.6%	Not detected
@1200 °C	Not detected	Dark red-brown

Table 2.7 - Temperature properties of Wealden clay (Worrall p80, 1969)

Samples of clay from Blunden's Wood, Knightons and Sidney Wood have been collected and tested by me. Experiments were carried out on samples of clay to show the colour change when heated up to 1400 °C (figs 2.4, 2.5 and 2.6). Also, a colour comparison with a fragment of crucible from each site can be seen. The volume and weight change of the clay from a dried state to fired state can be seen in Tables 2.8, 2.9 and 2.10. These results showed the maximum shrinkage was at 1200 °C, and that above 1200 °C the clay from all three glass-making sites began to move towards expansion. This resulted in the clay cracking, and breaking apart. The loss of weight during firing (from the as-received state) was between 26 and 32% in total, which indicated the high percentage of water within the clay. This compared very well with the average moisture content of 30.9% within Wealden clay (Worrall p80, 1969)

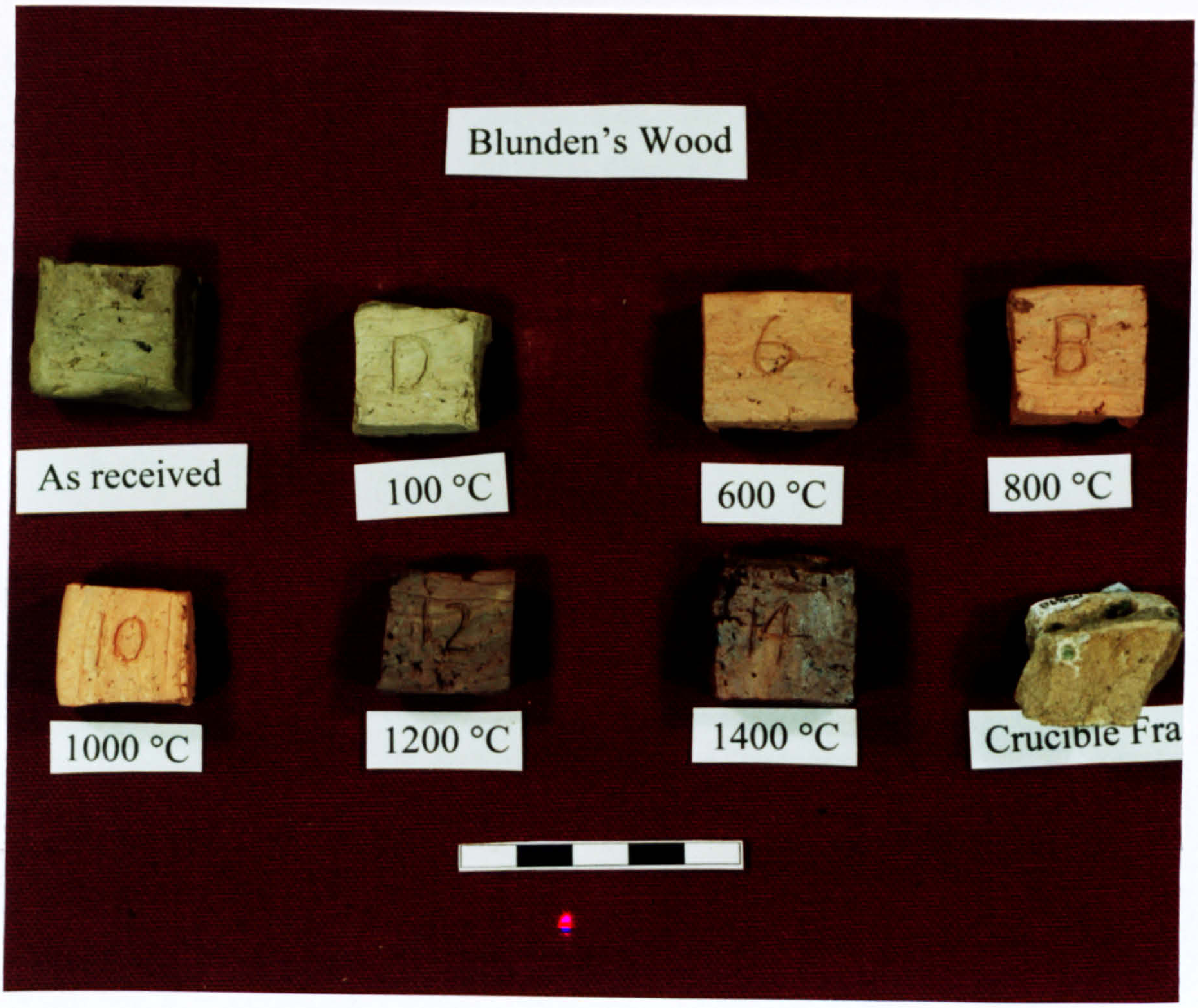

Figure 2.4 - Clay from Blunden's Wood, fired at different temperatures

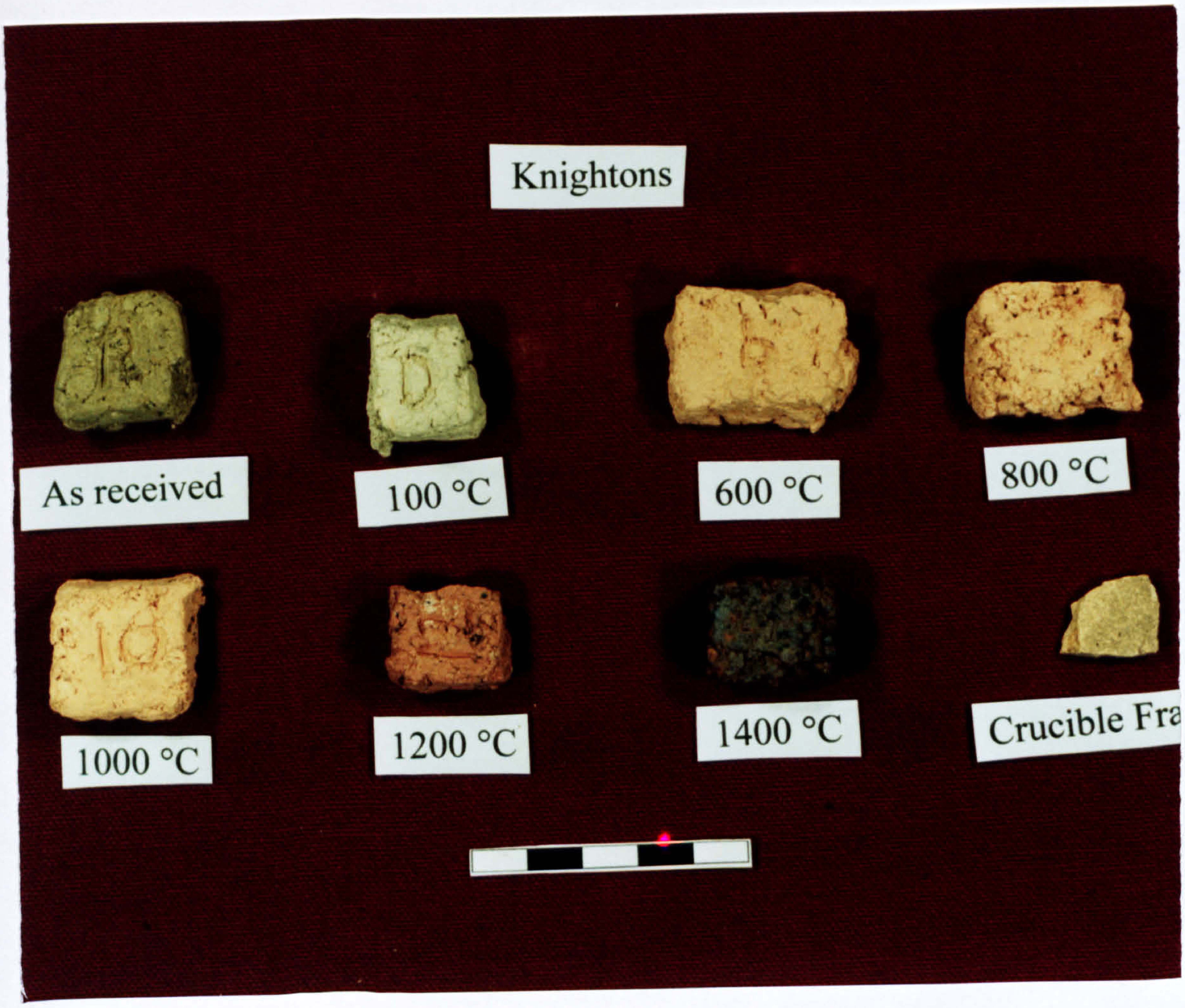

Figure 2.5 - Clay from Knightons, fired at different temperatures

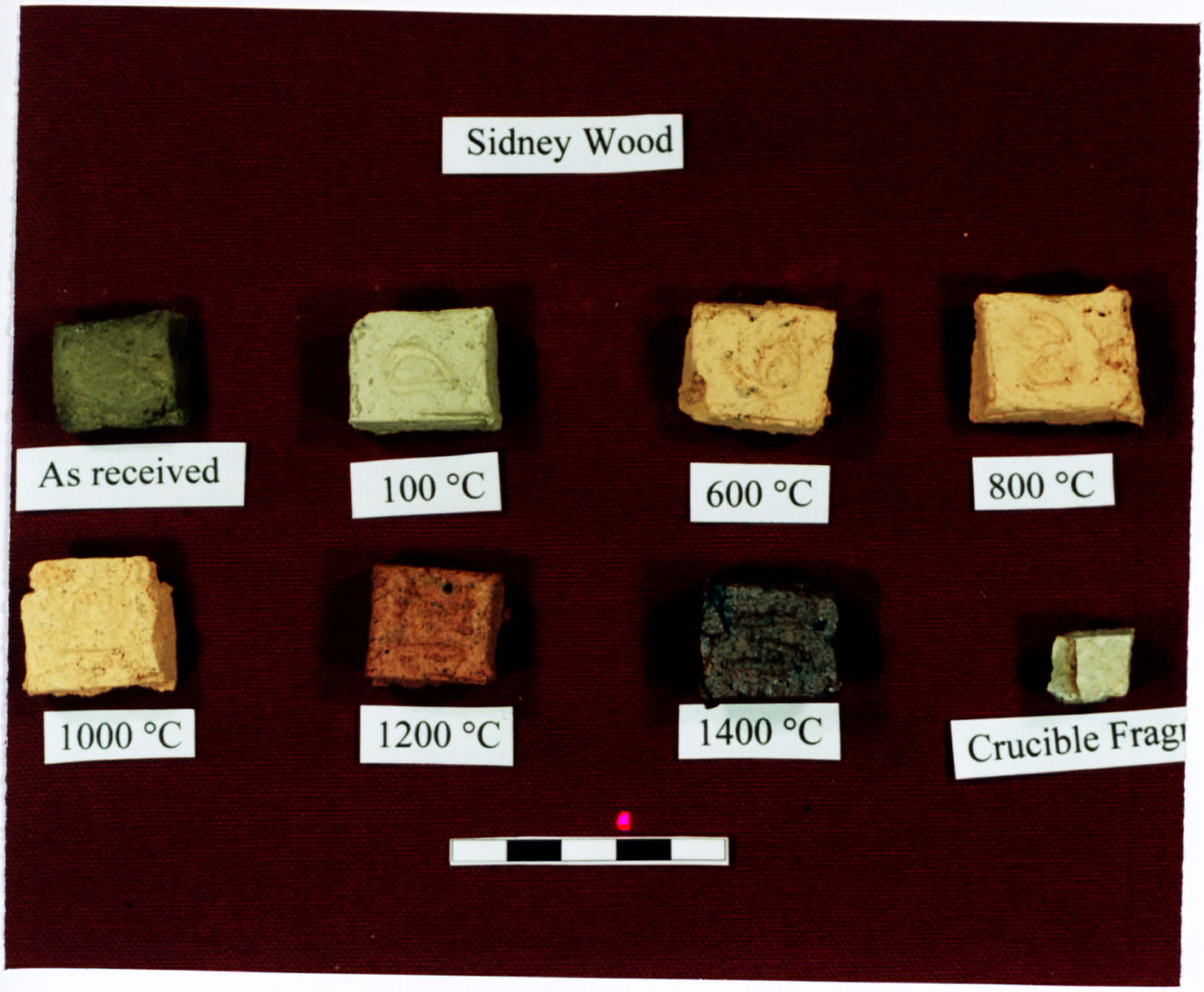

Figure 2.6 - Clay from Sidney Wood, fired at different temperatures

Firing Temperature/ °C	Volume change/%	Weight Change^1/ %	weight change^2/%	colour
110	-	-	-18.75	Light buff
600	0.00	-10.53	-26.09	Dark buff
800	-2.17	-12.50	-30.00	Red-brown
1000	-14.48	-13.33	-31.58	Red-brown
1200	-22.13	-13.33	-27.78	Dark-red-brown
1400	6.48	-11.11	-30.43	Dark-red-brown

1 = weight change from dried state to fired

2 = weight change from as received state to fired

Table 2.8 - Volume change, Weight change and Colour of fired Clay from Blunden's Wood

Firing Temperature/ °C	Volume change/%	Weight Change[1]/ %	weight change[2]/%	colour
110	-	-	-25.00	Light buff
600	-1.51	-9.09	-37.50	Light-red-brown
800	1.38	-8.33	-26.67	Light-red-brown
1000	-5.71	-9.09	-28.57	Light-red-brown
1200	-9.56	-14.29	-25.00	Red-brown
1400	-3.23	-9.09	-28.57	Dark-brown

1 = weight change from dried state to fired

2 = weight change from as received state to fired

Table 2.9 - Volume change, Weight change and Colour of fired Clay from Knightons

Firing Temperature/ °C	volume change/%	Weight Change^1/ %	weight change^2/%	colour
110	-	-	-23.53	Light buff
600	-3.03	-8.33	-31.25	Light-red-brown
800	-4.04	-7.14	-27.78	Light-red-brown
1000	-2.13	-8.33	-26.67	Light-red-brown
1200	-24.02	-7.69	-29.41	Red-brown
1400	-11.16	-7.69	-29.41	Dark-red-brown

1 = weight change from dried state to fired

2 = weight change from as received state to fired

Table 2.10 - Volume change, Weight change and Colour of fired Clay from Sidney Wood

Often ceramic bodies possess a memory for their process temperature. The ceramic material should remain volume-stable up to the temperature to which it has previously been fired at. Therefore, the crucible fragments were re-heated to temperatures between 600 °C and 1400 °C. It may have been possible to observe a temperature at which the volume stability of the fragment changed (Norton, 1968 and Ford, 1967).

The results of the re-firing experiments (fig 2.7) showed that the all the crucible fragments remained stable up to 1000 °C, and thereafter began to change in volume. This suggested that the temperature which the glass-melting furnace could reach was in excess of 1000 °C. The small change at 1200 °C indicated that the firing temperature was at least as high as this, which confirmed the estimation predicted by the presence of mullite laths within the crucible fabric. The large increase in volume when the fragments were re-heated to 1400 °C, and the obvious degradation of the crucible fabric (fig. 2.8) showed that the temperature would not have been as high as 1400 °C.

2.4 Medieval Glass Furnaces

Theophilus, writing in the twelfth century, in *De Diversis Artibus*, provided details of the industry during the medieval period, explaining how raw materials were collected, which types of plant ash were used, and finally, how the glass was melted and manufactured into finished products (Hawthorne and Smith p49-74, 1979).

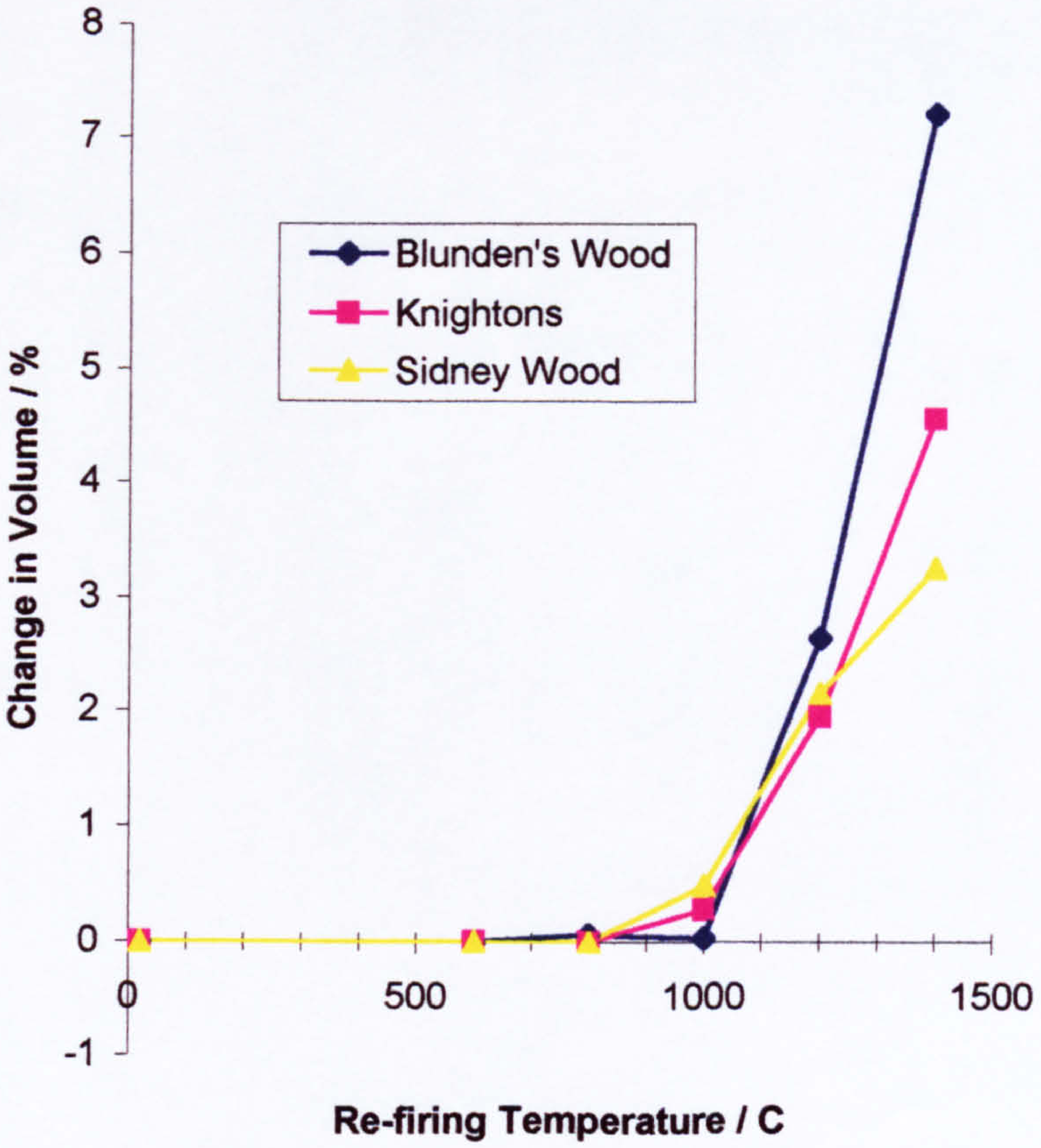

Figure 2.7 – The Volume Change of Crucible Fragments subject to re-firing at Temperatures between 600 and 1400 °C

Figure 2.8 – A Photograph of the Crucible Fragments fired to 1400 °C

Also, the furnace design was described as a typical 'northern' European style (fig. 2.9). This type of furnace had a hearth running through a rectangular structure and internal clay supports on either side of the hearth for the resting of crucibles on.

Of interest to the study of medieval glass production in England, was the illustration by Sir John Manderville, recorded while he was travelling throughout Europe in the fifteenth century (fig. 2.10). This showed a very good example of a glasshouse in Bohemia, with much information about the running of the glass-making site. It included a guide to the shape of a medieval furnace in northern Europe, broadly based on a rectangular structure. In addition to this the illustration showed many different functions that took place at a glass-making site, from the collection of raw materials to the trade of the finished articles.

The 'northern' style furnace was thought to have been used for the manufacture of 'forest' glass. The description of this type of structure within the text of Theophilus (Hawthorne and Smith p49-51, 1979), where the manufacture of wood ash glass was described, does suggest that this style of furnace was used in this manner.

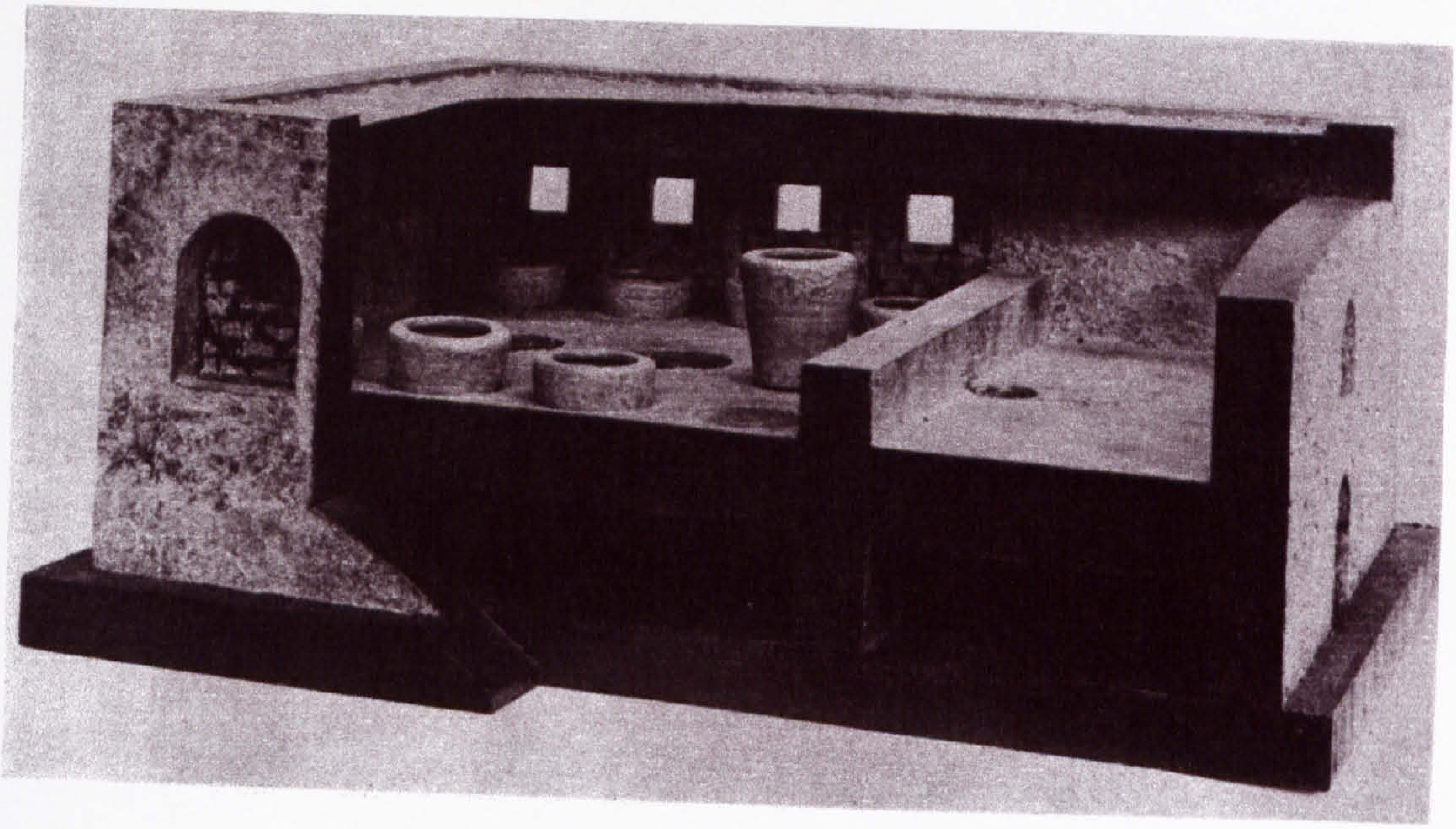

Figure 2.9 – Reconstruction of 'Northern' Style Furnace based on the Description by Theophilus (Kenyon Plate IX, 1967)

Figure 2.10 - Bohemian Glasshouse from the Travels of Sir John Manderville

(from British Library)

In *De Re Metallica* by Agricola, written in the sixteenth century (Hoover and Hoover p589, 1950), information concerning a different style of furnace can be seen. This was a 'southern' European style furnace. These structures had a circular base rising to a dome shape (figs. 2.11a and 2.11b). Though much of the description of glass furnaces by Merrett in the seventeenth century was based on the 'southern' style furnaces, there were references to a square furnace used to produce green glass (Turner p210-211, 1962). This suggested that the rectangular style furnace was most likely used for wood ash glass, in preference to the dome-shaped furnace.

An interesting circular-based furnace was found at Woodchester, in Gloucestershire, that was dated to the sixteenth century (Daniels p1-2, 1950). This structure was a typical design of the 'southern' furnace, in a period when all the other known furnaces in England were based on 'northern' style furnaces. Doubts as to the exact shape of this furnace have been raised and this furnace may not have been circular. If it was circular, as originally stated, it may have indicated that the furnace was designed by a glass-maker who had traveled throughout southern Europe where most of the furnaces he may have encountered would have been based on the dome-shaped design.

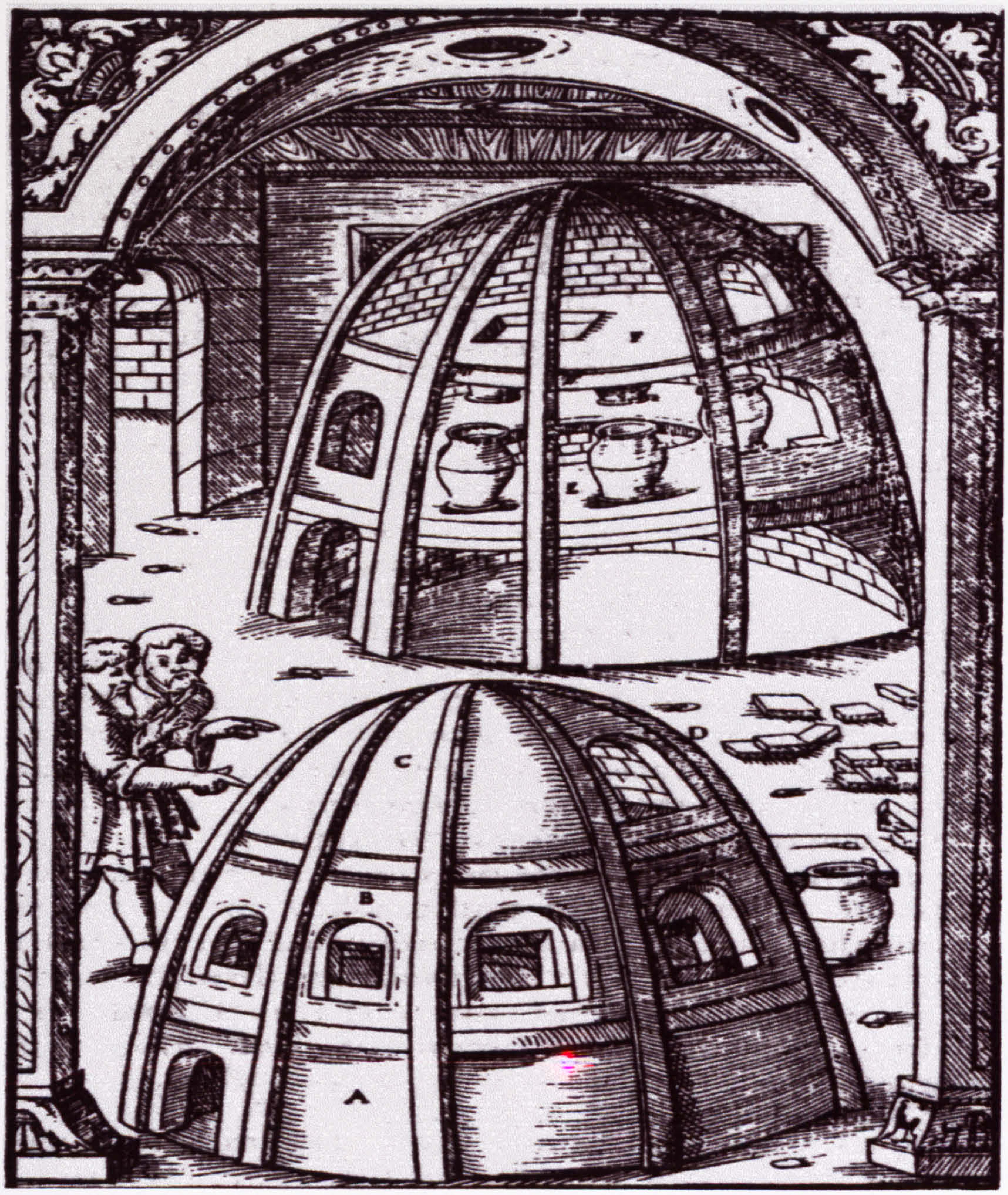

Figure 2.11a - 'Southern' Style Furnace based on the plate in *De Re Metallica* by Agricola (Hoover and Hoover p589, 1950)

Figure 2.11b - 'Southern' Style Furnace based on the plate in *De Re Metallica* by Agricola (Hoover and Hoover p590, 1950)

2.5 The Manufacture of Medieval Glass

The techniques used to manufacture glass during this period have been recorded by Theophilus (Hawthorne and Smith p52-74, 1979). The technique was relatively simple.

The medieval glass-making process took place in a number of stages. Firstly the ash was prepared by burning a suitable plant, as described in section 2.2.2. The ash must be purified, to eliminate any earth and stones from entering the glass melt. A mixture of sand and ash (two parts ash to one part sand by weight) was then heated to a moderately hot temperature (not very well defined, but, probably in the region of 700-900 °C) to produce a frit or 'fritt'. Thus, the fusion between the sand and ash has begun. The frit was heated in the furnace to melting temperatures (above 1000 °C). It was not always clear where colourants were added to the batch, though the usual practice seemed to be adding them to the molten glass, and left long enough to homogenise within the glass. The molten glass could then be fashioned into objects, using various techniques, depending on the requirements of the market and the properties of the glass (Turner, 1962).

The glass produced in this manner had a characteristic colour - green. This colour was as a result of the impurities from the sand or the ash, and was why Merret referred to 'green-glass' (also known as 'forest' glass, 'Waldglas' in Germany, or 'verre de fougère' in France (Turner, 1962). The production of 'forest' glass ceased in England in the first quarter of the seventeenth century, as will be discussed in more detail in chapter 3.

CHAPTER THREE

MEDIEVAL GLASS-MAKING IN ENGLAND

The production of glass originated in the eastern Mediterranean, with Mesopotamia or Egypt as the most likely regions (Newton and Davison p19, 1989). The earliest records of glass-making sites may have been at Tel-el-Amarna, dated to the fourteenth century BC (Charleston p9, 1978). However, this was over 2500 years earlier than the glass studied in this work. The glass industry migrated throughout the Mediterranean, and then throughout Europe. Therefore, by the thirteenth century AD, the period of this work, much would have been known about the techniques to produce glass.

3.1 Medieval/Post-Medieval Glass Manufacture

There were documentary sources that provided much information about glass-making during the medieval and post-medieval periods. These were written accounts by Theophilus (Hawthorne and Smith, 1979), Agricola (Hoover and Hoover, 1950), Neri (1612) (Turner, 1962) and Merrett (1662) (Turner, 1962). These sources have needed to be supplemented by excavations of glass-making sites, to discover information that cannot be obtained from these texts.

This work concentrated on the 'forest' glass manufacture in the Weald of Surrey and Sussex, though it was not the only area of glass manufacture during this period. High quality glass was being produced in London (Mortimer, 1991a) and by Jacob Verselini at Crutched Friars in the second half of the sixteenth century (Crossley p232, 1990).

The excavations must be studied in addition to documentary sources that enable some chronological order to be formed. This will enable the study of Blunden's Wood, dated to 1330 AD, Knightons, dated to 1550 AD and Sidney Wood, dated to 1610 AD, to be put into context.

The migration of glass-makers to England originated at the start of the twelfth century AD. The earliest records of glass-makers arriving in England from continental Europe came from a history of Bacton, a village in Norfolk. Here, Henry Daniel, a 'vitriarius' (glass-maker) was employed during the reign of King Stephen (1135-1154 AD). From this date onwards the documentary sources as to the scale of the glass industry increased, and the importance of the Weald in Surrey and Sussex became clear. (Douglas and Frank, 1972).

Records held in Guildford showed evidence of a glass-maker, Laurence Vitrearius being granted a plot of land in 'Chidingefalde' (GMR. 105/1/30) no later than 1240 AD. Early records of sales of glass from the Weald to various sources, including St. Stephen's Chapel, Westminster, came from accounts. They stated that glass from John de Alemayne was being supplied(Kenyon p26, 1967).

He was from Chiddingfold, according to the accounts, and the Godalming tax records of 1332 showed this was the case. The name suggests that his origin was Germany. Some of the Wealden glasshouses (fig. 3.1), with an estimation of the period in which they were operational can be seen in Table 3.1. Many of the early glasshouses have been discussed in detail (Winbolt p22-53, 1933 and Kenyon p146-222, 1967). The earliest site to be properly excavated is Blunden's Wood (Wood, 1965), which will be discussed in chapter 4. This site is dated 1330 AD. Other early sites, Broomfield Hanger and Fromes Copse (both in the parish of Chiddingfold) have evidence of furnace floors, and appear to have originated from the early period of glass-making in the Weald. However, these sites were not excavated fully. The glass from these glasshouses appeared to be milky green, typical of early thirteenth and fourteenth century Wealden glass.

The first documentary evidence concerning a glasshouse came in 1380. The deed following the death of the glass-maker John Schurterre stated that Joan, the wife of John, was to share a glasshouse at 'Shuerwode' in the parish of 'Keuredforde' with a glass-maker from Staffordshire, John Glazewryth (GMR 105/1/117). Other records showed that the son of the first John Schuterre, John, also had a glasshouse at 'Stroudwikeswoude' in 1385 (GMR 105/1/119).

Other examples of early glasshouses which showed the presence of a furnace floor (the only true method by which the location of the glasshouse can be proved) were at Wephurst Copse (in Kirdford parish) and Malham Ashfold (Wisborough Green parish).

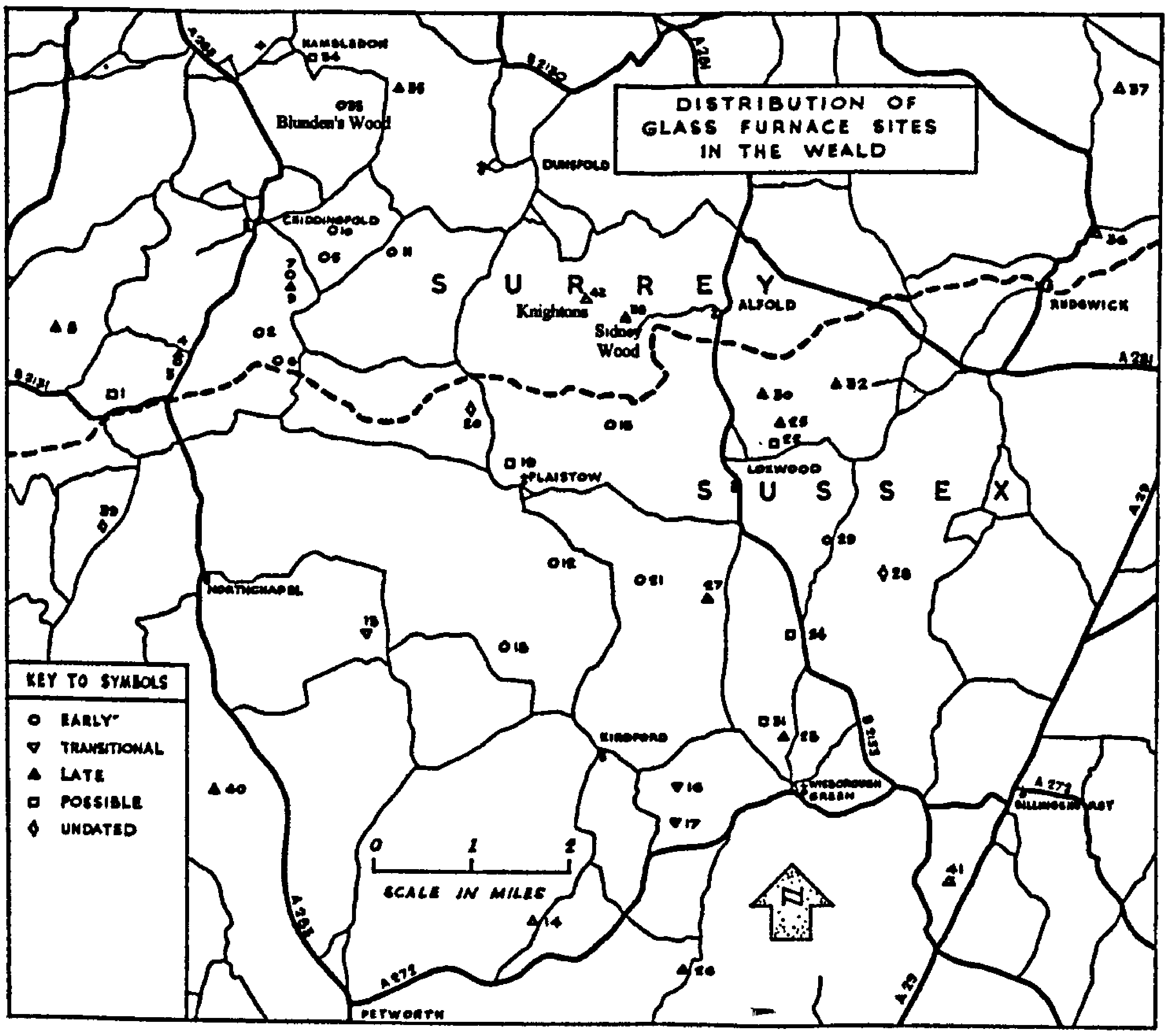

Figure 3.1 – Wealden Glasshouses (Kenyon back-page, 1967)

Number of Site	Name of Site	Parish of Site	Estimation of Date of Operation
2	Broomfield Hanger	Chiddingfold	E
3	Chaleshurst, upper	Chiddingfold	E
4	Chaleshurst, lower	Chiddingfold	L
5	Fromes Copse	Chiddingfold	E
7	Hazelbridge Hanger	Chiddingfold	E
9	Pickhurst	Chiddingfold	L
16	Idehurst Copse, N	Kirdford	T
17	Idehurst Copse, S	Kirdford	T
21	Wephurst Copse	Kirdford	E
29	Malham Ashfold	Wisborough Green	E
33	Blunden's Wood	Hambledon	E
34	Gunter's Wood	Hambledon	E
35	Vann Copse	Hambledon	L
38	Sidney Wood	Alford	L
42	Knightons	Alford	L

Key to Table:

Number of Site – As recorded by Kenyon

E = Early, T = Transitional and L = Late

Early = 1300 – 1550
Transitional = 1550 – 1560
Late = 1560 – 1620

Table 3.1 – A Selection of Wealden Glasshouses (after Kenyon p152-153, 1967)

The dating of Wephurst Copse was not clear, but the poor quality of the glass suggested that this site was operational before the end of the fourteenth century (Kenyon p182, 1967).

Malham Ashfold may have had three furnaces in operation, including a fritting furnace, and judging by the slightly improved quality of the glass (in comparison with earlier examples) the date of this site was probably in the fourteenth century. It was possible that Malham Ashfold had a winged furnace. This was similar in design to those observed at Vann Copse (dated to the sixteenth century) in the Weald (Winbolt p29-31, 1933), Buckholt in Hampshire (Kenyon p214-217, 1967), Kimmeridge (seventeenth century) in Dorset (Crossley p340-382, 1987) and Hutton and Rosedale in Yorkshire (Crossley and Aberg p107-159, 1972). These all date later than 1500 AD, much later than Malham Ashfold.

A gap in evidence concerning glass-making existed between the Schuterre family in the fourteenth century to the Peytowe family in 1536. It was known that this family was established in the parish of Chiddingfold, but there was no record of them producing glass until the will of John Paytowe in 1536. A glasshouse of John Paytowe 'at le Bridge' (in Chiddingfold) was left to his son, John (GMR105/2/9). Links between the Peytowe family and specific glass-making sites have been made. They may have run the glasshouses at Hazelbridge Hanger, Pickhurst and Broomfield Hanger (Kenyon, 1967). The Peytowe family may have operated both the furnaces at Chaslehurst while the land was in their possession between 1503 and 1614.

The Peytowes were important figures in the area, and therefore, were one of the most influential families between the end of the fifteenth century and the seventeenth century.

In the mid-sixteenth century one family has been definitely linked to the glasshouses at Idehurst. This family was the Strudwicks, and in 1557 Henry Strudwycke left a glasshouse at Idehurst to his son Robert (Surrey Record Society, vol.43, p.72). Other references to the family, and their association with glass, existed up to the middle of the seventeenth century. In addition to glass-making, this family farmed extensively throughout the area, and it was known that they owned an iron forge at Idehurst throughout this time.

The rest of the sites excavated in the Weald belong to the late medieval period, or more accurately post-medieval. This was a period of transition. One glasshouse that has been excavated fully, and was covered by this transitional period was Knightons glasshouse, dated to 1550 AD (Wood, 1982a and Wood, 1982b). This will be discussed in detail in chapter 4. Vann Copse glasshouse was thought to be in operation during this transitional period, though this site was not excavated to modern standards. However, as mentioned previously, this glass furnace was winged, which suggested a continental influence in the design of the furnace (Winbolt p29-31, 1933).

This transition was marked by the influx of immigrant glass-makers, probably the most influential being Jean Carré.

He arrived from Arras and established a glasshouse in London to make crystal glass (taken over by Jacob Verselini after the death of Carré in 1572) and two glasshouses at 'Fernefol' in Sussex for the manufacture of Lorraine and Normandy glass. In addition, he brought many other glass-making families to the Weald, including the Henseys from Lorraine and the Bungars from Normandy. He was buried at Alford church (on 25th May 1572) (Godfrey p16-25, 1975).

Carré wished to have a thirty year monopoly for the production of window glass, as seen in letters to Lord Burghley in 1567. These letters gave a good insight into the technology of the glass-makers, and the typical working year. He made it clear that he did not wish to use the trunks of trees, suggesting that he would only use the branches. Indeed, he even suggested that he would manage the wood by pollarding the trees. He gave an indication that the glass-makers had a time in the summer when the furnaces would not be operational, providing an annual working year of forty weeks (Kenyon p121, 1967). It was Carré who was responsible for the rapid expansion seen in the glass industry between his arrival in 1567 and the end of the sixteenth century. The influx of immigrant workers brought over by Carré may have assisted in the movement of the glass-makers within England, to the south coast, Staffordshire and beyond.

The close proximity of Alford to the Sidney Wood glasshouse may have suggested that this glasshouse was set up by Carré. It may have been taken over by an associate of his, John Vinion.

It was clear that by 1590 Vinion was joined by Peter Comely to produce 'drinking glass' at Alford (Godfrey p34, 1975), and this date tied in with the projected operation of the Sidney Wood glasshouse (Winbolt p37-40, 1933), and the reference to a glasshouse on John Speede's map of 1610. Sidney Wood glasshouse will be discussed in more detail in chapter 4.

The Henseys arrived from Lorraine in 1568, brought to the Weald by Carré, though the earliest reference to them was in the records of the Petworth parish register in 1592. The Hensey family came from Darny, in Lorraine, where they were established as glass-makers (Kenyon p126-127, 1967). It was possible that the Henseys were making glass at a furnace left by Carré, though this was uncertain (Kenyon p125, 1967).

The Henseys moved out of the Weald at the beginning of the seventeenth century. It was claimed that Jacob Hensey, mentioned in the Wisborough Green Parish register in 1599, moved to make glass at Wollaston in Stourbridge in 1615 for Sir Robert Mansell (Kenyon p128, 1967). However, this reference was probably mistaken, as the Middleton Collections referred to Jacob Hensey at Wollaton, Nottingham, in 1615 (Smith p30, 1962). It was possible that the family moved to Stourbridge, and then further north to Nottingham.

The Hensey family (Henzey) operated the glasshouse at Bagot's Park in Staffordshire at the end of the sixteenth century (Crossley p47-48, 1967).

The final important family to have arrived from Normandy was the Bungar family. They were thought to have joined Jean Carré in the Weald in 1568. It was possible that Issac Bungar operated the glasshouse at Sidney Wood, as he was a resident in Alford, the closest village. Also, in 1615 land in the manor of Sydney was sold by Issac Bungar, which suggested he could have had the glass-making site in Sidney Wood (Godfrey p54-59, 1975).

The migration of the industry away from the base of the Weald began before glass-making ceased in this area (1620). A monopoly was established by Sir Robert Mansell. This monopoly banned the burning of wood for glass-making purposes. The migration was from the heavily wooded Weald to coal-rich areas, such as the North-west of England, the Midlands, Yorkshire and Bristol. Examples of sixteenth century glasshouses have been found in Staffordshire, at Bagot's Park (Crossley p44-83, 1967), Bishops Wood (Pape p172-177, 1933) and Little Birches (Mortimer, 1991b). The movement to the south was seen at Kimmeridge (Crossley p340-382, 1987), while furnaces have been excavated to the east at Bristol (St. Clair Baddely, 1921) and as far north as Yorkshire, at Hutton and Rosedale (Crossley and Aberg p107-159, 1972). A glasshouse may have existed at Wollaton in Nottingham, where evidence in the Middleton Collections shows a plan of a glasshouse. Also, records of supplies for glass-making and correspondence with Sir Robert Mansell suggested that there was glass produced by Jacob Henzey and John Squire at the turn of the seventeenth century (Smith p30, 1962).

The industry was moving away from relatively small glasshouses to large cones, examples of which can be seen at the Stuart Crystal glass site at Stourbridge, Catcliffe in Sheffield and the furnace excavated at Gawber (Ashurst p92-140, 1987).

The distinct ending point of the 'forest' glass industry in the Weald in England was predominantly due to the competition for wood. The Weald was heavily wooded, which was ideal for the glass furnaces, as one of the major raw materials was the fuel source - wood. The competition for wood led to the approval of monopolies to control the production of glass. The search for an alternative fuel to wood forced the new glass-makers, or those licensed to produce glass, to look to coal.

In 1615 Sir Robert Mansell bought out the monopolies to produce glass using coal, taking over the first furnaces to attempt to coal-fire the glass-making process in the London furnaces owned by Sir Edward Zouch (Godfrey pp78-79, 1975). Mansell began to patent coal-fired furnaces in coal-bearing areas. These included the glasshouse at Wollaton in Nottingham in 1615 (Smith, 1962) and Kimmeridge (Crossley p340-382, 1987). The design of the Kimmeridge glass furnace was based on a style seen in Lorraine. This was a winged furnace with a central hearth. This retained some of the links with the 'forest' glass manufacture, but the move away from the wooded regions had begun.

It appeared that there was a definite starting point of around the twelfth century AD and finishing date (1620) to the 'forest' glass manufacture in Wealden England.

3.2 The Weald

Glass-makers in the Weald would have competed for raw materials for use in their furnaces. Fuel was an important factor in locating an industrial site, and as the Weald had a ready supply of fuel, wood, it became a significant industrial region during the medieval period. The Wealden iron industry seemed to run a parallel course with the glass industry to some extent. It was the influx of French iron workers which established the industry, prior to migration throughout Britain (Awty, 1981). The comparison between the migration of glass-makers and iron workers was good, as the migration from continental Europe took place at the same time, late fifteenth century (Crossley p156, 1990).

The location of the iron industry, in the iron ore-rich areas of Sussex, Surrey and Kent would have added prosperity to the region, which would have attracted the glass-makers to a thriving area (or it could have been the earlier migration of the glass-makers attracting the iron workers).

In addition to a thriving iron industry, pottery was being produced in the Surrey and Sussex area in this medieval period. The close proximity of London as the main market for the pottery made Surrey ideal for the production of wares. Cheam ware was produced from the middle of the fourteenth century, before its disappearance at the end of the fifteenth century (Crossley p248-249, 1990).

The link between immigrant workers was been seen at Parrock, Surrey, where the operation of the pottery kilns was by French workers (Freke p79-125, 1979).

This showed that it was not only the glass-makers migrating to the Weald during the medieval period, but other industries also. The reason for the migration was uncertain, though the religious turmoil throughout northern Europe at this time, such as the massacre of St. Bartholomew in 1 may have played its part (Kenyon p124, 1967)

The other form of employment in the Weald was farming, as noted by the fact that Strudwick family were farmers as well as glass-makers. The seasonal aspect of glass-making described earlier in this chapter (Kenyon p121, 1967) may have allowed farming to take place during the summer months. This system of a dual economy was not uncommon, and further examples of this were seen in the lead industry in Derbyshire (Blanchard, p121-122, 1971)

The Weald was ideally situated for the London market. The area itself had many advantages, including the presence of raw materials. Wood was readily available, and large areas of woodland can still be seen throughout the region today.

CHAPTER FOUR

THE SITES AND SAMPLES

4.1 Blunden's Wood

The glass-making site of Blunden's Wood lay undiscovered until 1959. In 1959 a low, square mound, with evidence of glass-making, was discovered (Wood, 1965). Some fragmentary evidence had been removed, and there had been some disturbance where a bank had collapsed.

4.1.1 The Location of Blunden's Wood (SU/974.374)

The location of the site was within a wooded area of oak, ash and hazel (Wood p55, 1965), south-east of Hambledon village as shown previously (fig. 3.1). The location of the glasshouse at Blunden's Wood can be seen (fig. 4.1), along with Gunter's Wood and Vann Copse glass-making sites.. The site was destroyed at the end of the excavation, when the Sussex and Dorking Brick Companies Limited began to quarry the clay for use in brick- making. The present woodland of Blunden's Wood consisted of mainly oak trees (English), though a small number of coppiced beech trees could be seen. All these were relatively recent, so the actual species present during the life of the glass furnace was unknown. The wood was the source of fuel for the glass furnaces and ash as a fluxing agent in the glass melting process.

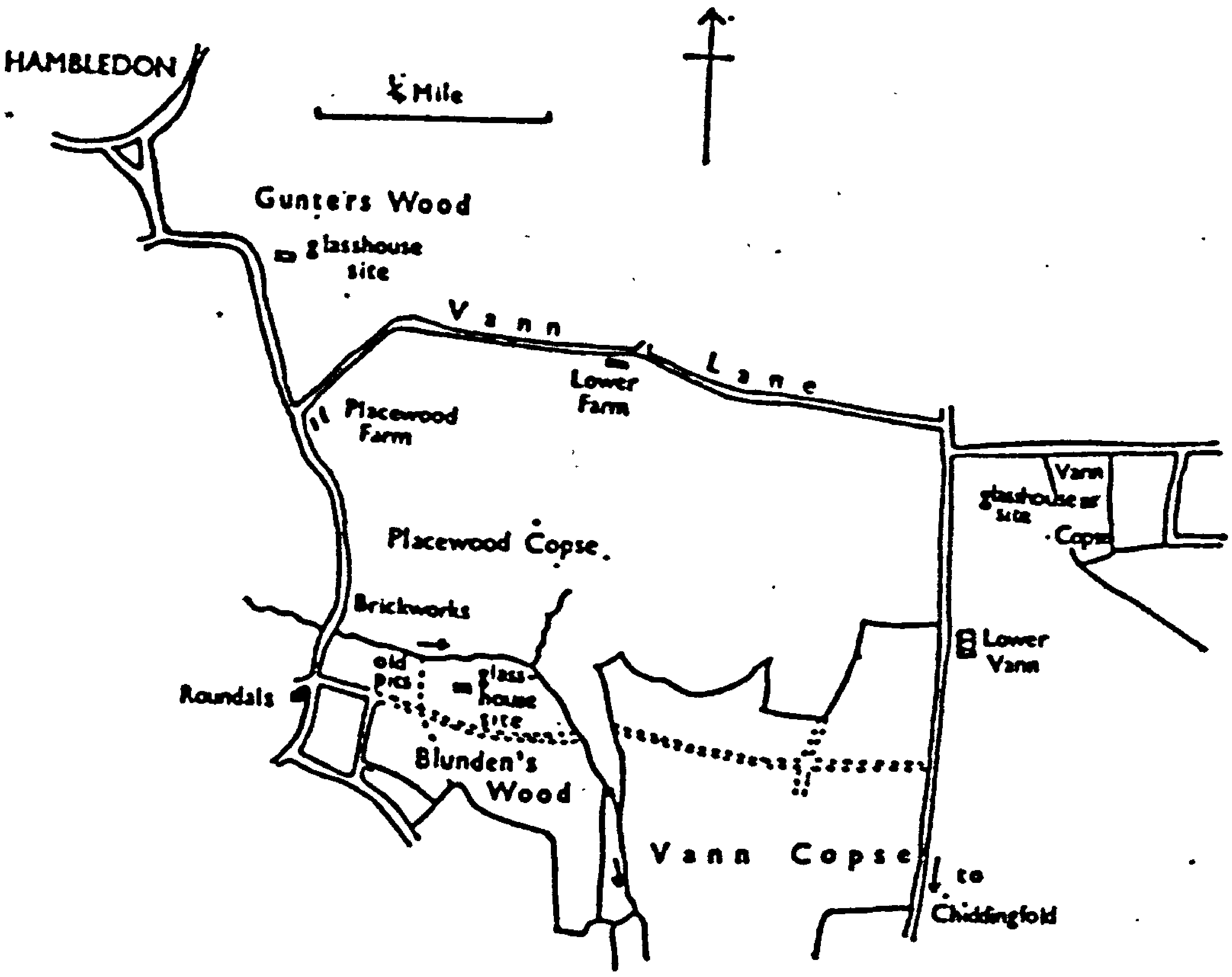

Figure 4.1 - Location of Blunden's Wood (Wood p55, 1965)

The source of sand for use in the manufacture of glass at Blunden's Wood may have come from Hambledon Common in Surrey, or Graffham in Sussex (Wood p55, 1965), but veins of Lower Greensand may have come to the surface closer to the site or even on it. Blunden's Wood glasshouse was situated on a bed of Wealden clay. This bed contained a mixture of sandy clay, calcarous sandstone and grey clay (Thurrell et al p53, 1968). Outcrops of sandy coloured clay can be seen less than 50 metres away from the original location of the glasshouse (fig. 4.2). Therefore, the raw materials required for the production of glass, ash and sand were available to the medieval glass-maker in Blunden's Wood. It must be stressed that if any raw materials were to be transported to the site it was highly likely that it would be the sand. This was because sand was relatively easy to transport, and only small quantities would have been required in comparison with ash, fuel and clay.

4.1.2 The Excavation of Blunden's Wood Glasshouse

The site was excavated in 1960 under the supervision of Mr E. S. Wood, prior to its destruction by Sussex and Dorking United Brick Companies Limited.

The excavated site showed three furnaces (fig. 4.3). First, there was the main furnace, 3.3 metres in length and with an original width of 2.4 metres. This furnace consisted of a central flue flanked by two benches, or sieges, made from sandstone, on which the crucibles were placed. This was surrounded by a stone wall. This wall was originally thought to have left a cavity between the sieges and itself. However, a re-interpretation of the structure indicated that the outer wall was contiguous to the sieges (Ashurst and Wood p93, 1973).

Figure 4.2 – Outcrop of Wealden Clay in the vicinity of Blunden's Wood

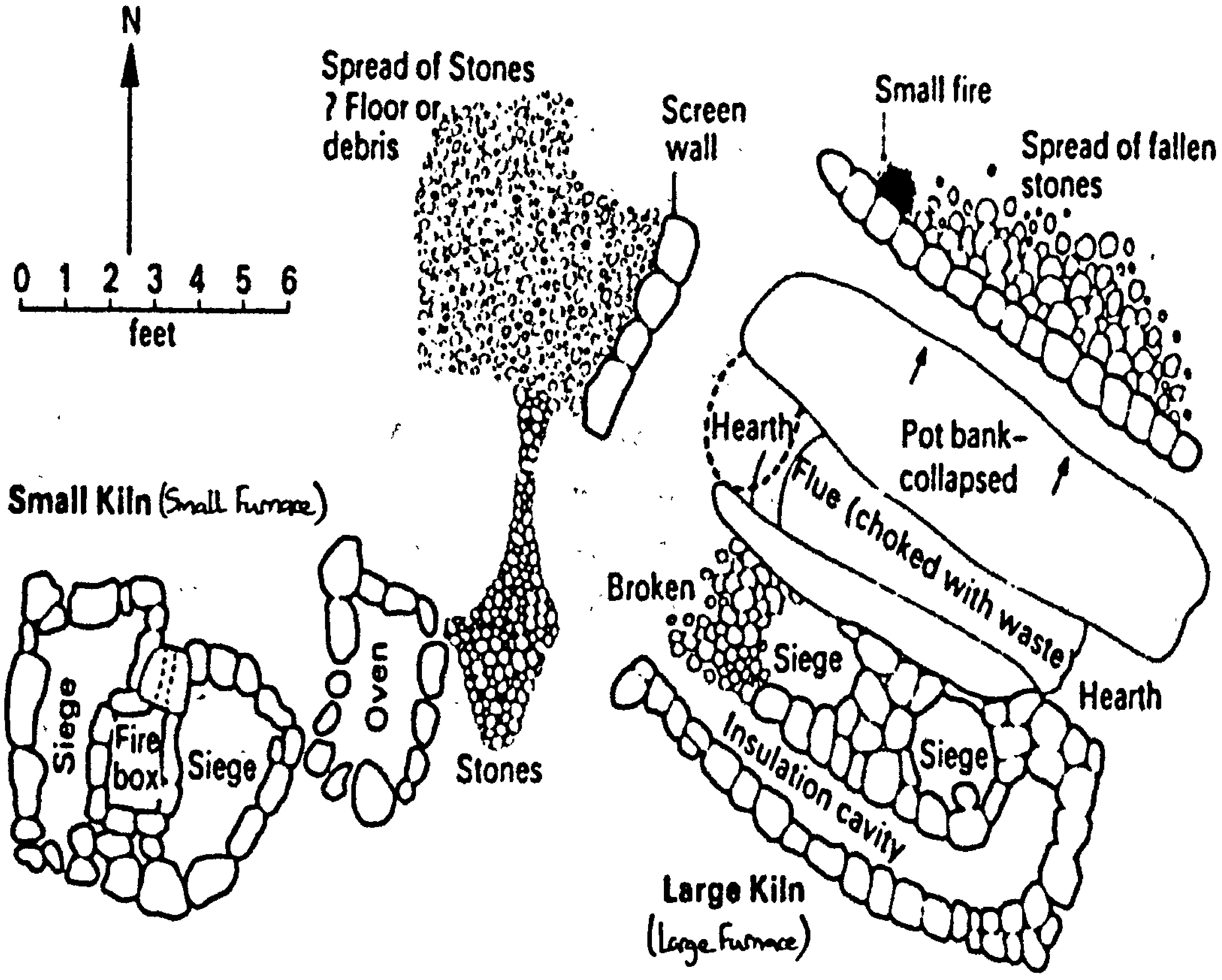

Figure 4.3 – Excavation Plan of Blunden's Wood Glasshouse (Wood p56, 1965)

There appeared to be a hearth at either end of the flue, which showed signs of two distinct layers of burnt material. This suggested the furnace had been operated in two phases (Wood p57-58, 1965).

No evidence of a roof could be found, although one idea suggested that a wooden frame was used on the outer edge of the sieges. This would have allowed the walls and a roof to be built. On firing the furnace this wooden structure would burn, which left the stone walls (Wood p59, 1965). This furnace was probably used for glass melting, with evidence of a highly burnt clay base suggesting that this furnace was where the highest process temperature was reached.

Second, a smaller round furnace (Small kiln) was uncovered, 2.4 metres long by 1.3 metres wide. The shape of this was more round than that of the main furnace, and there was evidence of a tuyere, which may have allowed bellows to be inserted into the furnace and produce a forced draught of air. This furnace was split into two chambers, separated by a cavity (fire-box) filled with burnt clay. This was the hearth for both chambers of the furnace. It has been suggested that fritting and annealing took place in this furnace. The left side, with evidence of splashed glass, may have been used for fritting (Wood p64-65, 1965).

Finally there was a small oven, 0.75 metres long and 0.45 metres wide. No hearth could be seen, just blackened soil. The lack of spilt glass, and no firing evidence suggested that this furnace was used for the pre-heating of the crucibles.

The site was destroyed after being excavated, and no new furnaces or structures were uncovered in subsequent levelling of the site. A model of a medieval glasshouse (fig. 4.4) was based partly on the excavation of the Blunden's Wood site, and has been displayed at the Pilkington's Museum of Glass.

4.1.3 Description of Glass Fragments

All the sample numbers in this work refer to the site excavation numbers. Most of the glass from this site was pale green in colour associated with 'forest' glass manufacture (fig. 4.5). These samples were of good quality - few bubbles and homogeneous - but the nature of the raw materials used produced a glass which was translucent rather than opaque. There was little colour variation in the fragments of vessel glass for this study, though samples that had a blue or yellow tint were found (Wood p65, 1965). The thickness of the fragments varied, although most appeared to be of a similar thickness, 2-3 mm. A few fragments of less than 0.5 mm in thickness were found, which suggested that the glass-maker was attempting to achieve glass of fine quality, but not always reaching his target. It was generally regarded that the finer the glass vessel, the higher quality of craftsmanship.

Figure 4.4 - Model of Glasshouse, based on Blunden's Wood

Figure 4.5 - Photograph of Fragments of Vessel Glass (AS3542)

Weathered fragments fell into two categories - slightly and heavily corroded. The slightly weathered samples (fig. 4.6) showed a fine pale coloured surface layer of weathering, where the surface depth is only a very small fraction of the total glass.

The heavily weathered samples (fig. 4.7) had a crust adhering to the glass. This crust was sandy-brown in colour, darker than the lightly weathered fragments. The major difference between the fragments was the depth of corrosion, where the sandy crust represented a significant fraction of the excavated glass. In some cases this outer layer was up to 3 mm, compared to the inner glass thickness of 2 mm. The inner glass was a rich green colour, with a texture similar to that of orange peel, pitted and dimpled.

Another type of glass was found amongst the weathered samples (fig. 4.7). This glass was a yellow-brown colour, and had a better clarity than the typical pale green glass from the site. It was unclear whether these were manufactured on the site, or were brought from outside, as there appeared to be too few fragments to ascertain the true origin of these pieces of glass.

The final group of glass fragments showed the extent of different types of waste that was generated at a medieval glass-making site. Fragments of opaque pale green material were found (fig. 4.8), which were probably pieces of devitrified glass.

Figure 4.6 - Fragments of Vessel Glass with Pale Weathering (AS3550)

Figure 4.7 - Fragments of Heavily Weathered and Yellow Glass[top-right] (AS3560)

Figure 4.8 – Fragments of Divitrified Glass (AS3554)

Other waste material (fig. 4.9) may have represented other processes of glass-making, as samples of glass which flowed prior to being discarded can be seen alongside the opaque glass. The rounded nature of these pieces suggested that the glass was poured from crucibles, possibly as a method of emptying the crucible at the end of a glass-making session.

4.1.4 Description of Crucible Fragments

There were two shapes of crucibles found at Blunden's Wood, bucket-shaped pots with straight sides, or more commonly, barrel-shaped pots with 10 mm or 6-8 mm thick walls. The internal, top-rim diameters of the pots varied from 250 mm to 300 mm (Wood p68-69, 1965). The majority of the crucible fragments were red-brown in colour (fig. 4.10). Many of the pieces had green glass adhering to the ceramic material. The adherence showed the pitted nature of the crucibles, probably caused by the glass attacking the crucible wall. Other fragments showed the problem of glass-making in respect of waste glass running down the outside of the crucibles as glass was poured from the crucible. This may have caused a problem in handling the crucible, as this glass would solidify quickly on removal from the furnace, resulting in a very sticky surface.

Figure 4.9 – Fragments of Glass Waste (AS3578)

Figure 4.10 – Fragments of Glass-making Crucibles (AS3498)

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A crucible fragment with glass adhering to the inner face was found (fig. 4.11). Again the red-brown colour of the clay body is visible. Fragments of glass from this crucible were taken for compositional analysis, as described in chapter 6.

The firing experiments carried out on the clay local to Blunden's Wood (see section 2.3.1) showed that the buff Wealden clay turned to a dark, red-brown colour at 1200 °C. The red-brown colour of Wealden clay, and the red-brown colour of the crucibles, may have indicated that the clay material was similar. However, initial comparison of the chemical composition of the crucible fragments and the clay from Blunden's Wood did not suggest this (Wood p71, 1965).

A slightly more pale brown crucible material was observed (fig. 4.12). Attached to it was a material which resembled frit - dark and semi-vitrified. It may be coincidence that this crucible material was different in colour to the known samples used in glass-making, or it may have shown that the glassmaker used different pots for fritting and glass melting. The presence of this material was evidence that fritting may have taken place, though further analysis will have to be carried out to clarify this.

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These samples represented the range of crucible fragments from Blunden's Wood, but it must be stressed that in the case of the ceramic pieces and the glass fragments, specimens were chosen to represent the whole assemblage excavated.

Figure 4.11 – A Crucible Base, with Glass adhering (AS207)

Figure 4.12 – A Fragment of Crucible, with Frit attached (AS3496)

4.1.5 Dating of the Site

Three separate methods of dating confirm that Blunden's Wood was probably operational in the second quarter of the fourteenth century. Firstly, magnetic dating of the main furnace provided a date of c. 1330 (Wood p76, 1965). Secondly, fragments of Cheam ware pottery were found at Blunden's Wood. Production of Cheam ware was thought to have started during the middle of the fourteenth century (Wood p76, 1965), which may have indicated that Blunden's Wood was operational between 1330 and 1350. Finally, a large fragment of an iron horseshoe was found which resembled one found at Tutbury, which was dated 1322 (Wood, 1965). An absolute date of operation of Blunden's Wood was not possible. However, the estimate that glass-making was taking place at 1330 appeared to be quite accurate, with a possible operation span of twenty years (between 1322 and mid-fourteeth century).

4.2 Knightons

The glasshouse at Knightons was excavated between 1965 and 1973, after the discovery of the site in May 1965 (Wooda p8, 1982). It has been preserved, and is a feature within the Forestry Commission owned Sidney Wood.

4.2.1 The Location of Knightons (TQ/0170.3410)

Knightons was located 400 m north of a seventeenth century house, Old Knightons, on the boundary between the parishes of Alford and Dunsfold (fig. 4.13).

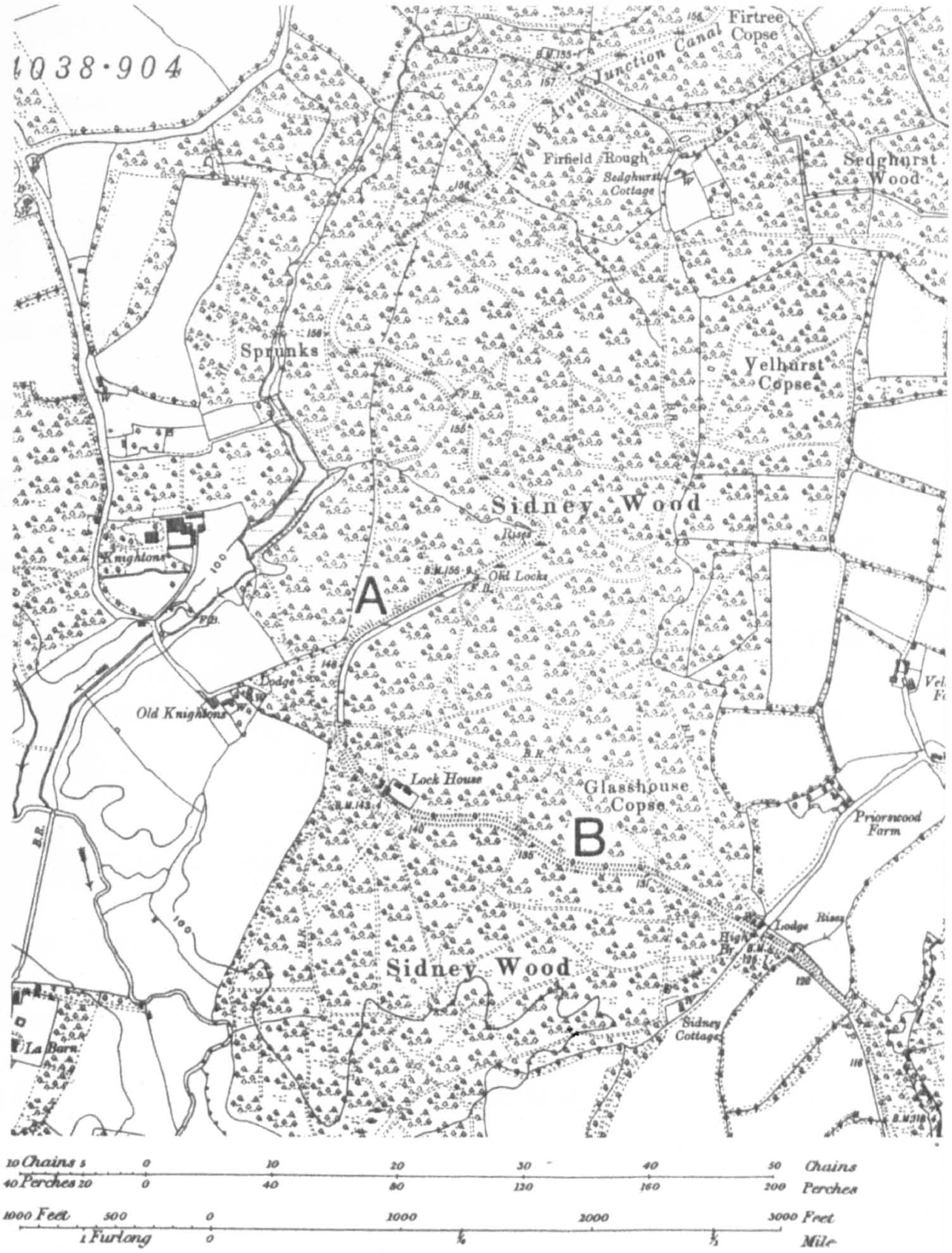

Figure 4.13 – The Location of Knightons Glasshouse within Sidney Wood

(A = Knightons, B = Sidney Wood) (Wood, 1982a)

A programme of clearance and tree re-planting has taken place recently in Sidney Wood, but, the trees covering Knightons were still predominantly established English oak trees. The site lay on a bed of yellow-buff Wealden clay within Sidney Wood. The area adjacent to Knightons glasshouse lay on a bed of grey laminated clay, with bands of silty mudstone. Near to the site was evidence of grey shaly clay, large beds of sandstone, as well as a fine sand (Thurrell et al p53, 1969).

4.2.2 The Excavation of Knightons Glasshouse

There were four furnaces excavated (Wood p8-12, 1982a) (fig. 4.14). Two furnaces were found to lie almost on top of one another. The first was similar in shape to that found at Blunden's Wood, typical for a 'northern' type glass furnace. It was rectangular with a bank of sieges either side of the fire trench. The lateral dimensions were similar to the Blunden's Wood furnace, 3.3 metres long and 2.3 metres wide. External dimensions were slightly larger, 4.46 metres by 3.23 metres.

The sieges had spaces for three crucibles, compared to two in the Blunden's Wood furnace. A hearth ran the length of the furnace, fired at one end only. The second furnace had replaced the first, having moved slightly north from the original position. The style was identical to the first furnace, however, the dimensions had been altered.

The width of this furnace had been reduced to 1.84 metres internally and 2.76 metres externally (Wood p9, 1982a). The reason for the reduction of dimensions was unclear.

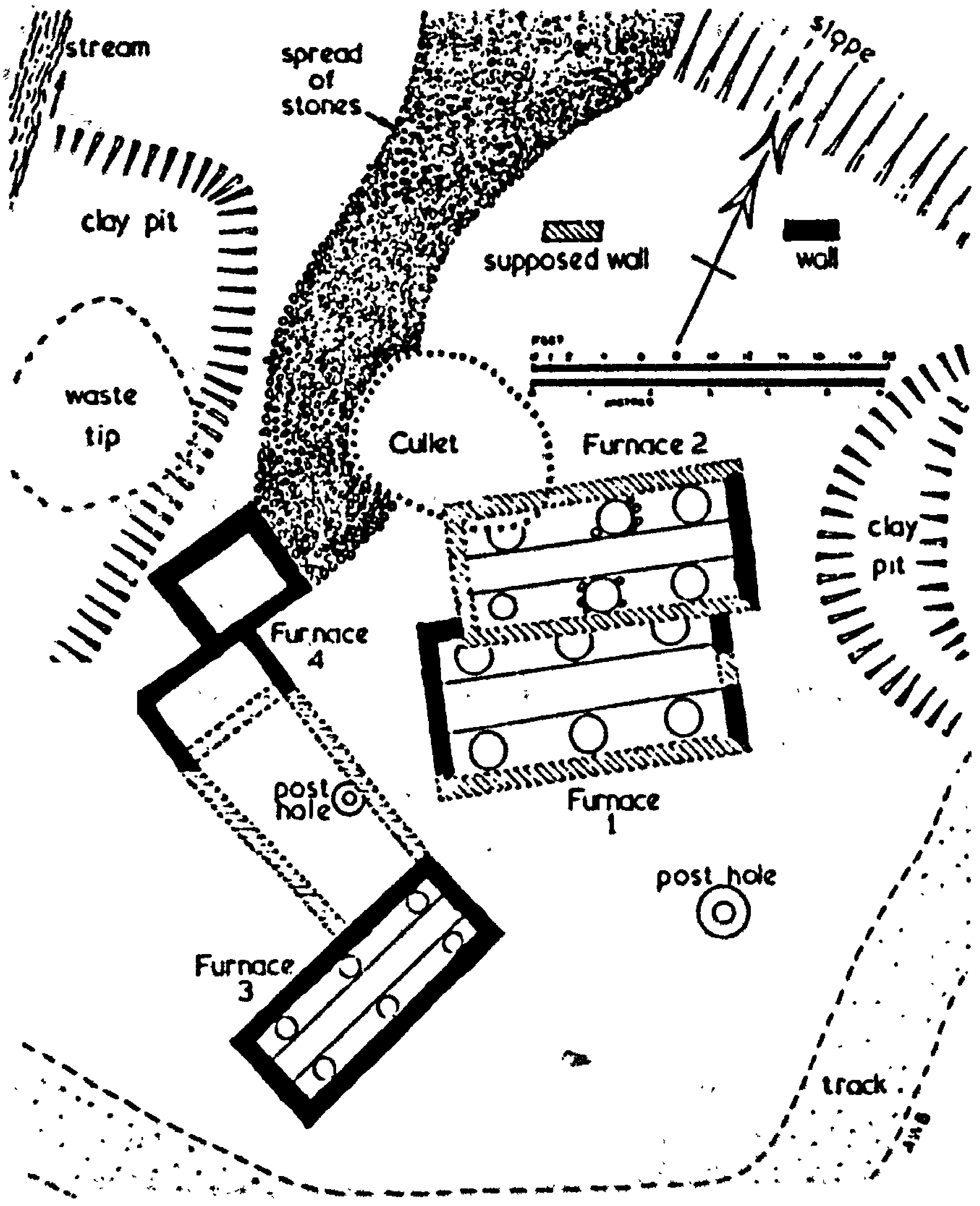

Figure 4.14 - Excavation Plan of Knightons (Wood, 1982a)

The third furnace was of similar design to the first two, except that the direction in which it lay was north to south. As before, three sieges banked either side of the hearth. Inside the furnace fragments of frit, and lump glass were found, which may have suggested that this third furnace was the fritting furnace, while furnaces one and two were primarily used for glass melting. Large fragments of crucible were also found in this furnace (Wood p17, 1982b).

The final, fourth furnace to be excavated was very different in structural design to the previous three furnaces. This furnace consisted of two square chambers that shared a common wall. They were not joined back to back, but were slightly offset. In the joining wall was a hole, 60 cm in width, which may have been to allow hot gas to pass from one side to the other (Wood p17, 1982b). There was evidence of crown glass within the chambers, so it appeared that this was a furnace dedicated to annealing. The dual chambers would have allowed continuous annealing of crown sheets where each side was fired alternately (Wood p10, 1982a). There was an expansion in use of window glass in houses at the start of the seventeenth century (Polak p359, 1978). This dedicated furnace structure for the production of window glass may have been the first indications that the glass-making sites had to cater for a new market, and be able to produce larger quantities of crown glass.

In addition to the main furnace structures, a cullet store, evidence of a shed, a working floor and clay-pits were found. These extra features give the suggestion that Knightons was a self-contained and well-ordered site.

As mentioned previously, this glasshouse has been preserved, and evidence of clay with glass adhering to it can still be seen littered over the site.

4.2.3 Description of Glass Fragments

There were nearly 12000 fragments of glass excavated from Knightons, with 0.33% of the total glass observed as 'late' type blue-green 'forest' glass (Wood p19, 1982a). The excavated glass forms showed a strong link with alchemy, with items of medical and distilling ware found (Wood p19, 1982a). Apart from this the glass consisted of window, vessel, bottle and domestic ware.

The number of fragments chosen for this study was tiny in comparison with the large assemblage. However, the fragments were chosen to best represent the glass produced at Knightons. The glass was a pale green colour, with few bubbles and inclusions (fig. 4.15). The clarity was similar to those found at Blunden's Wood, which showed that the window glass from Knightons was only partially transparent. The majority of glass fragments were approximately 2-3 mm in thickness.

Crown sheets were formed by placing a large gob of glass onto the end of a pontil, then spinning the glass to produce the sheet. This produced an inner segment that was larger in thickness than the rest of the plate of glass. Examples of this could be seen in the form of 'bulls-eyes' (fig. 4.16) where the pontil mark was clearly visible.

Figure 4.15 – Fragments of Window Glass (AS4931)

Figure 4.16 – Fragments of Window Glass (AS4934)

Some fragments of 'bulls-eyes' showed the presence of a sand coloured weathering layer, similar to the pattern of light weathering observed in many of the samples from Blunden's Wood (fig 4.17). In addition to this these fragments showed a great variation in thickness. The thickness of the centre portion of the glass in some of these crown sheets was as much as 15mm, which would have represented a very heavy piece of glass when this was being formed. This showed the great strength of the glass-maker, as well as the skill that would have been required to produce the crown sheets.

Examples of coloured glass and vessel glass were mentioned (Wood p19-33, 1982a), though no samples of either were analysed in this work.

4.2.4 Description of Crucible Fragments

The crucibles found at Knightons had a very distinctive shape. The rims of the vessels were pinched into a sharp edge, which provided a character different to crucibles found at other sites (Wood p18-20, 1982a). The crucibles showed a clay of light brown colour (fig. 4.18), which appeared to resemble the buff coloured, clay of the Weald, as found at Knightons, and described in section 2.3.1. However, the Wealden clay was much more red when fired to 1200-1400 °C than the crucible fragments were, which may have indicated that an alternative source of clay used in the manufacture of the crucibles was available.

Figure 4.17 – Fragments of Window Glass (AS4838)

Figure 4.18 – Fragments of Crucibles (AS4921)

Large fragments of a crucible base were found, (fig. 4.19), which provided a good measure of the size of the crucibles being used in the manufacture of glass. The external base circumference was estimated to be 120 cm. Given a height of crucible in the region of 0.5 metres, an estimated volume of glass produced in the crucibles was 0.3 m^3 (assuming the sides of the crucibles were relatively straight and the crucible was half filled). This crucible had glass adhering to the inner face of it. Fragments were taken for analysis, as described in chapter 6.

4.2.5 Dating of the Site

Knightons was dated to 1550, which suggest that it was one of the last medieval forest glasshouses to have been built. The glasshouse was dated to 1550 by pottery fragments that included salt-glaze stoneware found on the site. These were styles found in the sixteenth century (Wood p41, 1982a). Added to this was the discovery of a coin. A silver shilling of Edward VI was found with the date of 1550 on it (Wood p44, 1982a). It was this evidence which enabled an operational date of 1540 to 1560 to be estimated, a period of great activity in the glass industry. Archaeomagnetic dating was carried out on the furnace floors, which provided a date of 1550 (Wood p64, 1982b).

Figure 4.19 – A Crucible Base (AS4779) [Full-scale = 5cm]

4.3 Sidney Wood

This site was thought to be in operation at the end of the production of English 'forest' glass. This meant that it was immensely important in understanding the ending of 'forest' glass manufacture in the Weald.

4.3.1 The Location of Sidney Wood (TQ/0220.3372)

The glasshouse was located near to the Knightons glasshouse, within Sidney Wood, as shown in section 4.2.1 (Fig. 4.13). The geology was similar to that of Knightons, in that there was a buff-yellow stratum of Wealden clay at the surface. As at Knightons the clay was grey and shaly (Thurrell et al. p53, 1969).

There has been re-planting of trees very recently over the area that included the Sidney Wood glasshouse. The new trees are pine, though very close to the site there were established English oak trees. This did not aid the determination of the type of vegetation that was present while the glasshouse at Sidney Wood was operational, but the lack of beech trees may have indicated that the oak had always dominated the landscape in Sidney Wood.

4.3.2 The Excavation of Sidney Wood Glasshouse

Two excavations of the site took place in 1923 by the Vicar of the parish church in Alford, F.W. Cobb, followed in 1930 and 1931 by Samuel Winbolt. However, these were not excavations carried out to modern standards.

Evidence was not recorded in much detail, and the only record of the style of the furnaces was described by Winbolt (Winbolt p36-40, 1933). A sketched plan of the glasshouse (fig. 4.20) provided the size of the whole site (Winbolt p38, 1933), but not the size of the furnace.

Hearth bricks were found at the site, and they appeared to be well made. There was evidence that some of these bricks had been burnt. The fact that the furnace was drawn in the shape of a rectangle indicated that it was probably made in the 'northern' style of furnace, though this could not be proven. This was the extent of the published work by Winbolt, which made a comparison with the Knightons and Blunden's Wood sites slightly weighted. This was also the case with much of the glass and crucible evidence, where the lack of available material pose problems in a comparative study. Small fragments of material can still be seen in the area around the glasshouse, though these fragments appeared to be spread over a large area.

It was thought that coal cinders were found in the hearth which it has been suggested were as a result of coal being used as fuel (Winbolt p40, 1933). The period between 1615 and 1620 was dominated by the banning of wood as a source of fuel for glass furnaces, as described in chapter 3, and there was a need to establish coal-fired furnaces, under the monopoly of Sir Robert Mansell. Thus, the presence of coal cinders may have indicated that attempts were made to transform a wood-fired furnace into a coal-fired one. However, this could not be proven one way or the other.

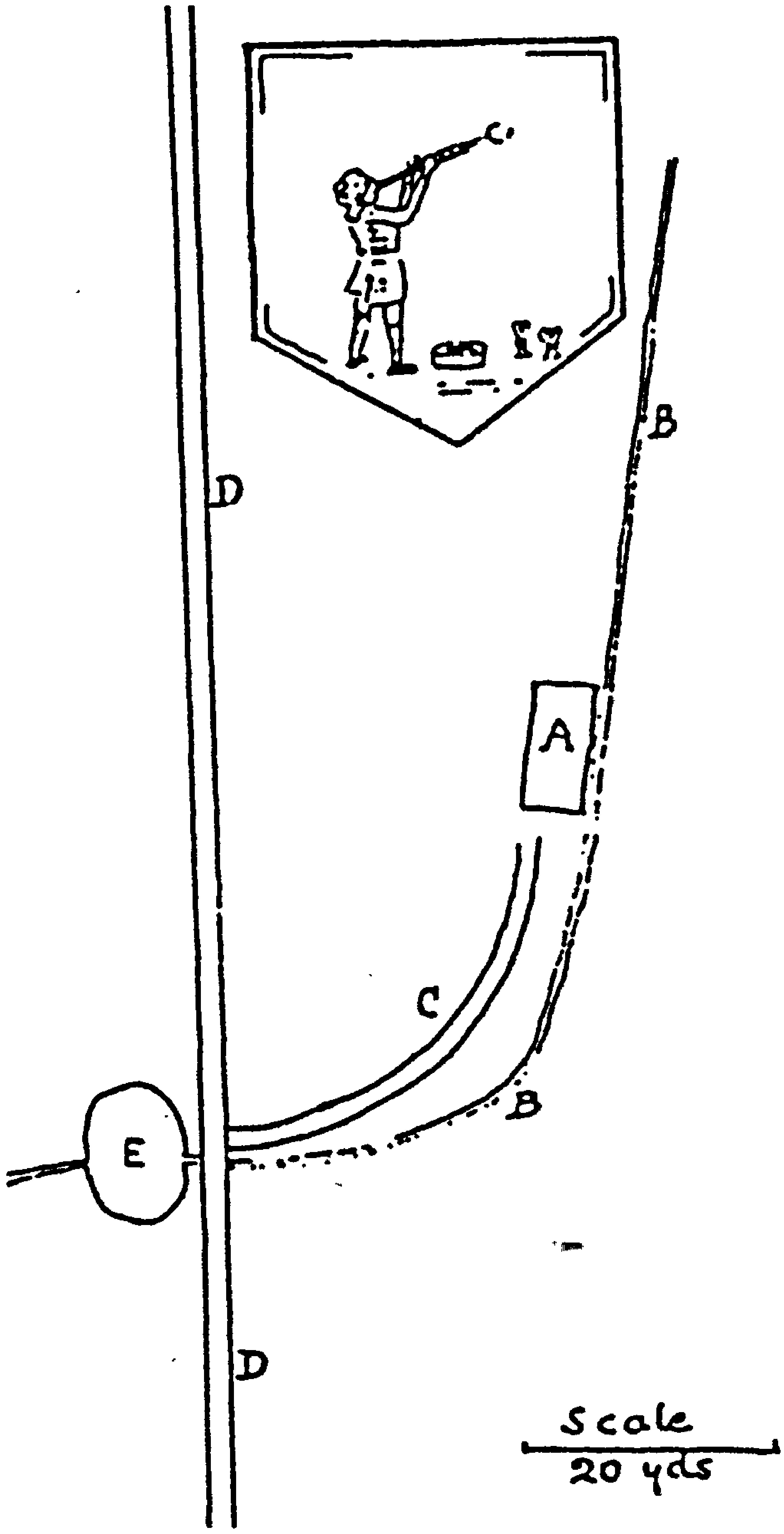

Figure 4.20 - Plan of the Sidney Wood glasshouse

There may have been a link with Jean Carré to the Sidney Wood glasshouse. He was buried at Alford parish church in 1572, about a mile away, as described in chapter 3. This may have indicated that he had some involvement in the site, though this may not be the case. The importance of Carré to the influx of immigrant glass-makers that transformed the English glass industry made this link most interesting.

Finally, evidence that the Sidney Wood glasshouse was operational at the start of the seventeenth century could be seen on a map of Surrey by John Speede in 1610 (fig. 4.21). From the location of the glasshouse, in comparison with the locations of known glasshouses, it appeared that the 'glashose' seen near to Sydney Wood was that of the Sidney Wood glass-making site. A glasshouse could also be seen on two earlier maps by Norden (1594 and 1607), that suggested that the Sidney Wood was an important feature at the end of the sixteenth century (Kenyon p203, 1967).

4.3.3 Description of Glass Fragments

It has been reported that the glass from this site was the finest medieval glass produced in the Weald. The nature of this glass was described as nothing 'comparable in quality with this Sidney Wood green glass' by Mr. F Buckley (Winbolt p40, 1933). Specimens of Sidney Wood glass are kept in The British Museum and the Science Museum, so the number of samples available for examination were more limited than the numerous samples open to investigation from Blunden's Wood and Knightons.

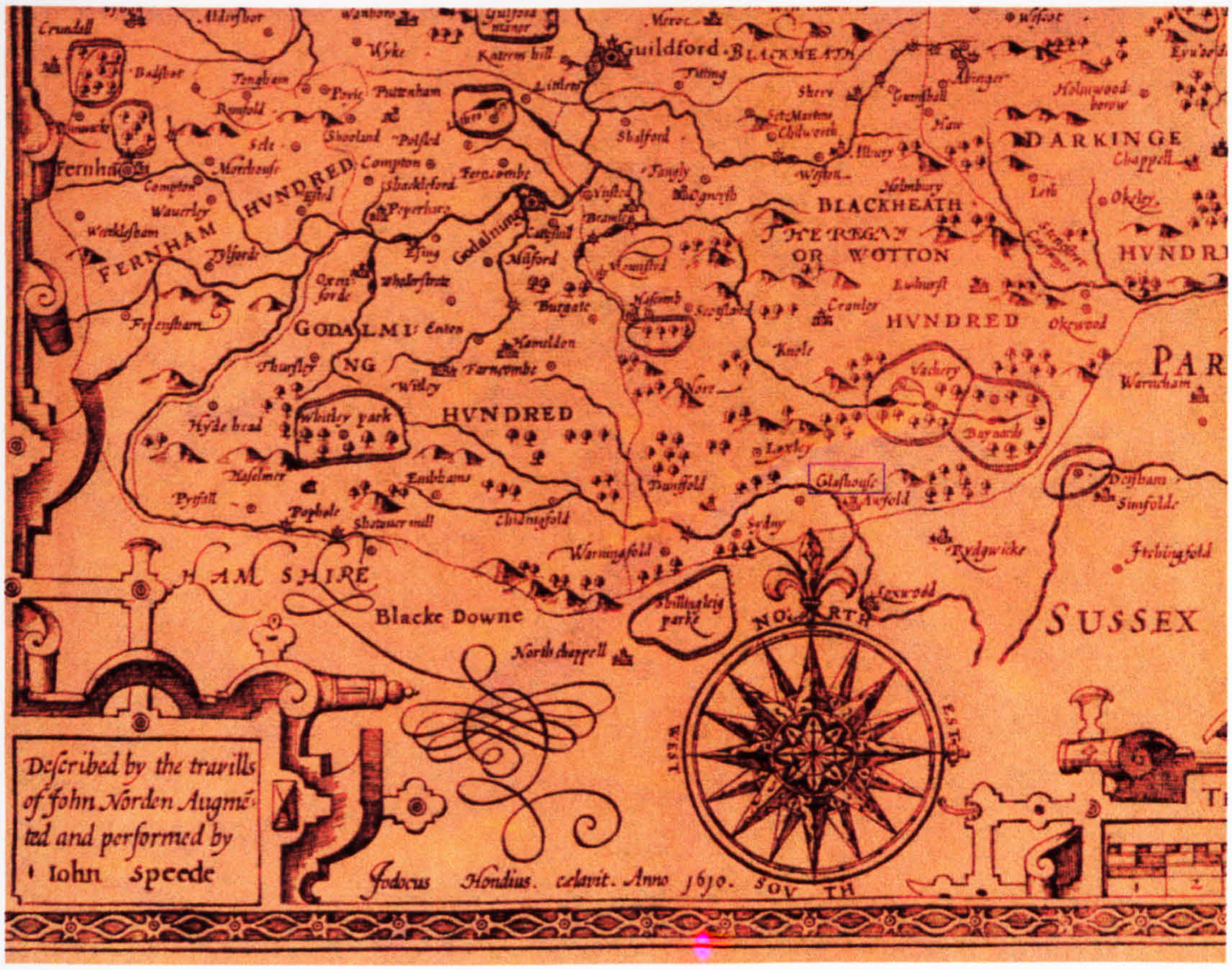

Figure 4.21 - Speed's map of Surrey in 1610

Samples of blue-green glass (fig. 4.22) showed the excellent quality. There was far greater clarity in the glass, in fact it is possible to describe the glass as transparent, not something which could be said of most 'forest' glasses. Also, the blue tinge to the glass was different, which may be due to tighter control of the glass-making process. There may have been more control of the redox reaction involving the oxides of manganese and iron. The clarity of the glass showed the high standard that the glass-maker attained, which suggested someone with considerable knowledge, such as Jean Carré, may have been responsible for the making of the glass at Sidney Wood.

The glass from Sidney Wood was later than Blunden's Wood, and may have been the cause for less decay to take place, and therefore, the clarity and quality would be better. However, the supposed difference in date of operation between Sidney Wood and Knightons, as well as their close proximity was not able to explain why the quality of the glass from Sidney Wood should have been so much better.

One problem associated with the analyses of the fragments from Sidney Wood, and this could be applied to the analysis of the crucible fragments also, was small number of samples. A small number of fragments could only provide sufficient details of the nature of the glass, but not much more about the raw materials. It had been mentioned that fragments of window glass were found at Sidney Wood, but no such samples were analysed for this study (Winbolt p38, 1933).

Figure 4.22 – Fragments of Vessel Glass (AS4966, AS4967 and AS4977)

4.3.4 Description of Crucible Fragments

Crucible fragments appeared to show different clay was used in their manufacture to that which was present locally. Fragments were grey-brown in colour (fig. 4.23). They had a very tight texture, which had the appearance of a more dense crucible than those observed at Blunden's Wood or Knightons. The appearance of the blue-green glass suggested that the atmosphere within the furnace was more reducing, which may account for the grey colour of the clay, where the ceramic material has been reduced.

The crucibles may have been slightly more brittle and prone to thermal shock than crucibles both from Blunden's Wood and Knightons, due to the more dense structure. The integrity of the ceramic material would have provided a high quality crucible for glass-making (based upon my own examination of modern refractory bricks from glass furnace materials). The blue-green glass could be seen within some of the crucible fragments, which suggested that these crucibles were used for the production of the high quality glass at Sidney Wood.

A piece of red-brown stone was found (fig. 4.24), to which purple glass was adhering. This may have been a piece of the hearth bricks (Winbolt, p38, 1933). This purple glass was of particular interest as it was the only fragment of non-green 'forest' glass analysed.

Figure 4.23 – Fragments of Clay Crucibles (AS4981, AS4982)

Figure 4.24 - Clay Floor with Purple Glass adhering to it (AS4998)

4.3.5 Dating of Sidney Wood

The date at which Sidney Wood glasshouse was operational could not be wholly proven. It was apparent from the maps by Norden and Speede that a glasshouse was an important feature of Sidney Wood between 1594 and 1610. However, this evidence did not establish whether the glass-making site was the Sidney Wood glasshouse, or that it was operating. It could have been a feature that was present in Sidney Wood, but had stopped production.

The other evidence that provided an estimate to the date of operation of the Sidney wood glasshouse was the evidence of coal cinders within the hearth of the furnace (Winbolt p40, 1933). Again, this could only prove as scant evidence that Sidney Wood was operational at the start of the era when coal-fuelled furnaces were in use (1615), even if the cinders were from the date of the operation. Therefore, the operation date of Sidney Wood has been put between the end of the sixteenth century and the start of the seventeenth century.

CHAPTER FIVE

OPTICAL MICROSCOPY

5.1 Optical Microscopy of the Fragments

Optical microscopy of the glass fragments provided a little information about the homogeneity of the glass, but not much more. However, optical examination of crucible fragments and frit enabled information about the processes involved in the production of glass. In order to carry out the optical microscopy it was necessary to prepare a sample for investigation.

5.1.1 Preparation of the Fragments

Samples that best represented the range of specimens from each site were examined. Small fragments were either cut from larger ones using a diamond-blade, or chippings taken where appropriate.

Specimens were mounted in epoxy resin and cured at room temperature for 24 hours. The epoxy resin chosen was a two-component system, providing low viscosity to flow around the specimens. To ensure specimens were completely impregnated with resin the filled moulds were placed under vacuum. This forced resin into the porous specimens, while air was eliminated during decompression. The epoxy resin had the specimens of glass and ceramic encased in it.

These samples then underwent a grinding and polishing regime, from 240 grit emery paper to 1 μm diamond paste, that varied according to the specimens. Ceramic fragments required more careful control in polishing as they were made up of many phases, which polished at different rates. Therefore, so that all the phases were well polished, it was necessary to polish with caution. The glass samples behaved in a very similar fashion to the resin, and thus, polished evenly. This demonstrated that longer grinding and polishing times were observed for ceramic fragments than glass fragments. It must also be stressed that any glass adhering to the face of a crucible had to be polished according to the regime set for ceramic pieces, as they behaved as multi-phase fragments. The finished samples were polished down to 1 μm.

5.2 Optical Examination of Glass Fragments

Samples from Blunden's Wood, Knightons and Sidney Wood can be grouped together for the purposes of optical examination, as the fragments of glass appeared to be similar. The appearance of the vessel glass fragments from Blunden's Wood and Sidney Wood and the window glass from Knightons showed remarkable homogeneity. There appeared to be few bubbles within the glass, which suggested that a high enough temperature, and a long enough heating time, had been used by the glass-maker during the melting stage.

No obvious layers had formed in the glass, and, at these relatively low magnifications (under 40 times), there did not appear to be any leaching of calcium or alkali ions to the atmosphere to produce a surface layer of corrosion.

These samples were also examined in more detail at higher magnifications, using the scanning electron microscope (Section 6.3.1).

5.3 Optical Examination of the Crucible Fragments

The crucible material was observed as a multi-phase system, that consisted of large grains within a fine grained matrix (figs. 5.1, 5.2 and 5.3). A quite high proportion of open porosity was seen. Examination of the larger grains showed the appearance of cracking within them. The appearance of this cracking may have highlighted the difference in thermal expansion between the fine clay matrix and the coarse grains, which may have indicated that these coarse grains were added to the clay during the manufacture of the crucibles. The spherical shape of these grains, indicated that they were silica (Shelley p241, 1985), though this will need to be confirmed using scanning electron microscopy.

It was difficult to see if any of the porosity was directional, which would have indicated the direction in which the crucibles were formed. The degree of porosity was difficult to assess though it was apparent that the crucible fragments from Sidney Wood had slightly less porosity than the fragments from Blunden's Wood or Knightons.

The matrix of the crucibles appeared to consist of two different phases. This was most obvious in the fragment from Sidney Wood (fig. 5.3). The first of these phases was glassy in structure, while the second phase showed signs of crystal. At these relatively low magnifications (under 40x) it was difficult to resolve these crystals.

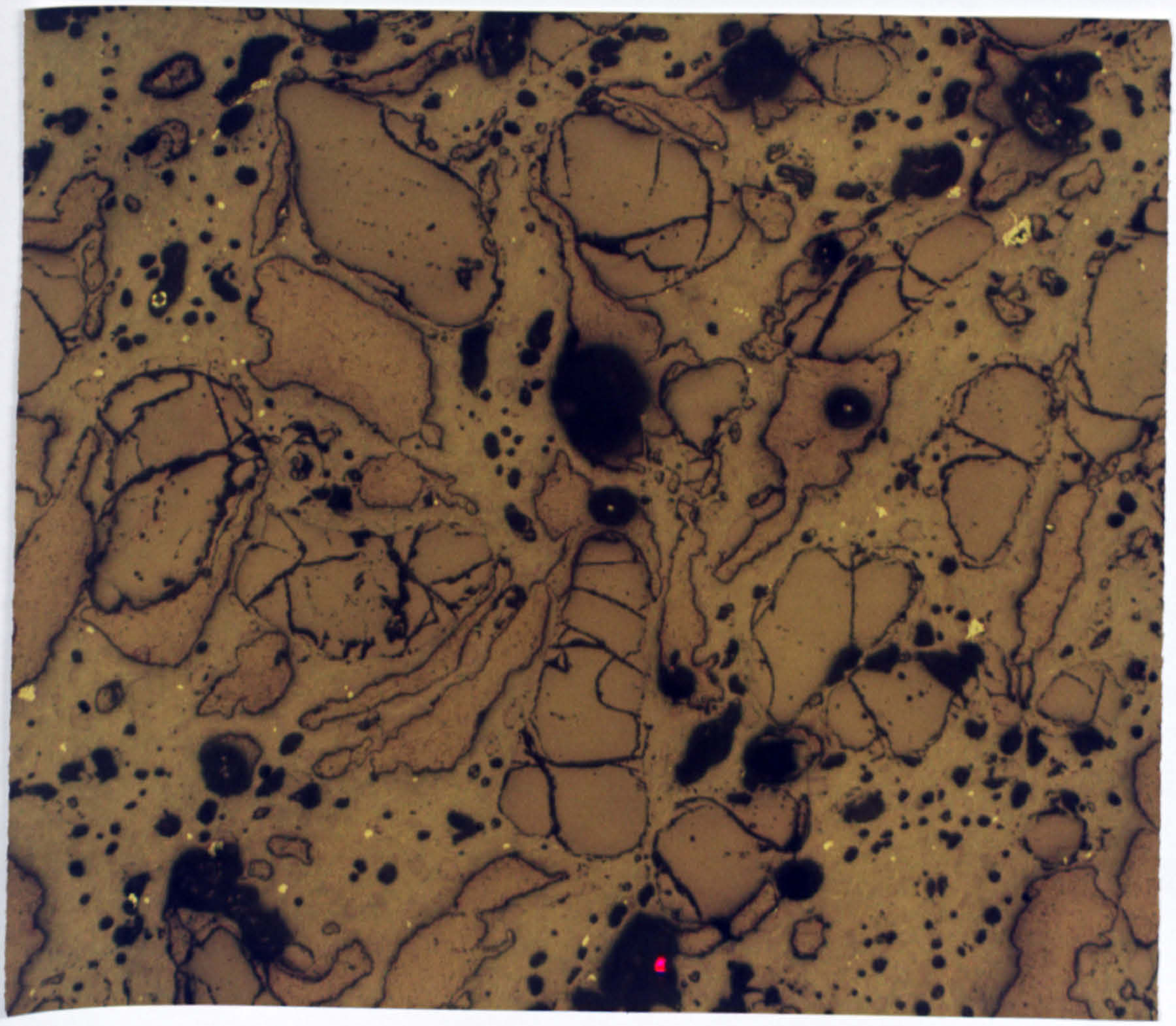

Figure 5.1 - Optical Micrographs of Crucible Fragments from Blunden's Wood

(Mag. = 10x)(AS3498)

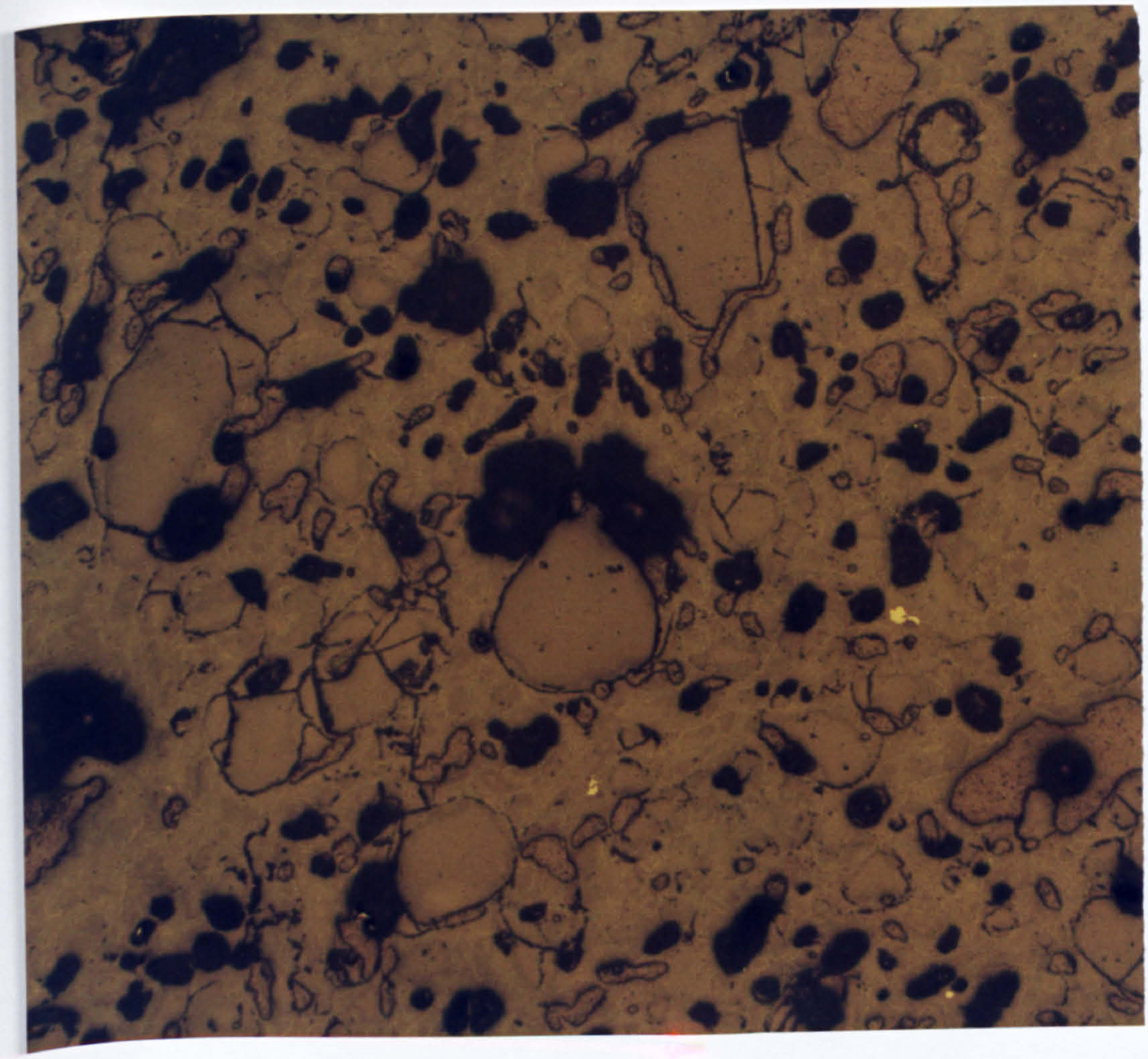

Figure 5.2 - Optical Micrographs of Crucible Fragments from Knightons

(Mag. = 10x)(AS4921)

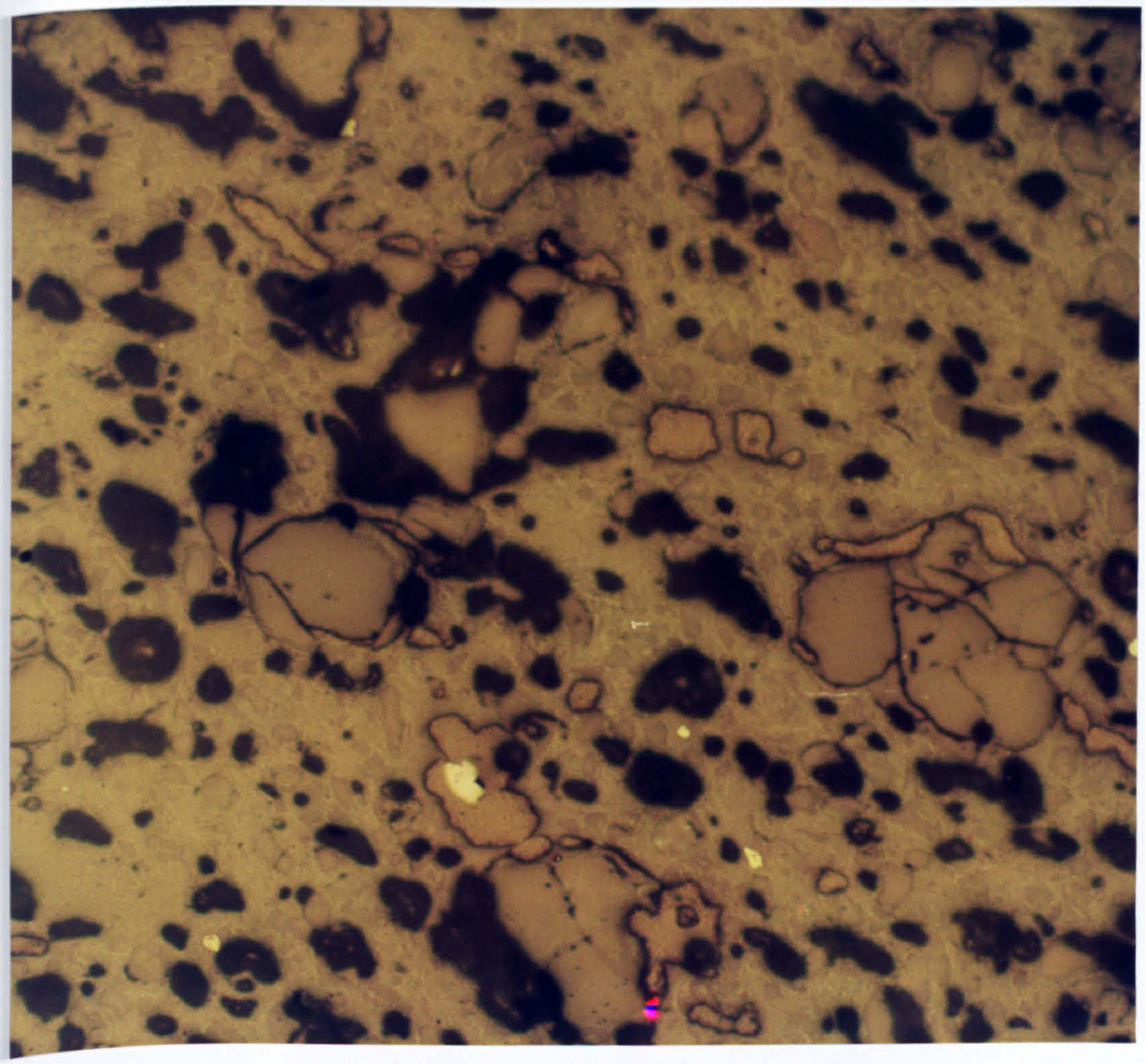

Figure 5.3 - Optical Micrographs of Crucible Fragments from Sidney Wood

(Mag. = 10x)(AS4982)

5.4 Optical Examination of Frit

A fragment of material that had the appearance of frit was found adhering to a crucible amongst the samples from Blunden's Wood. This fragment was examined using optical microscopy, and showed the structure of frit very clearly (fig. 5.4). Coarse spherical particles were observed in a matrix that showed a high degree of fusion. This fused material seemed to be holding the coarse grains in place. There appeared to be a reaction taking place between these spherical particles and a granular material surrounding them. This may have been the reaction of the wood ash and the sand, prior to the dissolution of the grains of sand. The spherical particles had the appearance of sand grains (Shelley p241, 1985).

When the frit was examined using polarising filters the three different phases could be seen (fig. 5.5). The most obvious phases were the slightly green particles of sand and the pink matrix material. This pink matrix was fused, which may have showed that the fritting process took the ash and the sand to the point of fusion but not to high enough a temperature for complete glass formation. The third phase present in the frit was a grey region surrounding the particles of sand, which had the appearance of a reactive zone between the sand and another material, probably ash.

No samples of frit were examined from Knightons or Sidney Wood, although there was reference to frit being found in Furnace three at Knightons (Wood p36, 1982b).

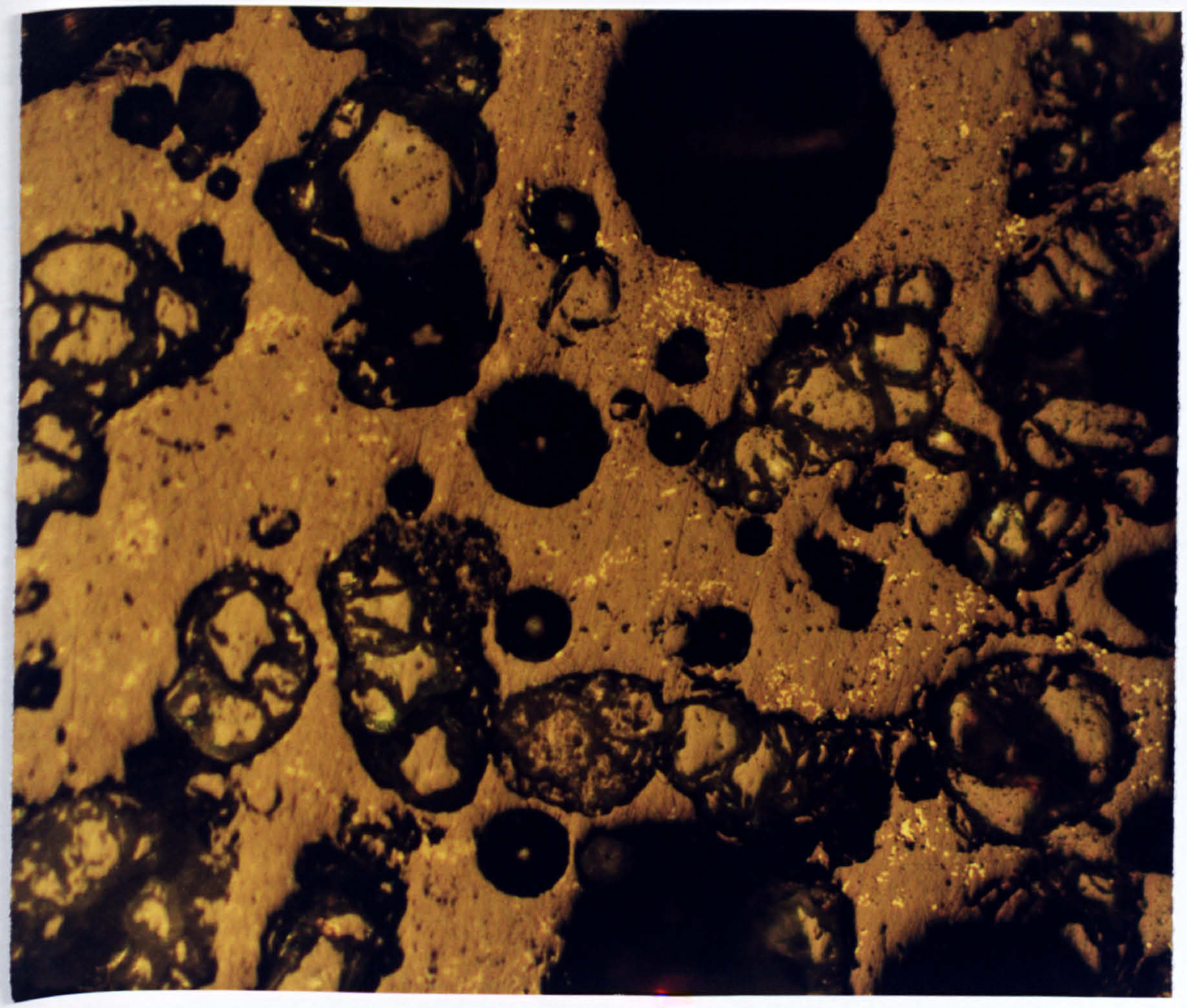

Figure 5.4 - Optical Micrograph of Frit from Blunden's Wood (Mag. = 10x)

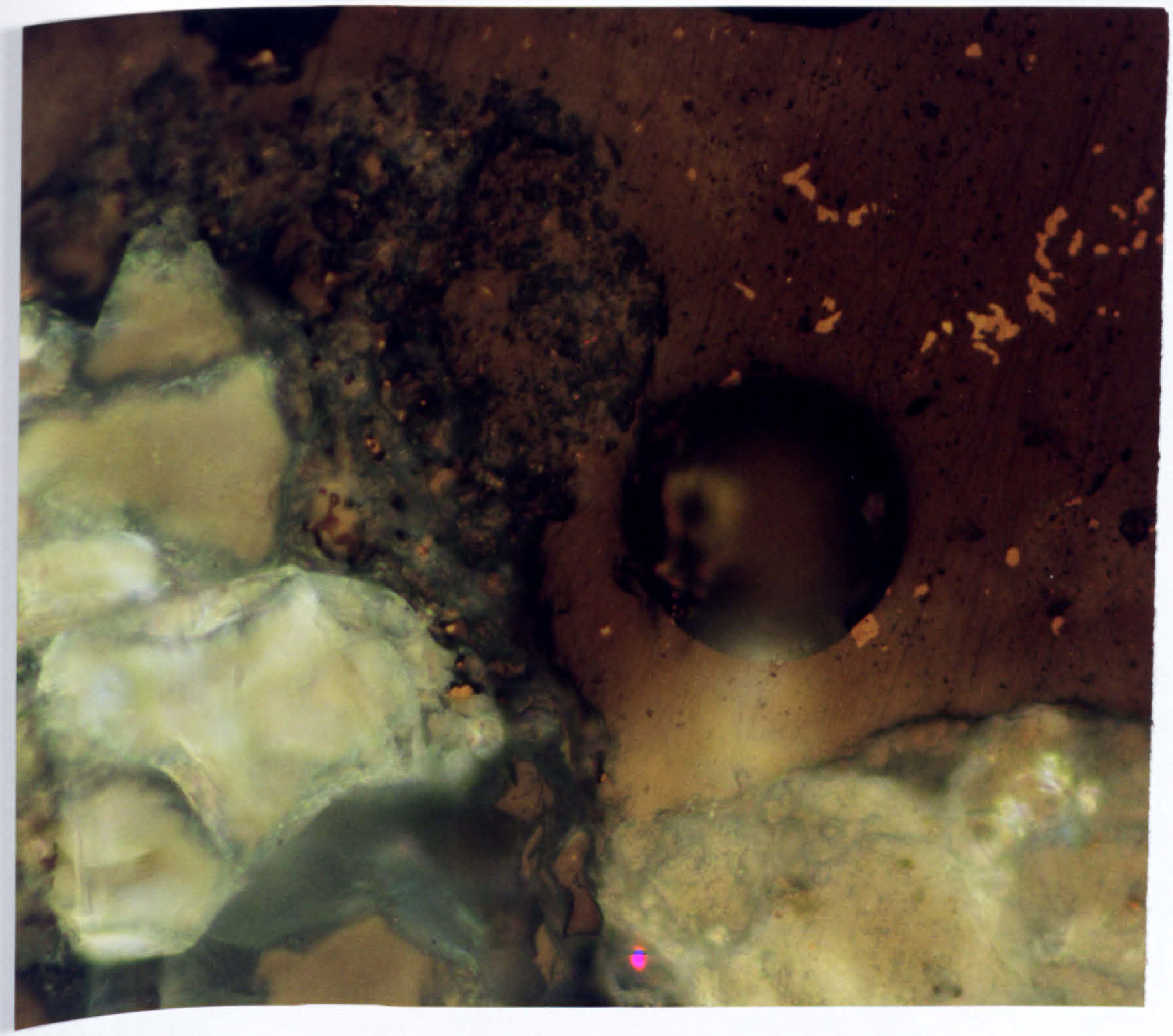

Figure 5.5 – Optical Micrograph of Frit from Blunden's Wood

(Mag. = 40x, polariser filter)

CHAPTER SIX

ANALYTICAL TECHNIQUES

Electrons will interact with a solid specimen in a number of ways, dependent on many material factors. If a beam of electrons hits a solid target, as is the case with a scanning electron microscope, the electrons are either deviated, or are scattered. Scattering can lead to absorption, reflection or transmission of electrons (fig. 6.1) (McKindley p156, 1988).

It is necessary to take the different forms of interaction separately to understand their uses. The interactions which take place will cause elastic or inelastic reactions, and depending how the interactions proceeds, there will be a different output - secondary electrons, back-scattered electrons, Auger electrons or x-rays. The energy of the distorted or deviated beam will determine how far they are able to travel, and thus, the higher energy interactions produce x-rays, while the lower energy interactions produce secondary or Auger electrons.

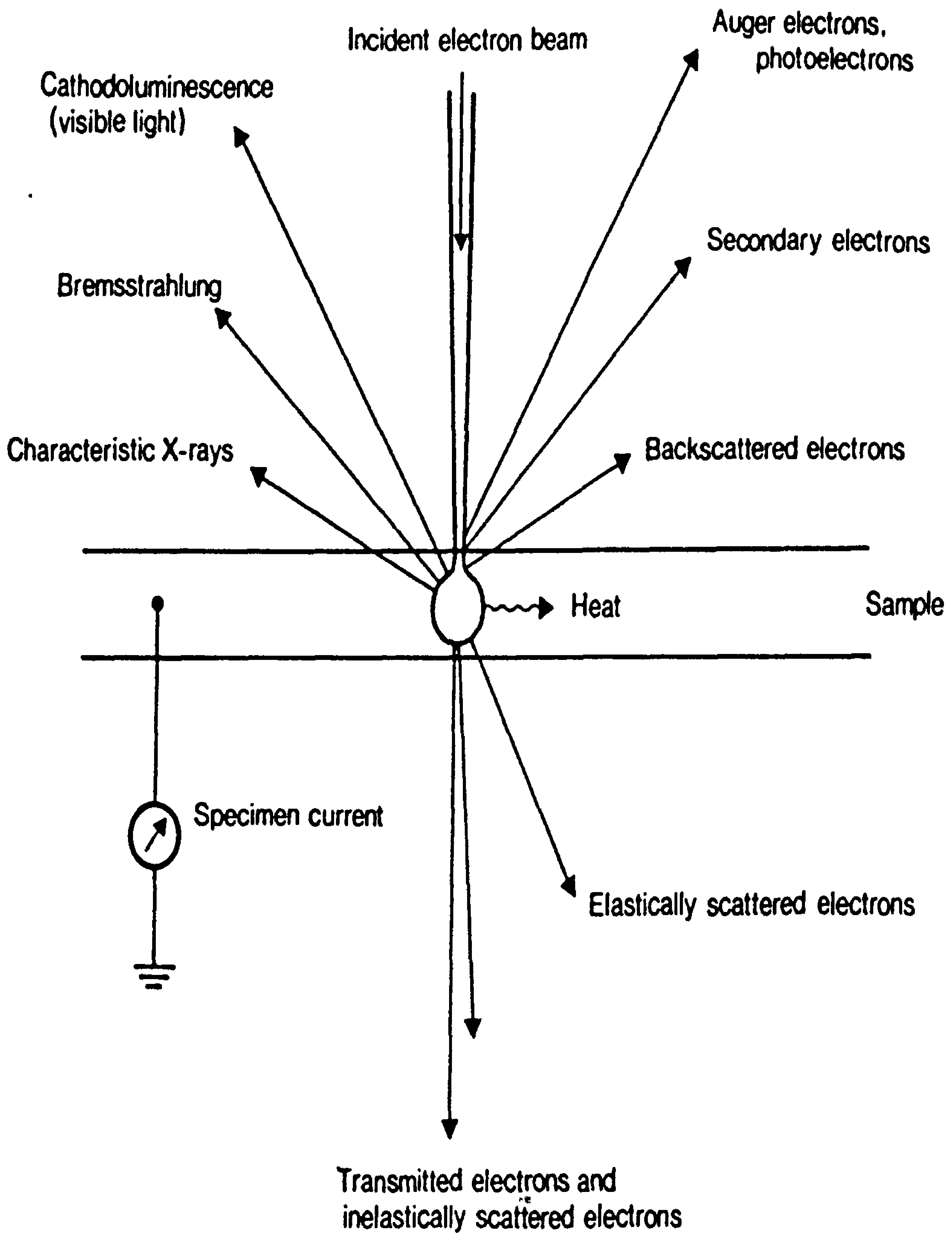

Figure 6.1 – The Bombardment of a Specimen by Electrons (McKindley p156, 1988)

One factor that must be taken into account when analysing archaeological materials, in particular those samples that are very small, is the interaction volume. This is the volume of material which is excited by the electron beam, and can be varied by the applied voltage, or the atomic number of the sample (Flegler et al. p71-72, 1993). The interaction volume is directly proportional to the applied voltage and inversely proportional to the atomic number. Therefore, in glass samples which have a high concentration of highly mobile low atomic number elements (sodium, magnesium etc.), it is most important not to apply too high a voltage, or the surface of the specimen will be destroyed and the compositional data will be inaccurate.

The depth to which the beam will penetrate to will produce different interactions, secondary electrons, back-scattered electrons, Auger electrons and x-rays.

Secondary electron images

The incident beam of electrons produced by the electron gun will interact elastically with the loosely bound electrons near to the specimen surface. This will cause secondary electrons to be produced, which will be collected by a detector and translated into an image. Approximately 99% of the secondary electrons are absorbed by the sample, leaving a depth of only 5 to 50 nm (depending on the material) to form an image.

Back-scattered electron images

Back-scattered electron images are formed when the incident beam of electrons undergoes an elastic interaction with the specimen, and electrons are scattered backwards. They have a high energy level (typically 60% to 80% of their initial energy) and therefore may require a dedicated detector to collect the emitted electrons, in order to maximise the count. The production of back-scattered electrons is strongly dependent on the atomic number of the sample, and is therefore a very useful tool in observing slight changes in internal composition of archaeological glasses where movement of atoms during weathering may be more apparent.

X-ray production

The incident beam of electrons, or in the case of an x-ray spectrometer the beam of primary x-rays, may remove an electron from the inner shell of the atom, in one of two ways. Firstly, and most importantly, is the production of x-rays. Their production, and detection, allows the determination of the chemical composition of a specimen. This is done by measuring the characteristic energy or wavelength of the x-ray, and enables the calculation of elemental compositions of atomic numbers between 8 and 99.

The use of secondary x-rays as a method to determine the composition of fragments relates to Planck's equation:

$$\lambda = hc/E$$

where λ is the wavelength of the x-ray, c is the speed of light, h is Planck's constant and E is the energy of the x-ray. In this way the secondary x-ray can be characterised by the energy, or the wavelength, produced by it (McKindley p125, 1988).

6.1 Scanning Electron Microscopy

In choosing a method for analysis it is necessary to look at the advantages of it over another. This is especially the case with a scanning electron microscope. Scanning electron microscopy offers the chance to analyse samples by forming an image of high resolution and high magnification, in comparison to an optical microscope, with the additional capacity to chemically analyse the fragments for compositional variations, assuming a form of x-ray detector is attached to the microscope.

6.1.1 Operation of the Scanning Electron Microscope

The operation of scanning electron microscopes has been covered in great depth (Flegler et al., 1993, Reimer, 1985, Belk, 1979, Goodhew and Humphreys, 1988 and Joy et al, 1986), so for the purpose of this work I must assume that some knowledge of scanning electron microscopes is known. I will discuss some elements which are important to the analysis of archaeological materials, and in particular some of the variables which are of most concern. A diagram of a scanning electron microscope (fig. 6.2) shows the five main components required to form an image (Flegler et al. p67, 1993).

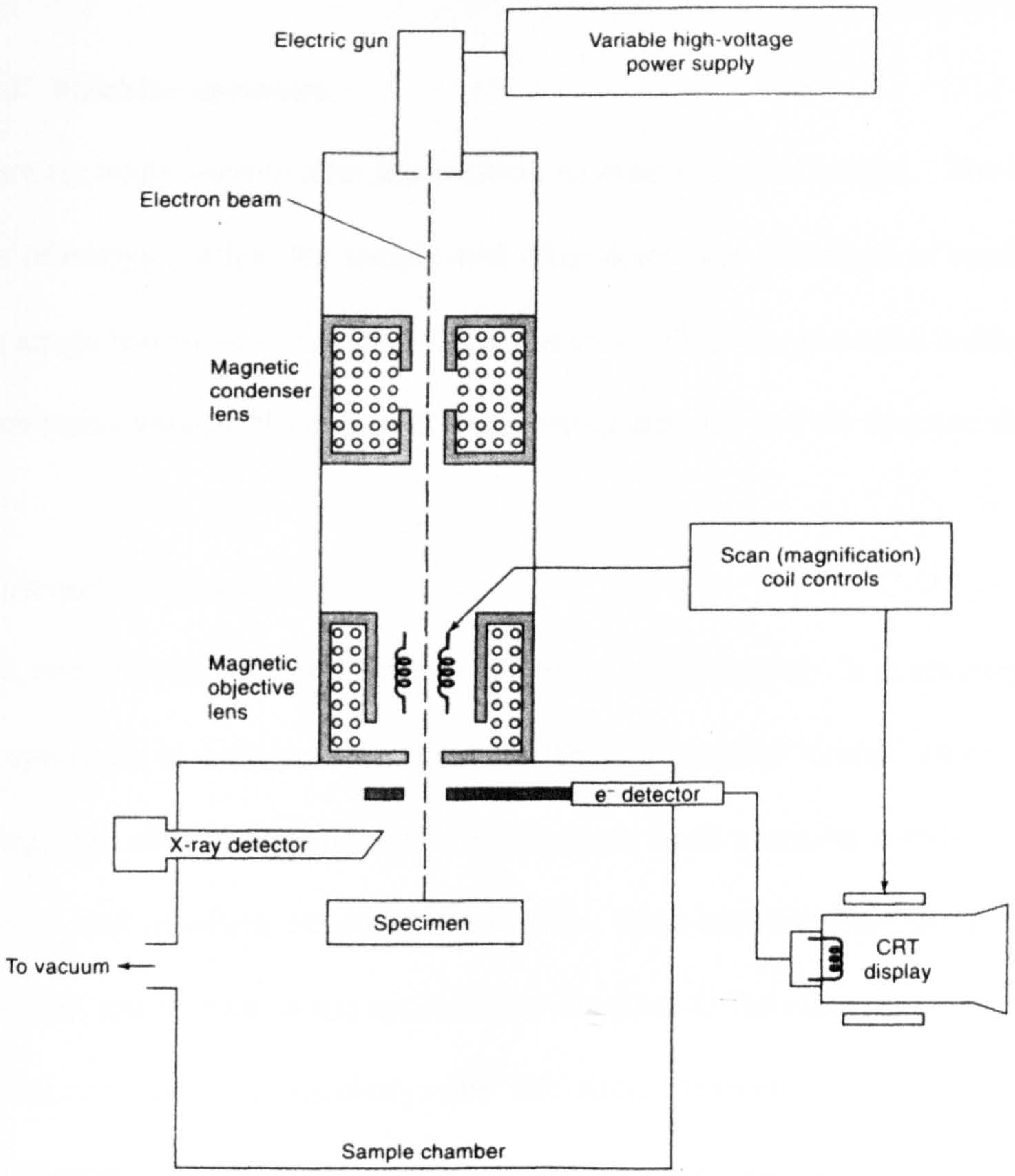

Figure 6.2 – The Components of a Scanning Electron Microscope

(Flegler et al. p67, 1993)

A beam of electrons must be generated by an electron gun, focussed to a fine point using condenser and objective lenses, and scanned over the surface of the specimen using magnetic coils. Electrons or x-rays are emitted from the specimen which are detected and translated into an image in the case of electrons, or composition data in the case of x-rays.

6.1.2 Machine variables

There are many ways to alter the analysis, to obtain the best results. The amount and type of energy put into the sample will often determine the output of results, whether it is image formation or compositional analysis. This energy can be controlled by the accelerating voltage, the spot size, the working distance and the aperture size.

Accelerating Voltage

First, and foremost, the accelerating voltage can be changed. It is necessary to excite the specimen in such a way to produce the best possible result. Generally, a high voltage will allow a better image to be obtained, as all elements within the sample are excited and produce secondary electrons, back-scattered electrons and x-rays. However, the surface of the specimen is sensitive to the electron beam, and can be burned. This is particularly true for light elements such as sodium, where volatilisation can take place, which makes the accurate analysis of glasses particularly difficult. A zone chemically analysed in the scanning electron microscope may show a depletion of sodium, which could either be a true representation of the level, or as a result of too high a voltage causing the mobile atoms to escape.

If it is established that the latter is the cause for depletion, then the voltage should be lowered for compositional analysis.

Spot Size

The spot size can be controlled by the condenser lenses within the microscope. Reduction of the spot size increases the resolution obtained, thus improving the image. Resolution between structures or phases is limited by the size of the beam, that is, the resolved spacing must be greater than the spot size. A disadvantage of a small beam is the increased level of electronic noise, produced as a result of a lower working current. Therefore, an increase in resolution must be balanced by the decrease in image quality when altering the spot size.

Working Distance and Aperture Size

Both of these variables can improve the depth of field of the image. As depth of field is an important advantage in using a scanning electron microscope instead of an optical microscope, then increasing the depth will increase the potential. The shape of the beam of electrons, cone-shaped, will alter the depth of field. A more narrow cone will increase the depth of field, this being produced by a reduction in aperture or an increase in the working distance.

Variables chosen for Glass Analysis

The conditions of analysis were optimised to excite the elements most likely to be present in the glass and ceramic fragments.

It required approximately two times the energy of the electron beam in order to maximise the excitation of the secondary emissions of x-rays or electrons (Philips PV9500, Edax manual). Therefore, in the case of a glass where the highest energy was likely to be that of the L-lines of lead (KeV=10.53), it was necessary to have an exciting energy of 20 KV.

The working distance, or the distance between the surface of the polished fragments and the detection apparatus of the electron microscope, could be altered. A working distance of 28 mm was chosen for the analyses, so that the intensity of the beam was great enough to excite the electrons within the specimen. A close enough distance was especially important when attempting to observe the image formed from back-scattered electrons, as they required a more intense beam to remove them from deeper inside the specimen.

In addition to this, there were fewer back-scattered electrons ejected from the specimen, so it was important to maximise this number by intensifying the beam to create as many electrons as possible, which can then be detected. It is important not to have too small a working distance, as the back-scattered electron detector has to be very close to the specimen within the chamber, to attempt to receive as many electrons as possible. If too small a distance is used, there is a possibility of the specimen touching the detector, or at least the close proximity of the detector to the specimen may result in an incomplete investigation. Therefore, it is necessary to balance one variable with another to optimise the settings that are used to analyse fragments within the scanning electron microscope.

Another factor taken into account when analysing specimens was 'dead time'. When a x-ray was detected it took time process the result. If another x-ray was emitted from the specimen during this time, and was to be detected there would be a problem for the detector distinguishing between the x-rays. In order to take this into account, both x-rays were ignored by the analyser, thus creating a 'dead time' (McKindley p137, 1988).

6.2 Preparation of Samples

Initial sample preparation of fragments of glass and ceramics for use in the scanning electron microscope was identical to the preparation for optical microscopy, as seen in chapter 5 (5.1.2).

To view the specimens using a scanning electron microscope, it was necessary for the surface of the fragment to be conducting. Therefore, a layer of carbon was applied. The carbon coating was applied under vacuum where an arc was formed between two carbon rods. This vaporised the carbon that was then directed towards the mounted specimen surface. The cooling effect of the surface allowed the carbon to adhere, and created a continuous layer. Finally, to guarantee conduction between the fragments of material and the microscope itself, a silver-based paint was trailed from the glass and ceramic samples to the edge of the mount, which was in contact with a brass holder fixed within the microscope chamber. The mounted specimens were now ready for examination using the scanning electron microscope.

6.3 Experimental use of the Cambridge 8 scanning electron microscope

Specimens were placed into the chamber of the electron microscope, and air was evacuated.

Two forms of analysis took place;

1/ Image analysis, and

2/ Quantitative Energy Dispersive Spectroscopy (EDS).

For glass fragments, image analysis was limited to checking the material for homogeneity. However, image analysis of the ceramic pieces needed more depth.

6.3.1 Image analysis of glass fragments

Little could be gained by viewing the samples of glass, except its homogeneity. In the case of the glass examined, it appeared that all glasses are homogeneous, with no elemental migration from the bulk glass to the edge. No weathering was apparent on any of the vessel glass samples.

6.3.2 Quantitative energy dispersive spectroscopy of glass fragments

Glass fragments were analysed using the energy dispersive spectrometer attachment on the Cambridge 8 scanning electron microscope. The machine was calibrated using cobalt of high purity. Re-calibration was carried out periodically, to ensure the results could be compared to one another, and their reliability maintained.

The fragments of glass were analysed for 180 seconds, with a count rate of greater than 1000 counts per second. If the count rate fell below this value the time was extended, ensuring that each analysis was comparable for the total number of counts.

Sample compositions were determined using a form of correction to account for the effect of the matrix of the material under test. This correction was the ZAF routine. This corrected for the effect of atomic number of each sample in comparison with a standard (Z), the absorption of x-rays in the sample and the standard (A) and the effect of fluorescence produced by secondary x-rays from high atomic numbers energising lower atomic number (F).

A Corning D standard was analysed to determine the degree of accuracy of the microscope, where a comparison with the known value could be made. The average value for each component of Corning D standard can be seen in Table 6.1, along with the standard deviation, accuracy and precision of the results.

Each glass fragment was analysed no less than three times, and an average calculated. A small area of sample was analysed, in preference to a spot, to try and eliminate the problem associated with the volatilisation of light elements. The results for Blunden's Wood, Table 6.2, Knightons, Table 6.3, and Sidney Wood, Table 6.4, showed the results for the fragments of glass.

	Mean Value /wt%	Standard Deviation	Precision[1] /%	Accuracy[2] /%
Na_2O	0.82	0.44	53.72	-37.58
MgO	3.59	0.28	7.75	-12.35
Al_2O_3	4.88	0.39	8.04	-10.08
SiO_2	52.83	0.61	1.15	4.35
P_2O_5	4.23	0.34	7.93	5.83
K_2O	12.02	0.29	2.45	4.90
CaO	16.36	0.13	0.81	8.70
MnO_2	0.64	0.11	17.13	12.67
Fe_2O_3	0.53	0.06	11.16	6.11
TiO_2	0.45	0.05	11.81	12.50
CuO	0.43	0.12	27.83	8.47

1: 100 x (Standard Deviation/Mean)

2: 100 x ((Actual Value – Quoted Value) / Quoted Value)

(Quoted value supplied by Corning Museum – See Appendix 1)

Table 6.1 – Glass Compositions of Corning D Standard (n=18)

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS3542	0.45 ±0.50	4.61 ±0.46	0.30 ±0.24	59.13 ±0.89	3.39 ±0.34	13.30 ±0.52	16.02 ±0.94	1.64 ±0.17	1.15 ±0.16	0.19 ±0.09	0.10 ±0.12
AS3542	1.39 ±0.88	4.31 ±0.49	0.12 ±0.08	59.91 ±1.19	3.43 ±0.20	12.40 ±0.67	15.99 ±1.01	1.56 ±0.22	1.27 ±0.23	0.15 ±0.09	0.02 ±0.02
AS3542	1.15 ±0.31	4.69 ±0.40	0.27 ±0.24	59.47 ±0.32	3.52 ±0.38	12.87 ±0.16	15.45 ±0.27	1.66 ±0.15	1.01 ±0.06	0.19 ±0.09	0.04 ±0.04
AS3542	0.74 ±0.26	4.46 ±0.35	0.11 ±0.11	60.09 ±0.87	3.57 ±0.28	12.68 ±0.43	15.61 ±0.80	1.73 ±0.25	1.05 ±0.36	0.21 ±0.12	0.09 ±0.15
AS3542	1.12 ±0.11	5.07 ±0.57	0.30 ±0.22	57.73 ±1.52	3.10 ±0.36	11.13 ±0.75	18.60 ±1.50	1.80 ±0.19	1.51 ±0.27	0.20 ±0.06	0.09 ±0.08
AS3542	1.22 ±0.74	4.36 ±0.41	0.06 ±0.09	60.65 ±1.25	3.06 ±0.13	12.72 ±0.71	15.36 ±1.05	1.72 ±0.15	1.30 ±0.25	0.16 ±0.07	0.10 ±0.12
AS3542	1.15 ±0.92	4.69 ±0.42	0.22 ±0.23	56.65 ±1.77	3.39 ±0.26	13.49 ±0.99	17.66 ±1.28	1.95 ±0.33	1.27 ±0.26	0.10 ±0.09	0.11 ±0.15
AS3542	0.79 ±1.05	3.98 ±0.51	0.21 ±0.25	61.33 ±3.51	2.90 ±0.46	13.10 ±0.50	14.88 ±2.95	1.86 ±0.34	1.23 ±0.35	0.08 ±0.08	0.12 ±0.17
AS3542	0.74 ±0.86	4.40 ±0.55	0.23 ±0.17	60.31 ±0.99	3.46 ±0.36	12.37 ±0.14	15.55 ±0.22	1.60 ±0.10	1.09 ±0.05	0.16 ±0.06	0.07 ±0.11
AS3542	0.57 ±0.33	4.45 ±0.23	0.22 ±0.24	60.83 ±0.68	3.11 ±0.12	12.32 ±0.04	15.42 ±0.24	1.68 ±0.07	1.08 ±0.06	0.14 ±0.13	0.11 ±0.05
AS3542	0.78 ±0.66	4.53 ±0.42	0.40 ±0.17	60.42 ±0.96	3.50 ±0.23	12.26 ±0.27	15.37 ±0.33	1.67 ±0.16	1.09 ±0.12	0.23 ±0.06	0.10 ±0.08
AS3542	0.56 ±0.93	4.53 ±0.41	0.22 ±0.24	59.86 ±0.74	3.38 ±0.23	12.53 ±0.28	15.99 ±0.71	1.70 ±0.30	1.21 ±0.14	0.21 ±0.12	0.03 ±0.04
AS3542	0.83 ±0.87	4.48 ±0.30	0.29 ±0.18	57.71 ±1.47	3.36 ±0.20	13.27 ±0.20	17.21 ±0.46	1.97 ±0.23	0.90 ±0.17	0.18 ±0.07	0.00 ±0.00
AS3542	0.45 ±0.44	4.31 ±0.68	0.34 ±0.13	61.37 ±0.50	3.35 ±0.28	12.44 ±0.38	14.95 ±0.53	1.56 ±0.16	1.14 ±0.13	0.19 ±0.09	0.09 ±0.08
AS3542	0.70 ±0.34	5.05 ±0.30	0.37 ±0.29	57.44 ±1.05	3.28 ±0.19	13.16 ±0.34	17.02 ±0.67	1.96 ±0.08	1.01 ±0.10	0.22 ±0.10	0.03 ±0.05
AS3542	0.66 ±1.08	4.91 ±0.31	0.39 ±0.23	58.38 ±0.80	3.36 ±0.14	11.15 ±0.26	17.95 ±0.71	1.64 ±0.07	1.47 ±0.28	0.26 ±0.07	0.06 ±0.06
AS3542	0.54 ±0.63	4.40 ±0.40	0.37 ±0.21	61.29 ±0.92	3.13 ±0.23	12.52 ±0.34	14.98 ±0.68	1.60 ±0.14	1.14 ±0.23	0.19 ±0.15	0.02 ±0.03
AS3542	0.62 ±0.46	4.68 ±0.48	0.09 ±0.09	57.54 ±0.95	3.54 ±0.29	13.24 ±0.41	17.34 ±0.77	1.89 ±0.27	1.05 ±0.05	0.11 ±0.05	0.07 ±0.09
AS3542	0.28 ±0.14	4.39 ±0.45	0.27 ±0.14	60.31 ±0.61	3.21 ±0.39	12.54 ±0.40	16.07 ±0.44	1.61 ±0.19	1.23 ±0.09	0.13 ±0.07	0.05 ±0.09
AS3542	0.80 ±0.78	4.60 ±0.25	0.29 ±0.17	59.88 ±1.12	3.35 ±0.15	12.51 ±0.33	15.63 ±0.57	1.70 ±0.21	1.20 ±0.07	0.16 ±0.08	0.11 ±0.19

Table 6.2 - Glass Compositions (± one standard deviation) for fragments from Blunden's Wood

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS207i	1.23 ±1.74	5.51 ±0.44	0.78 ±0.74	57.09 ±1.84	3.14 ±0.34	10.78 ±0.66	17.96 ±2.16	1.77 ±0.21	2.40 ±0.26	0.38 ±0.09	0.06 ±0.08
AS207i	0.90 ±1.10	4.72 ±0.47	0.36 ±0.25	57.49 ±1.83	3.38 ±0.22	10.87 ±0.56	18.12 ±1.60	1.78 ±0.28	2.49 ±2.00	0.24 ±0.03	0.10 ±0.09
AS207i	0.40 ±0.39	4.74 ±0.67	0.62 ±0.74	55.98 ±2.68	2.94 ±0.51	11.02 ±0.90	17.33 ±1.14	1.85 ±0.34	5.05 ±3.28	0.17 ±0.15	0.12 ±0.11
AS207i	0.22 ±0.38	5.08 ±0.54	0.53 ±0.08	58.23 ±0.21	3.46 ±0.25	10.34 ±0.12	18.45 ±0.28	1.69 ±0.13	1.92 ±0.30	0.20 ±0.16	0.01 ±0.01
AS207i	0.88 ±1.24	4.80 ±0.78	1.70 ±1.00	58.99 ±2.30	2.72 ±0.85	11.02 ±0.78	15.70 ±3.05	1.50 ±0.26	2.74 ±1.59	0.33 ±0.23	0.00 ±0.00
AS207i	0.62 ±0.63	4.44 ±0.38	0.67 ±0.35	56.95 ±1.67	3.38 ±0.38	10.44 ±0.24	17.40 ±0.87	1.85 ±0.21	4.17 ±2.81	0.23 ±0.21	0.07 ±0.12
AS207i	1.15 ±0.87	3.38 ±0.48	3.38 ±1.42	60.08 ±1.88	1.83 ±0.54	12.30 ±1.01	11.36 ±2.43	0.90 ±0.27	5.70 ±1.18	0.22 ±0.08	0.14 ±0.10
AS207i	0.54 ±1.93	4.00 ±0.93	1.46 ±0.52	55.99 ±1.32	3.00 ±0.46	10.85 ±0.64	16.05 ±0.64	1.59 ±0.24	6.24 ±1.27	0.38 ±0.18	0.13 ±0.14
AS207i	0.69 ±0.79	4.94 ±0.31	1.20 ±0.56	57.36 ±0.58	3.01 ±0.29	10.42 ±0.23	17.19 ±0.88	1.70 ±0.26	3.36 ±0.89	0.32 ±0.09	0.11 ±0.11
AS207i	0.85 ±1.02	4.53 ±0.57	0.79 ±0.19	57.79 ±0.33	3.10 ±0.08	10.62 ±0.28	17.51 ±0.68	1.59 ±0.08	3.20 ±1.17	0.17 ±0.13	0.20 ±0.21
AS207i	0.00 ±0.00	3.92 ±0.71	1.54 ±0.12	54.69 ±1.47	2.70 ±0.22	11.01 ±0.25	16.00 ±0.28	1.58 ±0.13	8.16 ±1.13	0.40 ±0.09	0.00 ±0.00
AS3550	0.61 ±0.78	5.13 ±0.24	0.46 ±0.28	56.02 ±0.62	3.59 ±0.31	13.16 ±0.21	18.24 ±0.30	1.77 ±0.19	0.89 ±0.16	0.20 ±0.05	0.12 ±0.20
AS3550	1.17 ±0.78	5.04 ±0.08	0.61 ±0.15	56.01 ±0.76	3.75 ±0.38	12.62 ±0.28	18.05 ±0.20	2.00 ±0.10	0.89 ±0.18	0.18 ±0.15	0.03 ±0.02
AS3550	0.38 ±0.50	4.87 ±0.40	0.19 ±0.17	57.56 ±0.50	3.40 ±0.10	13.65 ±0.28	17.14 ±0.56	2.06 ±0.08	0.73 ±0.15	0.06 ±0.08	0.05 ±0.09
AS3550	0.52 ±0.53	5.38 ±0.49	0.46 ±0.10	55.47 ±0.45	3.85 ±0.25	13.13 ±0.42	18.24 ±0.38	1.95 ±0.18	0.91 ±0.15	0.20 ±0.15	0.06 ±0.07
AS3550	0.82 ±0.73	4.90 ±0.45	0.35 ±0.15	56.99 ±0.87	3.69 ±0.24	13.35 ±0.37	16.95 ±0.27	1.98 ±0.17	0.92 ±0.09	0.12 ±0.12	0.15 ±0.09
AS3498i	0.17 ±0.25	1.10 ±0.30	4.64 ±0.41	60.62 ±0.83	0.50 ±0.21	20.01 ±1.15	5.09 ±0.33	0.72 ±0.22	7.39 ±1.00	0.29 ±0.07	0.14 ±0.08
AS3498i	0.78 ±0.81	2.57 ±0.37	3.78 ±1.25	58.71 ±1.13	2.25 ±0.18	20.27 ±1.34	8.63 ±0.87	0.88 ±0.17	2.01 ±0.45	0.39 ±0.09	0.09 ±0.09
AS3498i	0.63 ±0.66	2.14 ±0.68	3.67 ±1.35	58.22 ±1.60	1.96 ±0.28	20.62 ±1.37	9.69 ±1.22	0.90 ±0.22	1.88 ±0.42	0.34 ±0.17	0.03 ±0.03
AS3498i	0.19 ±0.33	2.78 ±0.35	3.96 ±0.88	59.62 ±0.76	2.07 ±0.53	17.20 ±0.39	10.85 ±1.32	1.17 ±0.17	1.81 ±0.32	0.42 ±0.08	0.07 ±0.12

Table 6.2 continued - Glass Compositions for fragments from Blunden's Wood

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS3498i	1.01 ±1.46	2.45 ±0.59	4.99 ±0.33	60.53 ±0.84	1.95 ±0.08	16.02 ±0.27	9.67 ±1.10	1.40 ±0.05	1.47 ±0.23	0.46 ±0.00	0.00 ±0.00
AS3498i	0.73 ±0.49	2.92 ±0.34	3.92 ±0.09	59.09 ±0.78	2.00 ±0.24	16.99 ±0.24	11.46 ±0.28	1.22 ±0.06	1.62 ±0.11	0.22 ±0.08	0.01 ±0.01
AS207o	0.54 ±0.94	2.01 ±0.51	4.08 ±0.83	70.01 ±1.06	0.77 ±0.16	8.83 ±0.96	9.07 ±1.93	0.77 ±0.25	3.77 ±0.31	0.46 ±0.06	0.08 ±0.10
AS207o	0.84 ±0.86	2.45 ±0.44	4.51 ±0.45	62.39 ±1.48	0.57 ±0.32	16.96 ±0.21	8.16 ±0.39	0.67 ±0.17	3.31 ±0.03	0.43 ±0.15	0.01 ±0.01
AS207o	0.60 ±0.81	2.14 ±0.44	5.21 ±0.28	63.68 ±0.52	0.35 ±0.29	16.58 ±0.18	7.75 ±0.49	0.70 ±0.11	2.69 ±0.26	0.53 ±0.11	0.04 ±0.06
AS207o	0.58 ±0.90	1.75 ±0.57	5.94 ±0.32	63.23 ±0.80	0.33 ±0.21	16.69 ±0.45	7.46 ±0.71	0.79 ±0.20	2.90 ±0.22	0.59 ±0.17	0.00 ±0.00
AS207o	0.37 ±0.36	2.20 ±0.45	5.47 ±0.57	62.52 ±0.29	0.36 ±0.23	16.90 ±0.56	7.90 ±0.22	0.69 ±0.03	3.20 ±0.25	0.56 ±0.05	0.00 ±0.00
AS207o	1.75 ±1.34	2.38 ±0.47	5.88 ±0.74	61.89 ±1.40	0.18 ±0.06	16.74 ±0.22	7.50 ±0.35	0.68 ±0.19	2.99 ±0.29	0.49 ±0.09	0.05 ±0.06
AS207o	0.97 ±0.93	1.30 ±0.28	4.46 ±0.62	70.36 ±1.39	0.55 ±0.20	10.57 ±0.55	7.59 ±0.90	0.60 ±0.23	3.47 ±0.34	0.43 ±0.10	0.00 ±0.00
AS3560^1	0.00 ±0.00	0.03 ±0.04	1.36 ±0.91	88.52 ±0.76	3.04 ±0.35	0.70 ±0.07	3.35 ±0.38	0.13 ±0.16	2.60 ±0.32	0.44 ±0.07	0.12 ±0.16
AS3560^2	1.79 ±0.59	4.72 ±0.30	0.36 ±0.30	45.88 ±1.48	6.14 ±0.30	23.92 ±1.38	14.79 ±1.01	1.94 ±0.36	1.17 ±0.18	0.32 ±0.04	0.03 ±0.04
AS3560^2	0.74 ±0.95	4.77 ±0.54	0.33 ±0.27	45.85 ±1.59	6.44 ±0.31	23.99 ±1.30	14.79 ±0.73	2.15 ±0.36	1.17 ±0.24	0.27 ±0.01	0.03 ±0.04

Key to Table 6.2:

AS3542: Fragments of Vessel Glass
AS3550: Fragments of Vessel Glass
AS3498i: Glass Fragments from the inner face of a Crucible
AS207i: Glass Fragments from the inner face of a Crucible
AS207o: Glass Fragments from the outside face of a Crucible
AS3560^1: Heavily Weathered Glass
AS3560^2: Fragments of Yellow Glass (unknown form)

Table 6.2 continued – Glass Compositions for fragments from Blunden's Wood

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS4921i	2.61 ±0.86	7.97 ±0.69	1.53 ±0.21	52.84 ±1.43	4.50 ±0.27	7.48 ±0.41	20.63 ±1.35	1.65 ±0.15	1.59 ±0.18	0.28 ±0.20	0.20 ±0.09
AS4921i	1.58 ±1.16	7.81 ±0.73	1.48 ±0.08	53.18 ±1.54	4.46 ±0.08	7.72 ±0.61	20.75 ±1.24	1.59 ±0.18	0.81 ±0.15	0.39 ±0.04	0.09 ±0.08
AS4921i	2.04 ±0.59	7.78 ±0.60	1.45 ±0.21	53.39 ±0.67	4.37 ±0.29	7.59 ±0.32	20.95 ±0.92	1.65 ±0.28	0.95 ±0.19	0.32 ±0.05	0.04 ±0.07
AS4921i	1.37 ±1.28	7.82 ±0.59	1.88 ±0.28	53.70 ±0.92	4.17 ±0.24	7.76 ±0.54	20.67 ±1.13	1.75 ±0.22	0.88 ±0.19	0.38 ±0.04	0.10 ±0.04
AS4921i	2.30 ±1.06	7.97 ±0.35	1.50 ±0.30	53.13 ±0.93	4.36 ±0.29	7.70 ±0.39	20.79 ±1.40	1.68 ±0.17	0.89 ±0.22	0.25 ±0.13	0.08 ±0.11
AS4921i	1.09 ±0.70	7.49 ±0.54	1.61 ±0.23	54.07 ±0.93	4.41 ±0.38	7.85 ±0.40	20.77 ±0.93	1.76 ±0.24	0.89 ±0.08	0.35 ±0.07	0.07 ±0.11

Key to Table 6.3:

AS4921i: Glass taken from the inside of Crucible Fragments

Table 6.3 - Glass Compositions (± one standard deviation) for fragments from Knightons

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS4966	1.03 ±0.88	1.80 ±0.69	2.27 ±0.22	57.50 ±0.93	1.93 ±0.12	4.65 ±0.18	27.24 ±0.51	1.29 ±0.17	1.80 ±0.27	0.44 ±0.11	0.02 ±0.03
AS4967	0.52 ±0.84	1.94 ±0.49	2.06 ±0.37	59.56 ±1.10	2.17 ±0.29	5.44 ±0.18	25.55 ±0.63	0.93 ±0.17	1.49 ±0.12	0.53 ±0.17	0.15 ±0.26
AS4967	0.38 ±0.75	2.00 ±0.40	1.84 ±0.19	59.86 ±1.14	2.24 ±0.13	5.52 ±0.13	25.60 ±0.90	0.84 ±0.22	1.48 ±0.16	0.54 ±0.10	0.13 ±0.13
AS4977	0.28 ±0.33	1.87 ±0.32	1.89 ±0.26	59.77 ±1.32	2.07 ±0.16	5.51 ±0.15	25.80 ±60	0.95 ±0.08	1.57 ±0.22	0.44 ±0.04	0.09 ±0.03
AS4977	0.65 ±1.08	1.83 ±0.28	1.91 ±0.25	59.84 ±1.07	2.39 ±0.22	5.33 ±0.07	25.46 ±0.49	0.98 ±0.11	1.48 ±0.15	0.32 ±0.10	0.11 ±0.11

Key to Table 6.4:

AS4966: Vessel Glass
AS4967: Vessel Glass
AS4977: Vessel Glass

Table 6.4 – Glass Compositions (± one standard deviation) for Fragments from Sidney Wood

6.3.3 Image analysis of the crucible fragments

The ceramic fragments were investigated for the most obvious forms of crystals - laths, equi-axed grains and agglomerations. Identification of the phases in the ceramic fragments was carried out, though it must be stressed that some of this was carried out in conjunction with the EDS analysis.

Crucible fragments from Blunden's Wood had glass adhering to the inside face. This allowed an assessment of the glass-making process to be made, and observations concerning the effect medieval glass had on the ceramic body.

The clay used for the crucibles from Blunden's Wood consisted of three phases (fig. 6.3). To exaggerate the contrast between the phases it was necessary to observe the clay using back-scattered electrons. The most dominant phase was a glassy structure, which produced the main form of bonding within the crucible. A network of closed porosity could be observed. The presence of the glassy structure may have indicated the temperature to which the crucible was taken during the melting of glass. The vitreous phase would be produced slowly at 1300 °C, but rapidly at 1350 °C, so a temperature between these might have been used to melt the glass (Travers p171, 1919 and Ford, 1967).

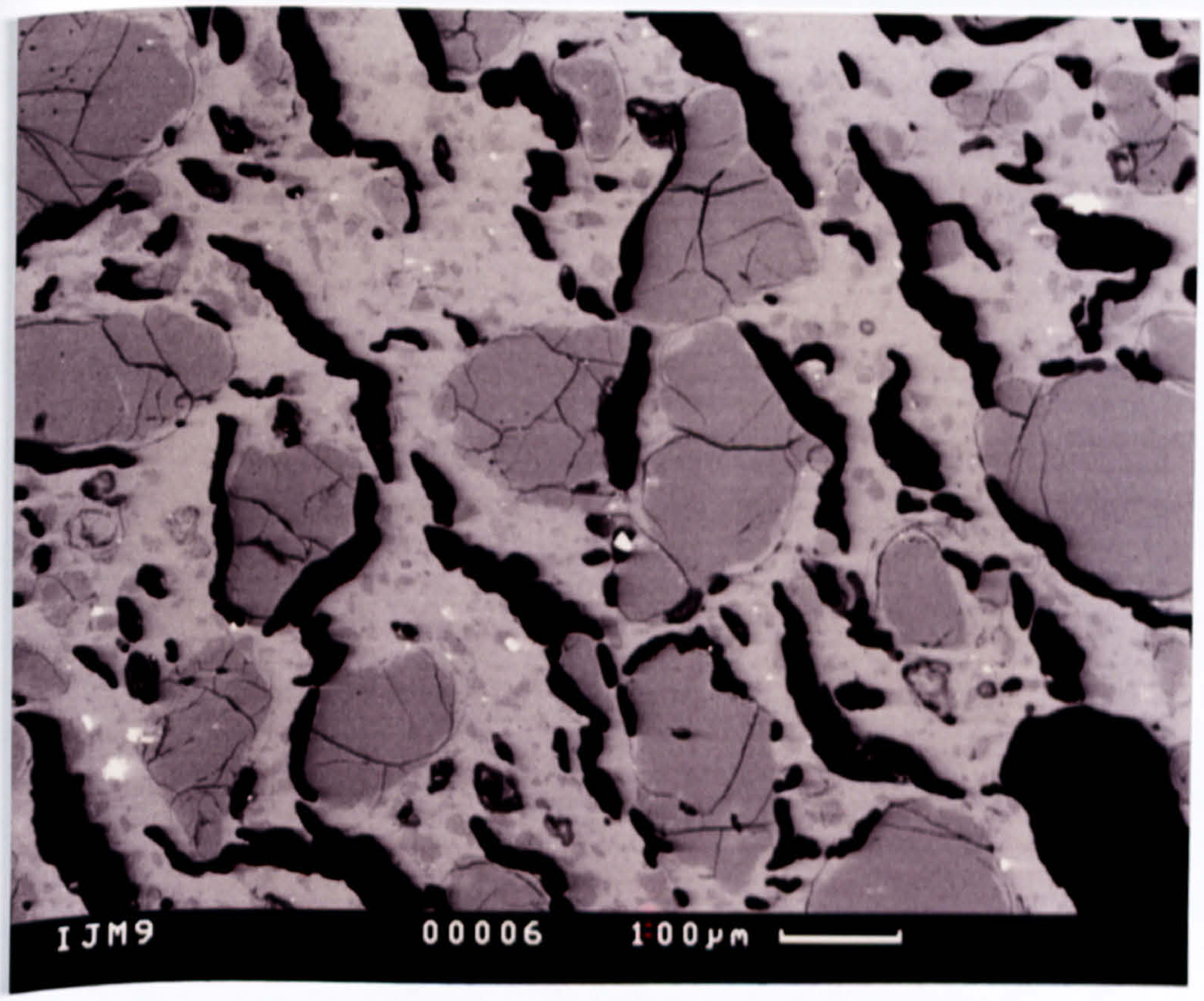

Figure 6.3 – Back-scattered Electron Micrograph of Crucible from Blunden's Wood

(AS3498)

At higher magnifications, in excess of 1500 times, it was possible to observe lath-like crystals, which appeared to have grown out of the glassy phase (fig. 6.4). Again a clearer image was obtained using back-scattered electrons. This suggested that there was a transformation taking place to produce the crystals, which resembled mullite laths (Shelley p165-166, 1985).

The laths were difficult to measure accurately, but an estimation of 1 μm in width by up to 10 μm in length showed the small size of these crystals. The final phase of material present in the crucible was silica grains. The grains varied in size, from as little as 5 μm up to 300 μm. There appeared to be a mixture of sizes in between these. The presence of cracking in the larger grains of silica suggested that these grains were added to the clay during the production of the crucible.

6.3.4 Quantitative energy dispersive spectroscopy of crucible fragments

Crucible fragments from Blunden's Wood were chosen for investigation by energy dispersive spectroscopy. Due to the multi-phase nature of the clay it was difficult to obtain a consistent bulk analysis. However, an attempt was made at a low magnification (20x), with an area scan, to take into account most of the phases present. At higher magnifications (4900x) it was almost possible to isolate the various phases, and analyse them using a small beam area. The results can be seen in Table 6.5. It was not possible to completely resolve the fine laths, but an analysis was obtained by accurately placing a small beam onto the lath. This composition contained some of the material from the surrounding area, but a calculation was made to remove the fraction of matrix contributing to the composition.

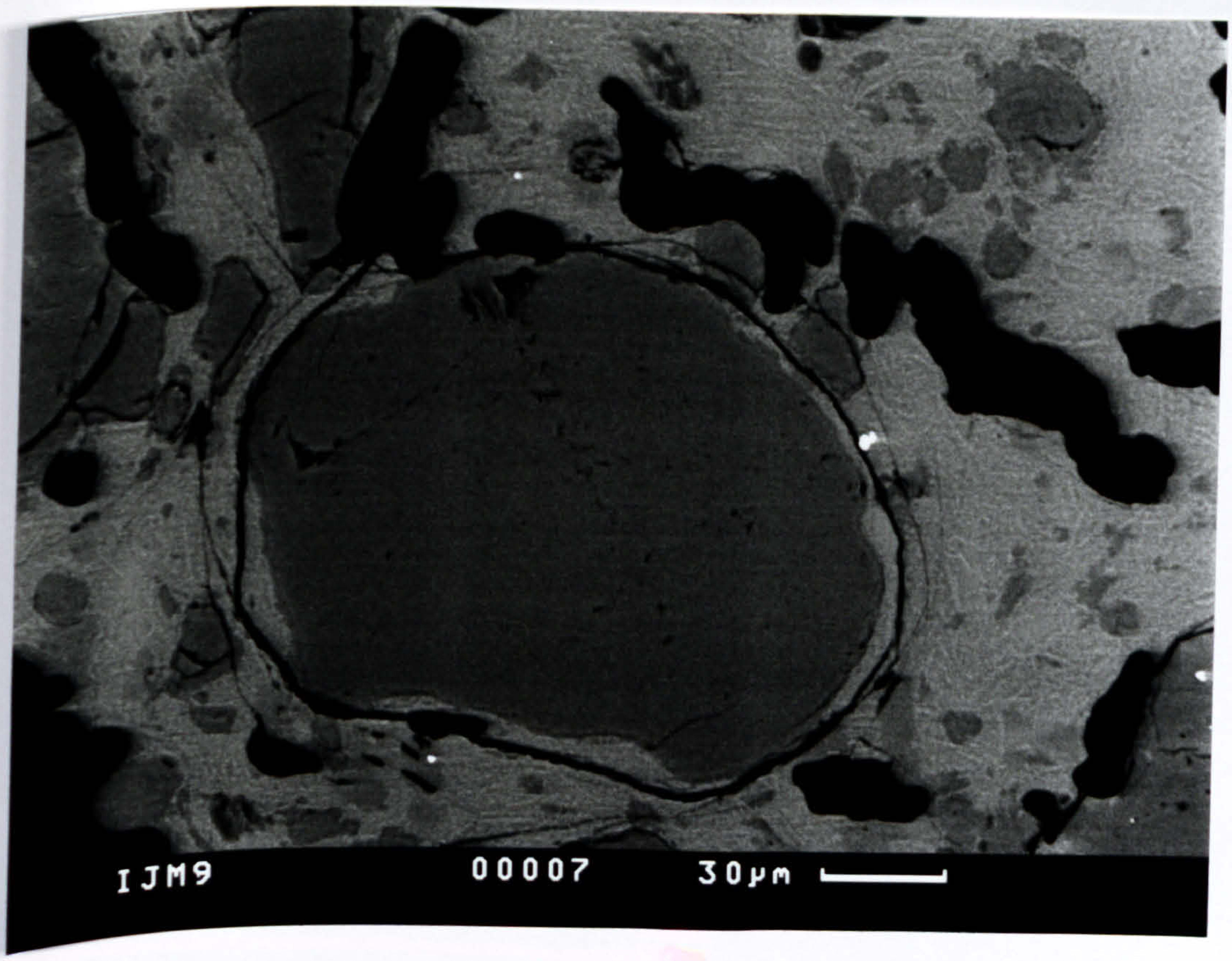

Figure 6.4 – Back-scattered Electron Micrograph of Crucible from Blunden's Wood

Showing large silica grain and laths within the matrix (AS3498)

Region of Crucible	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
Bulk Matrix – Back face	0.00	0.00	13.92	79.69	0.41	2.84	0.33	0.00	2.16	0.60	0.10
Bulk Matrix – Middle	0.31	0.11	11.60	80.18	0.20	4.18	0.21	0.10	2.16	0.70	0.03
Bulk Matrix – Front face	0.00	0.59	12.15	79.10	0.05	5.99	0.06	0.00	3.00	0.59	0.00
Laths	0.00	0.00	30.90	57.14	0.23	4.46	0.53	0.00	5.36	1.38	0.05
Large Grain	0.06	0.00	0.00	98.50	0.49	0.05	0.01	0.00	0.73	0.05	0.10

Table 6.5 – Chemical composition of regions within a Crucible (AS3498)

This allowed an estimate of the ratio between alumina and silica to be made. The calculation assumed the laths made up about 10% of the matrix (by observation). The crystals were based on a composition approximating to 3 parts Al_2O_3 and 2 parts SiO_2, which was the composition of mullite (Shelley p165-166, 1985).

Errors observed between each analysis of crucible material were large, which indicated a problem associated with the bulk analysis of multi-phase ceramics.

6.4 Investigation of the Glass-crucible Zone

The scanning electron microscope provided the ideal method for investigating areas where an interaction between phases was taking place. This has been done previously on medieval glass crucibles, with very good results (Henderson p249-252, 1991). One such case was the boundary between the glass and crucibles, observed in fragments where the inner face of crucibles from Blunden's Wood remain coated with a layer of glass. Unless all the glass was removed from the crucible after melting, the glass found in the crucible probably consisted of a few different melts. However, the most dominant should be the final glass melted in the crucible.

An investigation into the interface between the glass and crucibles was important as it provided a very good assessment of the glass-making process, and the type of attack that the glass imparted onto the ceramic body of the crucible. In particular, the crystalline phases present in the crucible at or near to, the boundary could lead to information about some of the process parameters - temperature, time and possibly raw materials (sand and wood ash).

Two forms of investigation were carried out on two crucible fragments excavated at Blunden's Wood. These were image analysis and quantitative compositional analysis of the interface between the glass and crucible.

Both these forms of analyses were carried out on two types of samples, one which appeared to have undergone aggressive attack by the glass (pitted crucible fragment) and a second which had a smooth glass layer over the inner surface of the clay crucible.

6.4.1 Image analysis of the Glass-crucible Zone

The samples were prepared using the method described earlier in section 5.1.2 and 6.2, ensuring that the whole sample was polished according to the regime for ceramic fragments. The pitted fragment showed a considerable depth of glass, up to 2000 μm in places, which allowed for any migration of light and highly mobile ions to be observed. The smooth layer of glass does not give this depth, which may have led to a problem in the analysis of the glass layer, as the migration of the mobile ions may not be detected. The thickness of the layer of glass adhering to the face of the crucible may have given an indication of the viscosity of the glass. The smooth layer of glass may have been the result of a highly fluid glass melt, while the thicker layer of glass could be attributed to a melt that was more viscous.

The images of the pitted specimens were observed using back-scattered electrons (fig. 6.5), which showed a complete interfacial zone. The atomic contrast between various elements observed with back-scattered electrons showed the interface in great detail. Observation of the interfacial zone provided three areas of interest. First, the glass, showed no change in contrast across the surface. This indicated there had been no apparent migration of light elements. Second, the multi-phase clay body could be observed in contrast to the homogenous glass. The final area to be seen was a zone between the glass and ceramic, an interfacial zone that consisted of the clay body whose porosity has been filled by the glass. This zone was measured to be between 130 and 200 μm. There was very little erosion of the clay by the glass, except that a few silica grains seemed to be within a glassy matrix, which indicated that they had been removed from the clay crucible. Also, it must be remembered that this analysis was carried out on a pit, so there had probably been erosion.

At a higher magnification (1500x) a line of bright crystals could be seen, running parallel with the surface of the glass, at a mid-point of the interfacial zone (fig. 6.6). At very high magnifications (5000-6000x) these rounded crystals were found to be sintering together. The smallest growths were about 1 μm in diameter, which rose to amalgamated forms in the region of 10 μm. The rounded structure and the way they have sintered together suggested that these crystals grew out of solution within the interfacial zone.

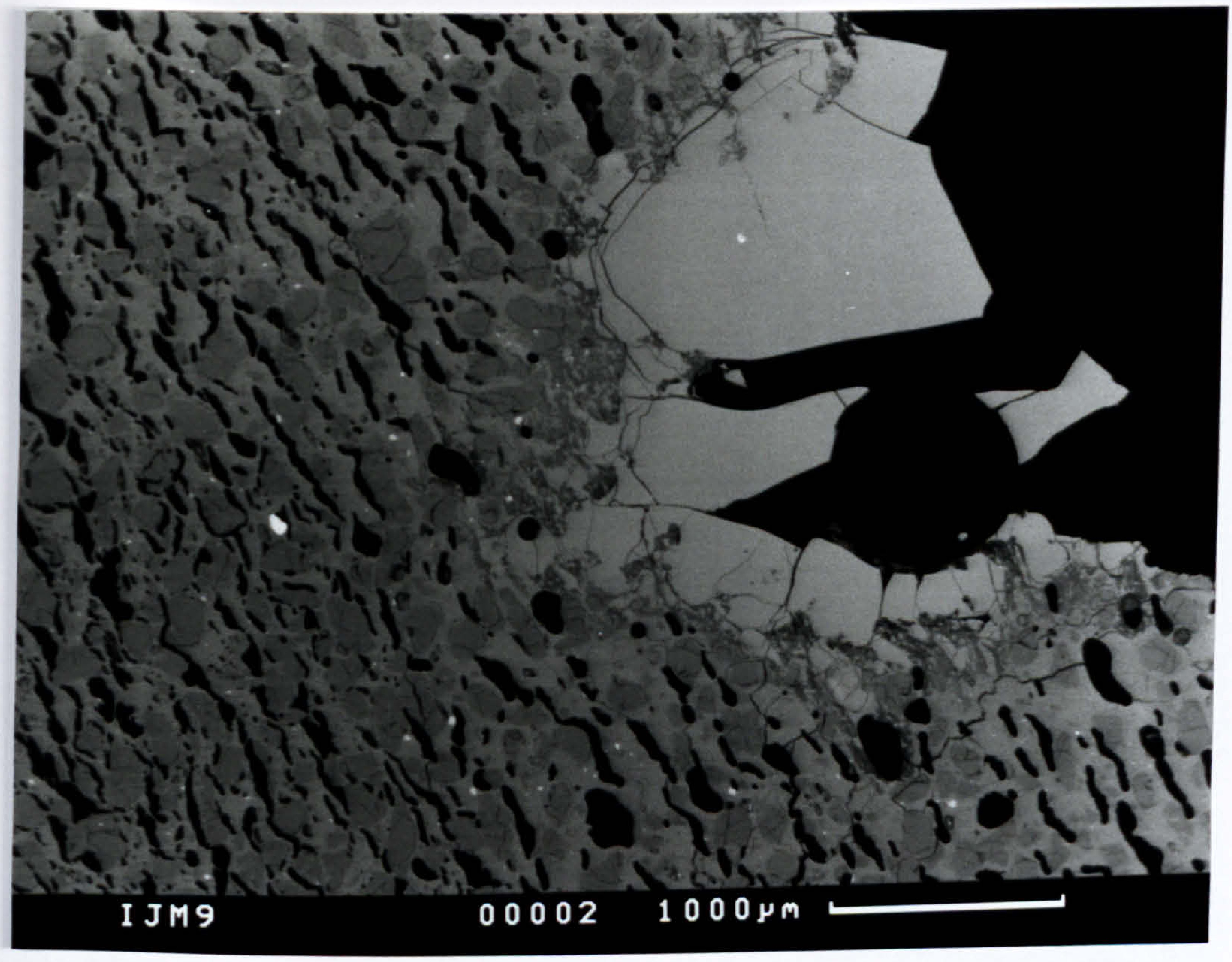

Figure 6.5 – Back-scattered Electron Micrograph of a Pitted Crucible (AS3498)

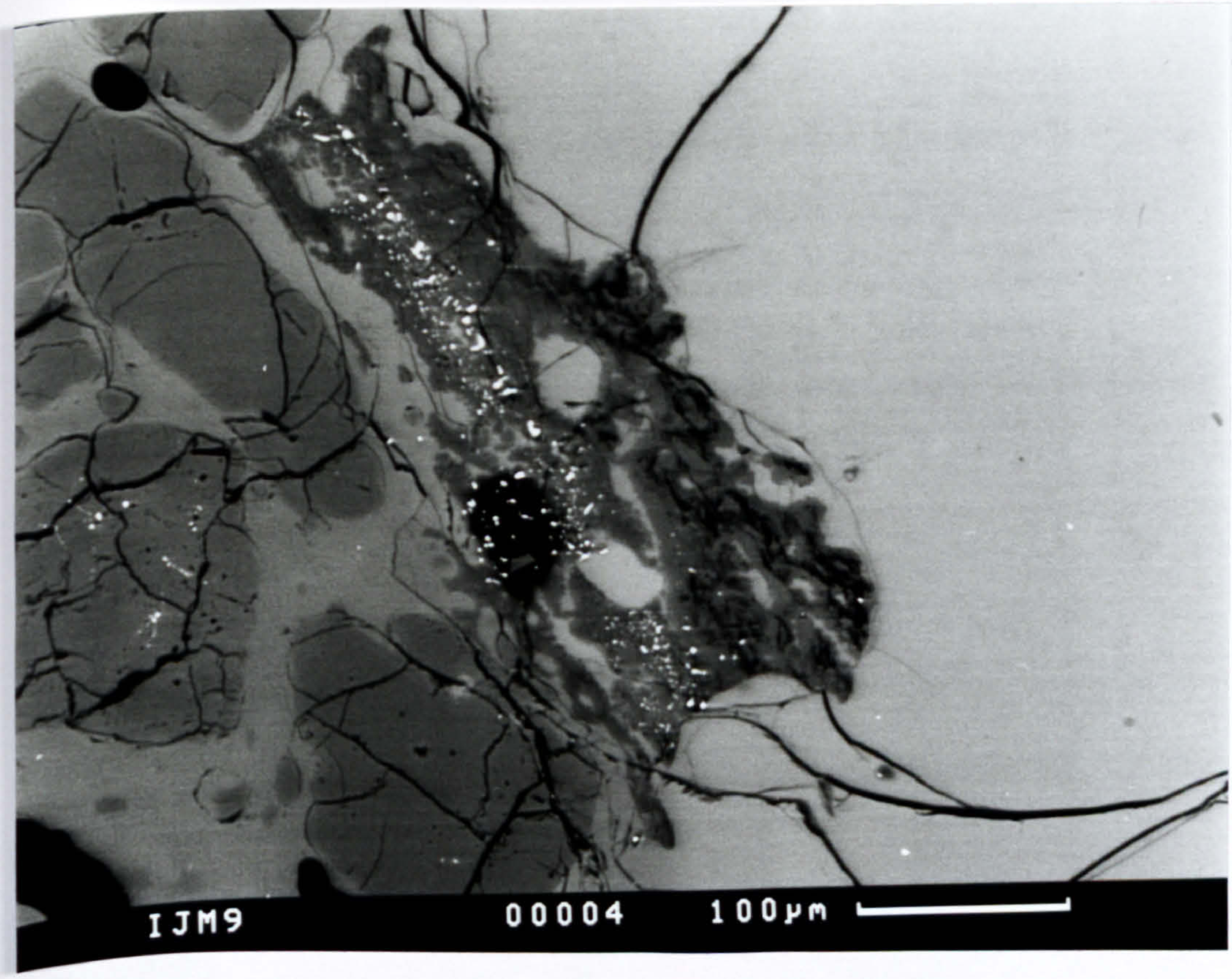

Figure 6.6 – Back-scattered Electron Micrograph of a Pitted Crucible (AS3498)

The crucible fragment with a flat layer of glass adhering to it appeared to have undergone very little attack by the glass. The glass was observed to be almost resting against the clay body, with only a very small region of interaction between the clay and the glass (fig. 6.7). The interface layer appeared to be very porous, and large areas of the layer of glass had come away from the clay crucible. This suggested that this glass had not penetrated to a very great depth, during the melting. These fragments may have come from the upper segment of the crucible walls, where the only contact with the glass would have been while the glass was poured from the crucible.

6.4.2 Quantitative energy dispersive spectroscopy of Glass-crucible Zone

Quantitative compositional analysis has been carried out on the fragments of crucible material with glass adhering to the inner face. Samples from Blunden's Wood were used for this method of analysis, and the conditions of 20 kV accelerating voltage and a working distance of 28 mm were used.

A spot analysis was made at intervals from the outer surface of the glass, through the glass, and into the clay crucible. The interval was shortened while passing through the zone between the clay and the glass. The results of the compositional analysis shown in Tables 6.6 and 6.7, showed that there was some transfer of components from the clay to the glass, and vice versa. This was the case for both the crucible that had a pitted structure and the crucible that had a layer of flat glass adhering to it.

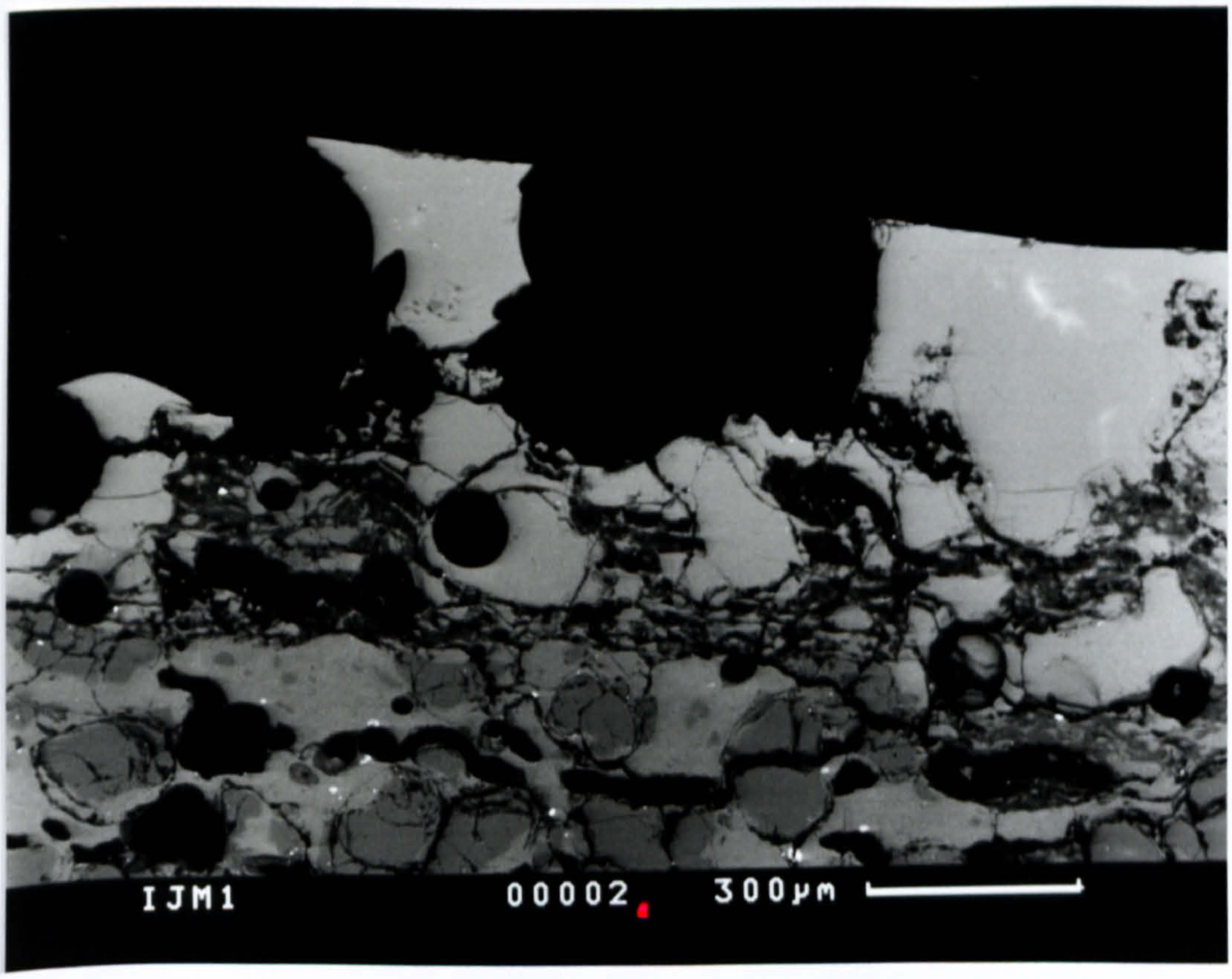

Figure 6.7 – Back-scattered Electron Micrograph of a Crucible with a flat layer of Glass adhered to it (AS3498)

Distance across Zone /microns	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2
1125 (glass)	1.06	2.99	3.25	56.64	1.82	19.7	11.04	1.05	2.14	0.25
900	0.12	2.74	3.81	58.0	2.18	20.2	9.68	1.00	1.94	0.27
750	0.54	2.37	4.47	58.8	2.13	20.2	8.09	0.95	2.00	0.39
675	2.76	2.71	3.50	58.2	2.19	19.0	10.66	1.19	2.03	0.42
600	0.70	2.64	4.35	59.0	2.04	20.2	7.91	0.84	1.90	0.36
500	0.91	2.68	3.74	58.6	2.07	20.5	7.89	0.98	2.35	0.24
450	0.94	2.66	4.65	58.8	2.06	20.1	8.09	0.49	1.77	0.30
400	0.08	1.77	4.23	58.7	2.21	20.5	8.40	0.70	2.56	0.62
300	1.19	1.16	6.28	61.2	1.92	18.5	5.49	0.61	3.13	0.43
225	0.44	1.38	6.02	60.1	1.22	20.3	6.19	0.77	2.19	0.31
200	0.00	1.45	4.70	59.3	1.67	20.5	7.54	0.73	2.39	0.50
150	0.26	1.07	5.89	61.7	0.33	20.5	5.89	0.15	2.75	0.84
100	0.08	1.51	5.56	61.9	1.64	20.4	5.32	0.62	2.44	0.35
50	0.00	1.12	5.22	65.4	1.39	20.2	2.92	0.32	2.71	0.38
0	1.58	1.10	11.46	65.6	0.53	17.7	1.16	0.09	4.03	0.67
-50	0.00	1.00	7.04	72.4	0.47	14.6	1.08	0.06	3.04	0.28
-100	0.29	0.07	6.05	75.8	0.57	12.1	1.28	0.22	3.00	0.29
-150	0.00	0.10	14.15	74.3	0.55	6.80	0.07	0.03	2.94	0.95
-200	0.16	0.00	13.20	69.8	0.03	9.66	0.41	0.00	2.78	0.91
-225	0.00	0.00	8.38	77.3	0.46	4.81	0.04	0.04	2.16	0.57
-300	0.61	0.00	12.96	75.3	0.29	6.10	0.04	0.05	3.65	0.77
-400	1.85	0.13	14.24	70.9	0.91	7.13	0.08	0.18	2.44	0.80
-450	0.00	0.00	10.20	83.5	0.00	1.66	0.13	0.00	1.88	0.65
-500	0.47	0.28	15.87	72.3	0.19	6.07	0.20	0.19	2.93	1.34
-600	0.68	0.16	11.23	83.0	0.31	3.02	0.14	0.00	1.68	0.73
-750	0.00	0.00	7.93	86.8	0.17	1.49	0.15	0.00	0.83	0.47
-1053	0.00	0.16	10.05	82.7	0.34	4.11	0.23	0.05	2.33	0.13
-1500	0.00	0.47	8.45	84.7	0.64	2.49	0.33	0.00	1.69	0.87
-2563	0.00	0.26	10.47	83.3	0.00	2.94	0.09	0.20	1.86	0.62
-3500 (crucible)	0.42	0.00	11.15	82.0	0.11	2.53	0.43	0.09	2.23	0.88

Table 6.6 – Chemical Compositions of Glass-crucible Zone of a Pitted Crucible (AS3498)

Distance across Zone /microns	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2
400 (glass)	0.57	0.29	7.02	72.28	0.61	13.5	1.18	0.10	3.70	0.54
300	0.00	0.56	7.61	67.00	0.32	17.1	1.12	0.07	5.57	0.49
200	0.05	0.10	7.43	72.43	0.52	15.9	0.61	0.00	3.00	0.76
100	0.96	0.47	8.05	70.08	0.37	14.9	0.66	0.00	3.61	0.70
0	0.55	0.00	11.68	78.46	0.36	7.27	0.15	0.05	1.61	0.72
-100	0.29	0.00	10.76	78.12	0.55	8.88	0.00	0.00	2.24	0.90
-200	0.00	0.04	10.52	80.88	0.16	5.03	0.14	0.04	2.09	1.03
-400 (crucible)	0.16	0.10	15.56	73.47	0.50	6.33	0.15	0.02	5.66	0.87

Table 6.7 – Chemical Composition of Glass-crucible Zone (with a flat layer of glass adhering to it) (AS3498)

6.5 Electron Probe Micro-analysis

If a localised composition, or variation over a short distance to be measured is required, then electron microprobe analysis has a distinct advantage over scanning electron microscopy (Birks p151, 1964). Electron probe micro-analysis uses a beam of electrons to excite the specimens. However, there are a number of differences. The main difference is that electron probe micro-analysers do not usually scan the beam of electrons across the surface of the specimen to create an image, but produce a stable beam of electrons to generate x-rays from within the specimen (Rowen p185-186, 1988). It is the production of the x-rays, as previously explained in section 6.1, which allows the compositional analysis of artifacts to be carried out.

Generally, electron probe micro-analysers measure the wavelengths of the secondary x-rays, to provide an accurate composition of a material. This requires more control of the incident beam and detection, making the electron micro-probe a better method to measure the composition of fragments (McKindley p139, 1988).

The electron micro-probe consists of many features seen in a scanning electron microscope but the coils that scan the beam across the surface of the specimen are not present (fig. 6.8). Also, a wavelength dispersive spectrometer will be seen. This spectrometer consists of a diffracting crystal that enables each x-ray to be separated into characteristic wavelengths (Rowen p190-194, 1988). This allows for a more direct measurement of the secondary x-ray, and therefore, the accuracy will be improved.

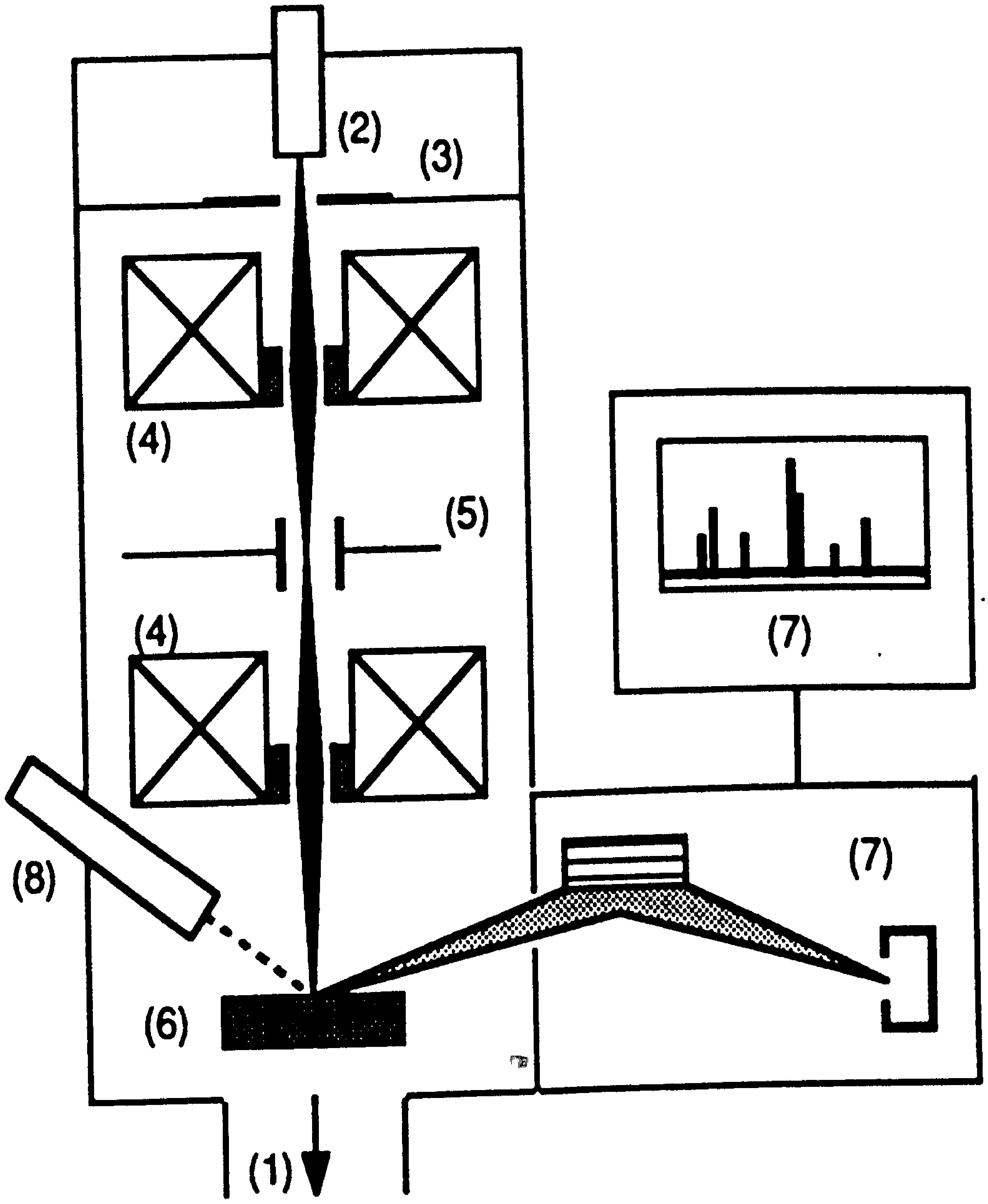

Figure 6.8 – Diagram of an Electron Probe Micro-Analysis System (Eberhart p305)

The wavelength dispersive spectrometer can alter the angle of detection, and therefore can resolve the x-rays. The detector then detects these individual x-rays, producing a relationship between the intensity of the x-ray and the characteristic wavelength (as a function of the angle of diffraction, θ), according to Bragg's Law (Rowen p185, 1988).

6.5.1 Preparation of glass fragments

Preparation of fragments for analysis in an electron micro-probe was the same as for scanning electron microscopes, and has been covered in sections 5.1.2 and 6.2. However, for electron probe micro-analysis work it was necessary to produce a similar thickness of carbon on the experimental samples to the layer on the standards against which the unknown was quantified.

6.5.2 Analysis of the glass fragments

The samples were placed into the chamber of a Cambridge Microscan 9 electron micro-probe. The conditions of each analysis were a 10 μm beam produced at 2.5×10^{-8} Amperes beam current. The accelerating voltage was15 kV.

The wavelength dispersive spectrometer measured the intensity of each element in turn, and the results obtained could then be calculated in weight percent. The beam of electrons could burn the surface of the specimen, which could lead to volatilisation of the lighter elements. This would produce errors in the results.

Therefore, one method developed (by Dr. F. Gibbs, Department of Earth Sciences at Sheffield University) to eliminate this problem, required the movement of the beam by a very small distance between each elemental analysis. The beam was moved within a 3 by 3 matrix between each analysis. Therefore, it was only on the tenth analysis that the glass underwent a second exposure to the electron beam.

The micro-probe was calibrated and the limits of detection were calculated, as can be seen in Table 6.8. The glass compositions were measured against both metal and ceramic standards. To discover the accuracy of the results, a standard glass, Corning D, was mounted with each set of unknown glass specimens. It was therefore treated as an unknown sample to see how the measured composition contrasts with the published values, shown in Table 6.9.

Analyses can be seen for a number of specimens from Blunden's Wood, Knightons and Sidney Wood in Tables 6.10. The number of oxides that were determined was based on the analyses obtained from the scanning electron microscopy. Therefore, the ten oxides of sodium, magnesium, aluminium, silicon, phosphorous, potassium, calcium, manganese, iron, titanium and copper chosen.

	Limit of Detection
MgO	0.02
Al_2O_3	0.01
SiO_2	0.05
P_2O_5	0.01
K_2O	0.01
CaO	0.01
MnO_2	0.04
Fe_2O_3	0.03
Na_2O	0.03
TiO_2	0.02
CuO	0.04
SO_3	0.02
Cl	0.01
ZnO	0.05
Cr_2O_3	0.03
SnO_2	0.03
CoO	0.03
Sb_2O_3	0.02
NiO	0.03
BaO	0.02
PbO	0.05
As_2O_3	0.04

Table 6.8 - Limits of Detection for Various oxides

	Mean Value /wt%	Standard Deviation	Precision[1] /%	Accuracy[2] /%
Na_2O	1.31	0.02	1.76	-1.14
MgO	3.71	0.03	0.77	-9.23
Al_2O_3	4.94	0.06	1.25	-9.12
SiO_2	54.83	0.36	0.66	-0.75
P_2O_5	3.96	0.07	1.72	-0.94
K_2O	11.46	0.14	1.21	-0.02
CaO	14.86	0.30	2.02	-1.28
MnO_2	0.56	0.04	7.04	-1.32
Fe_2O_3	0.47	0.05	10.19	-5.50
TiO_2	0.41	0.01	3.45	2.50

1: 100 x (Standard Deviation/Mean)

2: 100 x ((Actual Value – Quoted Value) / Quoted Value)

(Quoted value supplied by Corning Museum – See Appendix 1)

Table 6.9 – Glass Composition of Corning D Standard (n=4)

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS3542	2.12	6.29	0.83	60.51	2.97	10.42	12.85	1.13	0.75	0.07	0.00
AS3542	2.16	5.91	0.87	60.80	3.02	10.59	13.14	1.15	0.81	0.09	0.00
AS3542	2.15	6.11	0.89	61.12	3.00	10.35	12.56	1.05	0.74	0.09	0.00
AS3550	3.09	7.15	1.01	56.43	3.27	10.60	14.50	1.34	0.58	0.09	0.00
AS3550	3.03	7.17	0.99	56.16	3.27	10.75	14.53	1.21	0.56	0.11	0.00
AS3550	2.15	6.05	0.85	60.25	3.10	10.79	12.81	1.17	0.78	0.09	0.00
AS3498i	2.18	5.14	4.26	59.35	1.86	12.76	11.47	1.00	1.06	0.22	0.00
AS3498i	2.15	5.06	4.02	59.33	2.13	12.84	11.90	1.00	1.05	0.24	0.00
AS3498i	2.15	4.81	4.27	59.24	2.08	12.68	11.42	0.94	0.96	0.20	0.00
AS207i	2.57	6.52	1.49	58.11	2.99	8.84	13.92	1.08	2.66	0.11	0.00
AS4838	2.58	3.92	3.15	57.56	2.95	6.59	21.05	0.77	0.86	0.28	0.00
AS4838	2.59	3.96	3.05	56.42	3.00	6.77	20.83	1.04	0.88	0.28	0.00
AS4838	2.52	3.81	3.07	56.31	2.92	6.47	20.52	0.93	0.91	0.28	0.00
AS4931	1.92	6.06	1.77	57.26	3.62	10.28	16.08	0.94	0.72	0.18	0.00
AS4931	1.92	5.92	1.75	56.80	3.48	10.57	15.85	0.96	0.72	0.20	0.00
AS4934	1.97	5.97	1.74	56.32	3.61	10.20	15.56	0.91	0.80	0.18	0.00
AS4934	1.80	5.50	2.07	58.20	3.51	10.15	16.26	0.93	0.81	0.22	0.00
AS4934	1.73	5.37	2.16	57.23	3.40	10.18	16.30	0.96	0.74	0.20	0.00
AS4779i	4.62	9.53	1.88	52.01	3.75	9.35	16.02	1.01	0.72	0.20	0.00
AS4966	2.32	2.49	3.23	59.32	1.91	4.15	22.40	0.67	1.25	0.31	0.00
AS4966	2.35	2.60	3.46	58.84	1.86	4.06	22.72	0.80	1.14	0.31	0.00
AS4967	2.25	2.50	3.24	58.71	1.88	3.11	23.45	0.69	1.11	0.26	0.00
AS4967	2.29	2.49	3.33	58.73	1.83	3.05	23.46	0.66	1.19	0.26	0.00
AS4977	1.20	2.55	2.53	61.06	1.83	4.90	21.40	0.61	1.08	0.35	0.00
AS4981i	1.39	1.09	3.74	64.63	0.32	20.76	2.54	0.35	1.98	0.26	0.00
AS4982i	2.69	1.44	13.60	60.54	0.72	5.90	10.44	0.37	1.11	0.65	0.00
AS4998i	12.25	2.21	1.30	60.48	0.27	7.69	6.30	4.20	0.88	0.11	0.00

Table 6.10 – Chemical Composition of Glass Fragments

(see key below for numbers)

Key to Table 6.10:

AS3542: Vessel Glass from Blunden's Wood
AS3550: Vessel Glass from Blunden's Wood
AS3498i: Glass Fragments from the inner face of a Crucible from Blunden's Wood
AS207i: Glass Fragments from the inner face of a Crucible from Blunden's Wood
AS4838: Window Glass from Knightons
AS4931: Window Glass from Knightons
AS4934: Window Glass from Knightons
AS4779: Glass Fragments from the inner face of a Crucible from Knightons
AS4966: Vessel Glass from Sidney Wood
AS4967: Vessel Glass from Sidney Wood
AS4977: Vessel Glass from Sidney Wood
AS4981: Glass from face of Crucible Fragments from Sidney Wood
AS4982: Glass from the face of Crucible Fragments from Sidney Wood
AS4998: Purple Glass from a Fragments of Brick

6.6 X-ray Fluorescence

X-ray analysis has been touched upon earlier in this chapter, as a method of analysing the composition of the glass and ceramic fragments using scanning electron microscopy and electron probe micro-analysis. However, both of these sources use electrons to bombard the samples to produce secondary x-rays that can then be characterised and quantified. X-ray fluorescence spectrometers bombard the specimens with x-rays. The higher energy of these x-rays cause secondary x-rays to be emitted from the specimens which are then detected using an energy or wavelength spectrometer, and translated into meaningful quantitative results. X-ray fluorescence has the advantage that bulk samples can be analysed. This is particularly useful where crucible fragments are concerned, where the scanning electron microscope may not have been able to produce a large enough beam to account for all the phases within the clay.

X-ray fluorescence spectrometers consist of four main parts, a source of x-rays, a sealed chamber, a detector and a computer to calculate the results (fig. 6.9). The chamber must contain the x-rays, which can be harmful if humans are exposed to the intense rays. The source of x-rays comes from a tube. A high energy beam is generated within the tube and forced to move from the cathode to bombard a target material, the anode. The beam excites the target to produce x-rays, similar to those generated by an electron beam bombarding samples within a scanning electron microscope. The x-rays are then focussed onto the specimens within the chamber, using a collimator.

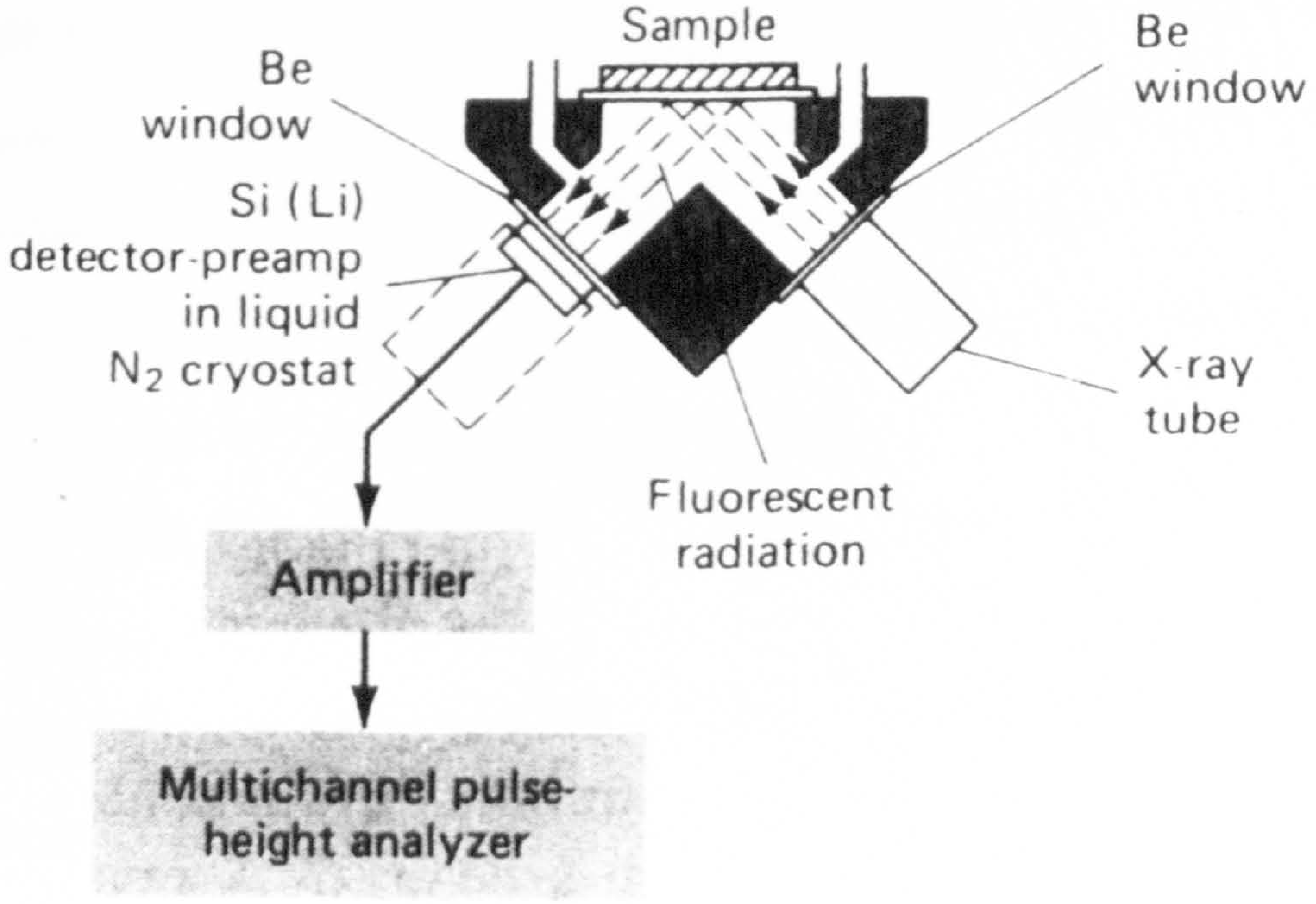

Figure 6.9 – X-ray Fluorescence Spectrometer (Skoog and Leary p374, 1992)

These x-rays will cause secondary x-rays to be emitted from the specimens that are then detected by a system that can measure the characteristic energy or wavelength of the x-ray of each element. This is done in the same way as the x-rays that are quantified using scanning electron microscopes or electron micro-probes.

The detection of x-rays in this work is based on a semiconductor counter. This system causes a flash of light to be given off when certain crystals, in the case of this work a lithium drifted silicon Si(Li) semiconductor, are bombarded with x-ray photons. The light is then detected, and multiplied, to produce a pulse of electric current. This pulse is now amplified and measured as the signal to quantify the number of secondary x-rays produced by the specimen (Skoog and Leary p370-371, 1992). The measurement of x-ray pulses is put in the form of count-rate. This measurement is usually counts per second, and the quantification process associated with the analysis of compositions, is able to calculate the number of counts from a given element. As with scanning electron microscopy, the detector of the x-ray fluorescence spectrometer can become saturated with pulses. Thus, the accelerating voltage must not be too high as to over-saturate the detector and cause too high a value of 'dead time'. Experiments carried out on a sample of Corning B showed that the detector could not be saturated with pulses (over 10,000 counts per second) while using a collimator.

6.6.1 Quantitative X-ray fluorescence analysis

Samples were prepared for analysis by breaking pieces from the glass fragments. Where possible specimens were mounted into epoxy resin, ground and polished in much the same way as microscopic samples are prepared. A flat surface was required to prevent the absorption of x-rays by neighbouring areas of a rough, undulating sample, (McKindley p148-149, 1988).

Analysis of the samples was carried out using a Phillips PV9500/PV9100 x-ray fluorescence spectrometer. To ensure a true spectra was recorded the machine was calibrated with a high purity alloy of aluminium and copper. The distance between the peaks was measured and calibrated to be 6.554 KeV (the difference between the energies of the aluminium peak (1.486 KeV) and the copper peak (8.040 KeV)). Calibration ensured that the aluminium and copper peaks were in the correct positions. An error in the calibration was calculated in the form of definable resolution. This was the level at which peaks can be distinguished from one another, and for the Phillips PV9500/PV9100 system for the duration of these tests it was between 160 and 170 eV. The samples were then placed inside the x-ray chamber, directly over the x-ray beam. A voltage of 30 KV and current of 300 μA was applied to the system to emit secondary x-rays from the glass samples. The beam was focussed using a 3 mm collimator. A count rate of 3000 counts per second was used for each analysis for a time of 300 seconds.

To determine the precision and accuracy of the tests a standard, Corning D, was tested as an unknown. The results, shown in Table 6.11, were good.

It was not possible to measure the value for sodium oxide, as the net intensity of the peak could not be measured above the background. The results for a number a glass fragments from Blunden's Wood, Knightons and Sidney Wood can be seen in Table 6.12.

	Mean Value /wt%	Standard Deviation	Precision[1] /%	Accuracy[2] /%
Na_2O	1.27	0.19	15.23	-4.17
MgO	3.73	0.21	5.50	-8.80
Al_2O_3	5.59	0.07	1.27	2.90
SiO_2	56.03	0.29	0.52	1.43
P_2O_5	4.21	0.08	2.01	5.19
K_2O	11.75	0.17	1.44	2.51
CaO	15.49	0.20	1.28	2.94
MnO_2	0.57	0.01	2.58	0.44
Fe_2O_3	0.51	0.00	0.84	2.50
TiO_2	0.40	0.01	2.83	-1.25

1: 100 x (Standard Deviation/Mean)

2: 100 x ((Actual Value – Quoted Value) / Quoted Value)

(Quoted value supplied by Corning Museum – See Appendix 1)

Table 6.11 – Glass Compositions of Corning D Standard (n=4)

Sample number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2	CuO
AS3542	2.27	6.29	2.37	63.18	2.21	10.19	11.57	1.08	0.81	0.03	0.00
AS3542	0.00	4.70	4.63	64.58	2.03	10.27	11.22	1.19	1.39	0.00	0.00
AS3550	1.08	10.97	1.21	45.34	5.42	21.18	11.99	1.60	1.11	0.00	0.00
AS3560	2.69	0.23	3.92	79.58	0.00	9.26	1.99	0.31	2.03	0.00	0.00
AS4931	1.60	4.04	4.40	60.65	2.21	9.85	14.56	1.00	0.85	0.23	0.00
AS4931	1.43	5.74	3.66	59.47	2.70	10.01	14.93	0.95	0.80	0.22	0.00
AS4931	1.40	7.58	2.54	58.03	3.65	10.37	15.53	0.94	0.78	0.22	0.00
AS4934	1.98	7.32	3.18	57.47	3.52	9.73	14.49	0.89	0.83	0.24	0.00
AS4934	2.10	6.64	3.15	58.07	3.44	9.97	15.27	0.89	0.80	0.22	0.00
AS4934	1.90	6.03	3.09	58.71	3.47	10.29	15.99	0.94	0.85	0.22	0.00
AS4966	1.38	2.61	3.52	60.14	2.04	4.77	21.33	0.60	1.17	0.32	0.00
AS4977	1.20	2.44	2.97	59.55	2.56	5.01	21.64	0.43	1.09	0.35	0.00

Key to Table 6.14:

AS3542: Vessel Glass from Blunden's Wood
AS3550: Yellow Glass Fragment
AS3560: Weathered Glass
AS4931: Window Glass from Knightons
AS4934: Window Glass from Knightons
AS4966: Vessel Glass from Sidney Wood
AS4977: Vessel Glass from Sidney Wood

Table 6.12 – Chemical Compositions of Glass Fragments

Samples of clay taken from the vicinity of Blunden's Wood, Knightons and Sidney Wood were analyses using x-ray fluorescence, in addition to fragments of crucible clay. The conditions for analysis were 30 kV, 300 µA and a test time of 400 seconds. The results were calculated against a Corning D glass standard, and therefore the results had to be normalised to counter the effect of the difference in surfaces and absorption of each material. The chemical compositions of the clay and the crucibles can be seen in Table 6.13.

6.7 X-ray diffraction analysis of the crucible fragments

X-ray diffraction analysis of materials allows the crystal phases present to be determined. In the case of glasses this technique is not used, unless inhomogeneous particles need to be determined. An incident x-ray produced by the x-ray generator will be diffracted as it passes through a crystalline structure. The degree of diffraction will depend on the crystal structure, in particular the atomic spacing. Thus, phases can be determined by observing and measuring the geometry of the diffraction pattern (Michette and Buckley p35, 1993).

When a beam of x-rays is directed at a material, they can be reflected, or in the case of the technique of phase determination using diffraction it passes through the material. The beam is deflected, or diffracted, from the original path. Depending on the internal structure of the material, the beam will be diffracted in a characteristic way. Each crystalline phase has a characteristic angle of diffraction, which enables different phases present in materials to be determined.

Sample number	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	TiO_2
Blunden's Wood Clay	0.00	17.49	67.75	0.25	4.25	0.78	0.12	9.07	0.40
Knightons Clay	0.00	12.18	78.54	0.33	1.66	0.02	0.16	6.56	0.56
Sidney Wood Clay	0.00	13.53	75.16	0.40	3.03	0.60	0.21	6.62	0.45
AS3498	0.00	17.50	68.30	0.20	9.70	0.30	0.20	3.40	0.40
AS4921	0.00	17.04	76.56	0.10	1.98	0.26	0.06	3.70	0.30
AS4982	0.00	20.34	73.19	0.05	2.28	0.39	0.09	3.31	0.35

Key to Table 6.13:

AS3498: Crucible from Blunden's Wood
AS4921: Crucible from Knightons
AS4977: Crucible from Sidney Wood

Table 6.13 – Chemical Compositions of Clay and Crucible Fragments

It is the internal structure (bond strength, atom size, etc) which causes the deflection of the x-ray beam from the original path. The intensity of the diffracted beam varies as a function of the amount of crystalline phase present, so a guide to the proportions of different phases in the material can be made.

X-ray diffraction analysis will only be used for the fragments of crucible from the glass-making sites, in addition to a fragment of frit from Blunden's Wood.

6.7.1 X-ray diffraction analysis

Small fragments of crucible were taken from the samples. They were then ground to a fine powder using a pestle and mortar. The purpose of this grinding stage was to ensure that the crucible material was broken down into as fine a material possible, to break the phases into their distinct units. It was necessary for the impacting x-rays to be diffracted through each crystal structure, which allowed each phase present to be determined. The samples were completely dried, so each powdered sample was placed into an oven at 100 °C for 24 hours.

The samples were placed into a brass holder, which was then put into the x-ray chamber of a Phillips PW1050 x-ray diffraction machine with a Hilltonbrooks generator. A voltage of 40 KV and current of 20 mA was used to produce a beam of x-rays. The x-rays had the characteristic of K-line radiation of copper (Cuk) and were fired at the powdered samples at a start angle of 5° (2θ). The angle of the incident beam is then increased up to 65° (2θ).

The speed of the scan is 2°/minute, and the step increase (fraction of degree) is 0.02. All the crystalline phases were found between these angles. As x-ray diffraction could only be used to determine crystalline phases in materials, this technique was used to investigate the nature of frit. A fragment of frit excavated from Blunden's Wood was subjected to x-ray diffraction. The plot of intensity against angle can be seen for the frit (fig. 6.10) and the crucible fragments (figs. 6.11, 6.12, 6.13 and 6.14).

As described previously, the intensity peaks allowed the determination of the various crystal phases present in the crucibles. From tables of characteristic angles the phases present in the frit and the crucible material, as shown in Table 6.17. The results of the phases present in the crucibles from Blunden's Wood, Knightons and Sidney Wood were similar. The proportion of each phase can only be determined in a subjective way. This will be discussed in chapter 7, when the technology of the glass-making process will be looked at.

The phases present in the frit are shown with the crucible fragments.

	Quartz	Tridymite	Cristobalite	Mullite	Cordierite
Blunden's Wood - AS207	Yes	Yes	Yes	Yes	Yes
Blunden's Wood - AS3498	Yes	Yes	Yes	Yes	Yes
Knightons - AS4779	Yes	Yes	Yes	Yes	Yes
Sidney Wood - AS4998	Yes	Yes	Yes	Yes	No
Frit – Blunden's Wood[1]	Yes	Yes	No	No	No

1 - It must also be noted that there is a curved base-line across the range of angles, denoting the presence of glassy material.

Table 6.14 - The Various Phases Present in Ceramic Crucible Fragments

CHAPTER SEVEN

DISCUSSION OF GLASS-MAKING TECHNOLOGY

7.1 Process Temperatures

There were two main temperatures for glass-making processes that could be determined from the analyses carried out in this work. These were the temperatures at which the glass was fritted, assuming that fritting was carried out, and the highest temperature reached in the furnace. Estimation of these temperatures could be important, as the technology of the furnaces, and the temperatures that could be attained, may have been a major factor in the type of glass that could be produced. It has already been stated in Chapter 2 that the addition of alkali, though reducing the temperature at which silica melts, degraded the quality of the glass. Therefore, if higher furnace temperatures could be reached, it may have been possible to reduce the amount of woodland ash.

7.1.1 The Fritting Temperature

The first temperature of interest was the temperature at which the frit was produced. The x-ray diffraction analysis carried out on the frit provided an insight into the behaviour of the mixture of sand and ash during the application of heat, assuming that this material was indeed frit.

The sand grains that were observed under the optical microscope in chapter 4 would have undergone a transformation as they were heated. This transformation, described in section 2.3, would have resulted in the change of phase within the silica, from quartz to cristobalite or tridymite. As tridymite was detected in the sample of frit it was highly likely that this material had been subjected to a heat in the region of 870 °C, the conversion temperature for tridymite.

Therefore, the detection of a small amount of tridymite in the frit led to the temperature of fritting being estimated to be in the region of 900 °C. This assumed that this piece of frit was representative of the frit produced at a glass-making site, or indeed, that it was a fragment of frit. The optical microscopy showed that it had all the appearance of frit, sand grains within a glassy matrix and signs of a reaction taking place around the silica grains. The presence of the glassy matrix was detected with x-ray diffraction, where a curved base-line could be seen. This represented a proportion of material that was not crystalline.

Was this piece of frit representative of medieval frit, and in particular frit of the type produced at Blunden's Wood, Knightons and Sidney Wood? Little evidence of frit has been found at glass-making sites, which could have two implications. First, all the frit was consumed in the glass-making process. Or second, samples of frit have been missed in excavations due to its appearance. The understanding of frit could be seen as fundamental in understanding the manufacture of medieval 'forest' glass, which suggested that excavators would look for this type of material.

Therefore, it must be assumed that very little frit has been found in recent excavations due to the consumption of it to produce the glass. The curved base-line, seen on the plot for the x-ray diffraction analysis of the frit, provided the evidence that the frit had begun to fuse, and therefore the formation of tridymite represented the absolute top temperature for the fritting process.

7.1.2 The Glass-melting Temperature

The scanning electron microscopy of the ceramic fragments enabled some knowledge of the process temperature of glass melting to be obtained. The crystalline structure of the clay body was observed in chapters 5 and 6 (figs. 5.1, 5.2, 5.3, 6.3 and 6.4). The phases that were identified could then be related to the break-down of the clay when subjected to heat. The mullite crystals and a glassy matrix, seen in the clay material, provided a basis for estimating a temperature in excess of 1000 °C. The formation of mullite from the hydrated clay has been discussed already, in chapter 3. The estimation of 1000 °C was at the lowest end of the scale. A temperature in the region of 1200 °C – 1300 °C would be far more likely, when mullite transformation was complete. This upper temperature would also account for the presence of a glassy phase observed in the crucibles, where the formation of the vitrified state would require a high temperature (Travers p171, 1918). Samples of other crucible material from Blunden's Wood and Knightons showed the presence of mullite, and a firing temperature in the region of 1100 – 1200 °C was estimated (Williams p12, 1995). The re-heating of the crucible fragments up to 1400 °C, seen in chapter 2, (Tables 2.8, 2.9 and 2.10 and fig 2.7), tended to support this estimation.

The crucible showed large expansion above 1200 °C, and showed signs of degradation at 1400 °C.

7.2 The Addition of Cullet to Glass Batches

No evidence concerning the addition of cullet to the glass batches was obtained for the analysis of the glass fragments. A sample of glass from Blunden's Wood had such a different composition to the vessel glass that was produced at the site was found. This fragment may have represented cullet, though this could not be proven as there were too few fragments to confirm this.

The reconstruction of the glass-making procedure did not provide much detail as to the addition of cullet. Glass was easily produced from the raw materials, as shown in experiments using beech ash and sand (chapter 2). However, it would be inconceivable that all the glass produced at a site would have been perfect. Therefore, waste glass would have been produced and may have been re-used in the glass batch.

7.3 The Quality of the Glass

It was very difficult to assess the quality of the glass, as the only fragments analysed were pieces that had remained at the site. However, what was apparent was the huge difference between the quality of the vessel glass made at Blunden's Wood and that made at Sidney Wood. The appearance of the glass from Sidney Wood was far superior to the cloudy, slightly weathered glass from Blunden's Wood.

The composition may have been largely responsible for this change in quality, as the Sidney Wood glass had a very high level of lime and very low level of alkali. This had produced a very durable glass, with a high degree of clarity.

In contrast, the vessel glass from Blunden's Wood had a higher potash and lower lime content, which had produced a poor quality material. This will be discussed further in chapter 8. The clarity and quality of the window glass from Knightons was similar to that of the vessel glass from Blunden's Wood. This similarity in quality showed the similar technology that would have been used to make vessel glass and window glass. Fragments of vessel glass were found at Knightons, but none were tested. Similarly, window glass was found at Sidney Wood, but not tested.

The reason for the improved quality of glass produced at Sidney Wood was most likely the change in composition of the ash, or possibly a different source of vegetation. What was also observed at Sidney Wood was the better quality of crucible. These two factors combined may have enabled the glass-maker to reach higher temperatures in the furnace, and therefore, may have allowed an ash that had a lower alkali content to be used. The better control of the process of glass-making may have produced a better quality glass.

7.4 The Transfer of Constituents between the Glass and the Crucible

Examination of the interface between the glass and clay was carried out to discover the transfer of components within the glass to the crucible and vice verse.

It may be important to discover the transfer of constituents of clay into the glass, as this may change the composition of the glass. In addition to this, the movement of components from the glass into the crucible may indicate the nature of the attack that the glass can have on the clay. This may provide an understanding of the ability of the crucible material to withstand this attack, and how it may have been designed to withstand the erosion.

Compositional analysis, using the scanning electron microscope, of the interface between a pitted crucible and the glass was carried out on a fragment of material from Blunden's Wood, as described in Chapter 6. A plot of the transfer of silica (fig. 7.1) showed that the silica content remained fairly constant throughout the glass (60%). There was a small increase at the boundary between the crucible and the glass, which suggested that there was a small level of silica moving from the clay to the glass. On the interior of the clay body the level of silica rises sharply to about 78%. This leveling off from 150 µm to 600 µm has been observed in modern refractory ceramics that have been subjected to corrosion by glass (Cable p293-294, 1994). The dissolution of the clay, as a result of the silica movement, may have been one of the main factors in determining the life of the crucible, though the small decrease may not have led to failure from erosion for a considerable length of time.

The level of potash in the glass (fig. 7.1) remained constant until the surface of the crucible was reached, before falling to 2-3% within the clay. The mobile ions of potash penetrated nearly 1000 microns into the clay.

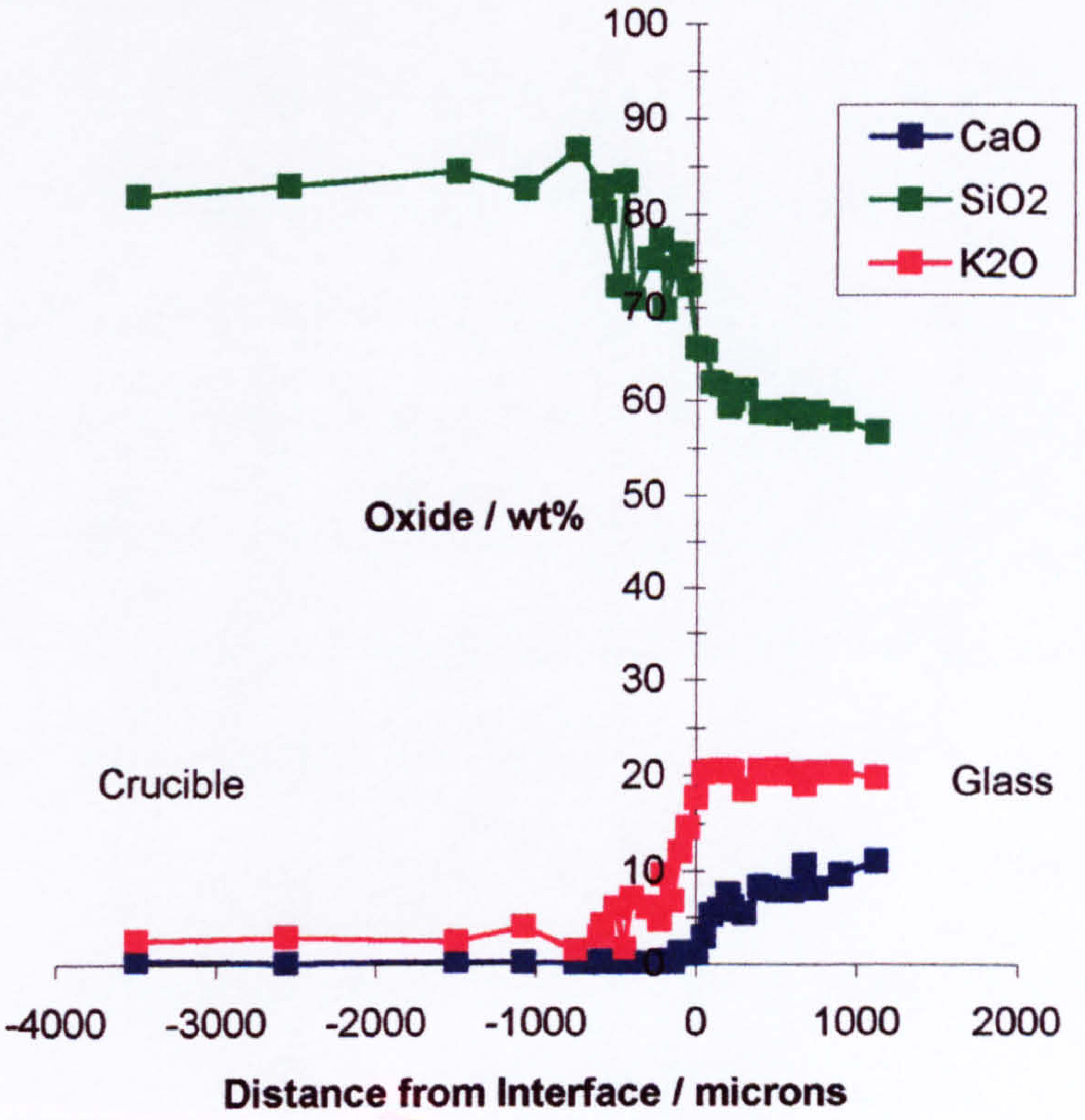

Figure 7.1 – The Change in Level of Silica, Potash and Lime across the Interface

AS3498 (Blunden's Wood)

These highly mobile ions were able to easily diffuse, and may have been the cause for the inflexion curve observed in the movement of silica. The preferential movement of the potash may have acted as barrier to the movement of the silica from the clay to the glass. The movement of lime (fig. 7.1) and magnesia (fig. 7.2) showed similar patterns to each other. The movement was from the glass into the clay, with a depth of penetration in the region of 250 μm. There was a large decline in the level of lime. This was from 10% at the outer surface of the glass to 2.5% at the interface between the clay and the glass (fig. 7.1). This showed that there was a large migration of calcium ions into the clay, which showed that the glass was corroding the ceramic crucible. A similar percentage fall was observed with the decline of magnesia (3 to 1.5%)(fig. 7.2). The abrupt stopping point of the lime and magnesia may indicate the presence of a freezing point. This was a point at which the clay was able to withstand the attack by the glass components, and the mobility of the calcium and magnesium ions was reduced to a point where they remained at a constant level, which was the same as the composition within the clay.

There was transfer of alumina from the clay to the glass (fig. 7.2). A reaction was taking place within the clay, between the interface and 1000 μm into the crucible. The alumina composition appeared to gradually increase from the outer face of the glass to the interface, rapidly rising at the border, reacting within the clay, and finally, leveling off towards the inner face of the crucible. The peak on the inside of the crucible was within the boundary layer, where the glass had filled the porosity of the clay.

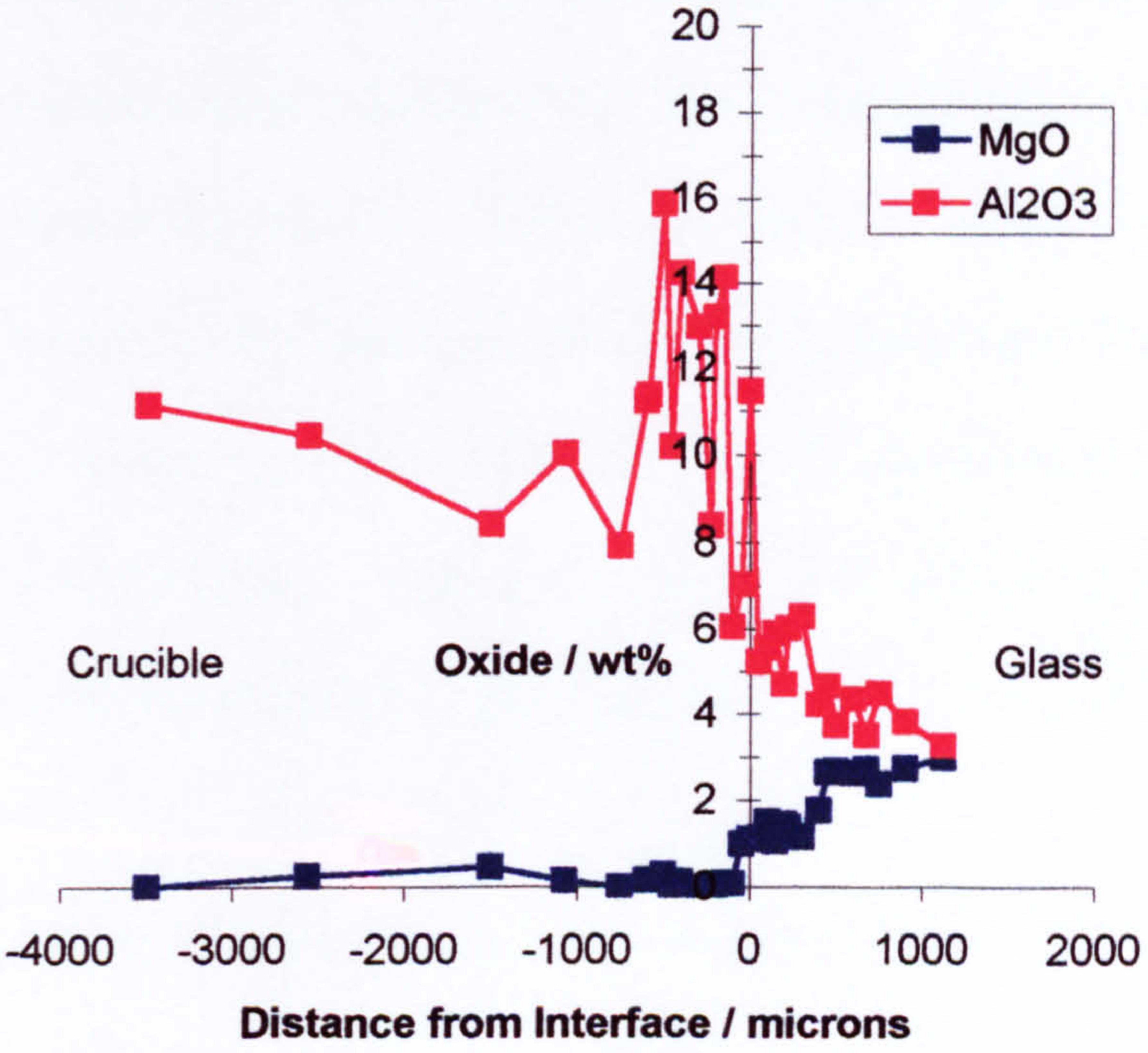

Figure 7.2 - The Change in Level of Magnesia and Alumina across the Interface

AS3498 (Blunden's Wood)

The ion movement into and out of the crucible was causing components to compete for spaces. The implication of this was that highly mobile ions were more likely to find the spaces, and therefore, the potash would be able to penetrate further into the glass.

This alumina dissolution showed similarities to observations made of Gallo-roman glasses, where a small transfer of material over the interface led to a contamination of the glass melt (Velde, 1990).

A peak of iron oxide occurred at the mid-point between the glass and clay (fig. 7.3). This peak corresponded with the composition of the bright crystals observed at the boundary of the glass and clay (seen in Chapter 6). There appeared to be a build up of titania just within the crucible (fig. 7.3). Some of the titania had dissolved out of the clay into the glass, but it was the build up at the boundary which had produced the bright crystals. The composition of the crystals was found to be around 50% iron oxide, 40% titania and 8% alumina. Early examination of glass-making sands in
and West-Oram, 1979
Britain revealed the presence of ilmenite ($FeTiO_3$) and rutile (TiO_2) (Boswell, 1917).

This may be where the iron oxide and titania were coming from, though they could also have been migrating from the clay crucible, which contained both iron oxide and titania. Silica grains were found in the boundary layer between the clay and the glass, so it was possible that this produced a layer that was rich in iron oxide and titania.

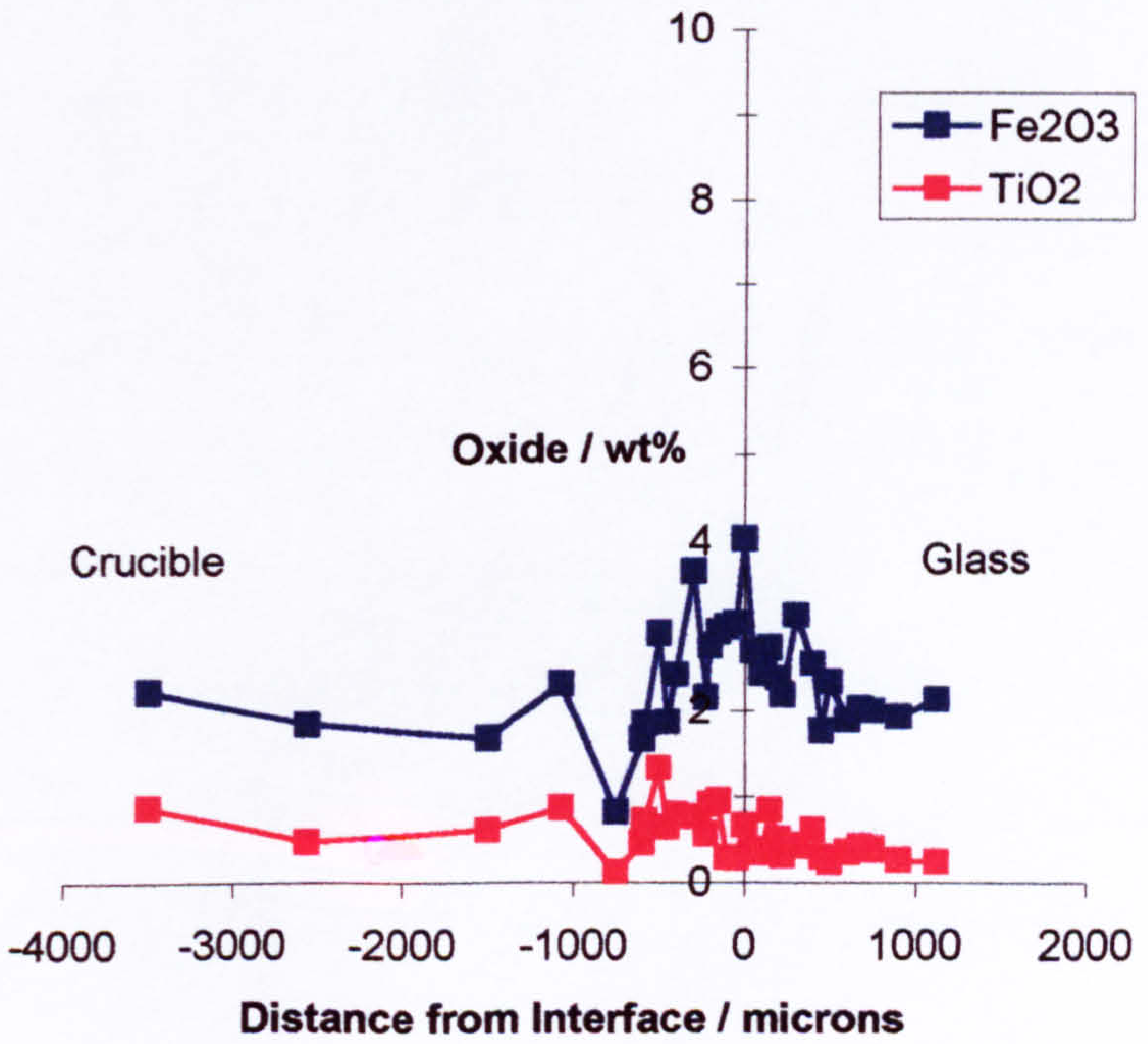

Figure 7.3 - The Change in Level of Iron Oxide and Titania across the Interface
AS3498 (Blunden's Wood)

7.5 Different Types of Attack

Some crucible fragments were pitted, as though the surface has been attacked by the glass, others had a flat surface, with a layer of glass adhering to the clay, showed little sign of corrosion. Examples of these two forms of surface have been investigated to ascertain any differences in the form of corrosion. As before, changes in chemical composition were measured at regular intervals through the pitted or flat surface using scanning electron microscopy.

The potash showed an increased level within the crucible with a pitted surface (fig. 7.4). This began to explain the different attack on the surfaces. The higher level of mobile alkali ions penetrated into the ceramic structure, disrupted it, and eroded the clay. The corrosion of the clay by the alkali from the glass may have caused sand grains within the clay to be released. Therefore, there should be an increase in the silica level in the glass. However, the opposite was observed. It was possible that the flat surface had been more weathered than the pitted surface, and that the increased level of silica in the glass from the flat layer was due to the migration of alkali ions out of the glass. This aside, it was apparent that the higher level of potash in the crucible was causing a more aggressive form of attack to take place, which was probably how the pits had formed.

The stability of the alumina (fig. 7.4) over the flat surface may also have explained the small level of attack by the glass. The clay structure was vital in halting the corrosion caused by the glass.

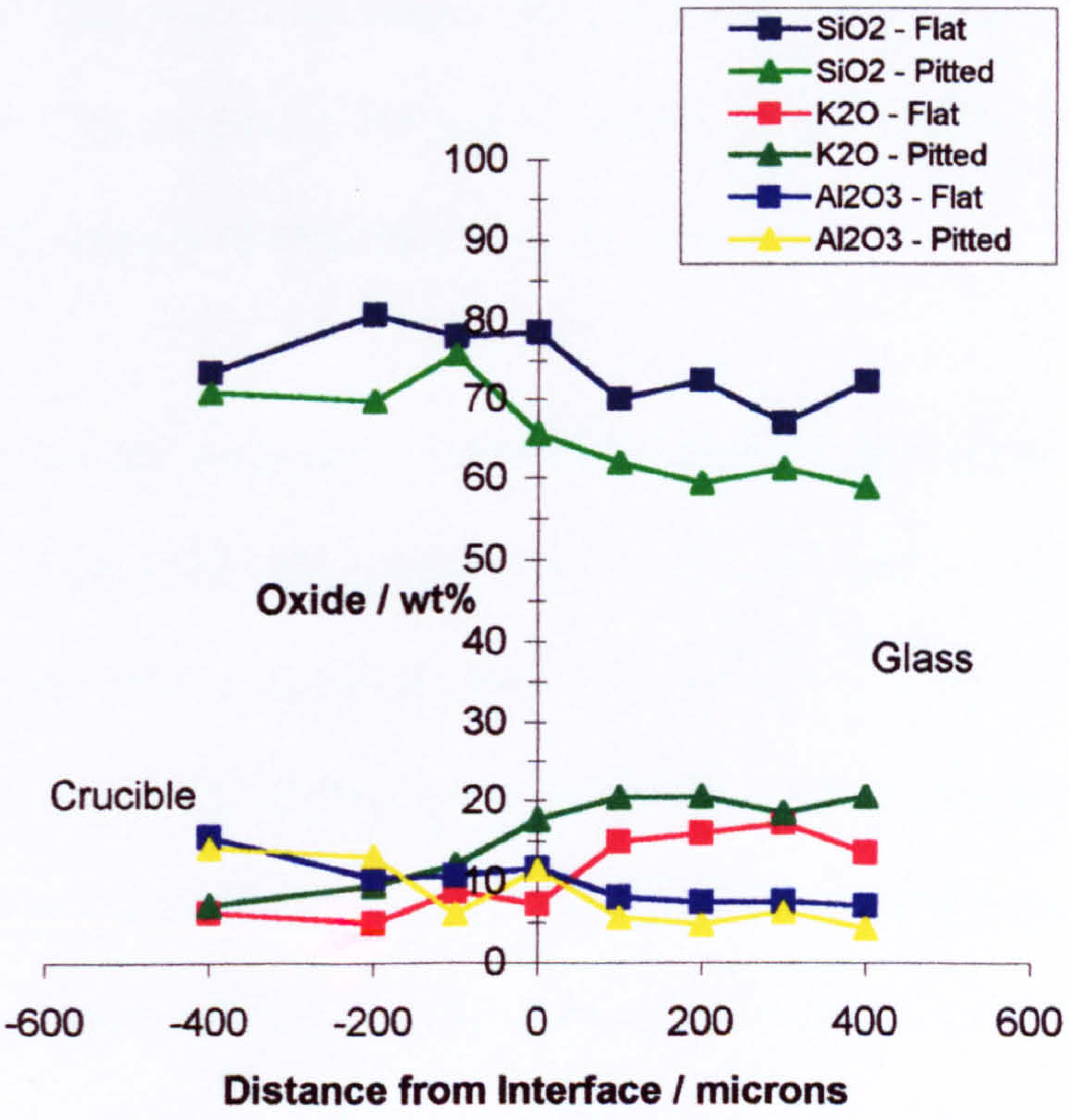

Figure 7.4 - The Change in Level of Silica, Potash and Alumina across Different Interfaces AS3498 (Blunden's Wood)

Therefore, if the clay matrix was able to remain intact, the crucible would be able to withstand the erosive effect of the glass. However, the increased dissolution of alumina from the clay into the glass may have indicated that the flat surface was undergoing a larger degree of attack, which had resulted in the total destruction of the outer layer of crucible. Conversely, the defined peak across the interface of the pitted surface shows that the alumina rich matrix was diffusing out at a lower rate, so although the surface was pitted, it had undergone localised attack by the glass.

The complexity of the erosion which took place on the two fragments of crucible was highlighted by the fact that there were conflicting conclusions as to which crucible had been eroded more. The exterior of the pitted crucible suggested that it was being ripped apart, with whole regions of clay dissolving into the glass.

Modern refractory bodies are designed to withstand corrosion and erosion by any molten, or semi-molten material with which they come into contact. Thus, the ability of the ceramic material to resist the attack may govern the economics of the process, and the behaviour of the refractories would be vital in furnace design, construction and operation (Cable, 1968). Medieval glass-makers may have located their glasshouse near a source of the clay used in furnace structures and crucibles, though this was not always necessarily true. It appeared that the glass-maker operating Blunden's Wood had found a clay which was able to withstand corrosion, and there was only a little dissolution of crucible into the glass. This final comment was important, as the medieval glass-making process relied on the production of glass from ash and sand.

Therefore, if there was a large amount of dissolution of the crucible, which contained silica grains, the glass would have become rich in silica. It would then have needed a higher temperature to melt the glass. Also, if there was dissolution of the crucible it would have become harder to control the composition of the glass batch.

CHAPTER EIGHT

DISCUSSION OF THE GLASS ANALYSES

8.1 Types of glass

The compositional analyses obtained using scanning electron microscopy, electron probe micro-analysis and x-ray fluorescence of the glass fragments Blunden's Wood, Knightons and Sidney Wood revealed that all were primarily potash glasses. The main constituents were silica, lime and potash. This was the base composition of glasses formed from sand and woodland plant ash.

8.2 Blunden's Wood

To fully understand how these glasses compare with other sites it was necessary to observe how the compositions formed patterns and correlation between each component. The first method of comparison was to use Pearson product moment correlation coefficients. This measured the linear association between two data sets, in this case the data sets were the various components within the glass. The formula can be seen in Appendix 2.

A value of 0 for the coefficient implies little, or no, correlation, while a value near to +1 or -1 indicated a strong linear relationship.

To test the significance of the correlation coefficients in relation to the sample size the significance level was determined. It was based on the calculation of the ratio of variances, to produce a significance level in regression analysis (Drennan p216-217, 1996). The formula, related to the Pearson product-moment correlation coefficient and the numbers of samples, can be seen in Appendix 2.

Calculation of the Pearson product moment correlation coefficients for glass fragments from Blunden's Wood, as shown in Table 8.1, provided a link between components. This statistical analysis was carried out on the samples analysed using scanning electron microscopy, as the data set was large enough for any correlation to be tested for significance. In fact the data set was large enough (n = 273) for all correlation coefficients above r = ±0.11 the significance was 0.1%, which showed that any linear relationships observed were valid. Even at the 10% significance level, the data set was large enough for correlation coefficients measured at r = ±0.07.

The cluster formations could cause a problem in the calculation of the correlation coefficient, so the value of r must be looked at in conjunction with graphical representation to distinguish whether clusters have caused the correlation or not (Baxter p46, 1985)

	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3	Na_2O	TiO_2
MgO		-0.73	-0.67	0.75	-0.08	0.95	0.91	-0.33	0.23	-0.58
Al_2O_3	-0.73		0.24	-0.82	0.36	-0.73	-0.75	0.41	-0.03	0.79
SiO_2	-0.67	0.24		-0.54	-0.52	-0.65	-0.72	0.16	-0.24	0.22
P_2O_5	0.75	-0.82	-0.54		0.01	0.75	0.82	-0.46	0.15	-0.56
K_2O	-0.08	0.36	-0.52	0.01		-0.16	0.02	-0.07	0.25	0.16
CaO	0.95	-0.73	-0.65	0.75	-0.16		0.94	-0.37	0.14	-0.55
MnO_2	0.91	-0.75	-0.72	0.82	0.02	0.94		-0.44	0.16	-0.59
Fe_2O_3	-0.33	0.41	0.16	-0.46	-0.07	-0.37	-0.44		-0.08	0.32
Na_2O	0.23	-0.03	-0.24	0.15	0.25	0.14	0.16	-0.08		-0.06
TiO_2	-0.58	0.79	0.22	-0.56	0.16	-0.55	-0.59	0.32	-0.06	

Table 8.1 – The Pearson Product-Moment Correlation Coefficients between the Components in Glass Fragments from Blunden's Wood

8.2.1 Components with High Positive Correlation

The values of the correlation coefficients immediately showed some to be highly positive. The highest correlation between the glass components was observed with magnesia and lime. A correlation coefficient of r = 0.95 suggested a very strong relationship. A test of significance of this value showed that the relationship was not due to vagaries of data points, but that there was a strong relationship between magnesia and lime. A plot of these components (fig. 8.1) showed this clear linear relationship, with a positive gradient to a line that could be drawn between the analyses of the glass fragments.

If both of these forms of analysing results were taken together it showed that it was highly probable that the magnesia and lime content in the glass from Blunden's Wood came from the same source. The source of raw material in medieval glass that contained lime and magnesia would most likely have been the ash. The analyses of various beech and oak ashes did show a high level of lime, and in the case of beech trunk, a high level of magnesia (shown in Table 2.4 (Turner p289, 1956)).

The correlation between lime and manganese dioxide was also very strong (r = 0.94). Again, this result was highly significant, which showed the strength of the linear relationship. These components were plotted against each other (fig. 8.2). This high level of relationship was observed in this plot, with a positive gradient to line that could be draw through the samples. This very high correlation showed once again that these two components were likely to have come from the same source of raw batch ingredient.

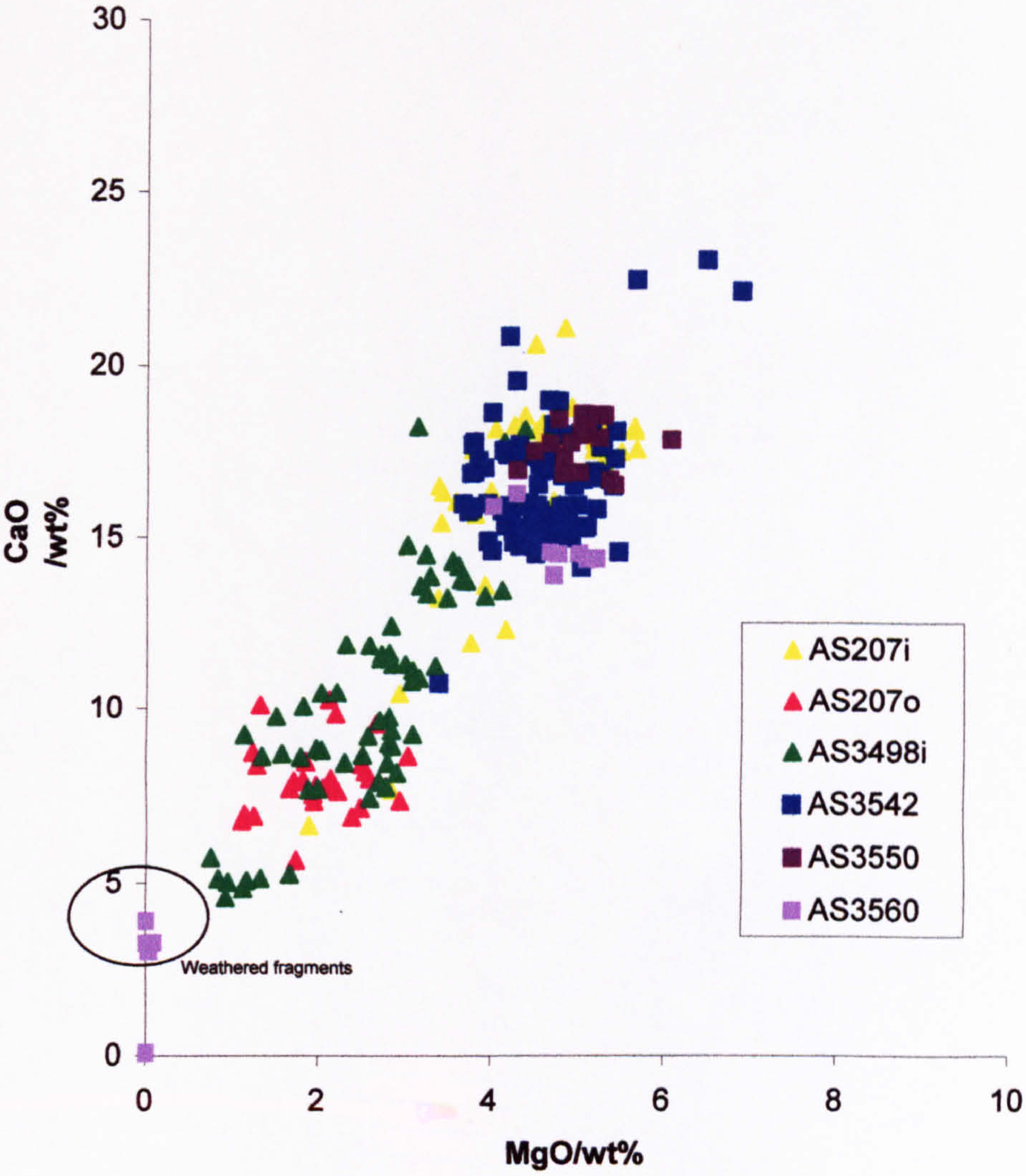

Figure 8.1 – A Plot of Magnesia and Lime for Glass Fragments from Blunden's Wood (Refer to Table 6.2 for Sample numbers)

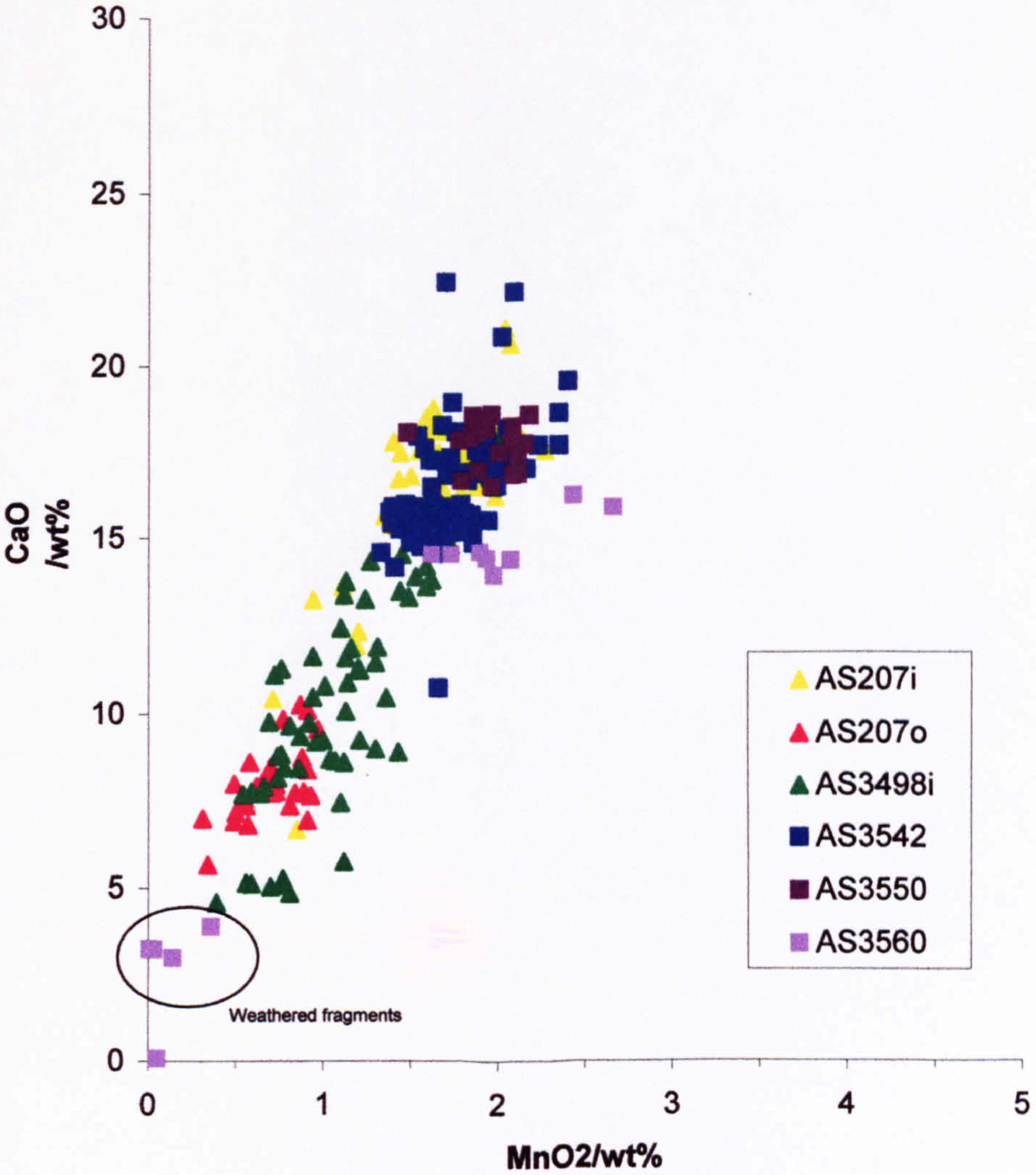

Figure 8.2 – A Plot of Manganese Dioxide and Lime for Glass Fragments from Blunden's Wood (Refer to Table 6.2 for sample numbers)

Manganese dioxide showed strong correlation with both magnesia (r = 0.91) and phosphorous pentoxide (r = 0.82). The correlation between manganese dioxide and magnesia re-affirms the suggestion that lime, magnesia and manganese were from the same raw material, as very high correlation coefficients were obtained for all combinations of these components. Therefore, if this was the case, and there was a high correlation between manganese and phosphorous pentoxide, it could be suggested that phosphorous pentoxide was also from the ash.

Lime and phosphorous pentoxide showed a correlation coefficient of r = 0.75. This was moving away from a solid relationship (+1), but still showed a high degree of correlation, and still highly significant. When these components were plotted against each other (fig. 8.3) there was a fairly strong linear relationship, but there was more spread of results.

Other components of the ash that showed a high degree of correlation were phosphorous pentoxide and magnesia (r = 0.75) and phosphorous pentoxide and lime (r = 0.75). Correlation coefficients below ±0.70 were taken to show slightly too much deviation from ±1 to form a valid linear relationship. In any case there were no other components that were likely to have come solely from the ash that showed a high degree of correlation.

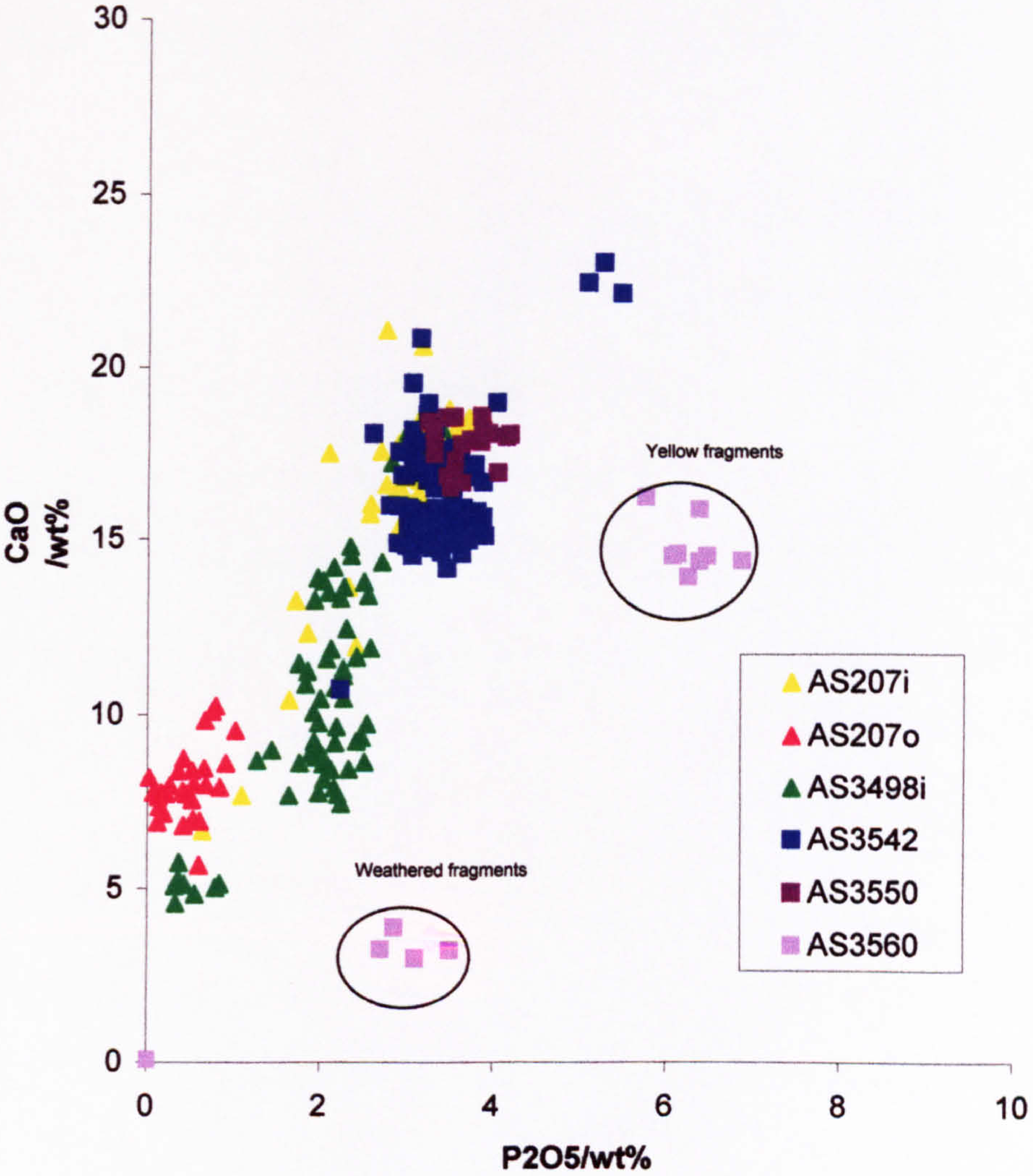

Figure 8.3 – A Plot of Phosphorous Pentoxide and Lime for Glass Fragments from Blunden's Wood (Refer to 6.2 for Sample numbers)

The correlation coefficient between alumina and titania was high (r = 0.79), and as with the other coefficients could be taken to be significant. The plot of these components (fig. 8.4) did show the good linear relationship. This result was of great interest as it provided the first evidence to the composition of the glass-making sand. No high positive correlation had been found between alumina or titania to any of the previously mentioned components (most probably from the ash), suggested that the second raw ingredient in the glass batch contained alumina and titania. The presence of alumina in glass-making sands has been discussed in section 2.2.

Other positive correlation coefficients of components that may have originated from the sand did not produce a very high value of r. It must be noted that there was positive correlation between alumina and iron oxide (r = 0.41), but the value was too low to suggest that these components were always from the sand. The lack of positive correlation between the alumina and the major components of the ash suggested that iron oxide may have been present in both the sand and the ash, which contributed to the low value.

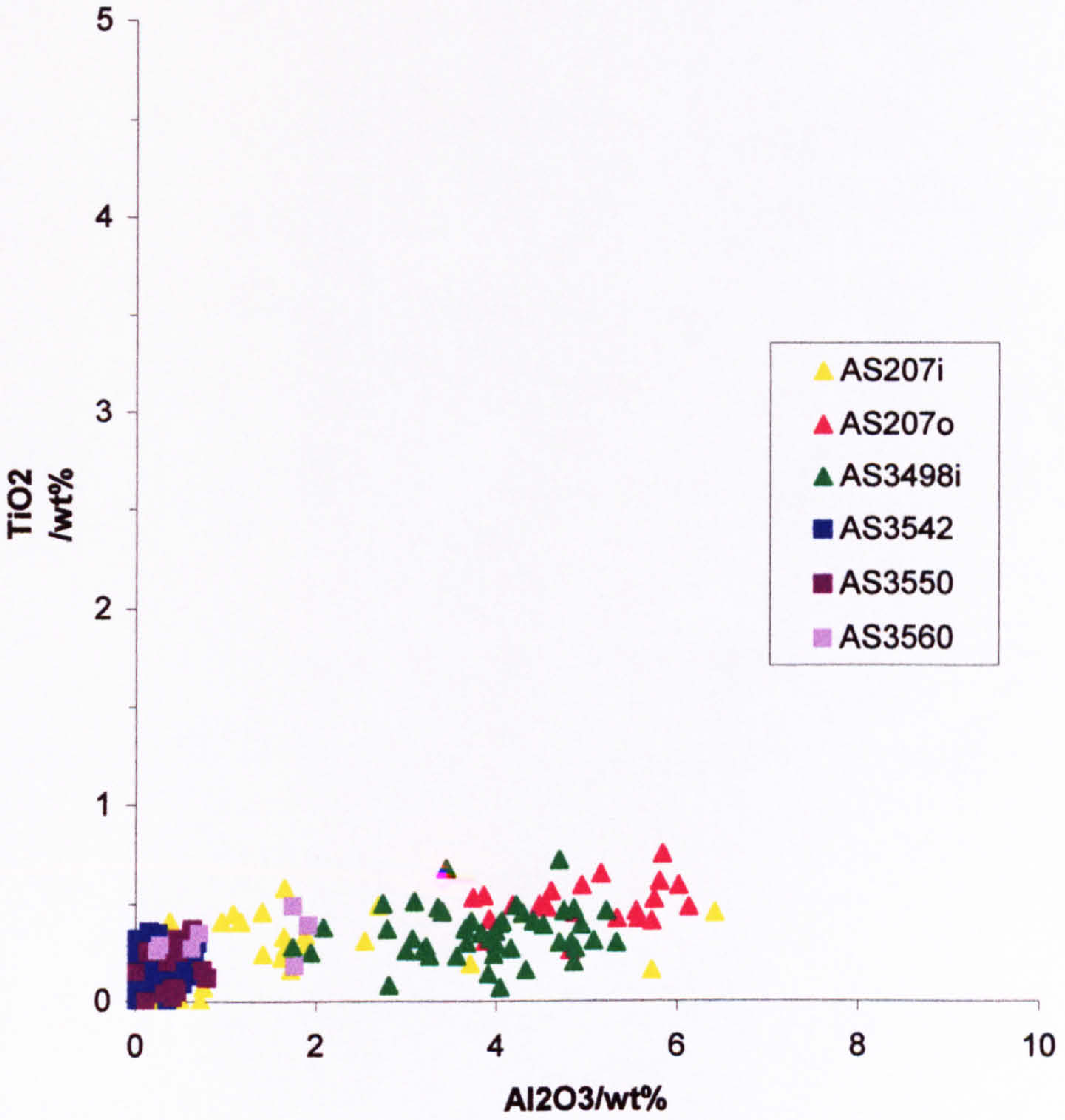

Figure 8.4 – A Plot of Alumina and Titania for Glass Fragments from Blunden's Wood (Refer to Table 6.2 for Sample numbers)

8.2.2 Components with High Negative Correlation

The previous section showed that certain components had a high level of positive correlation between them, and that the high value probably indicated that they were from the same source of raw ingredient to the glass batch. This section has grouped those components that showed a high degree of negative correlation, as shown in Table 8.1. These values indicated that the components with a high value of Pearson product-moment correlation coefficient, but were negative, were probably added to the glass batch separately.

The correlation coefficient was very high between alumina and phosphorous pentoxide (r = -0.82). When these components were plotted against each other, (fig. 8.5) a good linear relationship could be seen. The gradient of the line that could be drawn through the plotted analyses was negative. This suggested that the alumina content of the batch came from a different source to the phosphorous pentoxide.

As the previous section had indicated that alumina came from the sand, and phosphorous pentoxide had originated in the ash, this high negative vale re-affirmed the independence of these components.

This could be repeated for the correlation coefficients between alumina and manganese dioxide (r = -0.75), alumina and lime (r = -0.73) and alumina and magnesia (r = -0.73). The significance of these results showed that they were indeed true relationships. It suggested that lime, magnesia and manganese dioxide were added as part of the ash and alumina was added as an impurity in the sand.

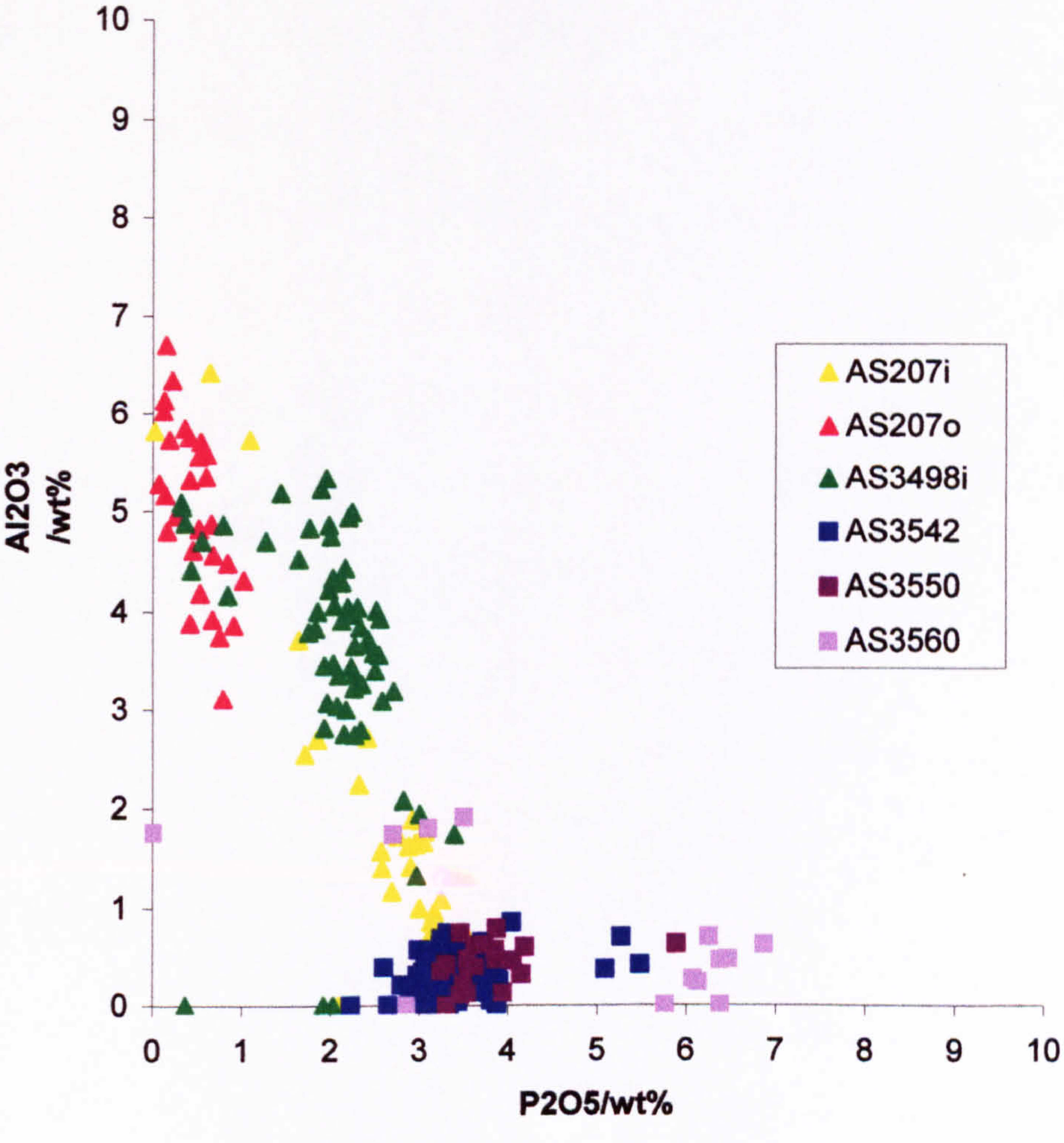

Figure 8.5 – A Plot of Alumina and Phosphorous Pentoxide for Glass Fragments from Blunden's Wood (Refer to Table 6.2 for sample numbers)

The highest correlation between silica and any other component was observed in its correlation coefficient with manganese dioxide (r = -0.72). This indicated that manganese dioxide was most likely independently added to the glass batch to the main component of the sand, silica. Therefore, it could be taken that the glass-making sand at Blunden's Wood did not contain manganese dioxide. However, it must be noted that silica may have been within the ash (see Table 2.4).

Other high negative correlation coefficients, but below –0.70, were those between silica and magnesia (r = -0.67), silica and lime (r = -0.65), silica and phosphorous pentoxide (r = -0.54) and silica and potash (r = -0.52). These values may have indicated the complex nature of a glass batch, and the contribution of silica to the ash.

8.2.3 Major Glass Compositions

There were many distinct glass compositions from the analyses of the fragments of glass from Blunden's Wood (Table 6.2). The first, and probably most important was the vessel glass composition, represented by the samples AS3542. It was clearly a high potash glass, typical of 'forest' glass. It had a mean silica level of 59.56%, potash of 12.62% and lime of 16.22%. Other vessel glass fragments analysed from Blunden's Wood, samples AS3550, had a similar composition. The silica was slightly lower (mean = 56.36%), but the mean values for the potash and the lime were close (13.13% and 17.77% respectively). This glass was slightly thicker than the vessel glass of AS3542, which could have been as a result of an altered composition. The glass-maker may have produced a glass to particular formula, and adapted it according to his needs.

However, the close values of the major components within both of these glasses suggested that the batch was predominantly the same. The other main components of the glass (magnesia and phosphorous pentoxide), and the trace components (alumina, manganese and iron oxides), indicated that these glasses were most likely using the same raw ingredients, and a very similar batch composition.

Fragments of glass were taken from the inner face of a crucible (sample AS207i). The results from the analyses of these fragments were able to confirm that the vessel glass discussed above was produced in crucibles found at Blunden's Wood. Glass batches could have been prepared using glass cullet from a number of different sources, which could result in fragments of glass not belonging to the site under study. However, crucible material was unlikely to have moved too far from the glass-making site, so the similar composition of glass from the inside of a crucible to the composition of vessel glass was most important. The composition of glass from the inside of the crucible was different in terms of alumina and iron oxide though (1.32% and 4.12% respectively). These very high values, in comparison to those obtained for the vessel glass, showed the possible contamination from the crucible, which was discussed in chapter 7.

The other crucible fragments that had glass adhering to the inside face produced similar results to those described above. The major difference were the levels of potash and lime in the glass fragments (mean = 18.34% and 10.42% respectively). This showed all the appearances of a different glass composition.

However, the analyses obtained from the inside of both crucibles had a much higher degree of standard deviation, especially in the case of lime and iron oxide. This has highlighted the problems of contamination of the glass batch from the crucible once more, and the skill of the glass-maker in accounting for the contamination.

The glass taken from the exterior of the crucible (sample AS207o) was highly likely to be from glass running down the side of the crucible. This may have reflected a composition that was melted in the crucible. However, the analyses of the glass from the exterior of this crucible showed all the features seen in the fragments from the interior. A high level of transfer of components from the crucible may have taken place, which resulted in a glass composition that bore little resemblance to the vessel glass from Blunden's Wood.

Other compositions of glass from Blunden's Wood included a very low silica glass (mean = 45.86%). Two fragments of a slightly yellow glass (sample AS3560^2) may have indicated the use of cullet on the site, or these could be rogue samples. There were only these two fragments, which did not appear to have any particular form to them, so while not being representative of glass from Blunden's Wood, they could not be ignored.

Samples of heavily weathered glass, AS3560^1, showed a fairly typical composition. The silica level was very high (mean = 88.52%), as a result of many of the other components being leached away.

As these heavily weathered samples were so different to the analyses obtained for the vessel glass it must be taken that the vessel glass had not undergone too much weathering. If this was the case it suggested that this vessel glass, while not possessing too great a clarity, it was durable.

In this case, it was possible that lime and potash were added independently to the glass batch, which raised the issue of the number of components within the glass batch. It has been stated that medieval glass was manufactured using sand and ash (Hawthorne and Smith p49-53, 1979). However, if there was no correlation between main the components within the ash, as seen above, and the level of ash remains constant in the batch then it was possible that three components were added to make glass. These would be sand, a source of potash (woodland ash) and a source of lime (a second form of woodland ash, or a lime-bearing mineral, such as chalk or limestone).

8.3 Knightons

The type of glass produced at Knightons glasshouse was window glass. The assemblages chosen for this work meant that the detailed correlation coefficient analysis carried out on the sample from Blunden's Wood could not be undertaken for Knightons, or for Sidney Wood. Part of the problem was the smaller number of glass fragments chosen. In addition to this there were definite clusters of analyses, which indicated that correlation coefficients would not be the best form of analysis to be carried out on the results.

For this reason, graphical representation of components plotted against one another could be made, which provided a basis for discussion for the compositions of the glass fragments. Results from all three methods of analysis of chemical composition, scanning electron microscopy, electron probe micro-analysis and x-ray fluorescence, were used in the discussion which follows.

When magnesia was plotted against lime (fig. 8.6) there appeared to be a wide spread of results. Most of the window glass compositions, represented by AS4931 and AS4934, had a lime content in the region of 15%, but the magnesia varied from 3.90% to 7.79%. What was also clear was the fact that the fragments of glass taken from the inside face of the crucible, AS4921i had a much higher level of lime in them (greater than 20%).

Some of the fragments of 'bulls-eye' glass that showed the signs of pitted weathering, AS4838, had a high level of lime also. This showed that although the lime was present in the glass as a stabiliser, it was not always possible to stop the process of weathering taking place.

The close compositional grouping of the glass fragments from Knightons was very evident when lime was plotted against manganese dioxide (fig. 8.7). This plot showed that all of the window glass, again except the 'bulls-eye' fragments mentioned above, provided a remarkably tight composition, at 15% lime and 0.90% manganese dioxide.

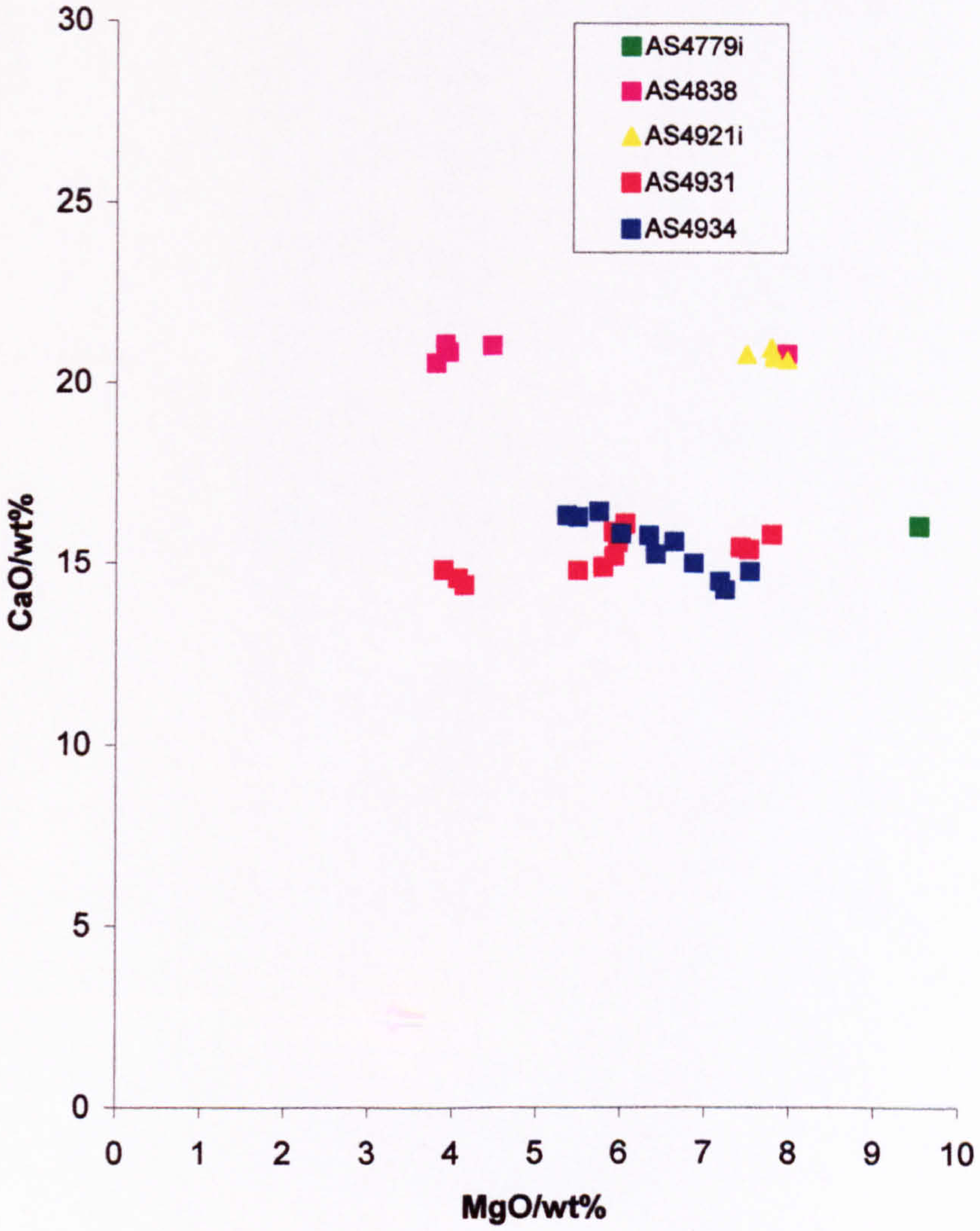

Figure 8.6 – A Plot of Lime and Magnesia for Glass Fragments from Knightons

(Refer to Table 6.10 for sample numbers)

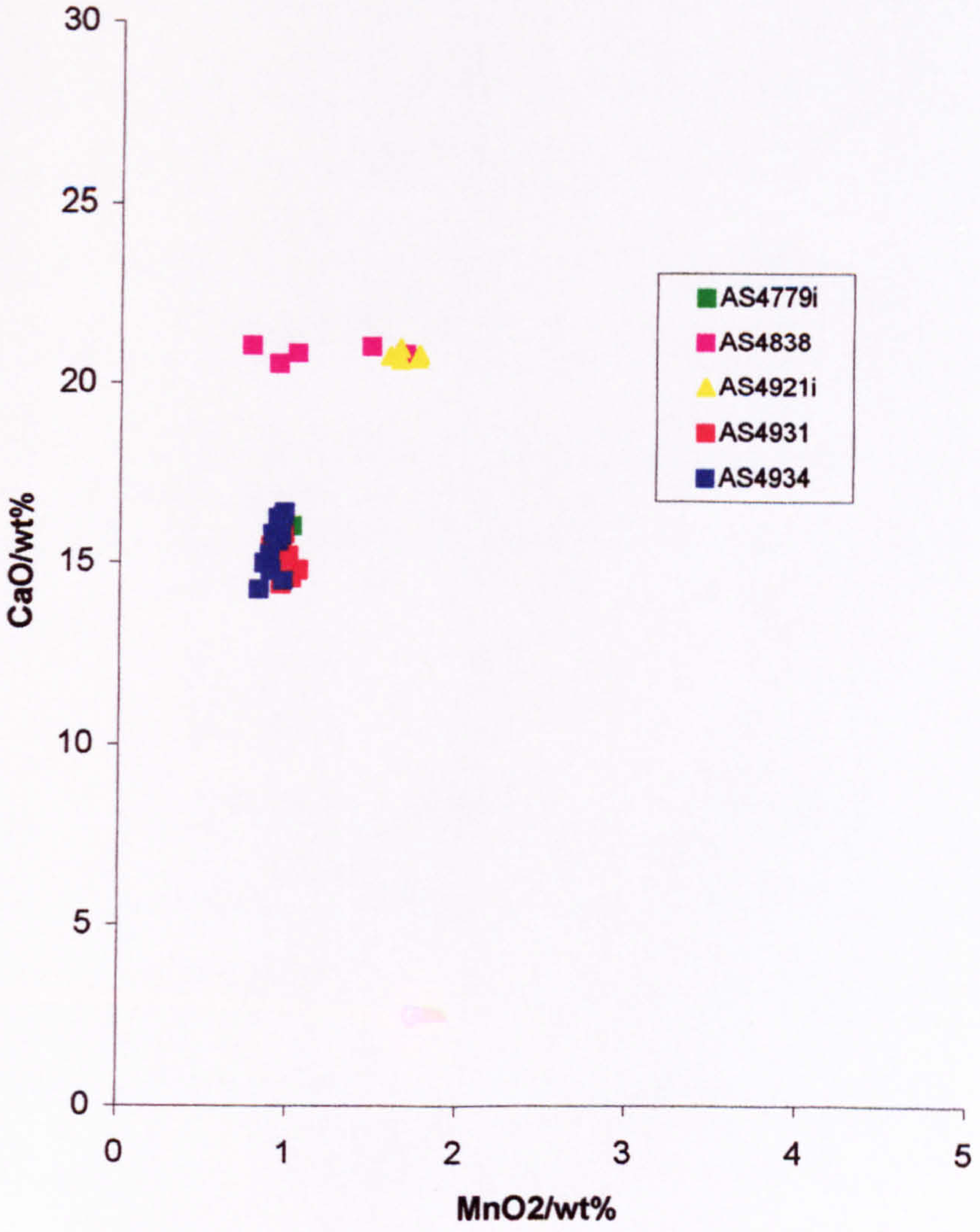

Figure 8.7 – A Plot of Lime and Manganese Dioxide for Glass Fragments from Knightons (Refer to Table 6.10 for sample numbers)

Though it was only possible to test one fragment from the interior of crucible AS4779, the analyses for this glass were also within this grouping. The close cluster grouping seen in this plot of lime and manganese results also indicated that correlation coefficients would not be suitable for these glass compositions.

One of the controlling factors in the determination of the colour of the medieval 'forest' glass was the ability of manganese dioxide to de-colourise the glass. Therefore a good comparison was obtained by plotting manganese dioxide against iron oxide (fig. 8.8), as the major impurity in medieval glass that would cause the green colour to be produced was iron oxide. As before this showed the very close cluster of results, centred on 0.95% manganese dioxide and 0.90% iron oxide. This showed that there was not an excess of manganese dioxide within the glass to reduce the effect of the iron oxide. Therefore, the result was a typical green glass, produced with wood ash.

Finally, in order to observe the relationship between two of the major components in the glass, silica was plotted against potash (fig. 8.9). Once again, the window glass fragments produced a very tight cluster. However, the plot showed that there was slightly more spread of results in the samples that had either come from the crucibles or from the 'bulls-eyes'.

The analyses of the glasses from Knightons were not able to shed much light on the raw materials used in the production of the glass, but these plots were able to show that there was close grouping between the fragments of window glass.

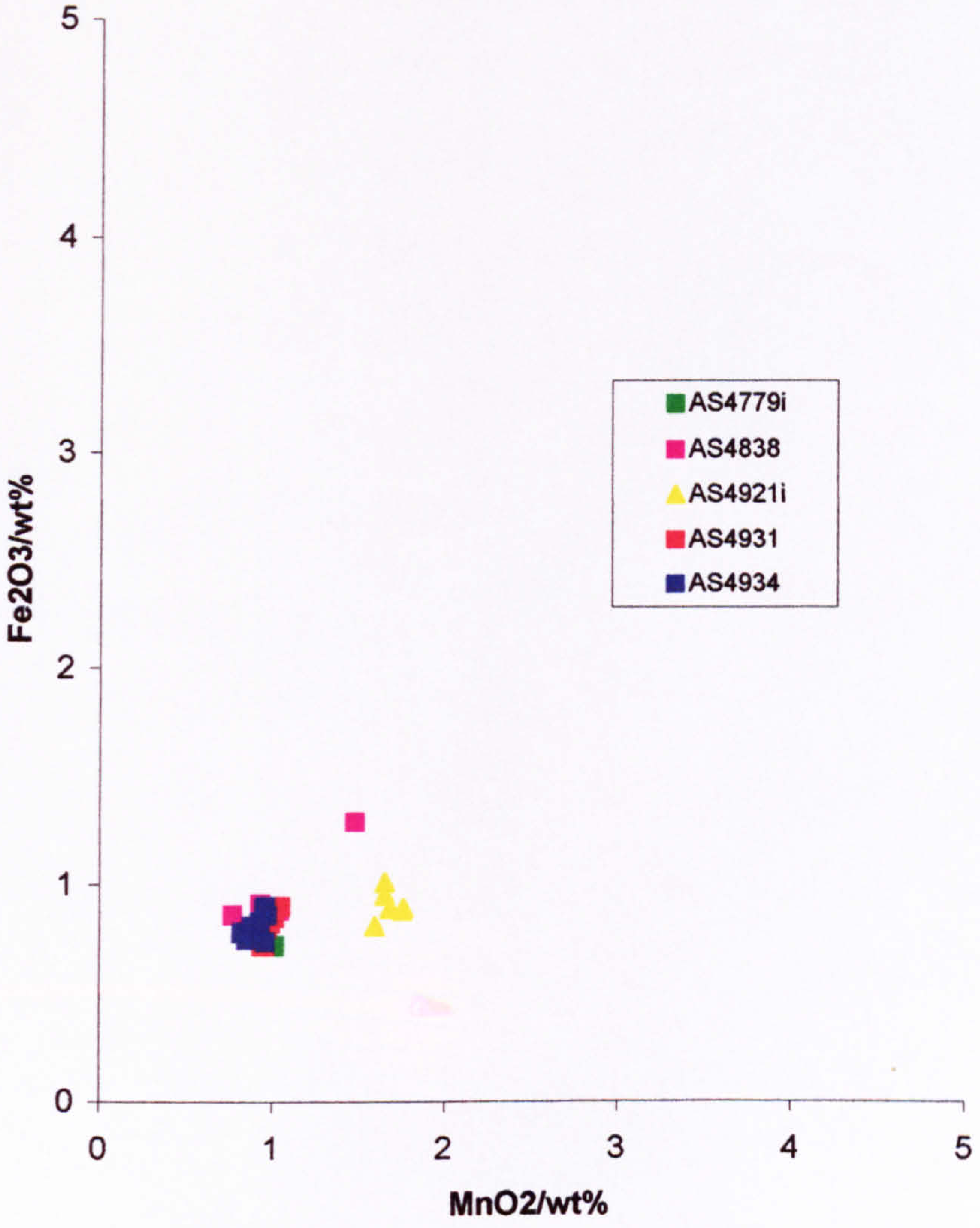

Figure 8.8 – A Plot of Iron Oxide and Manganese Dioxide for Glass Fragments from Knightons (Refer to Table 6.10 for sample numbers)

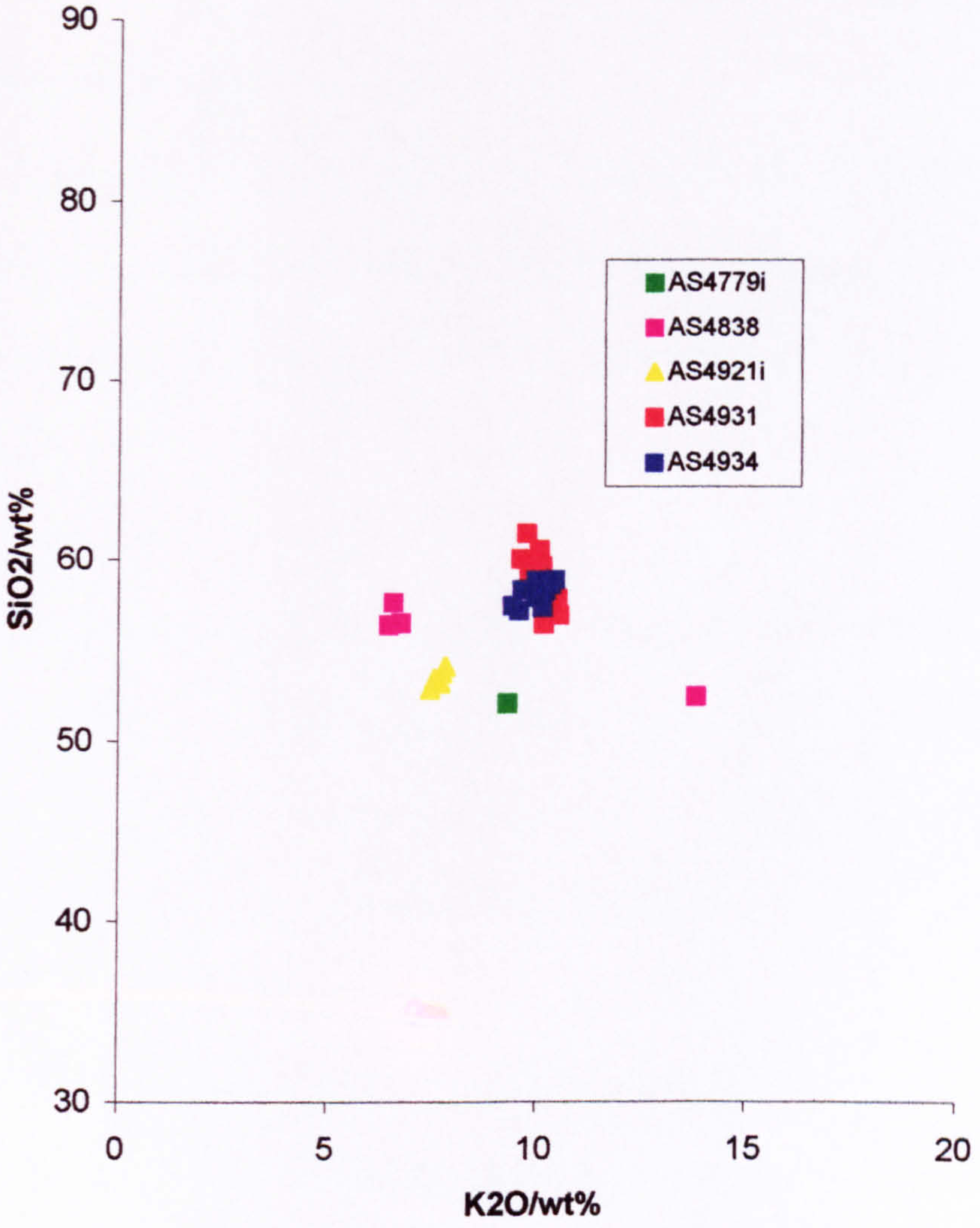

Figure 8.9 – A Plot of Silica and Potash for Glass Fragments from Knightons

(Refer to Table 6.10 for sample numbers)

It was unclear why the centre of the window glass ('bulls-eyes') should have had such a different composition, although the surface of these fragments were heavily pitted. This may have indicated that these glass fragments were more weathered than the good examples of window glass. There was some evidence of a reduced level of potash in the bulls-eye' fragments (fig. 8.9), which may have indicated that there had been dissolution of the alkalis within the glass.

8.3.1 The Major Glass Compositions

The glass from Knightons was a woodland ash glass, which contained silica, potash and lime as the main components. Less information concerning the raw materials could be gleaned from the analyses of the glass from Knightons than those from Blunden's Wood.

However a composition of window glass from this site could be determined, based on close cluster grouping. The analyses were able to show that the window glass of AS4931 and AS4934 was very close in composition. The window glass had a composition of about 58% silica, 10% potash and 15% lime.

The analyses of the glass fragments from within the crucible AS4921 were unable to corroborate the analyses of window glass, to confirm the window glass was manufactured at Knightons. However, the sole fragment that was taken from the interior of another crucible, AS4779, appeared to have a very close composition to the window glass.

Also, as there was evidence of a furnace specifically designed to anneal crown glass, it can be taken that this type of window glass was most likely manufactured by the glass-maker at Knightons.

One point of interest in the analyses of the glass from Knightons was the apparent differences in the compositions of AS4838 and AS4934 (Table 6.10). They both appeared to be fragments from the centre of the pontil, but their compositions were very different. The samples with a very high lime level, AS4838, were more weathered than the other samples. In addition to this the samples of AS4934 had a composition very close to the better examples of window glass fragments. This may have indicated that there were two compositions of window glass produced at Knightons, but it was more likely that this was not the case. The reason for the variation could not be determined by these analyses, as there were no other samples available to be chosen to analyse that could have provided the answer.

8.4 Sidney Wood

As was the case with the results obtained on the glasses from Knightons, the composition data from Sidney Wood could not be used to provide much information about the correlation between components in the glass. Plots of components against each other could be made, which showed the close composition of the vessel fragments from Sidney Wood.

These plots used the data from all forms of analyses. It was readily apparent that there was one cluster of composition, of vessel glass fragments AS4966, AS4967 and AS4977. This was seen in a plot of magnesia and lime values (fig. 8.10). There was quite a large degree of spread in the samples AS4977, which could not be explained. The level of lime in the Sidney Wood glass was much higher than that observed at Blunden's Wood, or Knightons.

There were a few analyses of glasses that had been adhering to the inner face of fragments of crucible. These differed widely to the vessel glass found at Sidney Wood, which reiterated the problems associated with the assemblage from Sidney Wood. The fragments of crucible material were assumed to have originated from Sidney Wood, but the analyses would offer an alternative explanation. This was that these fragments were not from Sidney Wood, which could not be proven. It was interesting to note that these crucible fragments appeared to be made from different clay to those made at Knightons, as discussed in chapter 2. Initially it was assumed that the glass-makers from each site may have used different clays, but the evidence of the analysis of the glass from the inside of these crucibles may have suggested otherwise. However, while I was walking around the location of the Sidney Wood glasshouse, I saw evidence of these light coloured crucibles.

When manganese dioxide and lime were plotted against each other (fig. 8.11), the first point of interest was that there was a cluster once again. Most of the manganese dioxide analyses were around 0.6-1%. However, the sample of purple glass (AS4998), taken from the surface of clay floor had a very different result.

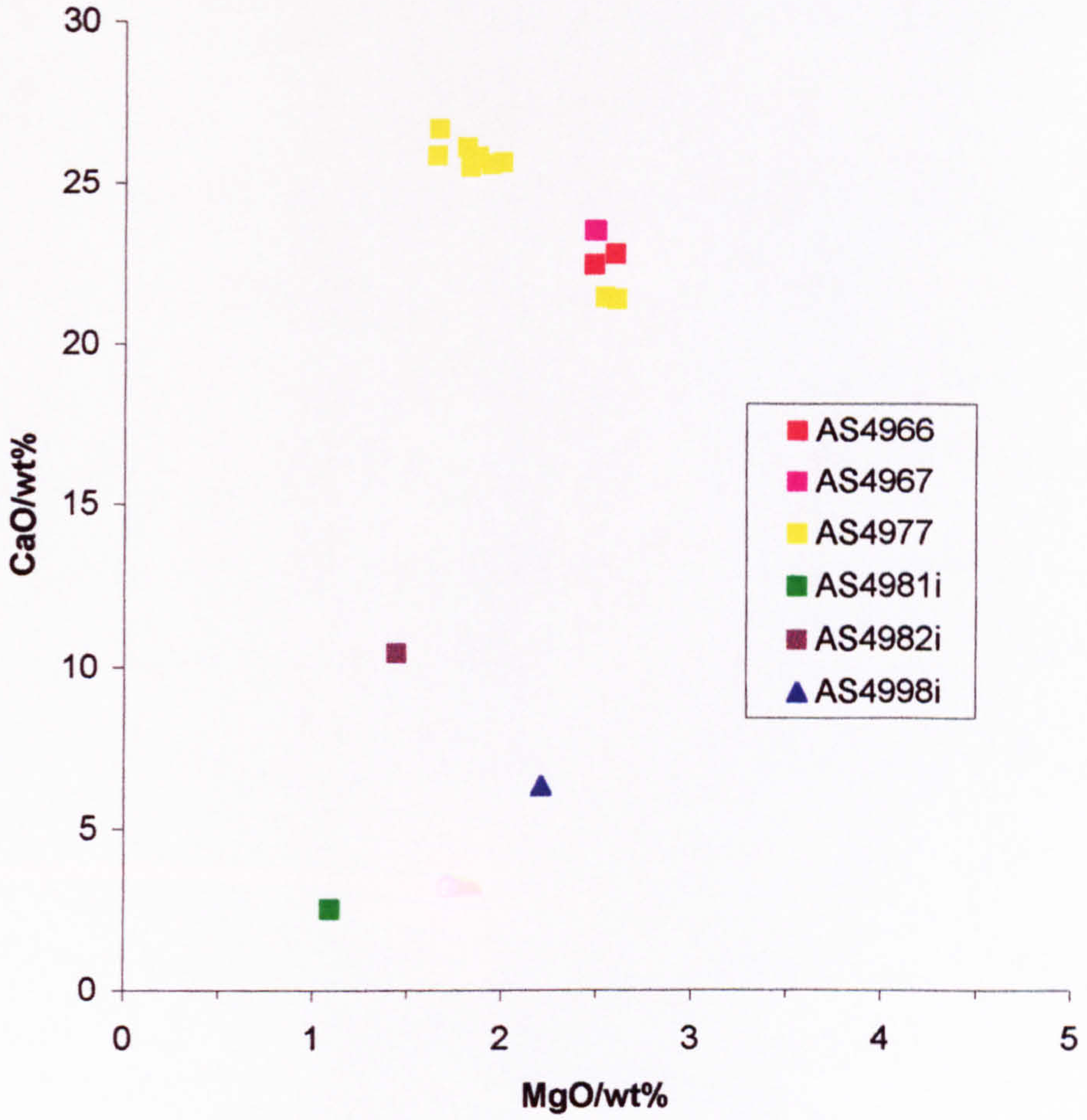

Figure 8.10 – A Plot of Lime and Magnesia for Glass Fragments from Sidney Wood (Refer to Table 6.10 for Sample numbers)

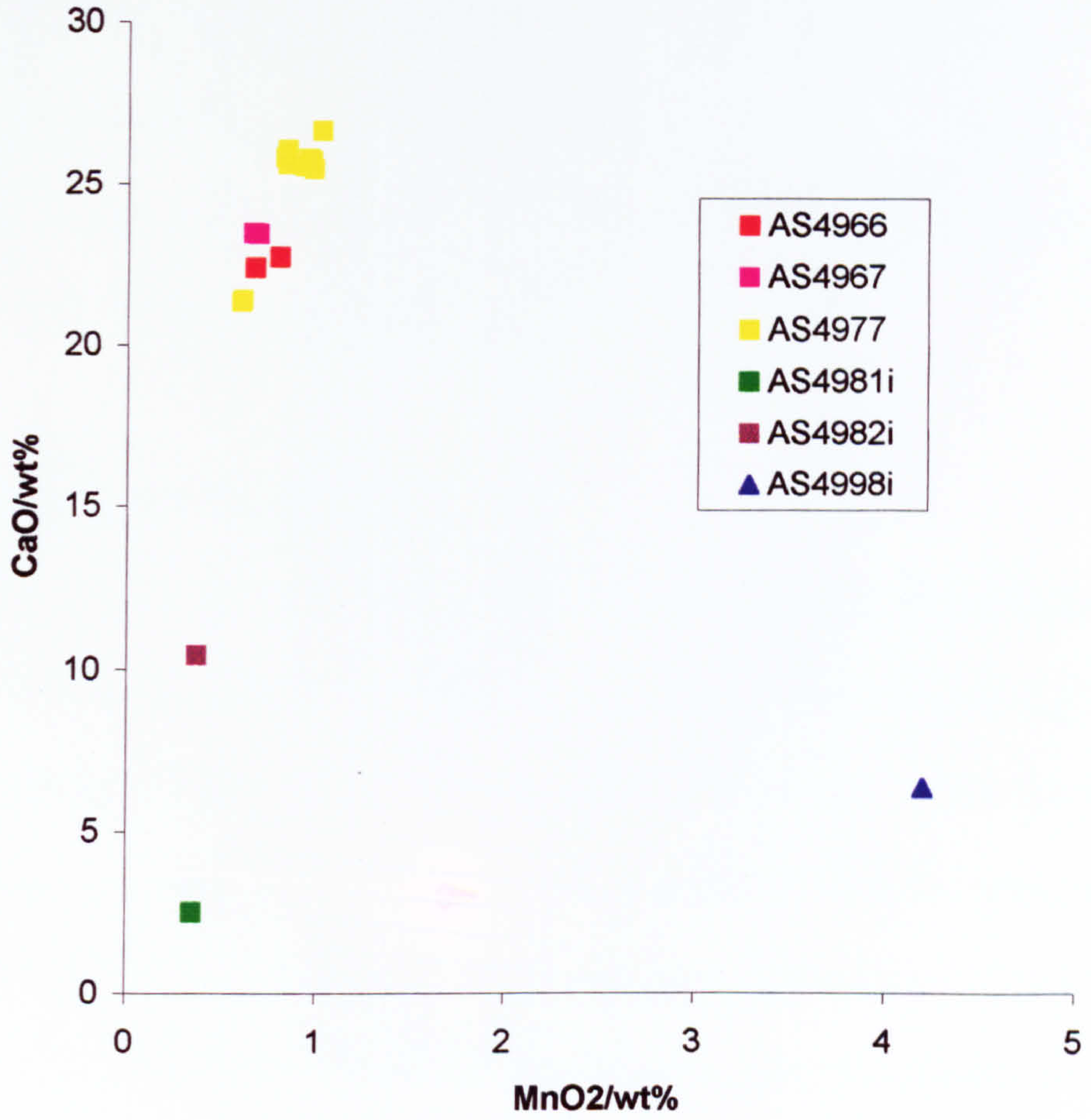

Figure 8.11 – A Plot of Lime and Manganese Dioxide for Glass Fragments from Sidney Wood (Refer to Table 6.10 for sample numbers)

When plotted on the graph it was seen to differ in composition to the vessel glass. The manganese dioxide level was over four times greater than that seen in the vessel glass. This excess level of manganese would have acted as a colourant, dominating the iron oxide to produce the purple colour.

Iron oxide was plotted against manganese dioxide (fig. 8.12), and the variation between the purple glass (AS4998), and the other samples was even more apparent. The fragments of vessel glass, and the fragments from the inside face of the pale crucibles showed a fairly tight cluster. However, the purple glass had a distinct composition, with a similar iron oxide content but a huge increase in manganese dioxide. With this excess of manganese dioxide over iron oxide the natural colour of the green glass would have been transformed, to produce the purple colour.

8.4.1 The Major Glass Compositions

The blue-green vessel glass from Sidney Wood was formed from a composition based on 60% silica, 4-5% potash and 23-25% lime. The high level of lime was significant, in that it was probably the cause of the high stability of this glass. As mentioned in Chapter 3 during the description of the fragments, the glass from Sidney Wood was of very high quality, and showed few signs of weathering. The low level of potash and high level of lime would have produced less weathering than that observed in most medieval 'forest' glass.

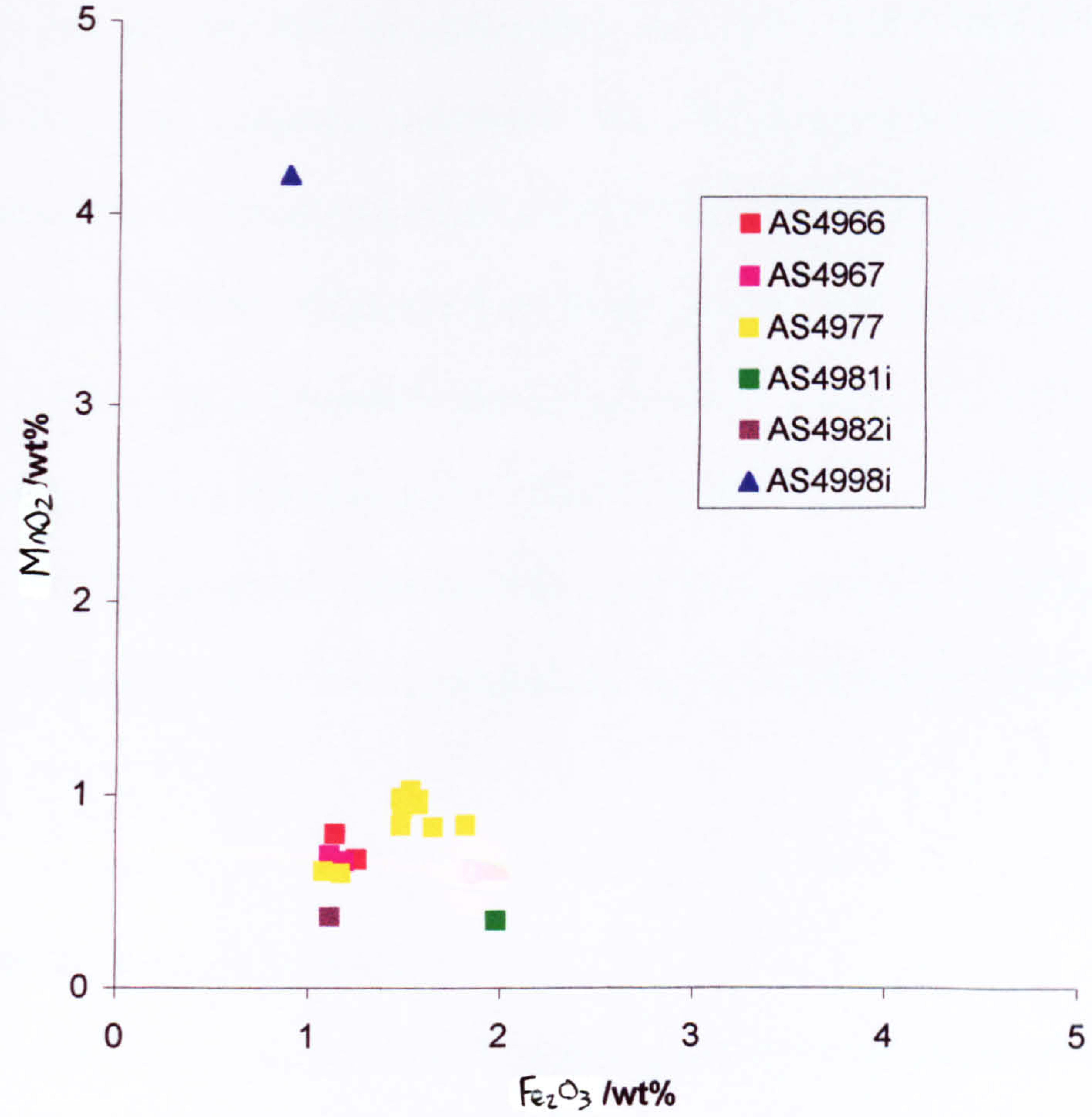

Figure 8.12 – A Plot of Iron Oxide and Manganese Dioxide for Glass Fragments from Sidney Wood (Refer to Table 6.10 for sample numbers)

No fragments of purple vessel glass were found at Sidney Wood, so it was not apparent whether the purple glass found adhering to the piece of furnace floor was formed intentionally or not. The size of the ceramic body suggested that it probably originated from Sidney Wood, and was not moved to the site. Once again, this analysis highlighted the problems of observing material from a site that had not been excavated to modern standards.

Sidney Wood was one of the last glasshouses to produce 'forest' glass in the Weald. Therefore it was possible that the glass-maker was experimenting with different batches. New raw materials may have been introduced into 'forest' glass manufacture, but the high level of sodium oxide suggested that there may have been a move to producing a glass without adding beech or oak plant ash to the batch. Alternatively, this fragment of purple glass may be what was left of a batch of re-melted cullet, which may have had a very different composition to the glass that was manufactured at Sidney Wood. The fact that it was found adhering to a large piece furnace floor may indicated that it ended up at Sidney Wood, but not that it originated from there.

8.5 Comparison between Wealden sites

This project spanned the whole period of glass manufacture in the Weald, from the beginning of the fourteenth century (Blunden's Wood) to the beginning of the seventeenth century (Sidney Wood). In between this, was a site of great importance, Knightons, where the boundaries of glass technology may have been stretched.

Therefore, comparison of analyses from the three sites may offer an insight into the changing technology.

A comparison of a mean composition of glass fragments from the three sites can be made. From the analyses it was apparent that there was one definite composition of vessel glass from Blunden's Wood, one definite window glass composition from Knightons and one definite vessel glass composition from Sidney Wood, shown in Table 8.2.

The first thing to note was the similarity between the main composition of vessel glass found at Blunden's Wood and the window glass found at Knightons. They were clearly based on 60% silica, 10-12% potash and 16% lime. Levels of magnesia, phosphorous pentoxide and iron oxide were comparable. The main differences were in the level of alumina, manganese dioxide and soda. This may have indicated that it may not have been the purpose for which the glass was being manufactured which was the dominant factor in determining the glass composition, but the raw materials which were available to the glass-maker. Therefore, although the technology remained fairly similar between 1330 AD and 1550 AD, the only difference between the glasses produced at two different sites were as a consequence of the varied composition of the raw ingredients. The close compositions of the glass from Blunden's wood and Knightons suggested that the glass-maker at each site was using the same raw ingredients.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3
Blunden's Wood	0.75	4.64	0.27	60.34	3.39	12.76	16.36	1.73	1.18
Vessel glass	±0.63	±0.66	±0.21	±4.62	±0.45	±1.07	±1.72	±0.22	±0.23
Knightons	1.86	5.69	2.63	58.13	3.33	10.19	15.75	0.96	0.80
Window glass	±0.23	±0.71	±1.00	±1.58	±0.51	±0.22	±0.61	±0.03	±0.05
Sidney Wood	2.08	2.54	3.22	59.47	1.89	4.01	22.46	0.67	1.16
Vessel glass	±0.49	±0.06	±0.31	±0.95	±0.05	±0.79	±0.94	±0.07	±0.06

Blunden's Wood Vessel glass - AS3542
Knightons Window glass - AS4931/AS4934
Sidney Wood Vessel glass - AS4966/AS4967

Table 8.2 - Glass compositions from Blunden's Wood, Knightons and Sidney Wood

The source of ash composition was seen to vary widely from each source of vegetation (Turner p289, 1956), which would have been apparent if the glass-makers at Blunden's Wood and Knightons had used a different ash. However, as the major components of the glass were very close, this indicated that the source of ash was the same.

Sidney Wood had a composition of vessel glass that was very different to both the vessel glass from Blunden's Wood and the window glass from Knightons. This could be seen when lime was plotted against potash (fig. 8.13). The glass from Sidney Wood was fundamentally different in composition to that from Blunden's Wood and Knightons. The potash was extremely low in comparison with the earlier sites, while the lime was higher. The vessel glass produced at Sidney Wood was of a far superior quality to that found at Blunden's Wood and Knightons, which could be attributable to the combination of the lime and potash. The low level of alkali and the high level of stabilising lime would have produced a highly durable glass.

In order to assess the effect the manganese dioxide had on decolourising the glass, or at least counter-acting the effect of the green colour produced by iron oxide, a plot was drawn of these components for Blunden's Wood, Knightons and Sidney Wood (fig. 8.14). In the case of Blunden's Wood there was an excess of manganese dioxide, which produced a ratio of Fe_2O_3:MnO_2 of approximately 0.7. The ratios for Knightons and Sidney Wood were 1.0 and 1.5 respectively. This showed that the iron oxide remained the dominant colourant even when there was nearly twice the amount of manganese dioxide.

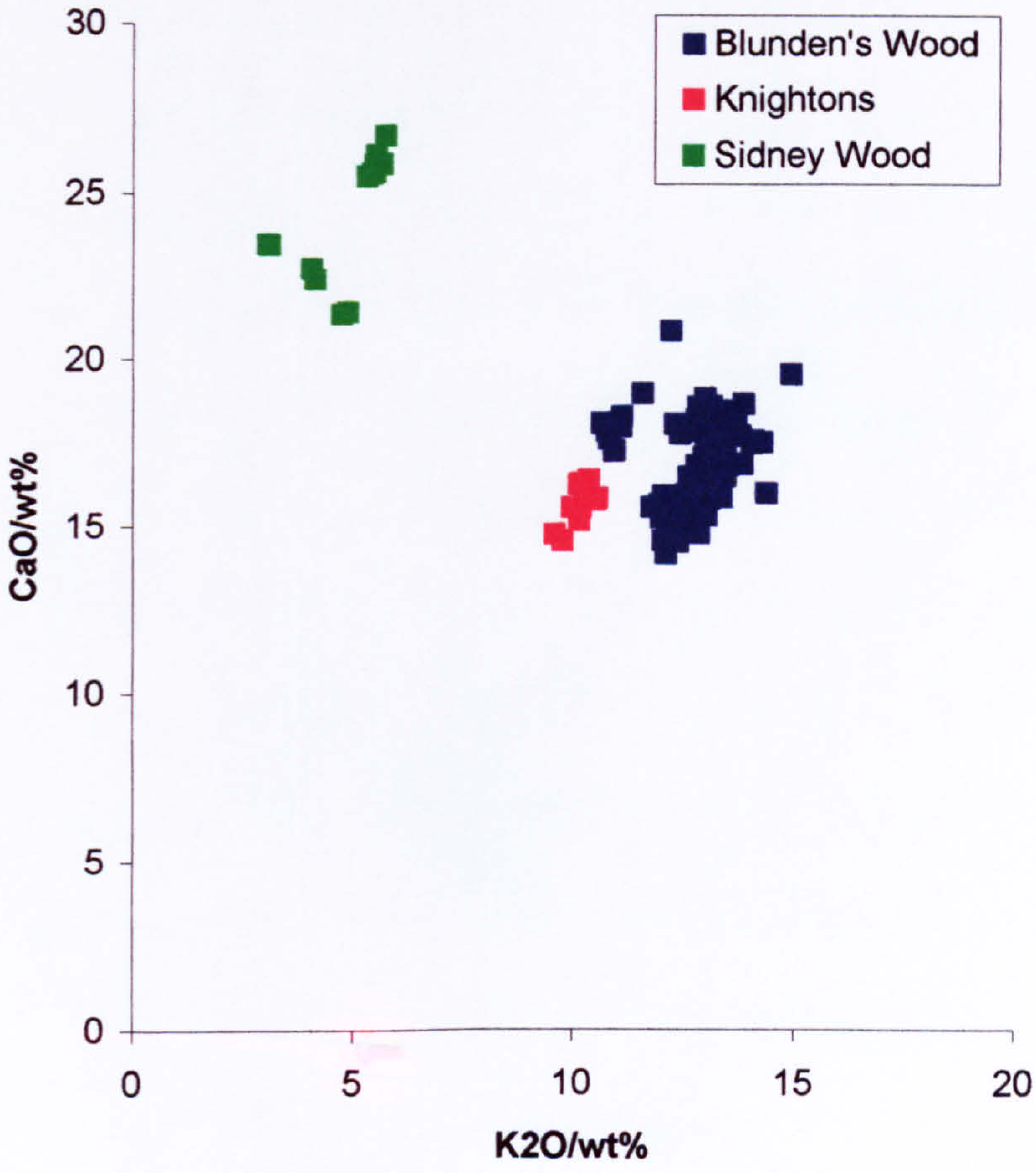

Figure 8.13 – A Plot of Lime and Potash for Glass Fragments from Blunden's Wood (AS3542), Knightons (AS4931 and AS4934) and Sidney Wood (AS4966, AS4967 and AS4977) (Refer to Table 6.10 for Sample numbers)

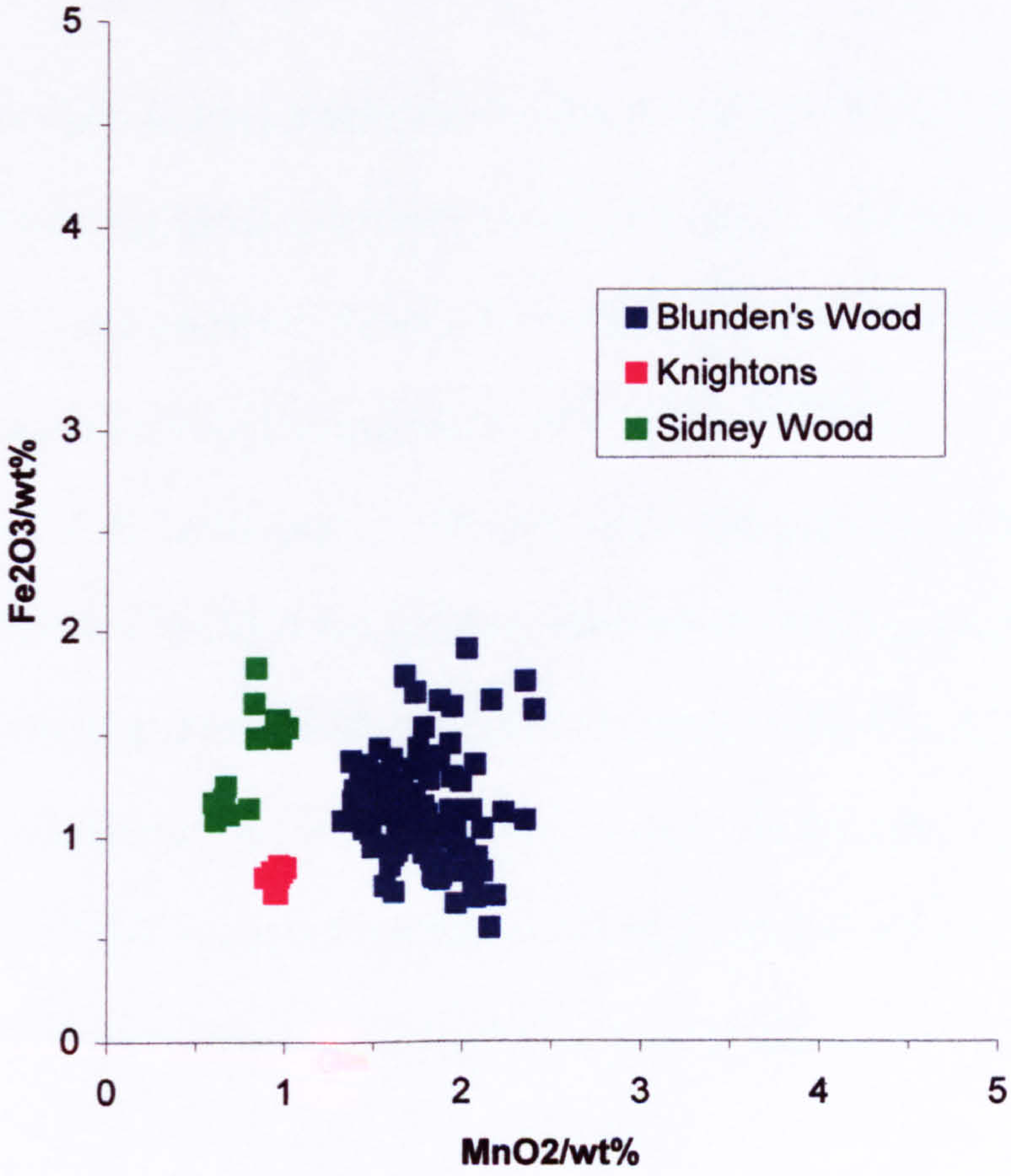

Figure 8.14 – A Plot of Manganese Dioxide and Iron Oxide for Glass Fragments from Blunden's Wood (AS3542), Knightons (AS4931 and AS4934) and Sidney Wood (AS4966, AS4967 and AS4977) (Refer to Table 6.10 for sample numbers)

It also showed that the excess of manganese dioxide in the vessel glass from Blunden's Wood did not produce a less green glass in comparison with Knightons. The furnace atmosphere may have played an important role in controlling the redox reaction between iron and manganese oxides, and the atmosphere may have allowed some control on the colour of the glass. It has been found that depending on the conditions within the furnace similar compositions of glass would be yellow in oxidising conditions and blue-green in reducing conditions (Newton p59, 1978).

Generally, the location of a glasshouse would have dictated the composition of glass produced, as the raw ingredients available to the glass-maker would have produced a glass with a certain composition. However, the close proximity of Sidney Wood to Knightons suggested that the raw materials may have differed, even though they were located in the same area. This may have indicated that different ashes were used in the production of these glasses. Analysis of ashed samples of oak and beech from Knightons and Sidney Wood indicated that the level of potash in the oak was marginally lower than the beech (Sanderson and Hunter p28, 1981). This tentatively suggested that the glass from Sidney Wood glasshouse was produced using oak ash, based on the very low level of potash found in the glass.

The level of silica in the glasses from Blunden's Wood, Knightons and Sidney Wood were very similar, which suggested that they may have used a similar composition of sand. As no source of sand could be located for any of the sites this could not be proven either way.

However, the alumina component in the Blunden's Wood glass was much lower than Knightons or Sidney Wood, and as alumina was an impurity found in glass-making sands it could be suggested that a low alumina sand was used in the Blunden's Wood glass batch.

By the end of the sixteenth century it could have been the purpose for which the glass was to be used which dictated the composition of the glass, and not the availability of the raw materials. This would have forced the glass-maker to look for alternative raw materials. This may be suggested as a reason for the large difference between the glass compositions from Knightons and Sidney Wood. The glass-maker at Sidney Wood may have brought in raw materials for the manufacture of the vessel glass. However, this could not be proven.

The difference in composition of glasses from Blunden's Wood and Knightons were small, even though the time-difference was over two hundred years. Conversely, the Knightons glass was very different in composition to the Sidney Wood glass where there was a time-difference of only fifty years. This may have shown the lack of progress made in the manufacture of 'forest' glass up to the middle of the sixteenth century. The influx of the immigrant glass-makers led by Jean Carré in 1567 may have caused the advances to take place. Therefore, the immigrant glass-makers may have brought new technology, which included the necessity to look for different raw materials. This may be corroborated by the presence of the high soda glass found at Sidney Wood (AS4998), which was of such a different composition to other medieval 'forest' glass that it may have contained a new source of ash.

This must be taken in the context that the glass may have ended up at Sidney Wood through the purchase of cullet which was been re-melted in the furnace.

8.6 Medieval and Post-medieval Glass

The previous section established links between the types of glasses produced at Blunden's Wood, Knightons and Sidney Wood. A further comparison could be made with other English late to post-medieval glasshouses and also two glass-making sites in Europe. These were Little Birches in Staffordshire (Mortimer, 1991b), Hutton and Rosedale in Yorkshire (Crossley and Aberg p107-159, 1972), Kimmeridge in Dorset (Crossley p340-382, 1987) and Bagot's Park in Staffordshire (Crossley p44-83, 1967), Bickerstaffe (Hurst p28, 1968), Denton (Hurst p28, 1968), Savenel in Belgium (Terlinden and Crossley p177-206, 1981) and Steimcke in Germany (Wedepohl p250, 1997). A final comparison was made between my own analyses of and those published for Blunden's Wood (Mortimer, 1993 and Vose, 1980) and Knightons (Wood, 1982b) glass-making sites. The results can be seen in Table 8.3.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3
Blunden's Wood (Mortimer) v 1330	2.80	6.80	0.50	59.10	2.90	9.70	13.00	1.20	0.70
Blunden's Wood, (Vose) v 1330	0.05	8.40	4.00	57.20	0.05	8.70	14.30	0.90	2.60
Blunden's Wood, (Vose) v 1330	3.40	6.95	4.78	57.00		9.00	17.50	0.20	1.32
Knightons, (Wood) w 1550	1.70	5.80	7.70	56.90		10.00	15.70	0.80	0.82
Little Birches (Mortimer) u 16C	2.50	7.30	1.50	57.30	2.90	12.10	12.20	1.40	0.50
Hutton (Crossley & Aberg) u 16C	1.84	2.28	4.98	58.98		5.16	24.59	0.37	1.51
Rosedale (Crossley & Aberg) u 16C	3.54	3.25	5.81	58.84		6.20	20.15	0.30	1.57
Kimmeridge (Crossley) u 17C	3.60	3.30	2.20	57.10		3.40	20.00	0.20	1.10
Bagot's Park (Crossley) u 16C	2.70	7.20		55.20		10.80	12.80		
Bickerstaffe (Hurst) v 16C	5.9	4.7	2.3	60.4	3.4	1.4	19.5	0.8	0.61
Denton (Hurst) v 16C	6.7	5.2	4.1	56.3	3.3	1.0	20.8	0.7	1.3
Savenel (Terlinden & Crossley) v 17C	1.00	3.60	2.00	57.80		8.70	19.30	1.20	1.10
Steimcke (Wedepohl) u 13C	0.24	4.74	2.18	46.04	3.07	18.05	22.01	1.92	0.52

v = vessel glass, w = window glass and u = unknown

Table 8.3 - Chemical Analyses of Glasses from Various Medieval and Post-medieval Glass-making Sites

It was immediately clear from the comparison with other sites that there was little change in the level of silica. A value between 55 % and 60 % was observed from all sites, except the glass from Steimcke. This consistent level of the major ingredient in the glass suggested that a similar recipe was probably in use throughout, which may, or may not, have been based on the 1 part sand to 2 parts ash described by Theophilus for the manufacture of glass (Hawthorne and Smith p52, 1979).

Most of the vessel glass found at fourteenth century glasshouse Blunden's Wood and the glass found at the sixteenth century glasshouse at Little Birches in Staffordshire showed a similar pattern between the magnesia and the alumina content. The pattern showed high levels of magnesia and low levels of alumina. In fact, there appeared to be quite close similarity of all oxides from the glass from these sites, with 3% phosphorous pentoxide, 12% potash and 1.5% manganese dioxide examples of very similar analyses. Bagot's Park had a similar composition, but there was not the full glass analysis to compare these results with to those that have been published.

The vessel glass composition which had been determined for Blunden's Wood, based on AS3542, compared favourably to that obtained previously (Mortimer, 1993). However, these compositions were very different to others (Vose, 1980). The latter compositions contain a very high level of alumina (4%) and only a very small amount of manganese dioxide (0.2%). It must be assumed that the composition of glass from Blunden's Wood (Vose, 1980) was not representative of the vessel glass from the site, as the other analyses (Mortimer, 1993) and my own show a high degree of correlation.

The other main constituents of the glass from all the sites, lime and potash, produced some of the clearest evidence that either different ash is used in the glass batches, or, that lime additions are made to the recipe. Sidney Wood produced vessel glass with over 20% lime and low alkali. This high level of lime was also seen at earlier sites to Sidney Wood, at Hutton (24.5%) and Rosedale (20%), and at similarly dated sites to Sidney Wood at Bickerstaffe (19.5%), Denton (20.8%) and Kimmeridge (20%). The high level of lime was matched by a corresponding low level of alkali at all of these sites. This suggested that there was a change in the raw materials used to manufacture the glass. There was a huge similarity in the glass from Sidney Wood to that at Bickerstaffe and Denton. The Bickerstaffe glass was described as clear, blue-green glass (Hurst p27, 1968), which was very close to the description placed on the Sidney Wood fragments which was producing glass at the same time as Sidney Wood. The glass fragments from Denton appeared to have similar forms also (Hogan p24, 1968). The high level of lime was measured at Savenel, in Belgium (19.3%), which was producing glass at the beginning of the seventeenth century. This may have suggested that similar technology may have been taking place across Flemish Europe and England, though the evidence of the analyses from this one site could not confirm this.

It was possible that by the end of the sixteenth century, it became apparent to the glass-makers that a more durable glass was required. Therefore, it was necessary to produce a glass with a high level of lime. The source of lime may have come from a particularly high level in the plant ash, or may have entered the batch as a result of an addition of lime-bearing mineral.

One of the highest sources of lime comes from oak, while a lower level can be seen in beech (Turner p289, 1956). This may have indicated that oak was the preferred source of 'forest' glass-makers towards the end of the sixteenth century, and beech was used before this.

The glass fragments from Steimcke in Germany were quite different to those from all the other sites. There was a large difference in the silica content, though the other components were similar. This may have suggested that a different type of sand was used in the manufacture of the German glass, based on a material with low silica.

8.7 A Comparison of Window Glass

A comparison of window glass, concentrating solely on 'forest' glass compositions can be made to observe the similarities and differences between material produced throughout England, Lorraine and Central Europe.

The comparison of the window glass from various sources provided information concerning the transfer of the glass-making technology from Central Europe and France to England during the medieval and post-medieval period. Analyses of green glass fragments were compared for glasses taken from Canterbury Cathedral (Newton p11, 1977), St. Michael's Church, Vienna (Newton p11, 1977), Rouen Cathedral (Newton p10, 1976), Ulm Minster (Brill p188, 1970), Avignon (Brill p188-189, 1970), York Minster (Brill p187, 1970),(Gillies and Cox p77, 1988) and Carlisle (Gillies and Cox p79, 1988). The comparative results can be seen in Table 8.4.

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	MnO_2	Fe_2O_3
Canterbury cathedral (Newton, 1977), 12C	1.4	4.2	1.1	54.3	4.8	13.7	16.9	0.83	0.40
St. Michael's Church, Vienna (Newton 1977), 14C	1.1	3.7	1.6	44.9	1.7	24.9	19.0	0.89	1.7
Rouen (Newton 1976), 17C	2.4	3.3	2.4	63.3	nd	4.2	11.3	nd	3.1
Ulm Minster (Brill, 1970), 15C	0.19	3.20	0.94	57	1.3	17.3	18.6	1.0	0.05
Avignon (Brill, 1970), 14C	3.0	5.16	2.51	45	1.5	16.2	25.0	1.2	0.8
York Minster Y (Brill, 1970), 12C	2.48	7.66	2.15	61	4.1	5.26	15.8	2.0	1.3
York (Gillies and Cox, 1988a), 12C	1.6	9.6	0.7	56.8	2.5	13.7	13.8	nd	nd
York (Gillies and Cox, 1988a) 14C	1.4	10.5	0.7	56.7	2.4	10.6	15.8	nd	nd
Carlisle (Gillies and Cox, 1988a) 14C	0.1	6.2	1.5	52.9	2.0	10.6	25.6	nd	nd

Table 8.4 - Chemical analysis of Window Glasses from Various Medieval and Post-medieval Churches

The first observation showed that 'forest' glass was used for making windows. Most of these window glasses appeared to have a high potash content. The material from Canterbury Cathedral showed a remarkable similarity in composition to typical 'forest' green glass. It had a close composition to the window glass from Knightons, as discussed in previous sections. From the dating of the fragments of glass from Canterbury Cathedral it has to be concluded that the glass from Knightons was used in the church. However, the close composition indicated that a site that used similar technologies to produce window glass could have made the glass. The twelfth century date of the window glass from Canterbury may have indicated that there were 'forest' glass-making sites in England at this time, though it was also possible that the glass could have come from France or Belgium.

Glass from Rouen dated to the seventeenth century had a low alkali level. As stated in the previous section the glass-makers at the end of the sixteenth century may have been attempting to make a more durable glass, with lower alkalis. However, the low level of lime was not a mirror of the observations made on the glass manufactured at Sidney Wood and other glass-making sites that had produced a low-alkali glass.

Fragments of glass from York Minster showed that many sources of glass may have been used in the church. The twelfth and fourteenth century fragments from York (Gillies and Cox p77, 1988) showed a similar composition to the Knightons window glass.

However, a glass from the twelfth century had a different composition (Brill p187, 1970). Whether these glasses were from different glass-making sites or were produced using different raw ingredients was not clear.

The glass from York Minster had a higher magnesia level than many of the other church glasses, and this was seen in the glass from Knightons also. This may have indicated that the glass-maker was trying to produce a glass with a high level of magnesia. This could have been done with a particular ash high in magnesia, which again pointed towards oak (from various analyses of ash from Sidney Wood and Knightons (Sanderson and Hunter p28, 1981).

The glass from Ulm Minster, Avignon and Carlisle were once more typical of high potash glasses, produced from wood ash and sand. Once more high levels of lime were seen in the glass from Avignon and Carlisle that continued the trend observed in the glass from Sidney Wood. This may have indicated that the glass used in some of the churches, with high levels of lime, were produced by the glass-maker with durability in mind. The fact that the window glass was from a much earlier date than Sidney Wood, suggested that a source of high lime ash could be found by the glass-maker.

CHAPTER NINE

CONCLUSIONS

This work showed the benefit of scientific analysis in the assessment of material excavated from archaeological sites. Evidence of both glass and ceramic fragments were analysed, and much was able to be determined by the composition of the glass material, the phases present in the crucible material and the interaction taking place between the two during the melting stage of the production of glass.

The assemblages of material from the sites varied. In the case of Blunden's Wood there was ample evidence to test, both for the composition of various glasses and the material associated with the manufacture of glass. Knightons and Sidney Wood were more limited. Some fragments of crucible with glass adhering to the inside face from Knightons did allow a relationship between the glass and the clay fabric to be looked at. The material from Knightons and Blunden's Wood was consistent. This could not be said for Sidney Wood, though the evidence obtained from the analysis of the glass was able to show how important this site was in observing the influx of immigrant glass workers.

All the major compositions of glass from Blunden's Wood, Knightons and Sidney Wood were typical green 'forest' glasses. They all had a silica content in the region of 60%, but did have different levels of lime and potash. The compositions of the glasses were seen to be similar to analyses from other English glass-making sites in the period from the thirteenth to the seventeenth centuries, which allowed a comparison to be made. This showed the migration of the immigrant glass-makers, not only through the Weald, but throughout England.

The Wealden glass-makers from these sites all used very similar techniques for the production of 'forest' glass. This method centred on the production of glass from a mixture of sand and wood ash. In the case of the three sites investigated in this project, Blunden's Wood, Knightons and Sidney Wood, it remained unclear whether the ash was produced from the burning of beech or oak trees. Initially, the successful replication of 'forest' glass using beech ash may have suggested that beech was used in the manufacture of glass between the thirteenth and seventeenth centuries in England. The lack of beech trees in the vicinity of all three sites today does not disprove this. However, the references to the production of 'forest' glass using oak ash, coupled with the overwhelming presence of English oak trees at Blunden's Wood, Knightons and Sidney Wood, may have provided an alternative source of vegetation for the production of glass. The chemical compositions also suggested that oak may have been used in the glasses, especially at Sidney Wood where very high levels of lime and low levels of potash were measured. This was consistent with studies that have taken place on ashes.

The similar level of silica in all of the glasses may have suggested that the composition of the sand used in the glasses was very similar. This did not suggest that the same source of sand was used, but that the glass-maker knew what the requirements were for a good glass-making sand.

The technology of glass production did not alter greatly during the medieval to post-medieval period. However, this would be to ignore the impact the immigrant glass-makers had on the glass industry during this time. The process of making a glass during this period was most likely based on the production of frit prior to melting the glass. This intermediate process most probably took place at Blunden's Wood, where evidence of a frit-like material was found. On testing this material it did appear to be frit, based on the observations that showed the beginnings of a reaction occurring between sand and ash, with the production of a partially fused material. An estimate of the fritting temperature was made, based on the presence of tridymite and glass in the frit material. This temperature was in the region of 900 °C, which was very close to the temperature that had been obtained by experiments carried out by myself.

The production of 'forest' glass from frit could then take place in the furnaces. The temperature at which the frit was taken, to melt and completely fuse, was estimated to be above 1200 °C. This was determined by the presence of high temperature phases in the crucible, mullite and cristobalite.

The latter phase, cristobalite suggested an even higher temperature (above 1400 °C), but the formation of cristobalite at lower temperatures would be possible in a system where impurities could lower the formation temperature. The effect of heating the crucible fragments from Blunden's Wood, Knightons and Sidney Wood showed that they would not have been able to withstand the temperature of 1400 °C, so a value below this seemed more likely.

These estimations of the temperature at which the processes took place were able to assist in the study of the structures excavated. The type of clay used in the crucibles had to withstand the arduous conditions that the processes demanded. Therefore, when excavating glass-making sites it would be important to observe the raw materials that were in the vicinity. While the Wealden clay may not be any more than a brick clay, it was very clear from this work that it was able to withstand the vigorous heating regime and the high temperatures. An interesting observation was made concerning the Wealden clay from Blunden's Wood, Knightons and Sidney Wood. The clay from all the sites appeared to be very similar. However, the crucible fragments showed differences. This may have suggested that crucibles were manufactured away from some, or all, of the sites, and transported to them. This could be an explanation for the difference in fired colour of crucible fragments obtained from Sidney Wood and the clay in the vicinity of the glass site.

The quality of the glass produced at Blunden's Wood, Knightons and Sidney Wood was assessed.

It appeared that there was little difference in quality in the majority of vessel glass and window glass fragments from Blunden's Wood and Knightons. The glasses were typical translucent green glass. Evidence of heavily weathered glass, with layers of weathering products, was seen in fragments from Blunden's Wood. This suggested a poorer quality glass. The similarity in quality of glass between Blunden's Wood and Knightons suggested that the technology of the glass production methods was alike. The main difference between fragments from these two sites may be that an extra degree of weathering has taken place at Blunden's Wood due to the increased time in the ground.

The quality of the vessel glass from Sidney Wood was far superior than that observed in glass from Blunden's Wood and Knightons. This uncovered two important factors. First, the close proximity of the Sidney Wood glasshouse to the Knightons glasshouse could not explain the apparent difference in quality of glass fragments from the sites. The geology of the ground would be similar, so this would result in the chemical composition of similar species of vegetation being comparable. Therefore, it was possible that there were differences in raw materials used to manufacture the glass. Alternatively it may have indicated that the glass-maker at Sidney Wood may have been able to control the glass-making process more closely. This suggested that by the end of the sixteenth century there would have been an influx of glass-makers from Lorraine and Normandy. This would have brought new technology, and clearly better glass-making practices.

The difference in quality of vessel glass produced at Sidney Wood and Blunden's Wood may have suggested that glass objects were made to different criteria. In the case of Sidney Wood the main criterion may have been durability and transparency, where as at Blunden's Wood the main criterion may have been the raw materials available.

The methods used in the scientific analysis of glass and crucible fragments showed advantages and disadvantages in all of them. The scanning electron microscope was a very good tool for the analysis of both glass and crucible fragments. It also allowed the opportunity to study the interaction between the glass and the clay, which was able to demonstrate the success that medieval clay crucibles had in containing the glass. Electron probe micro-analysis took longer to produce each result, but the accuracy of the final results was better. X-ray fluorescence spectrometry was a very good method to obtain a bulk analysis. For fragments of glass in this work I was able to use fairly large specimens for x-ray fluorescence, and was able to analyse the bulk chemical composition of the clay. Finally, x-ray diffraction allowed the determination of the phases present in the crucibles and the frit, which proved to be vital in estimating the temperatures at which the glass-making processes took place.

Future work must take place to increase the understanding of the glass-making process. This can be done by studying the fritting and melting processes, and all that this entails, and by extending the database of the chemical compositions of medieval 'forest' glass. There are many sites in the Weald that have not been fully excavated, but archaeological evidence is available.

This must be tested, partly to begin to attempt to fit 'unreliable' samples into context. It could be that information can be gained by forming a bigger picture about the glass industry of the Weald.

This work has provided further information about the production of 'forest' glass in England, but the continued analysis of fragments may uncover more.

The main conclusions can be summarised as;

- The compositions of the glasses were determined, and showed many aspects of the technology of glass-production.
- The glasses, all found to be typical 'forest' glass were most likely produced from two components – sand and wood ash.
- The local Wealden clay may have had sufficient refractory properties for use in the glass-making crucibles, though the exact location of the sources of crucible clay could not be ascertained.
- The source of wood ash may have been beech (from replication experiments), but high levels of lime and the abundance of oak may have indicated that oak was used in the manufacture the glass (especially at Sidney Wood).
- The consistent levels of silica (60%) seen in all the glasses may indicate that a similar composition of sand was used – the exact location of this source could not be determined.
- Similar glass compositions to the three Wealden sites, Blunden's Wood, Knightons and Sidney Wood were found throughout England and north-western Europe.
- The technology did not appear to alter greatly until the end of the sixteenth century. This coincided with the influx of immigrant glass-makers, which indicates the impact they had on the glass industry in England.
- A frit-like material was found at Blunden's Wood, which was estimated to have been formed in the region of 900 °C (similar to results obtained from my own experiments).
- An estimation of the melting temperature of the glass was estimated to be above 1200 °C and maybe as high as 1400 °C (due to high temperature phases present in the crucible material).
- The Wealden clay from Blunden's Wood, Knightons and Sidney Wood was similar in appearance and composition, but the crucibles from Sidney Wood were different. The pale-grey appearance may have suggested a different atmosphere within the furnace that may have been better suited to making glass.
- An assessment of the quality could be made from the compositions of the glass. The high quality of the Sidney Wood glass may have been as a result of the high lime and low potash providing a more stable material.
- The poor quality of the Blunden's Wood glass (relative to Sidney Wood) may have bee due to the high levels of potash.
- The difference in composition and quality of the glass from Knightons and Sidney Wood, bearing in mind their close proximity, may have suggested a different source of ash for each of them, and greater control of the glass-making process at Sidney Wood. This latter point once more suggested that the immigrant glass-makers had quite an impact on the production of English 'forest' glass.
- Future work must involve further study of the glass-making processes (fritting and melting).
- The data-base of glass compositions from English sites producing glass between 1200 and 1620 AD must be increased, so that more comparisons between regions can be made.
- Knowledge of the compositions in this thesis may be used as a source of data to model the viscosity behaviour of the glasses. This may allow accurate estimations of the glass melting and working temperatures to be made, similar to work on soda-lime-silica glasses (Lakatos et al, 1979).

APPENDIX I

Composition of Corning D Glass Standard

	Wt%
Na_2O	1.32
MgO	4.09
Al_2O_3	5.43
SiO_2	55.24
P_2O_5	4.02
K_2O	11.46
CaO	15.05
MnO_2	0.57
Fe_2O_3	0.50
TiO_2	0.40

APPENDIX 2

Pearson Product Moment Correlation Coefficient

$$r = \frac{n(\Sigma(xy)) - (\Sigma x)(\Sigma y)}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2][n\Sigma y^2 - (\Sigma y)^2]}}$$

Where r is the correlation coefficient,

n is the number of data points,

x is the first data set, and

y is the second data set.

Significance level

Ratio of Variances:

$$F = \frac{r^2 / 1}{(1-r^2)/(n-2)}$$

This value of F can then be read from the table shown below, to produce a level of significance.

Confidence	50%	80%	90%	95%	98%	99%	99.5%	99.8%	99.9%
	.5	.8	.9	.95	.98	.99	.995	.998	.999
Significance	50%	20%	10%	5%	2%	1%	0.5%	0.2%	0.1%
	.5	.2	.1	.05	.02	.01	.005	.002	.001
Degrees of freedom									
1	1.000	3.078	6.314	12.706	31.821	63.637	127.32	318.31	636.62
2	.816	1.886	2.920	4.303	6.965	9.925	14.089	22.326	31.598
3	.765	1.638	2.353	3.182	4.541	5.841	7.453	10.213	12.924
4	.741	1.533	2.132	2.776	3.747	4.604	5.598	7.173	8.610
5	.727	1.476	2.015	2.571	3.365	4.032	4.773	5.893	6.869
6	.718	1.440	1.943	2.447	3.143	3.707	4.317	5.208	5.959
7	.711	1.415	1.895	2.365	2.998	3.499	4.020	4.785	5.408
8	.706	1.397	1.860	2.306	2.896	3.355	3.833	4.501	5.041
9	.703	1.383	1.833	2.262	2.821	3.250	3.690	4.297	4.781
10	.700	1.372	1.812	2.228	2.764	3.169	3.581	4.144	4.537
11	.697	1.363	1.796	2.201	2.718	3.106	3.497	4.025	4.437
12	.695	1.356	1.782	2.179	2.681	3.055	3.428	3.930	4.318
13	.694	1.350	1.771	2.160	2.650	3.012	3.372	3.852	4.221
14	.692	1.345	1.761	2.145	2.624	2.977	3.326	3.787	4.140
15	.691	1.341	1.753	2.131	2.602	2.947	3.286	3.733	4.073
16	.690	1.337	1.746	2.120	2.583	2.921	3.252	3.686	4.015
17	.689	1.333	1.740	2.110	2.567	2.898	3.222	3.646	3.965
18	.688	1.330	1.734	2.101	2.552	2.878	3.197	3.610	3.922
19	.688	1.328	1.729	2.093	2.539	2.861	3.174	3.579	3.883
20	.687	1.325	1.725	2.086	2.528	2.845	3.153	3.552	3.850
21	.686	1.323	1.721	2.080	2.518	2.831	3.135	3.527	3.819
22	.686	1.321	1.717	2.074	2.508	2.819	3.119	3.505	3.792
23	.685	1.319	1.714	2.069	2.500	2.807	3.104	3.485	3.767
24	.685	1.318	1.711	2.064	2.492	2.797	3.091	3.467	3.745
25	.684	1.316	1.708	2.060	2.485	2.787	3.078	3.450	3.725
30	.683	1.310	1.697	2.042	2.457	2.750	3.030	3.385	3.646
40	.681	1.303	1.684	2.021	2.423	2.704	2.971	3.307	3.551
60	.679	1.296	1.671	2.000	2.390	2.660	2.915	3.232	3.460
120	.677	1.289	1.658	1.980	2.358	2.617	2.860	3.160	3.373
∞	.674	1.282	1.645	1.960	2.326	2.576	2.807	3.090	3.291

Distribution Table (Drennan p125, 1996)

APPENDIX 3

Table of Samples

Sample Number*	Site	Type of Fragment
AS3542	Blunden's Wood	Vessel Glass
AS3550	Blunden's Wood	Vessel Glass
AS3554	Blunden's Wood	Divitrified Glass
AS3560	Blunden's Wood	Heavily Weathered Glass
AS3578	Blunden's Wood	Glass Waste
AS207	Blunden's Wood	Crucible Base
AS3498	Blunden's Wood	Glass-making Crucibles
AS3496	Blunden's Wood	Crucible with Frit attached
AS4931	Knightons	Window Glass
AS4934	Knightons	Window Glass
AS4838	Knightons	Window Glass
AS4921	Knightons	Glass-making Crucibles
AS4966	Sidney Wood	Vessel Glass
AS4967	Sidney Wood	Vessel Glass
AS4977	Sidney Wood	Vessel Glass
AS981	Sidney Wood	Glass-making Crucibles
AS4982	Sidney Wood	Glass-making Crucibles
AS4998	Sidney Wood	Furnace Brick with Purple Glass adhering to it
AS4779	Sidney Wood	A Crucible Base

*Sample number from excavation

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