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Experimental Study of Glassmaking According to Historical Recipes

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“Piglia tanto cristal de montagna pesto, et minuto quanto gripola, et incorpora insieme, poi butta in fuogo, e ti venirà vedro in modo che tu potrai lavorarlo, et riceverà anco ogni color come gli altri vedri.”

Il Ricettario Darduin
Venice, 16th century

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1. MAN-MADE GLASS: PROPERTIES AND HISTORY

1.1. INTRODUCTION

1.1.1. GLASS DEFINITION

The glass definition does not deal with any specific substance, but describes a non crystalline amorphous solid. A more complete description is the one proposed by the Academy of Science of United States:
"Glass is the material that analysed by powder X-ray diffraction does not show peaks and that after a temperature changing, presents a variation in some thermodynamic properties as specific volume, enthalpy, specific heat, linear expansion. This temperature is called Glassy Transition Temperature T_G."
No material is cited, thus glass can be made by organic compounds as by inorganic compounds; therefore candies, cotton candy, some plastic material, can be defined glass. Second, nothing is said on preparation methods, but cooling of fluids is the most common technique. [1]

The glass success is due to its multi-applicability, it can contain, separate, protect and isolate without impose its materiality, thus it is considered an affordable and reliable material.
Glass can be modelled in countless shapes, can be colourless or colourful with every kind of shade, can be processed, cut, pulverised, in thin or thick layers, water soluble or chemical attack resistant. Glass can melt at 100°C or resist over 1000°C, can be mixed with other different materials as glazing for ceramics or in other plastic compounds; both high tension isolators and conductive materials can be made by glass. It is one of the most versatile materials and it has evolved and gone through human civilisation as no one else. [1]

1.1.2. GLASS MAIN COMPONENTS

In everyday language the word glass is referred to the material made of silica (SiO_2), commonly obtained from sand, which has a melting point around 1700°C when pure. To lower it, oxides of other elements (e.g. Ca, Mg, Na, Al) are added and the resulting glass is thus workable at more reasonable temperatures in the range 1100-1400°C. Modern float glass, silica-soda-lime glass, has a composition of about 70% SiO_2, 10% CaO, 15% Na_2O, 4% MgO and other minor elements (Al_2O_3, MgO, Fe_2O_3, SO_3, TiO_2, MnO, etc.) and it has not

changed much along millennia. Other oxides as B_2O_3, PbO o P_2O_5 can be added to obtain particular properties, e.g. thermal resistance and brightness. [2]

1.1.3. ARCHEOMETRY

Through the glass elemental analysis with SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-Rays) and LA-ICP-MS (Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry), it is possible to define geographical provenance and historical period, comparing its composition with the composition of glass already analysed before and, simultaneously, with the historical information on materials used during centuries and in different places.

1.1.4. INVESTIGATION PURPOSES

Following the whole glass-making process it is possible to study the fundamental parameters that characterise it, improving the compositional information with data dealing with type and quantity of initial ingredients and with heating curves. A wide database of analysed glass is available and with the help of ancient recipes, the aim is to produce a glass as much as possible comparable with real ancient glass. On the one hand it will be possible to connect the composition to a particular creative process providing the view on the historical evolution of materials and techniques; on the other hand from this survey glass handicraft/industry challenges will emerge.

In the present work particular attention is given to medieval and post-medieval glass, where the flux agent was K_2O instead of Na_2O. The artisans preferred it mostly for problems of availability and costs, thus ash was the raw material providing a good percentage of K_2O, in general beech ash [3]. Initially pure reagents have been used (K_2CO_3 as flux agent and $CaCO_3$ as stabiliser), because in the experimental work a methodology needed to be settled, e.g. trying different melting temperatures and amount of materials, and also avoiding the possibility to introduce other components as ash impurities. For this reason every kind of sand used has been previously analysed with FAAS (Flame Atomic Absorption) to define the composition. The most used sand was Chelford sand (UK), containing 5.5% of K_2O. A series of experiments with beech ash, raw and purified, will be realised only after the parameters optimisation and the certainty to achieve good results.

A first group of samples were realised to optimise temperatures and time of melting in relation with compositional ratios (K_2O : CaO : SiO_2). Medieval and post-medieval glass data, collected by SEM-EDX

analysis, were intersected with other coming from glass of which the melting temperature was known, therefore a set of temperatures and initial ratios could be delineated. Through an experimental work it has been reached a group of working conditions to realise a transparent and homogenous glass, both visually and with the electron microscope analysis (SEM-EDX).

The second part of this investigation deals with some challenges found during the first, previously considered secondary for the research of the useful working conditions, but now interesting to deepen: phenomena of cracking, colour formation, bubbling, loss of K_2O during melting, use of alkali mixtures. Therefore the second set of glass was produced to solve these problems, having a look on the methods used in the past, because of common obstacles in the glass-making.

Some glasses were realised with a mixed flux agent, K_2CO_3 and Na_2CO_3, the first in higher amount, to simulate real ash, usually containing both alkali.

A third set of glass gathers all the previous information and awareness to realise samples completely with raw materials, i.e. sand and ash, in particular beech ash. Indeed this type was the most common in the Middle Age, especially in North Europe. Three were the kind of sand used: Chelford (UK), Lommel and Dessel (Belgium), with different contents of SiO_2, respectively 93.6%, 99.7% e 99.4%, whereas ash was added both raw and purified (after being washed).

In the meanwhile the investigation is focused on the observation of the rare earth elements (REE) behaviour through elemental analysis with LA-ICP-MS. Simultaneously, with the same instruments, major and minor elements were also detected to verify the SEM-EDX reliability. Counting on initial ingredients and final glass, the qualitative and quantitative REE trends can be investigated; the idea is to prove the utility of ratios and amounts of REE in the raw materials investigation for glass production, and thus the glass provenance. Since it is still a “work in progress” part, no results will appear in this work dealing with REE behaviours.

In the end this survey resumes a methodical proceeding of making glass and analysing it, gathering a series of useful information on handicraft and a deeper awareness on the amorphous material. All these goals will be available to the Glass Conservation Department of Artesis Hogeschool of Antwerp, with the purpose to produce glass for research and/or conservation and restoration activities.

1.2. CHEMICAL STRUCTURE AND COMPOSITION

1.2.1. CRYSTALLINE AND AMORPHOUS SiO_2 STRUCTURES

The atoms in glass are linked together by strong forces, essentially the same as those in crystals, but the volume differences are fundamental to explain the glass amorphous structure. The volume changes occurring when a liquid is cooled to a crystalline solid and to glass are shown in figure 1.1.

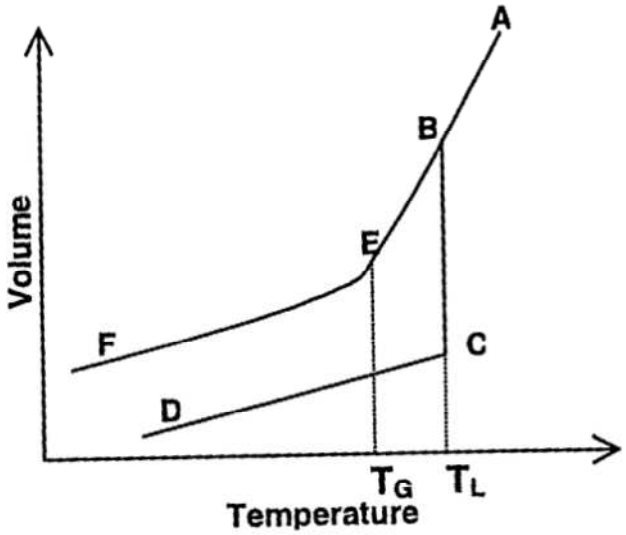


Figure 1.1 – Graph V vs. T to describe the formation of a crystalline solid (A-B-C-D) and glass (A-B-E-F) structures formation. [2]

At point A both systems are in a liquid form at high temperatures; cooling to point B thermal contraction and configuration shrinkage are the two means by which specific volume will decrease; further slowly cooling the liquid to C, at the T_L, it forms a crystalline structure and the volume will drop suddenly; this decrease is followed by thermal contraction to D. The second curve, passing by E, avoids crystallisation by faster cooling, crossing T_L; at E, corresponding to glassy transition temperature T_G, the slope of the curve changes and the specific volume varies only by thermal contraction to F. Thus the volume of a system after rapid cooling will be larger than a system that is cooled down slowly, since configuration shrinkage cannot keep pace with the cooling rate and consequent increasing viscosity.

The liquid cooled in the second case doesn't crystallize in an ordered rigid structure, but retains a random ordering as will be explained below. Crystalline solid have a precise melting/freezing temperature T_L, material such as glass features a range of temperatures in which the glassy transition temperature T_G is located. At this point the change happens from the viscous liquid to the amorphous solid. [2]

In theory every material can be worked and transformed in glass, but only materials with slow crystallization rate have the possibility to create a glassy structure, where the solid state is given by strong intermolecular binding and high viscosity.

The major constituent of most modern and ancient glass is silicon oxide (SiO_2), but several other oxides have the ability to form vitreous materials (e.g. B_2O_3, PbO). Silicon and oxygen in crystalline silica are arranged in the well defined pattern of a tetrahedron, where each silicon atom is surrounded by four oxygen atoms as represented in Figure 1.2 [4]. Two oxygen atoms are shared by each of the adjacent tetrahedrons, thus a three-dimensional network is formed by the tetrahedrons interconnected by Si-O bridges. The four bonds are strongly directional and tend to keep the same orientations, despite this the Si-O-Si angle between two tetrahedrons can vary and two tetrahedrons can rotate relatively to one another [5].
Silicon and oxygen are bound by a strong covalent-polar bond that forms a tightly braced structure in three dimensions. For this reason pure silica has a high melting temperature, since a great deal of energy is required to break the strong bonds [5][6].

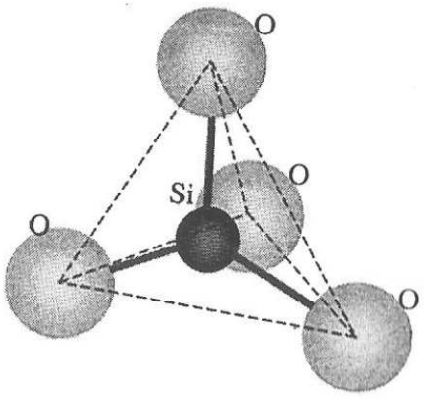


Figure 1.2 – Tetrahedral structure of silicon and oxygen atoms in a crystalline structure [2].

The regular crystalline structure of quartz can be destroyed if the material is molten completely, cooling down will appear the glassy semi-disordered structure. In Figure 1.3 their structural difference is displayed.
Indeed, when looking at a single or a few tetrahedrons, the glass and the crystal structure might appear the same, because the basic molecule is the same and glass presents a certain order at low distances, but when considering larger lattice portions, the difference is evident: the amorphous structure occupies a greater volume than the crystalline one, and hence the crystal is denser than the glass. The lattice structure is said not to have *a long-range order* [7].

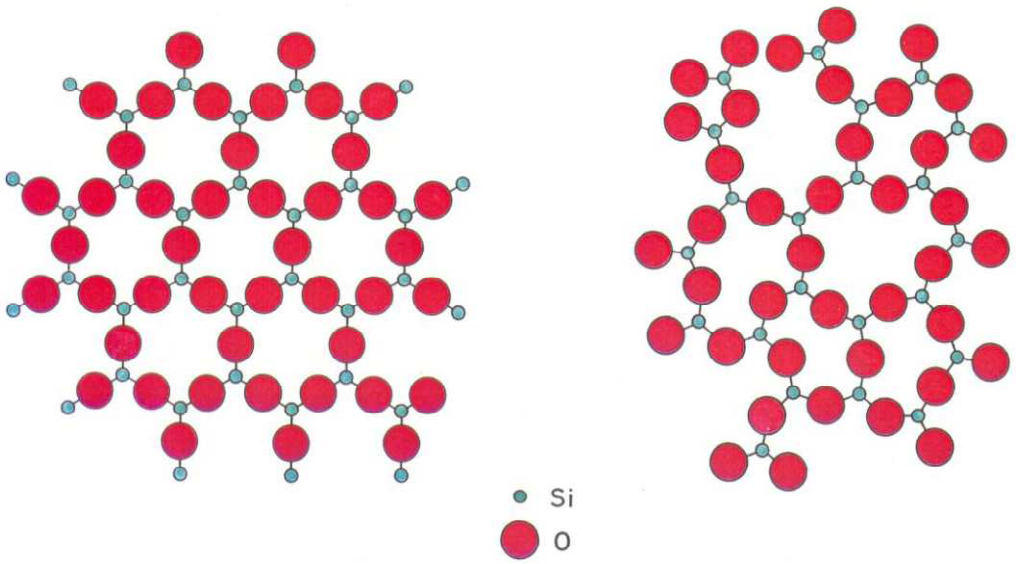


Figure 1.3 – Little grey dots represent Si atoms while the large circles represent O atoms: these structures are simplified in a 2D image, but qualitatively display the difference between quartz (left) and silica glass (right) [2].

1.2.2. MAIN ADDITIVES: FLUX AGENTS AND STABILISERS

Pure silica melts around 1700°C, a temperature that was not reachable in melting ovens for most of human history, but luckily raw materials had always contained some percentage of various impurities, mainly oxides, that lowered the melting temperatures, in order to obtain a glass more workable. Since other characteristics can vary depending on the impurities, from the moment artisans understood their presence, they also started to add different oxides deliberately as network modifiers, stabilisers and colorants, etc. The significant effects are to find upon the structure of the resulting product, as for flux agents and stabiliser.

When alkali as Na^+, K^+ used as flux agents, the negatively charged non-bridging oxygens are neutralised by the positively charged metal ions M^+ (ionic bond) which occupy spaces in the network near the non-bridging oxygens. The new bonds are weaker and non-directional and the continuity of the network is broken, making the structure less tight. There is a limit, which is the molar ratio 1 : 1 = silica : alkali, beyond which there would be two non-bridging oxygens per tetrahedron, avoiding the formation of a 3D structure.

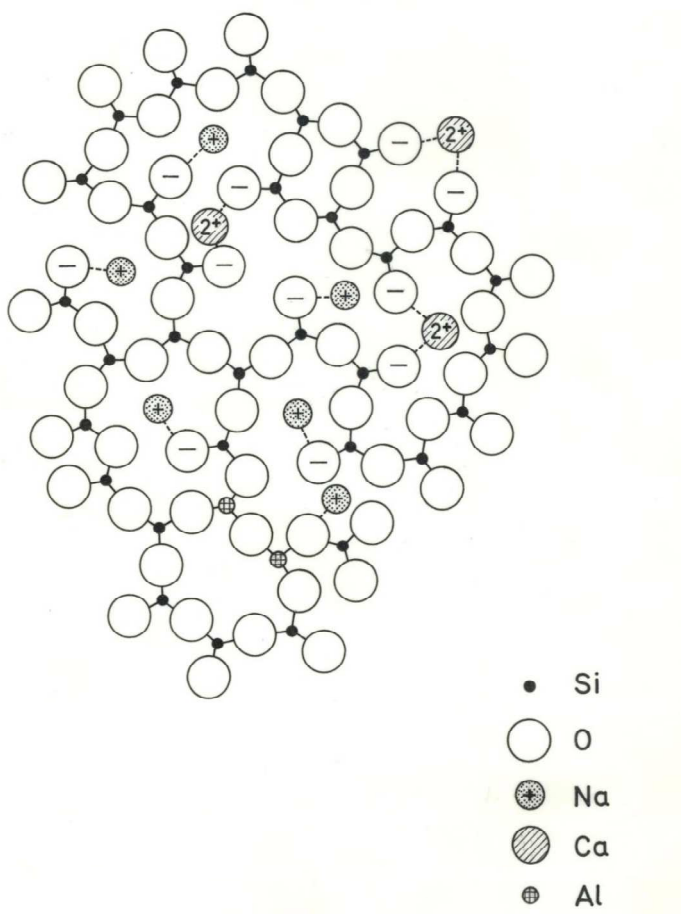


Figure 1.4 - A representation of a silica/soda/lime glass structure, with additional presence of Al. [2]

By adding mono-valent elements such as sodium or potassium, the resulting structure will be more open, because their ions are surrounded by several non-bridging oxygens: about five oxygens are found to be the average number surrounding a sodium ion, ten for potassium ions.

When divalent alkaline earth oxides, as for example lime or magnesia, are added, the divalent ions M^{2+} will neutralize two non-bridging oxygens, forming two ionic bonds. They are called stabiliser, because improve a general tightening of the structure and the chemical resistance of glass. [2]

1.3. HISTORY OF GLASS

Since silica exists in nature in three crystalline forms, quartz, tridymite and cristobalite, and some amorphous forms, obsidian, tektites, pumice and lechatelierite, as the result of melting at very high temperatures of the crystalline form, mankind had used naturally occurring glass for thousands of years, before the discovery how to produce it from raw materials. [2]

The glass origin is dated back millennia ago, and precise time and place are still unknown. In Pliny the Elder's *Naturalis Historia,* a legend talks about Phoenician merchants landing along Belus River spending a night. Instead of normal stones to create a cooking place on the sand, they used some big blocks of material they were transporting, natron ($Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$), an evaporation product from the alkaline natural water of Egyptian and Libyan lands. They made a fire and it burned slowly all night long, till the morning when they discovered a bright and diaphanous substance: glass, coming from melting natron with sand.
Anyway, this is still a legend, and the most probable hypothesis is that glass resulted from an accidental experiment of some potter in the Mesopotamian area, working with high soda content glazes at uncommon higher temperatures, ruining ceramic but producing glass. [1]

Since the first glass workshops were strictly connected with ceramic handicraft technologies, more than glass, a vitreous paste was obtained in little spheres, opaque and more or less colourful. Crystalline SiO_2 grains of partially or not melted sand are obtained, because in the III millennium B.C. a normal Mesopotamian furnace was unable to reach the sufficient temperatures for fusion and the complete homogenisation. An evolution of the production methods, observed in the following millennium, is noticed in Egyptian and Persian workshops, with a good control of transparency and a development of glass decorations. [1]
Important records of glass technology were found in Mesopotamia on cuneiform tablets dated from the 17^{th} century B.C., ensuring the glass-making tradition was already well established. Moreover it seems this awareness has been handed down unaltered for centuries, because on the tablets ancient technical words of the previous millennium appear. Thus glass technology tradition shows an extremely conservative mood about terms, and surely tried and tested formulae did not change often. [5]

These cuneiform texts reveal also shapes and structures of Mesopotamian furnaces, effectively made of three circular and subsequent "houses", the first to frit raw materials, the second to fuse completely the material before modelling, the third to anneal.

Fritting process was necessary because ancients kiln could not reach high enough temperature to melt completely the ingredients, especially silica with the highest fusion temperature. Probably temperatures of 1000°C were reachable, but not continuatively all along the glass making, that could last days. Hence the frit is a not complete amorphous glass, grinded and melted again to complete the homogenisation and to facilitate the eventual gas escape. This passage can be repeated several times before the final process of modelling glass in an object.
The last passage, annealing, reduces mechanical stress into the glass structure; it is normally conducted at temperatures lower than T_G, when glass has been already moulded. [5]

At the beginning very small and colourful glass objects were produced, because the technology of the time was very hard; since the processes were expensive, only the more affluent population classes could purchase for this new material valued as jewels.
It seems that Egyptians failed to learn the secret of fritting technique: not for any good technological reason, but for unawareness of the raw materials. Before glass became a low prized commodity it seemed inconceivable that this still precious material could be made from commonplace raw materials as sand and burnt vegetation. On the other hand Mesopotamians would have guarded their recipes, maintaining the status quo. Therefore in Egypt frit cullet was bought abroad and only the shaping process was in use by glass-maker, who probably used the same furnace for different scopes too, as pottery. [5]
In the II millennium B.C. two type of glass were mostly in use: from the East, an High Magnesium Glass (HMG), or vegetable soda-lime-silica glass, made with sand and soda-rich ashes of local salt-loving plants (e.g. of the *Salsola* and *Salicornia* genera), with a concentration of MgO and K_2O in the range 4-8%; in Europe, a Low Magnesia High Potash glass (LMHK), most likely made with a mixture of coastal and inland plants. [8]
In Roman times, the most consumed flux agent was natron, abundantly available, and the invention of glassblowing facilitated very much the shaping of objects, therefore glass turned into an affordable commodity and became the less expensive material by which obtain copies of objects made in precious natural materials. [9][10]
Glassworkers tended to locate their workshops in a strategic point for primary sources: e.g. near river deltas, where a plentiful supply of alkali from natron and unlimited sand reserve were available, even though sometime too rich in impurities. As much important to decide the furnace placement was the fuel supply, thus in general forests for wood.
The man-made soda glass is essentially composed by SiO_2 (60-70%), Na_2O (10-20%), CaO (5-15%), Al_2O_3 (1-3%) and other minor components, and it isn't changed greatly from the Roman period. Thus, materials for making ancient glasses were silica, alkali, and lime, this last one was often already present as impurity in one of the other ingredients, hence not always added voluntarily.

Depending from the collecting sites of sand, alkali and every other material used, different kind and/or amount of impurities are present into the glass and this information is useful for glass provenance. [2]

A Syrian manuscript dated around the 9th century A.D., describes a Roman furnace made of three compartments: a fire chamber at the bottom, a central chamber into which the heat rise and melt the glass and a vaulted upper compartment in which the glass may anneal and cool. The dimensions are variable with circular or rectangular shape, as well the number of holes giving access to glass pots. [5]

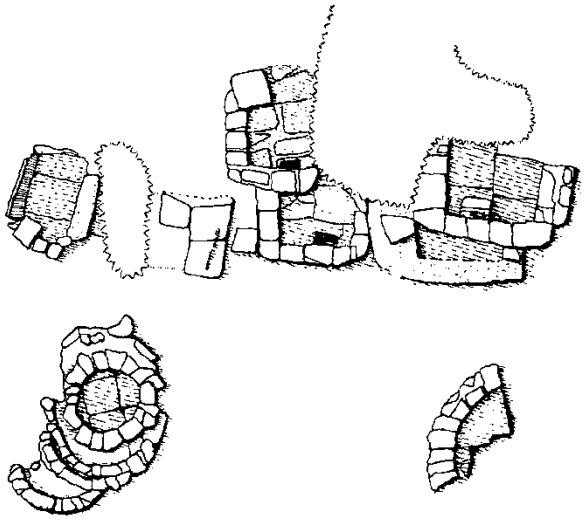


Figure 1.5 – The excavations of some furnaces founded in Europe reveals they had been rebuilt and each rebuilding being carried out over the previous furnaces which had been razed to their foundations. [7]

Temperatures till 1270°C seem to be achieved in the main furnace, devoted to melting. Then smaller furnaces for fritting and annealing lower temperatures were enough, since that sometime only one subsidiary furnace was used for both scopes. [5]

The alkalis were provided by natron until around the 9th century A.D., when this source became always less available on the market, probably due to exhaustion of the source and/or climate change that hindered salt precipitation, these reasons may be connected with the political instability during and after the Islamic conquest.

In the Byzantine period glass production continues following the Roman knowledge applied to the famous mosaic handicraft, where skills for making glass tesserae in different colours and with different decorations were developed.

The glass composition remained rather constant all over the Empire, before Roman and then Byzantine, due to the workshops organization based on homogeneous starting materials, but with the second millennium AD, a change in glass type between the Mediterranean and North Europe appears.

What particularly changes is the type of alkali sources, in generally characterised by K_2O and MgO content in vegetable ash, in place of natron. In Venice and Southern Europe, keeping close commercial ties with the Eastern Mediterranean, salt-marsh plants were used, giving rise to a 3-4% K_2O and MgO in the glass, in Northern Europe fern or beech ashes were utilized, obtaining higher percentages not only of such oxides in the glass, but also of lime. [2]

Venetian glass production started around the end of the first millennium AD with imported cullet from the Eastern Mediterranean, and from the beginning was focused on high quality glass. Indeed, by the 12^{th}-13^{th} century glass was made from raw materials, imported from other regions, like Ticino river pebbles for almost pure silica and Syrian ash. In venetian dialect is called “allume” or “allume catino”, and sometime it is purified before used, because composed mainly by Na_2CO_3 and $CaCO_3$, in minor amount by K_2CO_3 and Mg_2CO_3 and other salts as chlorides and sulphates. In parallel, a narrow part of the market was occupied from a potash glass obtained using the calcinations product of the tartar remaining inside the wine barrels. From the 15^{th} century in Venice another flux agents rich in soda were in use: it was called “cristallo di rocca” and produced boiling several times vegetal ash, the result was a white powder almost pure in Na_2CO_3. [11]

The Venetian Republic could purchased these purer raw material from far lands because its economic and politic power, otherwise normally artisans researched the closest, and therefore cheapest, sources available.

Potash glass, instead, with K_2O levels between 10 and 20% in weight, was the glass type used for the stained glass windows in the medieval cathedrals of Northern Europe, where local beech wood was probably richer in this alkali. The potash glass production peaks from 1000 to 1400 A.D.: A higher amount of ash was in use, in order to lower the melting temperature, but this also caused of faster deterioration processes. Hence from 1400 A.D. is dated the production of lime-potash glass starts, with lime as stabiliser in a 50-55% SiO_2 rich glass. [2]

From the 15^{th} century in different cities of the north, such as Antwerp, London, Amsterdam, a North European Venetian Style was established by Italian glassmakers escaped from the control of the Venetian glass guilds. They knew the fashion power of Venetian glass, known as glass “à la façon de Venise”. This glass was soda glass, with vegetable ash, both of the Levantine/Syrian type, or of the European (Spanish/west Mediterranean) type called *Barilla*. [2]

The furnaces evolution in the following centuries includes more organised working room, with walls and roof around two or more kilns equipped of several working pots. Thus an increment in production could easily reach, answering the business requests. [5]

Soda glass production remained popular till the late 17th century, when it was invented lead crystal, with better optical properties. Lead crystal and Bohemian potash glass remained the most popular European production, until the industrial revolution and the discovery of the Solvay process, leading to the production of affordable pure soda, which became the most common alkali source to produce glass, as it is nowadays for float and container glass. Another type of modern glass is borosilicate glass, used when high thermal resistance is required, while lead glass is produced for artistic-decorative purposes. [2]

Apart the industry world, investigating the contemporary handcraft, that issues from a continuity with the past is particularly interesting. In Venice, the glassworks in Murano melt the materials around 1400-1450°C, adding a 24% in weight of alkali, so the final ratio is SiO_2 (62%), Na_2O (18%), K_2O (6%), CaO (6%) and other minor components as $BaCO_3$, $NaNO_3$, borax, etc. Moreover a certain percentage is given to colour agent, since they are specialised in alloys manufacturing.

1.4. MEDIEVAL AND POST-MEDIEVAL GLASS

The main purpose of the present investigation is to produce glass as much as possible similar to medieval and post-medieval glass, thus it is appropriate to focus on this period, the raw materials in use and the glass changes.

Between the 7^{th} and the 9^{th} centuries A.D. a series of events provoked the shortage of natron sources with the following effect of the cessation of the import of alkali raw materials from East to Europe. Therefore in western part of the Carolingian Empire several glass-houses started to use ash of wood as the major flux agent for glassmaking. If before wood logs were burnt only to heat the furnaces, during Middle Age precise kind of them were selected to produce the precious reagent, e.g. beech wood. [3][12][13][14]

The major compounds in beech ash are Ca, Mg and K oxides; in particular this last replaces Na oxide as flux agent. The resulting glass is called wood ash glass, produced adding ash to quartz. Indeed, medieval manufacturers probably did not use river sand: since their glass-houses were located into the woods, they excavated sand from the soil. [12]
Of course different other elements, as Co, Cu and Fe oxides, were added to the molten to colour glass, because this was the period of windows panes for churches and cathedrals in Gothic style.

1.4.1. SAND

From the trace elements analysis of glass by LA-ICP-MS, it is possible to observe the distribution of Rare Earth Elements (REE) and compare them with distribution in quartz and quartz sand. Instead of import sand from coastal regions, the artisans of northern and western Europe preferred use more economic and available SiO_2 sources, maybe near the wood which supplied fuel and ash.
They excavated nearby Tertiary sands, decomposed Mesozoic sandstones and decomposed Triassic sandstones. The REE concentration differs between the types of sand because different processes of partial melting of the crustal and mantle rocks changed their composition, making possible to recognise the mineral as with fingerprints. For this reason the accessory elements in sands are more important indicators for silica source for glass than silica by itself. [3][12]
Medieval and post-medieval glass contains a percentage of SiO_2 in the range of 50-60%, depending mostly from the amount and the type of ash used, as it will be explained later.
Further studies are in progress on this topic, since the glassmaking permits to have both products and reagents. Trace analysis are planned by LA-ICP-MS on the samples produced and SN-ICP-MS (Solution Nebuliser-ICP-MS) on the used sands, but the results will not appear in this report.

1.4.2. ASH

Along centuries wood ash glass has changed in composition, depending generally on the type of ash used. In fact the ratio CaO/K_2O is used to identify subtype of potash glass. The lowest ratio indicates the highest quality of wood with a large proportion of beech trunks burnt, which corresponds to values between 1 and 2. Instead, increasing the quantity of beech barks and branches the ratio increases simultaneously till 9 or higher. [3]

The monk Theophilus Presbyter in his "Diversarum Artium Schedula", at the beginning of 12^{th} century, suggested to melt two parts of ash beech trunks with one part of quartz sand, therefore with an high K_2O level, around 15-20%, that helps to decrease the melting temperatures until 1200°C and thus, to facilitate the glass working. This kind of glass has been produced from the 9^{th} to the 15^{th} centuries and it can be called, properly, wood ash glass and the CaO/K_2O is 1-2. Already in the 14^{th} a certain amount of twigs and branches were burnt with beech trunks, with the consequent effect to increase the melting temperatures to 1350°C and the ratio CaO/K_2O until 3.4. The K_2O value is 7-8%, so that the alkali flux was supplemented by some sodium added as NaCl into the batch. This type of glass is called wood ash lime glass and will be prepared also later than the 17^{th} century. In the period 1400-1500 A.D. it has been produced another type of glass, made from only branches and beech barks, with higher CaO (25%) and lower K_2O (3%) content to get a ratio close to 9. The potassium level was so low that NaCl supplied the flux agent with 2.5% of Na_2O. [3]

Late medieval glass from window panels of English and French churches was prepared with fern ash instead of beech ash, because the rarer in these regions of Europe. It is revealed by the higher concentration of magnesium and phosphorus than beech ash glass. [3][12]

As sand, also ash will be analysed by SN-ICP-MS to investigate the trace element composition, although the ratio CaO/K_2O seems enough to indentify different subtypes of wood ash glass.

In Glass Experiment C (Section 3.3.3) the present information will be apply to prepare glass from sand and beech ash, with satisfactory results.

2. ANALYTICAL METHODS AND INSTRUMENTS

2.1. INTRODUCTION

Investigation on home-made glass has the initial purpose to check the effective quantity of major elements added by the raw materials, comparing theoretical and experimental values, and secondarily, but not less important, to compare these results with real ancient glass data. Due to the different types of materials characterised in this work (sand, frit, finished glass, etc.), several analytical techniques have been used. Major and minor elements were detected with Scanning Electron Microscope coupled with Energy Dispersive X-ray spectroscopy (SEM-EDX) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS): analysis with the second technique can assess the reliability of the first. This last technique is also necessary for trace elements analysis (work in progress).

Flame Atomic Absorption Spectroscopy (FAAS) was utilised to quantify some relevant elements in the three different types of sand used for glassmaking.

Thermo-gravimetric analyses (TGA) have been conducted to study the possible volatilisation of some glass components during the melting process.

In this chapter a brief description of every technique is followed by the working conditions kept during the analysis.

2.1.1. SAMPLES PREPARATION FOR SEM-EDX AND LA-ICP-MS

From each glass, a small fragment (5 to 10 mm^2) was sampled, usually with the help of a low speed diamond saw. Every fragment was positioned with its external surface on double-sided tape on the bottom of a plastic mould, with inner diameter of 2.5 cm, in which a bi-component cold-curing acrylic resin was poured (VersoCit-2). In this way, easily storable and transportable circular resin blocks were obtained: since the high glass availability due to the home-made production, quite big glass samples were collected, and every block contains one or two samples.

In order to obtain reliable information on the original glass composition, the analyses have to be performed on a flat and homogeneous glass surface. Thus the resin blocks were abraded with silicon carbide paper discs with decreasing grain size 320, 500, 800, 1200, 2400 grit class, and then polished with diamond spray of 3-1 μm particle size, to obtain a smooth and unaltered surface of glass. The same blocks of SEM-EDX

were used for LA-ICP-MS measurements. The carbon coating, needed for SEM-EDX analysis, can be easily removed with acetone prior to LA-ICP-MS measurements. [2]

In case of historical glass, additionally the surface area (e.g. 500-1000 μm) needs to be eliminated, because glass is known to suffer alteration, especially resulting in an alkali-depleted superficial layer. [2]

2.2. SCANNING ELECTRON MICROSCOPE - ENERGY DISPERSIVE X-RAY SPECTROSCOPY (SEM-EDX)

This reliable and versatile technique (called also SEM-EDS) couples an X-ray detector to an electron microscope, allowing to perform compositional analysis. Another useful and intrinsic SEM property is the possibility of obtaining highly magnified images of the samples. There are two possible modes: backscattered electron imaging (BEI) and secondary electron imaging (SEI).
Samples are bombarded with an electron beam in order to obtain element-specific X-rays; in fact a variety of interactions result from the collisions that can be divided in two groups, elastic and inelastic scattering [15].

Elastic scattering happens when the direction of the incident electrons changes without a significant change in energy. All the possible directions are allowed to travelling back towards the source. A backscattered electron is an electron deflected backwards, out of the sample, after one or more elastically interaction with the target. Higher the atomic number (Z) of the target, higher the possibilities of elastic interactions, therefore a backscattered electrons detector will show (BEI) images that display atomic number contrast, brighter for high Z and darker for low Z. This capability is commonly in use to study heterogeneous materials, e.g. not completely melted glass with sand and oxides grains. [15][16]

The second important kind of electron-target interactions produce inelastic scattering, where a significant amount of energy is transferred. The primary electron beam interacts with the target elements decelerating and losing kinetic energy; the same amount of energy is gathered by the nucleus or electrons of the bombarded sample. Consequently a series of related processes may occur: emission of secondary electron, X-rays, Auger electron, etc. [15][16]
Secondary electron emissions permit another type of SEM imaging (SEI). They are low energy electrons generated by the primary electron beam inelastic interaction with the atomic shells: a secondary electron can be expelled with certain energy, but before it can escape out of the surface further inelastic scattering and energy loss are possible. In general, most of the secondary electrons detected are produced close to the sample surface, where the escape path is shorter and thus also the energy loss. A secondary electron detector can give topographic information of the surface and it is normally the most used signal in SEM imaging. [17]
The interaction between primary electrons and the electrons of the inner shell of the target atoms originate characteristic X-rays and Bremsstrahlung radiation. The primary electron strikes an inner shell electron and ejects it: this creates a vacancy in that shell. Only if the kinetic energy of the primary electron is greater than the critical excitation energy of the concerned shell, a secondary electron is pushed out of

the atom and an ionised atom is created. The movement of an electron of an outer shell fills the inner vacancy, with the subsequently return to the ground state; the energy difference between the inner and the outer level is equal to the emitted radiation with X-ray wavelength. Since every element has a different electronic configuration, the emitted X-ray pattern will be unique for that element, permitting a qualitative and quantitative elemental analysis of the sample. [2]

The characteristics X-rays are superimposed on a continuum radiation called Bremsstrahlung, or braking radiation. This emission is caused by the interaction between the Coulomb field of the sample atoms and the incident electrons, which lose energy as X-rays. The spectrum is a continuum because the primary electron can lose several amount of energy (from 0 to the source energy) [18]. The continuum intensity varies with the average atomic number and the shape is the same for each excited material. X-ray absorption and lower efficiency of the detector at low energies provoke an intensity drop in the Bremsstrahlung spectrum [19].

2.2.1. INSTRUMENT CHARACTERISTICS

All the SEM-EDX analyses are performed with a JEOL6300 Scanning Electron Microscope equipped with a Princeton Gamma Tech (PGT) Energy Dispersive X-ray Si(Li) detector. The primary electron beam source is a tungsten filament heated to about 2700K. To prevent oxidation of the filament and scattering of the electrons caused by gas molecules in the air a high vacuum system is required, working at 10^{-4} or more Torr.

Secondary electrons are collected by an Everhart-Thornley scintillator detector, consisting in a Faraday cup with a scintillator inside. Backscattered electrons are recorded by a solid state electron detector, operating on the principle of electron-hole pair production induced in a semiconductor by energetic electrons.

As said before the X-rays are collected with an energy-dispersive Si(Li) detector, made of a nitrogen cooled pin Si(Li) crystal.

2.2.2. QUANTITATIVE ANALYSIS

Accelerating Voltage	20 KV
Current	2 nA
Takeoff Angle	30°
Detector Distance	60 mm
Spectrum Collection	200 s

Table 2.1 – SEM-EDX set up to collect X-ray analysis.

Because of the high heterogeneity of most of the samples, the microscope magnification is kept in a range between 200x and 500x. The number of spectra collected on every sample depends always from its heterogeneity and can vary from 4 to 10 spectra.

The fitting of the spectra is performed with the software AXIL (Analysis of X-ray spectra through Iterative Least squares), and then the quantification of the resulting intensities are done with a standardless ZAF method.

A normal ZAF method corrects the proportion between intensities and masses of unknown and standard with three factors: F_Z, correcting for the atomic number, F_A, correcting for the X-ray absorption by the matrix, F_F, correcting for the secondary fluorescence contribution. Since elemental standard collection is time consuming and, at the same time, a loss of detector efficiency due to contamination is observed as a function of time, a faster quantification has been used, requiring only collection of one multi-elemental standard. [2]

Briefly, an element yield value is calculated from the multi-standard material to correct the variations in detector efficiency. This yield is obtained from the ratio of the X-ray intensities of a precise element and its mass fraction, multiplied for the ZAF correction factors and normalised to beam current, collection time and solid angle. The spectrum of a multi-element standard permits to calculate all the element yields, therefore the calibration is valid on the entire composition of an unknown sample, so that the concentration of each element can be calculated. [20][21]

The validation of this method has been done with the analysis of several NIST standards, and the average relative error is 2.5% for major elements and 9% for minor (between 1% and 10% in mass). The limit of detection of the instrument of 0.1% in mass does not permit analysis on trace elements, indeed the error will be more than 70%. [20][21]

2.3. LASER ABLATION – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY (LA-ICP-MS)

This technique is normally associated with trace elements analysis, and it is complementary with SEM-EDX analysis, that is only dedicated to major (and minor) elements. The present work, however, is mostly focused on major and minor elements detected with La-ICP-MS, in order to compare the results previously obtained with the electron microscope and verify its reliability.

As explained before, there is no sample preparation, because the embedded and polished SEM-EDX samples fit perfectly with the sample-holder of the laser ablation chamber.

The laser ablation (LA) volatilises the solid sample by means of a pulsed laser beam. The vapour of the sample is pushed by a gas to the ICP-MS system to be directly analysed; these vapours arrive to the inductively coupled plasma (ICP) to be atomised and ionised before entering into the mass spectrometer (MS), where the ions are separated and counted as a function of their mass/charge (m/z) ratio. In an elemental analysis mono-charged ions correspond directly to chemical elements, thus almost all the periodic table can be explored. This technique has got very low limits of detection (LOD) (e.g. 100 ppb), and for this reason is recommended for trace elements analysis.

Because of the relative small dimension (from micrometers to millimetres) of the shots, this technique can be comprised in the field of micro-destructive analysis, i.e. the damage is almost not visible, which is very important in the cultural heritage sector, when often samples are unique and non replicable. [2]

Since only a part of the samples have been analysed at present, the trace elements results on REE will not be shown in this work, but only data referred to major and minor elements already analysed with SEM-EDX will be presented, in order to have a comparison between the two methods.

2.3.1. INSTRUMENT CHARACTERISTICS

The laser is a New Wave Research UP-193 ArF excimer laser with a standard ablation chamber. This type of laser is based on a molecule stable in an excited state and dissociated in the ground state (excimer gas), in particular the ArF complex. In this case for the analysis a raster mode was used. The gas carrier is He with a carrier gas flow rate of 0.30 L/min. In the next paragraph it will be shown the working set up. The laser is coupled with a Thermo Corporation X-Series 2 ICP-MS.

RF power	1400 W
Acq Time / mass	20 ms
Pts/mass	3
Plasma Gas Flow Rate	15 L / min
Aux gas flow rate	0.8 L / min

Table 2.2 – ICP-MS specifics.

It is important to notice that the laser ablation system works with He, while the ICP-MS uses Ar as carrier gas.

2.3.2. QUANTITATIVE ANALYSIS

Pre-ablation is needed to remove completely the carbon coating used for SEM-EDX analysis and eventual residual dirt/alteration on the sample.

	Relative Output Energy	Repetition Rate	Spot Size	Scan Speed	Depth/Pass
Pre-Ablation	50%	10 Hz	150 µm	70 µm/s	5 µm
Ablation	90%	20 Hz	100 µm	20 µm/s	5 µm

Table 2.3 – Working set up for pre-ablation and ablation.

To achieve a more stable signal, instead of spots, lines were shot on the glass samples. The analysis on the first 30 samples scheduled 3 lines of 2 mm. Two external standards were analysed in every session for the quantification, the NIST 610 and NIST 612 glasses. The calibration strategy includes also an internal standard, ^{43}Ca, using the concentration obtained from CaO SEM-EDX analysis. NIST 612 was added only to check the reliability of NIST 610. [2]

The concentration (µg/g) of each element is calculated following the equation:

$$c_j^{unk} = \frac{I_j^{unk} \Big/ I_{Int.Std.}^{unk}}{I_j^{std} \Big/ I_{Int.Std.}^{std}} * \frac{c_{Int.Std.}^{unk}}{c_{Int.Std.}^{std}} * \ c_j^{std}$$

Where c_j and I_j are concentration and intensity of the element of interest calculated in the unknown sample and in the standard NIST 610; $c_{Int.Std.}$ and $I_{Int.Std.}$ are concentration and intensity of internal standard ^{43}Ca presents in the unknown sample and in the standard NIST 610. The background is collected from measurement of a "gas blank", i.e. without ablation, performed as a precursor to initiating ablation. [2] Precision and LODs are correlated to signal and counting time, which are functions of a large number of

variables. Creating craters large enough to ensure that concentrations are well above LODs, with this internal standard method, the precision is between 2% and 15%, depending on the element of interest. [22]

If in the set of elements there is similar ablation behaviour and the internal standards are selected correctly, a high degree of accuracy can be obtained. On the contrary a much poorer accuracy is achieved for elements which fractionate significantly relative to the internal standard [23]. The fractionation is a dynamic, element-dependent process, mostly related to thermal properties of the element in different matrices, and influences LA-ICP-MS quantitative analysis. This well-known issue occurs between ablation and atomisation with ion-recombination of laser products. Therefore they are not anymore representative of the sample composition. [23][24]

2.4. FLAME ATOMIC ABSORPTION SPECTROSCOPY (FAAS)

Atomic absorption is a spectroscopic technique based on the quantification of chemical elements employing the absorption of optical radiation by free atoms in the gaseous state. Thus the sample has to be a gas or a vapour and subsequently atomised. Moreover the element investigated has to absorb a defined quantity of energy, i.e. light of a specific wavelength, to promote the electrons to higher orbitals; therefore the radiation source can change depending on the element to quantify. Modern instruments have continuum radiation source, so that a series of elements can be detected simultaneously. [25]
The quantification is obtained following the Beer-Lambert Law and measuring, first, the absorption of a set of standards with known element contents, secondly, the absorption of the sample. Normally a monochromator helps to separate and collimate the absorption lines directed to the detector, made of photomultipliers tubes. [25]

The samples preparation and the analysis have been conducted by Willy Van Mol from the University of Antwerp.
Almost 500g of each kind of sand (Chelford, Lommel and Dessel) were dried in an oven at 110°C for one night, and then they were weighed again two or three times in the following morning, every two hours, to check the stability of weight. During the night a certain amount of water was evaporated, thus the weight difference corresponds to the water content. This value is important for a correct calculation of concentrations. Thus they have been digested in a mixture of 3ml of HNO_3 and 5ml of HF. Afterwards, another mixture of 1ml HNO_3, 5ml HF and 1ml $HClO_4$ was added and heated till dryness. At the end the residue was dissolved in 1ml HNO_3 and 10 ml H_2O and diluted till 100 ml. Two solutions were prepared for each sand.

2.4.1. INSTRUMENT CHARACTERISTICS

The instrument is a Perking Elmer Atomic Absorption Spectrometer PEA analyst 300, working with an air-acetylene flame on the following wavelength: Fe 248.3 nm, Mn 279.5 nm, Cu 324.8 nm, Mg 285.2 nm, Ca 422.7 nm, Na 589 nm, K 766.5 nm.

2.5. THERMOGRAVIMENTRIC ANALYSIS (TGA)

This simple technique is useful to study the loss of material during a decomposition process. The resulting graph is a line with as much slope as the losses of material, and for each loss the amount of lost material and the relative temperature are given.

A series of 5 TG analyses were conducted to study the possible volatilisation of oxides from the crucible during the melting process. The problem comes from a systematic loss of K_2O% in almost every home-made glass. Consequently the SiO_2% increase of almost the same quantity 5-6%, making broader the discrepancy between theoretical and actual data on glass composition.

Since the initial ingredients, apart from sand, were carbonates, as K_2CO_3 and $CaCO_3$, a relevant CO_2 loss was expected, probably at different temperatures depending on decomposition temperature of every substance. Any other signal can be assigned to further volatile component.

The idea was to follow the melting process, therefore the samples had the same initial ingredients used in glass experiments. Different mixes were prepared, according to a precise plan, described in the dedicated paragraph (Section 3.3.2.6).

The instrument belongs to Karel de Grote Hogeschool of Antwerp, and the measurements have been conducted with the generous help of Prof. Dr. Christophe Vande Velde from Karel de Grote Hogeschool of Antwerp.

2.5.1. INSTRUMENT CHARACTERISTICS

The machine is a 2950 TGA HR V6.1A, with N_2 as purge gas and a standard oven. No specific detector is connectable to this source, thus a precise view on the volatile components is impossible.

The instrument is equipped with a Pt plate with the capacity of 50 mg; the range of working temperature is 0-1000°C.

3. GLASS EXPERIMENTS

3.1. INTRODUCTION

A considerable body of knowledge about glass has been gathered in the past years and collected in elaborated databases. In particular, compositional analysis has been used to assess the area/period of provenance [2][12][26][27][28][29][30]. Further information about historical glass is contained in the amorphous structure of this material, such as the ratios of the initial ingredients, properties of the glass melt and the heating curves used. Analysis of self-synthesised glass can improve this knowledge and help to reconstruct the recipes and heating procedures used in historical periods for glass making.

Several parameters are controllable during the glassmaking. In order to understand the correlations between these parameters and the characteristics of the final glass, it was appropriate to change one parameter of the glassmaking process at the time and to observe how such a change influences the glass characteristic. Since the aim of this work was to finally reproduce glass with a composition that is as closer as possible to that of ancient recipes, it was decided to follow a procedure of incremental changing the initial mixture of ingredients and the details of the heating procedure, until the resulting glass came close in composition to that used in historic periods.
A total of 57 glasses were prepared, divided in three sets of respectively 29, 22 and 6 samples; below, these experiments are referred to as Glass Experiments A, B, C. The first set was dedicated to the selection of the parameters of operation of the system; in the second set of experiments, the parameters were evaluated, improved and stabilised; in the third set of experiments, the raw materials employed were varied.
The samples resulting from every experiment are indicated by the experiment number: for example the glass made during the third experiment is called S03 (sample nr. 3).

Without compositional chemical analysis, conducted by SEM-EDX (Scanning Electron Microscope – Energy Dispersive X-Rays) on every sample, it would not have been possible to obtain an overview of the effect of all experimental parameters. With SEM-EDX it was relatively easy to monitor the percentage composition of the major elements oxides SiO_2, K_2O, CaO, Na_2O, MgO and of some minor elements such as Al_2O_3, Fe_2O_3, SO_3, TiO, P_2O_5, MnO that commonly are present in the glass. The electron microscope instrument provided the possibility to record electron micrographs and maps in secondary electron (SEI) and/or backscattering (BEI) mode, displaying discontinuities and heterogeneities present at the glass surface. This information allowed gaining insights into the nature of the glass that was synthesised; moreover, it facilitated the direction in which to adapt the parameters of the glassmaking process. LA-ICP-MS (Laser Ablation -

Inductively Coupled Plasma – Mass Spectrometry) is a powerful and helpful technique used to support the major and minor element concentration values obtained with SEM-EDX, with trace elements information.
To determine the elemental composition of Chelford, Dessel and Lommel sands, FAAS (Flame Atomic Absorption Spectroscopy) determination of Fe, Mn, Cu, Mg, Ca, Na and K were collected.
A series of TGA (Thermo-Gravimetric Analysis) measurements was realised to study when and which kind of volatile compound were released from the melt during the glass production.

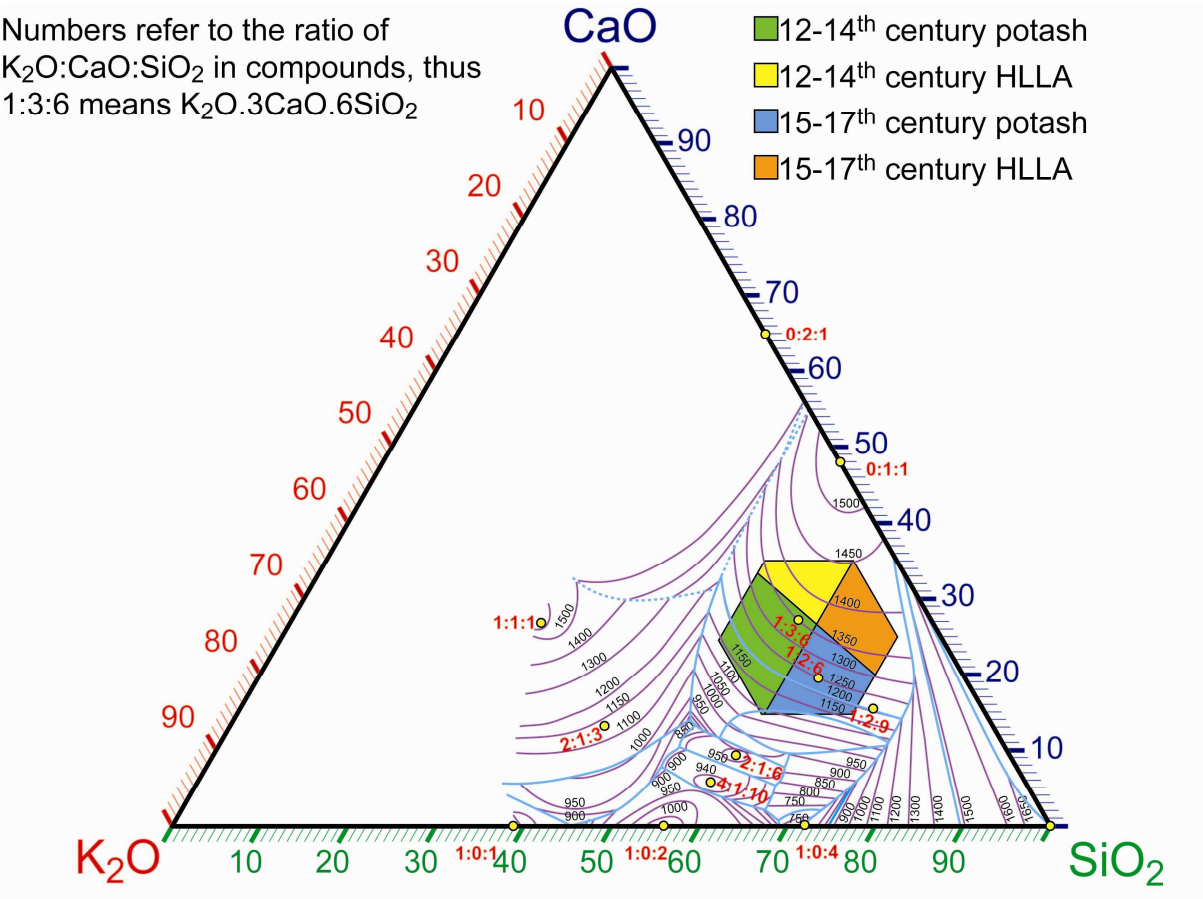


Figure 3.1 – Ternary system K_2O-CaO-SiO_2 with isotherm curves built on real glass; the hexagonal area included four different types of historical glasses. [31]

This work was particularly focused on potash glass: medieval and post-medieval glass as shown in Figure 3.1 of the ternary system K_2O-CaO-SiO_2 [31]. The hexagonal area includes four types of potash and high-lime low-alkali (HLLA) glass that are typical for the glass production in the 12-14th century or 15-17th century.

Where these regions meet the isotherms derived from data obtained from modern experimental glass, it is realistic to suppose that the corresponding temperature also has been used to produce the ancient glass. Starting with the boundary curves and the suggested compositions, a series of glassmaking experiments was realised. These are described below.

The first set of glass experiments were realised entirely by Dr. Olivier Schalm from the Glass Conservation Department of the Artesis Hogeschool, Antwerp, in the period March-July 2011 (Appendix A). His presence and knowledge helped the scheduling of experimental series B and C.

3.2. PARAMETERS

3.2.1. OVEN

The oven in which all the experiments have been realised is a Bottom Loading Furnace 161/2007 – Termolab (Fornos Electricos LDA-Portugal) present in the Metal Conservation Department of Artesis Hogeschool of Antwerp, with a power of 8 KW and limit temperatures of 1500°C, working in continuo, and at 1550°C for short periods. The useful chamber dimensions are 200x200x250mm (width x depth x height).

3.2.2. TYPE AND AMOUNT OF INGREDIENTS EMPLOYED

The commonly employed type of sand for glassmaking was Chelford sand (Courtesy Pilkington, UK), which contains a 93.6% of SiO_2; this sand therefore contains some impurities, and it is comparable with the sand used in the past for the same purpose. Also two other types of sand have been employed in the experiments: sand found in Dessel and Lommel (Courtesy Sibelco, Belgium), that have a SiO_2 content of respectively 99.4% and 99.7%. It was noticed by means of FAAS analyses that Chelford sand contains ca 5.5% in mass of K_2O; this additional source of potassium was taken in consideration when calculating the final expected K_2O content of the glass. At the time of Glass Experiment A this information was still unknown; however, good results have been achieved, and in later experiments the theoretical values have been changed with the new composition. Rather than real sand, pure silica was the main Si-bearing ingredient in experiments S24, S25 and S29.

The second most important ingredient needed to make glass is the flux agent, where the main chemical compound can be Na_2O or K_2O, obtained from different materials depending on the region and period of provenance. Since the present work was particularly focused on medieval potash glass, K_2CO_3 in the form of a pure reagent was used; secondly, some glass was prepared by means of a mixture of Na_2CO_3 and K_2CO_3; and finally, beech ash particularly rich in K_2O was employed as flux source.

The third component normally employed as major ingredient for glass making is CaO; inside the glass matrix it has stabilising properties. Since oxides, carbonates or other Ca salts could be present in both sand and ash, for long time it was unintentionally added to the melt; only in later periods, when the stabilising properties of CaO became more explicitly known, intentional addition of Ca-rich materials became common [5]. Similar to CaO, also MgO has stabilising properties, and sometime both compounds were present together for achieving this goal. In the glass experiments a series of samples were prepared with CaO (from

S01 to S23); in the later experiments, this ingredient was replaced by $CaCO_3$. Both were used in the form of pure reagents. For the experiments involving beech ash, no $CaCO_3$ was used. Ca- and Mg- oxides were already present into the ash, as became apparent from analyses of the glass.

In Glass Experiments A, the ratios between the three main ingredients were varied more than in the other two experimental series. In general, it can stated that SiO_2 was always the main component with its concentration in the range 40-70%, while K_2O (or $K_2O + Na_2O$) was in the range 7-30%, CaO (or CaO + MgO) in the range 9-30% and the remaining minor elements in the 0.1-10% range.
Due to the fact that K-, Na- and Ca-carbonates were used as ingredients, the amount of gas bubbles produced inside the glass was increased; however this phenomenon also assured that the glass-fusing reactions took place and facilitated the stirring of the melt. By beginning with pure ingredients, the intention was to reduce as much as possible unknown variables; nevertheless different problems needed to be overcome, so that only in Glass Experiments C, after having obtained several good glasses and having established an appropriate heating curve, beech ash was introduced as raw material.
Before use, all ingredients were dried for at least one day, in an oven at 40°C.

3.2.3. TYPE OF CRUCIBLE

Different material can be chosen for the crucible; in this case most of the experiments were realized in porcelain crucibles or silica carbide (SiC) crucibles. The first type of crucibles have a heating resistance until 1200°C, while the second type were used for heating curves at higher temperature, since they are resistant until 1500°C. Crucibles with different volumes (from 75 to 250 ml) were employed.
One glass synthesis experiment was conducted in a Pt crucible of 75 ml, but only after a good set of parameters was obtained and it was sure that a well melted transparent glass would result, because of the high cost of the Pt and its elaborated cleaning procedure.

Figure 3.2 – Three type of crucible used for glassmaking: porcelain (left), silica carbide SiC (centre) and platinum Pt (right).

Since the favourite heating curve worked at 1250°C, but SiC crucibles introduced too much impurities into the glass, as it will be explained later, the use of porcelain crucibles was preferred; to save the oven from any possible damage during the melting process, the porcelain crucible were put into a SiC.
The material of both the SiC and the porcelain crucibles was analysed by SEM-EDX, before and after use, to estimate the amount of minor and major elements that were present. In this way, a possible contamination of the glass that was synthesised in them can be evaluated; this is discussed in greater detail in Glass Experiment B (section 3.3.2).

3.2.4. TEMPERATURE AND TIME

The oven in use provided the possibility to specify a heating curve (H.C.) consisting of different steps in which temperature, holding time and heating rate were fixed. Three passages were selected, pre-heating, melting and annealing. All heating curves are numbered, from 1 to 22. Secondary heating curves differ from the primary curve when only the time of one step is changed, for example H.C.17 has a secondary series from 1 to 5 (named H.C.17(1), H.C.17(2), ...) because five experiments were conducted using a total of 1, 2, 10, 15 and 25 hours.

	Pre-Heating		Melting			Annealing			Glass
Curve	T [°C]	Time [h]	T [°C]	Time [h]	Rate [°C/min]	T [°C]	Time [h]	Rate [°C/min]	Nr.
1	600	1	1200	0.5					1
2	600	1	1200	2.5					2, 3, 4, 5
3	800	1	1450	1					6
4	800	5	1200	10					7
5	800	1	1500	1					8
6	800	5	1300	10					9
7	800	24	1300	10					10
8	750	1	1350	2					11, 12
9	800	1	1300	1	5				13
10	800	1	1300	1	0.5				14
11	800	1	1350	1	5				15
12	800	1	1400	1	5				16
13	800	1	1400	1	5	500			17
14	800	1	1450	1	5	500			18, 21, 23, 25
14(2)	800	1	1500	1	5	500	10		29
15	800	1	1500	1	5	500	5		19, 20
16	800	1	1250	1	5	500	5		22, 24, 26
16(2)	800	1	1250	1	5	500	5	5	27
16(3)	800	1	1250	1	1	500	10	15	28

Table 3.1 - Heating curves for Glass Experiments A.

	Pre-heating			Melting			1st step Annealing			2nd step Annealing			Glass
Curve	T [°C]	Time [h]	Rate [°C/min]	T [°C]	Time [h]	Rate [°C/min]	T [°C]	Time [h]	Rate [°C/min]	T [°C]	Time [h]	Rate [°C/min]	Nr.
16	800	1	15	1250	1	5	500	5	5				33
17(1)	800	1	15	1250	2	5	800	5	5				30, 37
17(2)	800	1	15	1250	10	5	800	5	5				31
17(3)	800	1	15	1250	1	5	800	5	5				32
17(4)	800	1	15	1250	15	5	800	5	5				35, 44,45,46,48,49,51-57
17(5)	800	1	15	1250	25	5	800	5	5				36
18	800	1	15	1450	2	5	800	5	5				34
19	800	1	15	1250	2	5	1000	5	5	500	5	5	38
20	800	1	15	1250	2	5	1000	5	5	800	5	5	39, 40, 41, 42
21	800	1	15	1250	2	5	100	1	5				43
22	800	1	15	1000	15	5	800	5	5				47, 50

Table 3.2 - Heating curves for Glass Experiments B and C.

One of the most used heating curves was the 17(4), displayed in the graph below (Figure 3.3). Pre-heating, melting and annealing steps are underlined with different colours. After the annealing process the oven started the free cooling down, without an imposed rate. The whole experiment lasted almost 40 hours.

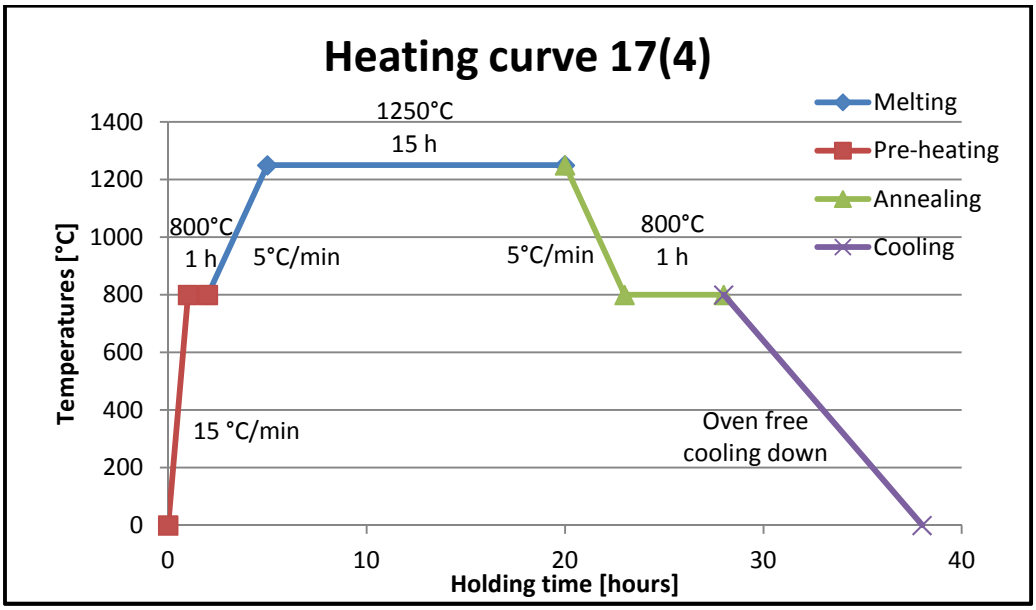


Figure 3.3 – Example of heating temperature. The graph represents the H.C. 17(4) used for many glass experiments.

The ternary system K_2O-CaO-SiO_2 (Figure 3.1) indicates which ingredient ratios to use at different temperatures (see Section 3.1). The isotherms, derived from data obtained from modern experimental glass, were used to determine the melting temperatures. The match between these isotherms and the K_2O-CaO-SiO_2 values suggested the ratios to use.

A range between 1200°C and 1500°C, from 30 min to 25 hours has been explored. Higher temperatures were considered inaccessible for the kilns of the past, and also for the furnace used during the present experiments.
These parameters were varied mostly in Glass Experiments A, as it will be explained later; yet also for Glass Experiments B, different times were tested in relation with some characteristics.

The pre-heating step permitted to prepare the oven for the melting process and at the same time it helped the uniformity of the molten mixture, because the structural impediment of the oven (i.e. closed chamber) itself made stirring impossible. The first 5 glass experiments had the pre-heating temperature at 600°C; all the others had the temperature of 800°C. The holding time of 1 hour appeared to be more suitable.

This third step of annealing was introduced only from the heating curve 13. Initially the temperature used was 500°C, with a holding time between 5 and 10 hours (H.C. 14, 15 and 16). With the heating curve 17, the temperature was increased to 800°C and the holding time was 5 hours. Some experiments with two steps of annealing will be discussed in greater detail in section 3.3.2 (Glass Experiment B). They have a first step at 1000°C and a second at 500/800°C. Their general aim was to avoid as much as possible cracking inside the synthesised block of glass.

3.3. GLASS

Each group of glass (Glass Experiments A, B, C) will be dealt separately to explain the main targets, the obstacles found and the solutions obtained, in order to achieve good results. They will be described in the order of execution, because the three groups were strictly connected and correlated. A complete and detailed description of each experiment is gathered in Appendix A (for Glass Experiments A) and Appendix B (for Glass Experiments B and C), with information on the initial composition in weight, the theoretical composition, the heating curve, the type of crucible, the method used and photographs of the resulting glass.

The next paragraphs summarise the information for a complete understanding of the home-made glass evolution; moreover, they show the most important steps and the challenges encountered and finally, they discuss the results reached.

The compositional ratios displayed are referred to the major compounds of the glass; these last are correlated with the initial ingredients and described in the ternary system K_2O-CaO-SiO_2, i.e. a ratio of 1 : 2 : 6 means 1K_2O : 2CaO : 6SiO_2.

Theoretical values of K_2O, CaO and Na_2O, added as K_2CO_3, $CaCO_3$ and Na_2CO_3 respectively, were calculated from the ratio of the molecular masses (MM) as follow.

$$g_{OXIDE} = \frac{MM_{OXIDE}}{MM_{CARBONATE}} * g_{CARBONATE}$$

For example:

$$g_{K_2O} = \frac{MM_{K_2O}}{MM_{K_2CO_3}} * g_{K_2O}$$

It was thus possible to work out a parameter of conversion for pair of compounds from the molecular mass ratio: 0.68 for K_2O/ K_2CO_3, 0.56 for CaO/$CaCO_3$ and 0.58 for Na_2O/Na_2CO_3.

3.3.1. GLASS EXPERIMENTS A

The series from S1 to S29 was called Glass Experiments A; it collects the first glass experiments realised with the particular scope of defining one or more efficient heating curves to produce glass that is as much as possible homogeneous and transparent. In particular, what had to be found was a connection between the temperatures and the initial composition of the ingredients mixed into the crucible.

Tables 3.4 and 3.5 summarise the information for each sample of Glass Experiment A. They display: the amount (in g) of initial reagents as raw materials; the expected amount (in g) of major compounds after

melting; the type of crucible; the heating curve to produce it; some qualitative observations on the obtained sample; the theoretical percentage of the major and minor elements calculated from the initial reagents; the actual percentage of the major and minor elements determined by SEM-EDX analysis with its relative standard deviation.

3.3.1.1. Group 1: S1 – S5

Since in the ternary system K_2O-CaO-SiO_2 (Figure 3.1) high-lime low-alkali (HLLA) glass matches the isotherms with temperatures around 1350-1400°C, it has been preferred to start with milder conditions, in an attempt to reproduce potash glass with an initial ratio of 1 : 1 : 6 and a melting temperature of 1200°C. The pre-heating temperature was fixed at 600°C for 1 hour, and the mixed ingredients were poured into a porcelain crucible. The SEM-EDX analysis shows that an actual ratio of 1 : 1 : 7 was obtained, for the non glassy material that contains different kinds of un-melted crystals, especially Ca oxides, as shown in Figure 3.3 (left). The BEI image emphasises the white parts of different types of Ca crystals of irregular shape. In order to eliminate the un-melted material, first, an attempt was made to increase the melting time from 30 min to 2h30min, considering the need of more heating to melt the mixture while, in second place, the composition was changed to a new ratio of 1 : 1.5 : 1.5, assuming that a too high amount of initial sand was the cause of the incomplete melting; in both cases however, these attempts did not achieve their goals.

3.3.1.2. Group 2: S6 – S16

Here the composition 1 : 1 : 6 was employed while the temperature of the set up was changed: the pre-heating was increased to 800°C per 1 hour, and a series of melting temperatures was tested (1300, 1350, 1450, 1500°C), in combination with shorter and longer holding times (1, 2, 10 hours). The results were no so encouraging: no homogeneous glass was formed, but always different crystalline compounds were found to remain present. Un-melted CaO, Al_2O_3 and SiO_2 were detected, creating a highly heterogeneous solid and making qualitative analyses difficult. In Figure 3.4 (right) a particle of un-melted sand, surrounded by glass, is shown in BEI mode.

Table 3.3 lists the five SEM-EDX analyses conducted on the S02 material, where S02_GL_3 shows a higher CaO content, referring to a white point in the BEI image (left) in Figure 3.4. In S02_GL_2, less SiO_2 attests the general heterogeneity of this group of samples. The quantitative results for S02 displayed in Table 3.5 are the average of the values of these five analyses. The standard deviations, in Table 3.5, were calculated to validate the averaged data, considering values with a relative standard deviation below 10% sufficiently reliable. Therefore, some individual analysis results were removed from the data sets in order to obtain a lower standard deviation, e.g. the analysis S02_GL_3.

S02 analysis nr.	SiO_2%	K_2O%	CaO%	Minor%
S02_GL_1	75.1	12.1	11.6	1.2
S02_GL_2	68.1	15.7	15.0	1.1
S02_GL_3	72.8	9.2	16.0	1.9
S02_GL_4	72.4	12.9	14.0	0.7
S02_GL_5	72.5	12.8	13.5	1.2

Table 3.3 – Five X-ray analysis by SEM-EDX on sample S02 with related composition in mass percentage divided between SiO_2, K_2O, CaO and minor elements.

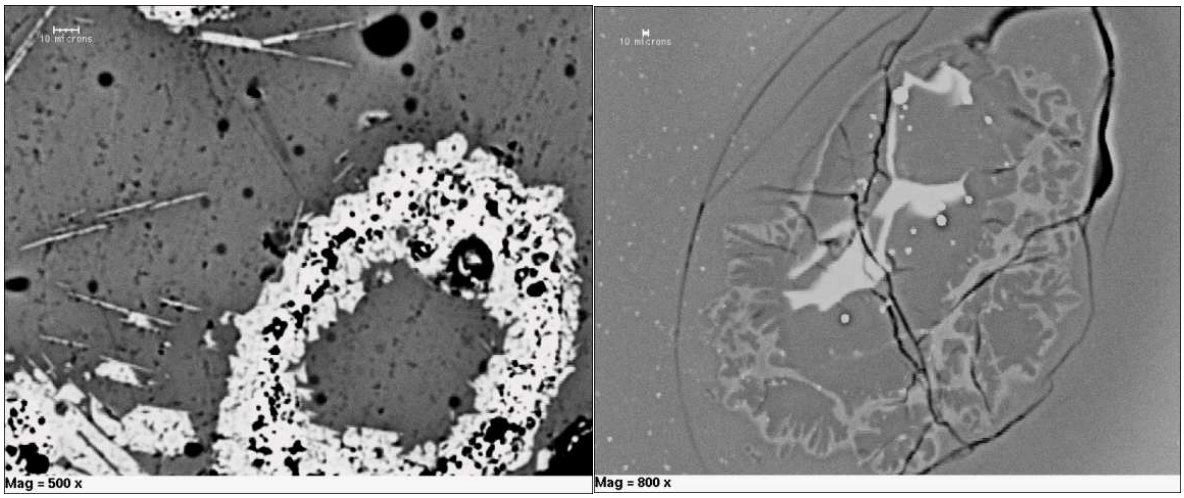


Figure 3.4 – Backscattering images (BEI) by SEM-EDX of two samples: S02, magnification 500x (left); S06, magnification 800x (right). In the first Ca crystals are displayed in the white shapes, in the second a not melted particle of sand is observed.

A new initial composition with ratio 1 : 1 : 3 was used from S7, with an heating curve composed by a pre-heating at 800°C for 1 hour and a melting temperature at 1300-1400°C for 1 hour. The crucible was a SiC crucible because of the higher temperatures. Still not good qualitative glass was collected, but some improvements in the homogeneity were recorded by SEM-EDX analysis. The following BEI map (Figure 3.5) displays the difficulty to involve Ca oxides in the reactions. Indeed an enough homogeneous material based on Si and K is visible between the Ca crystals, always in cigar and lumpy shapes.

	Ingredients [g] Room Temperature				Ingredients [g] High Temperature						
Nr.	**Sand**	**K_2CO_3**	**CaO**	**$CaCO_3$**	**SiO_2**	**K_2O**	**CaO**	**Minor**	**CRUC.**	**H. C.**	**OBSERVATIONS**
1	17.0	4.3	4.5	-	15.9	3.9	4.5	0.5	Porcel.	1	surface irregular, gas holes, no liquid glass obtained, K2CO3 was smeared out
2	17.0	4.4	4.5	-	15.9	3.9	4.5	0.5	Porcel.	2	rough surface with air bubbles, no liquid glass obtained, longer firing improved quality
3	10.0	7.8	8.0	-	9.4	5.9	8.0	0.3	Porcel.	2	probably glass created, grey layer on the inner crucible part
(3→)4	10.0	7.8	8.0	-	9.4	5.9	8.0	0.3	Porcel.	2	crucible and sample 3 refired, grey layer still, smoother surface
5	10.0	7.8	8.0	-	9.4	5.9	8.0	0.3	Porcel.	2	purple shade, medieval glass cullet mixed with ingredients
6	1.8	0.5	0.5	-	1.6	0.4	0.5	0.0	SiC	3	no white powder, dark colour (SiC), small as bubbles, crucible sticked on the brick
7	2.1	0.7	0.7	-	1.9	0.6	0.7	0.1	SiC	4	glassy material, white powder
8	3.4	1.0	1.0	-	3.2	0.9	1.0	0.1	SiC	5	glassy material with white/opaque lower layer, transparent upper layer
9	2.0	0.5	0.5	-	1.8	0.4	0.5	0.1	SiC	6	white powder on and sticked in glass, white and opaque surface
10	1.9	0.6	0.5	-	1.8	0.5	0.5	0.1	SiC	7	Irregular surface, no white powder, CaO part of the glass??
11	1.7	1.2	0.3	-	1.6	0.9	0.3	0.0	SiC	8	at 750°C turned into a porous solid, dark green glass, many gas bubbles
12	2.0	0.6	0.6	-	1.9	0.5	0.6	0.1	SiC	8	white inclusions on the top of the surface
13	1.8	1.3	0.3	-	1.7	1.0	0.3	0.0	SiC	9	Greenish glass, gas bubbles, higher transparency=homogeneity??
14	2.0	0.8	0.7	-	1.9	0.6	0.7	0.1	SiC	10	slow heating rate but gas bubbles, white powder, no complete melting process, refired
(14→)15	2.0	0.8	0.7	-	1.9	0.6	0.7	0.1	SiC	11	seems better than 14
(15→)16	2.0	0.8	0.7	-	1.9	0.6	0.7	0.1	SiC	12	opaque and shine surface
17	2.1	0.7	0.7	-	1.9	0.6	0.7	0.1	SiC	13	no transparency, many gas bubbles
18	2.2	0.8	0.7	-	2.0	0.6	0.7	0.1	SiC	14	well melted but gas bubbles and opaque white zones
19	2.0	1.2	0.5	-	1.9	0.9	0.5	0.1	SiC	15	at 1300°C viscous liquid formed, inner crucible vitrified, blisters, two different colour layer
20	2.1	0.7	0.7	-	2.0	0.6	0.7	0.1	SiC	15	blisters cause hight temperaure??
21	29.4	10.3	10.3	-	27.5	8.6	10.3	0.8	SiC	14	transparent top layer, white opaque layer at the bottom, yellow region between, top bubbles
22	26.9	16.4	6.7	-	25.2	12.6	6.7	0.7	Porcel.	16	transparent glass, many cracks, short annealing, fragile crucible
(21→)23	29.4	10.3	10.3	-	27.5	8.6	10.3	0.8	SiC	14	ball milling of 21, black parts of crucible, homogeneous black glass
24	24.3	14.9	-	10.8	24.3	10.1	6.0	-	Porcel.	16	transparent glass, some cracks in the crucible, small pits of 1 mm of gas bubbles
25	25.3	8.9	-	15.8	25.3	6.1	8.8	-	SiC	14	transparent top layer, white opaque layer at the bottom, yellow region between
26	24.3	14.9	-	10.8	22.7	11.5	6.0	0.7	Porcel.	16	transparent glass, some cracks in crucible and glass, small pits of 1 mm of gas bubbles
27	24.3	14.9	-	10.8	24.2	10.1	6.0	0.1	Porcel.	16(2)	transparent glass, some cracks in crucible and glass, NO small pits of gas bubbles
28	24.3	14.9	-	10.8	24.2	10.1	6.0	0.1	Porcel.	16(3)	many cracks in glass, no bubbles on the top
29	25.3	8.9	-	15.8	25.3	6.1	8.8	-	SiC	14(2)	thinner transparent top layer than 25, white opaque layer at the bottom, yellow region between

Table 3.4 – Glass Experiments A data: initial ingredients [g] and relative products after melting [g], type of crucible, heating curve and some observations for each sample.

	Theoretical % [%m/m]				Actual % [%m/m]							
Nr.	SiO_2	K_2O	CaO	Minor	SiO_2	Std.Dev.	K_2O	Std.Dev.	CaO	Std.Dev.	Minor	Std.Dev.
1	64.3	15.6	18.2	1.9	72.2	1.8	13.6	0.1	13.0	2.8	1.2	0.9
2	64.3	15.7	18.2	1.9	72.0	2.9	13.4	1.6	13.6	1.4	1.0	0.2
3	39.9	24.9	34.1	1.1								
(3→)4	39.9	24.9	34.1	1.1	49.4	1.8	24.6	0.9	23.0	1.4	3.0	0.5
5	39.8	24.9	34.1	1.1	52.0	1.3	13.2	1.5	32.7	3.7	2.1	0.9
6	62.5	16.3	19.4	1.8	69.1	0.8	10.5	1.0	17.9	1.9	2.5	0.5
7	60.0	18.0	20.3	1.7	66.7	0.1	17.3	0.6	14.5	0.3	1.4	0.1
8	61.3	17.0	19.9	1.8	66.7	2.1	11.3	0.6	20.1	2.6	1.9	0.3
9	64.4	15.8	18.0	1.9	73.1	0.7	9.1	0.3	15.4	0.9	2.3	0.3
10	63.3	17.1	17.9	1.8	75.3	2.4	10.2	1.4	10.3	1.2	4.3	0.9
11	55.6	31.4	11.4	1.6	66.0	0.4	20.1	0.3	9.8	0.4	4.0	0.3
12	63.2	16.1	18.9	1.8	69.1	3.2	11.8	0.5	17.5	2.3	1.6	0.5
13	56.1	32.5	9.8	1.6	65.0	0.7	23.8	0.9	8.2	0.5	3.0	0.1
14	57.3	19.4	21.7	1.7								
(14→)15	57.3	19.4	21.7	1.7	62.7	0.6	20.4	0.2	15.7	0.7	1.2	0.2
16	57.3	19.4	21.7	1.7	65.9	0.9	13.3	1.7	8.0	0.3	12.8	1.2
17	58.2	18.3	21.8	1.7	66.3	0.8	11.0	0.7	19.3	1.8	3.3	0.4
18	59.1	18.9	20.4	1.7	68.0	2.1	9.1	0.4	19.4	1.9	3.5	0.6
19	55.5	28.0	14.9	1.6	72.5	1.2	8.8	0.4	8.5	0.4	10.2	1.1
20	59.1	18.2	21.0	1.7	71.9	0.7	6.1	0.4	12.5	0.5	9.5	0.5
21	58.3	18.3	21.8	1.7	64.9	2.1	15.1	0.5	18.6	1.7	1.3	0.3
22	55.7	27.9	14.8	1.6	61.0	1.5	25.4	1.3	12.5	1.8	1.2	0.2
23	58.3	18.3	21.8	1.7	66.9	0.0	11.1	0.1	18.5	0.8	3.5	0.7
24	60.0	25.0	14.9	-	59.7	1.1	26.3	0.2	13.7	1.1	0.3	0.0
25	62.9	15.1	22.0	-	66.1	1.6	15.3	0.6	17.7	1.6	0.9	0.6
26	55.6	28.0	14.8	1.6	57.8	1.7	23.7	1.2	17.5	2.7	1.0	0.2
27	59.7	25.0	14.9	0.4	59.7	1.8	24.6	1.7	15.4	1.9	0.4	0.1
28	59.8	25.0	14.9	0.2	62.9	1.1	23.5	0.5	13.3	0.8	0.4	0.0
29	62.9	15.1	22.0	-	65.4	1.7	12.9	0.8	21.1	2.5	0.7	0.2

Table 3.5 – Glass Experiments A data: theoretical glass composition [%m/m] and actual one analysed by SEM-EDX [%m/m] with relative standard deviation [%m/m] for each sample.

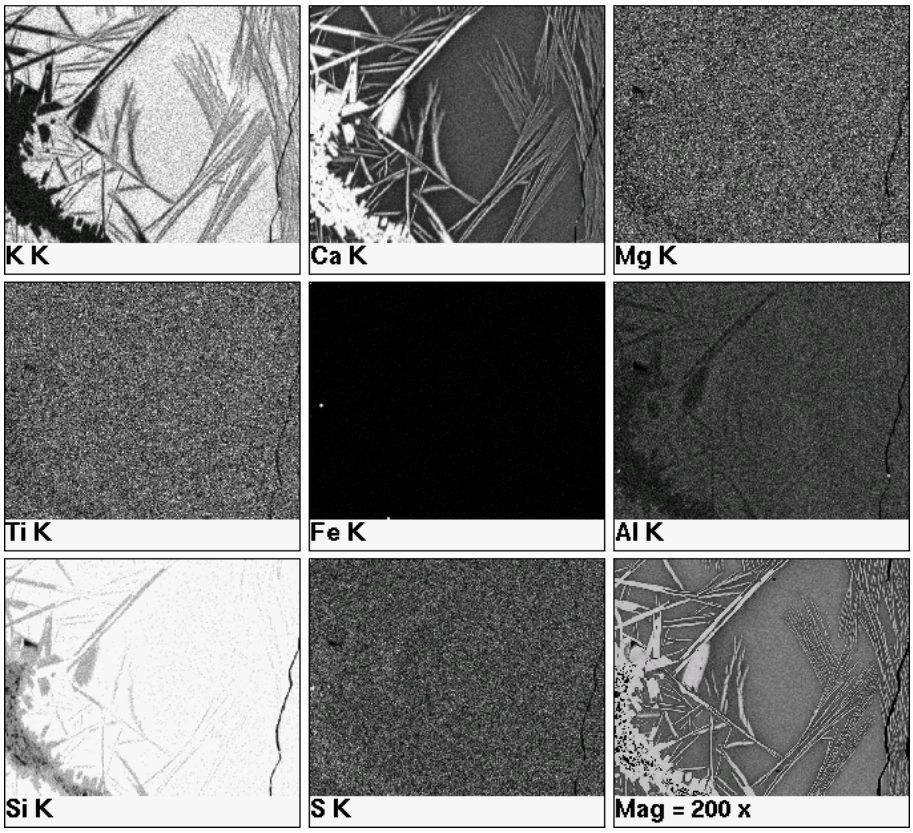


Figure 3.5 – Backscattering (BEI) image and maps by SEM-EDX, magnification 200x, on sample S09. K_α lines of the following elements: K, Ca, Mg, Ti, Fe, Al, SI, S.

3.3.1.3. Group 3: S17, S18, S21, S23, S25, S29

Qualitative better results were achieved with a group of samples synthesises in a new setting, referred to as H.C. 14. Melting temperatures around 1400-1500°C (H.C. 14), ratios variable from 1 : 1 : 3 to 1 : 1.5 : 4 (this second only for S25 and S29). This group shows a better, even if not perfect, matching between theoretical and actual percentage composition. Nevertheless the material formed can be defined as a glass, with a certain amount of bubbles; furthermore in almost every sample was present a yellowish shadow, as a separate inner layer (Figure 3.6). A crystalline layer was always present together with the glass, proving that problems of heterogeneity and melting were still present and the setting was not optimal.

The discordances on ratios see SiO_2% increasing and contemporary K_2O% decreasing. This behaviour will be more evident later and part of the research in Glass Experiment B will investigate to give it a meaning.

In any case, the partial success of this group can derive from the new step of annealing at 500°C for 5 hours.

Figure 3.6 – Picture of S21 with three different layers: a transparent top layer rich of bubbles, an intermediate inner yellowish layer, a bottom crystalline and opaque layer.

3.3.1.4. Group 4: S22, S24, S26, S27, S28

In parallel with this group, another group of samples was synthesised in the parameters set up of H.C. 16: a composition of 2 : 1 : 4 was mixed into porcelain crucible pre-heated at 800°C for 1 hour, than heated till 1250°C for another hour and, at the end, annealed at 500°C for 5 hours. Actually, also in this group it was observed by SEM-EDX, and confirmed by LA-ICP-MS, the opposite compositional trend of SiO_2 and K_2O, as previously explained. In general the effective composition was around 1.5 : 1 : 4. Nevertheless, from a qualitative point of view, a transparent well melted glass was obtained (Figure 3.7), with some bubbles inside and cracking. Even if the compositional matching between actual and theoretical values was not perfect, at least higher homogeneity has been achieved into the glass. It means that it has been found a good set of parameters.

Figure 3.7 – Picture of S24, made with H.C. 16 into porcelain crucible.

3.3.1.5. Discussion

A first consideration deals with the ternary system K_2O-CaO-SiO_2 (Figure 3.1) containing the hexagonal area. This area includes four types of potash and high-lime low-alkali (HLLA) glass that are typical for the glass production in the 12-14th century or 15-17th century. The ingredients ratios and the temperatures

suggested by the ternary system barely agree with the results achieved in this report. E.g., it suggested a ratio of 1 : 2 : 6 to produce a 15-17th century potash glass with the melting temperature of 1250°C. Instead, a melting temperature 1250°C produced good quality glass, as in the case of the samples of group 4, with an ingredients ratio of 2 : 1 : 4.

For group 3 the compositions used were on the edge between 12-14th century potash glass and 15-17th century potash glass, but the melting temperatures suggested by the ternary system are lower than those experimentally used. These temperatures have been tested from S10 to S16, which almost the same composition of group 3 was kept and no good glassy material was produced (Figure 3.8), but they are coloured, heterogeneous, foamy and never transparent.

Figure 3.8 – Picture of S11, still attached to the SiC crucible.
On the wall it is visible the volume change during melting.

No high-lime low-alkali (HLLA) glass has been realized, although their designed temperatures of 1400°C were gained for the glass in group 3: the presence of a crystalline layer into almost every sample could suggest that the amount of alkali was already at the lowest limit, and probably only with higher temperatures than 1450°C it could be possible to form a glassy compound. Two practical problems deny this possibility: on one hand the oven heating limit at 1500°C, on the other hand the crucible resistance at the same temperature.

Until now the main target searched was an optimal heating curve that could produce a well melted glass, with good homogeneity and transparency. The last two groups answered quite well to these requests, in particular the second one. Indeed their samples gained a good transparency without form multi-layers as in group 3, moreover the lower temperature at 1250°C than at 1450°C was preferable, because more feasible with the kiln of the past. Therefore the heating curve 16 with the group 4 parameters will be considered as base for the development of the next series.

It is important to mark that from S24 to S29 no more CaO, but $CaCO_3$ has been added to the initial mix; therefore a higher amount of carbonates into the molten could help in self-stirring and homogenisation. Further, S24, S25 and S29 have been melted with pure SiO_2 and not with Chelford or any other sand.

	Theoretical % [m/m]					Actual % [m/m]							
Nr.	SiO_2	K_2O	CaO	Minor		SiO_2	Std.Dev.	K_2O	Std.Dev.	CaO	Std.Dev.	Minor	Std.Dev.
6	62.5	16.3	19.4	1.8	SEM	69.1	0.8	10.5	1.0	17.9	1.9	2.5	0.5
					LA-ICP-MS	69.6		9.4		17.9		3.1	
8	61.3	17.0	19.9	1.8	SEM	66.7	2.1	11.3	0.6	20.1	2.6	1.9	0.3
					LA-ICP-MS	67.1		10.8		20.1		2.0	
9	64.4	15.8	18.0	1.9	SEM	73.1	0.7	9.1	0.3	15.4	0.9	2.3	0.3
					LA-ICP-MS	71.8		9.9		15.4		2.9	
10	63.3	17.1	17.9	1.8	SEM	75.3	2.4	10.2	1.4	10.3	1.2	4.3	0.9
					LA-ICP-MS	74.0		10.6		10.3		5.1	
11	55.6	31.4	11.4	1.6	SEM	66.0	0.4	20.1	0.3	9.8	0.4	4.0	0.3
					LA-ICP-MS	63.9		20.8		9.8		5.5	
24	60.0	25.0	14.9	-	SEM	59.7	1.1	26.3	0.2	13.7	1.1	0.3	0.0
					LA-ICP-MS	59.0		27.0		13.7		0.2	
25	62.9	15.1	22.0	-	SEM	66.1	1.6	15.3	0.6	17.7	1.6	0.9	0.6
					LA-ICP-MS	65.3		15.3		16.7		2.7	
26	55.6	28.0	14.8	1.6	SEM	57.8	1.7	23.7	1.2	17.5	2.7	1.0	0.2
					LA-ICP-MS	55.7		25.2		17.5		1.6	
27	59.7	25.0	14.9	0.4	SEM	59.7	1.8	24.6	1.7	15.4	1.9	0.4	0.1
					LA-ICP-MS	58.2		25.4		15.4		1.1	
28	59.8	25.0	14.9	0.2	SEM	62.9	1.1	23.5	0.5	13.3	0.8	0.4	0.0
					LA-ICP-MS	61.2		24.8		13.3		0.8	
29	62.9	15.1	22.0	-	SEM	65.4	1.7	12.9	0.8	21.1	2.5	0.7	0.2
					LA-ICP-MS	65.0		13.2		21.1		0.6	

Table 3.6 – SEM-EDX and LA-ICP-MS analysis, on some sample of Glass Experiments A, are compared to verify the reliability of the electron microscope on major and minor elements quantification. For LA-ICP-MS data the standard deviation is not shown because automatically calculated and applied in the quantification programme.

From the time the FAAS analysis furnished a new Chelford sand composition, with 93.6% of SiO_2 all the theoretical composition has been changed and adapted to overcome this little variation. Luckily the goals have been obtained despite this was unknown, and at the end it was just taken note of a new composition.

A particular problem noticed in any sample prepared with Chelford sand is a loss of K_2O% with respect to the theoretical expectations, with a correspondent increasing of SiO_2%. This strange behaviour did not vary the CaO%, making less understandable the causes, perhaps connected with the lack of homogeneity. It was started to be clear only with the last glasses, more homogeneous and comparable each other, before them the attention was focussed mostly on a qualitative good result that could justify a useful group of parameters. In Glass Experiments B this K_2O loss will be studied and some hypothesis will be discussed.

As already described in the instruments and methods chapter, LA-ICP-MS has been used to verify the reliability of SEM-EDX analysis for major and minor elements. This idea started from the systematic difference between theoretical and experimental data concerning the K_2O and SiO_2 concentrations.
Analysis on the first 29 samples have been done and a good matching between the two methods was gained as shown in Table 3.6, where just a group of data is display to represent the general trend. CaO data are the same because this oxide is the internal standard for La-ICP-MS quantification, and the value of concentration used was taken from SEM-EDX analysis.
The linear ablation produced a series of punctual data of concentration for each element, on which a standard deviation was calculated. Data exceeding more or less 10% of the averaged signal were discarded. This proceed is useful to avoid spikes interferences and defines the precision of concentrations.

The new awareness achieved after this first session is surely an important step that sheds a bit more light on the complex glass craft and permits to delineate the future decisions.

3.3.2. GLASS EXPERIMENTS B

This group contains 22 glasses, from S30 to S50 and S55, and seven new heating curves are proposed, some of them with different variations. Inside this group also samples taken from the two types of crucibles were included and the analyses carried out on them before and after use. These analyses were important for some topics that will be dealt in the next paragraphs, e.g. the coloured glasses and the K_2O absorption by the crucible.

Since in Glass Experiments A the best results were achieved with the ratio $2K_2O$: $1CaO$: $4SiO_2$ in combination with the H.C. 16 (group 4; Section 3.3.1.4), for all the glass realised in Glass Experiments B a mixture of initial ingredients was used, that corresponded to this kind of theoretical composition, also when a different sand was used or Na_2CO_3 was mixed with K_2CO_3 as flux agent. In this last case their contributions were summed. Anyway the compositional analysis revealed the effective ratio to be always around 1.5 : 1 : 4, due to the "loss of K_2O" that is discussed more in detail below.

The choice to keep only the group 4 parameters (H.C. 16; Section 3.3.1.4) was due to the lower working temperature at 1250°C and the transparency and homogeneity of most of its samples. A series of challenges needed to be faced in this chapter, all problems observed on Glass Experiments A samples, but not connected with the achievement of a glassy material. For example, all group 4 samples had cracks, but these did not influence the homogeneity and the transparency of the glass, nor did the presence of gas bubbles. Anyway, these effects, as others, were studied and it has been tried to control by observing the ancient techniques and finding experimental solutions. The principal scope was to understand the causes and, when it was possible, intervene.

Tables 3.7 and 3.8 summarise the information for each sample of Glass Experiment B. In this set also Na_2CO_3 and Na_2O are counted because it has been experimented a mixture of alkali sources.

3.3.2.1. Cracking

It was plausible to identify the thermal dilatation of the porcelain crucible as the cause for the glass cracking during the cooling down of the oven, because all samples of group 4 have been realised in this kind of crucible, while with SiC crucibles the cracking effect was almost never present. For this reason, and also for a matter of availability, from S30 to S36, SiC crucibles were employed.

Two ways to reduce cracking were selected: on one hand the annealing temperature was increased from 500°C (H.C. 16) to 800°C for 5 hours in order to be closer to the melting temperature and to reduce the thermal stress; on the other hand the crucible type was changed. Sample S33 was conducted with H.C. 16, whereas S30 was made using the higher annealing temperature and in a SiC crucible. In both cases the cracking effect was no longer present, but new problem surface, i.e. the fact that the resulting glass was

coloured (Figure 3.9, left): well melted pieces of brownish glass with many little bubbles inside were produced.

Nevertheless, the annealing temperature of 800°C was maintained in the next heating curves.

Figure 3.9 – Picture of S30 (left) and S40 (right). The first shows a brownish colour caused by Fe contamination of the glass coming from SiC crucible; the second has many cracks due to the porcelain crucible, but it is very transparent and almost without bubbles, because produced by fritting the material of S37.

A group of samples, S38 to S42, was synthesised in porcelain crucibles using two heating curves, H.C. 19 and H.C. 20, in which two annealing steps were introduced: the first at 1000°C for 5 hours, the second at 500°C (H.C. 19) or 800°C (H.C. 20) for 5 hours. The principal aim of these experiments was to study the variation of K_2O%, and in parallel observe the cracking, with the hope that a longer cooling down period reduced as much as possible the thermal stress of porcelain. Unfortunately, no effective differences were observed between experiments involving one annealing step and experiments using two annealing steps (Figure 3.9, right); however, if the cracking thickness is of the order of few microns, there are no problems with the analysis. Both SEM-EDX and LA-ICP-MS instruments have the possibility to observe the surface; therefore, it was possible to select the most appropriate points for analysis, so that heterogeneities, bubbles and also cracks can be avoided.

3.3.2.2. Colours

New heating curve number 17 involved pre-heating at 800°C for 1 hour, melting at 1250°C and annealing at 800°C for 5 hour; it was used with five different melting times (1, 2, 10, 15, 25 hours). These variants were tested in order to understand first, the origin of the colouring, and second, to verify whether or not this parameter was correlated with the amount of gas bubbles formed in the glass.

The five resulting glass showed different colours passing from yellow-brownish (shortest melting time) to blue-greenish (longest) (Appendix B); moreover the surface in contact with the SiC crucible was not separated from the crucible itself anymore, but part of the SiC material remained firmly attached to the glass. Therefore a contamination from the crucible was considered to be plausible, probably of Fe, because

the observed colours could correspond to FeO (brown-yellow) and Fe_2O_3 (blue-gree) [4]. SEM-EDX analysis of glass demonstrated the presence of Fe, which even at a low concentration can change the colour of the glass (Figure 3.10).

Figure 3.10 – Pictures of S31 (left) and S34 (right). The first with a bluish colour and bubbles on the top layer, the second greenish and melted at higher temperature (1450°C), that provoked the firm adhesion of pieces of crucible inside the glass.

SEM-EDX analysis conducted on SiC crucible samples could effectively explain the Fe contamination. A new (i.e. unused) SiC crucible contains 2.6% m/m iron (probably as Fe_2O_3); while, after melting a remainder of 1% m/m Fe_2O_3 was detected. Also from a qualitative point of view the passing of iron from the crucible to the glass could be verified: when Fe was present in the crucible from the beginning, a coloured glass was obtained, with the colour related to the presence of iron oxides. After melting the crucible always appeared damaged and particles of its surface were visible on the glass surface and sometimes inside the glass itself (Figure 3.10, right). When a porcelain crucible was used in the last experiment of this series (S37 with H.C. 17(1)), the resulting glass was colourless.

Because the Glass Experiments A samples, also realised in SiC crucibles, featured different other problems (e.g. incomplete melting, opacity, etc.), the colours of the glass were not so evident.

In the middle of this series, an experiment at higher melting temperature was performed to see if the contamination by the crucible could be removed by heating: in H.C. 18, a melting temperature of 1450°C was reached for 2 hours, but nothing more than more important damage to the crucible and a larger number of crucible inclusions inside the glass were observed (Figure 3.10, right).

From S37 till S57, in which highest temperatures than 1250°C were not used, porcelain crucible were again used.

	Ingredients [g] Room Temperature				Ingredients [g] High Temperature							
Nr.	**SAND***	**K_2CO_3**	**$CaCO_3$**	**Na_2CO_3**	**SiO_2**	**K_2O**	**CaO**	**Na_2O**	**Minor**	**CRUC.**	**H. C.**	**OBSERVATIONS**
30	24.5	15.4	11.0	-	22.9	11.8	6.1	-	0.7	SiC	17(1)	good glass, thicker than others, brownish, little bubbles inside
31	24.7	15.4	11.0	-	23.1	11.8	6.2	-	0.7	SiC	17(2)	good glass, thicker than others, greenish, bubbles
32	27.7	16.9	11.9	-	25.9	13.0	6.7	-	0.7	SiC	17(3)	good glass, good resistance, brownish, little bubbles, thin green-transparent layer
33	27.9	17.3	12.0	-	26.1	13.3	6.7	-	0.8	SiC	16	good glass, brownish color, little bubbles inside, on the surface greenish-transparent parts
34	24.5	15.4	11.0	-	22.9	11.8	6.2	-	0.7	SiC	18	good glass, greenish, bubbles and particles from the crucible, really ruined crucible
35	24.7	15.5	11.0	-	23.2	11.9	6.2	-	0.7	SiC	17(4)	good greenish glass, well-melted, bubbles on the top
36	24.7	15.5	11.0	-	23.1	11.9	6.2	-	0.7	SiC	17(5)	good greenish well-melted glass, bubbles on the top, more transparent in the edge with the crucible
37	12.4	7.8	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	17(1)	transparent glass, cracking, some bubbles
38	12.4	7.8	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	19	transparent glass, cracking, some bubbles
39	12.4	7.8	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	20	transparent glass, cracking, some bubbles
40	12.4	7.8	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	20	11.8 g of S37 ball milled; transparent bluish glass, well melted, no bubbles
41	12.4	7.8	5.5	-	12.3	5.3	3.1	-	0.1	Porcel.	20	Dessel Sand, transparent glass, cracks and bubbles
42	12.5	7.8	5.5	-	12.5	5.3	3.1	-	0.0	Porcel.	20	Lommel Sand; transparent melted glass, cracks and bubbles
43	12.4	7.9	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	21	transparent melted glass, cracks; many bubbles
Porc. Cr.	Porcelain crucible of S37, S38, S39 has been analysed to estimate to K% inside the material; the results are an average of the results of these 3 sample											
Porc. Cr.	a fragment of new crucible is analysed along the cross section: no particular differences; quantify data are affected by a low Ctot											
SiC Cr.	a fragment of new crucible is analysed along the cross section: no particular differences; quantify data are affected by a low Ctot											
44	12.1	3.5	5.3	4.9	11.4	3.1	3.0	2.9	0.3	Porcel.	17(4)	transparent melted glass; cracks, no many bubbles; brittle
45	12.1	2.0	5.2	6.5	11.4	2.0	2.9	3.8	0.3	Porcel.	17(4)	transparent melted glass; cracks, no many bubbles; brittle; a bit bluish
46	12.4	0.5	5.0	8.3	11.6	1.0	2.8	4.8	0.3	Porcel.	17(4)	bluish well melted glass, no bubbles, cracks, transparent
47	12.4	7.8	5.5	-	11.6	6.0	3.1	-	0.3	Porcel.	22	no glass formed; frit done and another experiment launched, but no glass resulted
48	12.2	2.1	5.3	6.5	12.1	1.4	2.9	3.8	0.1	Porcel.	17(4)	Dessel Sand; transparent well melted glass; cracks and no bubbles
49	12.1	2.4	5.3	6.6	12.1	1.6	2.9	3.8	0.0	Porcel.	17(4)	Lommel Sand; transparent well melted glass, cracks and no bubbles
50	12.2	2.1	5.2	6.5	11.4	2.1	2.9	3.8	0.3	Porcel.	22	no glass formed; frit done and another experiment launched, but no glass resulted
55	6.2	3.9	2.8	-	5.8	3.0	1.5	-	0.2	Pt	17(4)	Very good glass; few bubbles, transparent, no cracks

Table 3.7 - Glass Experiments B data: initial ingredients [g] and relative products after melting [g], type of crucible, heating curve and some observations for each sample.

	Theoretical % [%m/m]					Actual % [%m/m]									
Nr.	**SiO_2**	**K_2O**	**CaO**	**Na_2O**	**Minor**	**SiO_2**	**Std.Dev.**	**K_2O**	**Std.Dev.**	**CaO**	**Std.Dev.**	**Na_2O**	**Std.Dev.**	**Minor**	**Std.Dev**
30	55.1	28.5	14.8	-	1.6	61.7	1.2	22.6	0.9	13.9	1.2	-	-	1.7	0.5
31	55.3	28.3	14.7	-	1.6	62.1	0.5	21.2	0.8	14.7	0.5	-	-	2.1	0.2
32	55.9	28.1	14.4	-	1.6	61.1	0.9	22.6	0.9	15.1	0.9	-	-	1.2	0.2
33	55.7	28.4	14.3	-	1.6	60.4	0.5	23.2	0.8	14.7	1.2	-	-	1.6	0.4
34	55.1	28.5	14.8	-	1.6	62.5	0.6	21.5	0.3	14.0	0.8	-	-	2.1	0.3
35	55.3	28.4	14.7	-	1.6	63.3	0.5	20.3	0.4	13.8	0.5	-	-	2.7	0.5
36	55.3	28.4	14.7	-	1.6	64.3	0.2	19.2	0.3	13.8	0.2	-	-	2.7	0.2
37	55.2	28.5	14.7	-	1.6	60.6	0.7	23.0	0.3	15.1	0.8	-	-	1.3	0.2
38	55.2	28.5	14.7	-	1.6	58.9	0.9	22.8	0.3	16.2	1.3	-	-	2.1	0.2
39	55.2	28.5	14.7	-	1.6	58.8	0.3	24.0	0.2	16.2	0.4	-	-	1.0	0.2
40	55.2	28.5	14.7	-	1.6	61.2	0.1	22.5	0.2	15.1	0.2	-	-	1.3	0.3
41	59.3	25.5	14.8	-	0.4	58.9	0.2	24.8	0.5	15.1	0.5	-	-	1.2	0.2
42	59.5	25.5	14.8	-	0.2	59.7	0.5	24.0	0.3	15.5	0.5	-	-	0.8	0.3
43	55.1	28.6	14.7	-	1.6	58.1	0.7	24.2	0.3	16.3	0.5	-	-	1.3	0.1
Porc.	-	-	-	-	-	62.9	1.3	4.6	0.2	0.7	0.1	-	-	31.7	1.5
Porc.	-	-	-	-	-	64.5	0.5	3.8	0.2	0.8	0.1	-	-	30.9	0.3
SiC	-	-	-	-	-	72.8	1.9	1.5	0.4	0.5	0.1	-	-	25.3	1.6
44	55.2	14.9	14.5	13.9	1.6	61.0	1.1	10.1	0.5	15.1	1.1	11.9	0.4	1.9	0.5
45	55.7	9.9	14.3	18.5	1.6	64.9	0.5	6.9	0.2	10.7	0.5	16.1	0.2	1.5	0.2
46	56.4	5.0	13.6	23.4	1.6	59.2	0.4	2.4	0.1	12.3	0.5	22.6	0.5	3.5	0.7
47	55.2	28.5	14.7	-	1.6	no analysis because no glass formed during the experiments									
48	59.6	6.9	14.5	18.7	0.4	60.6	0.3	5.5	0.1	15.1	0.3	17.6	0.5	1.2	0.3
49	59.0	7.9	14.3	18.6	0.2	60.6	0.6	5.7	0.2	14.1	0.7	17.5	0.6	2.2	0.5
50	55.7	10.1	14.3	18.4	1.6	no analysis because no glass formed during the experiments									
55	55.2	28.5	14.7	-	1.6	61.2	1.7	22.3	0.3	15.4	2.1	-	-	1.1	0.2

Table 3.8 – Glass Experiments B data: theoretical glass composition [%m/m] and actual one analysed by SEM-EDX [%m/m] with relative standard deviation [%m/m] for each sample.

3.3.2.3. Eliminating gas bubbles

The heating curves 17(1), (2), (3), (4) and (5) were also of interest with the context of decreasing the amount of bubbles in the glass. The bubbling behaviour was studied by considering glass cross-sections; the direction of the flow of the bubbles was visible from the bottom to the upper layer (Figure 3.10, left): with the first two heating curves, this movement was not so evident, because they differed just by one hour of melting, but in the other three heating curves (10, 15, 25 hours of melting) the amount of bubbles significantly decreased and the remaining ones were more concentrated in the top layer (Appendix B). Thus, it can be concluded that by using a higher melting time, it will be possible to reach a glass without bubbles; whether such an extended time is compatible with the crucible lifetime or with the oven, is not clear.

In former times, these bubbles were eliminated by fritting the glass, one or several times, so that the carbonates (or other source of gas evolution such as sulphates and nitrates) were totally consumed [5][11]. An experiment involving fritting was performed to verify this process.

Part of the glass of S37 was ground by ball milling (MP100 instrument, 250rpm speed, 3 min time) and the glass prepared from this powder, S40, appeared to be without bubbles. Since the cleaning process of the grinding machine is long and may not allow avoiding contamination from the previous grinding, and also the presence of bubbles into the glass only changes the aesthetic qualities and not its composition, no other frits experiments were carried out. Nevertheless, this experiment allowed confirming the possibility of removing gas bubbles from the glass by fritting. Moreover, since most of gas bubbles originated from the use of K- and Ca-carbonates as starting ingredients, it is expected that once beech ash will replace K_2CO_3, carbonates effect will decrease.

Glasses produced from a mixture of Na_2CO_3 and K_2CO_3 featured a lower presence, or almost absence, of bubbles. This type of glasses is discussed in the next paragraph on mixed alkali glass.

3.3.2.4. Mixed alkali glass

A set of six experiments (S44, S45, S46, S48, S49 and S50) were prepared to verify the feasibility of the use of mixed flux agents; the properties of the resulting glasses were compared to those of potash glass [12][26]. These six experiments were produced from Na_2CO_3 and K_2CO_3 and contain different Na_2O and K_2O ratios; normally this ratio depending on the ash provenance (type of wood, type of soil, geographical region ...). In the first three samples (S44, S45 and S46) different ratios K_2O : Na_2O were tried, 1 : 1 (S44), 1 : 2 (S45), 1 : 5 (S46), whereas the heating curve was always number 17(4). The three resulting glasses were well melted and transparent with less bubbles than in the case where no Na_2CO_3 was used (Figure 3.11, left).

Figure 3.11 – Pictures of S46 (left) and S47(2) (right). The first, with a higher Na_2O content, has almost no bubbles, the second has been melted at 1000°C after fritting and no glass is obtained.

The alkali composition and heating curve of S45 was used again to produce two glasses with Dessel (S48) and Lommel (S49) sands, comparable to the other 4 experiments executed with these sands (S27, S28, S41 and S42).

A mixed Na_2CO_3/K_2CO_3 glass was melted at lower temperature (1000°C) by using H.C. 22, and together with another sample, rich only in K_2O, was prepared to investigate the possibility of using milder working conditions correlated to repeated melting processes. S47 and S50 were glasses prepared in a two-step procedure: after the first melting, a frit was prepared and re-melted with a heating curve that heats until 1000°C for 15 hours (always H.C. 22). After the first step, a crystalline material was formed that remained after the second step; after the second step the resulting material, however, was more transparent than before (Figure 3.11, right). Probably after several of such fitting and re-melting steps, it is possible to gain glass. In view of the limited amount of materials with which this experiment was started, it was not possible to continue this line of experiments.
This could be an interesting direction to investigate further in the future, because it may explain how glass could make at lower temperatures in former periods.

In what follows, attention is given to the unexpected and not completely understood behaviour of K_2O during the glass making. As mentioned already in Glass Experiments A, from the moment a series of glasses comparable to each other was produced, a discrepancy of 5-6% m/m in their K_2O and SiO_2 contents was observed, between the theoretical and experimental composition. The K_2O concentration showed a loss while SiO_2 gains in concentration. In terms of relative concentration, there was a change from 2 : 1 : 4 to 1.5 : 1 : 4 for the K_2O : CaO : SiO_2 ratio. In Glass Experiments B this trend was more evident because all the glass

produced were well melted and has a good transparency, even if coloured, and always the same ratios were used between flux agent, stabiliser and sand components.

Below, two possible explanations for the loss of material are investigated: K_2O absorption by the crucible and volatilisation of the alkali.

3.3.2.5. Loss of K_2O by absorption

From the beginning an exchange of materials between glass and crucible has been assumed because both for the SiC and the porcelain crucibles, the loss of K_2O was obvious; SEM-EDX analysis and imaging of the crucible-glass interface displayed a separation between the two parts that was not very well defined (Figure 3.12).

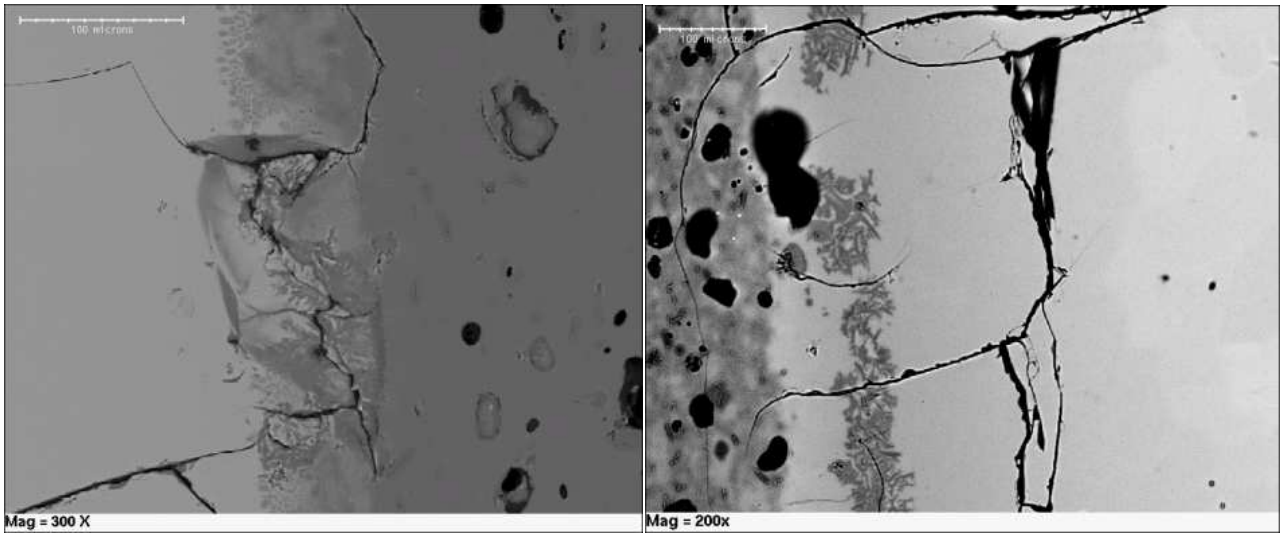
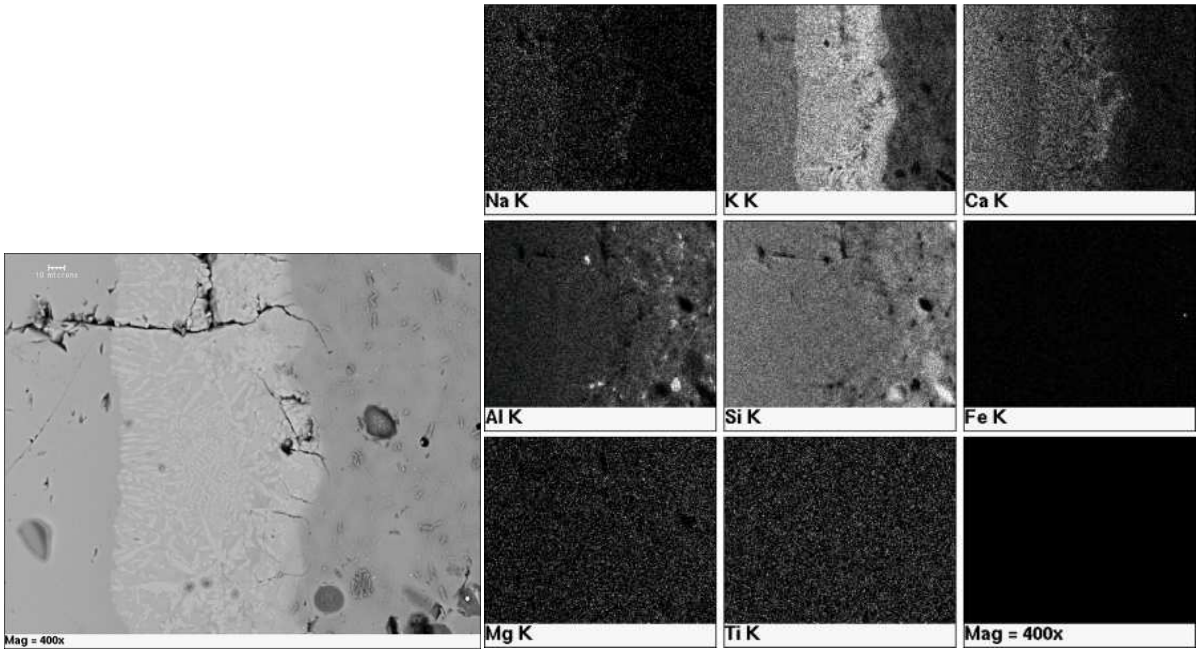


Figure 3.12 – BEI images by SEM-EDX of S41, magnification 200x (left), and S48, magnification 200x (right). In both cases the dark side is the porcelain crucible and the light part is the glass: cracks from the glass pass through to the crucible material. There is not clearly defined interface between both materials.

SEM-EDX BEI images conducted on the border between the porcelain crucible and the glass melted inside it showed several cracks passing from one to the other phase; sometime they also showed a clear intermediate layer richer in K_2O and Al_2O_3 than the glass itself (Figures 3.12 and 3.13). While Al_2O_3 was surely coming from the crucible matrix, the K_2O must originate from the molten glass. The top layers of (unused) porcelain crucibles have been analysed and it has been detected a K_2O concentration of 3.8% that increases to 5.3% after be used. On the other hand, the glass layers in contact with the crucible often contained a higher Al_2O_3 concentration than the rest of the glass body.

In Figure 3.13 the presence of an intermediate layer between glass and crucible, rich in K_2O, as the maps show, allowed to estimate the amount of material absorbed by the crucible. Since Si and Ca were also present (although at lower concentration), this layer was considered to have the same density as float glass (d=2.5 g/cm^3). Glass S44 differs scarcely in composition from float glass (Table 3.9).

The porcelain crucible was approximated to have a cylindrical shape so that the areas of the base and the wall covered by the molten material during the glassmaking (respectively A_{BASE} and A_{WALL}) could be calculated as a function of the cylinder radius r (2.5 cm). During the melting process the molten volume increased until it was more or less 4 cm high inside the crucible; thus A_{WALL} was the circumference multiplied with this height. The layer thickness l was set to be approximately 100 µm (Figure 3.13 (left)) or 0.01 cm.



Figures 3.13 – Backscattering image (left) and maps (right) of S44, magnification 400x. On the right side of every picture is the crucible, on the left glass and in between a layer rich in K. The maps are taken on the K_α lines of Na, K, Ca, Al, Si, Fe, Mg, Ti. The size bar is 10 µm, thus the K_2O rich intermediate layer is estimated to be almost 100 µm in thickness.

	FLOAT glass % [%m/m]	S44 values [%m/m]
SiO_2	68.0-74.5%	61.0%
$K_2O + Na_2O$	10.0-20.0%	22.0%
CaO	9.0-14.0%	15.1%
Minor	0.0-8.7%	1.9%

Table 3.9 – FLOAT glass general values are compared with S44 compositional values. FLOAT data are obtained [32].

Another parameter was the K_2O concentration of the material in the intermediate layer, as determined by SEM-EDX to be 21.3%. Finally, the K_2O molar mass (MM=94.2 g/mol) was used to convert to moles.

$$\boldsymbol{mol\, K_2O_{LAYER}} = \frac{[\boldsymbol{A_{BASE}} + \boldsymbol{A_{WALL}}] * \boldsymbol{l_{LAYER}} * \boldsymbol{d_{FLOAT}} * \boldsymbol{K_2O}\%}{\boldsymbol{MM_{K_2O}}}$$

Thus:

$$\boldsymbol{mol\ K_2O_{LAYER}} = \frac{[(\boldsymbol{\pi r^2}) + \ \boldsymbol{4} * (\boldsymbol{2\pi r})] * \ \boldsymbol{0.01} * \boldsymbol{2.5} * \ \boldsymbol{21.3}}{\boldsymbol{94.2}} \ = \boldsymbol{0.005\ mol}$$

This result (0.005 mol) must be compared with the amount of lost material analysed by SEM-EDX. In the experiment S44 the differences between the theoretical and the experimental concentration values were 6.7% for K_2O and 5.8% for SiO_2. To simplify the calculation it was decided to use the average 6.3% m/m between these two values (see Table 3.13). This figure represented the amount of lost material analysed by SEM-EDX, but must be converted to moles. In the conversion, the glass mass of experiment S44 (20.6 g) (see Table 3.7) and the molecular mass of K_2O (MM=94.2 g/mol) were used. This was an approximation, because it assumed that K_2O was the only material that is lost.

$$mol\ K_2O = \frac{Loss\% \ * \ glass\ mass}{MM_{K_2O}} = \frac{6.3\% * 20.6g}{94.2} = 0.01\ mol$$

The final value (0.01 mol) was the double of the quantity of material absorbed by the crucible and previously calculated (0.005 mol). Despite the fact that these values were approximate, the ratio of absorbed K_2O/lost K_2O (0.005/0.01) indicated that not all the lost K_2O was absorbed and that other causes were involved.

Figure 3.14 – Picture of S55, glass made into Pt crucible.

Since crucible materials were observed to interact in unwanted manners with the glass melt during the melting process, the availability of a Pt crucible was exploited to verify if indeed the type of crucible influenced the K_2O loss. In experiment S55 the loss of material was tested in a Pt crucible by employing H.C. 17(4) and a 2 : 1 : 4 compositional of K_2O : CaO : SiO_2. Unfortunately, also in this case, SEM-EDX analysis confirmed the discrepancy between the actual composition and what it was expected to find, being a loss of 5-6% of K_2O. A positive note was the qualitative aspect of this sample, very transparent and

homogeneous, despite the higher thickness due to the smaller dimension of the Pt crucible, without cracking and with just a few quite large bubbles (Figure 3.14).

3.3.2.6. Loss of K_2O by volatilisation

In parallel to the above experiments, another hypothesis was taken in consideration to explain the K_2O behaviour. In the literature the alkali content of glasses may be reduced by simply heating the glass itself a second time or during the annealing step; this decrease is explained by the volatilisation of the alkali from the glass structure [33][34][35][36][37].

			Theoretical % [m/m]				Actual % [m/m]							
H.C. 17	Melting time [h]	Nr.	SiO_2	K_2O	CaO	Minor	SiO_2	Std.Dev.	K_2O	Std.Dev.	CaO	Std.Dev.	Minor	Std.Dev
3	1	32	55.9	28.1	14.4	1.6	61.1	0.9	22.6	0.9	15.1	0.9	1.2	0.2
1	2	30	55.1	28.5	14.8	1.6	61.7	1.2	22.6	0.9	13.9	1.2	1.7	0.5
2	10	31	55.3	28.3	14.7	1.6	62.1	0.5	21.2	0.8	14.7	0.5	2.1	0.2
4	15	35	55.3	28.4	14.7	1.6	63.3	0.5	20.3	0.4	13.8	0.5	2.7	0.5
5	25	36	55.3	28.4	14.7	1.6	64.3	0.2	19.2	0.3	13.8	0.2	2.7	0.2

Table 3.10 – Series of 5 heating curves related to number 17, with different melting times.

In effect, glasses obtained via similar heating curves but with different melting times showed a variation in composition that influenced the discrepancy of 5-6% of lost material. The discrepancy between actual and theoretical K_2O and SiO_2 concentrations increased slightly with longer melting time. After 25 hours of melting, the actual K_2O concentration was almost 3% lower than after only 1 hour of melting; the SiO_2% concentration was almost 3% higher after 25 hours, so the discrepancy increased from 5-6% to almost 9% m/m (Table 3.10).

The glass S43 needed to be considered, obtained with a single, as fast as possible cooling down step (H.C. 21). The discrepancy was expected to be less large in this glass and to become larger with glass synthesised with a longer annealing time.

The data shown in Table 3.11 appear to confirm this for the S43 material: the differences between theoretical and analysed concentrations of K_2O and SiO_2 are almost 4% and not anymore as high as 5-6%.

In Table 3.11 the data of experiments S37 and S39 are also shown. The first was synthesised with H.C. 17(1) with one annealing step (800°C for 5 hours), the second was synthesised with H.C. 21 with two 5 hours annealing steps (at 1000°C and 800°C). Thus the discrepancy was expected to increase with S39; however, it became smaller.

		Theoretical % [%m/m]				Actual % [%m/m]							
Nr.	**H. C.**	**SiO_2**	**K_2O**	**CaO**	**Minor**	**SiO_2**	**Std.Dev.**	**K_2O**	**Std.Dev.**	**CaO**	**Std.Dev.**	**Minor**	**Std.Dev.**
37	17(1)	55.2	28.5	14.7	1.6	60.6	0.7	23.0	0.3	15.1	0.8	1.3	0.2
39	20	55.2	28.5	14.7	1.6	58.8	0.3	24.0	0.2	16.2	0.4	1.0	0.2
43	21	55.1	28.6	14.7	1.6	58.1	0.7	24.2	0.3	16.3	0.5	1.3	0.1

Table 3.11 – Some samples prepared with different annealing steps inside the heating curves.

Since from the compositional analysis of the glass it appeared difficult to recognise and estimate if a loss of material took place during the melting process, a set of Thermo-Gravimetric Analysis (TGA) was performed. The aim was to monitor the same heating curve used to produce a glass from the thermo-gravimetric point of view: every loss of material was recorded, including the amount lost and the temperature at which every process happens. All these data are displayed in a thermo-gravimetric curve.

The TA instrument can work up to 1000°C; this implies that the melting temperature of most heating curves, 1250°C, could not be reached. This parameter could influence negatively the analysis, because the two glasses realised with H.C. 22, with melting temperature at 1000°C, did not produce glass. It is also true that the decomposition of the carbonates was expected to take place before 1000°C, and if any other loss happened inside the oven, it would be visible in the thermo-gravimetric curve. Unfortunately the TA instrument was not connected to any detector for qualitative analysis of the volatile phases; therefore the considerations given below are only based on the mass loss and the temperatures at which this occurs.

As first mass loss step, the evaporation of water was observed at low temperatures, between 100-200°C, despite all the ingredients being dried in an oven at 40°C for at least one day. The second mass loss could be associated with the evolution of CO_2 generated during the decomposition of K- and Ca-carbonates. The K_2CO_3 decomposition was expected at 891°C and that of $CaCO_3$ at 825°C. Since these compounds and the sand were involved in a fusing process during the melting, in reality a drop relative to these tabulated temperatures was expected. Thus the matching of the observed mass loss steps with the corresponding substances was more difficult.

From the information found [36], the annealing step should be responsible for a possible loss of alkali; however, in every TGA curved recorded, after the step at 1000°C no other loss events were visible. Hence this kind of volatilisation, if it was real, had to take place during the previous steps of the heating curve.

The amount of carbonates present could be calculated from the quantity of initial ingredients, since the TGA instrument gave values in %weight; in Table 3.12 the theoretical data of CO_2 are worked out.

Two analyses were performed with a selected mixture of ingredients to observe separately the behaviour of K_2CO_3 and $CaCO_3$: TGA4 with Chelford sand and $CaCO_3$ and TGA5 with Chelford sand and K_2CO_3.

	mass [g]			Theoretical CO_2% [%m/m.]		
Nr. TGA	**Chelford Sand**	**K_2CO_3**	**$CaCO_3$**	**K - %CO_2**	**Ca - %CO_2**	**Tot - %CO_2**
1	12.4	7.8	5.5	9.7	9.4	19.1
2	2.5	2.0	0.5	12.9	4.3	17.2
3	Only Chelford Sand			-	-	-
4	2.5	-	2.0	-	19.5	19.5
5	2.5	2.1	-	20.0	-	20.0

Table 3.12 – For each TGA graph, the mass [g] of the three ingredients and the theoretical CO_2 percentage [%m/m] is shown, coming from the decomposition of, respectively, K-, Ca-carbonates and their sum.

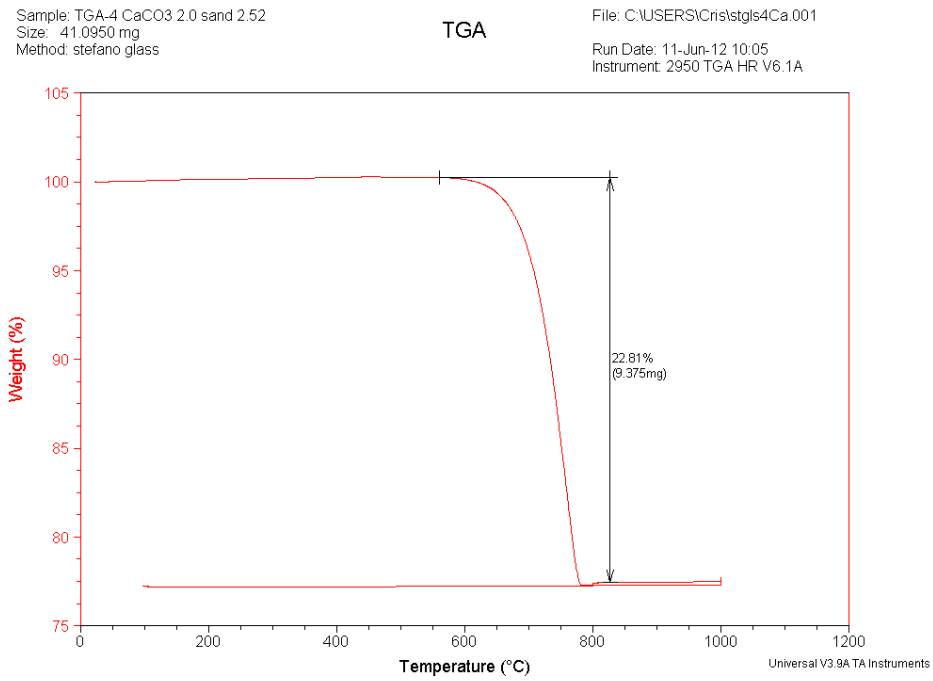


Figure 3.15 – Graphical display of the TGA4 experiment.

For TGA4 (Figure 3.14) the main mass loss event took place between 600 and 800°C, corresponding to a mass loss of 22.8%, close to the value of 19.5% calculated from the initial ingredients (Table 3.12). The 3% in excess could be due to stoichiometric water. For TGA5 (Figure 3.16) the main mass loss event took place at 800°C, and corresponded to a loss of 10.2%, almost the half of the amount of CO_2 (20.0%) calculated in Table 3.12. This incoherence was hardly explainable, unless the presence of sand caused a delay in K_2CO_3 melting, or trapped the CO_2 inside the structure of the future glass. In the first case the impossibility to exceed 1000°C did not permit to observe the complete reaction of the melt; in the second case it could be justified by the difficulties of removing gas bubbles from the glass.

A third experiment, TGA3, on Chelford sand only, was performed to verify the possible presence of volatile compounds in the sand itself, or a certain presence of water, but the designed curve did not show any of these possibilities, therefore every volatile came from another source.

In TGA1 (Figure 3.17) an experiment with the three glass components in a ratio similar to the one used in Glass Experiments B was performed; the resulting curve displayed 4 steps after a first mass loss step at 100-200°C, related to adsorbed water. The total loss in weight was almost the double of the expected CO_2 mass calculated from the initial ingredients' mixture (Table 3.12).

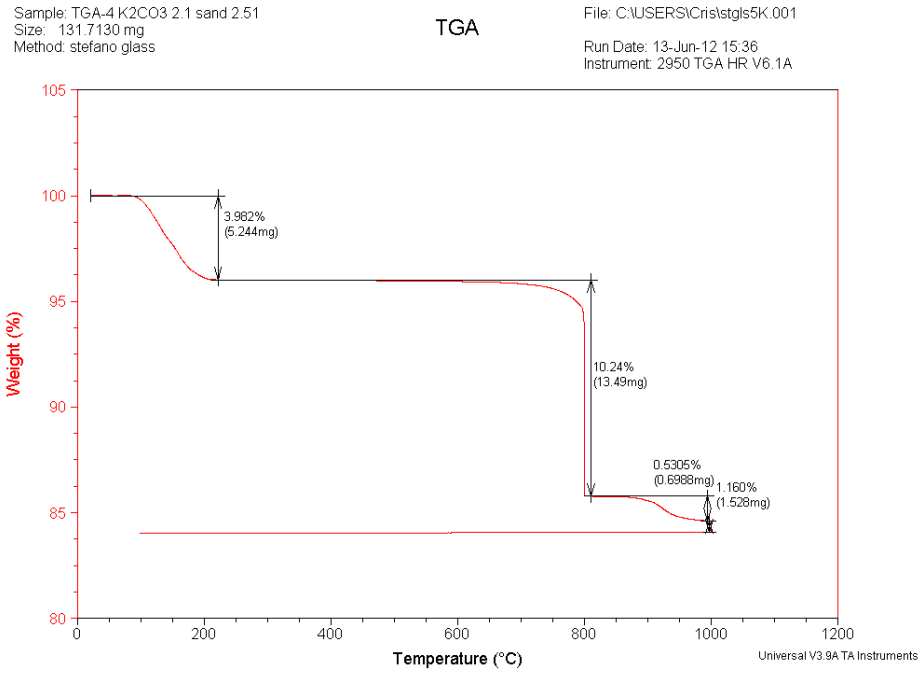


Figure 3.16 – Graphical display of the TGA5 experiment.

Taken together, the first two mass loss steps corresponded to a mass loss of 18.3%, close to the calculated total CO_2 value of 19.1%, with the first step corresponding to $CaCO_3$ and the second to K_2CO_3. The mass loss events in TGA4 and TGA5 occurred before 800°C and their shapes were similar to the first two in TGA1: starting from 600°C and going slower for $CaCO_3$, starting from 720-740°C and more steep for K_2CO_3. There was a problem with the relative amount of lost material, because the TGA1 assigned a higher amount to the first step and a lower one to the second step: 10.7% and 7.5% instead of 9.4% and 9.7%, values calculated from the initial mixture of ingredients (Table 3.12). To explain this, on the one hand it could be assumed that part of the CO_2 from K_2CO_3 began to form at lower temperatures together with Ca carbonate while, on the other hand, the CO_2 emission from K_2CO_3 could be delayed as in TGA5. Thus it was expected

to obtain half of the calculated value of 9.7% (Table 3.12), as the behaviour observed in TGA5; instead the mass loss was 7.5%.

The third slope had a mass loss corresponding to 5-6%, similar to the loss of K_2O analysed in the glass experiments; further consideration about it will be given together with the results of the following TGA (Figure 3.18). The fourth slope had a cut shape due to the oven limit of 1000°C, so it was not really clear how rapidly the last loss happened, because the heating curve stayed at 1000°C for 15 hours.

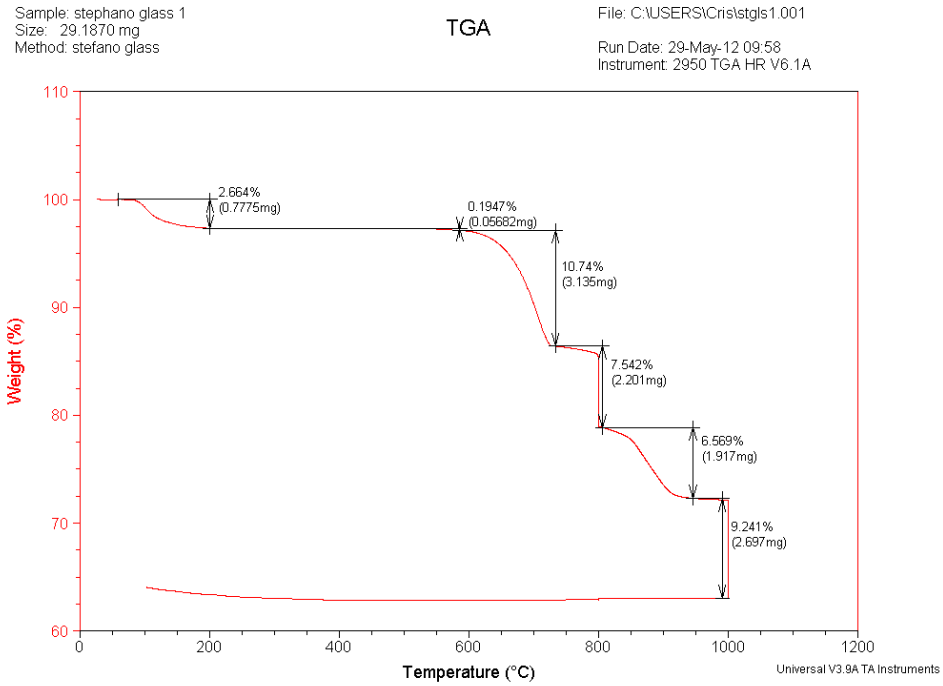


Figure 3.17 – Graphical display of the TGA1 experiment.

On the basis of these observations, some hypotheses could be formulated about the third and the fourth slopes. One hypothesis was to assume the presence of stoichiometric water in K_2CO_3, $CaCO_3$ and/or SiO_2, but in effect TGA3, TGA4 and TGA5 curves did not display any additional mass loss events. The other hypothesis was to assume the volatilisation of some other compounds such as K_2O.

A fifth analysis, TGA2 was conducted to understand the CO_2 contribution originated from K_2CO_3 and $CaCO_3$; this was done by changing the ratio of ingredients to $4K_2O$: 1CaO : $5SiO_2$ (Table 3.12). In the flow of the previous considerations the first slope fitted with the mass loss of CO_2 calculated for $CaCO_3$, the second could be explained as before, with a mass loss half than the expected for the CO_2 coming from K_2CO_3. The fourth slope had the same problem seen in TGA1, even if the mass loss was inferior. The third was for sure linked with the new ratio in favour of K_2CO_3, because it showed a higher amount of lost material. Thus a relation was investigated between the loss of K_2O of 5-6%, systematically recorded in many glass experiments, and the third mass losses observed in TGA1 and TGA2, respectively 6.6% and 10.4%. Since in

these experiments K_2O was produced only by K_2CO_3, it has been tried to refer the losses only to the mass of K_2CO_3 and not to the total mass of ingredients (Table 3.13).

First, the total mass of ingredients (Chelford sand, K_2CO_3, $CacO_3$ and Na_2CO_3) of some synthesised glasses was calculated. Second, the discrepancies between theoretical and actual concentration of SiO_2 and K_2O were displayed and their averages were calculated. Then, the mass of lost material was estimated by multiplying the average value with the total mass of ingredients of each glass. The last column in Table 3.13 displays the losses of K_2O related to the mass of K_2CO_3 (in %m/m) for each glass and, at the end of the column, the averaged value. This is 19.2%, thus almost 20% of K_2CO_3 was transformed and lost as K_2O during the glass synthesis.

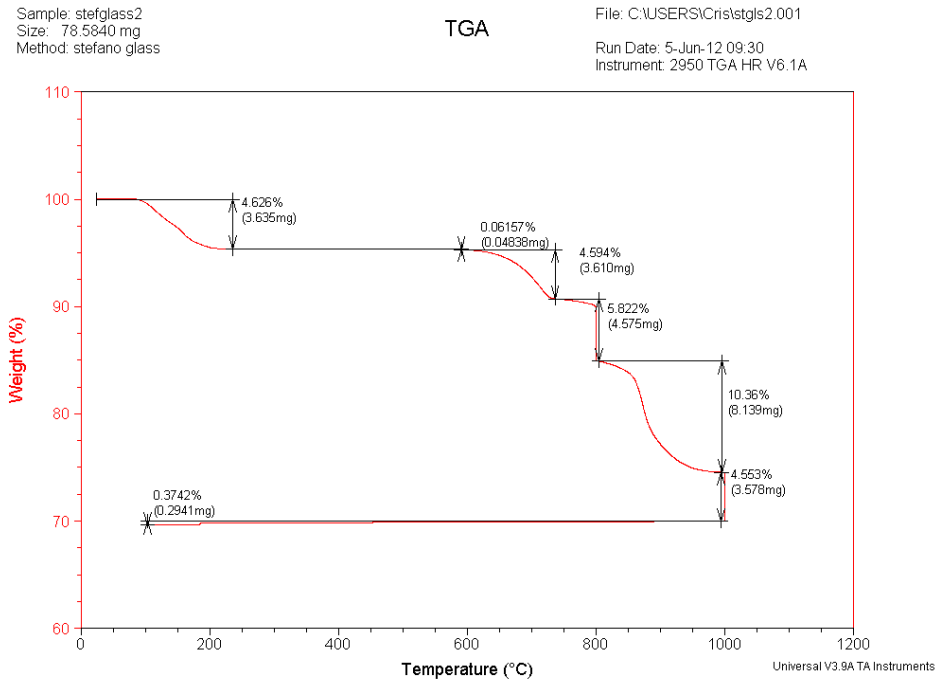


Figure 3.18 – Graphical display of the TGA2 experiment.

On the other hand, the same consideration must be done for the third mass losses observed in TGA1 and TGA2, respectively 6.6% and 10.4%. These values are referred to the total mass of ingredients (25.7 and 5.0 g) used in the two TG analyses. When the values only refer to K_2CO_3 masses (7.0 and 2 g) they correspond respectively to 21.7% and 25.7% of loss.

These values are comparable with the averaged value 19.2% of loss of K_2O in glass experiments. Although in most of them the loss is close to the average 19.2%, the extreme values are 9.1% and 30.3%. The lowest extreme was obtained with S46, synthesised from a mix of alkali, with higher Na_2CO_3 amount than K_2CO_3. The highest extreme was with the experiment S36, where it was used the longest melting time of 25 hours.

It can be concluded that many factors can influence (in both directions) the amount of volatilised K_2O and future investigations will need to be conducted to explore them in greater detail. For the aim of the present work, the fact that it is possible to demonstrate in a qualitative manner that volatilisation of K_2O effectively takes place, is considered sufficient.

Other four glasses were produced with Dessel and Lommel sands, two per type of sand. The first pair were synthesised with H.C. 20 parameters, containing two annealing steps; the second pair with a mixture of the fluxing agents K_2CO_3 and Na_2CO_3. In general, the glasses synthesised with Dessel and Lommel sands showed a better compositional match between actual and theoretical values than the glasses synthesised, in the same conditions, with Chelford sand. Further considerations will be drawn in the following chapter dealing with raw materials, in which glass is made with beech ash.

	Initial ingredients Mass [g]					Discrepancies related to Tot. [%m/m]				Related to K_2CO_3
Nr.	**Chelford Sand**	**K_2CO_3**	**$CaCO_3$**	**Na_2CO_3**	**Tot.**	**gain SiO_2**	**loss K_2O**	**average**	**Loss material mass [g]**	**loss K_2 [%m/m]**
30	24.5	15.4	11.0	-	50.8	6.6	5.9	6.3	3.2	20.6
31	24.7	15.4	11.0	-	51.1	6.7	7.1	6.9	3.5	23.0
32	27.7	16.9	11.9	-	56.5	5.2	5.5	5.3	3.0	17.9
33	27.9	17.3	12.0	-	57.2	4.7	5.1	4.9	2.8	16.3
34	24.5	15.4	11.0	-	51.0	7.4	7.0	7.2	3.7	23.8
35	24.7	15.5	11.0	-	51.2	8.0	8.1	8.1	4.1	26.7
36	24.7	15.5	11.0	-	51.2	9.1	9.3	9.2	4.7	30.3
37	12.4	7.8	5.5	-	25.7	5.3	5.5	5.4	1.4	17.7
38	12.4	7.8	5.5	-	25.7	3.7	5.7	4.7	1.2	15.4
39	12.4	7.8	5.5	-	25.7	3.6	4.5	4.0	1.0	13.2
40	12.4	7.8	5.5	-	25.7	5.9	6.0	6.0	1.5	19.7
43	12.4	7.9	5.5	-	25.8	3.0	4.4	3.7	1.0	12.3
44	12.1	3.5	5.3	4.9	25.9	5.8	6.7	6.3	1.6	19.2
45	12.1	2.0	5.2	6.5	25.9	9.2	5.4	7.3	1.9	22.2
46	12.4	0.5	5.0	8.3	26.2	2.8	3.4	3.1	0.8	9.1
55	6.2	3.9	2.8	-	12.8	5.9	6.2	6.1	0.8	20.0
Av.								5.9		19.2

Table 3.13 – From the total amount of initial ingredients [g] the amount of loss material [g] is calculated, passing by the averaged value of %wt. gained by SiO_2 and lost by K_2O. The last column shows the %wt. of lost alkali is all the loss material comes from K_2CO_3.

3.3.2.7. Discussion

This second part of the work, gathered under the name Glass Experiments B, aimed to find a correlation between some glass characteristics and the parameters chosen to produce them.

Most of the experiments belonging to this series were prepared with H.C. 17(4), involving 15 hours of melting time. In past periods, glass making was realised by stirring the molten mix of ingredients in a large

furnace, by continuously heating the oven, sometimes also for days; since the stability of the crucibles was not guaranteed over longer times, 15 hours of melting were considered a good compromise.

In this chapter the cracking behaviour was shown to be due to the thermal stress of porcelain crucible and it became clear that an annealing step helps to reduce this kind of stress.

The behaviour of bubbling was also studied and correlated to the high amount of carbonates in the initial ingredients. Its removal can be accomplished using a longer melting time, by fritting and by re-melting the glass itself.

In general it can be said that the glass of this set is homogeneous, but from one point of view certain heterogeneity was introduced by contamination from the crucible, e.g. a series of coloured glass samples it was caused by the passage of Fe from the SiC crucible into the melt. Also the porcelain crucibles were shown to react with the melt during the melting process, exchanging in particular, Al and K with the glass phase.

The most important aspect that needed explanation was the loss of K_2O, observed in almost all the samples prepared as a difference of 5-6% between the theoretical composition of K_2O and SiO_2 and the composition resulting from SEM-EDX analysis. The indications supporting the hypothesis of absorption from the crucible, both SiC and porcelain, did not agree with the results of experiment S55 involving a Pt crucible, where the same trend of loss of material was observed. A partial absorption of K_2O cannot be excluded, however, because some samples displayed a very clear intermediate layer, rich in K_2O between glass and crucible. Furthermore, the theoretical calculation on the thick layer rich in K_2O gave a lower amount of materials that can be lost in this manner than what was observed on the basis of the glass composition. It can be concluded from the above that probably the absorption process was not the only phenomenon causing the loss of K_2O.

Five thermo-gravimetric analyses were executed to gather evidences for loss of material by volatilisation. The expected volatile compounds have been connected with some of the mass loss events visible on TGA1 and TGA2 graphs (water and CO_2 from $CaCO_3$, K_2CO_3). Not every event observed matched with a specific substance and the absence of a qualitative detector did not help to recognise the unknowns, expected to be volatilised as K_2O or Na_2O. Since some authors [33][34][34][36][37] confirm this possibility and the data showed a systematic loss in almost every sample, the relative mass loss was calculated in relation only to the K_2CO_3 initial amount, corresponding to an average value of 19.2%. If the loss of material in the third

slope of TGA1 and TGA2 is only from K_2CO_3, the relative percentages are 21.7% and 25.7%, values comparable to the missing mass in the self-synthesised glasses.
Although a clear explanation still needs to be found, and further investigations are required to obtain a more complete understanding of the control over this behaviour, this did not affect the glass quality.

The experience with glassmaking achieved during this series was significant and sufficient to progress to the following step. This involved the use of mixed alkali glasses with different K : Na ratios, as often present in historical potash glass.

The melting temperature at 1250°C appears to work for every heating curve, in combination with different melting time, annealing steps and for different materials (Na_2CO_3, Dessel sand, Lommel sand, frits) and different crucibles. With a reasonable confidence the task of make glass with beech ash could be tackled, once the appropriate sand : ash ratios could be established.

3.3.3. GLASS EXPERIMENTS C

Since it is the intention in this section to explore the relation between the nature of the raw materials and the composition of self-synthesised glass, first the results with Chelford (UK), Dessel (Belgium) and Lommel (Belgium) sands for glass making will be considered (S27, S28, S41, S42, S48 and S49); in second place the results with beech ash will be discussed (S51, S52, S53, S54, S56 and S57; see Table 3.15).
The experiments with different types of sand were synthesised during Glass Experiments A and B.
Beech ash was used to synthesise glass samples with different ash: sand ratios and, afterwards, the ash was also purified in different ways in order to obtain a durable and transparent glass.

3.3.3.1. Types of sand

As explained above, the most frequently employed sand in all experiments up to now was Chelford sand; because of the higher amount of impurities that were present in its, it was similar to the types of sand used in the past centuries for glassmaking. From a qualitative point of view, different kind of grains, in various sizes and colours, were visible in a handful of this sand. On the other hand, Dessel sand had a more homogenous aspect, with fine grey grains, reflected its high SiO_2 purity (that was verified by means of FAAS analysis), as well as Lommel sand, even if its dark brown appearance can be misleading. In all experiments performed, always glass of good transparency and homogeneity was obtained.

S27 and S28 were the first two samples, realised in Glass experiments A, with Dessel and Lommel respectively, and comparable in composition with S26 (Table 3.14), made with Chelford sand and the same set of parameters. The composition of these glasses was determined with SEM-EDX and LA-ICP-MS.

	Theoretical % [%m/m]					Actual % [%m/m]									
Nr.	SiO_2	K_2O	CaO	Na_2O	Minor	SiO_2	Std. Dev.	K_2O	Std. Dev.	CaO	Std. Dev.	Na_2O	Std. Dev.	Minor	Std. Dev.
26	55.6	28.0	14.8	-	1.6	57.8	1.7	23.7	1.2	17.5	2.7	-	-	1.0	0.2
27	59.7	25.0	14.9	-	0.4	59.7	1.8	24.6	1.7	15.4	1.9	-	-	0.4	0.1
28	59.8	25.0	14.9	-	0.2	62.9	1.1	23.5	0.5	13.3	0.8	-	-	0.4	0.0
39	55.2	28.5	14.7	-	1.6	58.8	0.3	24.0	0.2	16.2	0.4	-	-	1.0	0.2
41	59.3	25.5	14.8	-	0.4	58.9	0.2	24.8	0.5	15.1	0.5	-	-	1.2	0.2
42	59.5	25.5	14.8	-	0.2	59.7	0.5	24.0	0.3	15.5	0.5	-	-	0.8	0.3
45	55.7	9.9	14.3	18.5	1.6	64.9	0.5	6.9	0.2	10.7	0.5	16.1	0.2	1.5	0.2
48	59.6	6.9	14.5	18.7	0.4	60.6	0.3	5.5	0.1	15.1	0.3	17.6	0.5	1.2	0.3
49	59.0	7.9	14.3	18.6	0.2	60.6	0.6	5.7	0.2	14.1	0.7	17.5	0.6	2.2	0.5

Table 3.14 – Theoretical and analysed composition [%m/m] by SEM-EDX, of Dessel (27, 41 and 48) and Lommel (28, 42, and 48) sands experiments, compared with similar Chelford sand experiments (26, 39 and 45).

What was striking was that a lower or no discrepancy at all remained between the theoretical and the actual composition of experiments S27 and S28. A justification of it could be found in the different composition of the three sands, having a different percentage of minor elements. In Chelford sand, in particularly a concentration of 5.5% of K_2O was present. One hypothesis was that the higher level of impurities could facilitate the volatilisation and/or absorption inside the SiO_2 melt.

At the same time this additional 5.5% of K_2O influenced the expected ratio calculated from the initial ingredients: its contribution was always taken in consideration during the calculation of the theoretical composition, but created a slight difference between the theoretical values of the Chelford and the other two types of sands. On the basis of Chelford sand, K_2O and SiO_2 concentrations of respectively 28.0% and 55.6% were obtained, while by means of Dessel and Lommel sands, respectively 25.0% K_2O and 59.7% SiO_2 will results. CaO concentration was always around 14.8% (Table 3.14).

The hypothesis was that the discrepancy between theoretical and actual concentrations in the Chelford sand was correlated with its elemental composition (93.6% of SiO_2, as determined by FAAS). The type of crucible, the heating curve and other parameters were kept identical for the three experiments (S26, S27 and S28), while the type of sand was changed. The main difference was the excess of 5.5% K_2O in Chelford sand, present from the beginning in the batch. It was possible that this excess was easily lost by absorption in the crucible and/or volatilisation.

The same kind of considerations can be done on the other two trios.

The second, composed of glasses S39, S41 and S40, respectively with Chelford, Dessel, Lommel sand, has been realised with H.C. 20 in porcelain crucibles. This heating curve has two 5 hours annealing steps at 1000°C and 800°C. In the third trio the glass experiments S45, S48 and S49 were synthesised with a mixture of alkali (using Na_2CO_3 and K_2CO_3), in combination with respectively Chelford, Dessel and Lommel sands.

As visible in Table 3.14 the major differences between the three sands were the different initial theoretical ratios, due to the presence of 5.5% of K_2O in the Chelford sand. On the other hand, a better matching between theoretical and actual concentrations for glass synthesised with Dessel and Lommel sands was observed.

3.3.3.2. Ash

The ash was prepared by burning beech wood as much as possible without any other kind of materials or type of wood, to be sure no contaminations took place. This work has been executed by Prof. Dr. Joost Caen from the Glass Conservation Department of Artesis Hogeschool of Antwerp.

The resulting ash was a heterogeneous mixture of grains of different shape, size and colour ranging from a fine grey-white powder to big black pieces of carbon.

Two modes of operation could be employed for glass making: on the one hand, mixing raw ash with sand and melting everything without other intermediate passages; on the other hand, purifying the raw ash by washing it, with the aim to remove as many undesired contaminants as possible. Both directions will be explored, to gain insights about the consciousness and knowledge of glassmakers in former period on the effective composition of ashes.

In this series of experiments, $CaCO_3$ was not added to the batch, because it was expected that CaO and/or MgO were present in the ash itself. Many recipes do not mention this ingredient in the initial mixture, but compositional analysis allows verifying their presence depending on the provenance of the glass and the raw materials that were available. Therefore the glass makers were sometimes unaware of adding hidden ingredients, with beneficial properties as stabilisers, to their glass.

In general it was decided to sift the ash with a 1 mm^2 textile sieve before use, in order to obtain a material of comparable homogeneity of the sand. The sifted ash still showed the presence of different components of various grey-scale colours ranging from white to black.

Four glasses were made with untreated sifted beech ash, in order to determine the appropriate ash to sand ratio. In addition, two glasses were synthesised after exposing the ash to washing treatments. As result of these treatments two main components (a precipitate and a solution) were obtained and these were used separately in the synthesis of the last two glasses. In the following paragraph the washing procedures are discussed and selected ash components described.

3.3.3.3. Washing Ash

It was known that several treatment steps were required to purify ash [5][11], but the exact proportion water : ash is not well documented, and neither the time nor the effective compounds that will be separated in such a procedure. It was expected that a precipitate, made of salts of mostly Ca-, Mg- and other less soluble elements, and a solution, rich in more soluble elements, such as K and Na are formed. Of course no pure ingredients will be isolated in this manner, but at least a partial removal of possible contaminants should take place.

The first experiment was intended to verify which kind of precipitate was formed after boiling ash in water. A series of 7 fractions of 1 L of water, in which 20 g of ash was placed, were purified by means of the following procedure. The ash was mixed in the first litre of water and boiled for 10 minutes, then the solution formed was filtered with a thin textile sieve and at the precipitate retained was added to the second volume of 1 litre of water. This second solution was brought to the boiling temperature for 5-10

minutes and filtered again. These operations were repeated seven times until the solution appeared quite transparent and the precipitate homogeneous. The latter appeared to be made up of two different powders, one black and one white.
Since 7 L of water was used in this process, long evaporation process was necessary to obtain the dissolved salts in the solution. Thus, a new washing process involving less water and more ash was also tested.

In the second try 40 g of ash were washed with 1 L of water in total. In the first step, the ash was mixed with 200 ml, boiled for 5 minutes and filtered; in the following, liquid fractions of 100 ml were used. When the cloudy solution of 500 ml of volume was filtered, a precipitate similar to the one obtained by means of the first procedure was obtained at the bottom of the recipient. A third component of muddy material was held back by the filter, probably due to the use of a higher ash concentration than in the previous washing procedure.
Since this muddy component appeared to be strongly heterogeneous, an additional 500 ml of water (in five fractions) was used to purify it. It was obtained another cloudy solution, a second fraction of precipitate and still a certain amount of muddy material remained behind.
In the resulting 1 L solution, a fine precipitate could be observed to form on the bottom of the holder; a slow evaporation of the solution permitted to save and store this precipitate. The two fractions of the precipitate collected from the recipient bottom were dried and stored. The third component was left to dry in an oven at 40°C and stored.

3.3.3.4. Experiments

The glass synthesis was in every case conducted by means of the H.C. 17(4) procedure, in a porcelain crucible.
For each glass experiment in Table 3.16, the Na_2O and K_2O concentrations were summed, as well as the CaO and MgO concentrations, since they have similar properties (as explained in Section 3.2.2 “Type and amount of ingredients employed”). Thus it was possible to calculate the K_2O : CaO : SiO_2 concentration ratio of the ternary system.

Figure 3.19 – Pictures of S52 (left), S53 (centre) and S54 (right).

In the four experiments S51, S52, S53 and S54, Chelford sand was mixed with sieved beech ash in ratios of 1 : 2, 1 : 3, 1 : 1 and 2 : 1. The resulting glass compositions are listed in Table 3.15.

	Initial ingredients [g]		Actual % [%m/m]											
Nr.	Sand	Ash	SiO_2	Std.Dev.	K_2O	Std.Dev.	CaO	Std.Dev.	Na_2O	Std.Dev.	MgO	Std.Dev.	Minor	Std.Dev.
51	12.0	6.0	72.5	2.2	6.3	0.1	13.4	1.3	0.4	0.3	4.1	0.6	3.3	0.4
52	15.1	5.0	71.6	0.6	6.3	0.3	14.1	0.8	0.3	0.2	4.1	0.2	3.5	0.4
53	5.0	5.0	65.7	1.3	6.5	0.3	17.0	1.3	0.9	0.4	4.8	0.3	5.2	0.2
54	5.1	10.0	49.9	0.6	13.9	0.5	11.0	1.4	2.0	0.5	13.4	0.6	9.9	0.9
56	7.1	7.0	66.6	0.7	18.9	0.4	6.9	0.2	2.2	0.3	2.2	0.2	3.1	0.2
57	7.1	7.1	62.0	0.5	2.1	0.2	21.9	0.7	0.4	0.2	6.2	0.2	7.4	0.4

Table 3.15 – Glass Experiments C data: initial ingredients [g], real analysed compositions with relative standard deviations [%m/m].

Initially, using higher amounts of sand were tried out, but the first attempts (S51, S52) did not result in a glassy material but in a crystalline compound with high heterogeneity and porosity (Figure 3.19, centre). On the other hand, experiment S53 resulted in a transparent glass with a brownish tone due to the impurities and a thin superficial opaque layer of material that, during the melting process, should be like foam on the surface (Figure 3.19, left). Material S54 was still glassy but not transparent (Figure 3.19, right). The higher amount of flux agent facilitated the melting but the higher amount of impurities present in the glass gave it an intense red-brownish colour.

The compositional analysis on S53 revealed a K_2O : CaO : SiO_2 ratio of 1 : 3 : 10 (Table 3.16), that inserted into the ternary system should correspond with HLLA glass from the 15-17th century. Indeed the amount of alkali was 7.4%, with a contribution of Na_2O of only 0.9% while then CaO and MgO concentrations were 17.0% and 4.8%. Minor elements reached 5.2%, with the main contribution from Al_2O_3. The presence of some minor elements such as P_2O_5 and MnO was noted. Manganese was probably responsible for the transparency of the glass, oxidizing the Fe^{2+} ions that were present to Fe_2O_3 [2][5][11][30].

	Actual % [m/m]			
Nr.	SiO_2	K_2O+Na_2O	CaO+MgO	Minor
51	72.5	6.7	17.5	3.3
52	71.6	6.7	18.2	3.5
53	65.7	7.4	21.7	5.2
54	49.9	15.8	24.4	9.9
56	66.6	21.1	9.2	3.1
57	62.0	2.5	28.1	7.4

Table 3.16 – Glass Experiments C data: flux agents (K, Na) and stabilisers (Ca, Mg) contributes are summed to simplify values in table 3.15.

The composition of S54 was $1K_2O : 1.5CaO : 3SiO_2$, corresponding to 12-14th century potash glass, even if not a high quality glass was obtained. The SEM-EDX analysis indicated the presence of two main phases, one with the composition mentioned above and another made up of 96.7% SiO_2 and CaO. This kind of secondary phase was unexpected, because the initial ingredient ratio, rich in ash should facilitate the fusing of SiO_2 with the flux agents.

The ingredient ratio employed in experiment S53 (i.e. a sand : ash ratio of 1 : 1) was retained during the last two experiments of this series. Instead of raw ash the solute and the precipitate obtained after washing the ash were added into porcelain crucibles to produce respectively materials S56 and S57.
S57 was not a glass, but a crystalline compound similar to S51 and S52, porous and with a very low amount of alkali, indicating that the washing process was effective. The compositional analysis revealed a total alkali content of 2.5%, a CaO + MgO content of 28.1%, a SiO_2 concentration of 62.0% and a minor elements amount of 7.4% (Table 3.15 and 3.16).
On the other hand a high quality glass was obtained by employing the solute. Glass S56 was transparent and well melted, without additional layers but with a slight purple shadow (referable to MnO) and having quite brittle consistence, due to the expected lower lime concentration. From SEM-EDX analysis, a concentration ratio of $2K_2O : 1CaO : 6.5SiO_2$ could be obtained, ascribable to a region in the ternary system outside the ancient glass hexagon, but directly below the region of the 15-17th century potash glass.

3.3.3.5. Discussion

While the number of synthesis experiments performed was not comparable to the first two Glass Experiments sets, the aims put forward could be achieved after just a few trials. A good matching between the heating curve and the raw materials was found.
Good results were obtained with Chelford sand while, such as also the case with Dessel and Lommel sands, as observed in the three trios of experiments realised.

Through the historical information in Section 1.4.2 “Ash” it was possible to connect these samples to the categories shown for wood ash glass. E.g. S53 had a CaO : K_2O ratio of almost 3 : 1, similar to wood ash lime glass, with a K_2O concentration of 6.5% m/m (Table 3.15). Although no NaCl has been added, yet it was present at around 0.9% m/m Na_2O. S54 could be considered to be a wood ash glass with a CaO : K_2O ratio of 1 : 1 (2 : 1 if the MgO concentration of 13.4% was added to CaO%, Table 3.15). Even though it has been prepared following the suggestion of the Monk Theophilus (“Diversarum Artium Schedula”), using two parts of ash and one of sand, this material did not appear to be a good glass, since it was brown and heterogeneous in composition. [3][12]

Instead S56 appeared to be a much more high quality glass, as described above, but too brittle. The CaO : K_2O ratio of 0.4 : 1 showed a low lime content that was too low in relationship with alkali. It did not interfere with the glass appearance but with its quality and durability. This glass has been produced from the solution part of washed ash, from which CaO and MgO were partially removed (Table 3.15). On the other hand in S57, made with the precipitate part of the washed ash, these two compounds were too concentrated in relation to the alkali, thus no glass could be produced.
For future experiments, it follows that solute and precipitate will need to be mixed again in different proportions. Hopefully, the majority of the impurities will remain behind in the third, muddy component of washed ash that will not be used for the glassmaking (Section 3.3.3.3).

The main goal of this work was the production of a high quality glass from sand and real ash. While surely additional experiments need to be done to improve the glass, it can be stated in a qualitative sense that by means of the materials produced during experiments S53 and S56, this goal was reached. This is remarkable in view of the fact that the effective composition of the ash, the precipitate and washing solution were (largely) unknown at the time the experiments were conducted.
Solution Nebuliser-ICP-MS (SN-ICP-MS) analysis on the sands and ash are in progress to enlarge our quantitative knowledge of the raw ingredients used during these experiments. This information will be useful to document all major and minor elements concentrations and secondly, to study the behaviour of trace elements.

4. CONCLUSIONS AND FUTURE DEVELOPMENTS

In the present survey the world of glassmaking has been explored, from the choice of the right quantity of ingredients, over the use of different heating curves to solving a series of technical challenges; by gradually improving the knowledge, a stable set of parameters could be established that permitted to achieve homogeneous and transparent glass. Special care was devoted to medieval and post-medieval glass, produced mainly from sand and wood ash.

The information gathered during the artisanal work was extended with elemental analysis by SEM-EDX and LA-ICP-MS, to follow the concentration of major and minor elements of every sample. By comparing these results with the expected theoretical values calculated from the initial reagents, it was possible to follow the evolution of the melting process, since recipes and heating procedures were known, and to shed light on the glassmaking art.

Only the LA-ICP-MS analysis results of a group of glass experiments (belonging to Glass Experiments A) were shown, relative to major and minor elements concentration. The analyses of the rest of glass experiments are in progress and they will be part of future investigations.

This work was connected with a project between Artesis Hogeschool and University of Antwerp on experimental glassmaking from raw materials, aimed at optimising a set of parameters to produce glass for restoration/conservation and research purposes. The first experiments involved the ternary system K_2O : CaO : SiO_2 (Figure 3.1) and were realised by Dr. Olivier Schalm from Artesis, where different ingredients ratios were matched with heating temperatures [31]. However the best working set up found had parameters which did not fit very well with the temperatures and the amount of ingredients suggested.

The most frequently used working temperature was 1250°C, not excessively high, but anyway elevated relative to common practice for a medieval furnace. Some experiments involving frits were performed at lower temperatures, but the low amount of initial material did not allow performing more than one re-melting cycle. If an initial larger quantity of reagents had been used, it would have been possible to achieve glass at a working temperature of around 1000°C or less.

The temperature of 1250°C has been employed during the three sets of glass experiments with a ratio 2 : 1 : 4 of the ingredients K_2O : CaO : SiO_2. At the same temperature, glass was produced employing real ash, but the resulting compositions were different, equivalent to a K_2O : CaO : SiO_2 as 1 : 3 : 10 (experiment S53) and 2 : 1 : 6.5 (experiment S56). Starting from these new ratios and the same heating curve, it was intention to verify whether different compositions could be used at the same working temperature; the

minor elements present into the beech ash, however, appear to play a fundamental role in the melting reactions.

From an historical point of view, observing Figure 3.1, glass with a ternary ratio K_2O : CaO : SiO_2 of 2 : 1 : 4 could be considered a 12-14th century potash glass, whereas with 1 : 3 : 10 and 2 : 1 : 6.5 glasses more representative for 15-17th century were obtained. Therefore the aim to reproduce medieval and post-medieval glass appears to have been achieved, even though the ratios CaO/K_2O for all of them is particularly low, apart for experiment S53, which the result could be defined as wood ash lime glass [3]. Low values of the ratio between Ca and K oxides are representative of early wood ash, typical of the 9-11th centuries.

Higher temperatures have been tested, with the aim of producing glass comparable with high-lime low-alkali glass (HLLA) shown into the ternary system in Figure 3.1. This resulting glass appeared more instable, because it was quite heterogeneous and had too high alkali content for HLLA glass.

Some challenges have been faced and solved: the glass cracking due to the thermal stress of porcelain crucibles, which continued to be used because SiC crucibles introduce iron contamination that colour glass. The use of Pt crucible have the advantage of producing glasses without contamination and it permits to economise on the use of disposable crucibles, that are impossible to reuse a second time.

Bubbles were always present due to the high CO_2 content, since K, Ca and Na carbonates were used as initial ingredients; however it has been shown that glass fritting can remove them.

The loss of K_2O remains without satisfactory explanation since both hypotheses (either loss through absorption and through volatilisation) were plausible but not convincingly demonstrated to take place. Other TGA analyses could improve the insight into the loss phenomenon in case specific detector for the volatile species would be used, e.g. a mass spectrometer coupled with the TG instrument.

Since medieval and post-medieval glass means potash glass, the last group of experiments was realised with sand and beech ash as starting materials. The ash was washed, resulting in a glass that appears transparent and homogeneous; it was also brittle, because of its very low lime content. Future investigations will start from this point and will involve the addition of Ca-containing stabiliser agents.

As already discussed in the previous chapter, it is possible to perform a step-by-step analysis of the synthesised glass, by choosing a specific heating curve and by halting the melting process at the most important steps. The evolution of the reactions can be followed in this manner, broadening the knowledge on the reaction order and on the crucial point of the fusion.

ICP-MS analyses are in progress to obtain the elemental compositions of the sands and ash employed in the glass making experiments. Solution Nebuliser-ICP-MS (SN-ICP-MS) is employed to determine the major, minor and trace constituents of these powders: no information on elemental composition of these initial reagents has been collected yet, apart from information obtained via FAAS analysis. Unfortunately due to the experimental set up: some minor elements cannot be detected such as Al; the Si content of the powders was calculated from the remaining percentage, and was not directly measured.

LA-ICP-MS has been used in this report to verify the reliability of SEM-EDX analyses, but this powerful method also allows collecting information on trace elements, especially of REE (Rare Earth Elements). The idea is to investigate how elemental concentrations and concentration ratios of REE in the raw materials influence the (trace) composition of the final glass, in order to capitalise on these insights during provenance studies.

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Appendix A - Logbook Experiments 2011

Descriptions of the experiments realized in the period April-July 2011

by Dr. Olivier Schalm from Glass Conservation Department of Artesis Hogeschool of Antwerp

in collaboration with AXiL -Antwerp X-Ray instrumentation and imaging Laboratory-

Chemistry Department of University of Antwerp

Academisation project Artesis – University of Antwerp

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For each sample are displayed the date of realisation, the recipe chosen, the working condition (crucible, heating curve, etc.), the theoretical composition of major and minor elements (%wt.), some picture of the resulted glass and related observations. The glass fragments shown in the pictures have dimensions between 5 and 2 cm.

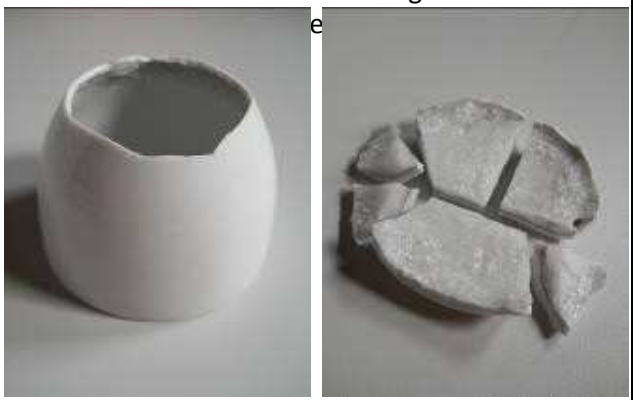
All experiments are conducted into Conservation Department of Artesis Hogeschool of Antwerp with a Bottom Loading Furnace 161/2007 – Termolab (Fornos Electricos LDA-Portugal) present in the Metal Conservation Department.

The awareness achieved will be available to the Glass Conservation Department, with the purpose to produce glass for research and/or conservation and restoration activities.

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
01	April 05	Sand (*): 17 g K_2CO_3: 4.3 g CaO: 4.5 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A glazed porcelain melting crucible W. Haldenwanger 79 MF -1a (c. 250 ml) was used. It is able to withstand 1250°C, although the glaze can dissolve into the glass melt. • Mixture in crucible was mixed with a metal spoon • **Heating curve 01** – preheating at 600°C for 1 hour; max temperature 1200°C for 30 minutes • The kiln was immediately opened, allowing the crucible to cool down rapidly. • Immediately after opening the kiln, the crucible emitted a yellow-orange light. During the cooling, you could hear the crucible or the glass inside cracking	SiO_2: 64.3% K_2O: 15.7% CaO: 18.2% Minor: 1.9%	• The glass surface appeared to be very shiny • The surface was very irregular containing several gas holes. This indicates that no liquid glass was obtained during the firing process • Some K_2CO_3 was smeared out on the inner side of the crucible just above the surface of the original mixture and it did not react with the glass. Therefore, the reactants did not increase in volume • Melting process requires longer melting times or higher temperatures (ex., 1400°C). For this, crucibles are needed that are able to withstand higher temperatures 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
02	April 07	Sand (*): 17 g K_2CO_3: 4.4 g CaO: 4.5 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• Glazed porcelain crucible (see exp. 01) • **Heating curve 02** – preheating at 600°C for • 1 hour; max temperature 1200°C for 150 minutes • The amount of SiO_2 was reduced in order to obtain a low melting liquid. It is comparable with a medieval glass composition	SiO_2: 64.3% K_2O: 15.7% CaO: 18.2% Minor: 1.9%	• The resulting mixture is hard and shiny, but the surface is very rough and contains air bubbles. This indicates that only a solid state reaction occurred without the formation of a liquid • Longer firing temperatures improved the quality of the mixture, although, it was not sufficient 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
03	April 11	Sand (*): 10 g K_2CO_3: 7.8 g CaO: 8 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• Glazed porcelain crucible (see exp.1) • **Heating curve 02** – preheating at 600°C for • 1 hour; max temperature 1200°C for 150 minutes • The next morning the kiln had still a temperature of c. 950°C although the program stopped at around 17:00 the day before. Apparently, the kiln cools very slowly	SiO_2: 39.9% K_2O: 24.9% CaO: 34.1% Minor: 1.1%	• A glass has been formed, although the surface is still rough and a white powder is present at the glass surface • The surface was facetted, suggesting that products did react with each but because there was no homogenization zones rich in K_2O, CaO and SiO_2 were probably created • A dull grey product about 1 cm above the glass surface is present on the inner side of the crucible 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
04	April 26	Sand (*): 10 g K_2CO_3: 7.8 g CaO: 8 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis (Same crucible as in Exp. 03, which is fired for a second time)	• **Heating curve 02** – preheating at 600°C for • 1 hour; max temperature 1200°C for 150 minutes • In this experiment a rather low temperature for a rather long firing temperature is employed	SiO_2: 39.9% K_2O: 24.9% CaO: 34.1% Minor: 1.1% (same as exp. 03)	• The crucible was broken and the bottom sticked to the plate • The next morning the kiln was already open • The glass at the bottom in the crucible is clearly facetted with a crystalline aspect. The surface is now much smoother and had a shiny appearance • Between the crucible and the glass a thin e 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
05	April 28	Sand (*): 10.0 g K_2CO_3: 7.8 g CaO: 8.0 g Glass cullet: 1.01 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis The glass cullet were crumbles of medieval glass from Canterbury	• **Heating curve 02** – preheating at 600°C for 1 hour; max temperature • 1200°C for 150 minutes • The kiln was switched off and the crucible was kept inside the kiln • The next day it was cold enough to remove it with your hands	SiO_2: 39.8% K_2O: 24.9% CaO: 34.1% Minor: 1.1% (same as exp.03 but this time mixed with medieval glass cullet) It is assumed that glass cullet has no influence on the composition	• At 1100°C (after the kiln was switched off and started to cool) it was not possible to pour the melt out of the crucible because it was too viscous, but by poking a metal stick into the melt it was clear that it behaved as a very viscous sirup. • The glass has a purple shade 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
06	May 17	Sand (*): 1.76 g K_2CO_3: 0.49 g CaO: 0.51 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 03** – preheating at 800°C for 1 hour; max T 1450°C for 1 hour • At 800°C the powder was still solid but it could not be • After the heating at 1450°C an attempt to pour the glass at 1000°C failed It was already solid	SiO_2: 62.5% K_2O: 16.3% CaO: 19.4% Minor: 1.8%	• The experiment resulted in a glassy material with a shiny surface • There was no white powder at the glass surface • The glass appears to be dark coloured (SiC inclusions?) and small gas bubbles • The crucible sticked to the refractory material. For that reason, the experiment was carried out on a thin plate 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
07	May 19	Sand (*): 2.1 g K_2CO_3: 0.7 g CaO: 0.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used. The crucible was placed in a larger crucible for security reasons. The small crucible resisted the firing process without any problems • **Heating curve 04** – preheating at 800°C for 5 hours; heating at 1200°C for 10 hours	SiO_2: 60.0% K_2O: 18.0% CaO: 20.3% Minor: 1.7%	• A glassy material has been formed but on top of the surface there is a white powder. Probably this is CaO-powder that floats on top of the silicate melt. 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
08	May 23	Sand (*): 3.4 g K_2CO_3: 1.0 g CaO: 1.0 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used on a thin plate of refractory material • **Heating curve 05** – preheating at 800°C for 1 hour; heating at 1500°C for 1 hour • At 1000°C the crucible was immersed in a basket filled with water. The cooling process was performed in a matter of minutes	SiO_2: 61.3% K_2O: 17.0% CaO: 19.9% Minor: 1.8%	• At 800°C the mixture can be considered as a porous solid, not possible to stir with a metal bar • The crucible sticked to the plate of refractory material • The crucible contained a thin slab of glass of 0.7 cm thickness but the inner sides of the crucibles covered with glass was 2.5 cm high. This was just 0.5 cm below the border of the crucible • A glassy material with a shiny surface has been formed. The slab appears to exist in two layers: (1) the lower part is white and opaque, and (2) the upper layer appears to be transparent.  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
09	May 26	Sand (*): 2.0 g K_2CO_3: 0.5 g CaO: 0.5 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used. The crucible was placed in a larger crucible for security reasons. The small crucible resisted the firing process without any problems • **Heating curve 06** –preheating at 800°C for 5 hours; heating at 1300°C for 10 hours	SiO_2: 64.4% K_2O: 15.8% CaO: 18.0% Minor: 1.9%	• Glass surface was covered by a white product that could be blown away. A part of that white product sticked in the glass. For that reason the surface appeared to be white and opaque. 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
10	May 27	Sand (*): 1.9g K_2CO_3: 0.6 g CaO: 0.5 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 07** – preheating at 800°C for 24 hours; heating at 1300°C for 10 hours	SiO_2: 63.3% K_2O: 17.1% CaO: 17.9% Minor: 1.8%	• There was no white powder on top of the surface. The glass surface was brown and had a very irregular surface. Longer firing temperatures did not improve the quality much, although the CaO appeared to be part of the glassy substance. 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
11	May 30	Sand (*): 1.7 g K_2CO_3: 1.2 g CaO: 0.3 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 08** - preheating at 750°C for 1 hour; heating at 1350°C for 2 hours • Experiment 11 and 12 were carried out during the same firing process	SiO_2: 55.6% K_2O: 31.4% CaO: 11.4% Minor: 1.6%	• The mixture turned into a porous, solid product after 30 minutes at 750°C. It was not possible to stir the mixture with a metal bar • A dark green glass has been formed, but it contains a large amount of gas bubbles 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
12	May 30	Sand (*): 2.0 g K_2CO_3: 0.6 g CaO: 0.6 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 08** - preheating at 750°C for 1 hour; heating at 1350°C for 2 hours • Experiment 11 and 12 were carried out during the same firing process	SiO_2: 63.2% K_2O: 16.1% CaO: 18.9% Minor: 1.8%	• The surface contains still white inclusions on top of the surface 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
13	June 6	Sand (*): 1.8 g K_2CO_3: 1.3 g CaO: 0.3 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 09** - preheating at 800°C for 1 hour; heating at 1300°C for 1 hour. The heating between 800°C and 1300°C was much slower (5°C/min) in order to avoid gas bubbles	SiO_2: 56.1% K_2O: 32.5% CaO: 9.8% Minor: 1.6%	• The mixture resulted in a greenish glass with gas bubbles. • The transparency is much higher, suggesting that the glass is much more homogeneous 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
14	June 7	Sand (*): 2.0 g K_2CO_3: 0.8 g CaO: 0.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 10** - preheating at 800°C for 1 hour; heating at 1300°C for 1 hour. The heating between 800°C and 1300°C was much slower (0.5°C/min) in order to avoid gas bubbles	SiO_2: 57.3% K_2O: 19.4% CaO: 21.7% Minor: 1.7%	• The melt has raised, suggesting that the slow heating between 800°C and 1300°C could not avoid the formation of gas bubbles in the silicate • The glass surface was covered with a white powder. The melting process was not completed 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
15	June 10	The crucible of exp. 14 was refired at 1350°C	• A SiC crucible was used • **Heating curve 11** - preheating at 800°C for 1 hour; heating at 1350°C for 1 hour. The heating between 800°C and 1350°C was much slower (5°C/min) in order to avoid gas bubbles	(SiO_2: 57.3% K_2O: 19.4% CaO: 21.7% Minor: 1.7%) Theoretical values for S14	• The glass appears to be a little bit better than S14 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
16	June 14	The crucible of experiment 14 was refired at 1400°C	• A SiC crucible was used • **Heating curve 12** - preheating at 800°C for 1 hour; heating at 1400°C for 1 hour. The heating between 800°C and 1400°C was much slower (5°C/min) in order to avoid gas bubbles	(SiO_2: 57.3% K_2O: 19.4% CaO: 21.7% Minor: 1.7%) Theoretical values for S14	• The glass appears to be well melted but the glass appears to have a white opaque but shiny surface 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
17	June 16	Sand (*): 2.1 g K_2CO_3: 0.7 g CaO: 0.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 13** - preheating at 800°C for 1 hour; heating at • 1400°C for 1 hour. The heating between 800°C and 1400°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 58.2% K_2O: 18.3% CaO: 21.8% Minor: 1.7%	• Glass appears to be formed but it contains many gas bubbles • The glass is not transparent 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
18	June 17	Sand (*): 2.2 g K_2CO_3: 0.8 g CaO: 0.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 14** - preheating at 800°C for 1 hour; heating at 1450°C for 1 hour. The heating between 800°C and 1400°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 59.1% K_2O: 18.9% CaO: 20.4% Minor: 1.7%	• Glass appeared to be well melted although the surface contained opaque white zones and a limited number of gas bubbles, hampering the transmission of the glass 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
19	June 27	Sand (*): 2.0 g K_2CO_3: 1.2 g CaO: 0.5 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A SiC crucible was used • **Heating curve 15** - preheating at 800°C for 1 hour; heating at 1500°C for 1 hour. The heating between 800°C and 1500°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 55.5% K_2O: 28.0% CaO: 14.9% Minor: 1.6%	• At around 1300°C a viscous liquid is formed • A brown circular spot was present around the crucible on the refractory stone. The inner side of the crucible is vitrified • The surface of the crucible was contained many blisters. Probably, the firing temperature was somewhat too high 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
20	June 27	Sand (*): 2.1 g K_2CO_3: 0.7 g CaO: 0.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• Fired together with S19 • A SiC crucible was used • **Heating curve 15** - preheating at 800°C for 1 hour; heating at 1500°C for 1 hour. The heating between 800°C and 1500°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 59.1% K_2O: 18.2% CaO: 21.0% Minor: 1.7%	• A glass has been formed • The surface of the crucible was contained many blisters. Probably, the firing temperature was somewhat too high 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
21	June 28	Sand (*): 29.4 g K_2CO_3: 10.3 g CaO: 10.3 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A large SiC crucible was used containing 50 g of batch • **Heating curve 14** - preheating at 800°C for • 1 hour; heating at 1450°C for 1 hour. The heating between 800°C and 1450°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 58.3% K_2O: 18.3% CaO: 21.8% Minor: 1.7%	• The glass consists a transparent top layer and a white opaque layer at the bottom • Between the two layers a yellow region is to be found • The top layer appears to be more gas bubbles 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
22	June 29	Sand (*): 26.9g K_2CO_3: 16.4 g CaO: 6.7 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A large **porcelain** crucible was used containing 50 g of batch • **Heating curve 16** - preheating at 800°C for 1 hour; heating at 1250°C for 1 hour. The heating between 800°C and 1250°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C	SiO_2: 55.7% K_2O: 27.9% CaO: 14.8% Minor: 1.6%	• Crucible was broken during the cooling process • A transparent glass has been formed • The glass contains many cracks. The annealing should be longer • Also the crucible was very fragile and could be broken by hand 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
23	June 29	With ball milling, the glass from exp. 21 was grinded to a fine white powder. 250 rpm for 5 minutes were used	• A small SiC crucible was used containing 50 g of batch • **Heating curve 14** - preheating at 800°C for 1 hour; heating at 1450°C for 1 hour. The heating between 800°C and 1450°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C for 10 hours	(SiO_2: 58.3% K_2O: 18.3% CaO: 21.8% Minor: 1.7%) Theoretical values of S21	• The small crucible was filled to 1 cm below the rim • The black SiC particles attached at the bottom of the glass was introduced into the batch during milling • A homogeneous black coloured glass was obtained 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
24	July 3	SiO_2: 24.3 g K_2CO_3: 14.9 g $CaCO_3$: 10.8 g High purity AnalaR Normapur reagents were used	• A large **porcelain** crucible was used containing 50 g of batch • **Heating curve 16** - preheating at 800°C for 1 hour; heating at 1250°C for 1 hour. The heating between 800°C and 1250°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C for 5 hours	SiO_2: 60.0% K_2O: 25.0% CaO: 14.9% Minor: /	• Transparent colourless glass is obtained • The crucible showed some cracks but did not break. The glass inside the crucible showed some cracks as well • On the glass surface small pits of 1 mm diameter due to gas bubbles were present 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
25	July 4	SiO_2: 25.3 g K_2CO_3: 8.9 g $CaCO_3$: 15.8 g High purity AnalaR Normapur reagents were used	• A small SiC crucible was used containing 50 g of batch • **Heating curve 14** - preheating at 800°C for 1 hour; heating at 1450°C for 1 hour. The heating between 800°C and 1450°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C for 10 hours	SiO_2: 62.9% K_2O: 15.1% CaO: 22.0% Minor: /	• This glass type has less fractures than the low melting glass of experiment 24 • The fabricated glass consisted of a white opaque layer at the bottom and a thin transparent layer at the top; in the centre a yellow region is present • The SiC particles attached to the bottom of the glass could partly be removed with a rasp 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
26	July 5	Sand (*): 24.3 g K_2CO_3: 14.9 g $CaCO_3$: 10.8 g (*) Chelford sand, Pilkington (UK) 93.6% Si_2O – FAAS analysis	• A large **porcelain** crucible was used containing 50 g of batch • **Heating curve 16** - preheating at 800°C for 1 hour; heating at 1250°C for 1 hour. The heating between 800°C and 1250°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C for 5 hours	SiO_2: 55.6% K_2O: 28.0% CaO: 14.8% Minor: 1.6%	• Transparent colourless glass is obtained • The crucible showed some cracks but did not break. The glass inside the crucible showed some cracks as well • On the glass surface small pits of 1 mm diameter due to gas bubbles were present 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
27	July 6	Sand (*): 24.3 g K_2CO_3: 14.9 g $CaCO_3$: 10.8 g (*) Dessel sand (Belgium) 99.4% Si_2O – FAAS analysis	• A large **porcelain** crucible was used containing 50 g of batch • **Heating curve 16/2** - preheating at 800°C for 1 hour; heating at 1250°C for 1 hour. The heating between 800°C and 1250°C was much slower (5°C/min) in order to avoid gas bubbles • The annealing is performed at 500°C for 5 hours but the cooling down from 1250°C to 500°C was reduced to 5°C/min	SiO_2: 59.7% K_2O: 25.0% CaO: 14.9% Minor: 0.4%	• A transparent glass with cracks was obtained • At the bottom of the crucible some cracks are visible 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
28	July 8	Sand (*): 24.3 g K_2CO_3: 14.9 g $CaCO_3$: 10.8 g (*) Lommel sand (Belgium) 99.7% Si_2O – FAAS analysis	• A large **porcelain** crucible was used containing 50 g of batch • **Heating curve 16/3** - preheating at 800°C for 1 hour; heating at 1250°C for 1 hour. The heating between 800°C and 1250°C was much slower (**1°C/min**) in order to avoid gas bubbles • The annealing is performed at 500°C for 10 hours • The cooling down from 1250°C to 500°C was 15°C/min • Cooling down between 500°C and 50°C was set to 0.3°C/min	SiO_2: 59.8% K_2O: 25.0% CaO: 14.9% Minor: 0.2%	• The Lommel sand is brown because it contained humic acids. All organic substances were burned and a clear and transparent glass is obtained • A very small heating rate of 1°C/min was used so that gases could be removed from the batch • The glass contained still cracks • At the bottom of the crucible some cracks are visible 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
29	July 12	SiO_2: 25.3 g K_2CO_3: 8.9 g $CaCO_3$: 15.8 g High purity AnalaR Normapur reagents were used	• A small SiC crucible was used containing 50 g of batch • **Heating curve 14/2** - preheating at 800°C for 1 hour; heating at **1500°C** for 1 hour. The heating between 800°C and 1500°C was set to 5°C/min • The annealing is performed at 500°C for 10 hours	SiO_2: 62.9% K_2O: 15.1% CaO: 22.0% Minor: /	• Still two glass layers with an opaque white one at the bottom and a transparent on top has been formed. The yellow zone appeared to be smaller 

Appendix B - Logbook Experiments 2012

Descriptions of the experiments realized in the period March-July 2012

by Stefano Barenghi, Erasmus Master Student from Ca' Foscari University of Venice

for AXiL -Antwerp X-Ray instrumentation and imaging Laboratory-

Chemistry Department of University of Antwerp

Master Thesis Project

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For each sample are displayed the date of realisation, the recipe chosen, the working condition (crucible, heating curve, etc.), the theoretical composition of major and minor elements (%wt.), some picture of the resulted glass and related observations. The glass fragments shown in the pictures have dimensions between 5 and 2 cm.

All experiments are conducted into Conservation Department of Artesis Hogeschool of Antwerp with a Bottom Loading Furnace 161/2007 – Termolab (Fornos Electricos LDA-Portugal) present in the Metal Conservation Department.

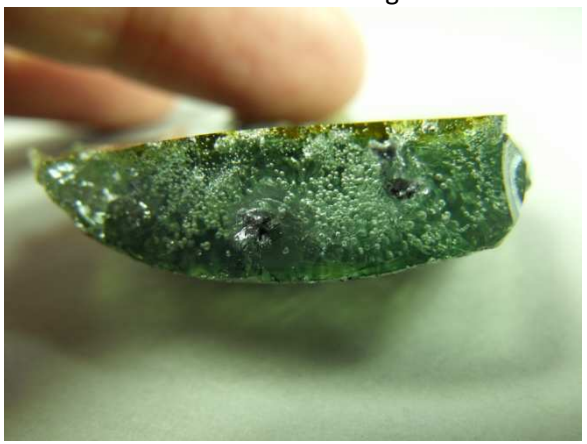
The awareness achieved will be available to the Glass Conservation Department, with the purpose to produce glass for research and/or conservation and restoration activities.

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
30	March 1	Sand (*): 24.45 g K_2CO_3: 15.40 g $CaCO_3$: 10.98 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible (300 ml) • **Heating curve 17(1)** – preheating at 800°C for 1h; max T 1250°C for 2h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Higher annealing T than before, in the way to avoid cracking	SiO_2: 55.1% K_2O: 28.5% CaO: 14.8% Minor: 1.6%	• Well melted glass without cracks: probably the new annealing T works good. • The glass has a good thick • It has a brownish color like beer bottle, not completely homogeneous • Little bubbles can be seen inside  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
31	March 2	Sand (*): 24.70 g K_2CO_3: 15.40 g $CaCO_3$: 11.00 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 17(2)** – preheating at 800°C for 1h; max T 1250°C for 10h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Trying to improve H.C. 17 a longer time of heating is used, looking for avoid bubbles; cracks problems seem solved with higher annealing T	SiO_2: 55.3% K_2O: 28.3% CaO: 14.7% Minor: 1.6%	• Well melted glass without cracks • Little bubbles in spite of longer heating time • Greenish color and transparent in some points  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
32	March 5	Sand (*):27.70 g K_2CO_3: 16.90 g $CaCO_3$: 11.90 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 17(3)** – preheating at 800°C for 1h; max T 1250°C for 1h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Trying to improve experiment 30 reducing melting time, to avoid the formation of iron sulfide (brown) or oxide (green)	SiO_2: 55.9% K_2O: 28.1% CaO: 14.4% Minor: 1.6%	• Well melted glass without cracks • Little bubbles inside like S30, S31, and brownish color like S30 • Short melting time take to brown , long melting time to green  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
33	March 13	Sand (*):27.89 g K_2CO_3: 17.30 g $CaCO_3$: 11.99 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 16** – preheating at 800°C for 1h; max T 1250°C for 1h; annealing at 500°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Trying to vary another parameter: not anymore melting time, but annealing T. It's used the H.C. 16 (used for S22, S24, S26) • The differences with S22, S24, S26 are the SiC crucible instead of the porcelain one, and the amount of ingredients (see 'glass experiment 2011') • S22, S24, S26 are transparent glasses, but with cracks	SiO_2: 55.7% K_2O: 28.4% CaO: 14.3% Minor: 1.6%	• Well melted glass, brownish color, no cracks, little bubbles inside • Greenish transparent color among the edge with the crucible • The variation of annealing T doesn't change nothing in color, it's not the right parameter to control it  

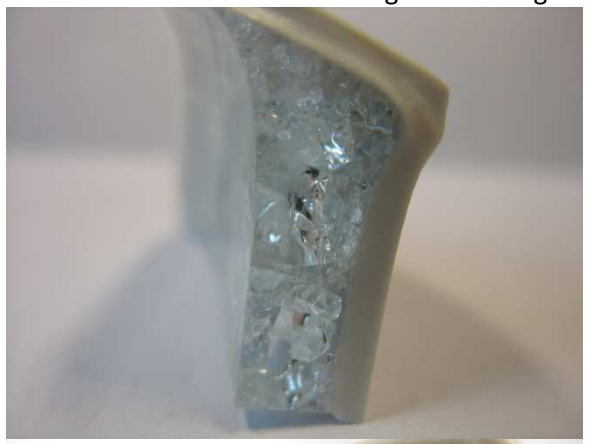
Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
34	March 14	Sand (*):24.50 g K_2CO_3: 15.44 g $CaCO_3$: 11.02 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 18** – preheating at 800°C for 1h; max T 1450°C for 2h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • This H.C is to compare with the number 17, because the only change is the melting T. All the experiment is to compare with exp.30: increasing melting T probably trace element will be discarded faster and there'll be no more color • In the same time is possible understand if melting T influences the amount of trace element (ICP-MS is necessary)	SiO_2: 55.1% K_2O: 28.5% CaO: 14.8% Minor: 1.6%	• Greenish glass, well melted, a couple of cracks (the sample was taken from the oven at 70°C and bring to room T), little bubbles • More transparent, but presence of particles from the crucible, that create little crystal inside • Crucible really ruined and fixed to the white stones of the oven • Thin yellow layer on the surface • Pieces of crucible inside the glass 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
35	March 15	Sand (*):24.70 g K_2CO_3: 15.49 g $CaCO_3$: 11.00 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • This experiment keep the H.C. 17 and change only the melting time: after 1, 2, 10 h of experiments 32, 30, 31, it's tried 15 h	SiO_2: 55.3% K_2O: 28.4% CaO: 14.7% Minor: 1.6%	• Greenish glass, well melted, a couple of cracks (the sample was taken from the oven at 230°C and bring to room T), little bubbles • The longer melting time doesn't change the color of glass.  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
36	March 21	Sand (*):24.70 g K_2CO_3: 15.50 g $CaCO_3$: 11.00 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• SiC crucible • **Heating curve 17(5)** – preheating at 800°C for 1h; max T 1250°C for 25h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • This experiment keep the H.C. 17 and change only the melting time: after 1, 2, 10, 15 h of experiments 32, 30, 31, 35 it's tried 25 h, because bubbles seem to move to the upper layer really slow	SiO_2: 55.3% K_2O: 28.4% CaO: 14.7% Minor: 1.6%	• Greenish well-melted glass, with transparent part on the edge with the crucible • Little bubbles in the top , close to the surface  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
37	April 17	Sand (*):12.4 g K_2CO_3: 7.8 g $CaCO_3$: 5.5 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(1)** – preheating at 800°C for 1h; max T 1250°C for 2h; annealing at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • The new porcelain crucible are experimented to avoid color coming from Fe contained into SiC crucible • The new porcelain crucible are smaller than SiC crucible have been used before: the total amount of initial ingredients is the half than previous experiments • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	SiO_2: 55.2% K_2O: 28.5% CaO: 14.7% Minor: 1.6%	• Transparent glass, well melted • Bubbles are present • Many cracks everywhere: for sure the crucible is responsible of this, because the same experiment with SiC crucible didn't produce cracking 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
38	April 18	Sand (*):12.4 g K_2CO_3: 7.8 g $CaCO_3$: 5.5 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 19** – preheating at 800°C for 1h; max T 1250°C for 2h; 1st annealing step at 1000°C for 5h, 2nd annealing step at 500°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Two annealing steps are experimented to avoid cracking • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	SiO_2: 55.2% K_2O: 28.5% CaO: 14.7% Minor: 1.6%	• Transparent glass, well melted • Bubbles are present • Many cracks everywhere. The oven was at 130°C when glass was taken: cracking due to the too fast cooling till room temperature 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
39	April 19	Sand (*):12.4 g K_2CO_3: 7.8 g $CaCO_3$: 5.5 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 20** – preheating at 800°C for 1h; max T 1250°C for 2h; 1st annealing step at 1000°C for 5h, 2nd annealing step at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Two annealing steps are experimented to avoid cracking: the second step has been increased to 800°C (differently from H.C. 19) • It waits room temperature before open the oven • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	SiO_2: 55.2% K_2O: 28.5% CaO: 14.7% Minor: 1.6%	• Transparent glass, well melted • Bubbles are present • Cracks everywhere. Two steps annealing are not enough to avoid them. Probably the crucible itself influences the glass cracking.  

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
40	May 03	Frit from glass S37: 11.8 g Ball milling: 3 min, 250 rpm (Instrument name: MP100, in Artesis) (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 20** – preheating at 800°C for 1h; max T 1250°C for 2h; 1st annealing step at 1000°C for 5h, 2nd annealing step at 800°C for 5h; both heating and annealing rates are 5°C/min • A frit has been done to remove all bubbles always present • It waits room temperature before open the oven • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	(SiO_2: 55.2% K_2O: 28.5% CaO: 14.7% Minor: 1.6%) Theoretical composition of S37	• Transparent bluish glass, well melted • No bubbles • Cracks everywhere. Two steps annealing are not enough to avoid them. Probably the crucible itself influences the glass cracking. 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
41	May 07	Sand (*):12.45 g K_2CO_3: 7.8 g $CaCO_3$: 5.5 g (*) Dessel sand (Belgium) 99.4% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 20** – preheating at 800°C for 1h; max T 1250°C for 2h; 1st annealing step at 1000°C for 5h, 2nd annealing step at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Two annealing steps are experimented to avoid cracking: the second step has been increased to 800°C (differently from H.C. 19) • It waits room temperature before open the oven • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	SiO_2: 59.3% K_2O: 25.5% CaO: 14.8% Minor: 0.4%	• Well melted glass, cracks, bubbles • No visible differences coming from the different sand 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
42	May 09	Sand (*):12.49 g K_2CO_3: 7.84 g $CaCO_3$: 5.54 g (*) Lommel sand (Belgium) 99.7% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 20** – preheating at 800°C for 1h; max T 1250°C for 2h; 1st annealing step at 1000°C for 5h, 2nd annealing step at 800°C for 5h; both heating and annealing rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Two annealing steps are experimented to avoid cracking: the second step has been increased to 800°C (differently from H.C. 19) • It waits room temperature before open the oven • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature	SiO_2: 59.5% K_2O: 25.5% CaO: 14.8% Minor: 0.2%	• Well melted glass, cracks, bubbles • No visible differences coming from the different sand 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
43	May 10	Sand (*):12.4 g K_2CO_3: 7.87 g $CaCO_3$: 5.53 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 21** – preheating at 800°C for 1h; max T 1250°C for 2h; no annealing, but cooling till 100°C, 1 h; heating and cooling rates are 5°C/min • Ingredients have been put in drying before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • No annealing to verify the possible volatilization of K_2O during this process	SiO_2: 55.1% K_2O: 28.6% CaO: 14.7% Minor: 1.6%	• Well melted glass, a lot of cracks and bubbles 

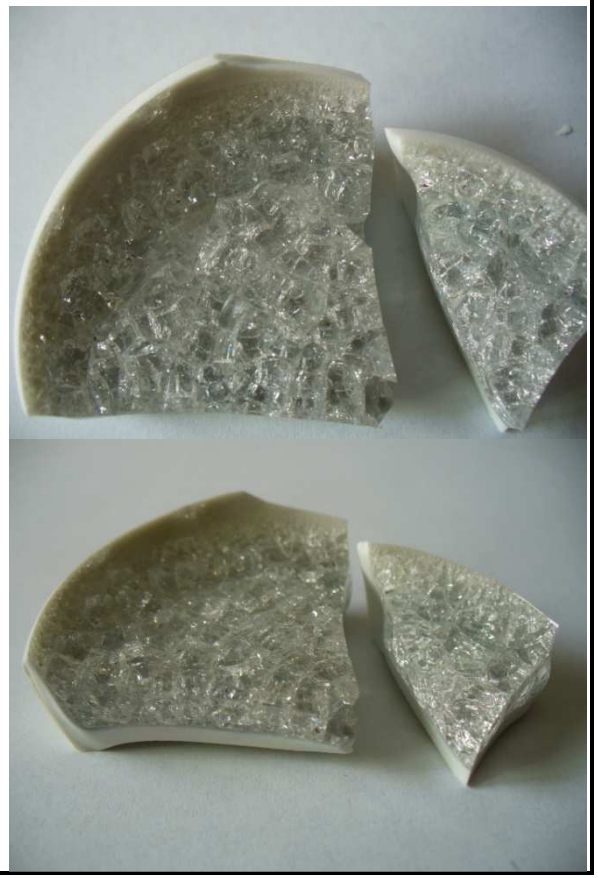
Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
44	May 22	Sand (*):12.1 g K_2CO_3: 3.5 g $CaCO_3$: 5.3 g Na_2CO_3: 4.9 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • First experiment with alkali mix: K and Na carbonate as initial ingredients	SiO_2: 55.2% K_2O: 14.9% CaO: 14.5% Na_2O: 13.9% Minor: 1.6%	• Good glass, transparent, with many cracks but not so many bubbles; it seems more brittle • The heating curve can be kept for the next experiments, with different K/Na ratio 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
45	May 24	Sand (*):12.14 g K_2CO_3: 2 g $CaCO_3$: 5.2 g Na_2CO_3: 6.52 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Different ratio between K and Na carbonate in comparison with S44	SiO_2: 55.7% K_2O: 9.9% CaO: 14.3% Na_2O: 18.5% Minor: 1.6%	• Good glass, many cracks but not so many bubbles; it appears a bit blues 

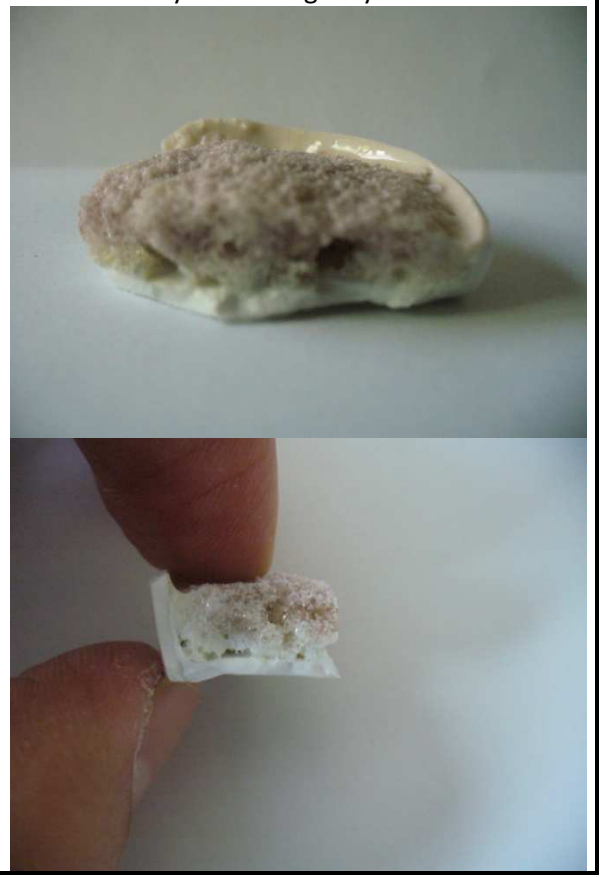
Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
46	June 4	Sand (*):12.04 g K_2CO_3: 0.5 g $CaCO_3$: 5.0 g Na_2CO_3: 8.3 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Different ratio between K and Na carbonate in comparison with S44 and S45	SiO_2: 56.4 % K_2O: 5% CaO: 13.6% Na_2O: 23.4% Minor: 1.6%	• Blueish transparent well melted glass, no bubbles, some cracks 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
47(1)	June 6 1st step	Sand (*):12.4 g K_2CO_3: 7.8 g $CaCO_3$: 5.5 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 22** – preheating at 800°C for 1h; max T 1000°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Melting T at 1000°C is experimented to check the temperature of vetrification	SiO_2: 55.2 % K_2O: 28.5% CaO: 14.7% Minor: 1.6%	• No glass but white porous cristalline material is formed 
47(2)	June 8 2nd step	Frit of June 6: 7.34g	• Porcelain crucible (150ml) • **Heating curve 22** – preheating at 800°C for 1h; max T 1000°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • A frit from the result of the first step (June 6) is prepared smashing that product • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • The same H.C. is kept	SiO_2: 55.2 % K_2O: 28.5% CaO: 14.7% Minor: 1.6%	• Still no glass bit white quite porous cristalline material; it seems a bit glassy and another frit should be tried, but the quantity of material is low and averything is very attached to the crucible 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
48	June 11	Sand (*):12.17 g K_2CO_3: 2.05 g $CaCO_3$: 5.26 g Na_2CO_3: 6.53 g (*) Dessel sand (Belgium) 99.4% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • K and Na glass with different sand: confront with S45 and S49	SiO_2: 59.6 % K_2O: 6.9% CaO: 14.5% Na_2O: 18.7% Minor: 0.4%	• Transparent well melted glass, no bubbles, some cracks 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
49	June 29	Sand (*):12.13 g K_2CO_3: 2.38 g $CaCO_3$: 5.25 g Na_2CO_3: 6.57 g (*) Lommel sand (Belgium) 99.7% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • K and Na glass with different sand: confront with S45 and S48	SiO_2: 59.0 % K_2O: 7.8% CaO: 14.3% Na_2O: 18.6% Minor: 0.2%	• Transparent well melted glass, no bubbles, cracks 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
50(1)	June 15 1st step	Sand (*):12.2 g K_2CO_3: 2.1 g $CaCO_3$: 5.2 g Na_2CO_3: 6.5 g (*) Chelford sand, Pilkington 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 22** – preheating at 800°C for 1h; max T 1000°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Melting T at 1000°C is experimented to check the temperature of vetrification • With Na carbonate the melting temperature should be lower, because the compound has a lower melting point	SiO_2: 55.7 % K_2O: 10.1% CaO: 14.3% Na_2O: 18.4% Minor: 1.6%	• No glass formed; white opaque cristalline material 
50(2)	June 2nd step	Frit of June 15: 8.30 g	• Porcelain crucible (150ml) • **Heating curve 22** – preheating at 800°C for 1h; max T 1000°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • A frit from the result of the first step (June 6) is prepared smashing that product • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • The same H.C. is kept	SiO_2: 55.7 % K_2O: 10.1% CaO: 14.3% Na_2O: 18.4% Minor: 1.6%	• After frit still no glassy material formed, but opaque and crystalline. • The melting T is still too low also for K+Na glass 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
51	June 20	Sand (*):12.01 g Beech ash: 6.0 g (*) Chelford sand 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash hasn't been purified, but just sifted out with a 1 mm^2 textile	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• No glass but a porous compound, brownish • Bottom layer almost glassy 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
52	June 22	Sand (*):15.09 g Beech ash: 5.0 g (*) Chelford sand 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash hasn't been purified, but just sifted out with a 1 mm^2 textile	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• No glass but brownish porous compound 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
53	June 25	Sand (*):5.04 g Beech ash: 5.0 g (*) Chelford sand 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash hasn't been purified, but just sifted out with a 1 mm^2 textile	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• Dirty transparent glass, with foamish material on the top layer 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
54	June 27	Sand (*):5.08 g Beech ash: 10 g (*) Chelford sand 93.6% Si_2O – FAAS analysis	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash hasn't been purified, but just sifted out with a 1 mm^2 textile	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• Dark brownish glass, opaque 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
55	July 02	Sand (*):8.94 g K_2CO_3: 3.89 g $CaCO_3$: 2.75 g (*) Chelford sand 93.6% Si_2O – FAAS analysis	• Pt crucible (75 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Pt crucible has been inserted into a SiC crucible: since it is the first use, I don't know how much the volume can increase during the melting process; in this way eventually flowing out will not ruin the oven	SiO_2: 55.2% K_2O: 28.5% CaO: c14.7% Minor: 1.6%	• Very good transparent glass, few bubbles and no cracks • Pt crucible works very good 

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
56	July 04	Sand (*): 7.09g Beech ash (**) (solute): 7.04 g (*) Chelford sand 93.6% Si_2O – FAAS analysis (**) The ash solute has been prepared on 02/07/2012	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash has been sifted and washed: the solution obtained has been dried	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• Good transparent glass, with purple shadows (Mn)

Nr.	Date	Recipe	Glass melting conditions	Theoretical composition (%wt.)	Observations
57	July 06	Sand (*): 7.05g Beech ash (**) (precipitate): 7.10 g (*) Chelford sand 93.6% Si_2O – FAAS analysis (**) The ash precipitate has been prepared on 02/07/2012	• Porcelain crucible (150 ml) • **Heating curve 17(4)** – preheating at 800°C for 1h; max T 1250°C for 15h; annealing at 800°C for 5h; heating and cooling rates are 5°C/min • Ingredients have been put in drying at 40°C before use, at least one day • Porcelain crucible has been inserted into a SiC crucible to prevent breaking of porcelain at high temperature • Beech ash has been sifted and washed: a precipitate is observed, stored and dried to be used	SiO_2: K_2O: CaO: Na_2O: MgO: Minor: These data are still unknown. Solution-ICP-MS on sand and ash will furnish them	• No glass obtained, but crystalline yellowish material • A glassy layer is visible on the edge with the crucible (glass or crucible's glaze?)