

A New Basaltic Glass Microanalytical Reference Material for Multiple Techniques

Steve Wilson, Alan Koenig, and Heather Lowers*

U.S. Geological Survey, MS973, Denver CO 80225

* hlowers@usgs.gov

Editor's Note: This article relates to the MAS Topical Conference, Microanalytical Reference Materials, to be held May 15–17, 2012, at the Colorado School of Mines. The use of firm, trade, and brand names is for identification purposes only and does not constitute endorsement by the U.S. government.

Introduction

The U.S. Geological Survey (USGS) has been producing reference materials since the 1950s [1]. Over 50 materials have been developed to cover bulk rock, sediment, and soils for the geological community. These materials are used globally in geochemistry, environmental, and analytical laboratories that perform bulk chemistry and/or microanalysis for instrument calibration and quality assurance testing. To answer the growing demand for higher spatial resolution and sensitivity, there is a need to create a new generation of microanalytical reference materials suitable for a variety of techniques, such as scanning electron microscopy/X-ray spectrometry (SEM/EDS), electron probe microanalysis (EPMA), laser ablation inductively coupled mass spectrometry (LA-ICP-MS), and secondary ion mass spectrometry (SIMS). As such, the microanalytical reference material (MRM) needs to be stable under the beam, be homogeneous at scales of better than 10–25 micrometers for the major to ultra-trace element level, and contain all of the analytes (elements or isotopes) of interest. Previous development of basaltic glasses intended for LA-ICP-MS has resulted in a synthetic basaltic matrix series of glasses (USGS GS-series) and a natural basalt series of glasses (BCR-1G, BHVO-2G, and NKT-1G). These materials have been useful for the LA-ICP-MS community [2] but were not originally intended for use by the electron or ion beam community. A material developed from start to finish with intended use in multiple microanalytical instruments would be useful for inter-laboratory and inter-instrument platform comparisons.

This article summarizes the experiments undertaken to produce a basalt glass reference material suitable for

distribution as a multiple-technique round robin material. The goal of the analytical work presented here is to demonstrate that the elemental homogeneity of the new glass is acceptable for its use as a reference material. Because the round robin exercise is still underway, only nominal compositional ranges for each element are given in the article.

Materials and Methods

Starting material for the preparation of the new reference material was obtained from a basaltic flow known today as Table Mountain, which is located near the town of Golden, Colorado. This material was used for years as a quality control standard for the USGS WDXRF laboratory, and a large supply of pulverized material was available (designated TB-1, see Table 1).

Glass production. Previous attempts to prepare a glass version of TB-1 (TB-1G) resulted in a viscous melt, which upon cooling produced a uniform glass that unfortunately had only low concentrations of most trace elements. Because the intent of this study was to produce a glass material with element concentrations useful for multiple analytical techniques, it was decided that 25 elements would be added to the original material. The additional elements were added to achieve concentrations in the 1,000–5,000 ppm level for EPMA and to increase the number of trace elements for LA-ICP-MS work (<1,000 ppm). To minimize the possibility that a heterogeneous glass would be produced, it was decided to lower the viscosity of the molten materials through the addition of specific major element oxides or carbonates (CaO, Fe₂O₃, K₂CO₃, Na₂CO₃, MgO).

Matrix-modified TB-1 material. A 150 g sample of TB-1 was combined with 30 g of major element oxides/carbonates (CaO, Fe₂O₃, K₂CO₃, Na₂CO₃, MgO), producing a matrix-modified basaltic material (180 g) with the desired major element composition. This matrix-modified material was transferred to a one-liter plastic bottle and mixed for

Table 1: Trial glasses with comments on the suitability of each as a reference material.

Batch	Description
TB-1	Powdered natural basalt glass used as WDXRF reference material.
WTB-1G	Glass produced from TB-1 powder. This glass contained iron dendrites and chromite inclusions.
WTB-2G	Modified version of WTB-1G to which dopants were added to achieve desired trace element concentrations. Additional chromium initially added to the WTB-1G batch was removed to prevent chromite formation. The platinum bowl that contained the molten glass was submersed in water. This glass had large iron-nickel spinels.
WTB-3G	This is the same composition of WTB-2G but without the melt, regrind, and remelt step.
WTB-2Ga	This is the final glass batch, which appears to be homogeneous based on BSE imaging, electron microprobe, and laser ablation analyses. It was prepared from a grind and remelt of the WTB-2G batch. The molten material was poured onto a platinum tray and then submerged in water.

5 minutes on a horizontal roller. To improve the homogeneity of this powdered material, portions of the blend (90 g) were ground in an agate shatter box (100 g capacity).

Trace element spiking solid. Trace elements were added to the matrix-modified TB-1 material using a specially prepared trace element spiking solid (TESS) material. This TESS material was designed to contain trace element concentrations, which were 10 times higher than required in the final glass. The TESS material was prepared by adding solid aliquots of the desired 25 trace elements to 25 g of TB-1, yielding a total mass of 50 g. This material was transferred to an agate shatter box and ground/mixed for 4 minutes. Because the final glass material was intended for multiple instrument platforms, element concentrations in the TESS material were added in amounts to produce a glass with selected trace elements to be detectable by electron microprobe and other element concentrations optimized for LA-ICP-MS and SIMS analysis. In the first preparation attempt (WTB-1G), a chromium concentration was used that would produce a Cr content in the final glass of 1,500 ppm. Because of a chromium heterogeneity problem encountered in WTB-1G, chromium was omitted from later blends.

In the final mixing step, a 20 g portion of the TESS material was combined with 180 g of matrix-modified TB-1 material and mixed for 5 minutes. To improve the homogeneity of this mixture, 100 g portions (2) were ground in the agate shatter box. The ground portions were recombined in a plastic bottle and mixed on a roller mill for 20 minutes.

Melting. The 200 g mixture was then transferred to a platinum bowl (9.7 cm D × 4.7 cm H). The powdered material completely filled the bowl (Figure 1). The bowl was transferred to a Lindberg heavy-duty box furnace operating at 1,300 C. A visual inspection of the heating chamber after 30 minutes revealed that the powder volume was reduced by a factor of 3. After 2 hours of heating, the bowl was removed from the oven, and the molten contents were mixed using a 12 cm platinum rod. Mixing continued for a period of 30 seconds until the cooling basalt became too viscous to stir. The bowl was returned to the oven for an additional melting cycle. After an hour, the bowl was again removed from the oven, mixed (30 sec) using the platinum rod, and then returned to the oven for the final melting cycle. Given the relatively small sample size, two different cooling procedures were used to evaluate the speed of cooling on element homogeneity.

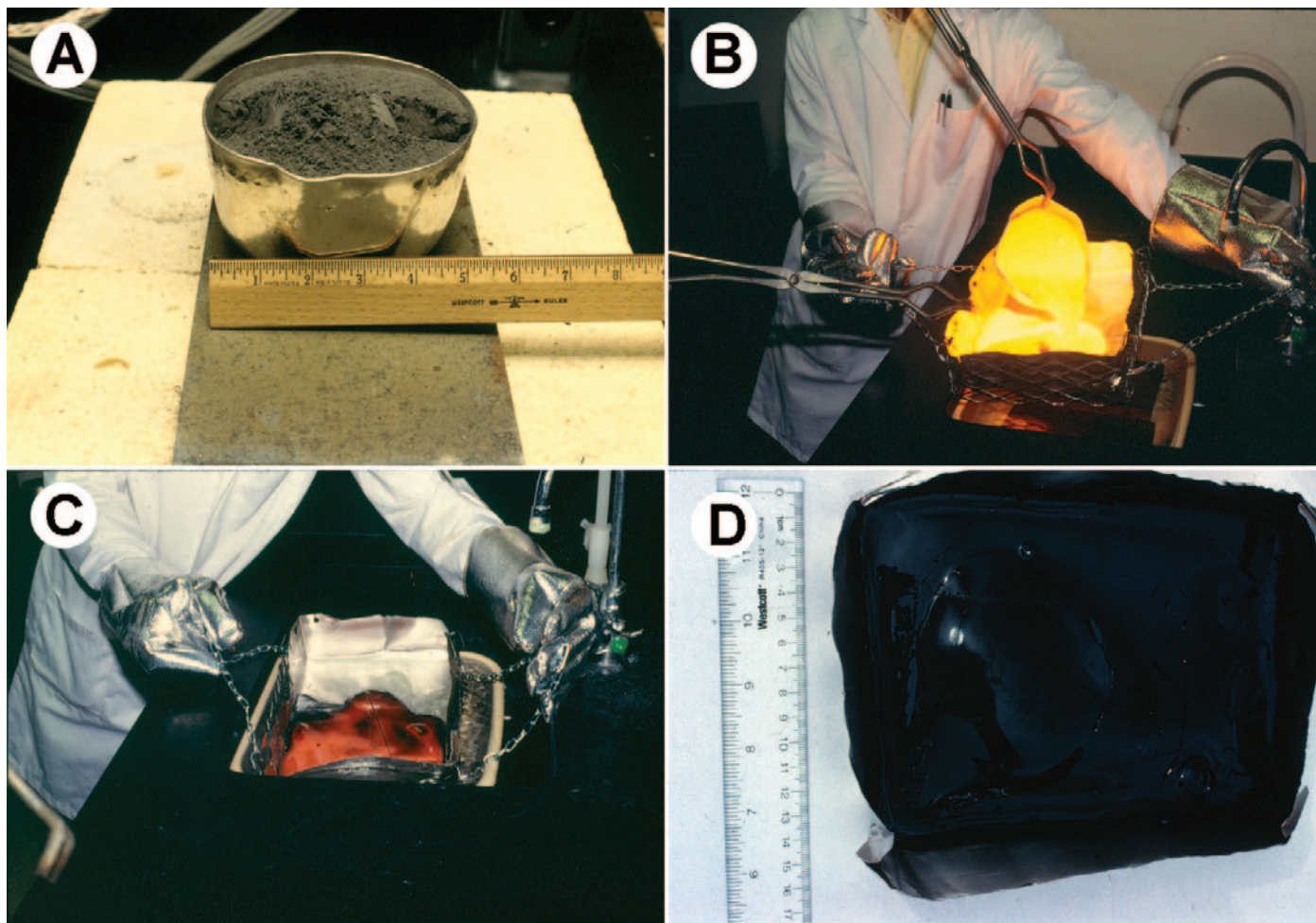


Figure 1: The preparation steps of WTB-2Ga glass. (A) The ground powder starting material is placed in a platinum crucible. (B) The molten material is poured into a shallow platinum boat supported by a steel cage. (C) The steel cage is lowered into a vessel of water. (D) The resultant glass disc is crushed to provide pieces for microanalysis.

Slow cooling WTB-2G. In the first attempt, the bowl was removed from the oven and slowly lowered into a water bath. During this quenching process, the center portion of the molten glass glowed red for an additional 10 seconds after complete submersion into the water bath. The persistence of this hot spot in the glass during the cooling process was a concern because of the possibility of crystallization occurring in this region of the glass, which was later confirmed by SEM imaging.

Fast cooling of WTB-2Ga. In an attempt to correct the above problem, the WTB-2G glass was recovered from the bowl, reground, and then remelted using the procedure outlined above. In this preparation procedure (WTB-2Ga, see Table 1) the quenching protocol involved pouring the molten glass into a shallow platinum boat, supported in a steel cage (Figure 1). The steel cage was lowered into a water bath, and the molten mixture solidified immediately with no obvious hot spots (Figure 1). After 15 minutes the WTB-2Ga glass slab (4 mm thick) was cool to the touch, and the glass fragments were removed for analysis.

Additional production without regrinding and re-melting, WTB-3G. Concern over the amount of useable WTB-2Ga material relative to potential demand prompted an additional production run identified as WTB-3G. In the production of WTB-3G, the mixing protocol and cooling procedure used in WTB-2Ga were followed exactly. The only difference was that the initial WTB-3G glass was not reground and remelted due to time constraints. Examination of this glass revealed large areas of “swirlies,” which were banded areas with heterogeneous major and trace element concentrations. Although it was believed that elimination of this heterogeneity problem would be corrected through regrinding and remelting, this work was never performed because of a better-than-expected recovery of premium (>4 mm) fragments of the WTB-2Ga material.

SEM imaging. Three epoxy grain mounts were prepared of each glass batch. Each mount, containing 8–10 glass chips, was polished to a 1 μm finish and coated with carbon for conductivity. Care was taken to discard chips that were in obvious contact with the platinum boat because of the well-known diffusion of platinum into iron bearing matrices. Backscattered electron (BSE) images were acquired with a field-emission SEM set to produce high beam currents (20 nA) at 15 and 20 keV. These BSE images were used to survey the quality of the glass batches because subtle changes in composition and non-glass inclusions can be observed.

Homogeneity assessment by EPMA. Electron microprobe data of the final WTB-2a glass were collected at 15 keV, 20 nA (cup) current, and with a 20 μm beam diameter. The following silicate mineral standards and crystals were used: Tiburon albite (Na:TAP, Si:TAP), an in-house orthoclase (K:PET), Miyake anorthite (Ca:PET, Al:TAP), Springwater forsterite (Mg:TAP), synthetic rutile (Ti:LiF), synthetic fayalite (Fe:LiF), synthetic spessartine (Mn:LiF), and synthetic nickel olivine (Ni:LiF). Depending on the area of glass exposed, 30 to 100 analyses were performed on 9 glass chips from one of the WTB-2a mounts. The level of homogeneity as a percentage

of the concentration of each element was calculated with the Probe for EPMA software package [3] using the following equation from Goldstein et al. [4]:

$$\pm \frac{W_{1-\alpha}}{C} = \pm \frac{(t_{n-1}^{1-\alpha})S_C(100)}{n^{1/2}N_{avg}}$$

where C is the actual concentration of the element in weight percent of the sample, $t_{n-1}^{1-\alpha}$ is the Student t for a $1 - \alpha$ confidence and $n - 1$ degrees of freedom, n is the number of data points acquired, S_C is the standard deviation of the measured values (count intensity), and N_{avg} is the average number of counts on the unknown.

Homogeneity assessment by mass spectrometry. LA-ICP-MS analyses for WTB-2Ga were conducted on 13 different grains from the 3 mounts. For two of the grains, analyses in rectangular grids of 100 and 120 spots, respectively, were conducted. Random analyses were made across the remaining 11 grains. LA-ICP-MS analyses were conducted using a 193 nm excimer laser ablation system coupled to a quadrupole ICP-MS. A spot size of 85 μm was used for the LA testing. The energy density was 5 J/cm², and the ablated material was transported to the ICP-MS in a stream of He (combined flow of 1.0 L/min). Ablation occurred in a 2-volume ablation chamber that is optimized for fast washout, allowing micro-inclusions to be easily resolved based on chemical differences. Instrument response was calibrated using the USGS synthetic basalts GSE-1G and GSD-1G as well as the

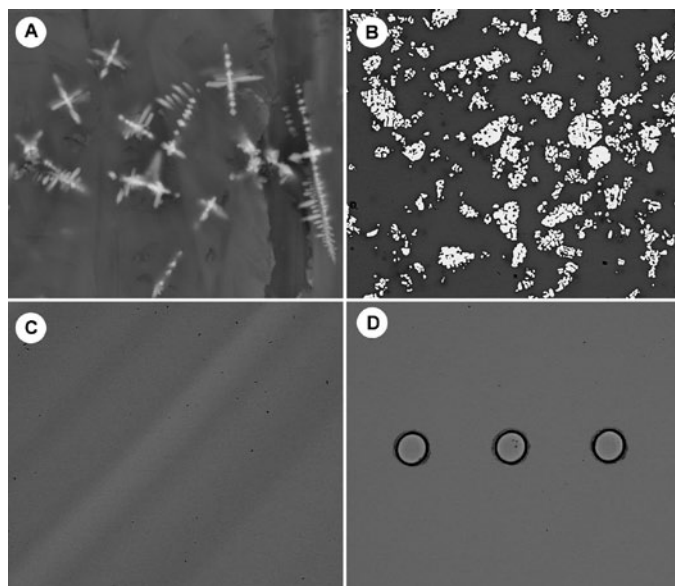


Figure 2: Scanning electron microscope BSE images showing progression from inclusions and chemical zoning to clean glass suitable as a reference material. (A) WTB-1G contained iron dendrites (shown) as well as chromite inclusions (not shown) (horizontal field width (HFW) = 14.4 μm). (B) Upon slow cooling, WTB-2G, produced iron- and nickel-containing spinels (HFW = 848 μm). (C) WTB-3G, which is the same composition as WTB-2Ga, was cooled by pouring the molten material from the platinum boat into the water bath. This produced a glass with noticeable chemical variations mainly due to iron (HFW = 851 μm). (D) WTB-2Ga resulted in a glass free of inclusions and free of noticeable chemical variations. This glass was further tested for homogeneity by electron microprobe (Table 2) and by LA-ICP-MS (craters in glass, also Figure 3) (HFW = 848 μm).

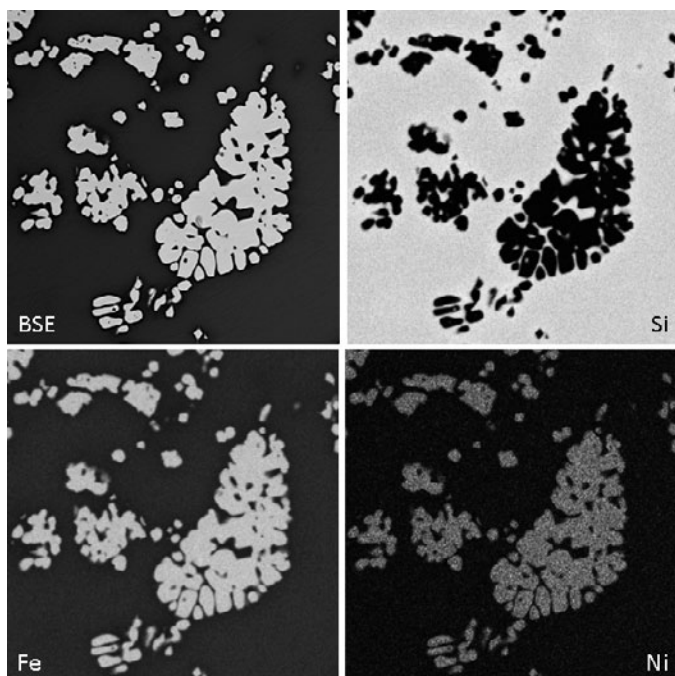


Figure 3: WTG-2G X-ray intensity maps of Si, Fe, and Ni and a BSE image. This glass iteration had large iron-nickel spinels (EDS determination) prohibiting its use as a reference material. The maps were acquired on a FESEM operated at 20 keV to excite the Ni Ka X-ray line [6], current set to 50 nA (cup), and 1-hour acquisition time (HFV = 323 μm).

natural basalts NKT-1G and TB-1G (the starting material for WTB-2a). Concentrations were calculated using the equations of Longrich et al. [5].

Results

SEM screening. The four glass preparations of Table 1 were initially screened by SEM. Backscattered electron imaging of WTB-1G revealed phases likely to be chromite (FeCr_2O_4) inclusions and iron oxide dendrites based on SEM/EDS spectra (Figure 2a). The presence of the chromite inclusions prompted removal of Cr as an added analyte

(above the natural concentration). BSE imaging of WTB-2G revealed large iron-bearing spinel inclusions (Figures 2b and 3). The presence of these inclusions made the glass unacceptable. Because the slower cooling of WTB-2 allowed the growth of these spinels, faster cooling should prevent this precipitation. Glass WTB-3G was rapidly cooled in a water bath; although it lacked mineral inclusions, it still showed significant compositional variations (Figure 2c). Energy dispersive analysis suggests the contrast variation in the BSE image is due to changes in iron concentration. The fast-cooled glass WTB-2Ga, which was a reground and remelted WTB-2G, was free of inclusions and noticeable compositional zoning in the BSE image. The success of this initial SEM screening of WTB-2Ga prompted further investigation of the homogeneity by electron microprobe and LA-ICP-MS.

EPMA homogeneity measurements. Initial homogeneity calculations for data collected with the electron microprobe for glass chips of WTB-2Ga are summarized in Table 2. All elements analyzed by electron microprobe were homogeneous within the 60% confidence interval. Furthermore, most major and minor elements (Si, Al, Fe, Mg, Ca, K, Na) in the nine glass chips were consistently homogeneous at the 99% confidence interval. The only exceptions were Mn, Ni, and for some grains Ti.

LA-ICP-MS homogeneity measurements. A total of 460 spot analyses across 13 grains of WTB-2Ga indicate sufficient homogeneity for most LA-ICP-MS work at the 85 μm scale. In general, the trace elements tested in the 1–100 ppm range exhibited less than 5–10% relative standard deviation. Elements spiked at higher concentrations, in the 500–2,000 ppm range, had less than 3% relative standard deviation. Figure 4 shows a summary of the homogeneity data for 460 spots across 13 grains for 2 elements: Co and Cu. The vertical axes are removed so as not to reveal the actual concentration in ppm because this material will be the subject of an upcoming round robin. A total of 66 elements were screened and all showed acceptable homogeneity for this material using LA-ICP-MS techniques. Testing of specimens from the

Table 2: Electron microprobe homogeneity results for WTB-2Ga. Values are the level of homogeneity at the 99% confidence interval (t-test) as a percentage of the average composition for major elements. The determination of homogeneity at the 1.0% precision level is in parentheses.

Chip	1	2	3	4	5	6	7	8	9
n	100	100	52	93	84	89	100	35	100
Si	0.1(yes)	0.2(yes)	0.6(yes)	0.6(yes)	0.1(yes)	0.1(yes)	0.6(yes)	0.2(yes)	0.1(yes)
Ti	0.9(yes)	1.1(no)	1.2(no)	1.2(no)	0.9(yes)	1.0(yes)	1.0(yes)	1.8(no)	0.9(yes)
Al	0.2(yes)	0.2(yes)	0.5(yes)	0.5(yes)	0.2(yes)	0.2(yes)	0.6(yes)	0.2(yes)	0.2(yes)
Ni	1.7(no)	1.6(no)	2.6(no)	2.6(no)	1.7(no)	1.4(no)	1.9(no)	2.4(no)	1.5(no)
Fe	0.2(yes)	0.2(yes)	0.6(yes)	0.6(yes)	0.3(yes)	0.2(yes)	0.3(yes)	0.4(yes)	0.2(yes)
Mn	2.0(no)	2.1(no)	2.6(no)	2.6(no)	2.6(no)	2.0(no)	2.0(no)	3.8(no)	2.2(no)
Mg	0.2(yes)	0.2(yes)	0.3(yes)	0.3(yes)	0.2(yes)	0.2(yes)	0.5(yes)	0.4(yes)	0.2(yes)
Ca	0.4(yes)	0.2(yes)	0.4(yes)	0.4(yes)	0.2(yes)	0.2(yes)	0.2(yes)	0.5(yes)	0.2(yes)
Na	0.6(yes)	0.4(yes)	0.9(yes)	0.9(yes)	0.4(yes)	0.3(yes)	0.6(yes)	0.6(yes)	0.4(yes)
K	0.5(yes)	0.2(yes)	0.4(yes)	0.4(yes)	0.3(yes)	0.3(yes)	0.3(yes)	0.5(yes)	0.3(yes)

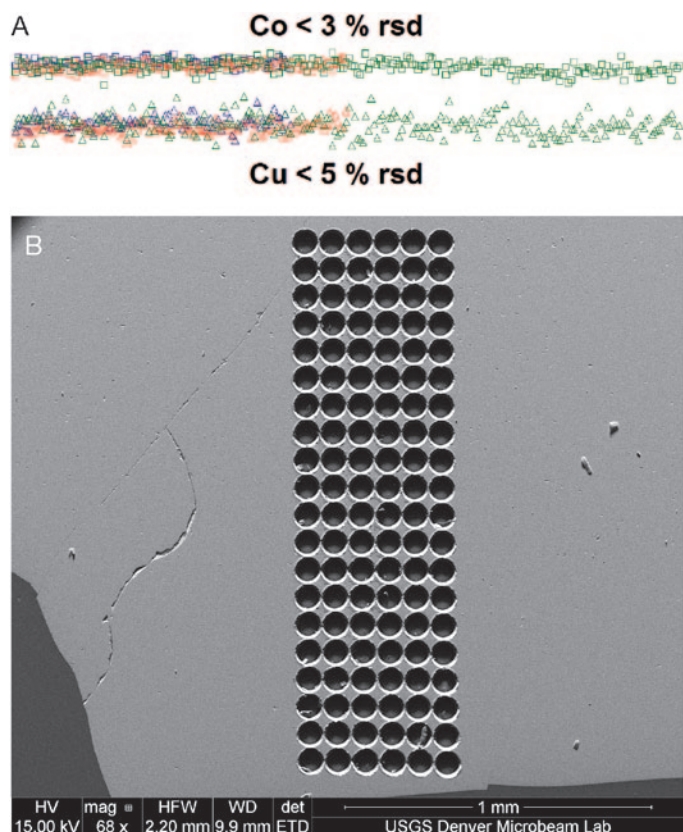


Figure 4: (A) A plot of Co and Cu concentrations determined by LA-ICP-MS for 460 spots over 13 grains of WTB-2Ga. The different groups refer to different LA data acquisition patterns (blue = 100-spot grid, red = 120-spot grid, and green = random spots on mount 3). The vertical axis is relative concentration. Actual concentration is not reported because this material is the subject of a round robin. (B) An SE image of the 120-spot LA-ICP-MS grid. Note the craters in the glass are round and have vertical walls and flat bottoms.

previous experiments in the WTB production runs (such as WTB-1G, WTB-2G, and WTB-3G) all revealed problems in trace or minor element heterogeneity that substantiated the initial screening by SEM imaging.

Discussion

Several iterations were necessary to achieve a glass that was free of inclusions and obvious chemical variations. Cooling history and composition were two variables that were changed to reach the desired glass characteristics. To avoid unwanted mineral inclusions, the glass must be quenched quickly. Thick pods of melt, such as WTB-2, will have high heat retention toward the middle. Such slower cooling in the middle of the pod allows spinel minerals to grow from the melt. Spinel incorporates transition metals as well as Mg and Al into their structure thus lowering the concentration of these elements in the neighboring glass (Figure 3). The presence of these minerals may create discrepancies between bulk chemical and microanalytical results. By pouring the molten glass into a thinner disc and immediately submerging in water, undesirable phase formation was suppressed in the final reference glass, WTB-2Ga.

The effect of pouring in atmosphere as opposed to in an oxygen-controlled atmosphere was not evaluated. Iron and perhaps manganese may display multivalent states depending

on the oxygen fugacity. However, for the targeted techniques, total iron concentration is the value that is measured. The valence state of such minerals would need to be better controlled and evaluated for reference materials to be useful for techniques such as X-ray photoelectron or Auger electron spectroscopies.

Although the development of glass reference materials for LA-ICP-MS has been successful for some time, the requirements of cross-platform reference materials useful for EPMA, SIMS, and LA-ICP-MS requires new materials to be developed with that purpose in mind that can be validated by all the techniques. The minor elements (0.05–1 wt%) present in this glass will provide crossover levels for comparison of EPMA and LA-ICP-MS data. Elements present in the trace element range (<0.05 wt%) will provide known levels for comparison with LA-ICP-MS and SIMS data. The addition of 25 elements (some at the 1,000s of ppm level) to the natural basalt composition also allows evaluation of the accuracy of interference correction procedures for all techniques.

Conclusion

The WTB-2Ga glass appears to be free of mineral inclusions and is homogeneous for major elements (Si, Al, Fe, Mg, Ca, Na, and K) at the 1% precision level for electron microprobe analyses. Examination by LA-ICP-MS determined that intergrain and intragrain variations standard deviations were less than 5–10% relative. The glass WTB-2Ga is ready for distribution to laboratories, capable of bulk or microanalytical quantitative analysis, that wish to participate in a round robin process to determine consensus values for the composition of this glass.

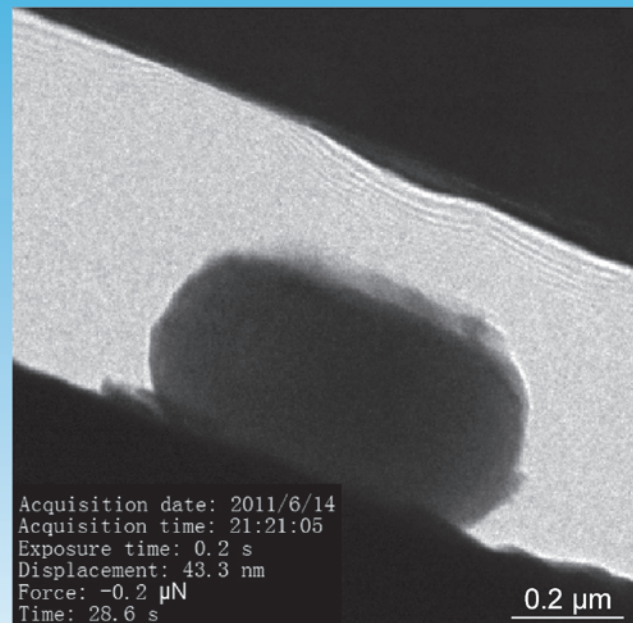
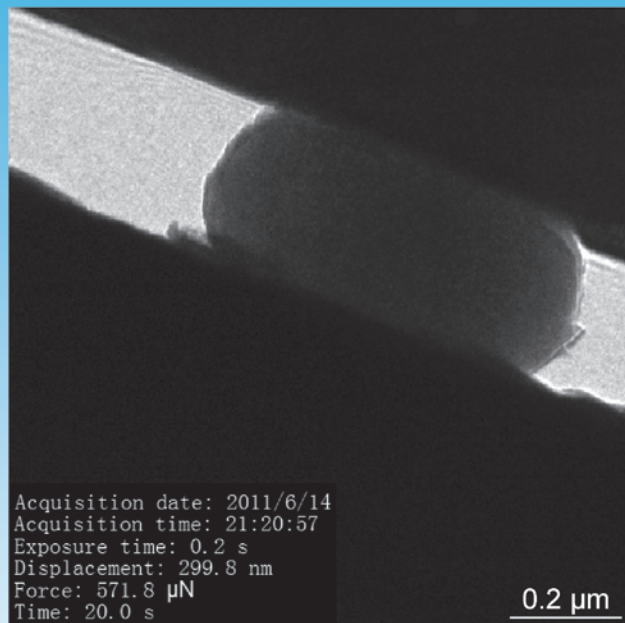
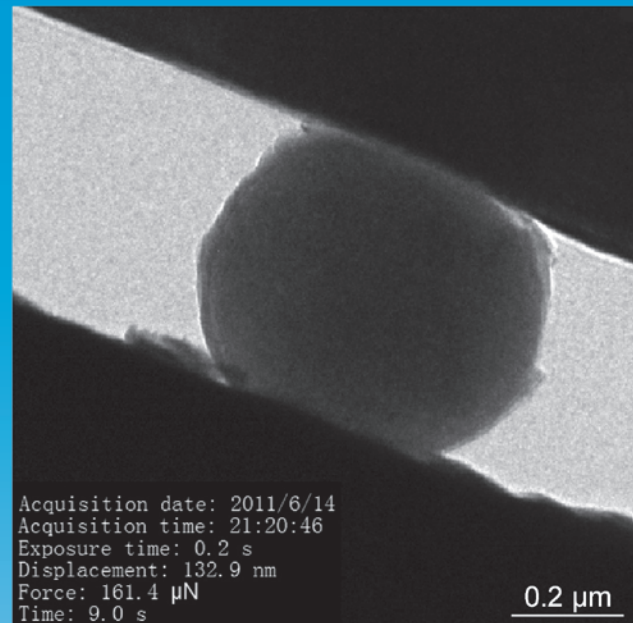
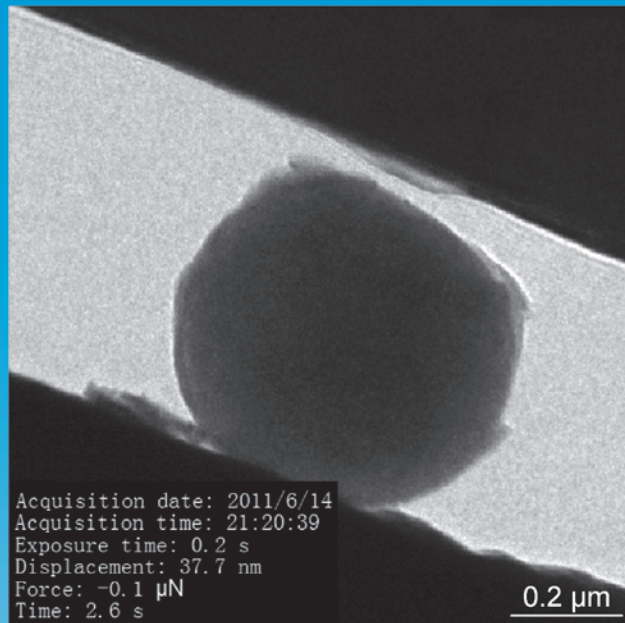
As new directions in microanalytical techniques continue to develop, the need will increase for homogeneous reference materials with a wide range of matrices and elemental concentrations. The development of reference materials such as this WTB-2Ga, intended for several techniques (EPMA, SIMS, LA-ICP-MS, and others), coupled with run round robin testing, provides better certainty of results for microanalysis. Making interlaboratory reference materials of appropriate homogeneity and in sufficient quantity is not a trivial exercise, but there is value in calibration and QC materials that are useful for a wide variety of instruments.

References

- [1] RE Wolf and SA Wilson, U.S. Geological Survey Fact Sheet 2007-3056. http://pubs.usgs.gov/fs/2007/3056/pdf/fs07-3056_508.pdf
- [2] KP Jochum, SA Wilson, W Abouchami, et al., *Geostandards and Geoanalytical Research* 35 (2011) 193–226.
- [3] JJ Donovan, Probe for EPMA, 1995–2011, <http://www.probesoftware.com/>.
- [4] J Goldstein et al., *Scanning Electron Microscopy and X-Ray Microanalysis*. 3rd ed., Springer Science+Business Media, New York, 2003.
- [5] H Longerich, S Jackson, and D Gunther, *J Anal Atomic Spect* 11 (1996) 899–904.
- [6] JJ Friel and CE Lyman, *Microsc Microanal* 12 (2006) 2–25.

Synchronizing images with data from *in situ* devices

In situ TEM/SEM **HD Video (AVI, MPEG4, WMV)** **Windows 7 (32 and 64 bit)**
Open architecture for 3rd party *in situ* devices **DM scripting**



In situ compression of a SiO_2 glass nanoparticle acquired with Gatan ORIUS[®] 830 CCD camera. A 500 nm amorphous SiO_2 glass particle is plastically deformed using a Hysitron Picoindenter (PI95). The loading rate of 15 nm/s was generated by driving the flat diamond punch seen in the lower left corner of the images. The indentation experiment was coordinated and recorded using Gatan's *In situ* Video Software, a new component of the Gatan Microscopy Suite[®]. Images courtesy of Prof. Zhiwei Shan, CAMP-Nano, Xi'an Jiaotong University, China.



www.gatan.com

ANALYTICAL TEM
DIGITAL IMAGING
SPECIMEN PREPARATION
TEM SPECIMEN HOLDERS
SEM PRODUCTS
SOFTWARE

***In situ* Video Software**
Gatan Microscopy Suite[®]