Analytical Conditions for the Induced Coupled-Plasma Atomic Emission Spectroscopy (ICP-AES)

ICP-AES analysis was undertaken to determine the concentration of the major elements in the individual glasses.

Samples were ground to icing-sugar grade (to aid dissolution) and then dried in an oven at 100^{o}C overnight.

ICP Analyses Bristol

Acid Digestion

0.1g of the glasses was weighed out into PTFE beakers (the exact weights were recorded so dilution factors could be calculated). 5ml of 70% Nitric acid was added followed by 5ml of 48% Hydrofluoric acid and 1ml of 70% Perchloric acid. They were left for 2 hours at 100^{o}C and then turned up to 200^{o}C to evaporate. When gel like 15ml of 1% Nitric acid was added to dissolve the gel. It was then made up to 100ml.

Lithium Metaborate Fusion

The fusion method used was similar to that in Gill (…). 0.1g of the glass was weighed out into a platinum crucible along with 0.3g of Lithium Metaborate ($LiBO_2$) Flux (which had also been dried at 110^{o}C). The exact weights were recorded so the dilution factors could be calculated. The contents of the crucible was then mixed and fused over a Meker Burner for between 5 and 15 minutes. The crucible was placed in a beaker and 100ml of 12.5% Nitric acid was added. A magnetic stirrer was then placed in the crucible and left overnight. The contents of the beaker were then washed into and made up to 250ml in a volumetric flask using milliwater from Milli-Q. This was then transferred into bottles. 2ml of the sample were added to 8ml of 1% Nitric acid which was then analysed.

Analysis

The analysis was carried out on a Horiba Jobin Yvon ULTIMA sequential ICP, using the Horiba Jobin Yvon ICP Analyst 5.2 software. A monochromator with a Czerny Turner spectrometer was used. The gas used was Argon.
The following wavelengths were chosen for each of the glasses:

Element	Wavelength (nm)
Y	224.306
La	379.477
Ce	446.021
Pr	529.263
Nd	430.357
Sm	446.734
Eu	381.965
Gd	342.246
Tb	367.635
Dy	353.171
Ho	339.898
Er	369.265
Tm	313.126
Yb	369.420
Lu	261.542
Ca	317.933
Al	396.152

Each result was an average of 5 measurements each of which had 45 acquisition readings. The number of repeats carried out depended on the amount of sample available. The details of this can be found in the full ICP data results.

ICP Analyses Royal Holloway

Acid Digestion

0.2g of the glasses was weighed out into a 25ml PTFE crucible. 6ml of a 1:2 mixture of Hydrofluoric acid and Perchloric acid was added to each crucible. They were placed on a hotplate and evaporated to dryness over approximately 3-4hours at 200°C. After being allowed to cool, 2ml of concentrated Hydrochloric acid was added. Each crucible was topped up with distilled water to about ¾ full and warmed on a hotplate for 15-20min. Once cool, using a pan balance, they were made up to 20.40g using distilled water.

Proceedural repeats were prepared (2 or 3), the number of repeats carried out depended on the amount of sample available.

Lithium Metaborate Fusion

20 mg of powdered sample was mixed with 1g $LiBO_2$ powder (doped with 200 mg/kg Ga) in a graphite crucible, and then fused at 950°C in a muffle furnace. The molten bead was then dissolved in 200 ml of 5% HNO_3.

The samples were analysed for Si, Al, Ca and the REE by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The instrument used was a Perkin Elmer Optima 3300RL, with an Echelle spectrometer and a segmented-array charge-coupled-device detector. The sample was introduced using a cross flow nebuliser and a Scott type spray chamber. The power on the RF coil was 1.5kW at 40Hz; the plasma was viewed radially. The instrument was calibrated using matrix matched reference materials (Si, Al, Ca) and matrix matched standard solutions (REE). Gallium was used as an internal standard for all analytes, and data are averaged from 5 replicate analyses.

Analysis at Royal Holloway

The analysis was carried out on a Perkin Elmer Optima 3300RL, using the Winlab32 software. The detector was a segmented-array Charge-coupled-device Detector (SCD). A polychromator with Echelle grating was used. The gas used was Argon.

The calibration standards used were 50ppm, 100ppm and 200ppm synthetics, the external standards were 200ppm synthetic and NIML and NIMG and 200 ppm synthetic standards for each element.

The following wavelengths were chosen for each of the glasses:

Element	Wavelength (nm)	Wavelength (nm)
Y	324.227	371.029
La	407.735	384.902
Ce	456.236	456.236
Pr	422.293	422.293
Nd	406.109	424.738
Sm	442.434	359.260
Dy	353.170	353.170
Gd	342.247	342.247
Tb	350.917	350.917
Er	349.910	349.910
Ho	339.898	347.426
Yb	289.138	289.138
Eu	381.967	381.967
Tm	313.126	346.220
Lu	291.139	219.554
Si	288.158	
Ca	315.887	315.887
Al	396.153	396.153