Titanium in quartz, gel making procedures

INTRODUCTION

Ti occurs naturally in quartz as a trace element; Ti^{4+} can substitute for Si^{4+} due to the tetravalent nature of both Ti and Si (Wark, 2006). Titanium concentrations in quartz can be used provide petrological information about the pressure and temperature (P-T) conditions quartz crystallised in, and thus the processes on going at these conditions (Spears and Wark, 2009; Thomas *et al*, 2010). The result is that Ti can be used as a geothermometer and geobarometer as its solubility in quartz has a strong dependence on P-T. It's therefore important to have an accurate set of synthetic quartz standards with known trace Ti concentrations, which can be used to calibrate natural samples against when using a Secondary Ion Mass Spectrometry (SIMS) instrument. A set of such standards, in gel form, were developed at Edinburgh Material and Micro-Analysis Centre (EMMAC), the University of Edinburgh, for this very purpose. This study explains the gel making process for a set of three amorphous and homogeneous synthetic quartz samples which were doped with 100ppm, 500ppm and 1000ppm titanium concentrations respectively. The most accurate source components for both silica and titanium were chosen, these were: tetraethyl orthosilicate (TEOS) with a quoted accuracy of 98% as a silica source and a AA titanium standard of 1000ppm Ti in ca. 2M hydrochloric acid. Accurate starting components were used in these initial stages as they result in a more accurate gel yield, and thus, a better standard. The titanium standard in a water and trace HCl solution wasn't used due to problems with solubility of titanium oxide.

SUMMARY OF PRODUCT

A set of 4 quartz glasses, each with a different concentration of Ti: 0% blank, 100ppm, 500ppm and 1000ppm were prepared from a synthetic gel.0.02-0.05g of each of the 4 glasses are available on request, and free of charge to Universities and other educational establishments. The synthetic gels were made from TEOS and Ti AA standard starting materials, ethanol was used to ensure the miscibility of TEOS Si(OC2H5)4), the silica source. Nitric acid was added to the weighed out Ti AA standard before this new solution was mixed into the TEOS and ethanol. Concentrated ammonia (0.88vol NH4OH) was then added to the amalgamated solutions to form a gelatinous precipitate of hydroxides. The gel was left partially covered over in the fume cupboard for 16hours to ensure the complete hydrolysis of the TEOS.

The gels were then slowly dried, starting at 70°C and increasing the temperature slowly over several days to 180°C in an oven. This was followed by a gradual heating to heating to around 400°C and finally roasting at 900°C, again this temperature was reached gradually to ensure the volatiles evaporated off slowly.

When dry and cooled to room temperature the gels were grounded into a fine powder. A small crucible was filled 1/2 to 1/3 full with the ground gel powder and fused in a furnace at 1735°C.On removal they were quenched with water. Hydrofluoric acid was used to digest any silica glass left in the platinum crucibles between fusions.

The doped values of 0ppm, 100ppm, 500ppm and 1000ppm Ti in a quartz glass have been verified separately by EMPA, SIMS and ICP OES instruments at the University of Edinburgh. Details of the exact values can be found in the Tables section of this document.

ADVANTAGES OF GEL STANDARDS

To overcome previous problems with glass preparation and difficulties from the nucleation of low-temperature phases from their high-temperature structures lead to the use of gel starting materials (Edgar, 1973). Gels are an amorphous solid which contains no birefringent material and gives no X-ray diffraction patterns. They are made by combining standardised aqueous solutions of hydroxides or metal nitrates with a source of silica which undergoes hydrolysis at suitable pH and temperature conditions. The minimum amount of containers should be used during the gel making process to minimise the loss of material to the container. The gel is then subjected to a gradual increase in heat to remove any unwanted compounds remaining from the addition of acids during hydrolysis and is then finally roasted. Using rutile in quartz standards, due to the slow diffusion of Ti through the quartz mineral structure, can produce local heterogeneities and have a long preparation time. In comparison, gel standards using Ti in solution produce a quick homogeneity and have a much lower preparation time.

PREPARATION OF GELS

CLEANING EQUIPMENT

3 parts hydrochloric acid and one part nitric acid were volumetrically measured using measuring cylinders. The hydrochloric acid was poured into a beaker and the nitric acid gradually added whilst stirring to make Aqua Regia, this was carried out in a fume cupboard and the temperature of the beaker was monitored because the two acids can boil if added too quickly. As the two were mixed the colour changed from clear to yellow, and when left over time, to an orange-red colour. This indicates that the compound which causes oxidation has been formed and the solution will clean the equipment properly.

De-ionised water of 18.2mΩ quality can be used along with bicarbonate, and plenty of water to neutralise any spills.

The Teflon beakers, Teflon beaker lids, Teflon coated magnetic stirrers, and Teflon large stirrers were all cleaned using Aqua Regia by swilling the solution over the surface, wiping the surface with tissue and rising with de-ionised water.

START MATERIALS

SiO_2 SOURCE

Tetraethyl orthosilicate (TEOS) was used as the silica source for the gels. The weight of TEOS needed to achieve a 99.99wt%, 99.95wt% and 99.9wt% of SiO_2 was calculated using the molecular weight of TEOS using its chemical formula: $Si(OC_2H_5)_4$ and the molecular weight ratio of the total value for TEOS and the value for just SiO_2. This was altered for the amount of Ti which was being added for each gel, and was found to be 34.66973268g, 34.6558634g and 34.6385268g, of TEOS for corresponding Ti concentrations of 100ppm, 500ppm and 1000ppm, respectively, in the individual

gels. A blank, pure silica, standard was also made which required 34.6732g of TEOS which yields a 10g gel output.

Ti SOURCE

Initially these experiments were going to be carried out using $TiCl_4$ (a liquid). However, when this was ordered from the manufacturers it was found to contain 20% HCl which wasn't accurately defined so this method was scrapped as an accurate ppm value of Ti would be impossible to achieve. Instead a 1000ppm Ti AA standard in water with trace amounts of HCl was used. The latter was accurately weighed out for each standard to achieve the desired weight percentages of Ti for 100ppm, 500ppm and 1000ppm in the final total 10g gel yield. To achieve 100ppm Ti, 0.01wt% of the 10g end product gel yield needs to be Ti. The calculated amounts for starting materials showed 1g of the AA solution added to 34.66973268g of TEOS gave the correct wt% of Ti for 100ppm in the final silica gel yield. 5g and 10g were added to 34.6558634g and 34.6385268g, respectively, of TEOS to achieve 500ppm Ti and 1000ppm.

100ppm GEL

The TEOS and Ti solution were weighed out into separate Teflon beakers using a Satorius MC 210 S Balance, situated on a spring balanced table, which has an accuracy of up to 0.00001 decimal places. To ensure the results were as accurate as possible the initial bulk values were pipetted in to just under the value required and the final decimal places achieved accurately using a syringe (Syringe Perfection, SGE Analytical Science model). Whilst the weight measurements were being made the door of the scales, and of the lab, remained shut to reduce any changes in air pressure. N.B. vibrations also affect the accuracy of this balance and care was taken to reduce this possibility by weighing the solutions out in quieter time periods where disturbances (such as trollies of equipment moving around the building) could be avoided.

The TEOS values were recorded as 34.66971g rather than 34.66973g (see table 2) and a lid placed on it immediately afterwards. When measuring out the 1000ppm AA Ti standard it was noted that the evaporation of Cl was continual and fast, therefore it's important to measure this quickly and put the lid onto the bottle and the beaker as quickly as possible. The recorded value for Ti was 1.0014g which rapidly reduced to 0.99957g and values below this, but no Ti was lost through evaporation so this isn't considered important (1g aim).

A small amount of de-ionised water was added to the measured Ti solution in a Teflon beaker before 20ml of nitric acid was pipetted slowly in and swilled together. 15ml of ethanol was pipetted into the TEOS and mixed well before it was added to the Ti and nitric solution. The Teflon beaker, which contained the TEOS, was then partially filled with de-ionised water which was swilled around and added to the Ti solution to ensure as little starting material was lost as possible during the transfer. 20ml of ammonium was pipetted into the combined Ti and TEOS solution whilst continually stirring, care was taken monitor the temperature of the beaker as this reaction is exothermic. It is this reaction between the nitric acid (HNO_3, 70%) that produces gelatination. The solution's consistency soon turns into a paste, at which point the Teflon stirring rod was left in the beaker and a loose lid fitted. The beaker was left to stand at the back of a fume cupboard overnight (or over a weekend) and the mixture checked after this settling period to see if there were any alterations or abnormalities before the next steps were undertaken.

500ppm GEL

34.65586g of TEOS was weighed out instead of 34.6558634 as the accuracy couldn't be achieved. 5.0002g of the 1000ppm Ti AA standard was weighed out to achieve the 0.05wt. % Ti desired. The preparation of this gel matches the procedures outline in the 100ppm Gel section above.

1000ppm GEL

34.63851g of TEOS was weighed instead of 34.6385268g due to accuracy and the difficulties of achieving the exact last decimal place. 10.001g of 1000ppm Ti AA standard was weighed out for the desired end product to contain 0.1 wt. % Ti. The preparation of this gel matches the procedures outline in the 100ppm Gel section above.

100% TEOS GEL: BLANK,

A blank standard with no titanium, 100% silica, was made to test the silica yield of the weighed out TEOS in the final gels. To achieve a 100% SiO_2 gel 34.673210g of TEOS was weighed out and used in the procedures outlines in 100ppm Ti.

NUMBER OF ATTEMPTS

Only 1 preparation attempt was made for each of the gels, as each 1^{st} attempt at making the gels was successful.

DRYING THE GELS

The gel samples were checked after a minimum of 24 hours for discolouration and texture. If these parameters were the same as when they were initially stored in the fume cupboard then the drying process could begin. The slow evaporation of ethanol was achieved by placing the gels (still in the loosely lidded Teflon beakers which still have the Teflon stirrer left in them) on a very accurate hot plate at 70°c, below the boiling point of ethanol, for 24 hours. The temperature of the hot plate was independently measured by a thermocouple, and a small gradient assumed throughout the beaker. This slow process is preferred, as rapid boiling off of ethanol could result in spitting and possible cross contamination as a result; if the gels are dried together, it is therefore important to cover the beakers with loose lids and keep them well spaced. In this case the gels were dried separately due to the size of the hotspot on the hot plate but fitted with loose lids anyway. After the initial 24 hours at 70°C the temperature was raised by 10°C every 2-3 hours until it reached 160°C. The gels were left at 160°C for a minimum of 24 hours to complete the initial drying process. This whole process took 2 and a half days for each gel.

ISO MANTLING HEATERS

The rest of the ammonium was then removed slowly by sublimation rather than boiling, the latter of which could result in expulsion of the gel from the beaker and into a neighbouring sample.

Any accumulation of material found around the top and lid of the beaker was loosened and returned to the beaker carefully, using a pinched grip between forefinger and thumb on a gloved hand. Or

within the beaker itself, mainly on the sides, by using the stirrer and then running a gloved finger along the side of the beaker and the stirrer to again loosen the dried gel.

All of the dried gel was then transferred from the Teflon beaker to a pyrex glass beaker. This was carried out over black non-absorbent paper, cleaned with acetone between usages, so any flecks of gels lost onto the paper from the beaker could be tipped back in without any contamination. The process was completed very carefully to ensure as little material was lost as possible, and any lost was gathered back in. Any material left in the teflon beaker after the initial transfer was then loosened and added to the pyrex beaker using the same methods as outlined in the previous paragraph.

The pyrex beakers were then transferred to an isomantle heater (Model: a blue Barnstead Electrothermal and a grey Fisher isomantle heater), which was initially set to 1.2. The reading was then increased by 0.2 every 2 hours (approximate) until 5.0 was attained. The full run time for one gel was 5 days (8 hour days), so several isomantle heaters were used so that more than one gel could be drying at the same time in order to reduce the overall run time of this stage of the experiment. Each temperature increase was measured independently using a thermocouple, this data was recorded to document any differences between isomantle heaters. Gels which dried on the same heater showed differences in the temperature increases recorded between readings (see table 1).

FURNACE STAGE 1 (100-400°C initial temperature ramping)

The gels were then transferred into palladium-gold PALAU (these also contain a small amount of silver, this was checked by analysing a small sliver of one of the containers on the SEM) containers with loose fitting PALAU lids. They were lowered by attaching a length of malleable thick metal wire, which was folded to into a hook and handle, to a thin wire attached to the container, the wires could easily carry the weight of the full container and lid. The attached thin wire was bent in the middle to ensure the container didn't rock too much as it was lowered into the furnace and also as a place to slot the hook wire onto when removing the sample. These were lowered into a furnace which was initially set to 100°C and then increased gradually by 50°C every hour until 400°C was attained, the gels were left at this temperature overnight. Each time the temperature was increased a thermal gradient within the furnace was recorded with an independent thermocouple as well as the set temperature and the green digital display temperature on the furnace (see tables 2-5). This was done in detail to record the changes in temperature as the gels were being heated up to 400°C. As a result any later anomalies which could be explained by problems with the heating the point at which the procedures needed to be reviewed could be easily traced. It's important to use a furnace underneath a fume extractor for both stage 1 and 2 of the drying procedure as a lot of fumes are driven off the gels during the drying process.

FURNACE STAGE 2 (400-900°C second temperature ramping to dry)

Using the same furnace the gels went through a second stage of drying as the temperature was increased from 400-900°C in 100°C increments every hour until they reached 900°C at which they were roasted for 24 hours. For both stages of drying and the final roasting temperature in the furnaces it's important to note that the temperature gradient profile within the furnace changed and quite often didn't match the setting or display readings given at the base of the furnace where the sample sat (See tables 2-5). The variation in temperature profile throughout the furnace meant that

raising the sample height to be exact for one temperature reading would be fruitless and so independent thermocouple readings were used instead to monitor and record these differences (which, in most cases, were minor).

On removal from the furnace the PALAU containers were placed in a, fresh and uncontaminated, desiccator and left to cool to room temperature. Once cooled it was noted that some of the aluminium oxide material that makes up the insulating block for the lid of the furnace had fallen into the small gaps at the side of the container where the lid and container sides didn't quite meet. It was suggested that the malleable but fragile containers were carefully shaped at the top to curve inwards to reduce this contamination possibility for future runs. However, this was difficult as the containers were fragile and bending of the sides of the container enhanced already developing cracks, not detrimental to the container as they were a maximum of 3mm in size. The furnaces used for this part of the process weren't extremely stable, their readings could vary to quite a high degree and the geotherm within them changed drastically throughout for each gel when it reached this point in the procedure.

N.B. For temperatures over 750°C the temperature with the furnace become very unstable, this was due to a probe, thermocouple, fault which gave the error code Er-01. This was the case for furnace A which was used in this study and furnace B (noted by another user) in the gel preparation lab.

POWDERING THE GELS

When the gels reached room temperature, in the desiccator, they were gradually transferred into a cleaned agate mortar and pestle with a metal spatula and ground into a fine powder. Black matt and un-absorbent paper was placed under and around the mortar so powder which went over the sides could be collected and returned to the mortar. The paper was cleaned with ethanol between different gels being ground to avoid contamination. A face mask and gloves were worn at this stage to reduce contamination, and because the dried gel made a very fine and airborne dust when ground. The gels were ground in small quantities at any one time to ensure as fine a powder as possible was produced. It's worthy of note that the gel powders are extremely static and are hard to remove from the mortar once ground, a metal spatula is the best implement to use. However, the powder still kicks up and adheres to the mortar again in another place or flicks off the side and on to the black paper. This part of the procedure is extremely fiddly. The 500ppm gel at this stage contained a lot of green-grey coloured crystals at the bottom only; the gel was ground in two stages so the gel free of these crystals at the top was bottled separately.

GLASSING THE GELS (1st)

A small amount of the powdered sample was transferred to a platinum crucible. The container for the gel was altered because platinum has a melting temperature of 1768°C, PALAU of 1076°C and Quartz of 1713°C. Glassing the gels at 1713°C needs to be very accurate as the container melts at 98°C above the melting temperature of the samples, therefore this needs to be done very accurately with a stable temperature. A Nabertherm 1750 furnace was used.

The Nabertherm was programmed to increase from 600-1200°C the day before use. An independent thermocouple was made using one pure platinum wire and one platinum 13% rhodium wire (Type R

thermocouple). This still produced a linear transfer of electrons from the two wires at high temperatures and therefore recorded the thermal gradient within the furnace using EMF and voltage readings which correlated with temperature. A Type R thermocouple can be used up to 1760°C. The initial thermal gradient within the Nabertherm at 1200°C was 30°C higher, where the sample sat, than recorded by the internally built thermocouple. However this discrepancy wasn't present for the experiment, instead the two varied by up to 4°C.

The platinum crucibles were filled to $^{1}/_{3}$ or a ½ full with the powdered gel sample initially to test how the sample behaves in the crucible at high temperatures. These crucibles were placed in an aluminium oxide cylinder shaped boat which is less delicate than the crucibles and easier to grab. N.B. the aluminium oxide boats were cleaned by wiping them with a dry tissue only, if water is used they absorb the water and swell as a consequence.

The samples were loaded at 1200°C, and then the temperature was gradually ramped from 1200°C to an initial temperature 1713°C (over the course of 2-3hours), and left at 1713°C for 10 minutes. A secondary test was also done to see how the gel behaved at 1713°C when left at this temperature for 1hour in the furnace, after 45 minutes at 1713°C the sample underwent an intermediate check to monitor how it and its container were dealing with this sustained high temperature. This ensured that the crucible wasn't damaged by increasing the temperature too much. It also gave an indication of the outcomes of running the experiments for longer timescale (1hour instead of 10minutes) and at this temperature.

The crucible within the boat was extracted and placed on ceramic blocks and cooled, a welding mask, safety glasses, heavy duty gloves, a lab coat, hand shield and tongues were used to do this. Sensible shoes were worn (which covered the entire foot e.g. full trainers etc.). An aluminium boat is placed under the crucibles which can be grabbed using the tongues.

POTENTIAL PROBLEMS

The crucibles must have lids as the furnace has been well used and therefore isn't clean, therefore this is the only way to reduce contamination. However, at high temperatures the crucible may deform under its own weight and mix as the lid presses down on the crucible. A plan B could use molybdenum, with a melting temperature of 2,623°C, in a high pressure cylinder press. This would negate the problems of oxidation and deformation as it's a high pressure reducing environment with lots of graphite which oxidises instead. The main problem with the platinum crucible and its lid at 1713°C is that they can stick together.

Another potential problem was how the gel sample would wet the crucible: possibly crawling up the sides and leaving a thin coat that wasn't easily extractable or even escaping the crucible entirely.

The type R thermocouple can only go up to 1760°C as platinum melts at 1768°C. If the furnace's temperature gradient was sufficiently different from the internal thermocouple readings rose to over 1760°C problems with the independent thermocouple and crucibles could arise. Using a tungsten-iridium thermocouple which can go up to 2100°C will negate the issue with the independent thermocouple.

1st GLASSING ATTEMPT RESULTS (100ppm)

Although the crucible and its lid had stuck together they were easily peeled apart. Throughout the experiment run and before in the temperature ramping there was no large discrepancies between the internal and independent thermocouple readings. The gel had shrunk in size and become dense at 1713°C but wasn't a glass, it was then analysed on the SEM and small melt globules could be seen interspersed with gel sample which hadn't melted. XRD analysis revealed that the gel had formed cristobalite, the high temperature polymorph of quartz, with a melting point of 1713°C. This occurred for both the 10 minute and 1hour experiment as the samples were loaded at 1200°C and didn't reach a high enough temperature above the melting point to glass the samples.

The XRD analysis diffracts the X-ray photons produced by ionised copper atoms to identify the distance between atoms in the crystal lattice present (d spacing), using the Bragg equation ($n\lambda = 2d \sin\theta$). The X-ray source and detector move constantly throughout the analysis to move from the maximum angle (θ) between them to the minimum. Minerals have a structure and therefore show peaks, if the sample had completely glassed there would have been a very broad arc with no sharp peaks. The results identified cristobalite only (no α quartz) but can't provide the ratio of this to glass present which was seen on the SEM images (Figure 1).

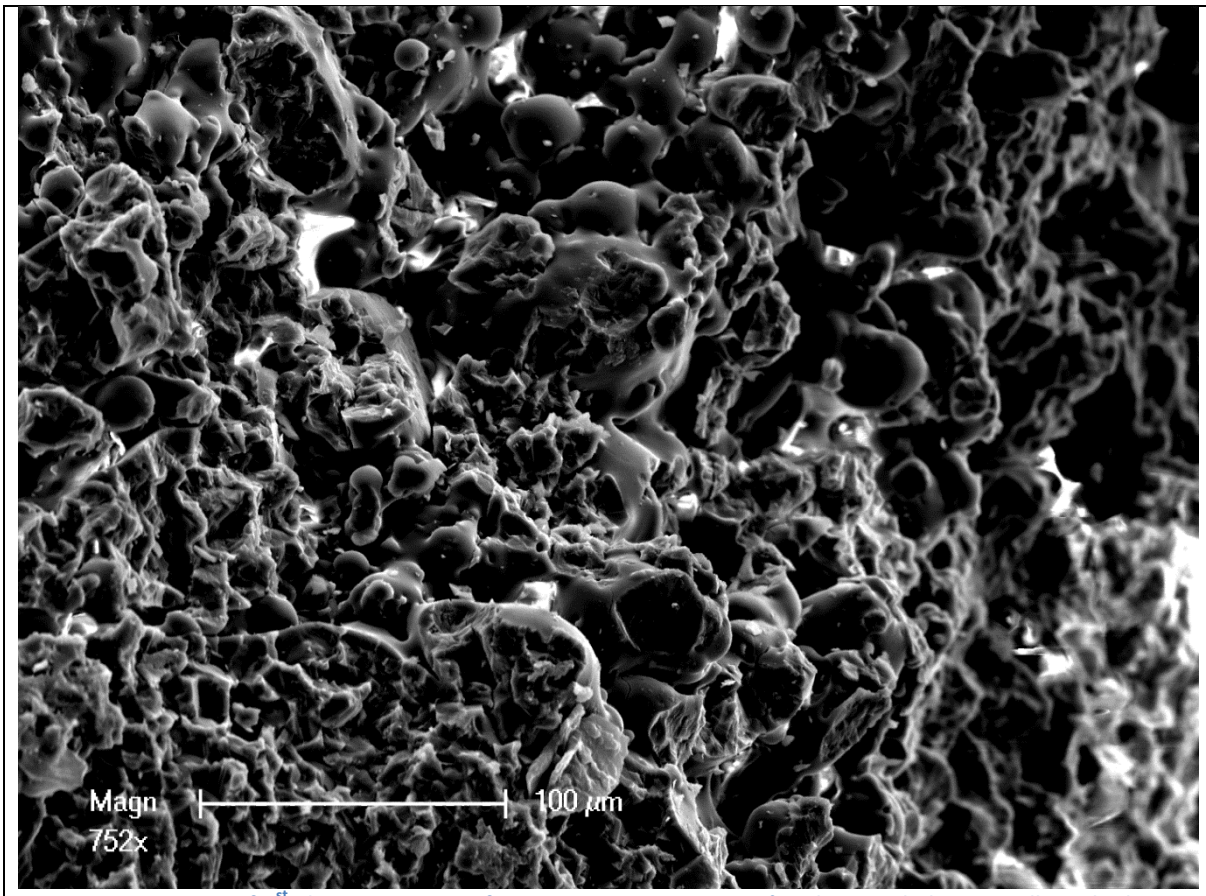

Figure 1: SEM image of 1st glassing attempt of 100ppm Ti in SiO_2 at 1713°C. The sample has partially melted, smooth globules of melt can be seen to interweave with a crystalline structure which, when analysed by XRD, was found to be cristabolite (high temperature quartz).

2nd GLASSING ATTEMPT RESULTS (100ppm) – 10 minutes

Another attempt was made loading the 100ppm gel as described previously but ramping the temperature to 1735°C (instead of 1713°C) for 10minutes. The gel had formed a glass which had a

high density of bubbles along with 4 dark brown hexagonal plates which could also be seen within the clear bubbly glass. The sample had fallen over but had not spilt within the aluminium oxide boat, this could be the source of contamination which has created the brown hexagonal flecks.

3rd GLASSING ATTEMPT RESULTS (100ppm) – 10 minutes

Procedures, previous two for methods and but again at 1735°C, like attempt 2. This time the crucible didn't fall over but the result was exactly the same as attempt 2. The contamination must be coming from elsewhere; it was considered at this point whether the brown flecks could be titanium which wasn't homogenised.

4th GLASSING ATTEMPT RESULTS (100ppm) – 100 minutes

As above. A 4th attempt at 10minutes was done for the 100ppm gel as the 1st didn't make a glass. A set of 3 glasses made at 1735°C for 10minutes for each gel was the aim.

5th GLASSING ATTEMPT RESULTS (100ppm) – 60 minutes

A test was also carried out for each gel at 1735°C but was left in the furnace for 1hour. The glassing was repeated at this higher temperature to see if: the brown plates were sourced from inhomogenised titanium which might homogenise further with the silica if left at a high temperature for longer, as well as to see if more bubbles were lost from the viscous molten gel when the crucible was left at 1735°C for an hour. The resultant bubbles were less densely spaced and smaller, 4 brown (maybe more rounded plates) were found within this glass. When this sample was loaded into the furnace at 1735°C, the thermal shock to the aluminium oxide boat caused the bottom to fall off when an attempt was made to remove it after 1 hour. The crucible was left standing on the base in the furnace which was then removed, so the sample run wasn't affected, but a note should be made to load the aluminium boats (containing samples) at a lower temperature and then increase it.

SIMS ANALYSIS OF 100ppm Ti ON THE 1270 (University of Edinburgh)

SIMS analysis was carried out on the 3rd glass attempt for 100ppm Ti in 100 wt. % SiO_2. The known standard SRM 610 was analysed alongside the glass as a reference standard and the count rates were compared. However, the although this wasn't ideal. Initially the counts for ^{28}Si (Farraday Cup) and ^{49}Ti (Electron Multiplier) were recorded (two detectors used for differences in counts low and high) and showed 100 wt. % SiO_2 with 65-66ppm (25-100ppm range) Ti were present in the glass. Tests for counts of Al, Ca and Na were also carried out and came back as negligible for Na, Al and a few ppm for Ca, so overall there is no contamination. 20 points were then manually pre-set to avoid the bubbles to test whether the same concentrations were detected throughout the sample. Each point is analysed 10 times (10 cycles).

CLEANING THE CRUCIBLES BETWEEN GLASSING

The crucibles were only cleaned between two different gels (i.e. a 100ppm and a 1000ppm gel, not between attempts at glassing the same gel more than once for tests).

Cleaning the crucibles after glassing was 1st attempted using nitric acid in a large beaker, where the crucibles were left in the nitric acid for 3 hours. The glass was still well attached to the crucible when they were removed from the beaker, washed with water and an attempt made to loosen the glass. The platinum crucibles were then cleaned using hydrofluoric acid (HF) to dissolve the silicate glass. It would also have been possible to clean the crucibles by adding lithium borate flux (containing La_2O_3

as a heavy absorber, used when making major element glasses) into the crucibles then heating them until the sample glass has melted. This could then be poured out of the crucible and the crucible washed in heated hydrochloric acid, then washed with water before being cleaned again using nitric acid. The latter option wasn't chosen for these samples due to the higher possibility of contamination of the crucibles.

HF dissolves glass, so Teflon beakers and plastic tweezers were used. Safety equipment for use with HF included: double layers of plastic gloves (inner, disposable neoprene; outer, heavy duty, elbow length black thick rubber gloves) to avoid pin hole sized leaks, a face shield, glasses, lab coat, plastic apron which was worn over the lab coat (all provided by Ann Mennim) and full cover shoes.

The crucibles were removed from the Teflon beaker containing HF and dunked (using the plastic tweezers and gloved hands) into a larger beaker filled with tap water. They were then washed and rinsed under the tap, using normal water (hands still gloved). The HF could also have been neutralised in the beaker using boric acid. The crucibles were then looked at under a microscope (ZEISS STEMI6 and a WILD MAKROSKOP M420 1,25x) to ascertain whether any of the silicate glass remained inside. After 1 hour in hydrofluoric acid the glass was still visibly attached, so the crucibles and lids were left in HF overnight.

FULL GLASSING OF REMAINING GELS

A set of 4 glasses were made for the other two titanium bearing gels 500ppm and 1000ppm gels, comprising of: 3 samples which were glassed at 1735°C for 10 minutes and 1 sample which was glassed at 1735°C for 1 hour. This procedure follows exactly the one adopted for the 100ppm glass sample production.

For the 0ppm, blank, 3 samples were glassed at 1735°C for 10 minutes, the longer roast time wasn't needed in this case as this sample contains no titanium.

RESULTS

It's worth noting that the quartz glasses produced are very viscous and thus all of the samples produced, even the ones which spent a longer amount of time at a high temperature, were very bubbly. This is probably due to the air trapped between the gel powders when they were measured out in to the crucibles.

The black/brown hexagonal speckles were also found in the 0ppm blank sample as well as the samples doped with Ti. It was initially suggested that these might have be silica nitrate compound source, which has spaces within the structure that are filled by electrons that absorb light and thus appeared opaque. However, when tested on the SEM the element peaks proved this wrong and that they were in fact Fe (see appendix 1, figures 4-14). The source of the Fe could be due to the TEOS which was only 98% accuracy.

Only anomaly was the 3rd glassing attempt of the 0ppm sample left a thin convex cristobalite blob at the base of the crucible where the rest turned to glass with no gradient. Thus the only the glass sample was taken out and used; the rest was disposed of using HF.

EMPA (RESULTS)

20 points for analysis were manually selected, to avoid bubbles and surface scratches (from polishing), for each sample. 15 samples were analysed overall; 3, 10 minute glasses for each 4 glass types and 3 1hour glass was analysed for those that contained Ti. 5 detectors recorded Ti values (both 49Ti and 48Ti) during the analysis of the glasses, along with Si and O and a total concentration of each in a percentage was recorded (see tables 9-15).

The recorded average values for each glass are as follows:

Doped Ti glass values	Percentage values detected by EMPA
0ppm	-0.00064
100ppm (10 minute fusion))	0.00895
100ppm (1 hour fusion)	0.00892
500ppm (10 minute fusion)	0.047369
500ppm (1 hour fusion)	0.045837
1000ppm (10 minute fusion)	0.095447
1000ppm (1 hour fusion)	0.0953

The results show relatively similar values for the 10minute and 1hour fusions however the ranges (see tables 9-15) indicate that a longer fusion time creates a more homogenised sample.

ICP OES ANALYSIS

PREPARATION OF SAMPLES FOR WET CHEMICAL ANALYSIS

Wet chemical analysis of 4 powdered glasses: 0ppm, 100ppm, 500ppm and 1000ppm (P, the primary samples which looked the best glasses out of each group) was carried out using ICP OES.

50-150 micrograms of glass were ground using an agate mortar and pestle into a very fine powder. The powder was then weighed accurately using a spring loaded Satorius MC 210 S balance into Teflon beakers with slot in lids that were pre-cleaned using 10% nitric solution. For ICP OES the sample needed to be dissolved in nitric acid, however as they're silicate samples they had to be first digested with HF. A finnpipette was used to measure out 2ml of HF and 1ml of nitric acid into Teflon beakers containing the powdered glass samples, these beakers were left on a hot plate for 24 hours. An assessment was made after 8 hours whether to add anymore HF, if the powdered glass wasn't fully digested, the HF evaporated off on the hot plate and the remaining solution contained the dissolved silicate sample. An acid blank was also made using the same method which was analysed alongside the glasses during ICP OES for calibration and tests for contamination. The remaining solutions were then diluted to 10ml volume in a glass flask with a stopper using distilled water.

RESULTS

The 5 out of 6 analysis results matched the external calibration of the EMPA and the SIMS analysis well, however one was consistently low in Ti. The average for all results can be seen below in table 1, standard deviation and percentage standard deviation can be seen below (also see Table 7):

Table 1: Shows the ppm results for ICP OES which were converted from Mgl-1 for each run, a more detailed table including the raw data and other parameters from the analysis can be found in table 21.

	0pm	100ppm	500ppm	1000ppm
	4.123784	105.8222	503.4306	989.2412
	-49.4813	85.55506	508.8279	1026.456
	-31.2963	92.21361	507.4388	1011.403
	-17.5489	96.91506	503.6735	1000.657
	-0.049	59.97265	168.362	641.9311
Average inc. poor run	-18.8503	88.09573	438.3466	933.9377
Std Dev (inc.poor run)	22.22697	17.36613	150.9442	163.8126
% Std dev (inc. poor run)	-117.913	19.71279	34.43489	17.54
Average (not inc. poor run)	-23.5507	95.1265	505.8427	1006.939
Std Dev (not inc. poor run)	22.61481	8.518514	2.706986	15.84831
% Std Dev (not inc. poor run)	-96.0262	8.954934	0.535144	1.57391

FURTHER SIMS ANALYSIS, on the 1270, (RESULTS)

Before each separate run on the 4F SIMS instrument BOG-QTZ and SRM 610 standards were analysed twice, to test the reproducibility for each analysis run and to use SRM 610 as a reference standard (tables 17-20). Each of the synthetic samples were analysed 24 times, avoiding areas with vesicles (table 17).

For the second day of analysis the beam current was increased and Mg was no longer analysed as a contaminant as this had proved to be unnecessary from the 1st day's analysis.

The average values for each synthetic quartz glass are as follows:

Doped starting values (ppm)	SIMS values, using the reference standard SRM 610
0ppm	0.338ppm
100ppm	69.3ppm
500ppm	335ppm
1000ppm	662ppm

The standard deviation increases for higher concentrations precisely because they larger values (see table 16 and figure 4. The % standard deviation is largest for the blank sample, as expected and between 4.9 and 5.9% for the other glasses. The synthetic glasses were compared to the reference standard SRM 610 which was unsuitable to achieve accurate Ti concentrations but it was the only

reference standard available, consequently the glass's Ti concentrations are consistently lower than their doped values (see above, and table 16).

The results for each of the Ti in quartz gels can be seen to follow a straight line with an R^2 value of 0.9995 (figure 4). This can then be used as a line of reference to convert the UHT rock Ti values, which were found using the inaccurate SRM 610 and BOG standards, into more accurate values of ppm concentrations.

4 quartz clusters within the host garnet, from an UHT rock sampled from the Napier Complex, Antarctica were chosen for analysis; their locations relative to each other within the garnet can be seen in figures 2 and 3. The synthetic standards were all re-analysed once more between the analysis of the known Ti concentration glass standards, SRM 610 and BOG, and the unknown Ti concentration Napier Complex rock (Figure 4), in order to test reproducibility. (See table 6 for raw data).

Using the synthetic quartz conversion line for Ti in quartz it was found the UHT rock contained 225ppm of Ti rather than the 150ppm recorded when calibrated with the SRM 610 values. This value can be taken and then put into a Ti thermometry and barometry calculator and the conditions of quartz crystallisation can be worked out.

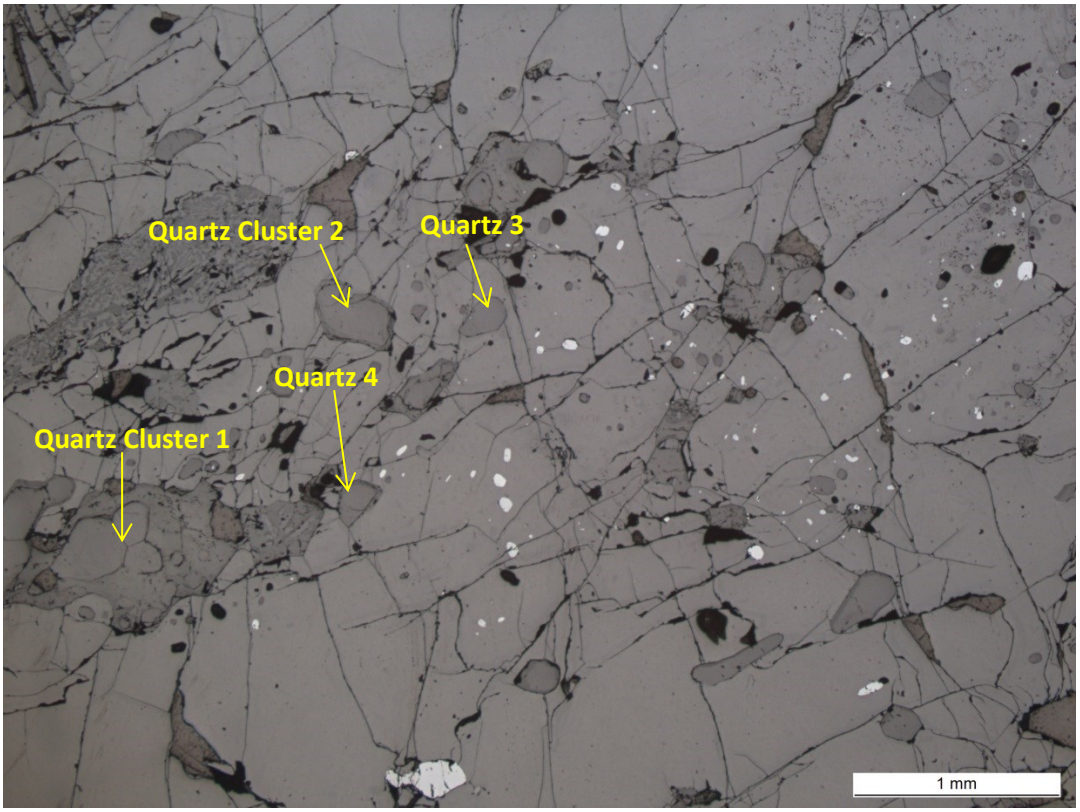

Figure 2: A reflected light photomicrograph of the UHT Napier Complex rock donated by Simon Harley. Location of quartz clusters analysed is indicated by yellow labels and arrows; they are all situated in a host garnet and have very fine plagioclase rims.

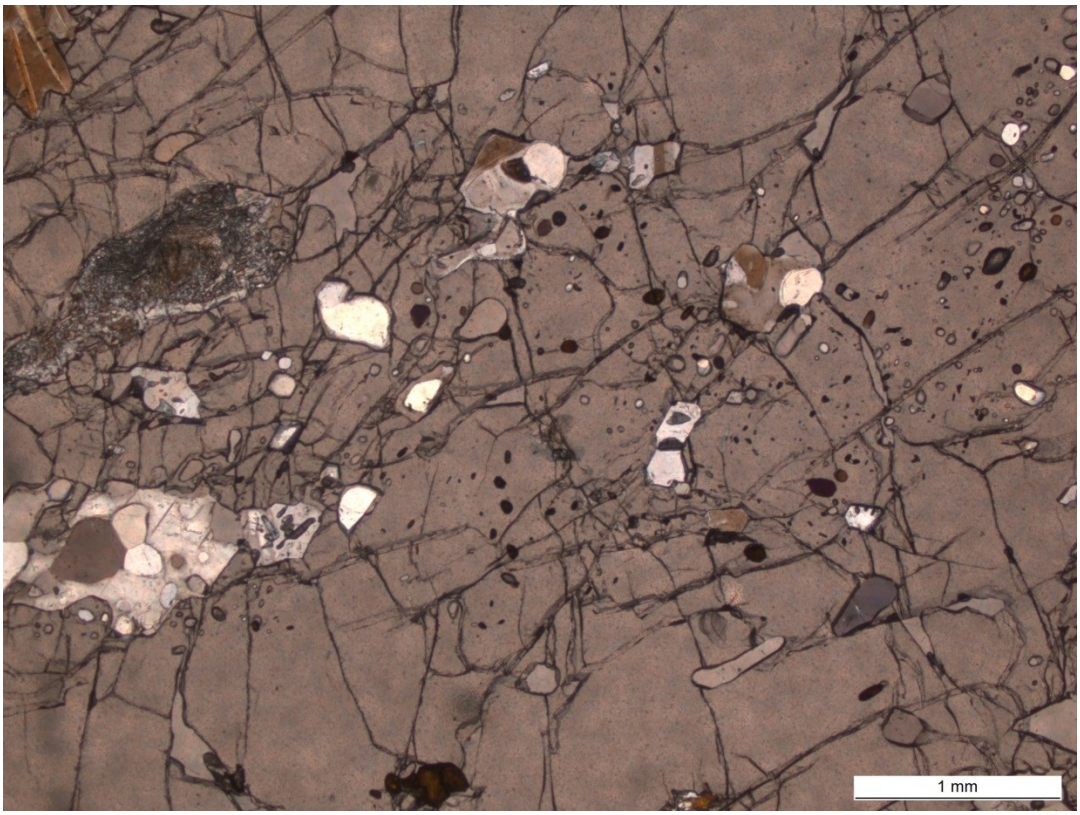

Figure 3: A transmitted light (cross polarised) photomicrograph of the UHT Napier Complex rock donated by Simon Harley. Plagioclase rims around the quartz clusters are better distinguished in XP light.

SIMS RESULTS

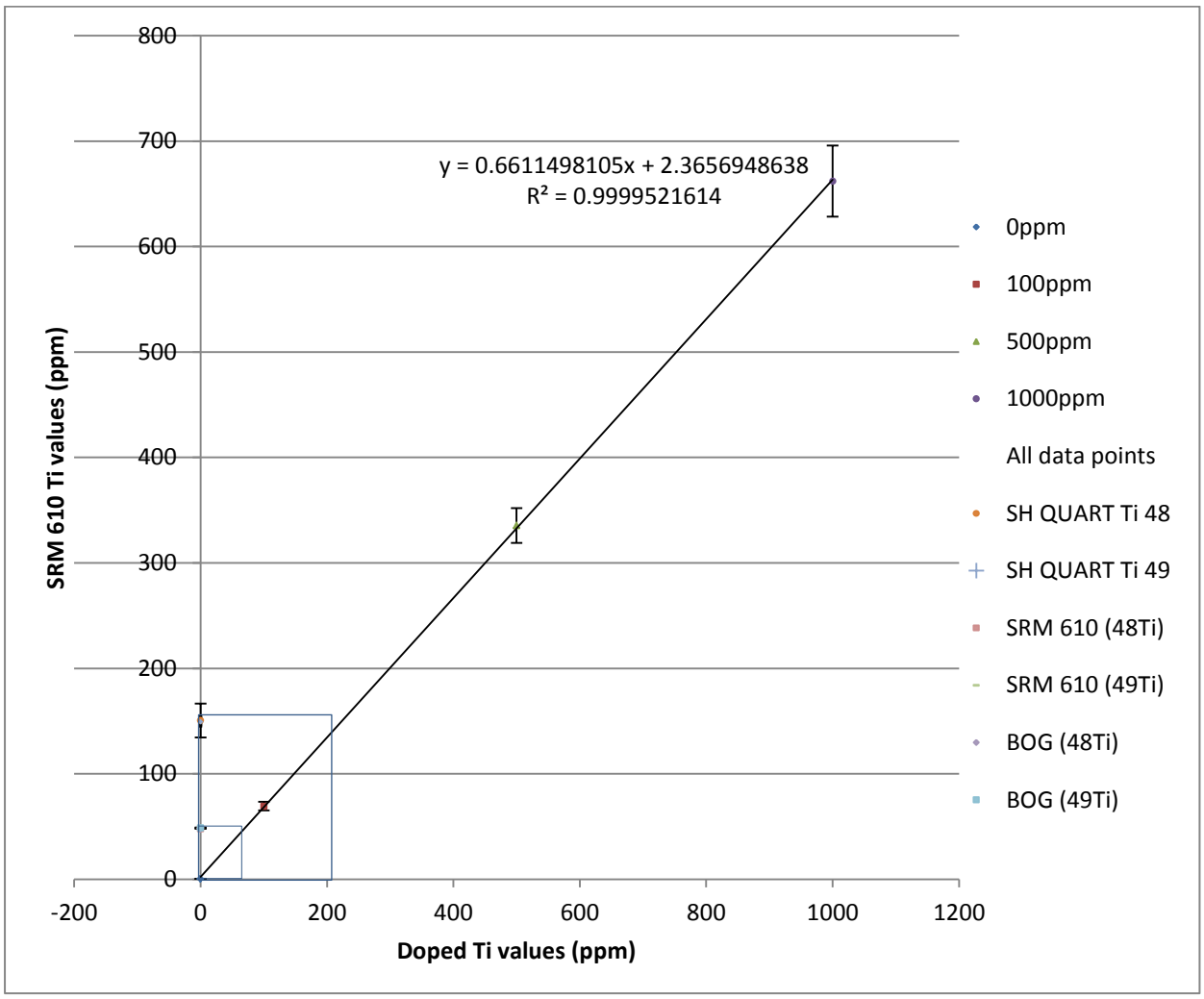

Figure 4: Excel graph of the SIMS results for the synthetic quartz standards, error bars were calculated using the standard deviation. The error is between 4.9-5.9% for 100-1000ppm samples, the error bars are larger for the higher concentrations exactly because the concentrations are larger. The synthetic samples were compared to the glass reference standard SRM 610. All the synthetic samples are consistently lower in their Ti concentrations (ppm) due to the reference standard being unsuitable to achieve this accuracy. The comparison can be seen on the X and Y axis. 4 different quartz clusters within a garnet were analysed from a Napier Complex UHT rock, these have been plotted on the Y axis (it's value found with SRM 610) with an X axis value of 0 but the blue box indicates where this rock's Ti concentration would lie using the new synthetic standards rather than the SRM 610. See table 6 for the raw SIMS Ti data,

LIST OF EQUIPMENT USED FOR Ti IN QUARTZ GELS

1) 5 Teflon beakers (without lips) with 5 lids. Gel prep lab.
2) Magnetic stirrers of several sizes. Gel prep lab.
3) Teflon stirrers. Gel prep. Lab.
4) Glass beakers (200ml) – several. Gel prep. Lab.
5) Plastic gloves for handling acids, green and purple. Gel prep lab.
6) Hydrochloric acid. Gel prep lab (cleaning grade for Teflon from Ian Bulter).
7) Nitric acid, Gel prep lab (from Chemistry).
8) Ammonium, Gel prep lab.
9) Ethanol, Gel prep lab.
10) Titanium oxide (Puratronic, 99.995% metals base), a -22 Mesh powder TiO_2, predominantly rutile and anatase, EMMAC – gel prep. Lab.
11) Titanium AA standard solution: 1000ppm and 10000ppm in ca. 2M hydrochloric acid, EMMAC – gel prep. Lab.
12) TEOS 98% x2, EMMAC – gel prep. Lab.
13) Titanium (III) Chloride solution 15%, EMMAC – gel prep. Lab.
14) 25g of Silicon (IV) oxide, Puratronic, metals base 99.999% (unused), EMMAC – gel prep. Lab.
15) 3 PALAU containers ONLY 1 lid, one has a couple of hairline fractures in the base which go through but water doesn't strip out. (Xp safe).
16) Furnaces in gel prep lab giving an error with code Er-01 (probe problem) at 900°C, causing temperature instabilities at over 750°C.
17) 3 isomantle heaters, gel prep lab.
18) 1 hot plate, supplied by Geoff Bromiley.
19) Agate pestle and mortar provided by EMMAC.
20) Glass vales with plastic lids provided by EMMAC.
21) Metal tweezers provided by EMMAC.
22) Metal spatula provided by EMMAC.
23) 2 2inch platinum crucibles with lids (Xp safe).
24) Tongues (High temperature furnace lab), platinum ones found in XRF glass making lab (Nick Oddling).
25) None absorbent black paper, for the transfer of gel powders both before and after grinding, provided by EMMAC.
26) Aluminium oxide cylinder boat (Geoff Bromiley).
27) Heavy duty gloves, high temperature lab.
28) Welding shield, high temperature lab.
29) Hand shield, high temperature lab.
30) Nabertherm furnace (for glassing only), high temperature lab.
31) Lab coat (several in gel prep lab).
32) Safety glasses, several, Gel prep lab.
33) Ceramic tweezers (EMMAC).
34) Hydrofluoric acid (40%) – cleaning grade, Ann Mennim's lab (locked safe).
35) Hydrofluoric acid (60%) higher grade, Ann Mennim's lab (locked safe).
36) Plastic tweezers (Ann Mennim).

37) Plastic pinnie (Ann Mennim).
38) Heavy duty black rubber gloves, elbow length, (Ann Mennim).
39) Carbon sample coating (EMMAC).
40) Gold sample coating (EMMAC).
41) Satorius MC 210 S Balance (Ann Mennim).
42) 5 small Teflon beakers with slot in lids (Ann Mennim).

TABLES

Table 2: Calculations done on excel to work out the molar ratios and therefore weights of TOES needed for the starting materials of gel preparation.

TEOS					
Si(OC2H5)4 molecular weight	=	208.329			
SiO2 only	=	60.083			
Ratio: 1 to	=	3.46732			
					100% SiO2
			500ppm	1000ppm	0 ppm
For a total yield of 10g with 100ppm Ti	=	9.999 SiO2	9.995	9.99	10
Therefore grams needed of TEOS	=	34.66973268	34.65586	34.63853	34.6732
liters needed	=	need to know density at room T and P			

Table 3: Calculations done on excel to work out weights of Ti (using AA standard) needed for the starting materials of gel preparation.

Using 1000ppm Ti aa standard instead in water with trace HCl				
		ppm		gram(s)
to dilute 1000ppm to 100ppm		100	=	1
to dilute 1000ppm to 500ppm		500	=	5
to dilute 1000ppm to 1000ppm		1000	=	10

Table 4: A record of temperatures variations for the same readings, different gradients between readings, start and end dates for different gel runs on the two isomantle heaters used.

Isomantle heaters (Barnstead Electrothermal - blue, and fisher scientific grey)						
1st Gel standards run						
2nd stage of drying						
	Temperature (°C)				Time	Run time
	blue heater	(was grey) Blue heater	blue heater	Grey heater		
Isomantle reading	100ppm	500ppm	1000ppm	Blank (0ppm)	(hrs)	(days)
1.2	T1 = 88	T1 = 87	T1 = 91	T1 = 134	2	1
1.4	T2 = 128	T2 = 120	T2 = 139	T2 = 179	4	
1.6	T3 = 191	T3 = 167	T3 = 152	T3 = 186	6	
1.8	T4 = 197	T4 = 221	T4 = 208	T4 = 216/7	8	
2	T5 = 215	T5 = 239	T5 = 232	T5 = 233	10	2
2.2	T6 = 241	T6 = 253	T6 = 255	T6 = 238	12	
2.4	T7 = 244	T7 = 268/9	T7 = 275/8	T7 = 263/4	14	
2.6	T8 = 261	T8 = 278	T8 = 298	T8 = 272	16	
2.8	T9 = 276	T9 = 306	T9 = 314	T9 = 303	18	3
3	T10 = 316	T10 = 338	T10 = 322	T10 = 314	20	
3.2	T11 = 327	T11 = 349	T11 = 332	T11 = 333	22	
3.4	T12 = 352	T12 = 356	T12 = 347	T12 = 346	24	
3.6	T13 = 375	T13 = 377	T13 = 366	T13 = 357	26	4
3.8	T14 = 388	T14 = 393	T14 = 378	T14 = 380	28	
4	T15 = 412	T15 = 407	T15 = 384	T15 = 392	30	
4.2	T16 = 423	T16 = 422	T16 = 394	T16 = 422/1	32	
4.4	T17 = 447	T17 = 431	T17 = 418	T17 = 438	34	5
4.6	T18 = 450	T18 = 441/2	T18 = 431	T18 = 457/8	36	
4.8	T19 = 463	T19 = 464/5	T19 = 451	T19 = 471	38	
5	T20 = 475	T20 = 473	T20 = 467	T20 = 490	40	
	Date started:	Date to start:	Date to start:	Date to start:		
	24/06/2013	03/07/2013	26/06/2013	09/07/2013		
	Date complete:	Date complete:	Date complete:	Date complete:		
	02/07/2013	09/07/2013	08/07/2013	17/07/2013		

Table 5: Temperature gradients for the drying furnaces for 100ppm.

	Left hand furnace temperature gradients (°C) for 100ppm sample											
(top)	88	138/9	156	192	246	292	366	423	475	602	791	826
	110	157	184	232	278	343	374	483	580	694	808	843
	114/3	158	194	247	296	344/3	402	490	580	716	806	874
Top of sample	106	158	181	241	300/299	342	405	513	604	725	822	890
Where the sample sits (base)	**104**	**160**	**200**	**244**	**305**	**357**	**415**	**513**	**629**	**727**	**837**	**893**
Set at	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**500**	**600**	**700**	**800**	**900**
Green digital display reading	**108**	**147/8**	**202 down to 198 (last 3 readings)**	**246/7 (6 in the middle, 7 at base and top)**	**301/299**	**347**	**400/1**	**493**	**599-601**	**685-692**	**779-800 av. around 789-797**	**871-898**

Table 6: Temperature gradients for the drying furnaces for 1000ppm.

	Left hand furnace temperature gradients (°C) for 1000ppm sample											
(top)	80/79	109	170	204/4	260/1	285	331	456/7	520	668	779	828
	87	126	192	248	291	331	392	517/8	585	717	811	841
	91	137	204	252	294/5	339	405	527	593/2	726/7	822	863
Top of sample	94	144	191	262	308	336	420	539	621/2	738	815	869
Where the sample sits (base)	**94**	**149**	**209**	**265**	**315**	**350**	**420**	**512**	**640**	**755**	**837**	**896**
Set at	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**500**	**600**	**700**	**800**	**900**
Green digital display reading	**98.4**	**153-152**	**204**	**245-49 (53 for highest two)**	**296**	**347**	**396/7-400**	**502-512 (latter for the 4th reading)**	**613 (602 for 2nd lowest)**	**696-723**	**793-800**	**854-894**

Table 7: Temperature gradients for the drying furnaces for 500ppm.

	Left hand furnace temperature gradients (°C) for 500ppm sample											
(top)	71	109	148	193	249/50	323	369	476/7	538	682	738	838
	82/1	126	190	238/9	270/69	331	372	458/9	584	669/700	768	881
	89	137	200/199	250/1	289/8	344	391	500/1	601	722	809	888
Top of sample	93	144	198	253	292/1	339	395	482	607	748	826	895
Where the sample sits (base)	**97**	**149**	**199**	**257**	**301**	**353**	**408**	**510**	**621**	**772**	**840**	**903**
Set at	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**500**	**600**	**700**	**800**	**900**
Green digital display reading	**101-100**	**153-152**	**200-206**	**248-251**	**296-301**	**344-347**	**392-400**	**498-501**	**593-600**	**715**	**790-799**	**849-899**

Table 8: Temperature gradients for the drying furnaces for 0ppm.

	Left hand furnace temperature gradients (°C) for 0ppm (just TEOS) sample											
(top)	86	112	136	153								
	92	132	162	225/6								
	96	149	190	243								
Top of sample	102/1	152	196	235								
Where the sample sits (base)	**103**	**148**	**191**	**248/9**								
Set at	**100**	**150**	**200**	**250**	**300**	**350**	**400**	**500**	**600**	**700**	**800**	**900**
Green digital display reading	**108/7**	**154-6**	**197-200**	**251/2**								

EMPA results

Table 9: 0ppm, 10 minute fusions, EMPA results. Values in percentages.

0ppm (BLANK) results	Ti	O	Si	Total	Glass number
	-0.0008	53.2652	46.75	100.0145	(13a) 1/4
	-0.0004	53.2655	46.75	100.0151	(13a) 2/4
	-0.0012	53.2649	46.75	100.0138	(13a) 3/4
	-0.0009	53.2652	46.75	100.0143	(13a) 4/4
	-0.0003	53.2655	46.75	100.0152	(13) 1/20
	-0.0004	53.2654	46.75	100.015	(13) 2/20
	-0.0007	53.2653	46.75	100.0146	(13) 3/20
	-0.0007	53.2653	46.75	100.0146	(13) 4/20
	-0.0007	53.2653	46.75	100.0146	(13) 5/20
	-0.0008	53.2652	46.75	100.0144	(13) 6/20
	-0.0006	53.2653	46.75	100.0147	(13) 7/20
	-0.001	53.2651	46.75	100.0141	(13) 8/20
	-0.0001	53.2656	46.75	100.0155	(13) 9/20
	-0.0007	53.2653	46.75	100.0146	(13) 10/20
	-0.0006	53.2653	46.75	100.0148	(13) 11/20
	-0.0011	53.265	46.75	100.0139	(13) 12/20
	-0.0007	53.2653	46.75	100.0145	(13) 13/20
	-0.0002	53.2656	46.75	100.0154	(13) 14/20
	-0.0006	53.2654	46.75	100.0148	(13) 15/20
	-0.0006	53.2653	46.75	100.0147	(13) 16/20
	-0.0009	53.2652	46.75	100.0143	(13) 17/20
	-0.0005	53.2654	46.75	100.015	(13) 18/20
	-0.0005	53.2654	46.75	100.0149	(13) 19/20

	-0.0003	53.2655	46.75	100.0152	(13) 20/20
	-0.0006	53.2653	46.75	100.0148	(14) 1/20
	-0.0004	53.2655	46.75	100.0151	(14) 2/20
	-0.0006	53.2654	46.75	100.0148	(14) 3/20
	-0.0008	53.2652	46.75	100.0144	(14) 4/20
	-0.0006	53.2653	46.75	100.0146	(14) 5/20
	-0.0007	53.2653	46.75	100.0146	(14) 6/20
	-0.0006	53.2653	46.75	100.0147	(14) 7/20
	-0.0003	53.2655	46.75	100.0152	(14) 8/20
	-0.0005	53.2654	46.75	100.015	(14) 9/20
	-0.0007	53.2653	46.75	100.0146	(14) 10/20
	-0.0007	53.2653	46.75	100.0146	(14) 11/20
	-0.0006	53.2653	46.75	100.0147	(14) 12/20
	-0.0006	53.2654	46.75	100.0148	(14) 13/20
	-0.0007	53.2653	46.75	100.0146	(14) 14/20
	-0.0009	53.2651	46.75	100.0142	(14) 15/20
	-0.0009	53.2651	46.75	100.0141	(14) 16/20
	-0.0007	53.2653	46.75	100.0146	(14) 17/20
	-0.0008	53.2652	46.75	100.0144	(14) 18/20
	-0.0004	53.2655	46.75	100.015	(14) 19/20
	-0.0008	53.2652	46.75	100.0144	(14) 20/20
St Dev.	0.000228				
Average	-0.00064				
Lowest	-0.0012				
Highest	-0.0001				
Range	0.0011				

Table 10: 100ppm, 10minute fusion, EMPA results. Values in percentages.

100ppm (10 minutes)	Ti	O	Si	Total	Glass Number
	0.0094	53.272	46.75	100.0315	(5a) 1/4
	0.008	53.2711	46.75	100.0291	(5a) 2/4
	0.0089	53.2717	46.75	100.0306	(5a) 3/4
	0.0092	53.2719	46.75	100.0311	(5a) 4/4
	0.0106	53.2728	46.75	100.0334	(7) 1/20
	0.0088	53.2716	46.75	100.0305	(7) 2/20
	0.009	53.2717	46.75	100.0307	(7) 3/20
	0.0092	53.2719	46.75	100.0311	(7) 4/20
	0.0091	53.2718	46.75	100.031	(7) 5/20
	0.009	53.2718	46.75	100.0308	(7) 6/20
	0.0078	53.271	46.75	100.0288	(7) 7/20
	0.0101	53.2725	46.75	100.0326	(7) 8/20
	0.0109	53.273	46.75	100.0339	(7) 9/20
	0.0092	53.2719	46.75	100.031	(7) 10/20
	0.0082	53.2712	46.75	100.0295	(7) 11/20
	0.0179	53.2777	46.75	100.0455	(7) 12/20
	0.0083	53.2712	46.75	100.0295	(7) 13/20
	0.0078	53.2709	46.75	100.0287	(7) 14/20
	0.009	53.2718	46.75	100.0308	(7) 15/20
	0.0103	53.2726	46.75	100.0329	(7) 16/20
	0.0088	53.2716	46.75	100.0304	(7) 17/20
	0.0065	53.2701	46.75	100.0266	(7) 18/20
	0.009	53.2717	46.75	100.0307	(7) 19/20
	0.0086	53.2715	46.75	100.0301	(7) 20/20
	0.0084	53.2713	46.75	100.0297	(10) 1/20
	0.0094	53.272	46.75	100.0314	(10) 2/20

	0.0087	53.2715	46.75	100.0302	(10) 3/20
	0.0063	53.2699	46.75	100.0262	(10) 4/20
	0.0093	53.272	46.75	100.0313	(10) 5/20
	0.0079	53.271	46.75	100.0289	(10) 6/20
	0.0078	53.2709	46.75	100.0287	(10) 7/20
	0.0112	53.2732	46.75	100.0343	(10) 8/20
	0.0086	53.2715	46.75	100.0301	(10) 9/20
	0.009	53.2718	46.75	100.0308	(10) 10/20
	0.0087	53.2716	46.75	100.0303	(10) 11/20
	0.0099	53.2724	46.75	100.0323	(10) 12/20
	0.0087	53.2716	46.75	100.0303	(10) 13/20
	0.0082	53.2712	46.75	100.0294	(10) 14/20
	0.0081	53.2711	46.75	100.0293	(10) 15/20
	0.0081	53.2711	46.75	100.0292	(10) 16/20
	0.0095	53.2721	46.75	100.0316	(10) 17/20
	0.0087	53.2715	46.75	100.0302	(10) 18/20
	0.0091	53.2718	46.75	100.0308	(10) 19/20
	0.0072	53.2706	46.75	100.0278	(10) 20/20
	0.0091	53.2718	46.75	100.0309	(11) 1/20
	0.0101	53.2725	46.75	100.0326	(11) 2/20
	0.008	53.2711	46.75	100.0291	(11) 3/20
	0.009	53.2717	46.75	100.0307	(11) 4/20
	0.0089	53.2717	46.75	100.0306	(11) 5/20
	0.0088	53.2716	46.75	100.0304	(11) 6/20
	0.0095	53.2721	46.75	100.0316	(11) 7/20
	0.0118	53.2736	46.75	100.0354	(11) 8/20
	0.0085	53.2714	46.75	100.0299	(11) 9/20
	0.0091	53.2718	46.75	100.0309	(11) 10/20
	0.0095	53.2721	46.75	100.0316	(11) 11/20

	0.0065	53.2701	46.75	100.0265	(11) 12/20
	0.0075	53.2708	46.75	100.0283	(11) 13/20
	0.0109	53.273	46.75	100.0339	(11) 14/20
	0.0087	53.2716	46.75	100.0303	(11) 15/20
	0.0081	53.2711	46.75	100.0292	(11) 16/20
	0.008	53.2711	46.75	100.0291	(11) 17/20
	0.009	53.2718	46.75	100.0308	(11) 18/20
	0.0101	53.2725	46.75	100.0327	(11) 19/20
	0.0086	53.2715	46.75	100.03	(11) 20/20
	0.0093	53.2719	46.75	100.0312	(12a) 1/4
	0.007	53.2704	46.75	100.0273	(12a) 2/4
	0.0081	53.2711	46.75	100.0292	(12a) 3/4
	0.0081	53.2711	46.75	100.0292	(12a) 4/4
Std Dev	0.001518				
Average	0.00895				
Lowest	0.0065				
Highest	0.0179				
Range	0.0114				

Table 11: 100ppm, 1 hour, EMPA results. Values in percentages.

100ppm (1hour)	Ti	O	Si	Total	Glass Number
	0.0087	53.2715	46.75	100.0302	(12) 1/20
	0.0091	53.2718	46.75	100.0309	(12) 2/20
	0.0092	53.2718	46.75	100.031	(12) 3/20
	0.0091	53.2718	46.75	100.0309	(12) 4/20
	0.0082	53.2712	46.75	100.0294	(12) 5/20
	0.0086	53.2715	46.75	100.0301	(12) 6/20
	0.0099	53.2723	46.75	100.0322	(12) 7/20
	0.0079	53.271	46.75	100.0289	(12) 8/20
	0.009	53.2717	46.75	100.0307	(12) 9/20
	0.0083	53.2713	46.75	100.0295	(12) 10/20
	0.0091	53.2718	46.75	100.0309	(12) 11/20
	0.0086	53.2714	46.75	100.03	(12) 12/20
	0.0092	53.2719	46.75	100.0311	(12) 13/20
	0.0094	53.272	46.75	100.0314	(12) 14/20
	0.0085	53.2714	46.75	100.0299	(12) 15/20
	0.0089	53.2717	46.75	100.0306	(12) 16/20
	0.0086	53.2715	46.75	100.0301	(12) 17/20
	0.0088	53.2716	46.75	100.0304	(12) 18/20
	0.0104	53.2727	46.75	100.0331	(12) 19/20
	0.0089	53.2717	46.75	100.0306	(12) 20/20
Std Dev	0.000568				
Average	0.00892				
Lowest	0.0079				
Highest	0.0104				
Range	0.0025				

Table 12: 500ppm, 10 minute fusion, EMPA results. Values in percentages.

500ppm (10minutes)	Ti	O	Si	Total	Glass Number
	0.0511	53.2999	46.75	100.101	(1) 1/20 at tip
	0.0325	53.2874	46.75	100.0699	(1) 2/20
	0.0467	53.2969	46.75	100.0936	(1) 3/20
	0.0477	53.2976	46.75	100.0953	(1) 4/20
	0.0471	53.2972	46.75	100.0944	(1) 5/20
	0.0431	53.2945	46.75	100.0877	(1) 6/20
	0.0422	53.294	46.75	100.0862	(1) 7/20
	0.0466	53.2969	46.75	100.0935	(1) 8/20
	0.0467	53.297	46.75	100.0937	(1) 9/20
	0.0357	53.2896	46.75	100.0753	(1) 10/20
	0.0471	53.2972	46.75	100.0943	(1) 11/20
	0.0496	53.2989	46.75	100.0985	(1) 12/20
	0.05	53.2991	46.75	100.0991	(1) 13/20
	0.0416	53.2935	46.75	100.0851	(1) 14/20
	0.0482	53.298	46.75	100.0962	(1) 15/20
	0.0512	53.2999	46.75	100.1011	(1) 16/20
	0.0468	53.297	46.75	100.0937	(1) 17/20
	0.0657	53.3096	46.75	100.1253	(1) 18/20
	0.0561	53.3032	46.75	100.1093	(1) 19/20
	0.0517	53.3003	46.75	100.1019	(1) 20/20
	0.0485	53.2981	46.75	100.0966	(2) 1/20
	0.0624	53.3074	46.75	100.1197	(2) 2/20
	0.0435	53.2948	46.75	100.0883	(2) 2/20
	0.047	53.2971	46.75	100.0941	(2) 3/20
	0.0457	53.2963	46.75	100.092	(2) 4/20
	0.0476	53.2975	46.75	100.0951	(2) 5/20

	0.041	53.2931	46.75	100.0841	(2) 6/20
	0.0484	53.2981	46.75	100.0965	(2) 7/20
	0.0468	53.297	46.75	100.0938	(2) 8/20
	0.047	53.2971	46.75	100.0941	(2) 9/20
	0.0536	53.3015	46.75	100.1051	(2) 10/20
	0.0481	53.2978	46.75	100.0959	(2) 11/20
	0.0465	53.2968	46.75	100.0932	(2) 12/20
	0.047	53.2971	46.75	100.0942	(2) 13/20
	0.0437	53.2949	46.75	100.0887	(2) 14/20
	0.0462	53.2966	46.75	100.0928	(2) 15/20
	0.0396	53.2922	46.75	100.0817	(2) 16/20
	0.0545	53.3022	46.75	100.1067	(2) 17/20
	0.0464	53.2967	46.75	100.0931	(2) 18/20
	0.0483	53.298	46.75	100.0962	(2) 19/20
	0.0479	53.2977	46.75	100.0956	(2) 20/20
	0.0459	53.2964	46.75	100.0923	(3) 1/20
	0.0456	53.2962	46.75	100.0918	(3) 2/20
	0.0405	53.2928	46.75	100.0834	(3) 3/20
	0.0438	53.295	46.75	100.0888	(3) 4/20
	0.0465	53.2968	46.75	100.0932	(3) 5/20
	0.0467	53.297	46.75	100.0937	(3) 6/20
	0.0462	53.2966	46.75	100.0929	(3) 7/20
	0.0494	53.2987	46.75	100.0981	(3) 8/20
	0.0492	53.2986	46.75	100.0978	(3) 9/20
	0.0497	53.2989	46.75	100.0987	(3) 10/20
	0.0453	53.296	46.75	100.0913	(3) 11/20
	0.0469	53.2971	46.75	100.094	(3) 12/20
	0.047	53.2971	46.75	100.0941	(3) 13/20
	0.0473	53.2973	46.75	100.0946	(3) 14/20

	0.0455	53.2961	46.75	100.0917	(3) 15/20
	0.0472	53.2973	46.75	100.0944	(3) 16/20
	0.0475	53.2974	46.75	100.0949	(3) 17/20
	0.0463	53.2966	46.75	100.0929	(3) 18/20
	0.0489	53.2984	46.75	100.0973	(3) 19/20
	0.057	53.3038	46.75	100.1109	(3) 20/20
Std Dev	0.005083				
Average	0.047369				
Lowest	0.0325				
Highest	0.0657				
Range	0.0332				

Table 13: 500ppm, 1 hour fusion, EMPA results. Values in percentages.

500ppm (1hour)	Ti	O	Si	Total	Glass Number
	0.0458	53.2963	46.75	100.0922	(4) 1/20
	0.0466	53.2969	46.75	100.0935	(4) 2/20
	0.043	53.2945	46.75	100.0874	(4) 3/20
	0.0432	53.2946	46.75	100.0877	(4) 4/20
	0.0457	53.2963	46.75	100.092	(4) 5/20
	0.0459	53.2964	46.75	100.0924	(4) 6/20
	0.0465	53.2968	46.75	100.0933	(4) 7/20
	0.0463	53.2967	46.75	100.093	(4) 8/20
	0.0496	53.2989	46.75	100.0985	(4) 9/20
	0.0462	53.2966	46.75	100.0928	(4) 10/20
	0.0457	53.2962	46.75	100.0919	(4) 11/20
	0.0478	53.2976	46.75	100.0954	(4) 12/20
	0.041	53.2931	46.75	100.0841	(4) 13/20
	0.0475	53.2974	46.75	100.0949	(4) 14/20
	0.0461	53.2965	46.75	100.0926	(4) 15/20
	0.048	53.2978	46.75	100.0958	(4) 16/20
	0.0477	53.2976	46.75	100.0952	(4) 17/20
	0.0424	53.2941	46.75	100.0864	(4) 18/20
	0.0459	53.2964	46.75	100.0923	(4) 19/20
Std Dev	0.002116				
Average	0.045837				
Lowest	0.041				
Highest	0.0496				
Range	0.0086				

Table 14: 1000ppm, 10 minute fusion, EMPA results. Values in percentages.

1000ppm (10minutes)	Ti	O	Si	Total	Glass Number
	0.0863	53.3234	46.75	100.1597	(5) 1/20
	0.0908	53.3264	46.75	100.1672	(5) 2/20
	0.101	53.3332	46.75	100.1842	(5) 3/20
	0.102	53.3338	46.75	100.1858	(5) 4/20
	0.0998	53.3324	46.75	100.1823	(5) 5/20
	0.0947	53.329	46.75	100.1737	(5) 6/20
	0.1013	53.3334	46.75	100.1846	(5) 7/20
	0.1235	53.3483	46.75	100.2218	(5) 8/20
	0.0906	53.3263	46.75	100.1668	(5) 9/20
	0.0988	53.3318	46.75	100.1806	(5) 10/20
	0.0977	53.331	46.75	100.1787	(5) 11/20
	0.0944	53.3288	46.75	100.1732	(5) 12/20
	0.0982	53.3313	46.75	100.1795	(5) 13/20
	0.0935	53.3282	46.75	100.1717	(5) 14/20
	0.0953	53.3294	46.75	100.1746	(5) 15/20
	0.0992	53.332	46.75	100.1811	(5) 16/20
	0.0932	53.328	46.75	100.1712	(5) 17/20
	0.0941	53.3286	46.75	100.1727	(5) 18/20
	0.095	53.3292	46.75	100.1742	(5) 19/20
	0.0904	53.3261	46.75	100.1665	(5) 20/20
	0.1009	53.3331	46.75	100.184	(6) 1/20
	0.0898	53.3257	46.75	100.1656	(6) 2/20
	0.0917	53.327	46.75	100.1688	(6) 3/20
	0.0908	53.3264	46.75	100.1672	(6) 4/20
	0.0931	53.3279	46.75	100.1711	(6) 5/20
	0.1016	53.3336	46.75	100.1852	(6) 6/20

	0.113	53.3412	46.75	100.2042	(6) 7/20
	0.0918	53.3271	46.75	100.1689	(6) 8/20
	0.0961	53.3299	46.75	100.176	(6) 9/20
	0.1006	53.3329	46.75	100.1835	(6) 10/20
	0.0968	53.3304	46.75	100.1771	(6) 11/20
	0.0965	53.3302	46.75	100.1767	(6) 12/20
	0.0927	53.3277	46.75	100.1704	(6) 13/20
	0.0919	53.3271	46.75	100.169	(6) 14/20
	0.0906	53.3262	46.75	100.1668	(6) 15/20
	0.0998	53.3324	46.75	100.1822	(6) 16/20
	0.0931	53.3279	46.75	100.171	(6) 17/20
	0.0907	53.3263	46.75	100.1671	(6) 18/20
	0.0924	53.3275	46.75	100.1699	(6) 19/20
	0.0895	53.3255	46.75	100.165	(6) 20/20
	0.0917	53.327	46.75	100.1686	(8) 1/20
	0.0961	53.3299	46.75	100.1761	(8) 2/20
	0.0923	53.3274	46.75	100.1697	(8) 3/20
	0.091	53.3265	46.75	100.1675	(8) 4/20
	0.0931	53.328	46.75	100.1711	(8) 5/20
	0.0845	53.3222	46.75	100.1568	(8) 6/20
	0.0927	53.3276	46.75	100.1703	(8) 7/20
	0.0896	53.3256	46.75	100.1652	(8) 8/20
	0.0972	53.3306	46.75	100.1778	(8) 9/20
	0.0978	53.331	46.75	100.1788	(8) 10/20
	0.0927	53.3277	46.75	100.1703	(8) 11/20
	0.1013	53.3334	46.75	100.1847	(8) 12/20
	0.0903	53.3261	46.75	100.1664	(8) 13/20
	0.099	53.3319	46.75	100.1809	(8) 14/20
	0.0875	53.3242	46.75	100.1616	(8) 15/20

	0.0908	53.3264	46.75	100.1672	(8) 16/20
	0.094	53.3285	46.75	100.1724	(8) 17/20
	0.0908	53.3264	46.75	100.1672	(8) 18/20
	0.0973	53.3307	46.75	100.178	(8) 19/20
	0.1139	53.3418	46.75	100.2057	(8) 20/20
Std Dev	0.006508				
Average	0.095447				
Lowest	0.0863				
Highest	0.1235				
Range	0.0372				

Table 15: 1000ppm, 1 hour fusion, EMPA results. Values in percentages.

1000ppm (1hour)	Ti	O	Si	Total	Glass Number
	0.0946	53.329	46.75	100.1736	(9) 1/20
	0.0953	53.3294	46.75	100.1747	(9) 2/20
	0.0924	53.3275	46.75	100.1698	(9) 3/20
	0.0855	53.3228	46.75	100.1583	(9) 4/20
	0.0931	53.3279	46.75	100.171	(9) 5/20
	0.0918	53.327	46.75	100.1688	(9) 6/20
	0.0949	53.3291	46.75	100.174	(9) 7/20
	0.0946	53.3289	46.75	100.1736	(9) 8/20
	0.0935	53.3282	46.75	100.1717	(9) 9/20
	0.0941	53.3286	46.75	100.1726	(9) 10/20
	0.1018	53.3338	46.75	100.1856	(9) 11/20
	0.096	53.3299	46.75	100.1759	(9) 12/20
	0.0937	53.3283	46.75	100.172	(9) 13/20
	0.0968	53.3304	46.75	100.1773	(9) 14/20
	0.0907	53.3263	46.75	100.167	(9) 15/20
	0.0916	53.3269	46.75	100.1685	(9) 16/20
	0.1115	53.3402	46.75	100.2017	(9) 17/20
	0.0925	53.3275	46.75	100.17	(9) 18/20
	0.096	53.3299	46.75	100.1759	(9) 19/20
	0.1056	53.3363	46.75	100.1919	(9) 20/20
Std Dev	0.005557				
Average	0.0953				
Lowest	0.0855				
Highest	0.1115				
Range	0.026				

SIMS, 1270, analysis results.

Table 16: Raw Excel data for all of the 4F SIMS analysis. BOG-QTZ and SRM 610 were analysed twice before each run, SRM 610 as a comparative reference standard and both SRM 610 and Bog as a measure of reproducibility within the analysis. The % StdDEV for the 0ppm is so high because the sample is a blank, the others lie within 4.9 and 5.9. Figure 4 shows the results in graph form including the interpreted temperature of the quartz from the UHT Napier Complex samples. The red values indicate extra analysis points for the 100ppm which were done on top of the set number for each of the other samples. Figures 3 and 4 are photomicrographs which show the location of the quartz grains which were analysed, situated within the larger a larger garnet within the thin section.

	Average for all runs						
	0	100	500	1000	**SH UHT QUARTZ**		
	2.35E-01	7.47E+01	3.36E+02	6.56E+02	QTZ-Cluster	48Ti	49Ti
	4.00E-01	6.57E+01	3.13E+02	6.18E+02	1a-1	1.71E+02	1.69E+02
	4.00E-01	7.05E+01	3.33E+02	6.31E+02	1a-2	1.78E+02	1.77E+02
	3.05E-01	7.33E+01	3.21E+02	7.39E+02	1a-3	1.73E+02	1.72E+02
	8.32E-01	6.68E+01	3.28E+02	6.29E+02	1b-1	1.56E+02	1.54E+02
	3.35E-01	6.88E+01	3.36E+02	7.15E+02	1b-2	1.66E+02	1.63E+02
	1.26E-01	7.18E+01	3.83E+02	6.44E+02	1b-3	1.56E+02	1.53E+02
	3.50E-01	6.78E+01	3.39E+02	6.71E+02	1c-1	1.63E+02	1.61E+02
	3.50E-01	8.08E+01	3.49E+02	6.79E+02	1c-2	1.55E+02	1.54E+02
	1.43E-01	6.29E+01	3.31E+02	6.58E+02	1c-3	1.58E+02	1.56E+02
	7.04E-01	6.81E+01	3.40E+02	6.70E+02	2a-1	1.47E+02	1.45E+02
	2.18E-01	6.82E+01	3.31E+02	6.61E+02	2a-2	1.47E+02	1.47E+02
	3.35E-01	7.41E+01	3.35E+02	6.52E+02	2a-3	1.56E+02	1.56E+02
	1.96E-01	6.48E+01	3.12E+02	6.13E+02	2b-1	1.37E+02	1.36E+02
	2.18E-01	6.91E+01	3.30E+02	6.26E+02	2b-2	1.34E+02	1.33E+02
	3.10E-01	7.36E+01	3.19E+02	7.29E+02	2b-3	1.38E+02	1.37E+02
	2.15E-01	6.63E+01	3.26E+02	6.27E+02	3-1	1.40E+02	1.38E+02
	6.77E-01	6.81E+01	3.36E+02	7.09E+02	3-2	1.50E+02	1.50E+02
	2.18E-01	7.20E+01	3.79E+02	6.39E+02	3-3	1.10E+02	1.09E+02
	1.10E-01	6.77E+01	3.36E+02	6.67E+02	4-1	1.36E+02	1.35E+02
	1.40E-01	8.03E+01	3.46E+02	6.76E+02	4-2	1.59E+02	1.59E+02
	1.54E-01	6.23E+01	3.29E+02	6.58E+02	4-3	1.34E+02	1.32E+02
	1.09E-01	6.74E+01	3.38E+02	6.66E+02			

	5.06E-01	6.71E+01	3.28E+02	6.59E+02			
		7.05E+01					
		6.74E+01					
		6.70E+01					
		6.73E+01					
		7.18E+01					
		7.04E+01					
		6.73E+01					
		6.64E+01					
		6.68E+01					
		7.05E+01					
Average	**0.338329**	**6.93E+01**	**3.35E+02**	**6.62E+02**		**1.51E+02**	**1.49E+02**
StdDEV	0.201172	4.086457	16.60139	33.71577		16.05296	16.02964
% StdDEV	59.46037	5.893647	4.948925	5.091686		10.65826	10.73119

Bog and SRM 610 results:

Both BOG and SRM 610 were used as reference standards to calibrate the values detected for the Ti in quartz synthetic gels and the Ti in SH UHT quartz.

Table 17: Values of SIMS analysis of BOG standard in ppm, results for run 1.

Run 1	BOG- 0813-1.DAT	BOG- 0813-2.DAT
26Mg	3.7434	4.8337
27Al	75.117	94.59
30Si	467390	467390
40Ca	8.393	11.444
48Ti	97.681	86.298
49Ti	97.866	86.09

Table 18: Values of SIMS analysis of BOG standard in ppm, results for run 2. To reduce the running time of each manually selected point of analysis the values for 26Mg weren't detected.

Run 2 and 3	BOG- 0813-3.DAT	BOG- 0813-4.DAT	BOG- 0813-5.DAT	BOG- 0813-6.DAT	BOG- 0813-7.DAT	BOG- 0813-8.DAT
27Al	26.98	26.98	26.98	26.98	26.98	26.98
30Si	29.97	29.97	29.97	29.97	29.97	29.97
40Ca	39.96	39.96	39.96	39.96	39.96	39.96
48Ti	47.95	47.95	47.95	47.95	47.95	47.95
49Ti	48.95	48.95	48.95	48.95	48.95	48.95

Table 19: Values of SIMS analysis of SRM 610 standard in ppm, results for run 1. Unlike BOG, 44Ca was also detected in the run 1 for SRM 610.

Run 1	SRM 610- 0813-1.DAT	SRM 610- 0813-2.DAT
26Mg	25.98	25.98
27Al	26.98	26.98
30Si	29.97	29.97
42Ca	41.96	41.96
44Ca	43.96	43.96
48Ti	47.95	47.95
49Ti	48.95	48.95

Table 20: Values of SIMS analysis of SRM 610 standard in ppm, results for run 2. To reduce the running time of each manually selected point of analysis the values for 26Mg and 44Ca weren't detected.

Runs 2 and 3	SRM 610- 0813-3.DAT	SRM 610- 0813-4.DAT	SRM 610- 0813-5.DAT	SRM 610- 0813-6.DAT	SRM 610- 0813-7.DAT	SRM 610- 0813-8.DAT
27Al	26.98	26.98	26.98	26.98	26.98	26.98
30Si	29.97	29.97	29.97	29.97	29.97	29.97
40Ca	41.96	41.96	39.96	41.96	41.96	41.96
48Ti	47.95	47.95	47.95	47.95	47.95	47.95
49Ti	48.95	48.95	48.95	48.95	48.95	48.95

ICP OES analysis results.

Table 21: Detailed ICP OES results, and the conditions of analysis table.

Sample ID	Analyte Name	Elem	Wavelength	Int (Corr)	RSD (Corr Int)	SD (Corr Int)	Conc (mgl-1)	RSD (Conc)	SD (Calib)	Volume of sample in solution(ml)	Weight (g)	Conc (ppm)
Calib Blank 1	Ti 334.940	Ti	334.94	186.7254411	44.20996411	82.55125049						
1 ppm Ti	Ti 334.940	Ti	334.94	484619.4496	0.342535323	1659.992795						
10 ppm Ti	Ti 334.940	Ti	334.94	4718642.172	0.556236803	26246.82435						
100 ppm Ti	Ti 334.940	Ti	334.94									
Acid Blank	Ti 334.940	Ti	334.94	4177.774028	0.886758286	37.04675738	-0.002	4.678	0.000	10		
1	Ti 334.940	Ti	334.94	2368348.722	0.780860584	18493.50166	5.249	0.783	0.041	10	0.05306	989.2412435
2	Ti 334.940	Ti	334.94	672321.7414	0.732191168	4922.680413	1.482	0.738	0.011	10	0.14006	105.8222435
10	Ti 334.940	Ti	334.94	21012.23564	0.679214876	142.7182301	0.036	0.890	0.000	10	0.0864	4.123783637
Unlabelled	Ti 334.940	Ti	334.94	1843530.023	0.29692033	5473.815424	4.083	0.298	0.012	10	0.08111	503.4305509
Calib Blank 1	Ti 336.121	Ti	336.121	-606.6764312	13.01002363	78.92874708						
1 ppm Ti	Ti 336.121	Ti	336.121	428788.7125	0.376524591	1614.494948						
10 ppm Ti	Ti 336.121	Ti	336.121	4189644.673	0.559609034	23445.6301						
100 ppm Ti	Ti 336.121	Ti	336.121	37053877.64	0.121676357	45085.80835						
Acid Blank	Ti 336.121	Ti	336.121	3793.428962	2.759557793	104.6818645	-0.469	0.063	0.000	10		
1	Ti 336.121	Ti	336.121	2097531.143	0.81350884	17063.60127	5.446	0.885	0.048	10	0.05306	1026.455745
2	Ti 336.121	Ti	336.121	594027.5494	0.710955234	4223.269954	1.198	0.996	0.012	10	0.14006	85.55505947
10	Ti 336.121	Ti	336.121	18616.00874	0.89070728	165.8141451	-0.428	0.110	0.000	10	0.0864	-49.48129834
Unlabelled	Ti 336.121	Ti	336.121	1630608.74	0.334593975	5455.918606	4.127	0.374	0.015	10	0.08111	508.8279343
Calib Blank 1	Ti 337.279	Ti	337.279	96.08882175	6.562077162	6.305422628						
1 ppm Ti	Ti 337.279	Ti	337.279	230736.8911	0.472262231	1089.68319						
10 ppm Ti	Ti 337.279	Ti	337.279	2264471.117	0.589084444	13339.6471						
100 ppm Ti	Ti 337.279	Ti	337.279	20803867.81	0.084783695	17638.28782						
Acid Blank	Ti 337.279	Ti	337.279	2067.214132	1.612475977	33.33333128	-0.310	0.054	0.000	10		
1	Ti 337.279	Ti	337.279	1131457.658	0.759125774	8589.186704	5.367	0.804	0.043	10	0.05306	1011.403364
2	Ti 337.279	Ti	337.279	320703.948	0.677424029	2172.525606	1.292	0.845	0.011	10	0.14006	92.21361474

10	Ti 337.279	Ti	337.279	9939.86711	0.796641277	79.18508429	-0.270	0.147	0.000	10	0.0864	-31.29631507
Unlabelled	Ti 337.279	Ti	337.279	882624.6012	0.406300956	3586.11219	4.116	0.438	0.018	10	0.08111	507.4388179
Calib Blank 1	Ti 368.519	Ti	368.519	-35.90937802	286.3963094	102.8431334						
1 ppm Ti	Ti 368.519	Ti	368.519	173884.0468	0.344148891	598.4200181						
10 ppm Ti	Ti 368.519	Ti	368.519	1712798.847	0.539811013	9245.876812						
100 ppm Ti	Ti 368.519	Ti	368.519	16209328.21	0.123577782	20031.12821		0.000	0.000			
Acid Blank	Ti 368.519	Ti	368.519	1428.438782	4.191335476	59.87066144	-0.191	0.202	0.000	10		
1	Ti 368.519	Ti	368.519	854910.0301	0.820798071	7017.085036	5.309	0.852	0.045	10	0.05306	1000.657059
2	Ti 368.519	Ti	368.519	241679.9881	0.720616644	1741.586219	1.357	0.827	0.011	10	0.14006	96.91506497
10	Ti 368.519	Ti	368.519	7532.431639	1.186623522	89.3816056	-0.152	0.380	0.001	10	0.0864	-17.5488761
Unlabelled	Ti 368.519	Ti	368.519	664957.3883	0.342173414	2275.307398	4.085	0.359	0.015	10	0.08111	503.6734523
Calib Blank 1	Ti 334.903	Ti	334.903	-132.552503	66.34633761	87.94373114						
1 ppm Ti	Ti 334.903	Ti	334.903	11135.67679	11.75781196	1309.311937						
10 ppm Ti	Ti 334.903	Ti	334.903	104839.0442	6.204041979	6504.258314						
100 ppm Ti	Ti 334.903	Ti	334.903									
Acid Blank	Ti 334.903	Ti	334.903	83.31075952	62.90407942	52.40586633	-0.021	25.045	0.005	10		
1	Ti 334.903	Ti	334.903	34314.12344	17.85257606	6125.954986	3.406	18.006	0.613	10	0.05306	641.9311204
2	Ti 334.903	Ti	334.903	8682.634383	17.69379913	1536.287887	0.840	18.311	0.154	10	0.14006	59.97265059
10	Ti 334.903	Ti	334.903	288.3274191	7.914153575	22.81867474	-0.0004	539.597	0.002	10	0.0864	-0.049001432
Unlabelled	Ti 334.903	Ti	334.903	13932.64295	42.378737	5904.478115	1.366	43.288	0.591	10	0.08111	168.3620054

References

Biggar, G.M. and O'Hara, M.J. 1969. A Comparison of gel starting materials for phase equilibrium studies. *Mineralogical magazine*, **37**, pp 198-205

Cairnes, E. 1983. Preparation of rare earth glasses. *Intern lab document* .

Thomas, J.B., Watson, E.B, Spear, F.S., Shemella, P.T., Nayak, S.K., and Lanzirotti, A. 2010. TitaniQ under pressure: the effects of pressure and temperature on the solubility of Ti in quartz. *Contributions to Mineral Petrology*. **160**. pp 743-759.

Spears, F.S. and Wark, D.A. 2009. Cathodoluminescence imaging and titanium thermometry in metamorphic quartz. *Journal of Metamorphic Geology*. **27**. pp 187-205/

Wark, D.A. and Watson, E.B. 2006. TitaniQ: a titanium-in-quartz geothermometer. *Contributions to Mineral Petrology.* **152**. pp 743-754

Appendix 1

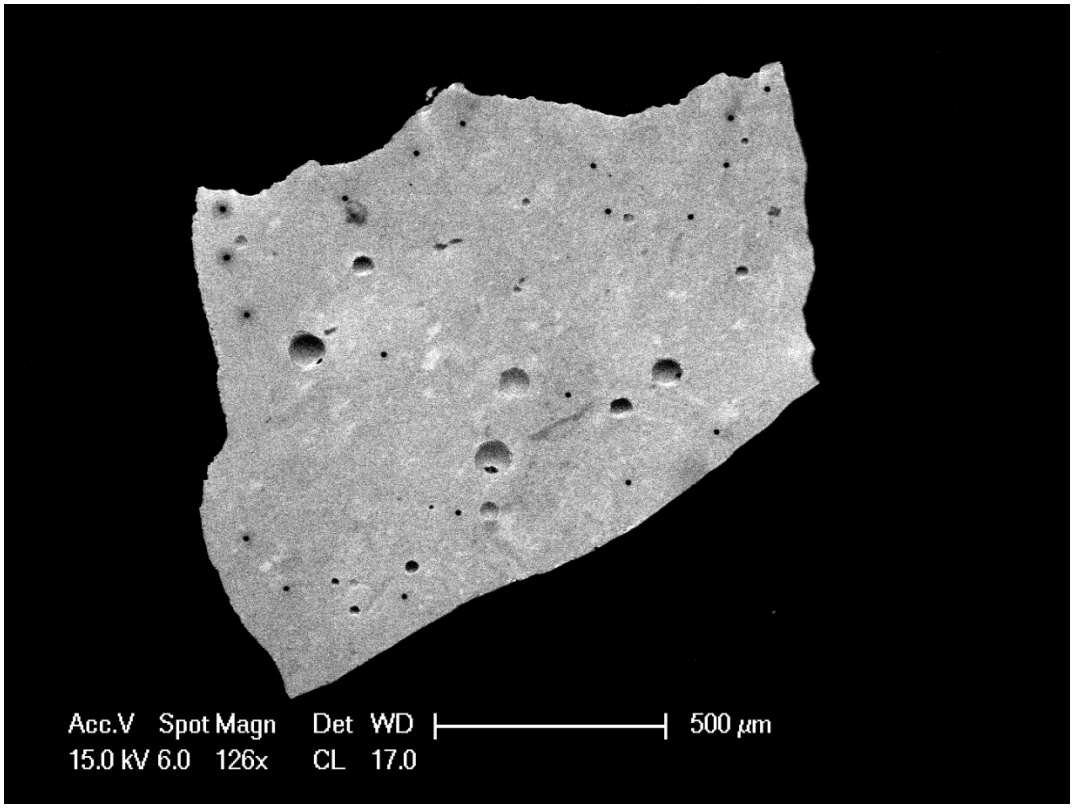

Figure 4: An image of Quartz glass 1 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

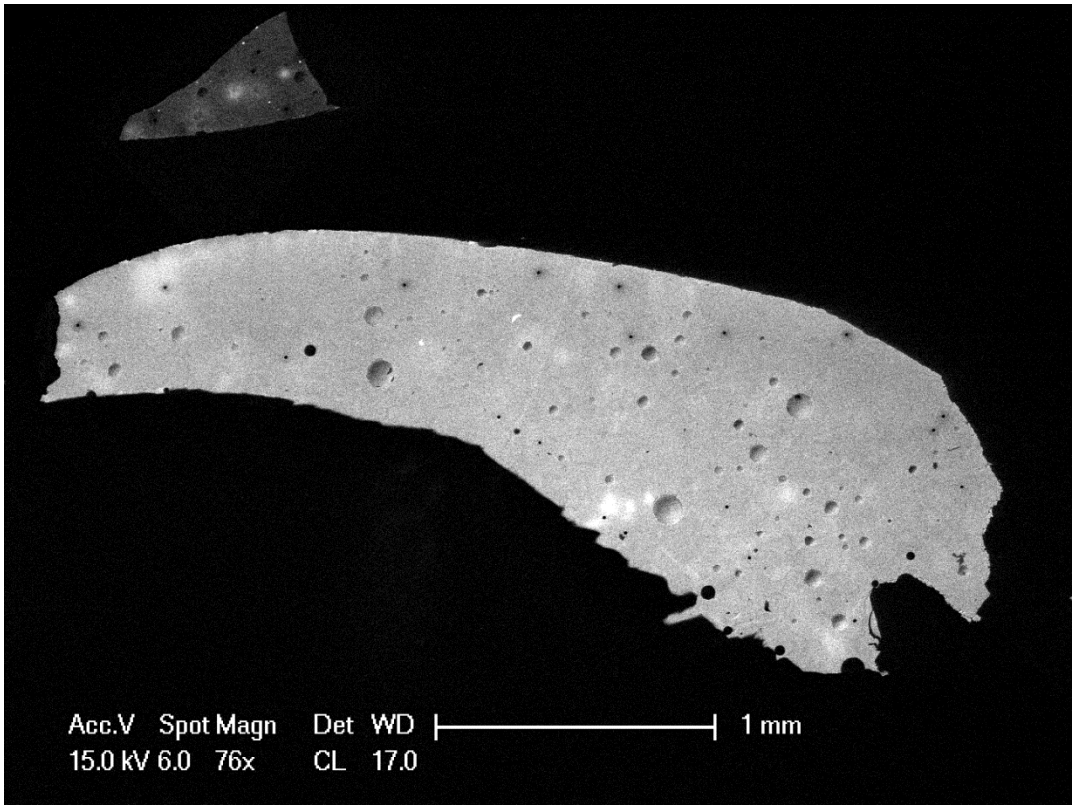

Figure 5: An image of Quartz glass 5a (top left) and 5 (centre) taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

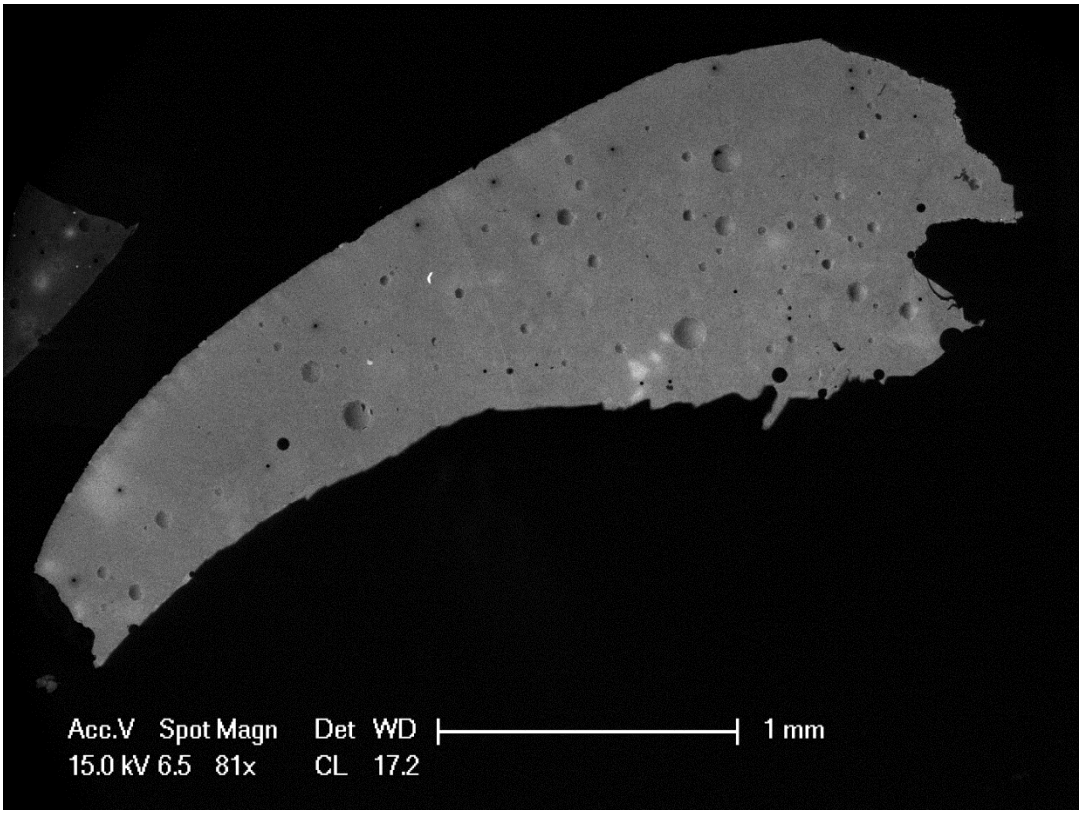

Figure 6: An image of Quartz glass 5 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

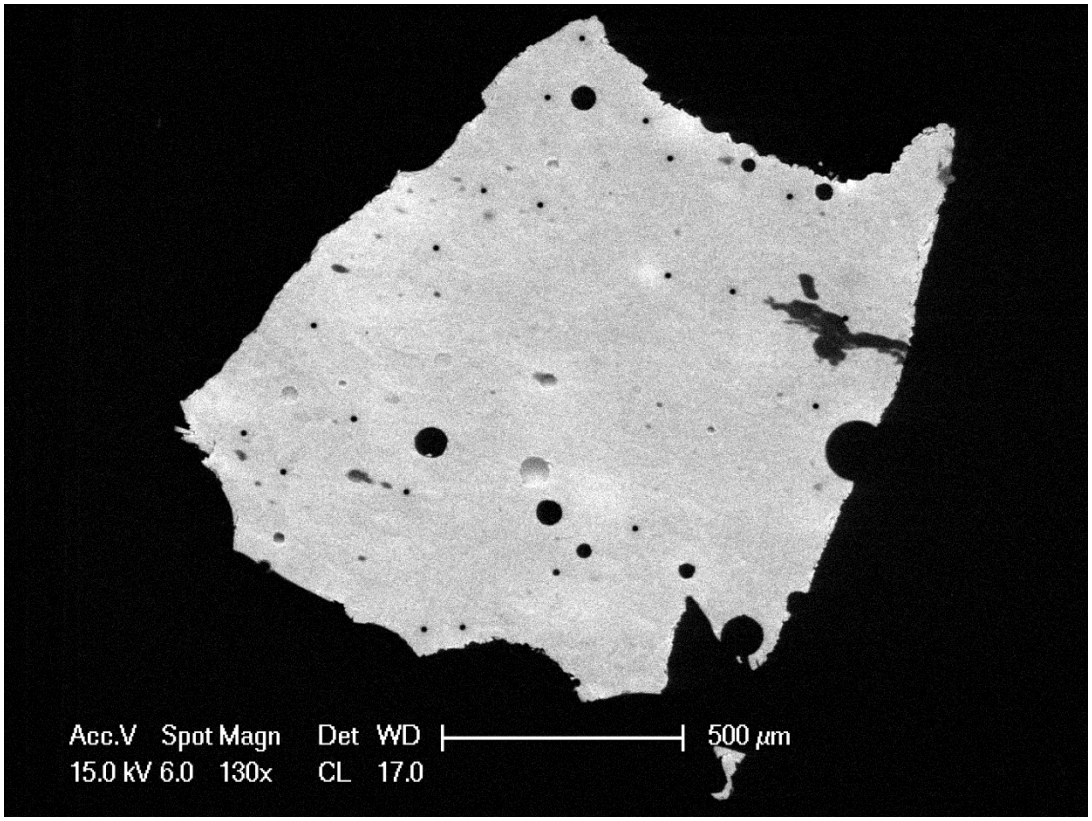

Figure 7: An image of Quartz glass 9 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

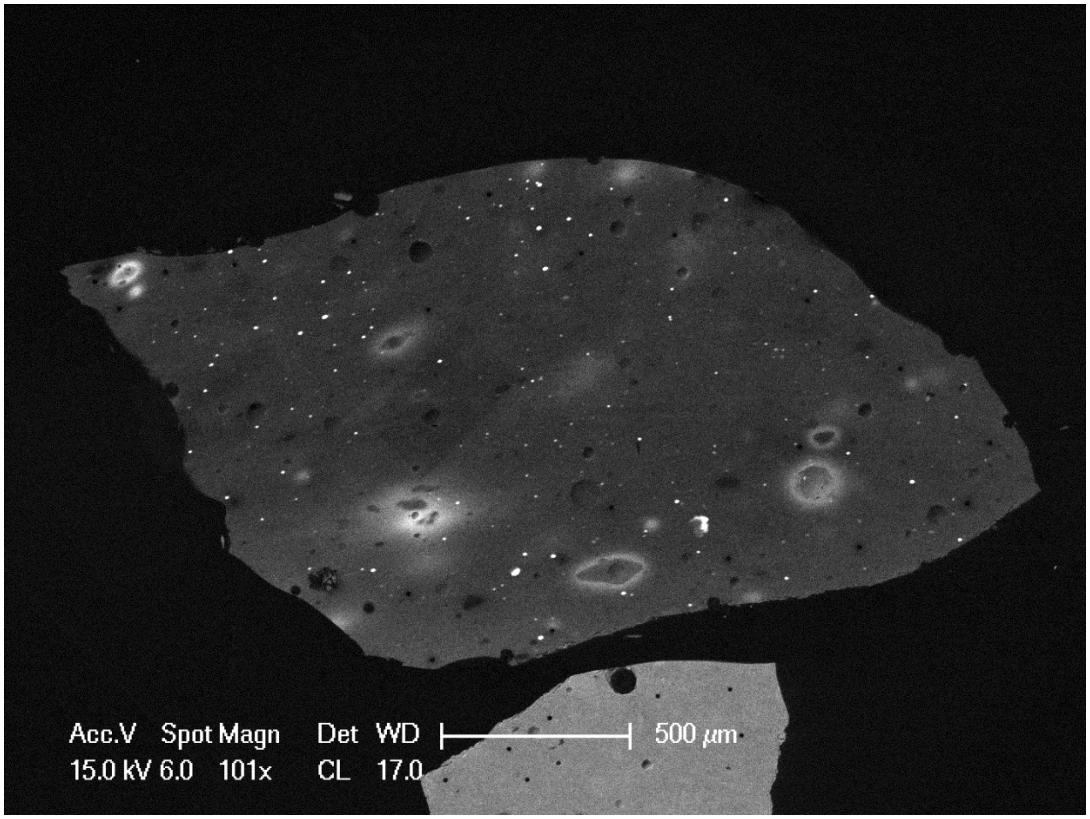

Figure 8: An image of Quartz glass 7 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

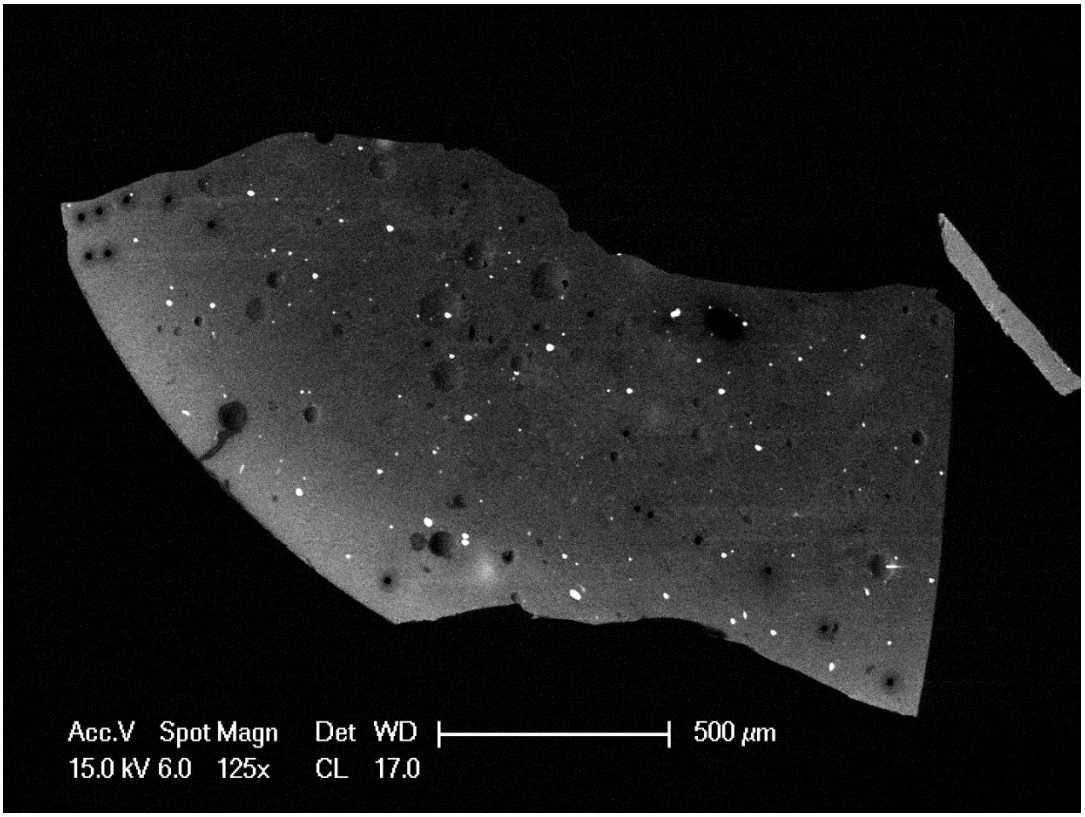

Figure 9: An image of Quartz glass 10 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

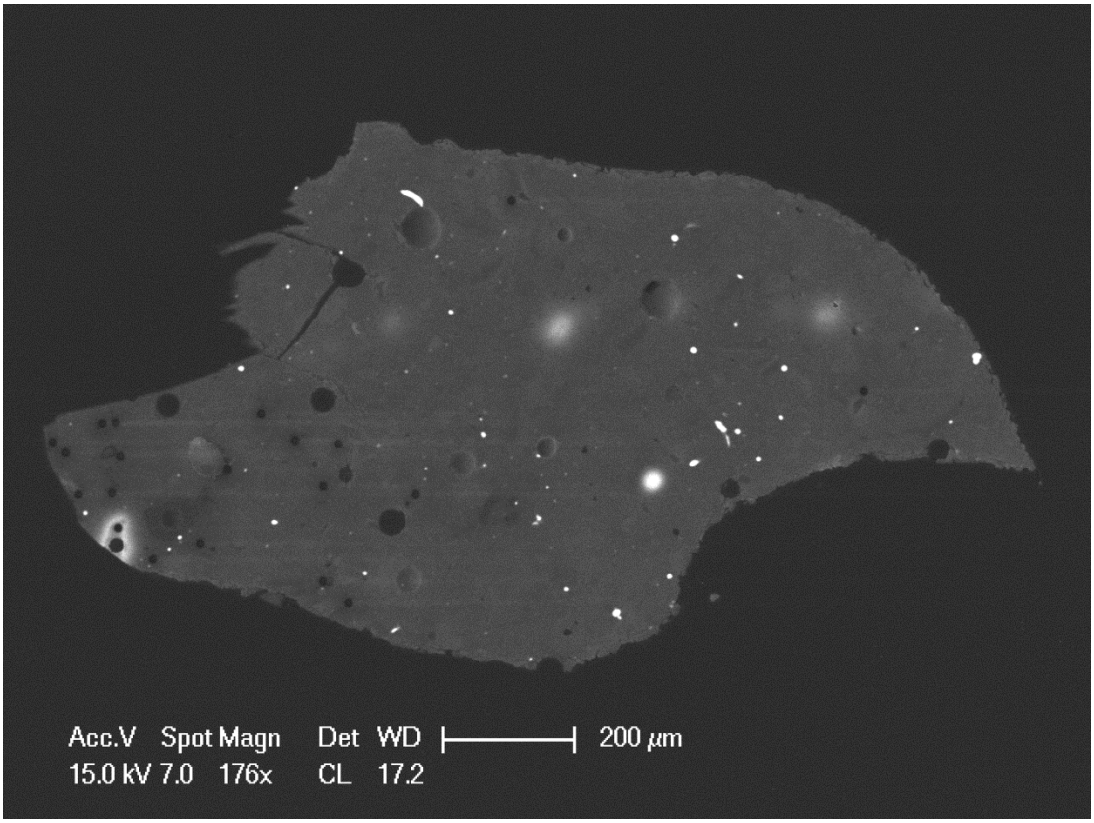

Figure 10: An image of Quartz glass 11 taken in CL on the SEM , EMMAC – University of Edinburgh. The lighter flecks are Fe, and not Ti that hasn't homogenised throughout the gel.

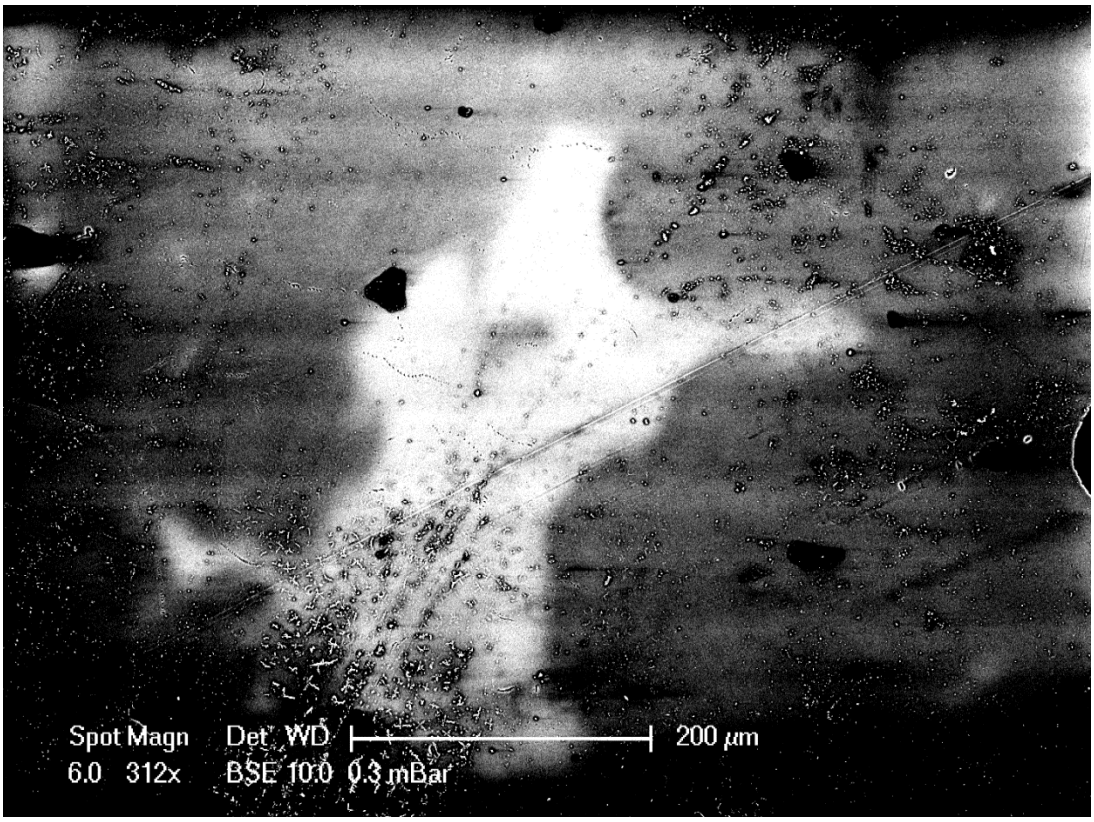

Figure 11: An image of FE brighter patch in one of the glasses, at the highest magnification ,taken in CL on the SEM, EMMAC – University of Edinburgh.

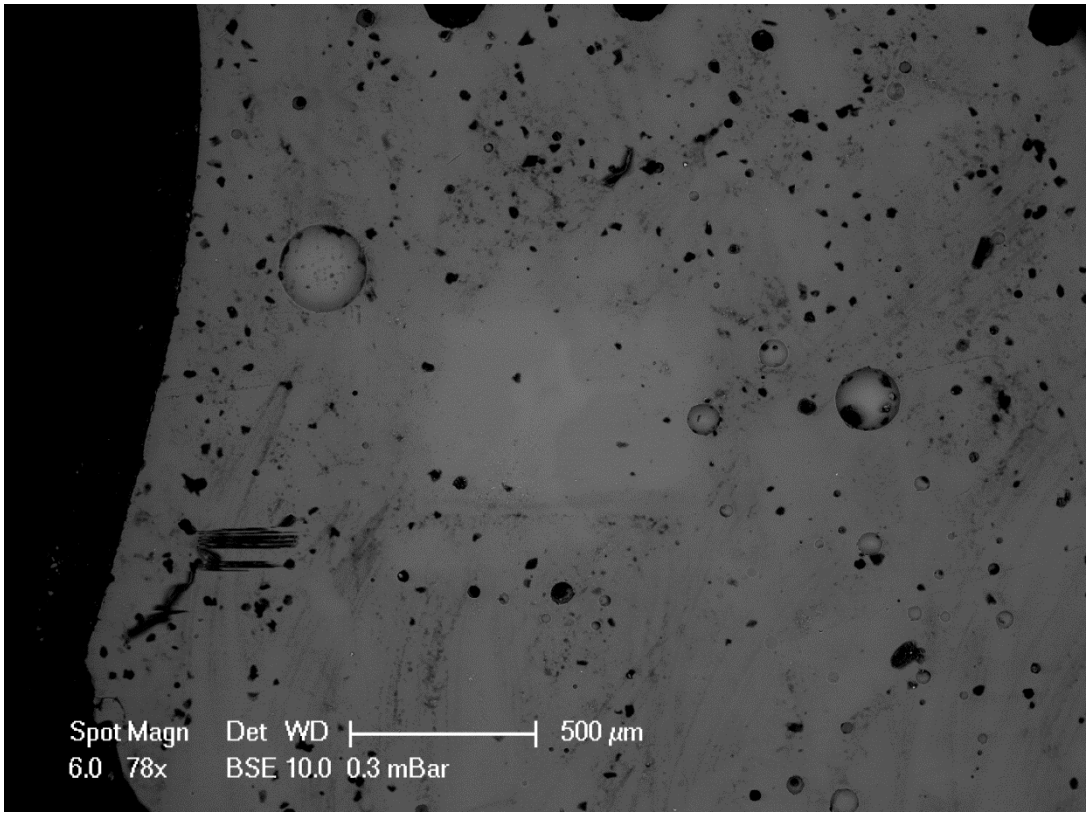

Figure 12: A zoomed image of FE brighter patch in one of the glasses, taken in CL on the SEM, EMMAC – University of Edinburgh.

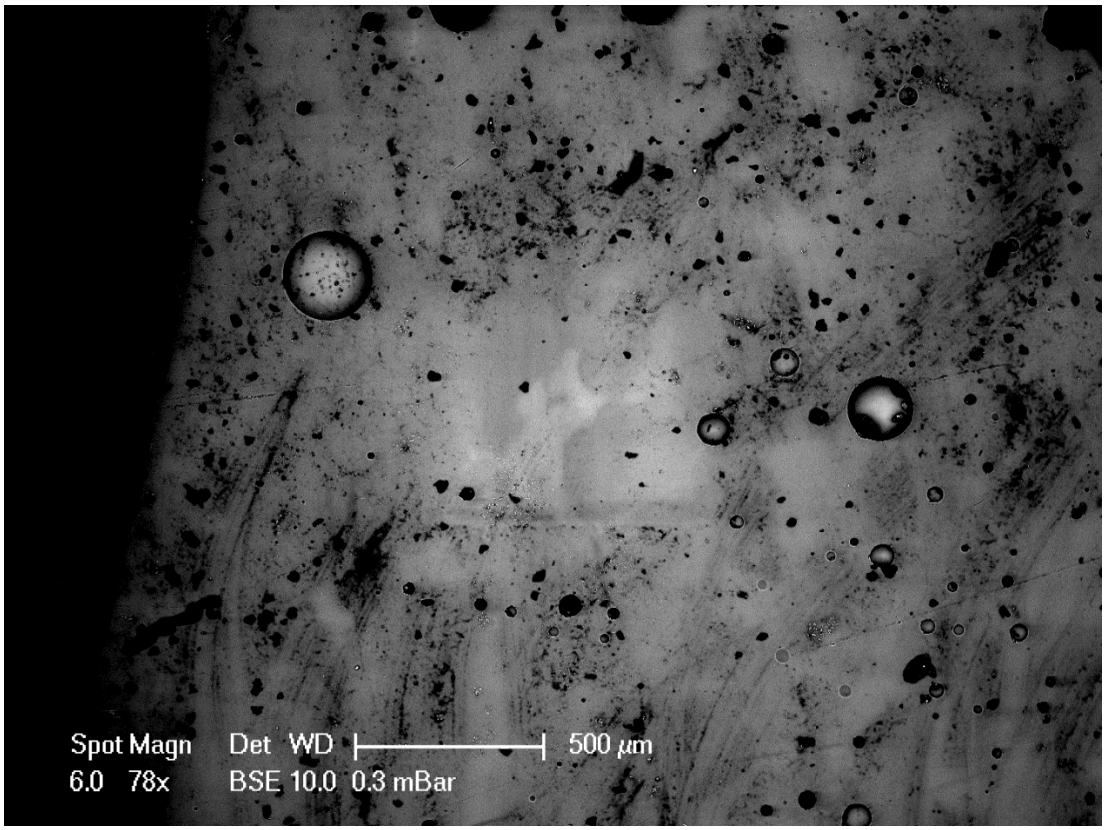

Figure 13: A close up image of FE brighter patch in one of the glasses, taken in CL on the SEM, EMMAC – University of Edinburgh.

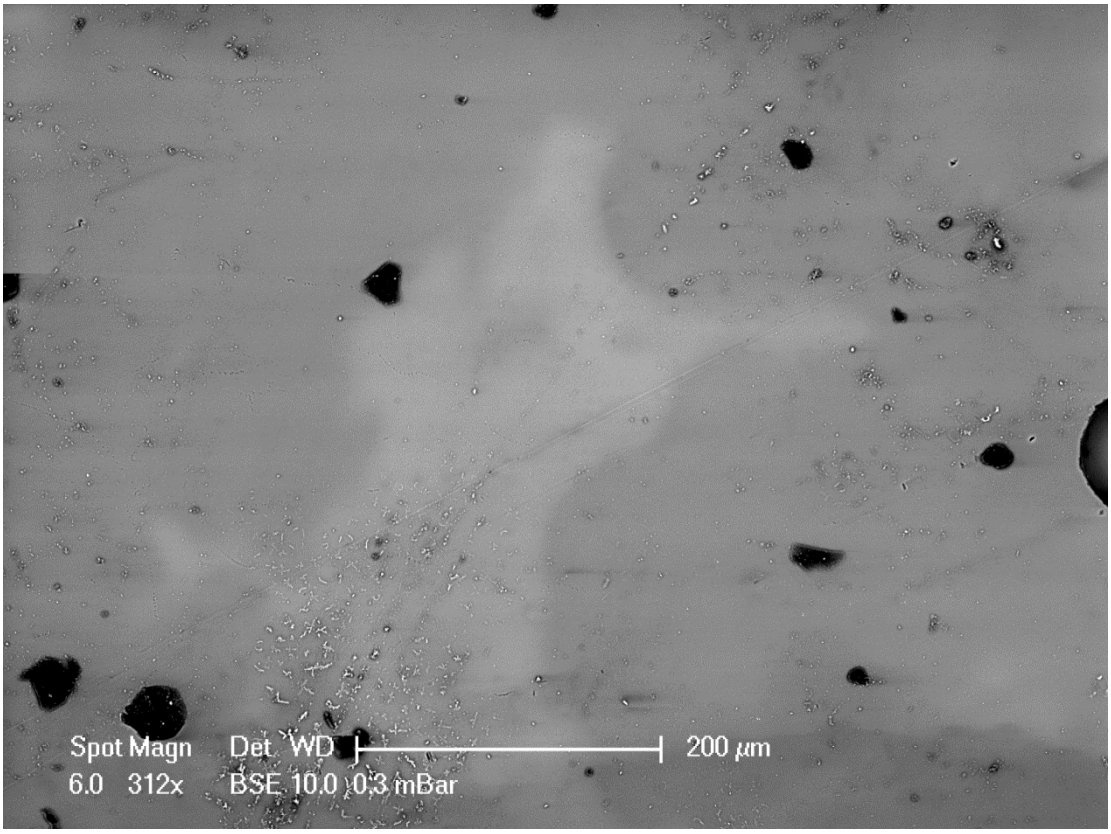

Figure 14: A close up image of FE brighter patch in one of the glasses, taken in CL on the SEM, EMMAC – University of Edinburgh.