

# Quantitative analysis of trace element abundances in glasses and minerals: a comparison of laser ablation inductively coupled plasma mass spectrometry, solution inductively coupled plasma mass spectrometry, proton microprobe and electron microprobe data<sup>†</sup>

Marc D. Norman<sup>\*a</sup>, William L. Griffin<sup>ab</sup>, Norman J. Pearson<sup>a</sup>, Michael O. Garcia<sup>c</sup> and Suzanne Y. O'Reilly<sup>a</sup>

<sup>a</sup>ARC National Key Centre for Geochemical Evolution and Metallogeny of Continents (GEMOC), School of Earth Sciences, Macquarie University, Sydney 2109, Australia

<sup>b</sup>CSIRO Exploration and Mining, P.O. Box 136, North Ryde 2113, Australia

<sup>c</sup>Hawaii Center for Volcanology, Dept. of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822, USA

Many geological, environmental and industrial applications can be enhanced through integrated microbeam and bulk geochemical determinations of major and trace element concentrations. Advantages of *in situ* microanalysis include minimal sample preparation, low blanks, information about the spatial distribution of compositional characteristics and the ability to avoid microscopic inclusions of foreign material. In this paper we compare trace element data obtained by laser ablation ICP-MS, solution ICP-MS, electron microprobe analysis and proton microprobe analysis for a variety of silicate glasses and minerals. New determinations for 36 trace elements in BCR-2G, a microbeam glass standard, are presented. Results obtained by the various microbeam and solution methods agree well for concentrations ranging over several orders of magnitude. Replicate analyses of BCR-2G demonstrate an analytical precision of 2–8% relative ( $1\sigma$ ) for all elements by laser ablation ICP-MS and  $\leq 3\%$  by solution ICP-MS, except for Li (5%). These data emphasize the utility of laser ablation ICP-MS as a quantitative microbeam technique capable of rapid, precise determinations of sub-ppm trace element abundances in a variety of targets.

**Keywords:** Trace element analysis; glass; mineral; laser ablation inductively coupled plasma mass spectrometry; solution inductively coupled plasma mass spectrometry; proton microprobe analysis; electron microprobe analysis

Integrated microbeam and bulk geochemical analyses of solids for their elemental and isotopic compositions can provide fundamental information to help solve diverse geological, environmental and industrial problems. Electron microprobe analysis is a mainstay technique for the determination of major and minor element compositions of minerals and glasses.<sup>1</sup> Proton microprobes,<sup>2–4</sup> ion microprobes<sup>5</sup> and laser ablation or glow discharge samplers coupled to ICP ionization sources and quadrupole or time-of-flight mass spectrometers<sup>6–9</sup> have been used for *in situ* trace element and isotopic analyses of solids. *In situ* microanalysis of solids provides several advantages over bulk analyses, including minimal sample preparation, low blanks and the ability to analyse very small (sub-mm) samples. Microbeam techniques also provide information on the spatial distribution of compositional characteristics and

can provide more accurate analyses than bulk methods by avoiding microscopic inclusions of foreign material.

Laser ablation ICP-MS is a relatively new microbeam technique that is rapidly gaining attention as a useful method for *in situ* microanalysis of solids because of the spatial resolution (10–100  $\mu\text{m}$ ), sub-ppm detection limits and rapid analysis times (typically  $\leq 5$  min per point analysis) that can be achieved. In addition, matrix effects are often trivial for a wide variety of target materials, allowing straightforward calibration of the analyses. These characteristics make laser ablation ICP-MS a versatile and cost-effective analytical tool for the determination of trace element abundances in solids. Applications of the technique are increasing, especially for geological studies such as those involving mineral exploration, isotopic age determinations and geochemical investigations of melting and mass transport in natural and experimental systems.

A laser ICP-MS microprobe was installed at Macquarie University in December 1994 and has been applied to several diverse geochemical and industrial problems, including the analysis of impact glasses to determine the composition of the continental crust,<sup>10</sup> the magmatic evolution of hotspot volcanoes<sup>11</sup> and investigations of the large-scale structure and evolution of the continental and oceanic lithosphere.<sup>12–14</sup> For this study, two silicate glasses were analysed by laser ablation ICP-MS, solution ICP-MS, electron microprobe analysis and proton microprobe analysis for their major and trace element abundances. One of these glasses (BCR-2G) is a standard prepared from Columbia River basalt by the US Geological Survey specifically for calibration of microbeam analyses. The other (I-102) is a natural glass tektite produced by a large meteorite impact into the continental crust of SE Asia. Both of these glasses contain trace element concentrations typical of those found in upper crustal rocks. This paper also compares laser ablation ICP-MS, electron microprobe, proton microprobe and thermal ionization isotope dilution MS data for a variety of silicate minerals, including pyroxenes, olivines, garnets, amphiboles and apatites. The results show excellent agreement among all of the techniques for concentrations extending over 3.5 orders of magnitude and demonstrate a close inter-calibration between the microbeam and bulk geochemical methods. This study emphasizes the capability of laser ablation ICP-MS to produce quantitative trace element abundance data for a wide variety of targets and element concentrations, with an analytical precision and accuracy comparable to that of other microbeam and bulk chemical methods.

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## EXPERIMENTAL

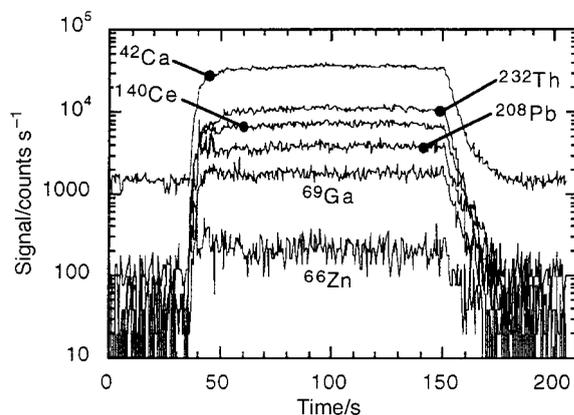
### Instrumentation and operating conditions

All analyses were conducted at Macquarie University except for the proton microprobe analyses which were carried out at the CSIRO Heavy Ion Analytical Facility.<sup>2-4</sup> The solution ICP-MS analyses were obtained using a Perkin-Elmer SCIEX Elan 6000. Data were collected by peak hopping, using 50 sweeps of the mass range per replicate, three replicates and a dwell time of 30 ms per mass. Prior to each session, rf power and ion lens voltage were optimized to maximum intensity on 10 ppb Rh in 2% HNO<sub>3</sub> and the nebulizer gas flow was adjusted so that CeO/Ce was <3%. Doubly charged ion production as measured by Ba<sup>2+</sup>/Ba<sup>+</sup> was ≤2%. Samples were introduced into the plasma *via* a cross-flow nebulizer and a Scott double pass spray chamber. The instrument was equipped with Ni sampler and skimmer cones and was operated in dual detector mode with the autolens on.

The laser ablation ICP-MS analyses were performed using a Perkin-Elmer Elan 5100 instrument coupled to a laser ablation microprobe as described below. Our standard operating conditions for laser ablation ICP-MS analyses have been described previously.<sup>7</sup> Briefly, the procedure involves focusing a UV laser beam onto the surface of a solid sample and using the ICP-MS instrument to determine trace element concentrations in the ablated material. Data were collected by peak hopping, using dwell times of 50–100 ms per mass to optimize instrument counting efficiency, one sweep of the mass range per replicate and 100–120 replicates per analysis, including 30–40 replicates on the dry gas to establish the background prior to ablation. Total analysis time was ≈5 min per spot, including backgrounds and washout of the sample prior to the next analysis. Data were collected in time-resolved graphics mode to monitor possible compositional heterogeneities that might be present in the sample at the scale of the laser sampling and to monitor the inter-element fractionation that can occur during a laser ablation analysis.<sup>6,7</sup> These counting parameters differ significantly from those used for the solution analyses, where the sample is presumed to be homogeneous and introduced at a steady-state without fractionation. Compared with solution analyses, oxide production is less efficient in the dry plasma used for laser ablation ICP-MS; it is minimized through adjustment of the nebulizer flow rates and forward power so that ThO/Th is <1%. Other potentially interfering oxides are then assumed to be negligible based on the relative efficiency of ThO production.<sup>15</sup> Platinum sampler and skimmer cones were used for all of these analyses.

The laser microprobe incorporates a Q-switched Nd:YAG laser with a fundamental wavelength in the infrared (1064 nm). This primary beam is converted to visible (532 nm) and UV (266 nm) wavelengths by two frequency doubling crystals.<sup>6</sup> UV light was used exclusively for the analyses reported here. Standards and samples were ablated using pulse rates of 4 Hz and beam energies of 1–2 mJ per pulse. Although laser ablation analyses are often considered to produce transient signals, these operating conditions produce a near-steady-state signal for up to 4 min (provided that the sample is sufficiently thick) with minimal inter-element fractionation during the analysis<sup>7</sup> (Fig. 1). Spot diameters are typically 30–50 μm and average drill rates are about 1 μm s<sup>-1</sup>, resulting in the consumption of ≤1 μg of material for a typical silicate.

The electron microprobe analyses were conducted using a Cameca SX-50 instrument equipped with five wavelength-dispersive crystal spectrometers and operated at an accelerating voltage of 15 kV and a beam current of 10 nA. Analyses of the glasses used a 10 μm diameter defocused beam to minimize Na loss; mineral analyses used a fully focused beam. Count times on peaks were 20–40 s for Si, Al, Fe, Mg, Ca, Na and K and 30–60 s for Ti and Mn; backgrounds were counted on



**Fig. 1** Typical laser ablation ICP-MS traces obtained on the NIST SRM 612 Glass. Backgrounds on the dry gas were counted for about 40 s prior to beginning ablation. The laser was turned off after 150 s allowing washout of the sample. The laser was operated at a 4 Hz repetition rate and 1 mJ per pulse. Note the steady-state signal that is produced under these conditions and the lack of inter-element fractionation during the run.

both the high and low wavelength sides of each peak for a total of 30 s. The proton microprobe analyses were obtained using a focused 30 μm diameter beam of 3 MeV protons. Beam intensities were measured indirectly from secondary-electron current and analyses were normalized to electron microprobe data for Fe, to compensate for any charge loss.

### Sample preparation

One of the glasses analysed for this study (BCR-2G) is basaltic in composition (Table 1) and was prepared and distributed by the US Geological Survey as a standard for microbeam analyses, including laser ablation ICP-MS (sample obtained from Dr. S. Wilson, US Geological Survey, Denver, CO, USA). According to notes distributed with the sample, the glass was prepared by fusing ≈1.5 kg of powdered basalt in a platinum crucible at 1350 °C and then quenching the melt by pouring it onto a platinum sheet. The other glass that was analysed (I-102) is a natural tektite obtained from Professor S. Ross Taylor of The Australian National University. This tektite is classified as an indochinite and it formed 0.8 million years ago by a meteorite impact into sediments comprising the upper continental crust of south east Asia.<sup>16</sup> As expected for a glass produced from upper crustal sediments, it is rich in SiO<sub>2</sub> and has a broadly granitic bulk composition (Table 1). Trace element data for this tektite by spark source mass spectrometry are given by Taylor and McLennan.<sup>17</sup>

**Table 1** Major element compositions of glasses BCR-2G and I-102 by electron microprobe analysis. Data in wt%, average of *n* points. FeO\* represents total Fe reported as FeO

	BCR-2G	1σ	I-102	1σ
SiO <sub>2</sub>	54.38	0.02	73.4	0.2
TiO <sub>2</sub>	2.28	0.04	0.80	0.01
Al <sub>2</sub> O <sub>3</sub>	13.6	0.1	13.0	0.1
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.01	0.01	0.01
FeO*	12.5	0.2	4.69	0.06
MnO	0.20	0.03	0.09	0.02
MgO	3.50	0.04	1.98	0.02
CaO	7.12	0.07	2.00	0.03
Na <sub>2</sub> O	3.15	0.07	1.24	0.03
K <sub>2</sub> O	1.79	0.04	2.53	0.03
P <sub>2</sub> O <sub>5</sub>	0.37	0.04		
NiO	0.01	0.01	0.01	0.01
Sum	98.87		99.67	
<i>n</i>	120		105	

For the solution ICP-MS analyses, small slabs of each glass (BCR-2G and I-102) were cut using a microsaw equipped with a diamond-embedded copper blade. Each sample was leached for  $\approx 20$  min in cold concentrated HCl in an ultrasonic bath, rinsed several times with ultrapure water and crushed with an agate mortar and pestle. A 0.1 g amount of each sample was weighed in duplicate into screw-top Teflon beakers and attacked with 2 ml of 1+1 distilled concentrated HF-HNO<sub>3</sub>. After drying on a hot-plate at 150 °C, the samples were allowed to reflux overnight in concentrated HF-HNO<sub>3</sub>, dried and refluxed again in 2 ml of distilled concentrated HNO<sub>3</sub>. Samples were then dried again and brought to a final volume of 100 ml with 2% HNO<sub>3</sub>. A 100 ppb concentration of Be and 10 ppb each of As, Rh, In, Tm, Re and Bi were added as internal standards and drift corrections for each analyte mass were applied by interpolating between the internal standards, except for Li which was normalized to Be, and Th and U which were normalized to Bi.

For the microbeam analyses (laser ablation ICP-MS, electron microprobe analysis and proton microprobe analysis), sample preparation consisted simply of mounting and polishing centimetre-size chips of each sample in 25 mm diameter epoxy mounts.

### Calibration

The solution ICP-MS analyses were calibrated against a single solution of the well characterized Hawaiian basalt standard BHVO-1 prepared identically to the unknowns, with the calibration forced through the origin. Calibration values for the analyte elements in BHVO-1 are those given by Eggins *et al.*<sup>18</sup> Calibration of solution ICP-MS analyses of geological materials against natural rock standards has the advantage of closely matching the matrix of the unknowns, which can significantly affect relative ionization efficiencies across the mass range in solution ICP-MS analyses.<sup>18</sup> Total procedural blanks were subtracted from each analysis.

For the laser ablation analyses, relative element sensitivities for each element were calibrated against the NIST SRM 610 glass using concentrations given by Norman *et al.*<sup>7</sup> with the addition of the following values: Ti 476 ppm, Cu 433 ppm, Zn 429 ppm, Mo 396 ppm, Pb 419 ppm. <sup>44</sup>Ca was measured with each analysis as an internal standard and the data were normalized to the CaO content of the sample as determined independently by electron microprobe analysis. The internal standard is used to correct for variations in the absolute amount of material ablated during each run. For each analysis, replicates representing the signal and background were selected graphically from the time-resolved spectra using off-line data reduction software and concentrations were calculated from the net count rate for each spot using eqn. (1). This assumes that the same isotope is used for both the sample and the calibration standard. Use of different isotopes for the sample and standard (*e.g.*, <sup>24</sup>Mg and <sup>25</sup>Mg) simply requires normalization for isotopic abundances.

$$c_{\text{sam}}^i = c_{\text{std}}^i \times (\text{cps}_{\text{sam}}^i / \text{cps}_{\text{std}}^i) \times [(\text{cps}_{\text{std}}^{is} / \text{cps}_{\text{sam}}^{is}) \times (c_{\text{sam}}^{is} / c_{\text{std}}^{is})] \quad (1)$$

where  $c_{\text{sam}}^i$  = concentration of analyte element  $i$  in the sample,  $c_{\text{std}}^i$  = concentration of analyte element  $i$  in the calibration standard,  $\text{cps}_{\text{sam}}^i$  = net count rate (peak minus background) of  $i$  in the sample,  $\text{cps}_{\text{std}}^i$  = net count rate of  $i$  in the calibration standard,  $\text{cps}_{\text{sam}}^{is}$  = net count rate of internal standard element  $is$  in the sample,  $\text{cps}_{\text{std}}^{is}$  = net count rate of  $is$  in the calibration standard,  $c_{\text{sam}}^{is}$  = concentration of  $is$  in the sample and  $c_{\text{std}}^{is}$  = concentration of  $is$  in the calibration standard.

Using these procedures, we have demonstrated an analytical precision of 2–5% relative ( $1\sigma$ ) for replicate laser ablation

ICP-MS analyses of the NIST SRMs 612 and 610 glass as unknowns and an accuracy of 1–2% for the average of these analyses relative to the calibration values.<sup>7</sup> These glasses have nominal concentrations of 35 and 450 ppm, respectively, for a variety of elements, making them especially useful for laser ablation ICP-MS calibration. Error analysis shows that counting statistics on the sample and the calibration standard and the external precision on the determination of the internal standard concentration account for the observed analytical uncertainties.<sup>7</sup> Detection limits for laser ablation ICP-MS analyses are a function of background levels, ICP-MS sensitivity (*i.e.*, counts ppm<sup>-1</sup>) and ablation rate. For the system used here, detection limits ranged from  $\leq 2$  ppm for low mass elements such as Ni to  $\leq 0.05$  ppm for higher mass elements such as Th, U, Ta and several of the REE.<sup>7</sup>

The electron microprobe analyses were calibrated against well characterized mineral standards and corrected for matrix compositions using the PAP procedure.<sup>19</sup> Proton microprobe data were obtained by deconvolution of the X-ray spectra using the GEO-PIXE software package, which provides standardless analysis by using the predictable nature of proton trajectories in solids to calculate X-ray yields directly.<sup>2–4</sup>

### RESULTS AND DISCUSSION

Table 1 presents the major element compositions of BCR-2G and I-102 determined by electron microprobe analysis. Tables 2 and 3 present trace element compositions of these glasses determined by solution ICP-MS, laser ablation ICP-MS and proton microprobe analysis. The solution ICP-MS data represent averages of all analyses of the duplicate solutions prepared for each sample. For BCR-2G, each solution was analysed three times ( $n=6$ ) and for I-102 each solution was analysed twice ( $n=4$ ). The  $1\sigma$  standard deviations of the six analyses of the two BCR-2G solutions are  $<5\%$  for all elements and  $\leq 2\%$  for most elements with  $Z \geq 85$  (*i.e.*, Rb to U). Solutions of the tektite I-102 show comparable agreement for most elements, although some elements are more variable, notably Ni, Zn, Ga, Pb and U. Mo shows a relatively large percentage deviation (12.8%), but the absolute value of both the Mo concentration and the standard deviation of these analyses is small ( $0.14 \pm 0.02$  ppm). The variability in the I-102 analyses appears to reflect sample heterogeneity on the 0.1 g scale in this impact-produced glass rather than instrumental error, because each of the duplicate solutions gave self-consistent results in separate runs, with the large standard deviations for these elements reflecting slight but measurable differences in composition between the two solutions. For example, one solution of I-102 gave  $1.27 \pm 0.01$  ppm Pb while the other gave  $0.88 \pm 0.01$  ppm Pb (averaging  $1.08 \pm 0.23$  ppm Pb; Table 2). Heterogeneous distribution of small grains of a sulfide phase and/or incompletely dissolved grains of refractory minerals such as zircon might account for the observed variability between the two splits of I-102. BCR-2G appears to be homogeneous at the 0.1 g scale for all of the elements determined here.

The composition of BCR-2G determined by laser ablation ICP-MS represents the average of 44 separate determinations by two different operators (M. D. N. and M. O. G.) for all elements except for Rb, Dy, Pb ( $n=38$ ), Zn ( $n=25$ ), Cs ( $n=20$ ) and Ti, Cu, Ga, Mo, ( $n=10$ ). These data were collected in five different sessions over a period of about 2 years. The  $1\sigma$  standard deviations of these analyses range from 2–8% relative (Table 2). The composition of I-102 determined by laser microprobe analysis represents an average of 23 separate determinations by one operator (M. D. N.) over a period of about 2 months.  $1\sigma$  standard deviations of these analyses range from 2–6% for all elements except for Ni (9%) and U (12.5%) (Table 3). As discussed above, some of this variability may

**Table 2** Comparison of solution ICP-MS, laser ablation (LA) ICP-MS and proton microprobe (PIXE) analyses of glass standard BCR-2G. All data in ppm, except for K and Ti in wt%. NA = Not analysed

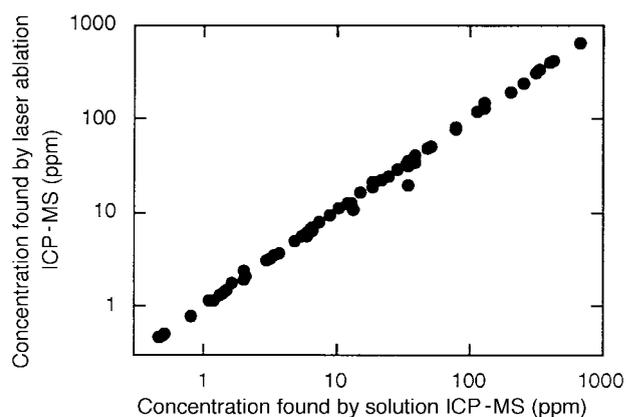
	Solution ICP-MS	1 $\sigma$	RSD (%)	LA-ICP-MS	1 $\sigma$	RSD (%)	LA-ICP-MS/ solution ICP-MS	PIXE	1 $\sigma$	RSD (%)
Li	9.6	0.5	4.9	NA						
K	1.49	63	0.4	1.49*			1.00			
Sc	33.5	0.4	1.2	33.0	0.8	2.3	0.99			
Ti	1.38	200	1.4	1.37	0.03	2.2	0.99			
V	429	7	1.7	414	8	2.0	0.97			
Co	38.0	1.0	2.6	35.8	1.3	3.6	0.94			
Ni	13.3	0.3	2.4	10.8	0.7	6.6	0.81	15	5	33.3
Cu	34.1	1.2	3.4	19.4	1.0	5.3	0.57	16.5	0.8	4.8
Zn	129	4	3.0	147	12	8.4	1.13	137	1	0.7
Ga	21.9	0.5	2.4	22.7	0.9	3.9	1.04	23.7	0.6	2.5
Rb	48.1	0.9	1.9	49	2	3.3	1.02	48	1	2.1
Sr	335	7	2.1	342	6	1.8	1.02	352	6	1.7
Y	39.4	0.8	1.9	35.3	0.7	2.1	0.89	32	1	3.1
Zr	201	2	1.2	194	4	2.1	0.97	192	4	2.1
Nb	13.1	0.1	0.8	12.8	0.4	3.0	0.98	11.3	0.8	7.1
Mo	255	4	1.6	244	7	2.9	0.96	268	3	1.1
Cs	1.18	0.01	0.8	1.13	0.08	6.7	0.96			
Ba	672	5	0.7	660	19	2.9	0.98	647	23	3.6
La	24.4	0.2	0.7	24.5	0.7	3.0	1.00			
Ce	51.9	0.3	0.5	50.5	1.6	3.1	0.97			
Pr	6.48	0.05	0.8	6.8	0.3	4.1	1.05			
Nd	28.4	0.2	0.9	29.0	1.1	3.9	1.02			
Sm	6.58	0.08	1.2	6.6	0.4	6.1	1.00			
Eu	1.98	0.02	1.3	1.92	0.12	6.4	0.97			
Gd	6.67	0.04	0.6	6.5	0.4	6.8	0.97			
Tb	1.06	0.02	1.9	NA						
Dy	6.33	0.07	1.1	6.5	0.4	5.8	1.03			
Ho	1.32	0.01	0.9	1.31	0.08	6.3	0.99			
Er	3.73	0.04	1.0	3.6	0.2	6.8	0.97			
Yb	3.34	0.04	1.1	3.5	0.2	7.0	1.04			
Lu	0.50	0.01	2.0	0.51	0.03	6.7	1.02			
Hf	4.90	0.05	1.0	5.0	0.3	6.5	1.02			
Ta	0.81	0.01	0.6	0.78	0.05	6.9	0.96			
Pb	10.3	0.2	2.1	11.5	0.6	4.8	1.12			
Th	6.03	0.08	1.4	6.1	0.3	5.0	1.01			
U	1.62	0.03	2.0	1.73	0.09	5.2	1.08			

\* Data from Table 1.

represent natural heterogeneity in this glass. These data represent a significant improvement over previous laser ablation ICP-MS studies of natural volcanic glasses which have reported an accuracy of <15% and a precision of 5–20%.<sup>20</sup> The proton microprobe data for BCR-2G represent summed spectra for ten replicate spot analyses.

Overall, the solution and laser ablation ICP-MS analyses of both glasses agree well, to  $\leq 5\%$  for most elements, which is well within the combined analytical uncertainties of both methods (Fig. 2; Tables 2 and 3). Larger deviations occur for some elements, notably Ni, Cu, Zn and Pb in BCR-2G (Table 2). Cu in this sample displays the greatest discrepancy between the laser and solution ICP-MS analyses observed in this study and may be reflecting either a  $^{48}\text{TiOH}$  interference on the  $^{65}\text{Cu}$  mass used for the solution analyses ( $^{63}\text{Cu}$  was used for the laser ICP-MS analyses), a solution blank problem or contamination from the saw blade used to slice the sample. Ni, Cu, Zn and Pb are also subject to possible fractionation during the laser ablation analyses<sup>6,7</sup> although we saw no obvious signs of this during the runs reported here. Ni, Cu and Zn suffer from relatively poor sensitivity by ICP-MS in general and are subject to interferences from the rock matrix and polyatomic gas species, resulting in relatively high detection limits for these elements (e.g.,  $\leq 2$  ppm for Ni by laser ablation ICP-MS<sup>7</sup>). This is reflected in Fig. 3 by the larger deviations from the 1:1 correlation line at low Ni concentrations.

Other discrepancies between the solution and laser ablation ICP-MS analyses may be ascribed to sample heterogeneity for



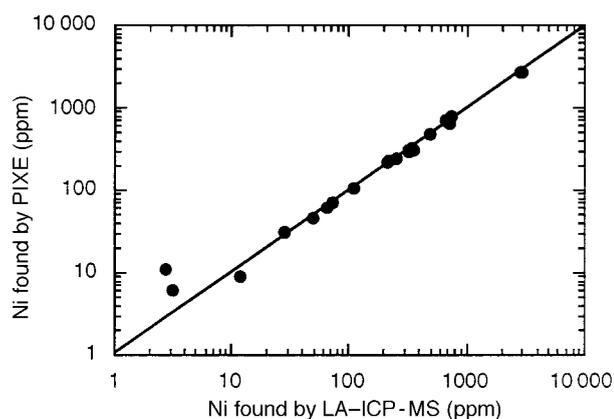
**Fig. 2** Comparison of trace element concentrations of the BCR-2G and I-102 silicate glasses determined by laser ablation ICP-MS and solution ICP-MS. The size of the points corresponds to a relative error of  $\approx 10\%$ . Data from Tables 2 and 3.

I-102, or to systematic differences in the values adopted for the calibration standards used for the solution *versus* laser ablation ICP-MS analyses. For example, compared with the solution data, Y by laser ICP-MS appears to be systematically lower by about 7–9% and U appears to be systematically higher by 10–20% (Tables 2 and 3). Systematic variations such as these suggest that the calibration values for these

**Table 3** Comparison of solution ICP-MS and laser ablation (LA) ICP-MS analyses of glass tektite I-102. All data in ppm, except for K and Ti in wt%. NA=Not analysed

	Solution ICP-MS	1 $\sigma$	RSD (%)	LA-ICP-MS	1 $\sigma$	RSD (%)	LA-ICP-MS/ solution ICP-MS
Li	49.6	0.8	1.6	NA			
K	2.08	0.03	1.5	2.11*			1.01
Sc	12.3	0.1	1.1	12.9	0.6	4.9	1.05
Ti	0.49	0.01	1.7	0.48*			0.98
V	79	3	3.5	79	3	4.2	1.00
Co	12.6	0.5	3.7	12.4	0.5	4.4	0.98
Ni	19	3	13.4	21	2	9.2	1.12
Cu	8.7	0.1	1.1	NA			
Zn	9.1	0.9	9.6	NA			
Ga	4.2	0.5	13.2	NA			
Rb	115	2	1.7	122	4	3.0	1.06
Sr	131	1	0.2	133	3	1.9	1.02
Y	34.3	0.1	0.3	31.1	0.6	2.0	0.91
Zr	309	1	0.2	309	7	2.1	1.00
Nb	19.0	0.1	0.3	19.3	0.4	2.3	1.02
Mo	0.14	0.02	12.8	NA			
Cs	6.5	0.2	2.6	6.7	0.3	3.8	1.04
Ba	400	2	0.5	404	10	2.5	1.01
La	39.0	0.2	0.4	41.4	0.9	2.1	1.06
Ce	79.0	0.5	0.6	83.4	1.6	1.9	1.06
Pr	8.87	0.03	0.3	9.5	0.2	2.0	1.07
Nd	34.0	0.2	0.6	35.5	0.8	2.2	1.04
Sm	6.67	0.03	0.4	6.9	0.3	4.8	1.03
Eu	1.29	0.01	0.6	1.31	0.06	4.4	1.01
Gd	5.99	0.02	0.4	5.7	0.3	5.8	0.96
Tb	0.94	0.01	1.1	NA			
Dy	5.44	0.02	0.4	5.6	0.2	4.3	1.02
Ho	1.10	0.01	0.5	1.12	0.04	3.3	1.02
Er	3.16	0.01	0.4	3.2	0.2	6.2	1.01
Yb	2.97	0.01	0.4	3.1	0.2	6.4	1.06
Lu	0.46	0.01	2.2	0.47	0.02	5.0	1.03
Hf	7.52	0.02	0.2	8.0	0.3	4.2	1.06
Ta	1.43	0.01	0.7	1.40	0.05	3.3	0.98
Pb	1.08	0.23	21.4	NA			
Th	15.2	0.1	0.5	16.4	0.5	2.8	1.08
U	1.98	0.13	6.5	2.4	0.3	12.5	1.20

\* Data from Table 1.



**Fig. 3** Comparison of Ni abundances determined by laser ablation ICP-MS (LA-ICP-MS) and proton microprobe analysis (PIXE) for a variety of minerals, including pyroxenes, olivines, garnets, amphiboles and apatites.

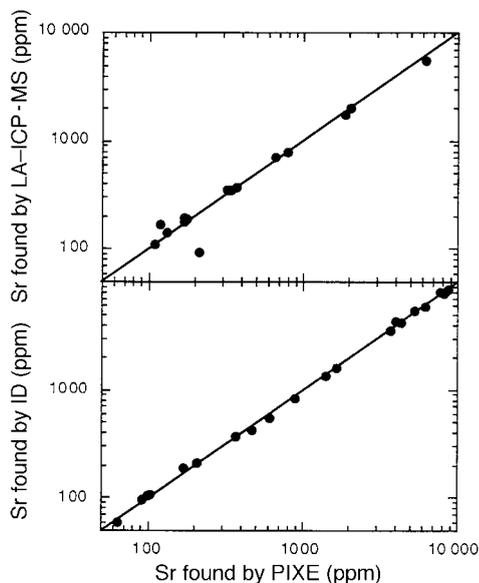
elements in the BHVO-1 and NIST SRM 610 standards may need further refinement.

A notable feature of BCR-2G is the high Mo concentration in this glass compared with the natural abundances in most basaltic rocks and this is confirmed by all of the methods (Table 2). According to the processing notes distributed with this standard, it is known that Mo was introduced during production of the BCR-2 rock powder from which the glass was prepared.

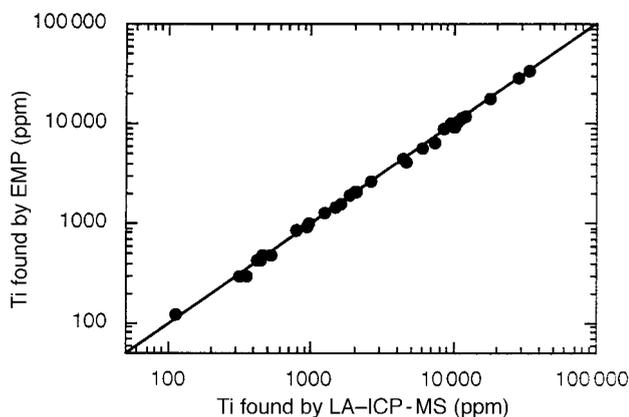
Ni, Sr and Ti abundances, determined by laser ablation ICP-MS, proton microprobe analysis and electron microprobe analysis, for a variety of minerals including pyroxenes, olivines, garnets, amphiboles and apatites are compared in Figs. 3–5 based on data compiled from the literature<sup>7,13,14,21</sup> and from our unpublished data. Fig. 4 also compares Sr data obtained by proton microprobe analysis and thermal ionization isotope dilution MS for various minerals, compiled from the same sources. For Ti, the laser ICP-MS and electron microprobe data show excellent agreement over concentrations ranging from 100 to 30000 ppm (Fig. 5), with a mean difference of 1.5% relative between the values obtained by the two techniques. Ni and Sr abundances determined by laser ablation ICP-MS and proton microprobe analysis also show good agreement over large ranges of concentration (Figs. 3 and 4), as do Ga, Zr and Y (not shown). The mean difference between the values obtained by laser and proton microprobe analysis is 4.6% for Sr and 5.1% for Ni. Sr abundances determined by isotope dilution MS over more than two orders of magnitude (Fig. 4), providing a link to absolute abundances determined by gravimetric calibration of the isotope spike. K abundances in BCR-2G and I-102 determined by solution ICP-MS also agree well with those determined for these glasses by electron microprobe analysis.

## CONCLUSIONS

Trace element analyses of a variety of silicate minerals and glasses by laser ablation ICP-MS, solution ICP-MS, electron



**Fig. 4** Comparison of Sr abundances determined by laser ablation ICP-MS (LA-ICP-MS), proton microprobe analysis (PIXE) and thermal ionization isotope dilution mass spectrometry (ID) for a variety of minerals, including pyroxenes, olivines, garnets, amphiboles and apatites.



**Fig. 5** Comparison of Ti abundances determined by laser ablation ICP-MS (LA-ICP-MS) and electron microprobe analysis (EMP) for a variety of silicate minerals, including pyroxenes, olivines, garnets and amphiboles.

microprobe analysis and proton microprobe analysis agree well with one another for concentrations ranging over several orders of magnitude. These data demonstrate a high degree of cross-calibration among the laboratories involved in this study and show that matrix effects for laser ablation ICP-MS analyses of silicates are not a serious problem. The precision of the laser ablation ICP-MS analyses is comparable to that of other standard geochemical methods. This study emphasizes the utility of laser ablation ICP-MS as a robust, quantitative microbeam technique capable of the rapid and precise determi-

nation of trace element abundances at the sub-ppm level in a variety of targets.

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