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The INTAV intercomparison of electron-beam microanalysis of glass by tephrochronology laboratories, results and recommendations

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Abstract

The INternational focus group on Tephrochronology And Volcanism (INTAV) of the International Union for Quaternary Research (INQUA) has conducted an intercomparison of tephrochronology laboratories with electron-beam microanalytical data on volcanic glasses submitted from 27 instruments at 24 institutions in 9 nations. This assessment includes most active tephrochronology laboratories and represents the largest intercomparison exercise yet conducted by the tephrochronology community. The intercomparison was motivated by the desire to assess the quality of data currently being produced and to stimulate improvements in analytical protocols and data reporting that will increase the efficacy of tephra fingerprinting and correlation. Participating laboratories were each supplied with a mount containing three samples for analysis: (1) rhyolitic Lipari obsidian ID3506, (2) phonolitic Sheep Track tephra from Mt. Edziza, British Columbia, Canada, and (3) basaltic Laki 1783 A.D. tephra. A fourth sample, rhyolitic Old Crow tephra, was also distributed.

Most laboratories submitted extensive details of their analytical procedures in addition to their analytical results. Most used some combination of defocused or rastered beam and modest beam current to reduce alkali element migration. Approximately two-thirds reported that they routinely analyze one or more secondary standards to evaluate data quality and instrument performance. Despite substantial variety in procedures and calibration standards, most mean concentrations compare favorably between laboratories and with other data. Typically, four or fewer data contributions had means for a given element on a given sample that differed by more than +/- 2 standard deviations from the overall means. Obtaining accurate Na_2O concentrations for the phonolitic tephra proved to be a challenge for many laboratories. Only one-half of the data sets had means within +/- 1 standard deviation of the ~8.2 wt% Na_2O value obtained by other methods. One mean is higher and 14 are lower. Three of the data set means fall below 7 wt% Na_2O. Most submissions had relative precision better than 1-5% for the major elements. For low-abundance elements, the precision varied substantially with relative standard deviations as small as 10% and as large as 110%. Because of the strong response to this project, the tephrochronology community now has a large comparative data set derived from common reference materials that will facilitate improvements in accuracy and precision and which can enable improved use of published data produced by the participating laboratories. Finally, recommendations are provided for improving accuracy, precision, and reporting of electron-beam microanalytical data from glasses.

Key Words: Electron microprobe, tephrochronology, geochemistry, microanalysis, volcanic glass, reference materials

In memoriam: This paper is dedicated to the memory of Dr Peter G. Hill, who helped numerous tephrochronologists over many years with his analytical skills, especially using the electron microprobe, and with his selfless personal support. Dr. Hill also co-led two previous intercomparisons which helped to inspire this work.

1. Introduction

Large, explosive volcanic eruptions disperse fine tephra hundreds to thousands of kilometers from their source, where they are rapidly deposited across widely distributed depositional systems forming isochrons. Consequently, tephrochronology is a powerful tool for correlation and geochronology with diverse applications in, for example, archaeology, paleoclimatology, paleolimnology, geomorphology, neotectonics, and volcanology. In addition, tephrochronology potentially offers chronostratigraphic precision that is unsurpassed by other geochronological techniques (Sarna-Wojcicki and Davis, 1991; Shane, 2000; Turney and Lowe, 2001; Lowe, 2011). Realizing this great promise, however, requires that individual tephra beds can be distinguished and identified with confidence.

For fingerprinting individual tephra beds and sparse cryptotephras, tephrochronology relies heavily upon the chemical characterization of individual volcanic glass shards by electron-beam (E-beam) methods: electron probe microanalysis (EPMA) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) (e.g. Smith and Westgate, 1969; Westgate & Gorton, 1981; Sarna-Wojcicki and Davis, 1991; Shane, 2000; Lowe, 2011). Similar methods are also widely used to characterize melt inclusions for petrologic studies (e.g. Rutherford et al., 1985; Thordarson and Self, 1996; Belkin et al., 1998; Frezzotti, 2001) and to characterize obsidians for archaeological studies (Merrick and Brown, 1984; Tykot, 2002). Microanalysis of individual glass shards for tephra fingerprinting has multiple advantages compared to analyses of bulk tephra and mineral grains (Smith and Westgate, 1969; Westgate and Gorton, 1981; Froggatt, 1992; Shane, 2000; Hunt and Hill, 2001). First, grain-discrete methods are necessary because (1) bulk samples may vary in composition with distance from the vent due to differential settling of phenocrysts and glass shards, (2) xenocrysts and detrital contaminants may be incorporated into tephra deposits, and (3) bulk analyses fail to distinguish multiple populations and other variations in the glass compositions. Second, glass compositions are potentially more distinctive than mineral compositions because (1) glass compositions are not limited by crystalline structures or stochiometry and (2) glasses, which represent the melt fraction of erupted magmas, are strongly influenced by fractional crystallization which can produce compositional differences between eruptions.

As compositional differences between glass shards from different eruptions can sometimes be subtle (e.g. Stokes and Lowe, 1988; Larsen and Eiriksson, 2007; Westgate et al. 2008; Kuehn et al. 2009), high levels of precision, accuracy, long-term intra-laboratory reproducibility, and inter-laboratory reproducibility are required for reliable identification of discrete tephras. Often, the use of published data is also complicated by small differences between results produced by different laboratories. Analyses of common reference materials are necessary to quantify these differences and thereby provide for more robust tephra correlations.

Among the many analytical challenges which must be overcome to obtain data of sufficient quality and a major focus of this intercomparison, is the phenomenon of alkali element migration (also known as “sodium-loss”) which affects Na-bearing silicate glasses and some minerals. It appears as an approximately exponential and irreversible decline in Na X-ray count rates with time during exposure to the electron beam (e.g. Lineweaver, 1962; Froggatt, 1992; Nielsen and Sigurdsson, 1981; Hunt and Hill, 1993, 2001; Morgan and

London, 2005). As the Na count rate declines, Si and Al X-ray count rates increase to a lesser degree. Other elements are affected relatively little. This phenomenon involves a physical migration of Na atoms out of the excitation volume (Lineweaver, 1962; Humphreys et al., 2006), that portion of the sample that is penetrated by the electron beam during analysis. Much of the “lost” Na is deposited deeper in the sample, below the excitation volume (Humphreys et al., 2006). Potassium may also migrate, but much more slowly. Silicon and Al atoms do not migrate, but their count rates are affected by the changing matrix composition.

The rate of alkali element migration is strongly affected by both analytical conditions and sample composition (Nielsen and Sigurdsson, 1981; Hunt and Hill, 2001; Morgan and London, 2005). Rhyolitic and phonolitic glasses, especially those that are secondarily hydrated (Shane, 2000), are much more strongly affected than basaltic glasses. Strategies for dealing with alkali element migration include lower beam currents and larger beam diameters (i.e. lower current densities), shorter analysis times, cryogenic temperatures, and explicitly measuring and correcting for the time-varying X-ray intensities.

Other analytical challenges include fine tephra grain sizes and highly inflated pumice which often limit the maximum beam diameter; the presence of microcrysts and microlites; secondary hydration of glasses (occurs in most tephra glasses older than ~200 years in temperate environments) resulting in variable analytical totals; and glass heterogeneity in some deposits which requires a large number of analyses to adequately characterize.

The objectives of the intercomparison are to :

(1) assess what the tephrochronology community is doing analytically, similar to surveys that the radiocarbon and geochemistry communities do regularly (e.g. Scott, 2003; Webb et al., 2009). Interlaboratory testing is one of the most effective ways for an individual laboratory to evaluate its performance against both its own expectations and the standards of performance set by other laboratories. Such testing provides a widely-used external form of quality control that helps to highlight reliable results as well as measurements that may be subject to unsuspected bias (Potts et al., 2002; Yip and Tong, 2009).

(2) distribute widely a uniform set of reference samples that will remain useful long after completion of the intercomparison. These samples may be routinely analyzed as secondary standards and the results reported together with unknowns in future publications. As published reference data on common samples accumulates, it will be possible to better compare data sets produced by different laboratories, reduce uncertainties, and make tephra correlations based on such data more robust.

(3) motivate improvements in analytical protocols that will enhance data quality and improve the efficacy of tephra fingerprinting and correlation. This directly addresses Objective 2 of the INTAV-led INTREPID project (enhancIng TephRochronology as a global research tool through improved fingErPrinting and correlation technIques and uncertainty moDeling): improved guidelines and protocols for compositional data acquisition and quality.

2. Reference Samples

As tephrochronology relies upon the characterization of natural materials, three homogeneous natural glasses were selected for inclusion in the intercomparison: (1) rhyolitic obsidian from Lipari Island, Italy, (2) phonolitic Sheep Track tephra from Mt. Edziza, British Columbia, Canada, and (3) basaltic tephra from the 1783 A.D. eruption of Laki volcano in Iceland. An additional sample, Old Crow tephra from Alaska, USA, was also distributed but not included in the intercomparison. These samples approximate the range of compositions typically found in tephra glasses and allow several elements to be compared across laboratories at both major- and minor-element concentrations. Samples were also selected to reveal inadequacies dealing with alkali element migration (Edziza) and inadequacies in dealing with microcrysts (Laki). Microcrysts and microlites are especially common in basaltic and andesitic glasses due to the relatively rapid nucleation and growth of crystals in low-viscosity melts (Szramek et al., 2010). Also included is one fine-grained sample (Edziza), which requires an electron beam diameter of no more than 10 μm to 15 μm.

2.1 Rhyolitic obsidian from Lipari, Italy

Obsidian sample ID3506 from Lipari Island, Italy, was obtained from the collections of Harvard University. It is highly homogeneous (tested using the procedure of Marinenko and Leigh, 2004), has a very low microcryst content, and is separately being developed as a reference material (Kuehn et al., 2009). The ID3506 sample is compositionally indistinguishable at 1 standard deviation (Kuehn et al., 2009) from that used in two previous intercomparisons by Hunt and Hill (1996) and Hunt et al. (1998). This allows direct comparison to those earlier results. Lipari obsidians have also received decades of use as primary (calibration) or secondary standards in several laboratories (e.g. Smith and Westgate, 1969, Reed and Ware, 1975).

Of the three glasses used in the intercomparison, the Lipari obsidian is the best-characterized. Multiple X-ray fluorescence (XRF), inductively-coupled plasma mass spectrometry (ICP-MS), and wet chemical measurements are available. The latter include alkalis by both atomic absorption and flame photometry. Also available are data from inductively-coupled plasma atomic (optical) emission spectrometry (ICP-AES) (Tables 1, S1, and S2). Additional bulk analyses by instrumental neutron activation (INAA) are in progress. Water content estimates from Fourier-transform infrared (FTIR) (S. Kuehn unpublished data) and from loss on ignition (LOI) for the XRF and ICP-AES analyses on the ID3506 sample average about 0.64 wt%.

2.2 Phonolitic Sheep Track tephra from Mt. Edziza, British Columbia, Canada

Samples of the late Holocene, phonolitic Sheep Track pumice erupted from the Mount Edziza volcanic complex in British Columbia, Canada (Souther, 1992; Lakeman et al., 2008) were provided by Jerry Osborn, University of Calgary. For the intercomparison, a high-purity glass separate (>99%) was prepared from a single 55 g proximal pumice clast. This clast was crushed using a rubber mallet, shattered in water using high-intensity ultrasound, wet sieved, and dried. The 75 to 150 μm size fraction was then purified using multiple passes on a

Frantz isodynamic magnetic separator followed by heavy liquids (a mixture of acetone and tetrabromoethane, TBE, with a density of ~2.4 g/ml). To obtain comparative analyses, not subject to the problem of alkali element migration, sub-samples of the glass separate were submitted to the Geoanalytical Laboratory at Washington State University for analysis by XRF (for methodology and validation see Johnson et al., 1998) and to the Geoanalytical Laboratory at Texas Tech University for analysis by ICP-AES (Tables 1, S1, and S2). One determination of LOI, 0.7 wt%, provides an estimated water content.

2.3 Basaltic Laki 1783 A.D. tephra from Iceland

Microcryst-bearing basaltic tephra from the 1783 A.D. eruption of Laki volcano was supplied by Thorvaldur Thordarson, University of Edinburgh. The sample was passed through a Frantz magnetic separator to remove the larger phenocrysts. Because of the significant microcryst content, this sample was not submitted for bulk analysis as the bulk composition may vary significantly from that of the matrix glass.

2.4 Additional sample: Old Crow tephra from Alaska, USA

Rhyolitic Old Crow tephra (OCt) from Alaska, USA was also distributed. This 124 ±10 ka tephra contains approximately 4 wt% H_2O, much of it the result of secondary hydration (Preece et al., 1999; Preece et al.,2011). The water content in Old Crow tephra demonstrates that low analytical totals do not necessarily indicate poor quality analyses. In contrast, water contents in younger and freshly erupted glasses are typically much lower (and analytical totals higher) because fresh tephra glasses represent largely degassed magma. OCt has been extensively analyzed for major and trace elements by EPMA, INAA, solution ICP-MS, laser-ablation ICP-MS, and secondary ion mass spectrometry (SIMS or ion microprobe) (e.g. Westgate et al., 1994; Preece et al., 2000; Kaufman et al., 2001; Begét and Keskinen, 2003; Pearce et al., 2004; Preece et al., 2011). It has also been used as a secondary standard in multiple laboratories for both major- and trace-element analysis. Splits of the same high-purity glass concentrate distributed to participants in the intercomparision has also been analyzed by XRF and ICP-AES (Tables 1, S1, and S2).

2.5 Quantification of alkali element migration in the reference glasses: Further defining the analytical challenge

To quantify the rate of alkali element migration under common analytical conditions, the Lipari, Edziza, and Old Crow glasses along with the basaltic Grimsvötn 2004 glass (which was tested as a candidate for the intercomparison before the Laki tephra sample was obtained) were studied on the Cameca SX-100 at the University of Alberta using conditions of 15 keV, 9 nA beam current, and 10 μm beam diameter. Results are illustrated in Fig. 1. As expected, the phonolitic Edziza glass poses the greatest analytical challenge as it is the most beam sensitive material with the greatest change in count rates. Instantaneous count rates for Na on Edziza tephra and the hydrated Old Crow tephra reach 50% of the initial count rate after a little more than 1 minute of exposure. Count rates on the Lipari sample are at 75% of the initial rate after the same amount of exposure. In contrast, count rates on the basaltic glass are relatively stable.

Because the Edziza glass has more than twice the Na content of the other glasses (Table 1), the magnitude of alkali element migration is greater than that of the other three samples. As a result, Edziza tephra displays the greatest increases in Al and Si count rates (Fig. 1). In the same time that the instantaneous Na count rates drop to 50% of initial on Edziza tephra, the Al and Si count rates are up nearly 5% and 4% respectively. This compares to increases of less than 2% on Old Crow, less than 1% on Lipari, and nearly constant count rates on Grimsvötn. Note that although the relative increase is greater for Al than Si, the absolute magnitude of the effect on the concentrations is greater for Si due to the greater SiO_2 content in the samples. Note also that thus far, this evaluation has assumed that the X-ray counting for all three elements begins shortly after beam exposure begins. Analyzing any of these as the second or subsequent element in the sequence increases the problem further. This is a common issue for EPMA facilities as many do not have spectrometer configurations capable of analyzing for Na, Al, and Si simultaneously.

For analytical procedures that do not explicitly measure and correct for time-varying X-ray intensities, it is the change in the cumulative count rate that matters as this is what ultimately leads to the reported concentrations. Cumulative count rates drop much more slowly than the instantaneous count rates (Fig. 1), and a quantification of these changes is useful for determining X-ray counting times that can produce data of sufficient accuracy. Using a 9 nA beam current and 10 μm beam diameter, analysis times for Na must be less than 10 s on Edziza and Old Crow and less than 20 s on Lipari to produce cumulative count rates that are 95% or more of initial count rates. To obtain Al and Si count rates that are inflated by no more than 2% and 1% respectively on the Edziza glass, analysis times under 40 s are required, assuming these are the first elements analyzed on their respective spectrometers. Obtaining count rates that are inflated by no more than 1% and 0.5% respectively requires analysis times under 20 s. Alternatively, lower currents and/or larger beam diameters may be used to allow for longer analysis times. Because SEM-EDS systems typically use much lower currents (e.g. ~1 nA) than is typical of EPMA, it is possible to use significantly longer count times with acceptable results provided that the beam is also rastered across a sufficiently large area (e.g. 5x5 or 10x10 μm). However, the goal of minimizing Na-loss may still impose some limitation on acceptable SEM-EDS analysis times thereby also limiting the obtainable precision on minor elements.

An approach that some laboratories use to deal with alkali element migration is standardizing for Na, Al, and Si (and perhaps K) on a rhyolitic glass (e.g. Lipari) so that migration during analyses of the standard compensates, at least in part, for migration in the unknowns. Essentially, a certain amount of Na-count-rate-decline as well as Al and Si gain is built into the standardization. This approach, however, assumes that all samples behave similarly to the calibration standards. Still, when combined with sufficiently short X-ray counting times and modest current densities (low current, defocused beam), this approach can be adequate on many glasses. Cumulative count rates for Na on the Lipari obsidian differ only modestly from the three other glasses for counting times close to 10 s or less (Fig. 1) when analyzed using a 9 nA current and 10 μm diameter beam. Cumulative count rates for Al and Si for the two rhyolites and the basalt also only diverge modestly for analysis times of several tens of seconds. Thus, when appropriate conditions are used, standardizing on a rhyolite like Lipari can compensate reasonably well for changes in Na, Al and Si count rates on other rhyolites and not inflate the Na concentrations or depress the Al and Si concentrations for basaltic compositions significantly. Aluminum and Si count rates on the phonolitic Edziza glass, diverge significantly from the others. Thus, the Edziza glass requires shorter count times and/or lower current densities than otherwise would be adequate.

The Edziza glass clearly poses a worst-case scenario as significantly longer count times and higher current densities can produce acceptable accuracy on the more commonly analyzed compositions represented by the other three samples. Consequently, if a laboratory can sufficiently minimize or correct for alkali element migration such that accurate results are obtained for Na, Al, and Si on the Edziza tephra, results are likely to be good for most tephra glasses. However, a laboratory that produces moderately low Na_2O concentrations on Edziza may still produce accurate data on less beam-sensitive samples.

3. Conducting the intercomparison

From conception to final reporting of results, this project has spanned approximately three years. In this time, it has also involved the efforts of more than forty individuals whose contributions of guidance, samples, data, and more made it possible to successfully achieve all major goals of the intercomparison.

3.1 Steering committee

S.C. Kuehn (Concord University, Athens, West Virginia, USA), D.G. Froese (University of Alberta, Edmonton, Alberta, Canada), S.M. Davies (University of Wales Swansea, Swansea, United Kingdom), B.V. Alloway (Victoria University of Wellington, Wellington, New Zealand), and P.A.R. Shane (University of Auckland, Auckland, New Zealand) with additional input from D.J. Lowe (University of Waikato, Hamilton, New Zealand).

3.2 Timeline

- Project development and selection of reference materials: Fall 2008 - Fall 2009
- Invitations and sample distribution: October - December 2009
- Deadline for initial data submissions: February 2010
- Compilation of results and submission of abstract for INTAV-Japan meeting: February 2010
- Distribution of preliminary report to participating laboratories: March 2010
- Presentation of results at INTAV-Japan meeting: May 2010
- Receipt of additional new and revised data submissions: until end of January 2011
- Final report submitted for publication: February 2011
- Revised manuscript submitted: August 2011

3.3 Website

http://www.env.auckland.ac.nz/uoa/intercomparison-of-tephrochronology-laboratories

3.4 Project development and operation

The INTAV interlaboratory comparison was inspired by earlier interlaboratory comparison projects for tephrochronology organized by John Hunt and Peter Hill (Hunt and Hill 1996; Hunt et al., 1998) and developed in part from a smaller intercomparison conducted for the Volcanism across the Arctic SysTem (VAST) collaboration. Experience with the latter aided in procedure development, reference material selection, and data evaluation. Protocols for data reporting were modeled largely after those of the ongoing G-Probe effort of the International Association of Geoanalysts (Potts et al., 2002).

A list of potential participants was developed from tephrochronology laboratories known to members of the steering committee as well as from a literature search for laboratories with an active publication record. Subsequently, an unpolished mount containing the four reference glasses was distributed to each of 29 institutions. Along with the samples, each institution received a printed packet describing the purpose and goals of the intercomparison, describing the protocols for analysis and data reporting, and including a copy of the data reporting form (see Supplemental materials).

Twenty-one institutions submitted 24 data sets (laboratory codes 1A through 23) from 23 instruments in time for inclusion in the INTAV-Japan abstract and preliminary report. Subsequently, a copy of the abstract, report, and a series of recommendations were distributed to the participants The participants were then invited to evaluate their submitted data in relation to the others, to make any necessary procedural changes, and submit revised data sets.

4. Results and Discussion

Results were received from 27 instruments at 24 institutions (Table 2). Twenty-one laboratories each submitted data from a single instrument. Of these, one submitted two sets of results based on the raw data but calculated using two different sets of calibration standards (designated 1A and 1B). Three laboratories each submitted data from two different instruments. One laboratory operated the same instrument under two different sets of conditions (laboratory numbers 26 and 27). Three laboratories submitted additional data based on revised procedures following distribution of the preliminary report. These revised submissions are designated by an “R” appended to the laboratory number. Four laboratories submitted their initial results following distribution of the preliminary report. These late-arriving new submissions are designated by an “n” appended to the laboratory number. This yields 28 laboratory numbers and 33 data sets from 27 instruments.

Mean concentrations with standard deviations are provided in Table 3 for each submitted data set. Complete analytical data and laboratory comments are available in Table S1. Most laboratories submitted procedural details including instrument type, analytical conditions, and software (Table 4); primary and secondary reference materials used (Table 5); spectrometer assignments and analytical sequence (Table 6); and peak and background analysis times (Table 7). In addition, a summary of spectrometer utilization (Table 8) was computed from the procedural data supplied by EPMA laboratories.

All 33 data sets include SiO_2, Al_2O_3, FeO_T, CaO, Na_2O, and K_2O (Tables 1 and 3). Thirty-two include TiO_2 and MgO. Thirty include MnO, 21 include Cl, and 16 include P_2O_5. Six data sets include F, four include BaO, and two include SO_2. ZrO_2, NiO, and directly-analyzed O are included in one data set each. Nineteen contributions also include data for the optional Old Crow tephra. Lab 28 supplied data on several well-characterized secondary standards that were analyzed together with the interlaboratory comparison samples (Table S3).

Of the 19 laboratories that analyzed for halogens, only 7 incorporated a correction for halogens=oxygen in their analytical totals. To remedy this, Tables 3 and S1 include a separate column providing halogen-corrected totals for all of the submissions, and Table 1 exclusively uses the halogen-corrected totals. Most laboratories used some combination of defocused or rastered beam and modest beam current to minimize alkali element migration (Table 4). Four laboratories (6, 13, 17, and 28) explicitly measured and corrected for changes in Na, Al, and Si X-ray intensities with time. Two laboratories included interference corrections, and two used multi-spectrometer analysis for specific elements to achieve better precision.

Procedures for removal of outliers varied. Most analysts checked their data manually for crystalline contaminants and very low totals. Others excluded all data with totals above or below a set value. At least one omitted all analyses for which a minor element (e.g. Ti) was not detected, and at least one used a form of cluster analysis to detect outliers. Some data sets include both positive and negative concentrations for minor elements whereas the data sets supplied by 15 other laboratories only include zero concentrations as their lowest values (Table S1). The former approach provides a more accurate representation of the analytical precision than the latter and therefore is preferable.

Reference materials used as primary calibration standards varied substantially and included a variety of glasses, silicate minerals, simple oxides, and other simple compounds (Table 5). Approximately two-thirds of the laboratories reported that they routinely analyze one or more secondary standards to evaluate data quality and instrument performance.

To compare the submitted compositional data, the individual oxide and element means and standard deviations were plotted by laboratory code (Figures 2 and S1). Nearly all of the submissions displayed good precision for the major elements. On the Lipari obsidian, for example, 85% of the contributions have relative precision better than 2% for SiO_2, 91% have relative precision better than 5% for Al_2O_3, and 70% have relative precision better than 5% for K_2O. For low-abundance elements such as Ti and Mg in the obsidian, the precision varied substantially with single relative standard deviations as small as 10% and as large as 110% of the reported concentrations (Figures 2 and S1, Table 3). As expected, EPMA laboratories tended to have better precision for minor elements than did SEM-EDS laboratories. Several laboratories reported mean analytical totals greater than 100% on one or more samples. This is particularly noticeable for the Edziza glass for which 5 of the contributions had mean totals exceeding 100.5% (Figure 2). Such consistent high totals indicate the presence of systematic error in the analyses. It should also be noted that there appears to be no systematic correlation between the reported concentrations and the matrix correction algorithms or software used. Therefore, the use of any of the common algorithms can produce data which is comparable to that produced by another laboratory, provided other analytical problems are absent.

The individual laboratory means were also used to calculate an overall mean concentration for each oxide or element on each sample along with related standard deviations and median values (Tables 1 and S1). To screen for outliers, z-scores were calculated in the same way as Potts et al. (2002) and Jochum et al. (2011) using a modified Horwitz function and an 'applied geochemistry' standard of performance (Table S2). This, however, results in the rejection of excessively large numbers of analyses, particularly for minor elements. On the Lipari obsidian, for example, approximately 80% of the MnO and MgO concentrations are rejected by this approach as they are more than 2 Horwitz-based target standard deviations from the overall median values (Table S2). Instead, we have used the overall standard deviations from the compiled results (Table 1) and rejected those laboratory mean concentrations which are more than +/- 2 standard deviations from the overall medians. This is less stringent than the +/- 1 standard deviation criterion used by Pearce et al. (1997) for NIST SRM 610 and 612 glass data. Typically 4 or fewer outliers were identified in this way for a given element on a given sample (Tables 1, 3, and S1). Thus, in most cases, 85% or more of the contributions were concordant under these criteria (Tables 1 and S1). Using the accepted data from this procedure, we have calculated preferred means and medians along with standard deviations (Tables 1 and S1). The preferred medians and their +/- 1 standard deviation ranges are indicated by horizontal gray bars in Figures 2 and S1. The resulting sets of mean and median concentrations are generally very close suggesting that the contributions approach a normal distribution in most cases. Sodium on the Edziza sample is an exception with a preferred median that is distinctly higher than then preferred mean (Table 1) suggesting a negatively skewed distribution. We have also tabulated the proportion of contribution means which overlap the overall medians at +/- 1 standard deviation of both values (Tables 1, S1, and S2). Under this criterion, more of the lower precision contributions are accepted.

In general, there is close agreement between the EPMA and SEM-EDS median concentrations and data from other methods (Tables 1, 3, and S1). XRF totals (and SiO_2 and Al_2O_3 values) do tend to be lower for Lipari and Edziza, and ICP-AES totals are lower for Lipari. LOI and FTIR estimates of water content are also available. As a subset of the tephrochronology community makes regular use of similarity coefficients (Borchardt et al., 1971, 1972), these were also computed between the individual contribution means and the preferred means on an oxide-by-oxide and element-by-element basis. The proportions of contributions having similarity coefficients (SCs) of 0.95 or greater to their respective overall means (i.e. the smaller number is at least 95% of the larger number) are included in Table 1. The complete set of SC values is contained in Table S4. These proportions are relatively high for most major elements, often 80% or more, but they are much lower for elements present at low concentrations. This difference is largely a function of the analytical precision. For the Edziza tephra, the apparent high level of agreement between data sets for Na_2O hides a large number of low concentrations. Only one-third of the data set means are within 1 standard deviation of the 8.2 wt% Na_2O value obtained by XRF, ICP-AES, and the six laboratories which most carefully minimized or corrected for alkali element migration. One data set is higher and 14 are lower (Figure 2). Three of the data set means fall below 7 wt% Na_2O. The laboratories with lower Na_2O concentrations tended to use longer counting times and/or higher current densities than laboratories which produced higher concentrations (Tables 4 and 7). Note that many of the laboratories with low Na_2O on the Edziza tephra did much better on the less demanding Lipari sample. Agreement is even better on the basaltic Laki tephra which should have relatively stable Na count rates.

The effects of alkali element migration on the Edziza tephra can also be clearly seen in the SiO_2 concentrations. Laboratory 3, which reported one of the two highest SiO_2 concentrations, also has one of the lowest Na_2O concentrations (Figure 2). In the case of laboratory 10, only the SiO_2 value is strongly affected. This can be directly attributed to the analytical procedure. Laboratory 10 analyzes for Si as the fifth element (after Na, F, Mg and Al on the same spectrometer) (Table 6). Analysis of Si begins after nearly four minutes of beam exposure (Table 7) and thus after a significant rise in Si count rates has occurred.

Several laboratories used a rhyolitic glass as the primary standard for Na. Some use this so that alkali element migration in the standard will compensate for migration in unknowns. To obtain good results, however, this approach requires that rates of alkali element migration on the samples are similar to or greater than the standard, but in practice, the rate can vary substantially. Standardization of Na on a rhyolite can also result in elevated Na_2O concentrations on less beam sensitive glasses (e.g. basaltic glasses), especially if current densities or count times are too long, because a certain amount of alkali element migration is built into the standardization. This problem does appear to be present among the contributed results. Note that only five laboratories reported Na_2O concentrations for the Laki tephra that are greater than one standard deviation above the overall mean (Figure 2). Of these, four used a rhyolitic glass for the Na standard (Table 5).

Concentrations of MgO obtained for the Laki sample appear to have a negatively skewed distribution (Figure 2). Twenty-six contributions are between 5.22 and 5.56 wt%, five are between 4.99 and 5.15 wt%, (laboratories 2, 4, 7, 20, and 22), and one is below 4.99 wt%. The difference cannot be clearly linked to the calibration standards (Table 5) or to software and matrix corrections (Table 4). At lower MgO concentrations, agreement is much greater (and relative precision lower), and a similar pattern in not apparent. A similar skewed distribution is not apparent in any of the other oxides on the Laki sample. Only the Na_2O concentrations for Edziza tephra also display a clear negatively skewed pattern.

There is much potential for optimizing counting times in the analytical routines. Few EPMA laboratories optimized their peak and background count times (Table 7) based on relative count rates, and very few utilized all time available on all spectrometers (Table 8). Considering that these optimizations are modest, one-time investments that benefit all future analyses, this is surprising. Although most did use different peak counting times for major and minor elements, the most common configuration for backgrounds was one-half of the peak count time at each of two background positions. Thus total peak counting time equals total background counting time for all or most elements at most laboratories. While such timings are near-optimal for minor elements like Mn, they are much longer than is needed for abundant elements like Si. This is the case because the quality of the background measurement contributes relatively little to the analytical precision when the peak to background ratio is high (major elements) but is very important when the peak rises little above the background (minor/trace elements). Thus, many laboratories could benefit from re-allocating time away from major-element backgrounds and applying that time to enhancing the precision of other elements on the same spectrometers or to the analysis of additional elements. Lab 9 implemented this optimization by calculating optimal ratios between peak and background count times based on their respective X-ray intensities and selecting count times appropriate to the lowest expected abundances of each element analyzed (e.g. optimized Ti count times for rhyolites and K count times for basalts). Only laboratories 2, 9, 15, and 19 have 30 s or less estimated idle time on all spectrometers (Table 8). The idle time, which in several cases exceeds 2 minutes (120 s) on a given spectrometer, could potentially be used to improve precision or to analyze additional elements. For elements present at concentrations of a few tenths of a wt% or higher, it is also possible to omit the background measurement and instead substitute a background correction modeled from the mean atomic number (MAN) of the sample (Donovan and Tingle, 1996). Lab 17 used this approach for 6 of the 14 elements analyzed.

After the initial round of contributions to the interlaboratory comparison was received and results and recommendations were distributed, three laboratories responded to an invitation to submit new data obtained using revised procedures. These revised contributions are designated by laboratory codes 16R, 18R-D, 18R-S and 21R. In all cases, the calibration standards were unchanged, but changes were made in spectrometer assignments and/or timing. Lab 16 increased most background count times and decreased peak count times for Na (from 10 to 6 s) and F (from 20 to 10 s) (Table 7). Lab 18 increased the raster size from 3 to 5 μm and implemented the two-part procedure that was among the suggestions provided to the participants following the initial data compilation. The new procedure includes a 30 s EDS analysis for Na, Al, Si, and K and a 150 s analysis for Mg, Ca, Ti, Mn, and Fe. Concentrations produced using this procedure are reported with code 18R-D (double-analysis procedure). Results using the 150 s analysis for all elements has the code 18R-S (single-analysis procedure). The same 150 s timings were used for the original submission. Lab 21 changed from a 2 μm beam with a 10 μm raster to a fixed 10 μm beam. Phosphorous was moved from the TAP to a PET spectrometer. Count times were increased for Mg, Si, Al, Mn, and Fe peaks and reduced for Na (from 20 to 10 s), K, and Ca. Measurement of Si was moved in the sequence to occur prior to Al instead of after it (Table 6)..

Many of the procedural changes implemented for the revised contributions produced clear changes in the analytical results. In the case of laboratory 16, decreasing the Na count time by 40% increased the resulting Na_2O concentrations on Edziza tephra from 7.2 wt% to 8.3 wt%, a significant improvement (Figure 2 and Table 3). Decreasing the count time for F by half, however, reduced the analytical precision substantially. In the case of laboratory 18, increasing the raster dimension from 3 μm to 5 μm alone (18R-S) raised the Edziza Na_2O concentrations from 7.2 to 8.0 wt%. Also reducing the counting time from 150 s to 30 s (18R-D) further increased Na_2O to 8.2 wt%. Surprisingly, the same reduction in counting time produced little change in the precision for Al_2O_3, SiO_2, and K_2O (Figure 2 and Table 3). In the case of laboratory 21, the P_2O_5 values improved dramatically from very high to within 1 standard deviation of the overall median. Na_2O concentrations increased slightly due to the reduced counting time. Analysis of Si before Al made little difference to the Al_2O_3 concentration, but resulted in significantly higher SiO_2 on all of the glasses, even the much less beam sensitive basaltic glass. In contrast, the expected result is little change on Laki and a reduction in SiO_2 on Lipari and Edziza due to reduced beam damage and therefore a smaller increase in the Si count rates. Perhaps the unexpected increase in SiO_2 concentrations across all samples is related to a change in the amount of beam damage on the SiO_2 standard used to calibrate for Si.

5. Preferred concentrations for the four reference glasses

Using data contributed to the interlaboratory comparison combined with additional data from several other analytical methods, including published data, we have assigned recommended compositions for the four distributed glasses (Tables 1 and S1). As in Potts et al. (2002), we have typically recommended the median values computed after the removal of outliers as the best estimate of the true sample composition. The median value, or middle number of a set of values, is preferred because it is less influenced by extreme values than is the mean value, especially when the number of determinations is small. Our E-beam data sets are large enough that the removal of a few outliers typically has little effect on the means and especially the medians. Because of their abundance, the E-beam data provide the primary control on the recommended compositions. In contrast, there are very few E-beam contributions for Ba and Zr which are present at low concentrations. For these elements, the bulk methods (e.g. XRF, ICP-MS, INAA) also have higher precision than E-beam methods and are likely to provide a better estimate of the true concentrations.

In addition to the E-beam outliers discussed in the previous section, we have rejected further data from the calculation of recommended values. This includes some additional outliers which became apparent when the E-beam and other methods data were considered together (Tables 1, 3, and S1). It also includes the rejection of data produced by procedures which may compromise the resulting concentrations. To develop the best estimation of the true SiO_2, Al_2O_3, Na_2O, and K_2O concentrations in the most beam-sensitive sample, Edziza tephra, we omitted all E-beam contributions for these oxides except for those produced by procedures which are least likely to result in data compromised by alkali element migration (Tables 1, 3, and S1). For Laki tephra, we omitted Na_2O concentrations from E-beam laboratories which calibrated for Na on rhyolite glasses.

For the Lipari obsidian and the Old Crow tephra, the resulting all-methods median values including analyzed (FTIR) or estimated (LOI) water produced halogen-corrected totals of 100.2 wt% and 100.5 wt% respectively. This indicates a systematic error in one or more of the median concentrations. In the Lipari case, the nearly 1 wt% difference in SiO_2 between the E-beam and other method preferred medians suggests that the problem lies there. All other major- and minor-element concentrations are essentially the same for the two method categories. In place of the all methods median, we recommend instead the average of (1) the E-beam preferred median and (2) the Other methods preferred median. In other words, we calculate the average of the medians from the two different types of methods (E-beam and bulk). This results in a concentration of 74.1 wt% SiO_2 and provides for an improved total. Twelve of the E-beam laboratories produced results within 1 standard deviation of this concentration. We also calculate a 74.1 wt% SiO_2 concentration for Old Crow tephra in the same way.

In Tables 1 and S1, we also distinguish between more robust reference values and less certain information values. Following the suggestion of Kane (2004), we designate reference values (R) where there are at least 10 individual laboratory results using at least two independent methods of analysis that agree within analytical error. Concentrations for those elements that were determined by fewer techniques or fewer laboratories are designated as information values (I). Information values have greater potential to change when additional data becomes available. For Laki, which was characterized only by E-beam methods, all concentrations are information values. Because the ID3506, UA 5831, and Hunt and Hill Lipari samples have indistinguishable major-element compositions (Kuehn et al., 2009), the recommended values for the Lipari obsidian found in Table 9 may be applied to all three. To quantify uncertainty at the 95% confidence level, we use a procedure similar to that followed by Jochum et al. (2011). This process considers three components of variance as recommended by Kane et al. (2003): (1) the standard deviation of the compiled concentrations, (2) a homogeneity component, and (3) a bias component. As the abundant microanalytical data includes a large number of data points on a large number of fragments, the standard deviations should already capture any homogeneity in the glasses so a homogeneity component is not needed. Because the E-beam and other methods agree within analytical error, the bias component may also be omitted. The remaining variance component, the standard deviation, is multiplied by the relevant value of the Student's t-distribution, t, to derive the 95% confidence level uncertainties - i.e. the uncertainties = σ x t (Jochum et al., 2011). The value of t is about 2.1 when the number of contributed data sets is larger than about 30 and increases for smaller quantities of data (e.g. about 2.5 for 7-8 contributions and 3.5 for 3 contributions). This results in greater uncertainties where less data is available. Uncertainties calculated using this procedure are included in Tables 1 and S1. For SiO_2 in Laki tephra, this procedure resulted in an uncertainty of +/- 0.8 wt% which we judge to be too small considering the single method and the larger uncertainties for SiO_2 obtained for the other three samples. We instead assign for SiO_2 in Laki tephra the larger uncertainty value of +/-1.4 wt% obtained for Lipari and Edziza.

6. Recommendations

Following are a series of recommendations intended to improve data quality, improve data reporting, and generally improve the efficacy of tephra fingerprinting and correlation. Several similar recommendations have been made previously by Froggatt (1992), Hunt and Hill (1993, 2001), Turney at al. (2004), Morgan and London (1996, 2005), and Westgate et al. (2008), whereas other recommendations are new. The above sources also provide several other valuable recommendations not repeated here. For all of these recommendations to widely take hold and influence the future published record of tephrochronology will require the participation of analysts, authors, reviewers, and editors. We sincerely hope that reviewers and editors will help to uphold these essential standards, particularly those related to data reporting, by requiring that they be met by all manuscripts in their care.

6.1 Recommendations Related to Accuracy and Precision

Although many of the submitted analyses are of high quality, much potential remains to improve accuracy and increase precision. The requirements for obtaining highly accurate data on tephra glasses are many. Among them are: (1) the use of analytical conditions and procedures that minimize alkali element migration, (2) the use of appropriate, well-characterized reference materials for standardization, and (3) the avoidance of microcrysts and the removal of microcryst-contaminated results. Precision, in contrast, is primarily a function of counting statistics. Increasing the X-ray counts by a factor of 4 ideally reduces the standard deviation by a factor of 2 because the standard error is determined by the square root of the total X-ray counts (e.g. Bertin, 1978; Reed 2002). Total X-ray counts may be increased by (1) lengthening the analysis time or by (2) increasing the raw count rate through increased beam current, use of multiple spectrometers, use of spectrometers with larger analyzing crystals, or the use of more sensitive detectors. Because of alkali element migration, however, precision and accuracy are often competing interests as increasing time and increasing current also increases the migration, often resulting in reduced accuracy.

Recommendation 1: Ensure that alkali element migration is adequately minimized or measure and correct for it.

a) Use a 5 μm to 20 μm defocused (or rastered) beam, a low beam current (the smaller the beam, the lower the current must be), short analysis times for Na, Al, and Si (lower currents allow for longer times), and/or directly measure and correct for the changing count rates (time-dependent intensity) (Nielsen and Sigurdsson, 1981;Froggatt, 1992; Hunt and Hill, 1993, 2001; Morgan and London, 1996, 2005). A combination of these approaches is most effective.
b) Analyze for Na, Al, and Si at the beginning of the procedure (i.e. as the first elements on their respective spectrometers) (Morgan and London, 1996, 2005). If this is not possible, analyze for Na first, analyze for Si and Al as early as possible, and analyze for Si before Al if both are assigned to the same spectrometer. If supported by the instrument and automation software, consider using WDS and EDS together. Al and Si may be assigned to EDS so that more elements may be analyzed at the very beginning of the procedure. Alternatively Si may be analyzed using a PET crystal for the same reason. (See laboratories 9 and 28 as examples of these two options respectively.)
c) Minimize the amount of beam exposure that occurs prior to the beginning of the analysis and ensure that this exposure is the same for all samples. Often, the sample is exposed to the beam for as much as several seconds before X-ray counting begins, and during this time significant alkali element migration can occur (Morgan and London, 2005).
d) For highly vesicular tephras and fine, distal cryptotephras, reducing the accelerating voltage below the commonly used 15 keV (e.g. to 10-12 keV) decreases the beam penetration depth and can reduce the occurrence of low totals and other problems which result when the beam penetrates through the sample. A reduced accelerating voltage, however, concentrates the beam energy in a smaller volume and therefore requires that greater care be taken to control alkali element migration.
e) Carefully validate the procedure using glass secondary standards to ensure that the resulting Na_2O, SiO_2, and Al_2O_3 concentrations are correct.

Recommendation 2: Ensure that calibration standards are appropriate and well-characterized.

a) Calibration standards must have accurate reference concentrations, and they must be sufficiently homogeneous.

b) Calibration standards must contain the elements to be analyzed at sufficient concentrations for relatively high precision to be obtained during standardization.
c) Beam-stable materials are preferable to those which undergo alkali element migration (e.g. alkali-bearing glasses) or which have other stability problems (e.g. F in apatite).
d) Because matrix corrections are imperfect, it is better to use materials which are compositionally similar to the samples that will be characterized provided that the above criteria have also been met.
e) Where a laboratory has multiple standards that may be suitable, it is useful to evaluate the standards in comparison to each other by incorporating raw count rates, magnitudes of the matrix corrections, and the reference concentrations to determine the most appropriate standards with the most accurate reference concentrations. (Lab 13 did this using the "Evaluate" function of Probe for EPMA.)

Recommendation 3: Optimize count times and spectrometer utilization to maximize precision.

a) Precision can often be improved by more optimally utilizing the spectrometers available during the time budget of the analysis. Idle time on any spectrometer represents wasted analytical resources that could instead be used to improve precision or to analyze additional elements.
b) For each spectrometer, add the peak and background counting times for all elements together with estimated spectrometer movement time. Compare the totals, and for any spectrometers with incomplete utilization, increase the count times for the least abundant of the assigned elements and/or add additional elements of interest. See the supplemental files that accompany this paper for a spreadsheet designed to aid in this optimization.
c) Use peak and background counting times and spectrometer assignments that are optimized for the relative abundances of the elements in the sample (or better to the measured peak and background intensities) (Bertin, 1978). Elements at minor and trace levels require long analysis times and similar peak and total background count times for optimal precision. For abundant elements, relatively short peak count times and even shorter background count times are sufficient (Reed, 2002). If similar count times are currently in use for both, re-allocating time from major to minor elements can improve the overall quality of the analysis. For example, 15 s peak and 3 s on a single background may be sufficient for Si in rhyolites analyzed with a 10 nA current. For Mg in the same material, good results could be obtained using 60 s peak and 30 s on each of two backgrounds (60 s total). In the case where Si or Al is analyzed after another major element, reducing the background counting time of the first element also has the advantage of starting the analysis of Si or Al sooner for better accuracy. See the supplemental files that accompany this paper for two spreadsheets designed to aid in optimizing the ratio between peak and background analysis times and to estimate the beam current and counting time needed to achieve a desired level of precision. If the automation software for the instrument includes the capability to substitute mean atomic number (MAN) based backgrounds for measured backgrounds, use it for the major elements. This method requires an additional calibration step to relate the intensity of the background under each X-ray peak to the MAN of the sample (Donovan and Tingle, 1996), but it can significantly reduce the analysis time for unknowns.

d) Consider aggregating intensities from multiple spectrometers to improve precision on minor and trace elements.

e) If an instrument is equipped with multiple spectrometers capable of analyzing the same elements with similar peak to background ratios but with significantly different count rates (e.g. both a TAP and an LTAP crystal), allocate elements which require short count times (e.g. Na) and lower abundance elements to the spectrometer with the greater raw count rate.

Recommendation 4 (SEM-EDS only): Implement a two part procedure to maintain accuracy on Na_2O and obtain good precision on minor elements when analyzing relatively beam-sensitive glasses.

a) Typically, a single analysis with the same count time for all elements is used on SEM-EDS instruments. Doing so may result in either an analysis time that is too long for accurate determination of Na_2O concentrations on the more beam-sensitive glasses or is too short for adequate precision on minor elements. One potential solution is to analyze each location twice. A shorter initial analysis (e.g. 30 s) may be used for Na_2O, Al_2O_3, and SiO_2 (and perhaps K_2O) to minimize the effects of alkali element migration. A longer subsequent analysis (e.g. 150 seconds or more) may then be used to obtain higher precision on the remaining elements. The precision for the latter elements would benefit further if the X-ray counts from both spectra could be combined.

b) Test the procedure to determine the optimal timing and analytical conditions required for the types of samples to be analyzed and the desired level of precision.

Recommendation 5: Analyze at least 20 points on homogeneous glass, more on less homogeneous samples.

a) The reproducibility of the mean concentration for a set of analyses generally improves as more analyses are included, although the additional incremental improvement declines as the total number of analyses increases (Froggatt, 1992). Thus, to adequately characterize homogeneous samples, we recommend 20 analyses as a reasonable minimum. This also provides a sufficient number of analyses to allow for the removal of a few outliers. If the sample is to be subsequently analyzed by LA-ICP-MS, additional data points would be beneficial as the larger analysis volume of LA-ICP-MS increases the chance of encountering a microcryst.

b) For less homogeneous samples, a larger number of analyses is necessary for adequate characterization. The more the glass composition varies, the more analyses are needed. In the case of a tephra produced through the mingling of basaltic and rhyolitic magmas, for example, sufficient data is needed to define both end members and the population distribution between them. In such a case, 50 to 60 analyses may provide a reasonable minimum for characterization. For tephras containing a scarce sub-population (e.g. 1 of every 10-15 shards as in Aniakchak tephra; Denton and Pearce, 2008), 100 or more analyses could be needed to sufficiently characterize the minor population.

<u>**Recommendation 6:**</u> **Carefully screen for and remove outliers prior to computing mean** concentrations**.**

a) Outliers in tephra data most commonly derive from crystalline contaminants or from points with low totals resulting from analytical problems (e.g. where part of the beam was on epoxy rather than glass or the shard was too thin) . Removing such points is essential for producing accurate mean concentrations. This can be accomplished using graphical methods (as recommended by Platz et al., 2007), z-scores (as used by Jochum et al.,2011 and this paper), or statistical methods such as cluster analysis.

b) Crystalline phases adjacent to but outside of the analysis volume can still affect the analysis due to X-ray absorption and secondary fluorescence effects, although the impact is much more subtle than when a portion of the electron beam directly excites a microcryst. This likely plays a role in the increased scatter often found in data from microcryst-rich samples even after obvious outliers have been removed. Where possible, positioning the margin of the electron beam *at least* 10-20 microns away from observed microcrysts and phenocrysts will substantially reduce this problem.

6.2 Recommendations Related to Secondary Standards and Data Reporting

The routine analysis of secondary standards is a powerful tool. Well-characterized secondary standards can be analyzed to test calibration quality and to provide a check on the reference compositions of the primary calibration standards. When interspersed with unknown samples throughout an analytical run, they can be used to identify and correct for drift. Furthermore, they can provide reference concentrations for publication. Published secondary standard data allows data quality to be independently verified and allows data to be compared between laboratories with greater confidence. By maximizing data accuracy and comparability, the use of secondary standards also makes tephra correlations based on such data more robust (Froggatt, 1992; Westgate et al., 2008). To ensure that they are widely used and reported, reviewers should require authors to provide analyzed concentrations on secondary standards (preferably those which are widely used) as a condition of publication.

Secondary standards can furthermore be used to maximize consistency between data collected at different times on the same instrument as well as between data from different instruments. When used in this way, small variations between calibrations and any drift can be removed to produce results that are highly consistent from run to run and over months to years (e.g. Kuehn et al., 2009). This approach works best when multiple secondary standards are analyzed several times throughout an analytical run such that the number of points analyzed is significantly greater than the number used in the initial calibration, and thus the means are more stable. Then, small adjustments can be made to the resulting concentrations so that they match the reference values or the laboratory’s long-term mean values. Applying the same adjustments to the unknowns analyzed during the same run produces results that are highly consistent over time. If different laboratories use common secondary standards, this approach can also be used to produce results that are highly consistent between laboratories, regardless of the primary calibration standards used, provided that alkali element migration has first been minimized.

Ideally, both mafic (e.g. Laki tephra or the U.S. Geological Survey glasses such as BHVO-2G, BCR-2G, and NKT-1G) and felsic secondary standard glasses (e.g. Lipari obsidian) should be analyzed. Other reference glasses are also available including the eight MPI-DING glasses (Jochum et al., 2006), those distributed through the G-probe proficiency testing program, and several additional glasses described in the GeoREM database <http://georem.mpch-mainz.gwdg.de/>.

Full disclosure of analytical conditions, automation software, matrix corrections, analysis sequencing and timing, calibration standards, and secondary standards is critical for fully evaluating the quality of any EPMA or SEM-EDS data set. Therefore, this information must be published (Froggatt, 1992; Hunt and Hill, 1993; Turney at al., 2004). Once published, later reports may include summary details (instrument, software, and analytical conditions) and cite earlier reports for complete details.

To evaluate tephra correlations, the analytical data must also be published. Therefore all publications which report new tephra correlations must include the analytical data. If space considerations preclude placing data in the paper body, the data must be provided as a supplemental file. Reporting mean concentrations alone is insufficient. Standard deviations, the total number of points analyzed, and the analytical totals (or water by difference) are also necessary (Froggatt, 1992). Water by difference provides only an estimation of the actual water content and is subject to errors resulting from the omission of other elements from the analysis, incorrectly-assumed oxidation states, the lack of a correction for the substitution of halogens for oxygen, poor sample positioning during analysis (both horizontal and vertical/focus), and the penetration of the beam through thin shards.

For samples which are heterogeneous, publication of the complete analytical data is essential. Publishing the complete data documents the full compositional range, population distribution, and any co-variation trends. This critical information is absent from the mean concentrations. Thus publication of means alone for heterogeneous samples is essentially useless. If necessary, summary data or plots may be placed in the paper body and compete data provided as a supplemental file (Froggatt, 1992). Because procedural details and analytical data are essential to substantiate any tephra correlation, reviewers should require authors to provide these details as a condition of publication.

Thickness and grain size data from tephra samples complement the analytical data and should also be reported (Turney at al., 2004). This additional information is helpful for mapping the distribution patterns of individual tephras and for locating eruptive sources. Thickness and grain size data also have volcanological applications – e.g. to understanding eruptive processes and atmospheric transport.

Recommendation 7: Analyze one or more secondary standards as a matter of routine, at the beginning of and several times throughout every analytical run.

Recommendation 8: Publish the analyzed and reference concentrations obtained from secondary standards as a matter of routine.

<u>Recommendation 9:</u> Fully disclose analytical conditions, primary and secondary standards, and all other relevant analytical parameters.

<u>Recommendation 10:</u> Publish all acquired compositional data including the analytical totals to substantiate new tephra correlations.

6.3 Additional comments and suggestions

Provided that other issues taken care of and the probe beam completely fits on the shard analyzed, incorporating water by difference into the matrix corrections can provide improved results for glasses with substantial secondary hydration. For accurate reporting, analytical totals should also account for the presence of any halogens (Cl, F) as halogens substitute for O. One O atom should be subtracted from the soichiometrically-determined O for every two halogen atoms present (Deer, Howie, and Zussman, 1992). Formulas which implement this correction are used in Table S1. Ideally, this adjustment should also be incorporated into the matrix correction procedure (e.g. ZAF, PAP, phi-rho-z) used to convert ratios of raw X-ray intensities into concentrations.

7. Availability of material

The Lipari obsidian sample ID3506 is available for distribution from the Harvard Mineralogical Museum. Small amounts of the UA5831 Lipari sample also continue to be available from commercial sources both as grains and in prepared multi-standard mounts. Small quantities of the Mt. Edziza Sheep Track tephra may be obtained from S. Kuehn. Samples of Old Crow tephra may be obtained from D. Froese.

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Figures and Tables – subsequent pages

Figure 1 – Time-dependent count rates on reference samples reported relative to the initial count rates. The curves are based on five analyses of each glass conducted on a Cameca SX-100 at the University of Alberta. The cumulative count rate is computed from total counts divided by total time. Analytical conditions are 15 keV and 9 nA with a 10 μm fixed beam.

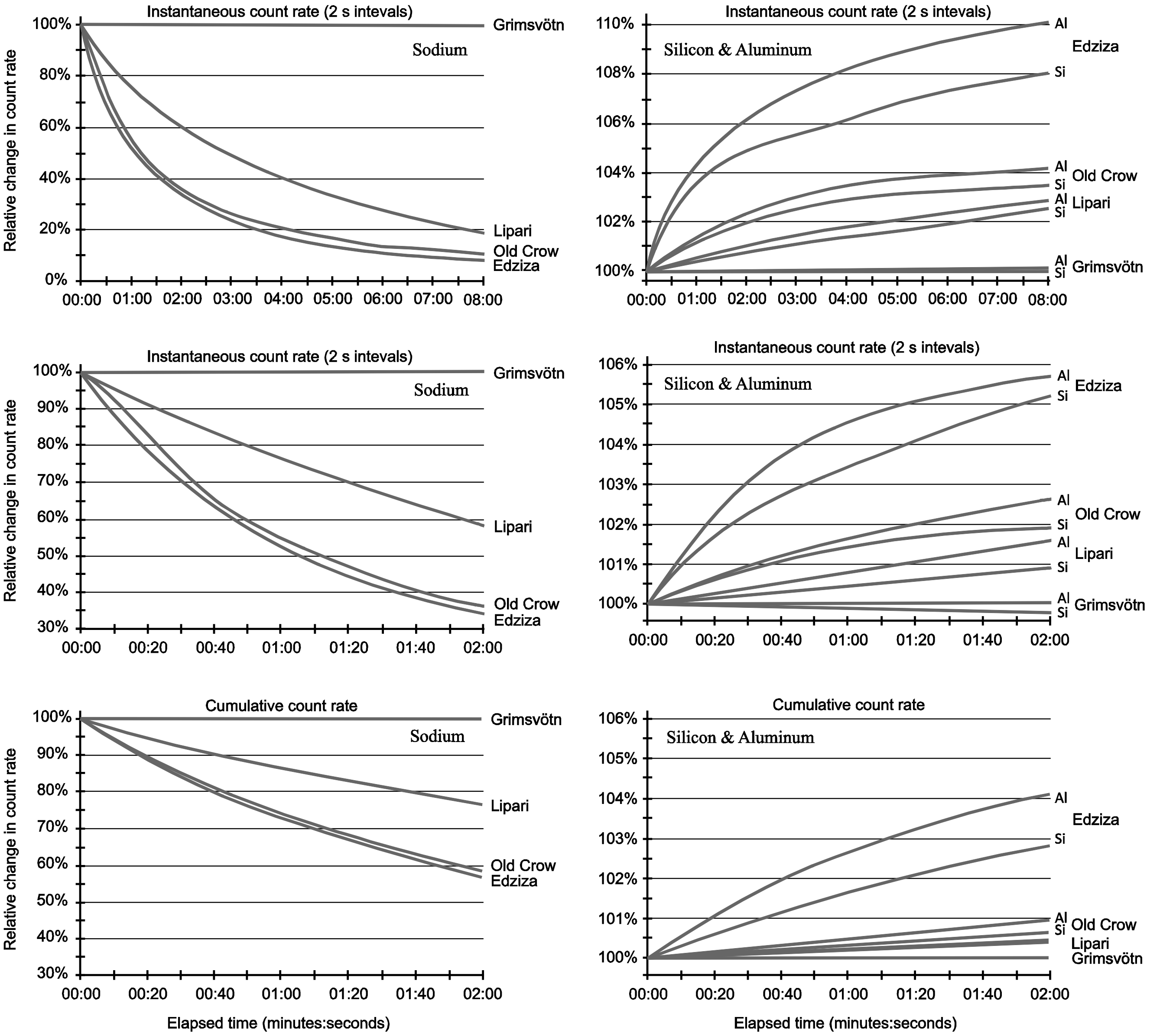
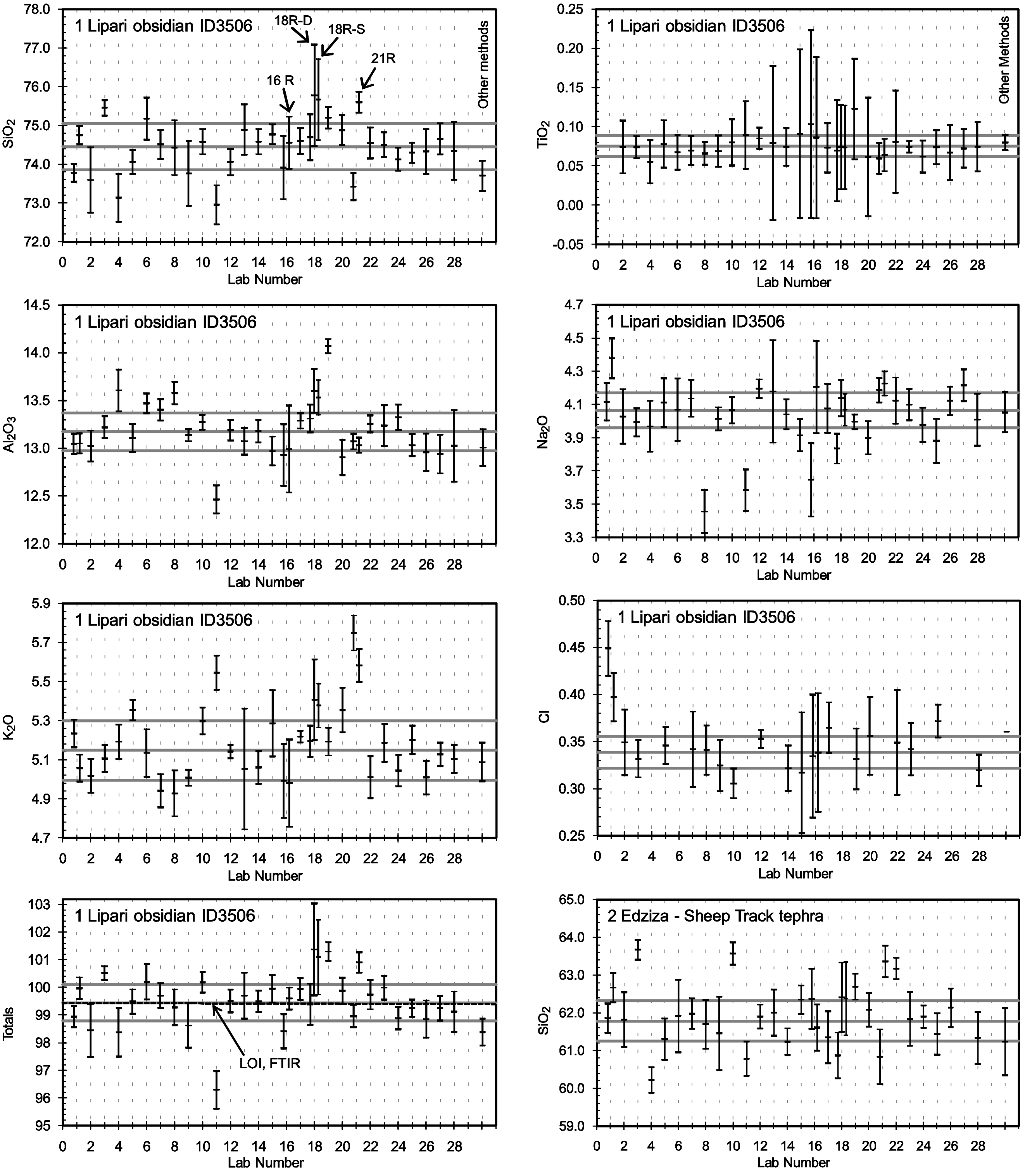
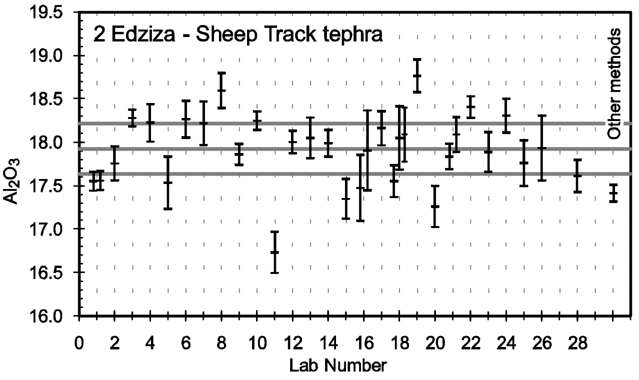
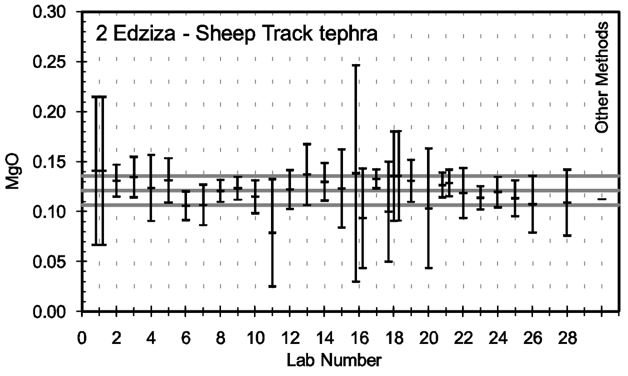
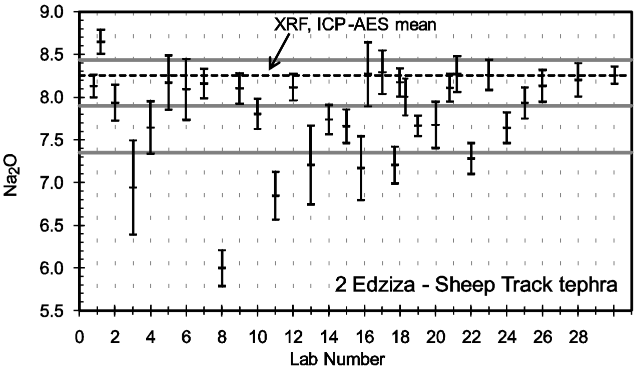


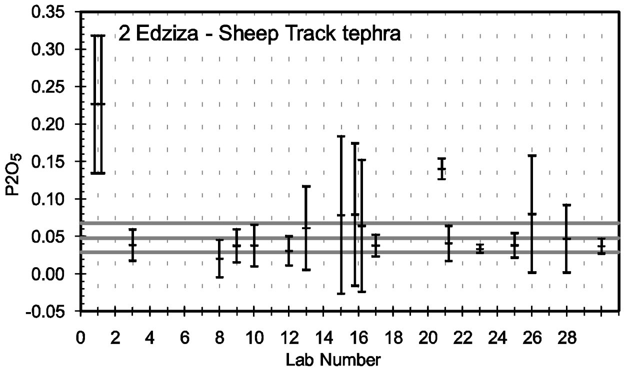
Figure 2 – Selected comparative plots of the submitted analytical data. Vertical bars represent the means +/- 1 standard deviation for each contribution. Horizontal gray bars represent the preferred overall medians +/- 1 standard deviation. A complete set of plots may be found in Figure S1.

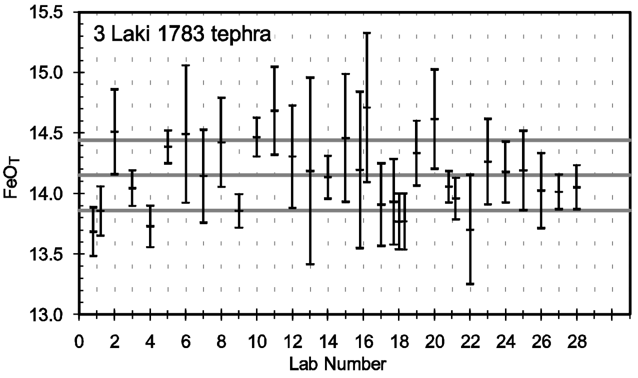


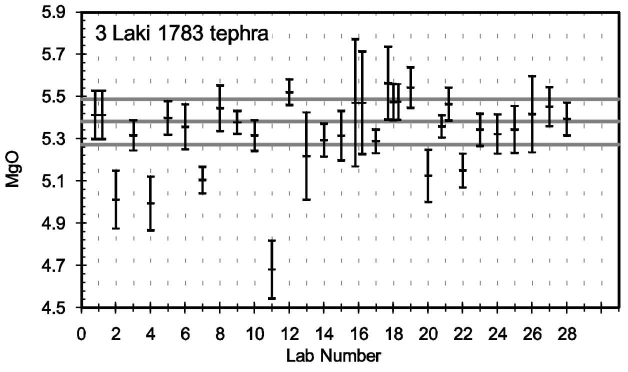

2 Edziza - Sheep Track tephra
Other methods
Al$_2$O$_3$
19.5
19.0
18.5
18.0
17.5
17.0
16.5
16.0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number

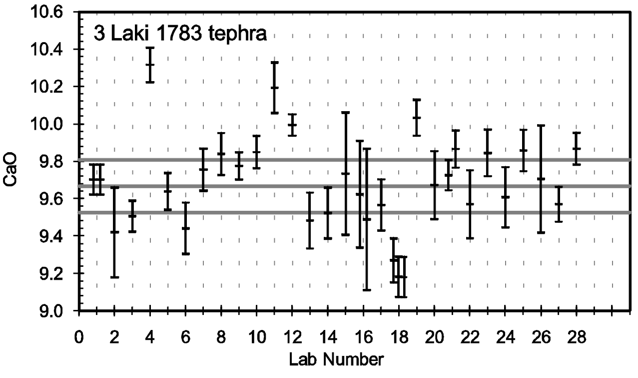

2 Edziza - Sheep Track tephra
Other Methods
MgO
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number


XRF, ICP-AES mean
2 Edziza - Sheep Track tephra
Na$_2$O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number


2 Edziza - Sheep Track tephra
P$_2$O$_5$
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number


3 Laki 1783 tephra
FeO$_T$
15.5
15.0
14.5
14.0
13.5
13.0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number


3 Laki 1783 tephra
MgO
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number


3 Laki 1783 tephra
CaO
10.6
10.4
10.2
10.0
9.8
9.6
9.4
9.2
9.0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number

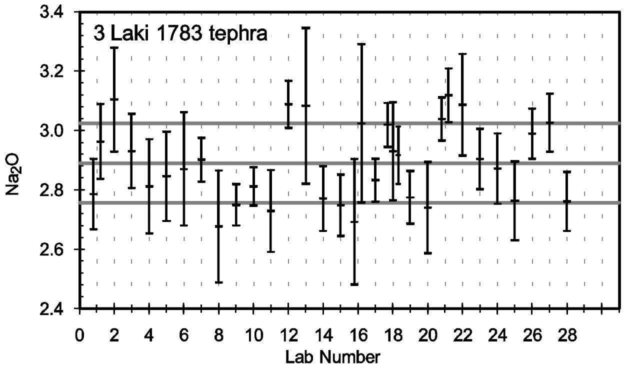

3 Laki 1783 tephra
Na$_2$O
3.4
3.2
3.0
2.8
2.6
2.4
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Lab Number

Table 1 – Summary data and recommended values for the four glasses. Included are overall means, medians, and standard deviations for the compiled data from electron-beam methods (E-beam: EPMA and SEM-EDS), for all other analytical methods, and for the electron-beam and other methods combined. FeO_T is total Fe reported as FeO. The Totals column contains overall means and standard deviations calculated from the totals of the individual contributions listed in Tables 3 and S1. The Sum column lists the sums of the compiled values found to the left in the same row. See the text and Table S1 for details regarding the determination of recommended values. In most cases, the recommended values are the medians computed from all available contributions from all available methods after the removal of outliers.

Table 1A Totals column lists means, medians, and standard deviations of the totals given in Table 3; Sum column lists the sums of the compiled values found to the left in the same row.

Lipari obsidian - Sample 1

Description	SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Totals (Cl,F=O adjusted)	Sum (Cl,F=O adjusted)
E-beam mean - All contribution means	74.5	0.076	0.021	13.2	1.55	0.045	0.066	0.039	0.71	4.03	5.18	0.024	0.35	0.15	0.007			99.50	99.77
E-beam median - All contribution means	74.5	0.074	0.021	13.1	1.54	0.036	0.065	0.041	0.73	4.07	5.14	0.011	0.34	0.15	0.007			99.50	99.78
1σ	0.7	0.013		0.3	0.04	0.040	0.019	0.009	0.13	0.19	0.19	0.029	0.03	0.02				0.97	
Number of Contributions	33	31	1	33	33	4	29	31	33	33	33	16	21	6	2			33	
% which overlap grand mean at +/- 1σ	85%	100%		91%	97%	100%	100%	97%	97%	88%	91%	94%	95%	100%				91%	
% of values within grand mean +/- 2σ	94%	94%		94%	91%	100%	97%	94%	97%	91%	91%	94%	95%	100%				97%	
Similarity coefficient >0.95	100%	37%		93%	90%		20%	19%	79%	83%	93%	0%	60%					100%	
E-beam preferred mean (outliers omitted)	74.6	0.073	0.021	13.2	1.55	0.026	0.064	0.039	0.73	4.07	5.14	0.018	0.34	0.15	0.007			99.60	99.84
E-beam preferred median (outliers omitted)	74.6	0.074	0.021	13.1	1.55	0.035	0.065	0.041	0.73	4.07	5.13	0.011	0.34	0.15	0.007			99.55	99.78
1σ	0.6	0.009		0.2	0.03	0.017	0.016	0.009	0.03	0.11	0.13	0.017	0.02	0.02				0.79	
Number of Contributions	31	29	1	31	30	3	28	31	32	29	30	15	20	6	2			32	
Omitted labs (outliers)	4, 11	16, 19		11,19	8, 7, 27	15	16		11	1B, 8, 11,16	11,21, 21R	21	1A					11	
Other methods mean (outliers omitted)	73.6	0.083	0.027	13.0	1.55	0.002	0.069	0.051	0.75	4.07	5.09	0.011	0.36			0.098	0.67	98.58	99.38
Other methods median (outliers omitted)	73.7	0.080	0.026	13.0	1.55	0.002	0.066	0.058	0.75	4.06	5.06	0.011	0.36			0.098	0.65	98.43	99.45
1σ	0.4	0.012	0.006	0.2	0.02	0.000	0.008	0.019	0.02	0.12	0.10						0.04	0.49	
Number of Contributions	5	4	4	5	4	4	5	3	5	7	7	1	1			1	3	5	
Methods included:	XRF, ICP-AES, Wet chem	XRF, ICP-AES, Wet chem	XRF, ICP-AES, ICP-MS, LA-ICP-MS	XRF, ICP-AES, Wet chem	XRF, ICP-AES	XRF, ICP-AES, ICP-MS, LA-ICP-MS	XRF, ICP-AES, Wet chem	XRF, Wet chem	XRF, ICP-AES, Wet chem	XRF, ICP-AES, Wet chem	XRF, ICP-AES, Wet chem	XRF	Wet Chem			XRF	FTIR, LOI	XRF, ICP-AES, Wet chem	
All methods mean - All contributions, except outliers	74.4	0.074	0.026	13.2	1.55	0.003	0.065	0.041	0.73	4.07	5.13	0.011	0.34	0.15	0.007	0.098	0.67	96.85	100.42
All methods median - All contributions, except outliers	74.5	0.074	0.024	13.1	1.55	0.002	0.065	0.041	0.73	4.07	5.11	0.010	0.34	0.15	0.007	0.098	0.65	99.43	100.40
1σ	0.7	0.009	0.006	0.2	0.03	0.002	0.015	0.010	0.03	0.11	0.13	0.008	0.02	0.02	0.01		0.04	0.83	
Number of Contributions	36	33	5	36	34	5	33	34	37	36	37	13	21	6	2	1	3	37	
Number of Methods	4	4	5	4	3	5	4	3	4	4	4	2	2	1	1	1	2	4	
Analyses omitted:	4, 11	16, 19		11, 19, XRF(HH)2	8, 7, 27, Wet chem	3, 15, 17	16	ICP-AES	11	1B, 8, 11, 16, ICP-AES	11, 21, 21R	15, 16, 16R, 21, Wet chem	1A						
Recommended values	74.1	0.074	0.024	13.1	1.55	0.002	0.065	0.041	0.73	4.07	5.11	0.010	0.34	0.15	0.007	0.098	0.65		100.03
Uncertainty at 95% confidence (σ * t)	1.4	0.020	0.016	0.5	0.05	0.006	0.031	0.022	0.06	0.22	0.27	0.02	0.05	0.05	0.026	0.012	0.15		
Value type	R	R	I	R	R	I	R	R	R	R	R	R	R	I	I	I	I		

Table 1B

Mt. Edziza - Sheep Track tephra - Sample 2

Description	**SiO_2**	**TiO_2**	**ZrO_2**	**Al_2O_3**	**FeO_T**	**BaO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**Cl**	**F**	**SO_2**	**Other Traces**	**OH, H2O**	**Totals (Cl,F=O adjusted)**	**Sum (Cl,F=O adjusted)**
E-beam mean - All contribution means	61.9	0.237	0.163	17.9	4.56	0.042	0.133	0.121	1.07	7.80	5.34	0.073	0.22	0.19	0.02			99.29	99.70
E-beam median - All contribution means	61.9	0.236	0.163	18.0	4.55	0.040	0.134	0.123	1.10	7.97	5.34	0.044	0.21	0.20	0.02			99.31	99.86
1σ	0.8	0.015		0.4	0.15	0.032	0.017	0.015	0.14	0.55	0.21	0.062	0.02	0.03	0.01			1.24	
Number of Contributions	32	32	1	32	32	4	28	32	32	32	32	18	21	6	3			32	
% which overlap grand mean at +/- 1σ	84%	100%		88%	97%	100%	100%	100%	97%	91%	94%	83%	95%	100%				84%	
% of values within grand mean +/- 2σ	91%	97%		97%	97%	100%	93%	94%	97%	94%	97%	89%	95%	83%				94%	
Similarity coefficient >0.95	100%	75%		96%	89%		38%	29%	68%	71%	89%	6%	45%					100%	
E-beam preferred mean (outliers omitted)	61.9	0.235	0.163	18.0	4.55	0.029	0.136	0.124	1.094	7.92	5.33	0.048	0.21	0.20	0.02			99.34	99.77
E-beam preferred median (outliers omitted)	61.9	0.236	0.163	18.0	4.54	0.030	0.136	0.124	1.098	8.09	5.34	0.039	0.21	0.21	0.02			99.31	99.99
1σ	0.6	0.012		0.4	0.14	0.022	0.013	0.012	0.058	0.37	0.19	0.019	0.02	0.02	0.01			0.78	
Number of Contributions	29	31	1	31	31	3	26	30	31	29	31	15	20	5	3			28	
Omitted labs (outliers)	3, 4, 10	16R		11	8	15	18, 26	11, 16R	11	3, 8, 11	21	1A, 1B, 21	1A	15				10, 11, 18, 21R	
Other methods mean (outliers omitted)	61.2	0.240	0.147	17.4	4.57	0.0040	0.131	0.149	1.053	8.24	5.32	0.035				0.118	0.7	98.60	99.32
1σ	0.9	0.006	0.006	0.1	0.04	0.0000	0.003	0.054	0.025	0.13	0.09	0.013						0.99	
Number of Contributions	2	2	2	2	2	2	2	2	2	2	2	2				1	1	2	
Methods included:	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES				XRF	LOI	XRF, ICP-AES	
All methods mean - All contributions, except outliers	61.8	0.236	0.153	17.9	4.55	0.005	0.135	0.123	1.09	8.17	5.33	0.040	0.21	0.20	0.018	0.118	0.70	99.29	100.71
All methods median - All contributions, except outliers	61.9	0.236	0.152	17.9	4.55	0.004	0.134	0.124	1.09	8.16	5.34	0.038	0.21	0.21	0.021	0.118	0.70	99.29	100.74
1σ	0.7	0.012	0.010	0.3	0.13	0.001	0.013	0.012	0.057	0.18	0.18	0.012	0.02	0.02	0.01			0.79	
Number of Contributions	31	33	3	31	33	3	28	31	33	19	33	14	20	5	3	1	1	30	
Number of Methods	3	3	3	3	3	3	3	2	3	3	3	3	1	1	1	1	1	3	
Analyses omitted:	3, 4, 10	16R		11, 19, 20	8	3, 15, 17	18, 26	11, 16R, ICP-AES	11	2, 3, 4, 8, 10, 11, 13, 14, 15, 16, 18, 19, 20, 22, 24, 25	21	1A, 1B, 15, 16, 21, 26	1A	15				10, 11, 18, 21R	
Selected E-beam labs mean - 1,5,17,18R-	61.7			17.8						8.21	5.40							99.48	
Selected E-beam labs median - 1,5,17,18R-	61.6			17.8						8.19	5.36							99.49	
1σ	0.4			0.3						0.06	0.09							0.41	
Recommended values	61.6	0.236	0.152	17.6	4.55	0.004	0.134	0.124	1.09	8.19	5.34	0.038	0.21	0.21	0.02	0.118	0.60		100.05
Uncertainty at 95% confidence (σ * t)	1.4	0.025	0.035	0.7	0.28	0.005	0.027	0.025	0.12	0.2	0.2	0.027	0.03	0.05	0.02				
Value type	R	R	I	R	R	I	R	R	R	R	R	R	I	I	I	I	I		

Table 1C

Laki 1783 AD tephra - Sample 3

Description	**SiO_2**	**TiO_2**	**ZrO_2**	**Al_2O_3**	**FeO_T**	**BaO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**Cl**	**F**	**SO_2**	**Other Traces**	**OH, H2O**	**Totals (Cl,F=O adjusted)**	**Sum (Cl,F=O adjusted)**
E-beam mean - All contribution means	49.7	3.097		13.0	14.15	0.043	0.221	5.328	9.68	2.89	0.47	0.357	0.020	0.13	0.10			98.79	99.14
E-beam median - All contribution means	49.7	3.081		13.0	14.14	0.046	0.229	5.359	9.70	2.87	0.47	0.347	0.019	0.11	0.09			98.71	99.10
1σ	0.6	0.128		0.3	0.29	0.016	0.033	0.183	0.25	0.13	0.02	0.048	0.008	0.06	0.02			0.90	
Number of Contributions	33	33		33	33	3	31	33	33	33	33	20	19	5	3			33	
% which overlap grand mean at +/- 1σ	88%	91%		91%	100%		97%	88%	85%	94%	91%	90%	100%	100%				82%	
% of values within grand mean +/- 2σ	91%	94%		97%	100%		87%	97%	91%	100%	91%	90%	95%	100%				94%	
Similarity coefficient >0.95	100%	83%		97%	100%		41%	86%	93%	72%	79%	44%	11%					100%	
E-beam preferred mean (outliers omitted)	49.7	3.11		13.0	14.2	0.043	0.223	5.37	9.68	2.86	0.46	0.343	0.019	0.13	0.10			98.80	99.13
E-beam preferred median (outliers omitted)	49.7	3.08		13.0	14.1	0.046	0.231	5.39	9.70	2.85	0.46	0.345	0.019	0.11	0.09			98.71	99.09
1σ	0.4	0.11		0.3	0.3	0.016	0.048	0.12	0.18	0.12	0.02	0.023	0.005	0.06	0.02			0.78	
Number of Contributions	33	32		32	33	3	28	29	29	29	30	18	18	5	3			31	
Omitted labs (outliers)	4, 18, 21, 21R	4		19			15, 18R, 27	4, 11, 20, 22	4, 11, 18R	2, 12, 13, 22	1A, 1B, 21	1A, 1B	16					4, 21R	
Recommended values	49.7	3.08		13.0	14.1	0.046	0.231	5.39	9.70	2.85	0.46	0.345	0.019	0.11	0.09				99.09
Uncertainty at 95% confidence (σ * t)	1.4	0.22		0.5	0.6	0.042	0.101	0.25	0.38	0.25	0.04	0.053	0.011	0.15	0.09				
Value type	I	I		I	I	I	I	I	I	I	I	I	I	I	I				

Table 1D

Old Crow tephra

Description	SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Totals (Cl,F=O adjusted)	Sum (Cl,F=O adjusted)
E-beam mean - All contribution means	72.5	0.313		12.5	1.63		0.064	0.276	1.40	3.63	3.61	0.064	0.28	0.18	0.012			96.05	96.34
E-beam median - All contribution means	72.5	0.298		12.5	1.61		0.052	0.272	1.42	3.67	3.60	0.045	0.27	0.19	0.012			95.83	96.31
1σ	1.0	0.031		0.2	0.06		0.033	0.013	0.05	0.23	0.16	0.039	0.04	0.05				1.15	
Number of Contributions	18	16		18	18		16	16	18	18	18	10	11	3	1			18	
% which overlap grand mean at +/- 1σ	94%	100%		94%	100%		100%	100%	89%	89%	89%	90%	91%	100%				89%	
% of values within grand mean +/- 2σ	94%	94%		94%	94%		94%	94%	83%	94%	94%	90%	91%	100%				100%	
Similarity coefficient >0.95	100%	37%		93%	90%		20%	19%	79%	83%	93%	0%	60%					100%	
E-beam preferred mean (outliers omitted)	72.6	0.308		12.5	1.61		0.057	0.274	1.42	3.66	3.59	0.055	0.27	0.18	0.012			96.05	96.46
E-beam preferred median (outliers omitted)	72.5	0.295		12.4	1.60		0.052	0.269	1.43	3.68	3.56	0.038	0.27	0.19	0.012			95.83	96.22
1σ	0.8	0.026		0.2	0.04		0.020	0.008	0.03	0.18	0.14	0.029	0.02	0.05				1.15	
Number of Contributions	17	15		17	17		15	15	15	17	17	9	10	3	1			18	
Omitted labs (outliers)	21	16		8	16		16R	16R	18, 18R	8	21	21	1A						
Other methods mean (outliers omitted)	71.6	0.301	0.033	12.7	1.74	0.108	0.061	0.299	1.42	3.62	3.59	0.039					4.12	95.63	99.66
Other methods median (outliers omitted)	71.6	0.301	0.033	12.7	1.74	0.107	0.061		1.42	3.62	3.59	0.039					4.12	95.63	99.36
1σ	0.0	0.005	0.003	0.1	0.04	0.010	0.003		0.00	0.05	0.09	0.004						0.10	
Number of Contributions	2	2	12	2	2	14	2	1	2	2	2	2					1	2	
Methods included:	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES, ICP-MS, LA-ICP-MS, INAA, SIMS	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES, ICP-MS, LA-ICP-MS, INAA	XRF, ICP-AES	XRF	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES	XRF, ICP-AES				XRF	LOI		
All methods mean - All contributions, except outliers	72.5	0.306	0.033	12.5	1.63	0.108	0.052	0.275	1.42	3.65	3.58	0.038	0.27	0.18	0.012	0.061	4.12	96.01	100.64
All methods median - All contributions, except outliers	72.4	0.297	0.033	12.5	1.62	0.107	0.052	0.275	1.43	3.66	3.56	0.036	0.27	0.19	0.012	0.061	4.12	95.79	100.54
1σ	0.8	0.025	0.003	0.2	0.06	0.010	0.007	0.010	0.02	0.17	0.13	0.007	0.02	0.05				1.09	
Number of Contributions	20	18	12	20	20	14	16	17	18	20	20	8	11	3	1		1	20	
Number of Methods	3	3	6	3	3	5	3	2	3	3	3	3	1	1	1	1	1	3	
Analyses omitted:	21	16		8	16	SIMS	16, 16R, 20	16R, ICP-AES	18, 18R	8	21	16, 16R, 21, 26	1A						
Recommended values	72.1	0.297	0.033	12.5	1.62	0.107	0.052	0.275	1.43	3.66	3.56	0.036	0.27	0.19	0.012	0.061	3.9		99.96
Uncertainty at 95% confidence (σ * t)	1.7	0.054	0.007	0.3	0.12	0.024	0.015	0.022	0.05	0.38	0.28	0.018	0.05	0.17					
Value type	R	R	R	R	R	R	R	R	R	R	R	R	I	I	I	I	I		

Table 2 – Contributing laboratories, contact persons, and analysts organized by geographic regions

Nation	Institution	Contact person(s)	Analyst(s) (if different)
Asia and New Zealand			
Japan	Hokkaido University	Mitsuhiro Nakagawa	Akiko Matsumoto
Japan	Tokyo Metropolitan University	Takehiko Suzuki	Masanori Murata
New Zealand	University of Auckland	Phil Shane	Ritchie Sims
Taiwan	Academia Sinica	Chang-Hwa Chen	Yoshiyuki Iizuka
Europe			
Belgium	Université catholique de Louvain	M. Jacques Wautier	
Germany	GeoForschungsZentrum (GFZ) Potsdam	Clara Mangili	Oona Appelt
Germany	IFM-GEOMAR	Christel van den Bogaard	Christel van den Bogaard, Maxim Portnyagin
Italy	University of Napoli	Paola Petrosino	Roberto De Gennaro, Paola Petrosino
United Kingdom	Queens University Belfast	Jonathan Pilcher	
United Kingdom	University of Edinburgh	Christopher Hayward	
United Kingdom	University of Oxford	Victoria Smith	
North America			
Canada	University of Alberta	Duane Froese	Stephen Kuehn
Canada	University of Toronto	John Westgate, Shari Preece	Shari Preece
United States	Arizona State University	Erin DiMaggio	
United States	Concord University	Stephen Kuehn	
United States	New Mexico Institute of Mining and Technology	Nelia Dunbar	Lynn Heizler
United States	Smithsonian Institution	Amelia Logan	
United States	U.S. Geological Survey, Menlo Park	David Wahl	
United States	University of Alaska, Fairbanks	Ken Severin	Jason Addison, Jim Beget
United States	University of Massachusetts	Michael Jercinovic	Nicholas Balascio
United States	University of Oregon	John Donovan	
United States	University of Utah	Barbara Nash	
United States	University of Wisconsin-Madison	John Fournelle	
United States	Washington State University	Franklin Foit Jr.	Franklin Foit Jr., Scott Cornelius

Table 3 – Mean concentrations by sample and laboratory for all samples from electron-beam methods and from all other methods with available data. FeO_T is total Fe reported as FeO. E-beam results in **bold-underline** are more than +/- 2 s from their respective overall medians and are considered outliers. Results in ***bold-italics*** are additional contributions omitted from the calculation of the All methods means and medians.

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
Lipari obsidian - Sample 1																					
EPMA and SEM-EDS summary results:																					
1A	Mean	73.8			13.0	1.53				0.79	4.12	5.23		**0.45**					98.94	98.84	22
	1σ	0.2			0.1	0.10				0.04	0.11	0.07		0.03					0.38	0.38	
1B	Mean	74.8			13.1	1.55				0.79	**4.38**	5.06		0.40					99.98	99.89	22
	1σ	0.2			0.1	0.10				0.04	0.12	0.07		0.03					0.39	0.39	
2	Mean	73.6	0.074		13.0	1.59		0.064	0.050	0.73	4.03	5.02		0.35					98.45	98.45	132
	1σ	0.8	0.034		0.2	0.09		0.027	0.019	0.04	0.16	0.09		0.03					0.97	0.97	
3	Mean	75.5	0.074		13.2	1.55	***0.037***	0.060	0.041	0.72	3.99	5.11		0.33					100.53	100.52	24
	1σ	0.2	0.014		0.1	0.05	0.033	0.028	0.015	0.02	0.09	0.07		0.02					0.25	0.25	
4	Mean	**73.1**	0.056		13.6	1.54		0.061	0.039	0.78	3.97	5.19							98.38	98.38	25
	1σ	0.6	0.028		0.2	0.10		0.088	0.019	0.04	0.15	0.09							0.87	0.87	
5	Mean	74.1	0.078	0.021	13.1	1.57	0.007	0.074	0.041	0.73	4.11	5.35		0.35	0.14				99.49	99.49	25
	1σ	0.3	0.030	0.034	0.1	0.06	0.012	0.017	0.012	0.02	0.15	0.05		0.02	0.03				0.44	0.44	
6	Mean	75.2	0.068		13.5	1.50		0.053	0.021	0.71	4.07	5.13							100.20	100.20	25
	1σ	0.5	0.022		0.1	0.18		0.030	0.009	0.03	0.19	0.12							0.64	0.64	
7	Mean	74.5	0.070		13.4	**1.46**		0.076	0.034	0.73	4.14	4.94		0.34					99.71	99.63	21
	1σ	0.4	0.019		0.1	0.20		0.038	0.016	0.02	0.11	0.08		0.04					0.46	0.46	
8	Mean	74.4	0.066		13.6	**1.67**		0.030	0.029	0.75	**3.46**	4.93	0.003	0.34					99.28	99.21	40
	1σ	0.7	0.015		0.1	0.07		0.018	0.010	0.03	0.13	0.12	0.007	0.03					0.65	0.65	
9	Mean	73.8	0.069		13.1	1.53		0.066	0.042	0.74	4.01	5.01	0.006	0.32					98.63	98.63	49
	1σ	0.8	0.020		0.1	0.04		0.017	0.006	0.02	0.07	0.04	0.023	0.03					0.81	0.81	
10	Mean	74.6	0.080		13.3	1.56		0.061	0.021	0.76	4.07	5.30	0.012	0.31	0.16	0.011			100.18	100.05	30
	1σ	0.3	0.030		0.1	0.08		0.025	0.012	0.04	0.08	0.07	0.014	0.02	0.07	0.010			0.37	0.37	
11	Mean	**73.0**	0.090		**12.5**	1.53		0.072	0.035	**0.03**	**3.58**	**5.55**							**96.29**	**96.29**	20
	1σ	0.5	0.043		0.1	0.10		0.057	0.026	0.03	0.12	0.09							0.69	0.69	
12	Mean	74.1	0.086		13.2	1.60		0.076	0.031	0.77	4.20	5.14	0.014	0.35		0.003			99.51	99.43	20
	1σ	0.3	0.013		0.1	0.12		0.034	0.020	0.02	0.06	0.03	0.015	0.01		0.005			0.41	0.41	
13	Mean	74.9	0.079		13.1	1.59		0.077	0.055	0.71	4.18	5.05	0.002						99.71	99.71	33
	1σ	0.7	0.098		0.1	0.29		0.065	0.026	0.05	0.31	0.31	0.045						0.84	0.84	
14	Mean	74.6	0.074		13.2	1.54			0.037	0.74	4.04	5.06		0.32					99.50	99.50	26
	1σ	0.3	0.024		0.1	0.04			0.013	0.03	0.09	0.08		0.02					0.39	0.39	
15	Mean	74.8	0.091		13.0	1.52	**0.102**	0.053	0.045	0.70	3.92	5.29	***0.041***	0.32	0.13				99.96	99.83	24
	1σ	0.3	0.108		0.2	0.21	0.164	0.069	0.031	0.08	0.10	0.17	0.063	0.06	0.05				0.49	0.49	
16	Mean	73.9	**0.104**		12.9	1.57		**0.124**	0.046	0.70	**3.65**	4.99	***0.051***	0.33	0.14				98.42	98.42	40
	1σ	0.8	0.120		0.3	0.26		0.144	0.046	0.09	0.22	0.19	0.064	0.07	0.19				0.62	0.62	
16R	Mean	74.6	0.086		13.0	1.49		0.077	0.049	0.75	4.21	4.98	***0.052***	0.34	0.18				99.60	99.60	40
	1σ	0.7	0.103		0.5	0.34		0.122	0.047	0.08	0.28	0.22	0.072	0.06	0.25				0.39	0.39	
17	Mean	74.6	0.073		13.3	1.54	***0.035***	0.053	0.043	0.72	4.08	5.22	0.007	0.36					99.94	99.93	20
	1σ	0.3	0.032		0.1	0.04	0.064	0.018	0.004	0.04	0.15	0.03	0.011	0.03					0.40	0.40	
18	Mean	74.7	0.070		13.3	1.55		0.034	0.054	0.65	3.83	5.20							99.39	99.39	22
	1σ	0.6	0.065		0.1	0.14		0.043	0.038	0.05	0.09	0.08							0.74	0.74	
18R-D	Mean	75.8	0.074		13.6	1.56		0.091	0.046	0.69	4.14	5.41							101.38	101.38	15
	1σ	1.3	0.054		0.2	0.16		0.067	0.036	0.06	0.11	0.21							1.67	1.67	
18R-S	Mean	75.7	0.074		13.5	1.56		0.091	0.046	0.69	4.07	5.38							101.10	101.10	15
	1σ	1.0	0.054		0.2	0.16		0.067	0.036	0.06	0.09	0.11							1.36	1.36	
19	Mean	75.2	**0.123**		**14.1**	1.59			0.050	0.75	4.00	5.19		0.33					101.30	101.23	20
	1σ	0.3	0.064		0.1	0.10			0.016	0.04	0.04	0.07		0.03					0.34	0.34	
20	Mean	74.9	0.062		12.9	1.55		0.092	0.046	0.73	3.90	5.35		0.36					99.88	99.80	34
	1σ	0.4	0.076		0.2	0.18		0.106	0.039	0.09	0.10	0.11		0.04					0.47	0.47	

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
21	Mean	73.4	0.060		13.1	1.53		0.066	0.038	0.73	4.19	**5.75**	**0.115**						98.96	98.96	20
	1σ	0.4	0.020		0.1	0.08		0.022	0.014	0.03	0.07	0.09	0.010						0.41	0.41	
21R	Mean	75.6	0.064		13.0	1.54		0.060	0.040	0.75	4.23	**5.58**	0.010						100.91	100.91	20
	1σ	0.3	0.021		0.1	0.05		0.020	0.010	0.03	0.07	0.08	0.017						0.37	0.37	
22	Mean	74.5	0.081		13.3	1.53		0.059	0.046	0.75	4.12	5.01		0.35					99.75	99.67	22
	1σ	0.4	0.065		0.1	0.08		0.044	0.019	0.04	0.14	0.11		0.06					0.53	0.53	
23	Mean	74.5	0.075		13.2	1.52		0.070	0.046	0.73	4.10	5.19	0.005	0.34	0.18				100.00	99.84	25
	1σ	0.3	0.007		0.2	0.10		0.008	0.018	0.04	0.09	0.10	0.003	0.03	0.02				0.43	0.43	
24	Mean	74.1	0.062		13.3	1.54		0.062	0.036	0.71	3.98	5.04							98.89	98.89	37
	1σ	0.3	0.020		0.1	0.07		0.022	0.010	0.03	0.10	0.08							0.41	0.41	
25	Mean	74.3	0.074		13.0	1.53		0.074	0.028	0.75	3.88	5.20	0.011	0.37					99.25	99.16	40
	1σ	0.3	0.022		0.1	0.09		0.035	0.014	0.04	0.13	0.07	0.013	0.02					0.31	0.31	
26	Mean	74.3	0.067		13.0	1.57		0.036	0.025	0.71	4.12	5.01	0.025						98.86	98.86	20
	1σ	0.6	0.035		0.2	0.07		0.034	0.016	0.04	0.09	0.09	0.046						0.68	0.68	
27	Mean	74.7	0.073		12.9	**1.43**		0.043	0.025	0.72	4.22	5.13	0.027						99.25	99.25	40
	1σ	0.4	0.025		0.2	0.07		0.019	0.012	0.03	0.09	0.06	0.034						0.44	0.44	
28	Mean	74.3	0.074		13.0	1.56		0.065	0.038	0.75	4.00	5.10	0.008	0.32					99.13	99.15	37
	1σ	0.7	0.032		0.4	0.06		0.013	0.029	0.03	0.14	0.07	0.021	0.02					0.73	0.73	

Other methods summary results:

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
XRF (ID3506) - this paper	Mean	73.3	0.080	0.0223	12.9	1.55	0.0022	0.0658	0.058	0.75	4.07	5.06	0.011	> 0.17			0.0977		98.03		7
	1σ	0.3	0.002	0.0006	0.1	0.02	0.0003	0.0003	0.018	0.01	0.04	0.03	0.001				0.0008		0.40		
ICP-MS (ID3506) - this paper	Mean			0.0243			0.0021														7
	1σ			0.0001			0.0001														
ICP-AES (ID3506) - this paper		73.0	0.073	0.036	13.3	1.54	0.0029	0.0726	***0.089***	0.75	***4.31***	5.28	***0.0***						98.9		1
LA-ICP-MS (ID3506) - Kuehn et al. (2009)	Mean			0.0267			0.0018														45
	1σ			0.0025			0.0001														
Loss on ignition (LOI) (ID3506) - this paper	Mean																	0.65			
	1σ																	0.15			
FTIR (ID3506) - S. Kuehn unpublished data	Mean																	0.64			10
	1σ																	0.11			
XRF (HH) 1 - Hunt and Hill (1996)		73.7			13.0	1.57		0.06	0.03	0.76	4.06	5.06							98.3		
XRF (HH) 2 - Hunt and Hill (1996)		74.0	0.08		12.7	1.56		0.08		0.72	4.06	5.18							98.4		
Wet chem (HH) 1 - Hunt and Hill (1996)	Mean										4.06	4.99									
	1σ										0.15	0.13									
Wet chem (HH) 2 - Hunt and Hill (1996)	Mean										3.89	5.01									
	1σ										0.17	0.07									
FTIR (HH) - Humphreys et al. (2006)																		0.72			
Wet chem (UA5831) - A. Stelmach, U. Alberta		73.9	0.10		13.1	***1.72***		0.07	0.07	0.76	4.06	5.04	***0.05***	0.36					99.3		

Mt. Edziza - Sheep Track tephra - Sample 2

EPMA and SEM-EDS summary results:

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
1A	Mean	61.9	0.241		17.6	4.41			0.14	1.17	8.13	5.35	**0.227**	**0.28**					99.35	99.29	21
	1σ	0.4	0.074		0.1	0.11			0.07	0.08	0.13	0.13	**0.092**	0.04					0.63	0.63	
1B	Mean	62.7	0.241		17.6	4.46			0.14	1.17	8.65	5.16	0.227	0.24					100.54	100.48	21
	1σ	0.4	0.074		0.1	0.11			0.07	0.08	0.14	0.12	0.092	0.04					0.64	0.64	
2	Mean	61.8	0.232		17.8	4.52		0.123	0.131	1.01	**7.94**	5.09		0.20					98.77	98.77	39
	1σ	0.7	0.032		0.2	0.14		0.027	0.016	0.05	0.21	0.11		0.02					1.01	1.01	

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
3	Mean	**63.7**	0.249		18.3	4.69	***0.050***	0.143	0.135	1.10	**6.94**	5.27	0.039	0.21					100.74	100.74	19
	1σ	0.3	0.030		0.1	0.15	0.054	0.026	0.020	0.07	0.55	0.08	0.021	0.01					0.28	0.28	
4	Mean	**60.2**	0.211		18.2	4.50		0.126	0.124	1.19	**7.65**	5.24							97.47	97.47	23
	1σ	0.3	0.038		0.2	0.21		0.063	0.033	0.14	0.31	0.11							0.54	0.54	
5	Mean	61.3	0.233	0.163	17.5	4.74	0.006	0.130	0.131	1.10	8.17	5.53		0.22	0.21				99.42	99.34	22
	1σ	0.5	0.053	0.076	0.3	0.14	0.014	0.034	0.022	0.08	0.32	0.09		0.02	0.06				0.87	0.87	
6	Mean	61.9	0.237		18.3	4.82		0.138	0.106	1.09	8.09	5.31							99.99	99.99	21
	1σ	1.0	0.026		0.2	0.36		0.050	0.014	0.11	0.36	0.14							0.94	0.94	
7	Mean	62.0	0.209		18.2	4.29		0.114	0.107	1.13	8.16	5.00		0.20					99.42	99.38	18
	1σ	0.4	0.028		0.3	0.45		0.037	0.020	0.09	0.17	0.13		0.04					0.45	0.45	
8	Mean	61.7	0.236		18.6	**4.88**		0.155	0.121	1.07	**6.00**	5.09	0.021	0.22					98.10	98.05	38
	1σ	0.6	0.017		0.2	0.13		0.029	0.011	0.06	0.21	0.13	0.025	0.02					0.77	0.77	
9	Mean	61.5	0.209		17.9	4.43		0.125	0.124	1.03	8.10	5.06	0.038	0.21					98.60	98.60	23
	1σ	1.0	0.020		0.1	0.06		0.020	0.011	0.05	0.18	0.07	0.022	0.02					1.12	1.12	
10	Mean	**63.6**	0.244		18.2	4.71		0.137	0.115	1.16	***7.80***	5.55	0.038	0.19	0.18	0.021			**101.98**	**101.86**	30
	1σ	0.3	0.025		0.1	0.08		0.023	0.016	0.06	0.18	0.09	0.028	0.01	0.08	0.019			0.44	0.44	
11	Mean	60.8	0.234		**16.7**	4.63		0.149	**0.079**	**0.37**	**6.85**	5.73							**95.57**	**95.57**	18
	1σ	0.5	0.064		0.2	0.17		0.062	0.054	0.11	0.28	0.10							0.81	0.81	
12	Mean	61.9	0.247		18.0	4.64		0.154	0.122	1.19	8.12	5.39	0.031	0.22		0.021			100.04	99.99	20
	1σ	0.3	0.018		0.1	0.18		0.043	0.019	0.08	0.15	0.06	0.019	0.01		0.011			0.44	0.44	
13	Mean	62.0	0.238		18.1	4.66		0.166	0.137	1.12	***7.21***	5.56	0.061						99.20	99.20	25
	1σ	0.6	0.142		0.2	0.45		0.075	0.031	0.13	0.46	0.31	0.056						0.79	0.79	
14	Mean	61.2	0.241		18.0	4.58			0.130	1.09	***7.74***	5.12		0.20					98.29	98.29	28
	1σ	0.4	0.038		0.2	0.09			0.019	0.07	0.17	0.11		0.02					0.48	0.48	
15	Mean	62.3	0.227		17.4	4.46	**0.081**	0.107	0.123	1.13	***7.66***	5.50	***0.079***	0.19	**0.13**				99.38	99.28	25
	1σ	0.4	0.199		0.2	0.27	0.171	0.146	0.039	0.12	0.20	0.21	0.105	0.05	0.06				0.50	0.50	
16	Mean	62.4	0.224		17.5	4.56		0.138	0.138	1.14	***7.17***	5.18	***0.079***	0.22	0.22				98.78	98.78	40
	1σ	0.8	0.170		0.4	0.45		0.164	0.108	0.13	0.37	0.22	0.095	0.05	0.16				0.62	0.62	
16R	Mean	61.6	**0.284**		17.9	4.38		0.141	**0.094**	1.07	8.27	5.34	0.064	0.20	0.18				99.55	99.43	20
	1σ	0.6	0.125		0.5	0.35		0.132	0.050	0.15	0.38	0.18	0.088	0.04	0.28				0.71	0.71	
17	Mean	61.4	0.231		18.2	4.66	***0.030***	0.129	0.133	1.06	8.29	5.38	0.038	0.23		0.01			99.65	99.65	28
	1σ	0.7	0.044		0.2	0.12	0.075	0.023	0.010	0.09	0.25	0.10	0.015	0.02		0.01			1.00	1.00	
18	Mean	60.9	0.226		17.6	4.42		**0.090**	0.100	1.02	***7.21***	5.37							**96.85**	**96.85**	23
	1σ	0.6	0.092		0.2	0.14		0.076	0.050	0.11	0.21	0.20							0.91	0.91	
18R-D	Mean	62.4	0.253		18.1	4.36		0.146	0.136	0.98	8.17	5.51							100.02	100.02	14
	1σ	0.9	0.078		0.4	0.18		0.096	0.045	0.08	0.16	0.16							1.38	1.38	
18R-S	Mean	62.4	0.253		18.1	4.36		0.146	0.136	0.98	8.01	5.52							99.86	99.86	14
	1σ	1.0	0.078		0.3	0.18		0.096	0.045	0.08	0.21	0.11							1.51	1.51	
19	Mean	62.7	0.251		***18.8***	4.63			0.131	1.15	***7.67***	5.36		0.20					100.84	100.79	31
	1σ	0.3	0.092		0.2	0.20			0.021	0.07	0.12	0.13		0.03					0.50	0.50	
20	Mean	62.1	0.222		***17.3***	4.79		0.127	0.104	1.14	***7.68***	5.41		0.21					99.02	98.97	40
	1σ	0.4	0.118		0.2	0.24		0.111	0.060	0.13	0.27	0.12		0.05					0.58	0.58	
21	Mean	60.8	0.239		17.8	4.55		0.132	0.127	1.14	8.11	**5.86**	**0.140**						98.97	98.97	20
	1σ	0.7	0.024		0.1	0.05		0.023	0.012	0.09	0.16	0.12	0.014						0.95	0.95	
21R	Mean	63.4	0.233		18.1	4.45		0.133	0.129	1.11	8.27	5.70	0.041						**101.52**	**101.52**	22
	1σ	0.4	0.031		0.2	0.31		0.021	0.013	0.17	0.21	0.21	0.024						0.52	0.52	
22	Mean	63.2	0.251		18.4	4.45		0.127	0.119	1.04	***7.28***	5.19		0.21					100.26	100.21	18
	1σ	0.3	0.096		0.1	0.10		0.045	0.025	0.05	0.18	0.12		0.04					0.48	0.48	
23	Mean	61.8	0.249		17.9	4.49		0.144	0.114	1.05	8.26	5.34	0.034	0.23	0.21				99.87	99.71	22
	1σ	0.7	0.009		0.2	0.13		0.010	0.012	0.05	0.18	0.09	0.006	0.01	0.02				0.58	0.58	

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
24	Mean	61.9	0.247		18.3	4.53		0.142	0.120	1.09	***7.64***	5.22							99.20	99.20	25
	1σ	0.3	0.025		0.2	0.15		0.025	0.015	0.10	0.18	0.09							0.51	0.51	
25	Mean	61.4	0.231		17.8	4.54		0.135	0.114	1.06	***7.93***	5.33	0.038	0.24					98.83	98.77	40
	1σ	0.5	0.030		0.3	0.17		0.034	0.018	0.04	0.18	0.08	0.016	0.02					0.74	0.74	
26	Mean	62.1	0.227		17.9	4.64		**0.094**	0.108	1.10	8.14	5.07	***0.080***						99.52	99.52	20
	1σ	0.5	0.037		0.4	0.16		0.036	0.029	0.16	0.19	0.10	0.078						0.56	0.56	
27	Mean																				0
	1σ																				
28	Mean	61.3	0.230		17.6	4.67		0.125	0.109	1.05	8.21	5.31	0.047	0.21					98.85	98.85	26
	1σ	0.7	0.032		0.2	0.09		0.013	0.033	0.04	0.19	0.09	0.045	0.02					0.73	0.73	
Other methods summary results:																					
XRF - this paper		60.6	0.236	0.152	17.5	4.60	0.004	0.128	0.11	1.04	8.15	5.26	0.045	> 0.15			0.118		97.9		1
ICP-AES - this paper		61.8	0.244	0.143	17.3	4.55	0.004	0.133	***0.19***	1.07	8.33	5.39	0.03				0.069		99.3		2
Loss on ignition (LOI) - this paper																		0.70			
Laki 1783 AD tephra - Sample 3																					
EPMA and SEM-EDS summary results:																					
1A	Mean	49.8	3.15		13.0	13.7		0.234	5.41	9.70	2.79	**0.54**	**0.481**						98.79	98.79	20
	1σ	0.2	0.11		0.1	0.2		0.084	0.11	0.08	0.12	0.03	0.083						0.42	0.42	
1B	Mean	50.5	3.15		13.0	13.9		0.234	5.41	9.70	2.96	**0.52**	**0.481**						99.78	99.78	20
	1σ	0.2	0.11		0.1	0.2		0.084	0.11	0.08	0.13	0.03	0.083						0.42	0.42	
2	Mean	49.2	2.92		13.2	14.5		0.221	5.01	9.42	***3.10***	0.45		0.02					98.09	98.09	47
	1σ	0.5	0.08		0.2	0.4		0.043	0.14	0.24	0.18	0.03		0.02					0.78	0.78	
3	Mean	50.1	3.08		12.7	14.0	0.026	0.229	5.32	9.51	2.93	0.45	0.354	0.01					98.73	98.73	24
	1σ	0.2	0.05		0.1	0.1	0.038	0.032	0.07	0.08	0.12	0.03	0.031	0.01					0.27	0.27	
4	Mean	**48.3**	**2.69**		13.3	13.7		0.218	**4.99**	**10.32**	2.81	0.47							**96.73**	**96.73**	25
	1σ	0.3	0.08		0.1	0.2		0.083	0.13	0.09	0.16	0.04							0.53	0.53	
5	Mean	49.1	3.09		12.6	14.4		0.251	5.40	9.64	2.85	0.49	0.368	0.02	0.16				98.35	98.35	29
	1σ	0.3	0.12		0.1	0.1		0.026	0.08	0.10	0.15	0.02	0.030	0.01	0.02				0.33	0.33	
6	Mean	49.7	3.07		13.2	14.5		0.252	5.36	9.44	2.87	0.47							98.84	98.84	20
	1σ	0.6	0.06		0.1	0.6		0.040	0.11	0.14	0.19	0.03							0.66	0.66	
7	Mean	49.6	3.01		13.1	14.1		0.235	5.10	9.76	2.90	0.44		0.02					98.26	98.26	16
	1σ	0.3	0.07		0.1	0.4		0.059	0.06	0.11	0.07	0.03		0.02					0.47	0.47	
8	Mean	50.3	3.07		13.2	14.4		0.239	5.44	9.84	2.68	0.44	0.343	0.02					100.02	100.01	39
	1σ	0.6	0.09		0.2	0.4		0.035	0.11	0.11	0.19	0.02	0.051	0.01					0.71	0.71	
9	Mean	49.2	3.00		12.8	13.9		0.226	5.38	9.78	2.75	0.46	0.346	0.02					97.85	97.85	33
	1σ	0.8	0.05		0.1	0.1		0.020	0.05	0.07	0.07	0.02	0.039	0.01					0.73	0.73	
10	Mean	50.3	3.06		13.2	14.5		0.218	5.32	9.85	2.81	0.48	0.353	0.02	0.10	0.09			100.32	100.28	30
	1σ	0.2	0.08		0.3	0.2		0.035	0.07	0.09	0.06	0.03	0.049	0.01	0.07	0.02			0.49	0.49	
11	Mean	49.6	3.29		12.5	14.7		0.261	**4.68**	**10.19**	2.73	0.48							98.42	98.42	18
	1σ	0.4	0.08		0.2	0.4		0.073	0.14	0.14	0.14	0.04							0.71	0.71	
12	Mean	49.5	3.08		13.0	14.3		0.239	5.52	9.99	***3.09***	0.47	0.295	0.02		0.12			99.69	99.69	20
	1σ	0.3	0.04		0.1	0.4		0.045	0.06	0.06	0.08	0.01	0.035	0.01		0.02			0.54	0.54	
13	Mean	49.8	3.09		12.9	14.2		0.212	5.22	9.48	***3.08***	0.47	0.336						98.80	98.80	26
	1σ	0.8	0.29		0.2	0.8		0.073	0.21	0.15	0.26	0.10	0.092						0.75	0.75	
14	Mean	49.2	3.02		12.8	14.1			5.29	9.52	2.77	0.44		0.01					97.18	97.18	31
	1σ	0.3	0.11		0.1	0.2			0.08	0.14	0.11	0.03		0.01					0.46	0.46	
15	Mean	49.8	**3.44**		12.6	14.5	0.046	**0.145**	5.31	9.73	2.75	0.45	0.369	0.02					99.15	99.14	25
	1σ	0.3	0.34		0.2	0.5	0.131	0.102	0.12	0.33	0.10	0.07	0.155	0.03					0.45	0.45	

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
16	Mean	49.6	3.08		12.8	14.2		0.279	5.47	9.62	2.69	0.48	0.369	**0.05**	0.11				98.70	98.70	40
	1σ	0.7	0.37		0.4	0.6		0.205	0.30	0.29	0.21	0.06	0.148	0.04	0.13				0.51	0.51	
16R	Mean	49.7	3.08		12.9	14.7		0.221	5.47	9.49	3.03	0.43	0.323	0.02	0.21				99.49	99.49	28
	1σ	0.7	0.30		0.4	0.6		0.193	0.24	0.38	0.27	0.08	0.130	0.02	0.20				0.49	0.49	
17	Mean	49.6	3.06		13.0	13.9	0.058	0.237	5.29	9.57	2.83	0.47	0.325	0.02		0.09			98.41	98.44	44
	1σ	0.6	0.09		0.2	0.3	0.110	0.026	0.06	0.14	0.07	0.01	0.026	0.01		0.02			0.98	0.98	
18	Mean	**51.0**	3.33		13.5	13.9		0.176	5.56	9.27	3.02	0.46							100.28	100.28	20
	1σ	0.3	0.12		0.1	0.4		0.102	0.17	0.12	0.07	0.05							0.33	0.33	
18R-D	Mean	50.1	3.26		13.3	13.8		**0.153**	5.47	**9.18**	2.93	0.49							98.68	98.68	15
	1σ	0.4	0.09		0.2	0.2		0.077	0.09	0.11	0.17	0.06							0.57	0.57	
18R-S	Mean	50.2	3.26		13.3	13.8		**0.153**	5.47	**9.18**	2.92	0.48							98.71	98.71	15
	1σ	0.2	0.09		0.1	0.2		0.077	0.09	0.11	0.10	0.04							0.47	0.47	
19	Mean	50.1	3.17		**13.7**	14.3			5.54	10.03	2.77	0.48		0.02					100.17	100.16	21
	1σ	0.3	0.18		0.1	0.3			0.10	0.10	0.09	0.02		0.01					0.48	0.48	
20	Mean	49.8	3.13		12.5	14.6		0.232	**5.12**	9.67	2.74	0.48		0.03					98.41	98.41	40
	1σ	0.4	0.21		0.2	0.4		0.132	0.12	0.18	0.15	0.08		0.05					0.59	0.59	
21	Mean	**48.5**	3.06		12.9	14.1		0.230	5.36	9.73	3.04	**0.52**	0.384						97.85	97.85	20
	1σ	0.3	0.05		0.1	0.1		0.026	0.05	0.08	0.07	0.02	0.008						0.44	0.44	
21R	Mean	**51.1**	3.06		13.0	14.0		0.237	5.46	9.87	3.12	0.50	0.343						**100.60**	**100.60**	23
	1σ	0.3	0.04		0.1	0.2		0.028	0.08	0.10	0.09	0.03	0.045						0.45	0.45	
22	Mean	49.3	3.13		12.9	13.7		0.229	**5.15**	9.57	***3.09***	0.45		0.01					97.51	97.50	19
	1σ	0.4	0.19		0.1	0.5		0.048	0.08	0.18	0.17	0.03		0.03					0.45	0.45	
23	Mean	49.7	3.11		13.1	14.3		0.239	5.34	9.85	2.90	0.46	0.307	0.02	0.06				99.37	99.27	23
	1σ	0.4	0.04		0.3	0.4		0.011	0.08	0.12	0.10	0.03	0.010	0.00	0.01				0.59	0.59	
24	Mean	49.6	3.06		13.2	14.2		0.253	5.32	9.61	2.87	0.45							98.48	98.48	31
	1σ	0.4	0.08		0.2	0.3		0.028	0.09	0.16	0.12	0.02							0.73	0.73	
25	Mean	49.3	3.09		12.6	14.2		0.229	5.34	9.86	2.76	0.47	0.358	0.02					98.29	98.28	40
	1σ	0.3	0.07		0.1	0.3		0.044	0.11	0.11	0.13	0.02	0.021	0.01					0.59	0.59	
26	Mean	49.6	3.04		13.3	14.0		0.183	5.42	9.70	2.99	0.44	0.320						98.96	98.96	20
	1σ	0.9	0.18		0.4	0.3		0.052	0.18	0.29	0.08	0.03	0.123						1.25	1.25	
27	Mean	49.9	2.98		12.8	14.0		**0.160**	5.45	9.57	3.03	0.45	0.337						98.64	98.64	40
	1σ	0.5	0.16		0.4	0.1		0.035	0.09	0.09	0.10	0.02	0.062						0.57	0.57	
28	Mean	49.5	3.12		12.9	14.1		0.224	5.39	9.87	2.76	0.46	0.347	0.02					98.70	98.71	44
	1σ	0.4	0.04		0.2	0.2		0.020	0.08	0.09	0.10	0.03	0.078	0.01					0.48	0.48	

Old Crow tephra

EPMA and SEM-EDS summary results:

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Totals (Cl,F=O adjusted)	n
1A	Mean	71.5			12.4	1.54				1.43	3.79	3.68		**0.37**					95.34	94.61	23
	1σ	0.7			0.1	0.07				0.06	0.11	0.07		0.04					0.96	0.96	
1B	Mean	72.4			12.4	1.56				1.43	4.03	3.55		0.32					96.38	95.66	23
	1σ	0.7			0.1	0.07				0.06	0.12	0.06		0.03					0.97	0.97	
2	Mean	71.6	0.289		12.4	1.62		0.052	0.266	1.36	3.32	3.40		0.26					94.50	94.50	31
	1σ	0.8	0.036		0.2	0.06		0.024	0.031	0.06	0.23	0.09		0.04					1.17	1.17	
6	Mean	73.0	0.291		12.7	1.59		0.048	0.263	1.36	3.72	3.55							96.52	96.52	20
	1σ	0.9	0.024		0.2	0.21		0.026	0.010	0.06	0.18	0.17							1.28	1.28	
8	Mean	72.5	0.301		**12.9**	1.69		0.042	0.292	1.45	**3.01**	3.39	0.052	0.27					95.83	95.77	29
	1σ	0.7	0.024		0.2	0.07		0.030	0.021	0.05	0.21	0.12	0.026	0.02					0.97	0.97	
9	Mean	72.0	0.278		12.4	1.59		0.057	0.281	1.40	3.67	3.46	0.038	0.26					95.41	95.41	27
	1σ	1.1	0.023		0.2	0.06		0.016	0.009	0.04	0.12	0.06	0.028	0.02					1.30	1.30	

Lab or Description		SiO_2	TiO_2	ZrO_2	Al_2O_3	FeO_T	BaO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Cl	F	SO_2	Other Traces	OH, H2O	Reported Totals	Sum (Cl,F=O adjusted)	n
10	Mean	73.2	0.289		12.7	1.65		0.052	0.266	1.43	3.64	3.64	0.036	0.25	0.13	0.012			97.28	97.17	29
	1σ	1.1	0.037		0.2	0.05		0.023	0.020	0.05	0.13	0.07	0.028	0.02	0.09	0.011			1.45	1.45	
16	Mean	73.9	**0.381**		12.4	**1.82**		***0.094***	0.281	1.44	3.45	3.52	***0.088***	0.28	0.19				97.76	97.76	20
	1σ	0.6	0.210		0.4	0.39		0.109	0.119	0.12	0.25	0.16	0.109	0.06	0.14				0.73	0.73	
16R	Mean	72.9	0.338		12.6	1.68		**0.167**	**0.315**	1.43	3.64	3.56	***0.074***	0.27	0.22				97.05	97.05	20
	1σ	0.9	0.174		0.4	0.26		0.222	0.090	0.13	0.26	0.15	0.069	0.05	0.30				0.83	0.83	
18	Mean	72.6	0.353		12.7	1.56		0.052	0.280	**1.31**	3.48	3.70							95.95	95.95	20
	1σ	0.9	0.061		0.2	0.13		0.054	0.051	0.07	0.12	0.08							1.20	1.20	
18R-D	Mean	72.0	0.349		12.6	1.60		0.047	0.268	**1.29**	3.74	3.71							95.61	95.61	15
	1σ	1.2	0.056		0.3	0.12		0.038	0.046	0.05	0.11	0.13							1.74	1.74	
18R-S	Mean	72.0	0.349		12.6	1.60		0.047	0.268	**1.29**	3.68	3.69							95.47	95.47	15
	1σ	1.1	0.056		0.2	0.12		0.038	0.046	0.05	0.11	0.12							1.55	1.55	
20	Mean	72.5	0.323		12.2	1.67		***0.112***	0.269	1.41	3.38	3.70		0.29					95.92	95.86	40
	1σ	0.7	0.111		0.2	0.18		0.086	0.066	0.09	0.20	0.12		0.05					0.98	0.98	
21	Mean	**69.9**	0.290		12.4	1.58		0.058	0.275	1.39	3.78	**3.99**	**0.144**						93.78	93.78	20
	1σ	0.9	0.022		0.1	0.05		0.023	0.021	0.05	0.15	0.07	0.012						1.14	1.14	
21R	Mean	73.8	0.300		12.6	1.58		0.056	0.281	1.42	3.91	3.87	0.037						97.87	97.87	22
	1σ	0.8	0.021		0.1	0.04		0.019	0.014	0.05	0.17	0.09	0.025						1.10	1.10	
25	Mean	72.8	0.289		12.4	1.62		0.058	0.268	1.43	3.68	3.66	0.027	0.30					96.56	96.49	40
	1σ	0.7	0.033		0.2	0.11		0.031	0.015	0.04	0.16	0.09	0.013	0.02					1.01	1.01	
26	Mean	73.9	0.291		12.8	1.65		0.036	0.267	1.43	3.61	3.48	***0.110***						97.65	97.65	20
	1σ	0.7	0.045		0.3	0.10		0.030	0.021	0.05	0.16	0.07	0.081						0.59	0.59	
28	Mean	72.4	0.295		12.4	1.64		0.052	0.282	1.43	3.78	3.38	0.034	0.25					95.81	95.81	24
	1σ	0.9	0.027		0.3	0.05		0.014	0.042	0.04	0.18	0.09	0.059	0.02					1.17	1.17	
EPMA - Preece et al. (2011) - 27 samples	Mean	71.9	0.286		12.4	1.64		0.057	0.277	1.42	3.55	3.52		0.27					95.35		924
	1σ	0.3	0.080		0.1	0.08		0.040	0.030	0.07	0.15	0.11		0.04					1.34		
Other methods summary results:																					
XRF - this paper		71.6	0.298	0.0323	12.6	1.77	0.105	0.059	0.299	1.43	3.66	3.65	0.042	> 0.19		> 0.007	0.0605		95.70		2
ICP-AES - this paper		71.7	0.304	0.0343	12.7	1.71	0.102	0.063	***0.355***	1.42	3.58	3.52	0.036				0.0356		95.56		1
Loss on ignition (LOI) - this paper																		4.12			1
ICP-MS - Preece et al. (2011) - 27 samples	Mean			0.0338			0.108														27
	1σ			0.0008			0.002														
INAA - Kaufman et al. (2001)				0.0301			0.099														2
INAA - Preece et al. (2000)							0.119														1
INAA - Preece et al. (1999), 8 samples							0.098														
SIMS - Begét and Keskinen (2003)	Mean			0.0395			***0.139***														
	1σ			0.0004			0.003														
LA-ICP-MS - Westgate et al. (1994)	Mean			0.0317			0.107														54
sample UT613 1991	1σ			0.0032			0.010														
LA-ICP-MS - Westgate et al. (1994)	Mean			0.0315			0.108														122
sample UT613 1992	1σ			0.0050			0.009														
LA-ICP-MS - Westgate et al. (1994)	Mean			0.0354			0.107														49
sample UT 502 1991	1σ			0.0038			0.013														
LA-ICP-MS - Westgate et al. (1994)	Mean			0.0326			0.107														7
sample UT 502 1992	1σ			0.0019			0.007														
LA-ICP-MS - Pearce et al. (2004)	Mean			0.0278			0.097														16
sample UT1434	1σ			0.0017			0.006														
LA-ICP-MS - Pearce et al. (2004)	Mean			0.0346			0.109														13
sample UT1407	1σ			0.0032			0.005														
LA-ICP-MS - Pearce et al. (2004)	Mean			0.0358			0.108														10
sample UT815	1σ			0.0030			0.006														

Table 4. Instrument type, analytical conditions, and software used for each data contribution.

Lab	Type	Model		Voltage keV	Current nA	Diameter µm	Raster µm	Automation Software	Matrix Corrections
1	SEM	JEOL	JSM-840A	15	0.8	17		Moran Scientific	ZAF
2	EPMA	JEOL	JXA-8900	15	6	10		JEOL	ZAF
3	EPMA	CAMECA	SX 100	15	20	15			
4	SEM	JEOL	JEM-6500F	15	5		4x5	INCA (Oxford)	
5 - Lipari	EPMA	Cameca	SX-50	15	25	20		Cameca	PAP
5 - Edziza	EPMA	Cameca	SX-50	15	10	10		Cameca	PAP
5 - Laki	EPMA	Cameca	SX-50	15	25	15		Cameca	PAP
6	EPMA	JEOL	JXA-8900R	13	10		5	Probe for EPMA	Phi Rho Z
7	EMPA	JEOL	JXA-8600	15	10	15		Voyager	ZAF
8	EPMA	Cameca	SX-50						
9	EPMA	Cameca	SX-100	15	9	10		Cameca	Phi Rho Z
10	EPMA	CAMECA	SX100	15	10	20		Peaksight	X-Phi
11	SEM	JEOL	SEM-6390	15	0.3	10	20		ZAF
12	EMPA	JEOL	JXA 8900	15	6	5			CITZAF
13	EPMA	Cameca	SX 51	15	6	5		Probe for EPMA	Phi Rho Z
14	EPMA	JEOL	JXA 8500F	15	12	8		Probe for EPMA	Phi Rho Z
15	EPMA	CAMECA	SX50	15	6	10			PAP
16	EPMA	JEOL	JXA-8500F	12	1	2		JEOL	oxide ZAF
17	EPMA	Cameca	SX100	15	10	10		Probe for EPMA	Phi Rho Z
18	SEM	JEOL	JSM-5310	15	1		3	LINK/ISIS (Oxford)	ZAF
18R	SEM	JEOL	JSM-5310	15	1		5	LINK/ISIS (Oxford)	ZAF
19	EPMA	Cameca	SX-50	15	10	10		Probe for EPMA	Phi Rho Z
20	SEM	JEOL	5310	15			10	INCA (Oxford)	ZAF
21	EPMA	JEOL	JXA-8800R	15	10	2	10	JEOL	ZAF
21R	EPMA	JEOL	JXA-8800R	15	10	10		JEOL	ZAF
22	EPMA	Cameca	SX-50	15	6	10		Probe for EPMA	ZAF
23	EPMA	Cameca	SX100	15	0.7, 2, 80	5 and 8		PeakSight	X-Phi
24	EMPA	JEOL	8800L	15	10.05 -9	10	10		ZAF
25	EPMA	JEOL	8600	15	6	10		SAMx	PAP
26n	EPMA	JEOL	JXA-8900R	15	5	5			
27n	EPMA	JEOL	JXA-8900R	15	10	10			
28n	EPMA	ARL	SEMQ	15	15	10		Probe for EPMA	Phi Rho Z

Table 5. Primary reference materials used for each element in each data contribution and any secondary standards also used.

Lab	Si	Ti	Al	Fe	Ba	Mn	Mg	Ca	Na
1 A	Average of several minerals	Rutile	Average of several minerals	Almandine		Bustamite	Average of several minerals	Average of several minerals	Albite
1 B	KN-18 obsidian	Rutile	KN-18 obsidian	KN-18 obsidian		Bustamite	Average of several minerals	Average of several minerals	KN-18 obsidian
2	Lipari obsidian	Ilmenite	Lipari obsidian	Pyrope		Willemite	Pyrope	Diopside	Lipari obsidian
3	Orthoclase	Rutile	Orthoclase	Fe_2O_3	Barite	Rhodonite	Periclase	Wollastonite	Albite
4	Orthoclase	TiO_2	Orthoclase	Rhodonite		Rhodonite	MgO	$CaSO_4$	Albite
5	MM3 obsidian	Rutile	MM3 obsidian	Hematite	Barite	Rhodonite	Diopside	Diopside	Albite
6	Anorthite (NMNH 137041)	Hornblende, Kakanui (NMNH 143965)	Anorthite (NMNH 137041)	Hornblende, Kakanui (NMNH 143965)		Manganite (NMNH 114887)	Hornblende, Kakanui (NMNH 143965)	Anorthite (NMNH 137041)	Hornblende, Kakanui (NMNH 143965)
7	Los Posos Rhyolite	Rutile	Los Posos Rhyolite	Fayalite (synthetic)		Rhodonite	San Carlos Olivine	Wollastonite	Amelia Albite
8									
9	Lipari obsidian	Kaersutite, Saudia Arabia (H 131928)	Lipari obsidian	Kaersutite, Saudia Arabia (H 131928)		Willemite	Kaersutite, Saudia Arabia (H 131928)	Kaersutite, Saudia Arabia (H 131928)	Lipari obsidian
10	Orthoclase (Zircon for basalt)	Ilmenite	Anorthoclase	Magnetite		MnO	Forsteritic olivine	Apatite, Beeson	Albite
11	Quartz	Rutile	Corundum	Hematite		Manganese	Periclase	Wollastonite	Albite
12	Rhyolite	VG-A99	Rhyolite	VG-A99		Rhodonite	VG-A99	VG-A99	Rhyolite
13 Lipari	Corning Haplogranite (dry)	Rutile, Mineas Gerais (UCLA)	Corning Haplogranite (dry)	Hematite, Okahandja		Tephroite (synthetic)	Olivine, Kilbourne Hole	Wollastonite, Diana	Corning Haplogranite (dry)
13 Edziza	NIST K412	Rutile, Mineas Gerais (UCLA)	NIST K412	Hematite, Okahandja		Tephroite (synthetic)	Olivine, Kilbourne Hole	Wollastonite, Diana	Na-rich andesite (synthetic, Hanchar)
13 Laki	NIST K412	Rutile, Mineas Gerais (UCLA)	USGS BHVO-2G	Hematite, Okahandja		Tephroite (synthetic)	NIST K412	NIST K412	Corning Haplogranite (dry)
14	Lipari obsidian	Sphene #1A (Taylor)	Lipari obsidian	VG A-99 (NMNH 113498/1)			NIST K-411	NIST K-411	Lipari obsidian
15	Wollastonite	Rutile	Sapphire (synthetic)	Hematite	Barite	Rhodonite	Olivine	Wollastonite	Oligoclase
16	Wollastonite	Rutile	Corundum	Hematite		Tephroite	Periclase	Wollastonite	Albite
17	USGS BIR-1G	TiO2 synthetic	Nepheline	Magnetite (U.C. 3380)	BaF_2	MnO synthetic	MgO synthetic	Diopside (Chesterman)	Nepheline
18	Wollastonite	TiO_2	Al_2O_3	Forsteritic olivine		$MnTiO_3$	MgO	Wollastonite	Albite
19	Wollastonite	Ilmenite (68ILM)	Orthoclase OR10 CT (Taylor)	Hematite			MgO	Wollastonite	Albite, Tiburon
20	Albite	Rutile	Albite	Almandine		Rhodonite	Dipside	Wollastonite	Albite
21	SiO_2	TiO_2	Al_2O_3	Fe_2O_3		MnO	MgO	Wollastonite	Albite
22	Lipari obsidian	TiO_2 (syntetic, ASTIMEX)	Lipari obsidian	Pyrope, Kakanui (USNM 143968)		Bustamite, Broken Hill (ASTIMEX)	Pyrope, Kakanui (USNM 143968)	Bustamite, Broken Hill (ASTIMEX)	Lipari obsidian
23	Wollastonite	Rutile	USGS BIR-1G	Fayalite	Barite	Mn	Spinel	Wollastonite	Jadeite
24	GSC glass (Corning)	TiO_2	GSC glass (Corning)	GSC glass (Corning)		Mn_2O_3	GSC glass (Corning)	GSC glass (Corning)	GSC glass (Corning)
25	Wollastonite	Rutile	Jadite	Hematite		Fowlerite	Periclase	Wollastonite	Jadeite

Lab	K	P	Cl	F	S	Zr	O	Secondary
1 A	Sanidine	Apatite	Tugtupite					
1 B	KN-18 obsidian	Apatite	KN-18 obsidian					
2	Lipari obsidian		Tugtupite					Lipari obsidian, Old Crow tephra
3	Orthoclase	Apatite	Tugtupite	Fluorite				
4	Orthoclase							Lipari obsidian
5	MM3 obsidian	Apatite	Tugtupite	Fluorite		Cubic zirconia	MM3 obsidian	MPI-DING KL2, MPI-DING ML3B, USGS BCR2
6	Microcline (NMNH 143966)							VG-568 (NMNH 72854), VG-2 (NMNH 111240/52), VG-A99 (NMNH 113498/1)
7	Orthoclase		Durango Apatite					Los Posos Rhyolite
8								
9	Lipari obsidian	Apatite	Tugtupite					Lipari obsidian, Old Crow tephra
10	Orthoclase	Apatite, Beeson	Scapolite	Phlogopite	Scapolite			VG-568 (NMNH 72854), VG-2 (NMNH 111240/52), KN-18, KE-12
11	K-Feldspar							
12	Rhyolite	VG-A99	Scapolite		Scapolite			
13 Lipari	NIST K412	Apatite, Durango (Wards)						
13 Edziza	K-rich andesite (synthetic, Hanchar)	Apatite, Durango (Wards)						
13 Laki	K-rich andesite (synthetic, Hanchar)	Apatite, Durango (Wards)						
14	Lipari obsidian		KCl					
15	Leucite	Apatite	Vanadinite	LiF				
16	Adularia	Apatite	Sodalite	Fluorite				Obsidian, JB-1 glass
17	Orthoclase MAD-10	$Ca_{10}(PO_4)_6Cl_2$	$Ca_{10}(PO_4)_6Cl_2$					NIST K-412, NIST K-411
18	K-Feldspar							
19	Orthoclase OR10 CT (Taylor)		Scapolite (USNM R6600-1)					Old Crow tephra, KN-18, VG-2 (USNM 111240/52), Indian Ocean basalt (USNM 113716)
20	Orthoclase		NaCl - Natural					
21	K-Feldspar	KTP - $KTiOPO_4$						
22	Lipari obsidian		Tugtupite, Greenland (ASTIMEX)					Old Crow tephra
23	Orthoclase	Apatite	Halite	RbMn-Fluoride				USGS BHVO-2G , Lipari obsidian
24	GSC glass (Corning)							RLS-132 obsidian
25	Othoclase	$NdPO_4$	BFCl					MPI-DING glasses
26, 27	Adularia	Apatite	Sodalite	Fluorite				Obsidian, JB-1 glass
28	Sanidine	Apatite, Wilberforce	Tugtupite					Lipari, Sheep Track tephra, BHVO-2G, ATHO-G, VG-A99, VG-2

Abbreviations: H - Harvard; MPI-DING - Max-Planck-Institut für Chemie, Geochemistry Division; NMNH - U.S. National Museum of Natural History (Smithsonian); NIST - U.S. National Institute of Standards and Technology; UCLA - University of California, Los Angeles; USGS - U.S. Geological Survey

Table 6. Spectrometer assignments and analytical sequence for each element in each contribution. The data format is as follows: spectrometer number / sequence on spectrometer / analyzing crystal (or EDS).

Lab	Si	Ti	Al	Fe	Ba	Mn	Mg	Ca	Na	K	P	Cl	F	S
1	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		
2	4 / 1 / TAP	1 / 2 / PET	4 / 2 / TAP	5 / 1 / LIFH		5 / 2 / LIFH	2 / 2 / TAP	3 / 1 / PET	2 / 1 / TAP	1 / 1 / PET		3 / 2 / PET		
3	5 / 2 / TAP	4 / 3 / PET	5 / 3 / TAP	2 / 2 / LIF	4 / 2 / PET	2 / 1 / LIF	5 / 4 / TAP	3 / 2 / PET	5 / 1 / TAP	3 / 1 / PET	3 / 3 / PET	4 / 1 / PET	1 / 1 / PC1	
4	2 / 1 / EDS	1 / 3 / PET	2 / 1 / EDS	2 / 1 / EDS		1 / 4 / LIF	1 / 2 / TAP	2 / 1 / EDS	1 / 1 / TAP	2 / 1 / EDS				
5 - Lip	2 / 2 / TAP	4 / 1 / LIF	2 / 3 / TAP	4 / 3 / LIF	3 / 4 / PET	4 / 2 / LIF	2 / 4 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET	3 / 5 / PET	3 / 3 / PET	1 / 1 / PC1	
5 - Edz	2 / 2 / TAP	4 / 1 / LIF	2 / 3 / TAP	4 / 3 / LIF	3 / 4 / PET	4 / 2 / LIF	2 / 4 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET		3 / 3 / PET	1 / 1 / PC1	
5 - Laki	2 / 2 / TAP	4 / 1 / LIF	2 / 3 / TAP	4 / 3 / LIF	3 / 4 / PET	4 / 2 / LIF	2 / 4 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET	3 / 5 / PET	3 / 3 / PET	1 / 1 / PC1	
6	2 / 1 / TAP	4 / 2 / PETJ	2 / 2 / TAP	3 / 1 / LIF		3 / 2 / LIF	1 / 2 / TAP	5 / 1 / PETH	1 / 1 / TAP	4 / 1 / PETJ				
7	1 / 2 / TAP	3 / 2 / PET	1 / 3 / TAP	4 / 1 / LIF		4 / 2 / LIF	1 / 4 / TAP	2 / 1 / PET	1 / 1 / TAP	3 / 1 / PET		2 / 2 / PET		
8														
9	6 / 1 / EDS	5 / 1 / LPET	1 / 2 / LTAP	3 / 1 / LLIF		3 / 2 / LLIF	1 / 3 / LTAP	2+4 / 2 / PET+PET	1 / 1 / LTAP	2+4 / 1 / PET+PET	2+4 / 3 / PET+PET	5 / 2 / LPET		
10	2 / 5 / TAP	1 / 6 / PET	2 / 4 / TAP	3 / 2 / LLIF		3 / 1 / LLIF	2 / 3 / TAP	1 / 5 / PET	2 / 1 / TAP	1 / 4 / PET	1 / 1 / PET	1 / 3 / PET	2 / 2 / TAP	1 / 2 / PET
11	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS				
12	4 / 1 / TAP	5 / 3 / PETH	4 / 2 / TAP	3 / 1 / LIF		3 / 2 / LIF	1 / 2 / TAPH	2 / 3 / PETH	1 / 1 / TAPH	2 / 2 / PETH	2 / 1 / PETH	5 / 2 / PETH		5 / 1 /
13	4 / 1 / TAP	5 / 3 / LIF	4 / 2 / TAP	5 / 1 / LIF		5 / 2 / LIF	1 / 2 / TAP	3 / 2 / PET	1 / 1 / TAP	3 / 1 / PET	3 / 3 / PET			
14	1 / 1 / TAP	2 / 2 / PETJ	1 / 2 / TAP	3 / 1 / LIFH			5 / 2 / TAP	2 / 1 / PETJ	5 / 1 / TAP	4 / 1 / PETJ		4 / 2 / PETJ		
15	1 / 1 / TAP	3 / 3 / LIF	1 / 2 / TAP	3 / 1 / LIF	3 / 4 / LIF	3 / 2 / LIF	1 / 3 / TAP	2 / 2 / PET	4 / 1 / PC0	2 / 1 / PET	2 / 4 / PET	2 / 3 / PET	4 / 2 / PC0	
16	1 / 1 / TAP	2 / 1 / PETJ	1 / 2 / TAP	5 / 1 / LIFH		2 / 2 / PETJ	3 / 2 / TAPH	4 / 2 / PETH	3 / 1 / TAPH	4 / 1 / PETH	5 / 2 / PETH	4 / 3 / PETH	3 / 3 / TAPH	
16R	1 / 1 / TAP	2 / 1 / PETJ	1 / 2 / TAP	5 / 1 / LIFH		2 / 2 / PETJ	3 / 2 / TAPH	4 / 2 / PETH	3 / 1 / TAPH	4 / 1 / PETH	5 / 2 / PETH	4 / 3 / PETH	3 / 3 / TAPH	
17	5 / 1 / TAP	2 / 1 / LLIF	4 / 2 / TAP	1 / 2 / LIF	2 / 4 / LLIF	2 / 2 / LLIF	5 / 2 / TAP	1 / 1 / LIF	4 / 1 / TAP	3 / 1 / LPET	3 / 3 / LPET	3 / 4 / LPET		3 / 2 /
18	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS			
18R-D	1 / 1 / EDS	1 / 2 / EDS	1 / 1 / EDS	1 / 2 / EDS		1 / 2 / EDS	1 / 2 / EDS	1 / 2 / EDS	1 / 1 / EDS	1 / 1 / EDS				
18R-S	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS			
19	4 / 2 / TAP	3 / 1 / LIF	4 / 1 / TAP	3 / 2 / LIF			2 / 2 / TAP	1 / 3 / PET	2 / 1 / TAP	1 / 2 / PET		1 / 1 / PET		
20	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS	1 / 1 / EDS		1 / 1 / EDS		
21	1 / 2 / TAP	3 / 3 / PET	1 / 1 / TAP	4 / 1 / LIF		4 / 2 / LIF	2 / 2 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET	1 / 3 / TAP			
21R	1 / 1 / TAP	3 / 4 / PET	1 / 2 / TAP	4 / 1 / LIF		4 / 2 / LIF	2 / 2 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET	3 / 3 / PET			
22	1 / 2 / TAP	2 / 3 / LIF	1 / 3 / TAP	2 / 1 / LIF		2 / 2 / LIF	1 / 4 / TAP	3 / 3 / PET	1 / 1 / TAP	3 / 1 / PET		3 / 2 / PET		
23	1 / 2 / TAP	2 / 3 / LLIF	1 / 1 / TAP	2 / 1 / LLIF		2 / 2 / LLIF	5 / 2 / LTAP	3+4 / 2 / LPET+PET	5 / 1 / LTAP	3+4 / 1 / LPET+PET	3+4 / 4 / LPET+PET	3+4 / 3 / LPET+PET	1+5 / 3 / TAP+LTAP	
24	3 / 1 / TAP	2 / 1 / LIFH	3 / 2 / TAP	4 / 1 / LIF		2 / 2 / LIFH	1 / 2 / TAP	5 / 2 / PETJ	1 / 1 / TAP	5 / 1 / PETJ				
25n	1 / 1 / TAP	3 / 4 / PET	1 / 2 / TAP	4 / 2 / LIF		4 / 1 / LIF	2 / 3 / TAP	3 / 2 / PET	2 / 1 / TAP	3 / 1 / PET	2 / 2 / TAP	3 / 3 / PET		
26n	1 / 1 / TAP	4 / 1 / PETJ	1 / 2 / TAP	3 / 3 / LIFH		4 / 2 / PETJ	2 / 2 / TAPH	3 / 2 / PETH	2 / 1 / TAPH	3 / 1 / PETH	4 / 3 / PETJ			
27n	1 / 1 / TAP	4 / 1 / PETJ	1 / 2 / TAP	3 / 3 / LIFH		4 / 2 / PETJ	2 / 2 / TAPH	3 / 2 / PETH	2 / 1 / TAPH	3 / 1 / PETH	4 / 3 / PETJ			
28n	1 / 1 / PET	1 / 3 / PET	2 / 1 / RAP	3 / 2 / LIF		3 / 3 / LIF	2 / 2 / RAP+TAP	3 / 1 / LIF	4 / 1 / TAP	1 / 2 / PET	1 / 5 / PET	1 / 4 / PET		

Abbreviations and notes: R appended to the lab number indicates a revised submission (round 2); n appended to the lab number indicates a new submission from a lab that had already received a copy of the report from round 1; Lab 5 also analyzed for Zr (2 / 5 / TAP) and O (1 / 2 / PC1).

Table 7. Peak and background analysis timing in seconds for each element in each contribution. The data format is as follows: peak / background + / background -

Lab	Si	Ti	Al	Fe	Ba	Mn	Mg	Ca	Na	K	P	Cl	F	S
1	100 / - / -	100 / - / -	100 / - / -	100 / - / -		100 / - / -	100 / - / -	100 / - / -	100 / - / -	100 / - / -	100 / - / -	100 / - / -		
2	20 / 10 / -	20 / 10 / 10	40 / 18 / -	30 / 10 / 10		20 / 14 / -	35 / 23 / -	20 / 10 / 10	20 / 10 / -	20 / 10 / 10		20 / 10 /		
3	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	20 / 10 / 10	20 / 10 /	20 / 10 / 10	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	30 / 15 /	20 / 10 /	20 / 10 /	
4	120 / - / -	30 / 5 / 5	120 / - / -	120 / - / -		20 / 5 / 5	20 / 5 / 5	120 / - / -	10 / 1 / 1	120 / - / -				
5 - Lip	15 / 7.5 / 7.5	25 / 12.5 / 12.5	15 / 7.5 / 7.5	25 / 12.5 / 12.5	20 / 10 / 10	25 / 12.5 / 12.5	20 / 10 / 10	20 / 10 / 10	4 / 4 / 4	15 / 7.5 / 7.5	20 / 10 / 10	20 / 10 / 10	20 / - / 10	
5 - Edz	15 / 7.5 / 7.5	25 / 12.5 / 12.5	15 / 7.5 / 7.5	25 / 12.5 / 12.5	20 / 10 / 10	25 / 12.5 / 12.5	20 / 10 / 10	20 / 10 / 10	4 / 4 / 4	15 / 7.5 / 7.5		20 / 10 / 10	20 / - / 10	
5 - Laki	15 / 7.5 / 7.5	25 / 12.5 / 12.5	15 / 7.5 / 7.5	25 / 12.5 / 12.5	20 / 10 / 10	25 / 12.5 / 12.5	20 / 10 / 10	20 / 10 / 10	4 / 4 / 4	15 / 7.5 / 7.5	20 / 10 / 10	20 / 10 / 10	20 / - / 10	
6														
7	10 / 10 / 10	30 / 30 / 30	10 / 10 / 10	30 / 30 / 30		30 / 30 / 30	30 / 30 / 30	30 / 30 / 30	10 / 10 / 10	30 / 30 / 30		30 / 30 /		
8														
9	25 / - / -	35 / 15 / 15	16 / 5 / -	32 / 18 / -		42 / 34 / -	34 / 17 / 17	20 / 6 / 6	6 / 3 / 3	20 / 6 / 6	22 / 9 / 9	27 / 11 /		
10	20 / 10 / 10	20 / 10 / -	20 / 10 / 10	20 / 10 / -		20 / 10 / 10	20 / 10 / 10	20 / 10 / -	20 / 10 / 10	20 / 10 / -	20 / 10 /	40 / 20 /	60 / 30 / -	40 / 20 /
11														
12	20 / 10 / 10	30 / 15 / 15	20 / 10 / 10	20 / 10 / 10		40 / 20 / 20	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	30 / 15 / 15	20 / 10 /	30 / 15 /		30 / 15 /
13	10T / 5 / 5	10 / 5 / 5	10 / 5 / 5	10T / 5 / 5		10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10T / 5 / 5	10T / 5 / 5	10 / 5 / 5			
14	10 / 10 / 10	10 / 10 / 10	10 / 10 / 10	40 / 20 / 20			10 / 10 / 10	10 / 10 / 10	10 / 10 / 10	10 / 10 / 10		10 / 10 /		
15	10 / 5 / -	6 / 3 / -	10 / 5 / -	6 / 3 / -	6 / 3 / -	6 / 3 / -	10 / 5 / -	6 / - / 3	6 / 3 / -	6 / 3 / -	6 / - / 3	6 / 3 / -	20 / - / 10	
16	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5		10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	20 / 5 / 5	
16R	10 / 10 / 10	10 / 10 / 10	10 / 10 / 10	10 / 10 / 10		10 / 10 / 10	10 / 10 / 10	10 / 10 / 10	6 / 6 / 6	10 / 10 / 10	10 / 10 /	10 / 10 /	10 / 10 /	
17	40 T / M	20 / 12 / 12	40 / M	120 / M	30 / 30 / -	20 / 20 / 20	60 / M	90 / M	60 T / M	40 / 20 / 20	20 / 20 /	20 / 20 /		20 / 20 /
18	150 / - / -	150 / - / -	150 / - / -	150 / - / -		150 / - / -	150 / - / -	150 / - / -	150 / - / -	150 / - / -	150 / - / -			
18R-D	30 / - / -	150 / - / -	30 / - / -	150 / - / -		150 / - / -	150 / - / -	150 / - / -	30 / - / -	30 / - / -				
18R-S	150 / - / -	150 / - / -	150 / - / -	150 / - / -		150 / - / -	150 / - / -	150 / - / -	150 / - / -	150 / - / -	150 / - / -			
19	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10			20 / 10 / 10	10 / 5 / 5	20 / 10 / 10	10 / 5 / 5		10 / 5 / 5		
20	50 / - / -	50 / - / -	50 / - / -	50 / - / -		50 / - / -	50 / - / -	50 / - / -	50 / - / -	50 / - / -		50 / - / -		
21	20 / 10 / 10	30 / 10 / 10	20 / 10 / 10	20 / 10 / 10		20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	60 / 20 /			
21R	30 / 10 / 10	30 / 15 / 15	30 / 30 / 30	35 / 15 / 15		30 / 10 / 10	45 / 20 / 20	15 / 5 / 5	10 / 10 / 10	15 / 5 / 5	20 / 10 /			
22	20 / 16 / 16	20 / 20 / 20	20 / 16 / 16	50 / 50 / 50		20 / 20 / 20	20 / 20 / 20	20 / 20 / 20	20 / 16 / 16	20 / 20 / 20		20 / 20 /		
23	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	40 / 20 / 20		50 / 25 /	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 /	20 / 10 /	60 / 50 /	
24	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	20 / 10 / 10		20 / 10 / 10	20 / 10 / 10	20 / 10 / 10	10 / 5 / 5	20 / 10 / 10				
25n	30 / 15 / 15	30 / 15 / 15	30 / 15 / 15	30 / 15 / 15		40 / 20 / 20	30 / 15 / 15	30 / 15 / 15	10 / 5 / 5	30 / 15 / 15	60 / 30 /	50 / 25 /		
26n	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	20 / 5 / 5		10 / 5 / 5	20 / 5 / 5	20 / 5 / 5	5 / 5 / 5	20 / 5 / 5	20 / 5 / 5			
27n	10 / 5 / 5	10 / 5 / 5	10 / 5 / 5	20 / 5 / 5		10 / 5 / 5	20 / 5 / 5	20 / 5 / 5	5 / 5 / 5	20 / 5 / 5	20 / 5 / 5			
28n	42 T / 4 / -	28 / 10 / 10	42 T / 5 /	40 / 10 / 10		52 / 26 / 26	117 / 50 /	60 / 12 / 12	42 T / 5 / 5	10 / 3 / 3	30 / 12 /	21 / 6 / 6		

Abbreviations and notes: T - time dependent intensity correction; M - modelled background from mean atomic number of sample; Lab 5 also analyzed for Zr (20 / 10 / 10) and O (20 / 10 / 10)

Table 8. Spectrometer utilization summary for EPMA laboratories. Only laboratories 2, 9, 15, 19, and 28 have 30 s or less estimated idle time (U) on all spectrometers. The idle time, which in several cases exceeds 2 minutes (120 s) on a given spectrometer, could potentially be used to improve precision or to analyze additional elements.

	Spectrometer 1					**Spectrometer 2**					**Spectrometer 3**					**Spectrometer 4**					**Spectrometer 5**				
Lab	N	C	M	T	U	N	C	M	T	U	N	C	M	T	U	N	C	M	T	U	N	C	M	T	U
2	2	80	30	110		2	88	20	108	2	2	80	30	110		2	88	20	108	2	2	84	25	109	1
3	1	40	10	50	260	2	80	30	110	200	6	200	110	310		4	80	70	150	160					
5 - Lipari	2	70	30	100	180	5	152	90	242	38	5	190	90	280		3	190	50	240	40					
5 - Edziza	2	70	30	100	142	5	152	90	242		4	150	70	220	22	3	150	50	200	42					
5 - Laki	2	70	25	95	185	4	112	70	182	98	5	190	90	280		2	100	30	130	150					
6	2					2					2					2					1				
7	4	180	70	250	0	2	180	30	210	40	2	180	30	210	40	2	180	30	210	40					
9	2	101	35	136	18	3	104	50	154		2	126	20	146	8	3	104	50	154		2	114	30	144	10
10	6	290	95	385		5	250	85	335	50	2	70	25	95	290										
12	2	80	30	110	120	3	140	50	190	40	2	120	30	150	80	2	80	30	110	120	3	180	50	230	
13	2	40	30	70	40						3	60	50	110		2	40	30	70	40	3	60	50	110	
14	2	60	30	90		2	60	30	90		1	80	10	90		2	60	30	90		2	60	30	90	
15	3	45	35	80	6	4	36	50	86		4	36	50	86		2	39	20	59	27					
16	2	40	30	70	50	2	40	30	70	50	3	70	50	120		3	60	50	110	10	2	40	30	70	50
16R	2	60	30	90	50	2	60	30	90	50	3	78	50	128	12	3	90	50	140		2	60	30	90	50
17	2	210	10	220	110	4	224	65	289	41	4	260	70	330		2	100	10	110	220	2	100	10	110	220
19	3	60	50	110		2	80	30	110		2	80	30	110		2	80	30	110						
21	3	180	50	230		2	80	30	110	120	3	130	50	180	50	2	80	30	110	120					
21R	2	140	30	170	50	2	115	30	145	75	4	150	70	220		2	115	30	145	75					
22	4	216	70	286	34	3	270	50	320		3	180	50	230	90										
23	3	240	50	290		3	195	45	240	50	4	160	70	230	60	4	160	70	230	60	2	240	30	270	20
24	2	60	30	90	20	2	80	30	110		2	80	30	110		1	40	10	50	60	2	80	30	110	
25n	2	120	30	150	200	3	200	50	250	100	4	280	70	350		2	140	30	170	180					
26n	2	40	30	70	70	2	45	30	75	65	3	90	50	140		3	70	50	120	20					
27n	2	40	30	70	70	2	45	30	75	65	3	90	50	140		3	70	50	120	20					
28n	5	197	85	282	19	2	262	25	287	14	3	248	50	298	8	2	271	30	306						

Abbreviations and notes: N - number of elements, C - total counting time, M - estimated spectrometer movement time, T - total analysis time, U - unused (idle) time on spectrometer; All times in seconds; R appended to the lab number indicates a revised submission (round 2); n appended to the lab number indicates a new submission from a lab that had already received a copy of the report from round 1; Estimated spectrometer movement time was calculated by assuming 10 seconds for each new peak position after the first and 5 seconds for each background position.

Supplemental Materials

(1) Figure S1 Comparison plots for all elements on all samples. Vertical bars represent the means +/- 1 standard deviation for each contribution. Horizontal gray bars represent the preferred overall medians +/- 1 standard deviation.

(2) Table S1 Overall mean and median compositions, recommended compositions, summary data, and complete analytical data for all samples and all methods.

(3) Table S2 Spreadsheet implementing three criteria for outlier detection: (1) identification of contributions which are more than +/- 2 sigma from their respective overall medians, (2) identification of contributions which do not overlap their respective overall medians at +/- 1 sigma of both values, (3) identification of outliers from z-scores using Horwitz-function-based target standard deviations.

(4) Table S3 – Analyses of BHVO-2G, VG-A99, VG-2, and ATHO-G glasses conducted together with the interlaboratory comparison samples by laboratory 28.

(5) Table S4 Similarity coefficients between individual mean concentrations (Table 3) and the preferred overall means (Table 1).

(6) Packet distributed to all laboratories which received the interlaboratory comparison samples (rationale, protocols, mount description, data reporting form) and sample invitation e-mail message.

(7) Spreadsheet with alkali element migration data and calculations used to generate Figure 1.

(8) Spreadsheet for optimizing spectrometer utilization.

(9) Spreadsheet for calculating optimal peak and background count times. Requires raw peak and background intensity data and total time budget as inputs.

(10) Spreadsheet for estimating precision for multiple time and current combinations. Requires raw peak and background intensity data, sample composition, and beam current as inputs.