DR. DAVID EVANS (Orcid ID : 0000-0002-8685-671X)

Automated Extraction of a Five-Year LA-ICP-MS Trace Element Dataset of Ten Common Glass and Carbonate Reference Materials: Long-Term Data Quality, Optimisation and Laser Cell Homogeneity

David **Evans** (1, 2)* and Wolfgang **Müller** (1, 3)

(1) Department of Earth Sciences, Royal Holloway University of London, Egham, TW20 0EX, UK

(2) Present address: School of Earth and Environmental Sciences, University of St Andrews, St Andrews, KY16 9AL, UK

(3) Present address: Institute of Geosciences, Goethe University Frankfurt, Frankfurt am Main, Germany

* Corresponding author. e-mail: de32@st-andrews.ac.uk

LA-ICP-MS is increasingly applied to obtain quantitative multi-element data with minimal sample preparation, usually achieved by calibration using reference materials. However, some ubiquitous reference materials, e.g., the NIST SRM 61x series glasses, suffer from reported value uncertainties for certain elements. Moreover, no long-term dataset of analyses conducted over a range of ablation and tuning conditions exists. Thus, there has been little rigorous examination of the extent to which offsets between measured and reported values are the result of error in these values rather than analytically induced fractionation. We present new software ('*LA-MINE*'), capable of extracting LA-

ICP-MS data with no user-input, and apply this to our system, yielding over five years of data (~ 5700 analyses of ten glass and carbonate reference materials). We examine the relative importance of systematic analytical bias and possible error in reported values, through a mass-specific breakdown of fourteen of the most commonly determined elements. Furthermore, these data, obtained under a wide range of different ablation conditions, enable specific recommendations of how data quality may be improved, e.g., the role of diatomic gas, the effect of differential inter-glass fractionation factors, and choice of transport tubing material. Finally, these data demonstrate that the two-volume Laurin ablation cell is characterised by no discernible spatial heterogeneity in measured trace element ratios.

Keywords: laser ablation, ICP-MS, 193 nm ArF excimer, laser cell homogeneity, calibration, accuracy, data-reduction software.

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is the fastest and least expensive quantitative tool capable of measuring ng g^{-1} to per cent elemental mass fractions at μm spatial resolution in a wide variety of geological, environmental, biological and material science substrates (Becker 2002, Russo *et al*. 2002, Heinrich *et al*. 2003, Jackson *et al*. 2004, Srinivasan 2015, Müller and Fietzke 2016). The popularity of LA-ICP-MS is the result of its capability for fast, quantifiable determination of multiple elements at %-level accuracy and precision, with minimal sample preparation requirements. Accurate quantification is possible at μm lateral and sub-μm vertical spatial resolution (e.g., Eggins *et al*. 2003, Lazartigues *et al*. 2014).

Despite the increasing popularity of LA-ICP-MS, little is known about the long-term quality of the large volumes of data produced. Quoted uncertainties are frequently derived from short periods of analysis and are therefore likely to underestimate error (particularly precision), especially when comparing temporally separated sample data. Whilst it is normal practice to quote long-term reproducibility for single-element isotopic determination (e.g., Thirlwall 1991), a similar approach has not been adopted by the LA-ICP-MS community, mostly because of the versatility of sample types

and range of potential analytes. Treating matrix-matched "external" reference materials (RMs) as unknowns often results in a favourable estimate of accuracy (Evans *et al*. 2015), provided the RM is well characterised, yet sample data may be biased as these may have a different (and possibly variable) matrix.

Ubiquitous reference materials such as the doped NIST SRM 61x glasses are known to be spatially heterogeneous for some elements of wide interest in the Earth and Environmental Sciences, for example B, As, Pb (Eggins and Shelley 2002). Furthermore, there has been little systematic study of the effect of ablation parameters, such as spot versus track analyses, spot size, repetition rate and gas type on long-term data quality, although many studies have investigated the influence of these and other parameters within single or closely-spaced sessions (e.g., Mank and Mason 1999, Gonzalez *et al*. 2002, Guillong and Günther 2002, Jackson and Günther 2003, Jochum *et al*. 2012). Because other factors influence the reliability of data collected over short time periods, such as ICP-MS tuning and sensitivity, a long-term view is required in order to (1) accurately gauge how such parameters may be optimised for certain elements and sample types and (2) assess the comparability of analyses separated temporally. Furthermore, there has been a recent trend towards ablation cells with increasing volume in order to improve routine analysis-throughput (Fricker *et al*. 2011). Whilst these large cells typically contain a low-volume, partially-isolated space within which ablation takes place (Eggins and Shelley 2002, Müller *et al*. 2009), thus minimising spatial variability in transport gas flow dynamics, there are few studies that have assessed the extent to which ablation cells are homogeneous in terms of elemental fractionation.

In order to address these concerns, and to provide a comprehensive long-term overview of both matrix and non-matrix matched calibration using a 193 nm excimer (ArF) laser ablation system with two-volume LA cell, we present a Matlab program capable of 'mining' all the data from a system over any specified period. Crucially, it runs automatically without user input, which means that, depending on computing power, years of data acquisition can be processed in a few hours.

We apply this program to all of the data produced by our laser ablation ICP-MS system at Royal Holloway University of London (Müller *et al*. 2009) between January 2010 and June 2015, during which the RESOlution M-50 prototype was connected to an Agilent 7500ce ICP-MS (subsequently replaced with an Agilent 8800 ICP-QQQ). This constitutes a dataset of ~ 5720 standard analyses of routinely utilised NIST61x, silicate (MPI-DING) and phosphate (STDP) glasses as well as a pressed-powder carbonate (MACS-3) (Eggins and Shelley 2002, Jochum *et al*. 2006, 2011, Klemme *et al*. 2008). Whilst a wide range of materials were analysed over this period, we focused on the determination of trace elements in carbonates and phosphates. Consequently, our dataset is naturally biased towards elements and reference materials that are commonly associated with such analyses, although a significant amount of time has been dedicated to other applications, for example tephra (Tomlinson *et al*. 2010) and ice core analysis (Müller *et al*. 2011, Della Lunga *et al*. 2014). Because many of the analyses carried out over this period were line-scans (tracks) across relatively large growth-banded carbonate samples – to our knowledge – we present the first extensive dataset of laser ablation line-scan ('track') data of RMs. Whilst some analyses of this type of data have been reported (Jochum *et al*. 2014), virtually all previous studies examining LA data quality focus on (vertical) spot analysis. Furthermore, we present a significant new dataset of the STDP phosphate glasses for which little inter-laboratory comparative data are available compared with many other RMs. Finally, as well as a detailed investigation of long-term data quality and the implications of observed offsets for LA or ICP-MS-induced fractionation (versus potential error in the reported value of these RMs), this dataset uniquely enables us to examine the effect of ablation parameter, including additional diatomic gas type, on long-term accuracy and precision. We utilise this to give a non-exhaustive set of recommendations for improving data quality, in order to highlight specific situations in which ablation parameters strongly influence accuracy and/or precision. Furthermore, because stage coordinates are available from the LA log files, we also discuss the homogeneity of the Laurin two-volume ablation cell.

Experimental procedure

Laser ablation-ICP-MS

The LA-ICP-MS system is described in Müller *et al*. (2009). Briefly, it features the RESOlution M50 prototype laser ablation system (193 nm ArF) with Laurin two-volume LA cell, connected to an Agilent 7500ce/cs ICP-MS. Tuning conditions vary according to application, although the underlying premise is always on achieving robust plasma conditions (i.e., ThO/Th < 0.3%, Th/U ~ 1 in NIST SRM 612). For example, tephra analyses require sensitivity optimisation across the mass range (Tomlinson *et al*. 2010), whereas data associated with the analysis of biogenic carbonates are typically characterised by optimised low-mass sensitivity in order to improve Li and B counting statistics in small, fragile samples (Evans *et al*. 2015). The principal change to the system since it was described is the installation of an H_2 gas line, which means either N_2 or H_2 can be selected as additional diatomic gas, added downstream of the ablation cell. Although this information is not written into the log file produced by the laser ablation control software (GeoStar), the optimal tuning conditions differ between these diatomic gases which means the gas type for each analysis can be identified using the flow rate of this mass flow controller; N_2 flow rates are routinely 6 ml min^{-1} whereas H_2 is optimised around 8.5 ml min^{-1}. Scan speed, repetition rate and spot size varied between 0–50 μm s^{-1}, 1–25 Hz and 15–96 μm respectively across the five-year period. Fluence was typically 3–5 J cm^{-2}. The He flow rate was set to 850 ml min^{-1} irrespective of other variables without exception. The design of the Laurin cell is such that the entire He flow enters at the lower rear of the large volume cell, splits into a top-down and bottom-up He flow within the inner 'funnel' and exits the latter through a pipe (see Müller *et al*. 2009). GeoStar records almost all of the critical ablation condition parameters required to assess this dataset with the exception of the presence or absence of the 'squid' signal-smoothing device. Similarly, ICP-MS dwell times and use of the ICP-MS collision cell are not recorded in the log files utilised here, instead we indirectly assess these variables using signal/background ratios. Therefore, it is not possible to assess the benefits of in-line signal smoothing or optimisation of sweep time versus repetition rate, although the squid is used the majority (~ 90%) of the time.

Matlab program: '*LA-MINE*'

Our newly developed Matlab program, referred to as '*LA-MINE*' below, is designed to analyse all Agilent and GeoStar csv files created by the LA-ICP-MS system at RHUL between January 2010 and June 2015, ($\sim 10^4$ of each). A key advantage of this software in this context over existing LA-ICP-MS data reduction programs (e.g., Guillong *et al*. 2008, Paton *et al*. 2011, Rittner and Müller 2011) is that it is designed to require no user input whilst extracting large quantities of LA data spanning a long period of time, as the large number of files involved means that it was impractical to individually assess each manually. Previously available software is not designed to achieve this for two principal reasons: (1) it is difficult to define criteria in the data alone which unambiguously identify a specific RM rather than samples, as user labels cannot always be relied upon to be correct, and (2) the LA and ICP-MS hardware are usually controlled by different programs running on separate computers which are typically isolated, and therefore have an associated non-constant offset in machine time. Whilst it may be prohibitively time consuming to produce a program that is capable of dealing with any data, we simplify this problem in several ways in order to produce a script that is capable of successfully differentiating between samples and RMs in almost all cases.

Before detailing these simplifications, we briefly outline the characteristics of the LA-ICP-MS data examined here. Users typically program a set of analyses using the laser ablation software (GeoStar) which produces a csv log file containing information regarding timing (start and end of each analysis), coordinates within the ablation cell, laser repetition rate, spot size, scan speed and the gas flow rate through the mass flow controllers. After selecting all or part of the sequence for analysis, ICP-MS data acquisition is initiated manually by the user. In virtually all cases each Agilent csv file contains all RMs and samples that the user intends to form part of the same sequence. Similarly, fluence and gas flow rates were always held constant within an analysis sequence. Thus, the program assumes that each Agilent csv file also contains every standard analysis that the user wishes to use to manipulate the sample data, such as the calibration material(s), typically NIST61x, and the secondary reference materials used to assess data quality. ICP-MS data are essentially always exported as a counts per second (cps) time series for each analysed *m/z*; at present the program cannot read data exported as

raw counts because it relies on intensity ratios to identify NIST glasses (see below). Before data processing, all sequences were automatically split into sub-sequences wherein every analysis was carried out under identical ablation conditions (spot size, repetition rate, scan speed). Data reduction without user input is achieved in five basic steps:

(1) The program reads in all Agilent csv data files from a specific day and then finds all GeoStar csv log files that fall within the time given by the first and last line of the data file.

(2) The start and end of each analysis within the data file is located using the times derived from the GeoStar logs. Before this can be done, the computer time offset between the start of the analysis on the laser ablation and ICP-MS computers must be calculated. As described above, this is not constant, as the computers are not synchronised. Attempts to achieve this by, for example, assuming that gas blank analyses between samples is characterised by a total ion beam intensity below a certain threshold (akin to Iolite's 'detect from beam intensity' option) are not accurate in some cases, for example when a track is placed across a discontinuous sample filled with clean resin (Evans and Müller 2013) or when depth profiling breaks through the base of the sample to the resin below. Our program overcomes this issue in the following way. First, the total ion beam (TIB) for a given analysis sequence (Figure 1A) is replicated 2000 times. The beginning of each such replicate dataset is assigned a machine time that is offset from the previous by one ICP-MS sweep time. For example, the dataset TIB_1 is assigned a start time of that written into the ICP-MS file minus 1000 dwell times, the dataset TIB_2 is assigned a start time of that written into the ICP-MS file minus 999 dwell times, and so on, so that dataset TIB_{2001} start time = machine time + 1000 ICP-MS dwell times. This allows a possible machine time offset between the ICP-MS and LA computer of $\pm$ 1000 ICP-MS sweep times (equivalent to ~ 3–6 minutes). Then, the location of the gas blank portions of the dataset given by the timestamps of the LA (GeoStar) log file are deleted from all of these replicate TIB datasets (Figure 1B). Note this is simply a deletion of these data from the file in a temporary step to match the LA and ICP-MS data, and is not the same as gas blank subtraction described below. In most cases the portions of data removed do not match with the location of the actual gas blank data, i.e., 2000 out of these

2001 datasets will be misaligned to differing degrees (this is a temporary intermediate step simply to align the datasets from the two computers). In order to find TIB_x, i.e., the dataset in which the analysis time of the computers are aligned, the sum of the total ion beam of the remaining data is calculated for each of these possible offsets. The actual sequence-specific computer time offset is then given by the time difference that results in the greatest sum of the total ion beam for the remaining segments, as this will be the offset that results in the best match between the analysis times given by the GeoStar logs and the data peaks in the Agilent data file (Figure 1C). Whilst the accuracy of this technique is limited to ± 0.5 ICP-MS sweep times, this is usually < 0.25 s and always < 0.5 s, which is sufficient resolution given that the initial and final portions of each analysis are discarded because they represent times of signal increase and decrease respectively.

(3) NIST glasses are identified based on fairly broad ranges of *raw* Sr/Ca and U/Sr intensity ratios (NIST SRM 612: $2 > {}^{88}Sr/{}^{43}Ca > 0.55$; $2 > {}^{238}U/{}^{88}Sr > 0.4$; NIST SRM 610: $8 > {}^{88}Sr/{}^{43}Ca > 4$; $6 > {}^{238}U/{}^{88}Sr > 0.8$). The factor of 2–6 range in these ratios is necessary as session-specific low/high mass tuning parameters may result in relatively large differences in sensitivity of these three masses. Ratios derived from Ca, Sr and U were chosen because at least one isotope of all three of these elements was analysed in > 82% of the Agilent files, and these elements show low ablation parameter-specific or down-hole fractionation, and negligible ICP mass load effects (Fryer *et al*. 1995, Kroslakova and Günther 2007, Jochum *et al*. 2014), which means that raw intensity ratios based on these elements are likely to show relatively little ablation-condition dependent variation (see also Jochum *et al*. 2012). Whilst more complex algorithms could use a variety of ratios to increase the percentage of files analysable in this way, we targeted 80% as an acceptable point at which sufficient standard analyses were retrieved whilst minimising the time taken to produce this code. Figure 2 shows the range of raw (background corrected only) ${}^{88}Sr/{}^{43}Ca$ and ${}^{238}U/{}^{88}Sr$ intensity ratios for all commonly analysed RMs. Despite a wide range of ICP-MS tuning conditions, ablation conditions and gas flow parameters, the RM analyses are grouped into definable clusters. Crucially, all RMs occupy Sr/Ca-U/Sr space, which is distinct from most other RMs as well as virtually all samples analysed. The STDP-3 phosphate glasses (Klemme *et al*. 2008) are an exception: STDP3-150 overlaps NIST SRM 612 and STDP5 and

1500 overlap NIST SRM 610 (Figure 2). To overcome this, NIST-STDP analyses were differentiated using two mechanisms. If more than one NIST analysis was identified within a specific sequence, then the U signal intensity was used to check whether all analyses were of the same material, as the STDP glasses have (Sr) and (U) ~ 3–5 times higher than NIST SRM 610/2. If the intensities were different by > 5×, then the analysis with a lower U intensity was identified as the NIST glass. If all analyses had similar U intensities, or there was only one analysis, then the user analysis labels from the laser ablation software were used to identify the RM(s). Whilst user labels were avoided as far as possible because of potential errors, the design of the code beyond this point (see below) means that if a RM is misidentified, or a sample is identified as a RM, it is not possible for such data to form part of the dataset that we present here. In addition, some volcanic glasses have similar Sr/Ca and U/Sr ratios to NIST SRM 610/2. This problem was overcome using U/Th ratios, which are always tuned to ~ 1 in the NIST glasses but not in tephra. Very long analyses (> 1000 ICP-MS sweep times) were also assumed to represent samples. Whilst these constraints may not be directly relevant to other laboratories, element/element ratios may easily be tailored to suit the needs of a specific laboratory, for example by choosing alternative ratios that are reasonably infrequently encountered in samples, or by defining additional criteria for samples which are similar to NIST61x with respect to these chosen ratios. The code is designed so that such criteria may be easily inserted, and we again stress that standard misidentification does not propagate through to the final dataset but instead results in data for the entire analysis session being excluded.

(4) Once the location of all NIST glasses has been ascertained, data reduction is performed following conventional procedures (Longerich *et al*. 1996, Heinrich *et al*. 2003) using Ca as an internal standard element. Primary calibration was performed using both NIST glasses, yielding separate NIST SRM 612 and NIST SRM 610-calibrated datasets. A drift correction was never applied, even in instances where more than one NIST glass analysis was available, because unknowns are never routinely separated from NIST analyses by more than one hour; drift over this time frame is never distinguishable from RM heterogeneity. For track analyses, the mean of all available NIST values was used for data reduction. For spot analyses, linear intensity-depth regressions with respect to ^{43}Ca are

calculated for each analysed *m/z*, and these regressions are then used to produce depth-specific intensity/mass fraction ratios for calibration. Outliers are removed from all background and signal analyses (3*s* from the mean).

(5) Non-NIST reference materials were identified by initially assuming that all analyses could be any secondary RM. NIST-calibrated X/Ca ratios are then compared with the literature values for each of the ten secondary RMs that were routinely analysed. Analyses are assigned to specific RMs when the mean offset between the measured and reported values is no more than 30% for all *m/z*, with no more than 20% of the analysed masses differing by > 30% from the reported values. These conditions are never met if non-NIST analyses are accidentally identified as NIST glasses because although such analyses have similar Sr/Ca and U/Sr intensity ratios, this is never the case for all the other element/Ca ratios analysed within a particular sequence. As an additional check, user analysis labels were also monitored in order to evaluate how many standard analyses were never identified. Assuming that these labels are correct, and these analyses really do represent missed RMs, the program is 96.4% effective. In order to ensure that unidentified RMs were not excluded from the final dataset, those analyses identified using user labels were included but were of sufficiently small number (~ 200) to be manually checked for errors. We incorporated these because they are likely to represent the worst data, as analyses were not recognised as RMs only if the measured values deviated from the reported values by > 30% on average. Furthermore, although there were too many files to process individually, all ~ 5700 analyses were checked to ensure that each represented a RM, and did not mistakenly include any gas blank data. Following this, 43 analyses (0.8%) were excluded, mostly as a result of signal washout taking longer than usual, resulting in incorrect gas blank intensities.

The NIST61x analyses were performed on twelve different wafers; therefore our dataset accounts for heterogeneity between NIST wafers, whilst only one set of the MPI and STDP glasses were used. Two MACS-3 pellets were analysed.

Results and discussion

Dataset statistics

In total, 5724 analyses of reference materials (RM) were mined from the period 01/01/2010 to 25/06/2015 of which 5572 were identified without resorting to user analysis labels. A breakdown of this total between the twelve most commonly analysed reference materials is shown in Table 1, including the ratio of spot to track analyses and the approximate ratio of analyses conducted using N_2 and H_2 as the additional diatomic gas. The NIST glasses are by far the most commonly analysed RM because one or both of NIST SRM 610/2 are used as bracketing calibrators for almost every sequence of analyses. The STDP-3 phosphate glasses (Klemme *et al.* 2008) are almost entirely represented by track analyses. The MPI-DING glasses ATHO-G and StHs6/80-G are predominantly represented by spot analyses associated with tephra data (Tomlinson *et al.* 2010), whereas MACS-3 and the remaining MPI-DING RMs are often analysed with carbonates which may be either tracks for larger, growth-banded material (Stoll *et al.* 2012, Evans *et al.* 2013, Warter *et al.* 2015) or spots for small fragile specimens such as foraminifera (Evans *et al.* 2015).

Within the NIST SRM 612-calibrated dataset, a total of seventy-nine *m/z* values were monitored at some point within the five-year period, with forty-three measured over 100 times and thirty measured over 1000 times, from ^{7}Li to ^{238}U. We focus the results and discussion of our dataset on a subset of all the masses analysed, specifically those for which a sufficient number are available to make an assessment of long-term data quality over a range of ablation conditions. Of the thirty-seven analytes for which well over 1000 measurements of reference materials exist, nineteen are distributed approximately equally between the RMs whilst the remaining eighteen was frequently associated with the analysis of volcanic glasses. In this latter group the MPI-DING glasses ATHO-G and StHs6/80-G were primarily used as secondary RMs. Because these *m/z* (^{29}Si, ^{45}Sc, ^{47}Ti, ^{60}Ni, ^{90}Zr, ^{93}Nb and the REE with the exception of La, Ce and Nd) were not routinely analysed other than in relation to tephra, we omit these from our discussion because Tomlinson *et al.* (2010) assess the quality of these data in detail.

Fractionation factors

Mean fractionation factors of all spot analyses from the entire period are shown for NIST SRM 612 in Figure 3a. Following Fryer *et al*. (1995) the fractionation factor for each analysis is defined as $F = (X/Ca_{0.5 < t < 1})/(X/Ca_{0 < t < 0.5})$, i.e., the mean X/Ca value for the second half of the analysis divided by the mean X/Ca value of the first half. Whilst Figure 3 utilises data collected under a range of analytical conditions, the vast majority of the depth profiling analyses were collected with a spot size of 44 μm and 2 Hz laser repetition rate. Exceptions to this are *m/z* 29, 47, 51 and the heavy rare earth elements, which were predominantly associated with analyses with a higher repetition rate (5 Hz) and may not be directly comparable.

For NIST SRM 612, most fractionation factors are close to 1, demonstrating little or no depth-dependent analyte fractionation with respect to ^{43}Ca. However, elements with a low condensation temperature (^{85}Rb and ^{208}Pb), that suffer from memory problems (^{11}B and ^{23}Na), with a large carrier gas interference (^{29}Si and ^{31}P, characterised by typical signal/background ratios of < 10), or other polyatomic interference (e.g., ^{60}Ni and $^{44}Ca^{16}O$ or $^{43}Ca^{16}O^{1}H$) are characterised by mean fractionation factors between 1.02 and 1.06. Whilst this is small compared with at least some 213 nm solid state LA system data (e.g., Jochum *et al*. 2014), fractionation relative to Ca is detectable. Moreover, we find significantly different fractionation factors between the most commonly analysed RMs here. Figure 3b–e shows fractionation factors relative to NIST SRM 612 for NIST SRM 610, MACS-3, and GOR132/128-G. There is no resolvable difference between NIST SRM 610-612 fractionation factors, which is unsurprising given their similar matrix. Encouragingly, we also observe little difference between the NIST glasses and the carbonate pressed powder MACS-3, with the possible exception of ^{89}Y (which may suffer from an ^{88}SrH interference in high-Sr carbonates, see section for ^{88}Sr). This implies that differential down-hole fractionation between carbonates and the NIST glasses is unlikely to be a source of error when calibrating carbonate samples to these synthetic RMs using a 193 nm ArF laser, although MACS-3 is relatively heterogeneous and poorly characterised for some elements (see *Accuracy and precision*). This is in agreement with previous work demonstrating that matrix-

matching is not necessary when analysing refractory lithophile elements in carbonates, in contrast to volatile chalcophile/siderophile elements, for which matrix-matching is desirable even when using 193 nm LA systems (Czas *et al*. 2012).

In contrast, GOR132-G and GOR128-G show significantly different fractionation factors for some elements compared with the NIST glasses. Specifically, ^{7}Li, ^{23}Na and ^{57}Fe are 4–6% greater, and ^{140}Ce is 3% lower for both GOR reference materials. The two GOR glasses are characterised by fractionation factors within error of each other for all masses shown in Figure 3, hence this finding is not a unique feature of either of them. We also find elevated ^{7}Li and ^{23}Na fractionation factors for KL2-G compared with NIST SRM 612, albeit with a smaller (3%) offset (these data are not shown in Figure 3 because this RM was not utilised as often). If this result is broadly applicable to volcanic glasses, it may imply that such data are less likely to be accurate than analytes that are not characterised by different fractionation factors to the NIST RMs. There is insufficient data available under equivalent conditions for ATHO-G and StHs6/80-G; hence we are unable to make this comparison for more felsic glasses. Overall this highlights that fractionation factors for certain masses may be more different between glasses of very different composition than between some glasses and carbonates. It should not be assumed that all glasses are matrix matched, or that using one glass to calibrate another will result in accurate data. Conversely, it cannot be assumed that inaccuracies in secondary RM glass data based on spot analysis of the NIST wafers reflects an inaccuracy in the reported value of one of those RMs.

Accuracy and precision

Where this dataset is discussed in relation to the GeoReM database (http://georem.mpch-mainz.gwdg.de/), version 21 of this database was used (January 2017). When comparing our long-term accuracy and precision to the reported or information values for a specific element/RM combination it is important to bear in mind that many of these reference values are – to differing extents – themselves based on LA-ICP-MS measurements, (Table 2). This is particularly the case for

elements heavier than Sr in the MPI-DING glasses, and all elements in the phosphate glasses STDP3-150 and STDP5. In these cases, any differences between the reported and our measured value are unlikely to be the result of an issue with the NIST glasses typically used for calibration. Rather, these could reflect different laser ablation and/or ICP-MS parameters (e.g., wavelength, particle size distribution, tuning conditions), unless the NIST value has been updated (e.g., Mg, see below) or an alternative calibration technique was used.

Accuracy and precision for all RMs for which more than twenty analyses are available for a given set of ablation conditions are shown based on NIST SRM 612 calibration in Tables 3–4 and NIST SRM 610 calibration in Tables 5–6. Similar spot sizes were pooled; data are shown for both spot and track analyses in bins containing 20–25 μm, 44–57 μm and 74–96 μm diameter spots. Whilst these pooled accuracy and precision data are based on analyses performed using a range of repetition rates and/or scan speeds, these were broadly invariant through time. Specifically, almost all spot analyses were performed at either 2 or 5 Hz whilst the majority of the track data (56.7%) were acquired at 15–20 Hz and a scan speed of 1 mm min^{-1}, with 20.8% acquired at 2 mm min^{-1}. Therefore, whilst spot and track accuracy and precision are not comparable in terms of ablation conditions, spot and track data of different RMs were obtained using broadly equivalent ablation parameters throughout the five-year period. Accuracy data are given relative to the reported values (accuracy = measured/reported, while precision (reproducibility) = (2s measured)/reported). We stress that the values given in Tables 3–6 do not represent the best possible data quality achievable by LA-ICP-MS, but do give an indication of the extent to which data are comparable when separated by large amounts of time, and collected under ablation and ICP-MS conditions which change as they are optimised daily.

A detailed analysis of this dataset including all individual analyses is displayed with respect to time in Figure 4 for *m/z* [25]Mg, [66]Zn, [88]Sr, [208]Pb and [238]U, a representative selection that includes masses that are relatively straightforward to measure and some with known complicating factors (discussed below). See the online supporting information for similar overview figures of other analytes. In the following sub-sections ([7]Li–[238]U) we examine the dataset by *m/z*, giving an overview of long-term

accuracy and precision, comparison with previous datasets and specific considerations. We envisage that this may be used as a reference guide when data quality of a particular analyte is important. The data discussed here are given in Tables 3–6, whereas most overview figures are in the supporting information apart from the *m/z* shown in Figure 4. We make the assumption that Ca is well characterised and homogeneously distributed in all of these RMs, which is likely to be the case given that it is a major constituent of all of them.

[7]Li: Calibrating NIST SRM 612 to NIST SRM 610 shows that matrix-matched Li determination produces accurate and precise data at tens of $\mu g\ g^{-1}$ mass fraction. Taking the mean of all data, track and spot long-term accuracy was better than 2% and 1% respectively, and there is no significant offset between the two techniques. In contrast, GOR128-G and GOR132-G, the only MPI glasses for which > 200 analyses are available, are consistently offset to higher values by 8–10% and 17% respectively when calibrating to NIST SRM 612 across all ablation conditions; NIST SRM 610 calibration produces values ~ 2% worse than this (Tables 3 and 5). This is consistent with the original MPI-DING dataset (Jochum *et al*. 2006), wherein LA-derived values are positively offset from the reported overall mean by 17% and 8% for GOR128-G and GOR132-G respectively, compared with both solution ICP-MS and other micro-analytical techniques.

In order to explore whether this difference is an artefact of LA spot analysis rather than an issue with the reported Li value of the MPI glasses, we plot accuracy as a function of the analysis-specific signal/background ratio in Figure 5. Doing so demonstrates that the lower Li mass fraction of the GOR glasses or the broadly lower signal/background ratios of spot analysis can be excluded as the cause of the difference in accuracy between techniques. The overall poorer accuracy for GOR128/132-G when depth profiling, is consistent with our observation of differential Li fractionation factors between the NIST and GOR glasses (Figure 3). Furthermore, the accuracy offset between spot and track analysis cannot result from spot analyses more frequently being carried out using H_2 rather than N_2 as the additional diatomic gas, as accuracy and fractionation factors are statistically indistinguishable for analyses performed using both gases. Our consistently higher

measured value compared with the reported value for the MPI glasses may indicate that LA depth profiling overestimates Li mass fraction in some materials compared with SIMS and solution ICP-MS; an accuracy correction may be appropriate when calibrating volcanic glasses to NIST RMs if positive fractionation factors are also observed (Figure 3 and 5C). The MACS-3 pressed powder carbonate does not show this analytically-derived offset (Figure 5), which has a Li fractionation factor very close to NIST SRM 612 (Figure 3), further indicating that differential down-hole fractionation is the largest source of inaccuracy in these measurements, rather than broad matrix type or inaccuracy in the reported values. Nonetheless, the overall positive offset between our measured value for GOR132/128-G track analyses and the reported value indicates that this issue could, to a lesser extent, arise from a GOR (Li) reported value that is ~ 5% too low.

Measured MACS-3 values are higher than the reported value by 5% and 6% for spot and track analyses respectively, a similar finding to Jochum *et al*. (2014) using both 200 nm fs and 213 nm Nd:YAG LA systems. This pressed carbonate powder may be sufficiently homogeneous (precision 11–15%) for most purposes, although given that accurate MACS-3 calibration to the NIST glasses is possible (see also Tabersky *et al*. 2013), directly calibrating carbonate samples to NIST will likely result in better precision, given that these are more homogeneous and the NIST61x and MACS-3 Li fractionation factors are not resolvably different (Figure 3).

[11]B: Boron data quality shows significant trends through time, directly related to the control exerted by the boron background intensity on signal/background ratios. A significant drop in the typical B background from ~ 6000 cps in early 2011 to ~ 250 cps by mid-2013 (Figure 6) was associated with the replacement of the major tubing components within the laser ablation system, including the squid smoothing device, with nylon-6. This tubing material was originally installed in order to improve sulphur data quality, as nylon-6 is produced without the use of sulphur in the manufacturing process, which is not the case for nylon-11 or nylon-12. However, we find that another significant advantage of this material is that it also results in improved B data, either as a result of a lower propensity for boron memory due to particles sticking to the transport tubes, or directly from

the nylon. The timing of this tubing change is associated with an improvement in NIST SRM 610-calibrated NIST SRM 612 B accuracy from a measured value 26.2% greater than the reported value prior to June 2011 (2s precision 17.8%), to 7.8% (precision 8.4%) after June 2012, and demonstrates how tubing can have a significant effect on data quality. Taking into account only data collected after mid-2012, NIST SRM 610-calibrated measured values are $16.9 \pm 10.7\%$, $5.9 \pm 7.7\%$ and $8.4 \pm 10.9\%$ higher than reported for GOR132-G, GOR128-G and NIST SRM 612 respectively (all ± ranges are 2RSD precision), for track analyses averaged over all ablation conditions. Given that NIST SRM 612 and GOR128-G calibrated to NIST SRM 610 result in precise long-term data despite B heterogeneity in the NIST glasses (Eggins and Shelley 2002), this indicates that the reported B value for GOR132-G may be too low. MACS-3 is comparatively far more heterogeneous (2RSD of all analyses is 42.0%, n = 111), which is similar to that calculated from all data in the GeoReM database (48.8%, or 33.2% minus one outlier). Based on the mean of all analyses on our system after mid-2012, we measured a MACS-3 B mass fraction of 9.1 ± 3.8 µg g^{-1} (2s) calibrated to NIST SRM 610, within the range of previously reported LA values (Chen *et al*. 2011, Jochum *et al*. 2012). In summary, B data may be both reasonably accurate and precise, provided careful attention is paid to factors such as variable gas blanks from sample tubing. Nylon-6 is recommended for all applications for which high quality B data are desirable. We observe no significant offset between track and spot analyses of the same material, indicating that matrix-dependent down-hole fractionation is not an issue. MACS-3 is characterised by ± 42% heterogeneity, and therefore is not likely to be useful for calibration or assessing B data quality.

[23]**Na:** NIST SRM 610-calibrated NIST SRM 612 Na data are both accurate ($< 1\%$) and precise ($< 2.5\%$), even averaged over all ablation conditions and analysis type. In contrast, the MPI glasses GOR132-G, GOR128-G and KL2-G are all characterised by a significant accuracy offset between spot and track analyses, irrespective of spot size (Tables 3 and 5). On average, spot analyses are offset to values 7–10% higher than reported whilst tracks are offset to the same degree in the opposite direction. It is not possible to distinguish between the relative effects of analysis type and

repetition rate in our dataset, as almost all track data acquisition is carried out at higher repetition rates than spot analyses. However, we observe no such offset for MACS-3, which is characterised by similar spot and track accuracy and precision (not shown in Tables 3–6 because there are fewer than twenty analyses under a given set of ablation conditions; see the supplementary material). The offset we observe for the MPI glasses is consistent irrespective of the diatomic gas. Jenner and O'Neill (2012) also observe a similar accuracy offset (6.4% greater than the reported value) for laser ablation depth profiling (calibrated using the USGS basaltic glass BCR-2G) compared with EPMA analysis. Together, these observations imply that similarly to Li, Na fractionation is not equivalent for glasses with different matrices, which is also clear from our fractionation factors (Figure 3). Therefore, we suggest that this commonly observed offset is more likely to be a result of differential Na fractionation during LA depth profiling than a problem with the EPMA data of the MPI glasses or BCR-2G (Melson *et al*. 2002). However, our track data at high repetition rates is characterised by a consistent negative offset compared with the reported value, which cannot be explained by down-hole fractionation and may imply an issue with the reported Na value for GOR132-G, GOR128-G and KL2-G. We note that our value measured by LA-ICP-MS line-scans, e.g., 557 ± 59 μg g^{-1} (2s) for GOR132-G calibrated using NIST SRM 612, is in much better agreement with the originally reported values of Jochum *et al*. (2000) than those updated by Jochum *et al*. (2006). The fact that these offsets are not observed for MACS-3 may imply that these issues do not need to be considered for NIST-calibrated carbonates. Long-term MACS-3 Na accuracy and precision are < 5% and 10–13% averaged over all ablation conditions.

Mg: Long-term Mg precision is better than expected given that both NIST glasses are known to be characterised by significant Mg heterogeneity (7.5% and 6.7% for NIST SRM 612 and 610 respectively based on the data of Jochum *et al*. (2011)). NIST SRM 610-calibrated NIST SRM 612 precision is 4–6% (Table 3), somewhat better than expected based on the above-mentioned heterogeneity of the calibration RM. Averaged across all ablation conditions, long-term (5-year) Mg accuracy for ^{25}Mg is < 4% for spot analysis of NIST SRM 612 and MPI glasses for which data are available, and < 3% for track analyses of the phosphate glasses STDP3-150/1500. The fact that NIST-

calibrated GOR128-G and GOR132-G accuracy from the same analysis sequence are highly correlated demonstrates that even more precise Mg data are possible if more homogeneous glasses are used for calibration (see the supplementary material of Evans *et al*. 2015, who demonstrate better than 2% precision when calibrating using GOR128-G). We see no evidence for Mg heterogeneity resulting from the possible presence of micro-olivines in our GOR128/132-G chips (Jochum and Enzweiler 2014).

In contrast to the long-term NIST precision, NIST-calibrated accuracy is consistently poor for all RMs. The MPI glasses GOR132/128-G and KL2-G, MACS-3 and STDP3-150/1500 are all offset to values ~ 7–10% lower than reported using NIST SRM 610 for calibration, which is itself inconsistent with the even poorer NIST SRM 610-calibrated NIST SRM 612 accuracy in this dataset (measured NIST SRM 612 (Mg) is 12–17% below the reported value of Jochum *et al*. 2011). Together, this implies that Mg values in both NIST SRM 610 and 612 require revision, in particular because the consistent offset between six other RMs with very different matrices demonstrates that this discrepancy does not have its origin in matrix-matching or ablation parameters. Taking the average of all ^{24}Mg and ^{25}Mg data calibrated using NIST SRM 610 (excluding NIST SRM 612) gives a mean NIST SRM 610 measured value 7.5% below reported. Therefore, based on our data NIST SRM 610 (Mg) is 467 ± 0.9 µg g^{-1} (2SE, $n = 933$). Using a similar approach (based only on ^{25}Mg, see below), NIST SRM 612 (Mg) is 62.4 ± 0.19 µg g^{-1} (2SE, $n = 2245$). Interestingly, our NIST SRM 610 value is indistinguishable from that of Pearce *et al*. (1997) (465 µg g^{-1}), widely used before Jochum *et al*. (2011) revised many of the NIST mass fraction values, including that of Mg to 432 µg g^{-1}. Whilst the compiled values of Jochum *et al*. (2011) resulted in greatly improved NIST characterisation, both the analyses we report here, as well as the mean of all LA-ICP-MS data in the GeoReM database suggest that the NIST SRM 610 value given by Pearce *et al*. (1997) could be readopted. However, neither the value of Pearce *et al*. (1997) or Jochum *et al*. (2011) result in accurate NIST SRM 612-calibrated data, and we therefore suggest that the NIST SRM 612 value given here be used in this case (62.4 µg g^{-1}). Using our recommended NIST values, accuracy in the other RMs reported here is better than 5% for most ablation conditions, with the exception of ^{24}Mg when using NIST SRM 612. The ^{48}Ca^{2+}

interference on ^{24}Mg has been described previously (Jochum *et al*. 2012), and is also obvious in our dataset, re-emphasising that this mass should not be used for samples with less than ~ 100 µg g^{-1} Mg and a high Ca mass fraction.

As for many other analytes, MACS-3 is characterised by a relatively poor precision of 12–16%, which makes this RM more heterogeneous than any of the glasses we routinely analyse for Mg and precludes its use in place of the NIST glasses for carbonate calibration in its present form (but see Garbe-Schönberg *et al*. 2014). Using the Mg value for NIST SRM 610 of Pearce *et al*. (1997), the mean measured MACS-3 value is 0.8% and 2.5% higher than the information value for spot and track analyses respectively, within the long-term precision. Therefore, we do not observe the same offset when calibrating carbonates to glasses reported by Hathorne *et al*. (2008); our dataset indicates that accurate carbonate data are possible using the NIST glasses for calibration.

^{27}**Al:** Calibration of Al in phosphate and volcanic glasses at per cent mass fraction to NIST SRM 610/2 is both accurate (broadly better than 3–4%) and precise (sub-3%, some ablation conditions characterised by long term accuracy of ~ 1%, Tables 3 and 5). There is no significant benefit of preferentially using either NIST SRM 610/612 for calibration, unsurprising given their similar Al mass fractions and matrices. We find MACS-3 to be considerably more heterogeneous (precision 32–38%) than previously reported by Chen *et al*. (2011) (< 10%), although our result is in agreement with studies that use an internal standard rather than bulk component normalisation (Jochum *et al*. 2012, Lazartigues *et al*. 2014).

^{31}**P:** Phosphorus determination by LA-ICP-MS is challenging because of the interference of ^{15}N^{16}O, ^{14}N^{16}O^{1}H, ^{15}N$_2$^{1}H, and at least three others on m/z = 31. Despite the hydrogen-containing polyatomic masses, our data demonstrate the importance of using H$_2$ instead of N$_2$ as an additional diatomic gas for the purposes of precise determination of P. Averaged over all RMs and ablation conditions for which diatomic gas-type data are available, we observed an improvement in precision from 109% using N$_2$ to 12% with H$_2$, similar in quality to that of Jenner and O'Neill (2012). NIST

SRM 612-calibrated P data for NIST SRM 610, GOR128-G and KL2-G yield measured values within 10% of those reported, demonstrating that reasonably accurate and precise P data at ~ 100 µg g^{-1} is possible.

^{55}Mn: At mass fractions above ~ 10 µg g^{-1}, Mn can be accurately and precisely measured by laser ablation across a range of matrices. Long-term accuracy and precision for all glasses is generally better than 5% and 3% respectively (Tables 3–6). The MPI glasses are consistently offset to values 1–4% above reported, which probably results from matrix-induced differential down-hole fractionation rather than a systematic error in these values, given that this offset is more pronounced for spot analyses compared with tracks, and is independent of which NIST glass is used for calibration. Irrespective of the cause, a small accuracy correction when calibrating glass data to NIST SRM 610/612 may be justified. The 5–6% lower measured Mn value compared with the information value for MACS-3 is identical to that of Jochum *et al*. (2012) using a 193 nm laser. Therefore, this may indicate that the MACS-3 information value is 5% too high given that this is equally the case for spot and track analyses, and we report > 200 ^{55}Mn determinations on two MACS-3 pellets.

Because *m/z* 55 suffers from a large gas blank correction as a result of ^{40}Ar^{15}N, it is more challenging to accurately quantify Mn in samples at low/sub µg g^{-1} mass fractions. Using H$_2$ as an additional diatomic gas reduces the *m/z* = 55 gas blank by almost two orders of magnitude (from > 4×10^5 to < 1×10^4 cps on average on the Agilent 7500ce). This improvement is a necessity for Mn determination when low repetition rates or small spot sizes are desirable (e.g., Evans and Müller 2013). For example, the detection limit for slow depth-profiling (44 µm, 2 Hz) is improved from 87 to 6 µg g^{-1} on average, comparable to that of Chen *et al*. (2011) derived from a LA system with no diatomic gas but using a higher repetition rate (8 Hz).

^{57}Fe: Fe determination by calibration to NIST SRM 612 is not possible because of the interference of ^{40}Ca^{16}O^{1}H. NIST SRM 610-calibration of the MPI glasses produces data in the broad region of reported values (i.e., within ± 50%), but with significant offsets that means accurate or

precise Fe mass fractions are not feasible on our system using NIST for calibration, and calibration using high-Fe mass fraction glasses was not developed because there was no requirement to do so. Previous studies have reported accurate Fe data and good LA-EPMA agreement when calibrating to high-mass fraction reference materials such as BCR-2G, or by using a multi-RM calibration line (Liu *et al*. 2008, Arevalo *et al*. 2011, Jenner and O'Neill 2012).

[66]**Zn:** Track data are severely compromised by Zn contamination, the most likely cause of which is zinc stearate powder, apparently present even on powder-free gloves (Friel *et al*. 1996, Evans and Müller 2013). Whilst samples are routinely pre-ablated, it may be that not all users pre-ablate RMs in the same way, which could lead to remnant surface contamination. NIST SRM 610-calibrated track data are offset to measured mass fractions up to 50% too high, whilst NIST SRM 612-calibrated data are reasonably accurate but imprecise because it has a more similar (Zn) to MACS-3 and the MPI glasses (NIST SRM 612 (Zn) = 39.1 µg g^{-1}, MACS-3 111 µg g^{-1}, GOR132-G 74.7 µg g^{-1}). This precludes further discussion of data obtained by LA tracks. However, depth profiling does not suffer from surface contamination, which allows the assessment of Zn data quality on our system using this method (Figure 4B). Calibrating the NIST glasses to each other produces data that is both accurate (< 4%) and precise (< 6%). NIST-calibrated GOR132/128-G data are of a similar quality (precision < 6% and accuracy ~ < 10%). On average, GOR132-G and GOR128-G data are offset to values -5% and +5% from reported, respectively. This may be a result of differential NIST-MPI fractionation factors at smaller spot sizes (Jochum *et al*. 2012, Kroslakova and Günther 2007) and the magnitude of the observed offset is not large enough to warrant recommendation of an accuracy correction. The limited data available for MACS-3 indicate accuracy comparable to the MPI glasses, albeit with a higher precision (20%), in common with most other elements in this RM.

[85]**Rb:** Long-term Rb accuracy was better than 3% for all RMs and ablation conditions (Tables 3 and 5), with the exception of small spots and track data of the MPI and STDP glasses (7–14%), although we note that much of the reported value data are based on LA-ICP-MS analysis (Table 2). Long-term Rb precision of sub µg g^{-1} samples is 15–20%. Spot size-dependent variation in

fractionation indices is a known feature of LA in general for the volatile elements (e.g., Tomlinson *et al*. 2010), differential NIST-MPI fractionation factors for the alkali metals (Figure 3) is the most likely explanation for the ~ 15% higher measured value of spot analyses on GOR132/128-G and KL2-G compared with track data. The STDP3-150/5 phosphate glasses were consistently offset (our measured value is 10% lower than reported) although there is little data with which to place this in context. The low Rb mass fraction of MACS-3 (along with likely heterogeneity) means that it is difficult to assess accurately by LA-ICP-MS. However, as a preliminary working value, the mean of all spot and track analyses from two different MACS-3 pellets is 58 ± 8 ng g^{-1} ($n = 64$, 2SE, range of individual analyses = 40–200 ng g^{-1}). This is within error of that reported by Jochum *et al*. (2014) using a 200 nm fs LA system (70 ± 8 ng g^{-1}).

[88]Sr: NIST SRM 612-calibrated analyses of both NIST SRM 610 and all the regularly analysed MPI glasses are generally characterised by accuracies of < 1% and precision of < 4% (Tables 3–6, Figure 4C); calibration using NIST SRM 610 produces data of equivalent quality. Spot analyses of ATHO-G and StHs6/80-G are equally accurate but considerably less precise (11% and 5% respectively), indicating that these RMs are less homogeneous than both NIST SRM 610/612 and the more basic MPI glasses despite their higher Sr mass fraction. This is in agreement with the SIMS data of Jochum *et al*. (2006), which indicates μm-scale heterogeneity of a similar magnitude. There are insufficient analyses to break STDP phosphate glass data quality down by ablation parameter. Based on the mean of all data, long-term accuracy is 2–4%. The small inconsistent offset (measured STDP3-1500 Sr is lower than reported whilst the others are higher) indicates that this is unlikely to be a result of differential NIST/phosphate glass fractionation. There is little previous data with which to compare, although we note the observed offset for STDP5 (i.e., a Sr mass fraction of 1496 μg g^{-1}) is in much better agreement with the 200 nm fs-LA data of Jochum *et al*. (2014) than the recommended value (Klemme *et al*. 2008). Further data from more laboratories is required to verify this, however our analyses indicate that these offsets are rooted in the STDP reported values, which may require minor revision in the future. MACS-3 is considerably more heterogeneous than the other RMs (precision of 8–13%) and consistently offset to values 5% lower than the reported value. This is in

poor agreement with previous 193 nm LA studies (Chen *et al.* 2011, Tabersky *et al.* 2013, Jochum *et al.* 2012), which broadly agree with the information value of 6760 μg g^{-1}. The 200 nm fs-LA data of Jochum *et al.* (2014) further support these existing datasets, which may suffer to a lesser extent from bias resulting from the use of a calibration RM with a different matrix. The reason for this offset is not entirely resolved, but cannot be an artefact of our data processing given that we demonstrate excellent Sr data for other RMs. Instead this may be due to minor detector nonlinearity at high count rates for ^{88}Sr at > 6000 μg g^{-1}, noticeable despite careful dead time and daily detector voltage calibration. In any case, the relatively poor MACS precision prevents us from recommending an accuracy correction when analysing Sr in carbonates.

^{89}**Y:** The accuracy for yttrium was generally better than 2–3% for track analyses and ~ 4% for spots. All NIST SRM 612-calibrated measured Y mass fractions in the secondary RMs are negative irrespective of matrix (except STDP3-150), indicating that the NIST SRM 612 Y value may be too low by 2.9% (this is not a feature of the NIST SRM 610-calibrated dataset). Whilst this is well within the range of previously reported and compiled values, which are 38.5 ± 3.9 μg g^{-1} and 38.3 ± 2.5 μg g^{-1} for solution and LA-ICP-MS respectively based the GeoReM database, our NIST SRM 612 Y value is derived from twelve different NIST wafers calibrated to seven other well-characterised RMs. The accuracy of the other RMs is better than we can assess given possible uncertainties of this magnitude (~ 3%) in the preferred value of the NIST glasses. Ablation parameter-specific precision is better than 5% for all RMs with the exception of MACS-3 (6–16% depending principally on spot size).

Diatomic gas type exerts no discernible control on accuracy for most RMs, which is unsurprising for RMs with Sr/Y ratios of ~ 1. However, MACS-3 (Sr/Y = 302) measured (Y) increases by 8.0% when H$_2$ instead of N$_2$ is used as the diatomic gas (*n* = 138 and 62 respectively, Figure 7). Given that these data represent the average of a range of spot sizes, mostly at 15 Hz repetition rate, it is unlikely that other factors could lead to this bias. An 8% positive increase in MACS-3 Y is equivalent to 1.8 μg g^{-1}, which equates to a ^{88}Sr^{1}H$^+$production rate of 0.027% for carbonate ablation using H$_2$. This may be a significant Y bias for carbonates or phosphates (e.g., the shells of marine organisms or tooth enamel)

which often have Sr mass fractions > 1000 μg g^{-1}. Given that Y/Ca (and other REE/Ca) ratios have been used as an indicator of diagenesis in such material (Müller *et al*. 2009, Evans *et al*. 2013), this should be taken into account when adding H$_2$ to the carrier gas stream. Whichever diatomic gas is used, our data indicate that the MACS-3 Y value requires revision (N$_2$ accuracy is 0.871, equivalent to a mass fraction of 19.5 μg g^{-1}), which is consistent with the mean of all data in the GeoReM database. Whilst H$_2$ results in an apparently better accuracy (0.951), see Figure 7, this is likely to be the combined result of a reported value that is too high, and does not indicate that H$_2$ should be used for accurate Y determination.

[138]**Ba:** Ba data quality in RMs with > 10 μg g^{-1} is both accurate and precise. The NIST, STDP and MPI glasses with relatively high (Ba) have long-term accuracies of < 6%, and < 2% is possible for certain ablation conditions. Long-term precision is better than 5% for most conditions. The consistent negative offset of NIST SRM 612-calibrated data may indicate that NIST SRM 612 (Ba) should be ~ 2% higher, or at least that the ID-TIMS data published in Jochum *et al*. (2005) (1% higher than the compiled value) should be adopted. The only other notable offset within the set of RMs presented here is for the phosphate glass STDP5 (measured values are 6% higher than reported). This is in broad agreement with the 200 nm fs-LA value of Jochum *et al*. (2014), which is offset from the recommended value of Klemme *et al*. (2008) by +3%. In contrast to the higher mass fraction RMs, GOR132/128-G accuracy is dependent on analysis type (spot/track). This offset is more pronounced for GOR132-G (0.82 μg g^{-1} Ba; characterised by a 15% difference) than GOR128-G (1.1 μg g^{-1}; 7%), where track analyses are characterised by measured values further offset from reported values than spots. The reason for this offset may either be surface contamination, to which ablation tracks are more susceptible than spots, or a problem with the extrapolation of the NIST mass fraction-intensity ratio to glasses with a far lower (Ba), although we note the MPI-DING reported Ba values are largely based on LA-ICP-MS measurements (Table 2).

Rare earth elements: Spot analysis of the REE in many of the MPI glasses is discussed in detail by Tomlinson *et al*. (2010), with minor differences here mostly relating to the use of [43]Ca

instead of [29]Si as an internal standard element. Track data of KL2-G and GOR132/128-G indicate data quality equivalent to spot analyses, with principal differences due to the low mass fraction of the REE in GOR132/128-G (the higher repetition rate of track analyses results in overall more precise data). The GOR132-G [139]La data showcases the ability of LA-ICP-MS to produce accurate and precise data at a mass fraction of 84 ng g^{-1} (overall < 15% and < 30% respectively). For most REE, present at μg g^{-1} mass fraction in these glasses, sub-5% long-term accuracy and precision is routinely possible. Measured mass fractions on both GOR132/128-G are consistently offset to 10% below the reported value for [146]Nd, although this is within the range of the LA data of Jochum *et al.* (2006) and subsequent studies (e.g., Jenner and O'Neill 2012). The STDP glasses are characterised by excellent homogeneity for [140]Ce (precision 2–4% when calibrated using NIST SRM 610), although our data indicate that the STDP3-1500 Ce information value is too high by 8%. Similarly, we measure a more precise STDP3-150 Nd mass fraction of 0.17 ± 0.004 μg g^{-1} ($n = 30$, 2SE, calibrated using NIST SRM 610), indicating that the reported value of 0.2 μg g^{-1} is too high (this was given to one significant figure (Klemme *et al.* 2008)). We find all three of these phosphate glasses to be considerably more homogeneous for Nd than original reported, STDP3-150/1500 are characterised by 2RSD Nd of 14% and 9% respectively ($n = 30$ in both cases). Finally, the lanthanides are one part of the periodic table to which the MACS-3 carbonates may have particular application. NIST-calibrated MACS-3 data are reasonably precise in comparison with most other elements in this pressed powder. La, Ce and Nd have 2RSD of ~ 10% which may be sufficiently homogeneous for most applications. However, we measure MACS-3 values ~ 10% lower than the information value for all the REE reported here, and observe offsets for some STDP3 glasses (e.g., our STDP3-1500 measured value 8% lower than reported), suggesting minor revisions to some reported values may be required. Tanaka *et al.* (2007) report data of similar quality.

[208]**Pb:** The volatility of Pb is a well-known issue for LA (Jackson 2001), exemplified by the inter-RM differences in fractionation factors (Figure 3). The overall higher and more variable fractionation compared with most other analytes evident in Figure 3 and reported many times before (e.g., Jochum *et al.* 2014), results from variation in the crater depth-dependent particle size

distribution as a function of ablation conditions (Jackson and Günther 2003). Nonetheless, at > 10 µg g^{-1} (GOR132-G, StHs6/80-G and the STDP glasses) reasonably precise (< 10%) Pb data are possible with a 193 nm ArF laser (Figure 4D). Precision may be further improved by using a reference material with improved Pb homogeneity than the NIST glasses (see Eggins and Shelley 2002). We do not attempt to assess the accuracy of the MPI glasses, as the offsets we observe are likely smaller than what may be expected from differential NIST-MPI fractionation factors, given the GOR132-G and StHs6/80-G accuracy of < 5%, much less than the long-term precision of these analyses (although we note that the MPI-DING reported values are largely based on LA-ICP-MS, Table 2). In contrast, our data may suggest the Pb information values of both STDP3-150/1500 require downwards revision, which are characterised by mean measured values 8% above and 13% below Klemme *et al.* (2008) respectively (both greater than long-term precision). The agreement of our data for STDP5 with the recommended value indicates that these offsets are not matrix-induced. In the case of STDP3-150, our measured value (139 µg g^{-1}) is in excellent agreement with the original solution ICP-MS data (145 µg g^{-1}) (Klemme *et al.* 2008), and we recommend the use of this when analysing phosphates. Spot analyses of MACS-3 indicate heterogeneity of 8% (collected from the first 1.5 years only), although track data are considerably worse (28%), limiting its use as a primary or secondary RM.

[232]**Th:** ATHO-G and StHs6/80-G Th data are discussed in Tomlinson *et al.* (2010). At high mass fractions in well-characterised RMs (the NIST glasses), accuracy and precision are < 2% and < 6% respectively. Approximately fifty analyses of KL2-G indicate that acceptably accurate and precise (< 10% and 5–7% respectively) measurements are possible at 1 µg g^{-1}. MACS-3 precision is ~ 20%, although our data indicate that the Th mass fraction in this RM requires downward revision of 13%; the mean value based on our dataset is 46 µg g^{-1}. This is in agreement with the 213 nm data of Jochum *et al.* (2014), whereas the 200 nm fs LA data of that study, along with most other data in the GeoReM database is in agreement with the information value (Chen *et al.* 2011, Jochum *et al.* 2012, Tabersky *et al.* 2013). Given that there are insufficient analyses in our dataset to assess the MACS-3 Th fractionation factor, possible Th fractionation as a result of ablation parameters and/or ICP-MS tuning conditions should be borne in mind when calibrating carbonates to the NIST glasses.

[238]U: High-mass fraction matrix-matched calibration (NIST SRM 612-610) is accurate and precise. The higher mass fraction MPI RMs (1–2 µg g^{-1}, ATHO-G and StHs6/80-G) have a long-term precision of 14–15% (Figure 4E), and reasonable (~ 20%) precision is still possible for GOR132-G (48 ng g^{-1}). However, at lower mass fractions (GOR128-G = 12 ng g^{-1}) only analytical conditions associated with relatively high ion beam intensities (high repetition rate, large diameter beam) produce useful data (track and spot precision are 23% and 63% respectively). MPI glass accuracy is good, given the low U mass fractions, characterised by a long-term average of < 5% except for GOR132/128-G (< 10%). The higher mass fraction STDP glasses are all characterised by precisions of 4–7%. Our measured values for STDP3-150 is in excellent agreement with the reported/information, whereas our STDP3-150/STDP5 data indicate that these information values require revision, or that differential U/Ca fractionation becomes an issue at mass fractions greatly exceeding that of the NIST glasses. MACS-3 data are characterised by a long-term precision of ~ 30%, around double that of glass RMs with comparable U mass fractions (Figure 4E) and our long-term data are consistently offset to lower values than reported. We measure a mean value of 1.25 µg g^{-1}, similar to the data of Chen *et al*. (2011) calibrated using the NIST glasses and the 213 nm LA data of Jochum *et al*. (2014). Whilst this is not the case for the 200 nm fs-LA data of that latter study (mean measured (U) = 1.50 µg g^{-1}, *n* = 4), U heterogeneity is a known issue of MACS-3, which is further highlighted by our long-term precision based on ~ 250 analyses. This implies that a large number of analyses are required to approach the mean value, and therefore our data indicate that the MACS-3 information value may require minor revision.

Further discussion

Long-term trends

We observe no long-term trend in data quality for any analyte in the dataset (e.g., Figure 4), demonstrating that appropriately calibrated, blank-corrected 193 nm laser ablation measurements do not suffer from long term biases. Therefore, we confirm that with careful hardware maintenance and

appropriate data processing, there should be no discernible temporal drift in long-term LA data. The only exception to this is the data for boron, for which we expect and observe an improvement in accuracy through time reflecting the installation of nylon-6 tubing (see above [11]B, and Figure 6). Furthermore, despite variation in ICP-MS tuning between sessions many of the long-term values for precision we report (Tables 4 and 6) are well below 10%, demonstrating that despite the challenges LA must overcome in order to improve data quality, such as the availability of well-characterised homogeneous RMs with a variety of matrices, long-term drift is not an issue.

Cell homogeneity

Because *x*–*y* stage coordinates are available for each analysis, potential spatial variation in data quality, fractionation factors or sensitivity can be investigated. The location of all the analyses described in this study are shown in Figure 8A. To maximise the amount of data available for the assessment of possible heterogeneity in element/element fractionation, all analyses were normalised to the mean measured value for that RM (i.e., accuracy was forced to 1 on a RM by RM basis). This ensures that the unavoidable preferential placement of some RMs in certain places in the ablation cell due to sample holder constraints (e.g., NIST SRM 612, Figure 8A) does not produce apparent spatial variation as a result of an issue with, for example, the reported value or differential fractionation factors of these RMs.

As an example, the ^{25}Mg/Ca offset normalised in this way is shown as a function of analysis position in Figure 8B. This provides a visual indication that there is no significant bias in Mg data depending on the location of the RM, for example close to the corners of the ablation cell where He flow dynamics might be expected to be impacted by the proximity of the cell wall. Even amongst the subset of analyses with relatively large deviations from the mean (up to $\pm$ 10%), possibly resulting from occasional more extreme ablation conditions, there is no obvious spatial trend.

Extending this analysis of cell homogeneity to more challenging analytes, Figure 8C shows NIST SRM 612-calibrated NIST SRM 610 Th/U ratios as a function of distance from the cell centre, chosen because these elements are well-known to exhibit significant down-hole fractionation with respect to each other (e.g., Paton *et al*. 2010). As for Mg/Ca, there is no detectable fractionation as a function of distance from the centre of the cell. Because NIST SRM 610 and 612 are usually contained within the same 25 mm mount, this cannot be an artefact of potentially different fractionation between spatially separated NIST glasses cancelling out when many measurements are considered. Finally, extending the method used to assess Mg/Ca cell homogeneity in Figure 8B to all analytes for which sufficient data exist (Figure 8D) demonstrates that the two-volume Laurin cell does not induce discernible spatial fractionation for any element when using Ca as an internal standard. Nonetheless, this should be viewed in the context of the long-term precision of these analyses; data derived from a number of RMs over a long time-period are unlikely to be able to resolve sub-% differences in accuracy when analytical parameters and/or limitations induce overall precision around an order of magnitude higher than this.

Diatomic gas type

The addition of small amounts of the diatomic gases N_2 or H_2 have been established as an effective method of improving sensitivity and signal/background ratios in LA-ICP-MS (e.g., Durrant 1994, Guillong and Heinrich 2007, Hu *et al*. 2008), following earlier work exploring a similar strategy for solution analysis (e.g., Lam and Horlick 1990). The basis of this is that both diatomic gases raise the temperature of the plasma, and it has been demonstrated that the element-specific sensitivity increase correlates with first ionisation potential (Guillong and Heinrich 2007). On our system, N_2 is slightly more effective at increasing sensitivity than H_2, so that H_2 is used only when a specific N-containing polyatomic interference must be avoided, or a polyatomic interference must be shifted to a different mass by reaction with H_2 (e.g., $^{40}Ar^{15}N$ on ^{55}Mn or $^{15}N^{16}O$ on ^{31}P).

Whilst specific instances of data quality significantly influenced by diatomic gas type were given above (*Accuracy and precision*), the dataset also allows broader trends to be recognised. Of these, the most obvious target is to evaluate potential differences in long-term accuracy and precision when using H_2 rather than N_2 for spot analyses. Examples of this are shown for NIST SRM 610 and GOR132-G in Figure 9, calibrated using NIST SRM 612. The NIST SRM 610 data are broadly characterised by similar accuracy and precision irrespective of diatomic gas, which is unsurprising given that the mass fraction of most analytes is high, and it is matrix-matched to NIST SRM 612. Notable exceptions to this are that ^{55}Mn precision is substantially better using H_2 (as discussed above), whereas ^{11}B precision is almost three times better using N_2. In both cases this primarily results from an improvement in the signal/background ratio, which is overall higher using N_2 except in specific cases where H_2 aids in the removal of a polyatomic interference. It is difficult to explain why H_2 apparently results in more precise data for *m/z* 89 and 140, which may be an artefact of the number of analyses in each dataset. NIST SRM 612-calibrated NIST SRM 610 accuracy is broadly equivalent when using H_2 or N_2 (Figure 9C).

An equivalent exercise for GOR132 calibrated using NIST SRM 612 is shown in Figure 9B. As for NIST SRM 610, ^{55}Mn precision is greatly improved when using H_2, but worse for all other analytes. This is especially the case for ^{11}B and ^{238}U which are characterised by a low signal/background ratio and signal intensity respectively; clearly H_2 should not be used if the quality of sub µg g^{-1} mass fraction elements (or those with high background intensities) is important, if N_2 is also available and there is no specific reason for doing so. The broader scatter in accuracy for GOR132-G (Figure 9D) is discussed extensively above, and results from a number of specific factors, principally related to likely issues with the reported values for some analytes in NIST and differential fractionation factors between the NIST and GOR reference materials for the alkali metals (Figure 3). The fact that most analytes lie close to the 1:1 line demonstrates that the data discussed in the section *Accuracy and precision* largely do not suffer from a diatomic gas-derived bias. Nonetheless, the lowest mass fraction elements in GOR132-G (e.g., U) are characterised by moderately improved accuracy using N_2, whereas ^{55}Mn accuracy is better using H_2. Again, this most likely results from the improved signal

intensity and signal/background ratio respectively, highlighting that maximising these can result in better precision *and* accuracy, but see Figure 7 for an example of a specific case where the use of H_2 is less appropriate.

Conclusions

The LA-ICP-MS trace element data 'mining' program (*LA-MINE*) presented here highlights the need to consider large datasets in order to representatively report accuracy and precision, and to assess reported RM values. However, whilst we show that precision may be worse than typically reported based on a limited number of analyses conducted under a specific set of ablation conditions, this long term (5 year) dataset of ~ 5700 analyses of reference materials also highlights that excellent trace element data is possible even when large differences in ablation conditions and ICP-MS tuning between measurement sessions are taken into account. If careful attention is paid to the choice of reference materials, sub-5% reproducibility (2*s*) and accuracy are easily possible for some analytes even if ablation conditions are varied across those routinely used in the Earth and Environmental sciences. Our mass-specific breakdown of data quality in ten commonly analysed reference materials, including the NIST glasses, highlights where care must be taken in order to produce good data (for example boron), and enables us to assess the relative effects of LA-ICP-MS-induced fractionation and error in the reported value of some elements in certain RMs (e.g., NIST Mg). We observe no long-term temporal trends in accuracy and precision for any analyte in any of the reference materials we routinely analysed, demonstrating that data acquired over long time periods are comparable, provided that long-term accuracy and precision are appropriately characterised. However, in certain cases we observe significant differences in both accuracy and precision depending on ablation conditions, particularly relating to the use of either H_2 or N_2 as the additional diatomic gas. Given that our dataset was collected over a long period under a variety of laser ablation parameters and ICP-MS tuning conditions, any such differences are highly likely to be real and warrant further exploration. Finally, because stage coordinates are available for each analysis, we are able to assess long-term ablation cell homogeneity for the first time. We find no significant centre-edge gradient in any element/Ca ratio,

providing good evidence that the Laurin two-volume cell does not suffer from spatially varying fractionation at a level likely to significantly bias trace element data. The Matlab program may be especially useful for inter-laboratory comparison, as similar datasets from other LA-ICP-MS systems could be produced in a short period of time. Because our data are derived from commonly analysed reference materials, pursuing this line of enquiry would give a comprehensive overview of the comparability of trace element data between LA-ICP-MS systems.

Acknowledgements

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Supporting information

The following supporting information is available online:

Data appendix containing: Tables S1–S4 (mean measured mass fractions for all reference material and ablation parameter combinations), fractionation factors; Figures S2–S73.

This material is available as part of the online article from:
http://onlinelibrary.wiley.com/doi/10.1111/ggr.00000/abstract
(This link will take you to the article abstract).

Figure captions

Figure 1. Automatic calculation of the time offset between laser ablation and ICP-MS computers. (A) An example ICP-MS file, showing the total ion beam (TIB) intensity as a function of time. (B) The TIB is shifted incrementally in steps of one ICP-MS dwell time to create 2001 version of the dataset that each begin at incrementally different machine times. Lightly shaded areas are deleted portions of the matrix according to the start and end times of each analysis given by the laser log file. (C) Summing the TIB of the remaining data for each dwell time shift provides an effective mechanism of calculating the time offset between the LA and ICP-MS files, as this is maximised only when the deleted portions of data match the location of the background segments of the TIB (see text for details).

Figure 2. Raw Sr/Ca and U/Sr ratios for the most commonly analysed reference materials (colour, except NIST), shown in the context of all sample analyses (grey). All other RMs and the majority of samples are distinct from the NIST glasses in Sr/Ca-U/Sr space, with the exception of the phosphate glasses STDP3-150 and STP3-1500/STDP5 which overlap with NIST SRM 610 and NIST SRM 612 respectively (see text for details of the resolution to this problem and minor overlap with some sample types). These ratios therefore provide a robust means of identifying NIST analyses without user confirmation. Note that the scatter in raw element/element ratios of the RMs is larger than that of the final mass fraction data, as raw ratios are calculated prior to data exclusion based on the LOD, and depend on LA-ICP-MS tuning parameters.

Figure 3. (a) Mean NIST SRM 612 fractionation factors from all depth-profiling analyses. The vast majority were conducted with a 44 μm spot size and 2 Hz repetition rate. Colour is shown as a function of the number of analyses used to calculate each data point, see scale in lower right. Error bars are 2s. (b) NIST SRM 610 fractionation factors relative to NIST SRM 612, i.e., NIST SRM 610 fractionation divided by NIST SRM 612 fractionation, values greater than 1 imply a larger fractionation factor for NIST SRM 610 than NIST SRM 612. Fractionation factors relative to NIST SRM 612 are plotted to aid identification of significant differences between reference materials, see the supporting information for raw fractionation factors. Here, error bars are 95% confidence intervals as they are derived from the combined uncertainty on the fractionation factor for both RMs. (c–e). As panel B, except for MACS-3, GOR132-G and GOR128-G respectively. Masses greater than [146]Nd are not shown for GOR128-G as not enough analyses were available to calculate statistically meaningful factors. Gaps in the data are associated with fewer than 10 depth-profiling analyses for that mass and RM combination.

Figure 4. (a) All NIST SRM 612-calibrated data for m/z 25. See panels b–d (for ^{66}Zn, ^{88}Sr, ^{208}Pb and ^{238}U, respectively) and the supporting information for similar figures of other analytes discussed in the text. Open and closed symbols represent spot and track analyses respectively. Marker size is shown as a function of spot size and colour is shown as a function of repetition rate. Accuracy ± precision (2s) is shown in the bottom left of each panel (values > 1 denote a measured mass fraction greater than the reported value), with the number of analyses above the limit of detection in brackets. In all cases, data were calibrated using the NIST SRM 612 mass fraction values of Jochum *et al.* (2011). Reported analyte mass fractions in each RM are shown in the top left of each panel in μg g^{-1}.

Figure 5. ^{7}Li accuracy as a function of signal/background ratio for each analysis. Symbol size is shown as a function of spot size. (a) Track (line scan) analyses for the five most commonly analysed RMs. (b) Spot analyses; see legend in panel (a). (c) The same data shown in panel (b), with colour as a function of fractionation factor. These data indicate that the accuracy offset of the GOR glasses is a result of differential fractionation factors between the RMs, rather than a function of mass fraction or an issue with the reported values. Data acquired using both N_2 and H_2 as a diatomic gas are shown, as this parameter does not significantly affect Li accuracy or fractionation factors in our dataset.

Figure 6. The effect of installing nylon-6 tubing on ^{11}B background intensity. Following an initial sharp rise during 2010, attempts were made to reduce the B background by replacing the tubing, torch and thorough cleaning of the ablation cell, resulting in a modest reduction. On replacement of the entire tubing (including the squid gas signal smoothing device) with nylon-6, the gas blank on $m/z = 11$ reduced by more than an order of magnitude over a period of ~ 1 year. The GOR128-G signal/background ratio when depth profiling increased by more than an order of magnitude as a result.

Figure 7. ^{89}Y accuracy in the pressed powder carbonate reference material MACS-3, using either N_2 or H_2 as an additional diatomic gas. The use of H_2 when analysing this RM results in a positive accuracy shift of 8 ± 2%, which is most easily explained by the formation of ^{88}Sr^{1}H$^+$ (MACS-3 Sr/Y = 302), see text for details. Light shaded regions represent 2SE of each dataset. Note that whilst the use of H_2 results in an apparent improvement in ^{89}Y accuracy, this is indicative of an issue with the reported (Y) value, rather than true improvement when using H_2.

Figure 8. (a) The location within the ablation cell of all the RM analyses presented here (only the start points of ablation tracks are shown). These are biased towards the right-hand side of the cell as certain sample holders only allow RMs to be placed on this side. (b) Example homogeneity exemplified by ^{25}Mg/Ca offsets as a function of analysis position, shown by colour. Data for all RMs are shown, normalised to the mean value measured for each RM in order to remove any accuracy offset associated with reported value error. This illustrates the absence of and positional accuracy bias within the sample holder. (c) Measured NIST SRM 610 Th/U calibrated using NIST SRM 612 as a function of distance from the cell centre, again demonstrating the absence of positional artefacts and

illustrating how centre-edge gradients are calculated. (d) Centre-edge gradients for all m/z relative to ^{43}Ca with > 1000 total analyses, i.e., accuracy change as a function of distance from the cell centre. The gradient is shown as accuracy change per mm. None of these slopes are significant, and are displayed only to illustrate this point.

Figure 9. (a) The effect of diatomic gas type on precision and accuracy for NIST SRM 612-calibrated NIST SRM 610 analyses as a function of the mean N_2 signal/background ratio. H_2 precision relative to N_2 precision is the ratio of the mean precision of all data collected using H_2 to the mean precision of all data collected using N_2, where e.g., a value of 2 denotes a 2× better precision using N_2 compared with H_2. H_2 results in improved precision for masses with polyatomic interferences (e.g., ^{55}Mn), but lower precision when sensitivity was significantly reduced compared with N_2 (^{11}B). There is no significant difference for most analytes. (b) As panel (a) except based on GOR132-G calibrated using NIST SRM 612. (c) A comparison of accuracy for the masses shown in panel A in NIST SRM 610 when using N_2 and H_2, demonstrating that there is little change in most cases (but note ^{55}Mn and see Figure 7 for another example of an exception to this). The poor Mg accuracy is best explained by an issue with the reported value for the NIST glasses, see text for details. (d) As panel (c) except based on GOR132-G. In all panels, only masses with more than forty data points available for both diatomic gas types are shown. Note that the calculated signal/background ratios for m/z characterised by ~ 0 cps gas blank results in arbitrary values (e.g., GOR132-G ^{238}U, which is high because the mean background is almost 0 cps, even though the signal intensity is also low).

Table 1.

The number of analyses of each secondary reference material, using either NIST SRM 610 or 612 as a primary RM. Analysis type spot/track (S/T) ratios show that almost all STDP analyses were tracks, whereas most ATHO-G and StHs6/80-G analyses were spots (a value of 0.5 would indicate an equal number of spot and track analyses). H_2/N_2 values denote the ratio of the number of analyses conducted with H_2 to those with N_2 (virtually all analyses were performed with one of these diatomic gases). These are an estimate only, as data from this mass flow controller is sometimes missing from the GeoStar log files.

	NIST SRM 610 calibrated			NIST SRM 612 calibrated		
	n	S/T	H_2/N_2	n	S/T	H_2/N_2
NIST SRM 610				1085	0.46	0.23
NIST SRM 612	1026	0.47	0.26			
NIST SRM 614	22	0.00	0.00	25	0.12	0.00
MACS-3	180	0.30	0.03	290	0.42	0.03
GOR132-G	356	0.67	0.10	431	0.68	0.09
GOR128-G	348	0.66	0.09	503	0.72	0.07
KL2-G	99	0.31	0.03	113	0.29	0.03
ATHO-G	16	0.81	0.00	365	0.98	0.00
StHs6/80-G	13	0.75	0.00	532	0.99	0.00
STDP3-150	35	0.00	0.00	68	0.00	0.00
STDP3-1500	39	0.05	0.00	70	0.03	0.00
STDP5	39	0.05	0.00	76	0.04	0.00

Table 2.

A brief overview of the degree to which the reference materials assessed here are well characterised. For each element and RM combination three numbers are given. In order, these denote the number of techniques used to characterise that element/the number of analyses on which the reference value is based/the number of those analyses that were laser ablation. For example, the reported (Li) of NIST SRM 610 (Jochum *et al*. 2011) is based on three techniques and eight analyses in total, of which four were LA-ICP-MS measurements. Bold numbers denote reported values that are characterised by only two techniques, where > 50% of the data that went into the reported value are based on LA-ICP-MS measurements. Underlined numbers are reported values which are based on more than two techniques, where > 50% of the data on which these are based come from LA-ICP-MS measurements. When comparing our results to the reference values, in very broad terms, element-RM combinations in bold may be considered an exercise in inter-laboratory LA-ICP-MS comparison, whereas others may inform us of inter-technique biases. Data were compiled from Jochum *et al*. (2006, 2011), Klemme *et al*. (2008). Note that further data may be available from the GeoReM database.

	Li	B	Na	Mg	Al	Si	Mn	Fe	Zn	Rb	Sr	Y	Ba	La	Ce	Nd	Pb	Th	U
NIST SRM	3/8/4	3/5/3	2/8/3	6/15/4	2/9/3	1/6/0	10/23/9	6/16/7[*]	6/19/9	6/23/8[*]	8/23/10[*]	5/18/6	4/16/8	6/29/10	7/23/7	8/26/8	6/22/9[*]	6/27/10[*]	5/19/7[*]
NIST SRM	<u>3/13/8</u>	5/8/4	2/8/4	**2/10/8**	2/6/2	2/9/3	<u>5/19/12</u>	3/8/4[*]	4/15/7	4/18/8[*]	<u>5/25/15</u>[*]	3/20/1	6/21/9	6/32/15	<u>4/31/16</u>	5/25/11	<u>3/23/16</u>[*]	<u>3/19/13</u>[*]	<u>4/20/14</u>[*]
MACS-3	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0	1/1/0
GOR132-G	4/8/4	3/5/3	3/12/0	3/12/0	2/11/0	2/12/0	4/18/5	3/14/0	4/7/3	<u>4/17/13</u>	4/22/15	<u>4/20/1</u>	<u>4/19/15</u>	<u>5/21/15</u>	<u>4/21/15</u>	<u>5/21/14</u>	**2/12/11**	<u>4/15/12</u>	<u>4/17/13</u>
GOR128-G	<u>4/11/6</u>	3/7/5	4/9/0	2/10/0	2/9/0	2/11/0	4/14/3	3/11/0	4/6/3	4/18/14	5/21/15	<u>4/21/1</u>	<u>4/20/17</u>	<u>5/23/17</u>	<u>5/21/15</u>	<u>5/22/16</u>	<u>3/14/12</u>	<u>4/15/12</u>	<u>3/18/14</u>
KL2-G	2/9/4	**2/5/3**	3/14/0	3/13/0	3/13/0	3/13/0	7/22/5	5/15/0	6/10/5	<u>6/27/16</u>	8/32/15	<u>7/27/1</u>	<u>9/32/17</u>	<u>9/32/17</u>	9/30/15	<u>9/30/16</u>	<u>5/18/11</u>	<u>6/32/17</u>	<u>6/27/16</u>
ATHO-G	4/12/6	**2/7/5**	6/14/1	4/16/1	4/17/1	3/16/0	7/24/6	6/20/1	6/12/5	<u>7/26/18</u>	<u>9/34/20</u>	<u>6/31/2</u>	<u>9/34/19</u>	<u>7/34/20</u>	<u>7/34/20</u>	<u>9/23/19</u>	<u>5/20/15</u>	<u>6/29/20</u>	<u>5/26/19</u>
StHs6/80-G	4/10/5	3/7/3	3/13/0	3/13/0	2/12/0	2/12/0	7/21/5	4/15/0	6/10/3	<u>7/25/16</u>	8/30/17	<u>6/26/1</u>	8/28/17	<u>6/28/18</u>	<u>7/28/17</u>	<u>7/28/17</u>	<u>4/16/12</u>	<u>5/25/18</u>	<u>4/24/18</u>
STDP3-150	**2/6/4**	1/4/0	-	1/1/0	1/1/0	1/1/0	-	-	-	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**	**2/6/4**
STDP3-	1/5/0	1/5/0	-	1/1/0	1/1/0	1/1/0	-	-	-	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0	1/5/0
STDP5	**2/7/5**	**1/5/5**	-	-	-	-	-	-	-	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**	**2/7/5**

[*]Analytes for which certified values are available, in these cases the reference value is not composed of the mean of all available data.

Table 3.

Ablation parameter and reference material-specific accuracy, based on primary calibration to NIST SRM 612. ^{43}Ca was used as an internal standard element in all cases. Data are only shown where > 20 analyses were available for a given RM and specific set of analytical conditions. Accuracy is measured/reported, i.e., values > 1 denote a higher measured mass fraction compared with the reported value. See the supporting information for the same data alternatively formatted as measured mass fraction ($\mu g\ g^{-1}$)

Spot size **Spots**		^{7}Li	^{11}B	^{23}Na	^{24}Mg	^{25}Mg	^{27}Al	^{29}Si	^{55}Mn	^{57}Fe	^{66}Zn	^{85}Rb	^{88}Sr	^{89}Y	^{138}Ba	^{139}La	^{140}Ce	^{146}Nd	^{208}Pb	^{232}Th	^{238}U
74–96	NIST SRM 610	0.992	0.942	0.995	1.185	1.205	0.988	-	1.026	0.279	0.991	0.986	0.998	0.993	0.989	1.008	1.005	0.981	0.994	1.003	0.996
	GOR132-G	1.170	1.076	1.060	1.060	1.112	1.037	-	1.021	-	0.920	-	0.980	0.999	1.103	-	1.066	0.931	-	-	0.830
44–57	NIST SRM 610	0.987	0.924	0.991	1.172	1.211	0.988	0.986	1.008	0.413	0.990	0.980	0.985	0.976	0.981	0.984	0.984	0.993	0.977	0.972	0.984
	MACS-3	-	-	-	-	1.080	0.955	-	0.944	0.354	-	-	0.928	0.873	0.965	0.933	0.918	0.906	1.013	-	0.835
	GOR132-G	1.169	1.089	1.069	1.089	1.127	1.029	1.104	1.023	0.341	0.952	-	0.974	0.971	1.064	0.819	1.007	0.894	1.029	-	0.774
	GOR128-G	1.103	0.975	1.092	1.099	1.136	1.031	-	1.039	0.353	1.045	-	0.999	0.971	0.933	0.800	0.867	0.856	-	-	0.698
20–25	GOR128-G	-	-	-	-	-	-	1.205	-	0.337	-	-	1.002	0.989	0.938	0.879	0.877	0.856	-	-	-
Tracks																					
74–96	NIST SRM 610	-	-	-	-	1.173	0.979	-	1.007	0.394	-	0.984	0.988	0.987	0.989	0.992	0.992	-	0.987	0.991	0.992
	MACS-3	-	-	-	-	1.104	0.964	-	0.991	-	-	-	0.951	-	0.994	-	0.960	-	1.159	-	0.835
44–57	NIST SRM 610	0.999	0.860	0.989	1.174	1.188	0.986	-	1.016	0.411	0.881	0.986	0.997	0.991	0.991	0.995	1.000	0.986	0.985	1.012	1.001
	MACS-3	1.034	-	-	0.977	1.016	0.993	-	0.957	-	1.016	-	0.917	0.909	0.931	0.976	0.959	0.923	1.102	-	0.846
	GOR132-G	-	1.107	0.905	1.046	1.101	1.040	-	1.020	-	0.981	0.877	0.994	0.979	1.187	0.987	1.092	-	1.020	-	0.889
	GOR128-G	-	0.980	0.924	1.053	1.106	1.037	-	1.032	-	1.025	-	1.011	0.980	1.019	0.920	0.915	-	-	-	0.971
	KL2-G	-	1.054	0.871	1.055	1.048	1.025	-	1.025	-	0.897	0.862	0.993	0.921	0.951	0.967	0.975	-	1.051	-	0.949
	STDP3-150	-	-	-	-	1.063	1.008	-	-	-	-	0.897	1.039	1.049	0.961	-	0.984	0.831	0.913	-	0.991

	STDP3-1500	-	-	-	-	1.012	0.975	-	-	-	-	-	0.971	0.999	0.949	-	0.915	0.962	0.873	-	0.964
	STDP5	-	-	-	-	-	-	-	-	-	-	0.951	1.021	0.994	1.037	-	0.977	-	1.046	-	1.062
20–25	NIST SRM 610	0.980	0.924	-	1.131	1.180	0.987	-	1.001	-	0.861	-	0.983	0.988	0.980	0.986	0.982	-	-	-	0.984
	MACS-3	1.098	-	-	1.097	1.140	-	-	0.980	-	1.107	-	1.007	0.878	0.968	0.963	0.906	-	-	-	0.654
	GOR132-G	-	1.123	-	1.048	1.105	1.042	-	1.032	-	1.109	-	0.985	0.948	1.206	-	1.072	-	-	-	-
	GOR128-G	1.082	-	-	1.085	1.132	1.055	-	1.041	-	1.057	-	1.003	0.941	0.985	0.864	0.896	-	-	-	-

Table 4.

Ablation parameter and reference material-specific precision, based on primary calibration to NIST SRM 612. Precision is defined as 2s of all data for a given set of conditions divided by the mean, e.g., 0.02 is equivalent to a 2% 2s around the mean measured value. See the supporting information for the same data alternatively formatted as measured mass fraction (µg g^{-1})

Spot size / Spots		^{7}Li	^{11}B	^{23}Na	^{24}Mg	^{25}Mg	^{27}Al	^{29}Si	^{55}Mn	^{57}Fe	^{66}Zn	^{85}Rb	^{88}Sr	^{89}Y	^{138}Ba	^{139}La	^{140}Ce	^{146}Nd	^{208}Pb	^{232}Th	^{238}U
74–96	NIST SRM 610	0.023	0.167	0.020	0.061	0.032	0.021	-	0.085	0.177	0.047	0.039	0.048	0.049	0.046	0.048	0.045	0.026	0.053	0.053	0.058
	GOR132-G	0.086	0.146	0.083	0.069	0.063	0.041	-	0.096	-	0.186	-	0.036	0.037	0.094	-	0.129	0.130	-	-	0.145
44–57	NIST SRM 610	0.032	0.202	0.025	0.053	0.050	0.023	0.023	0.041	0.192	0.066	0.041	0.028	0.034	0.032	0.029	0.034	0.037	0.040	0.037	0.060
	MACS-3	-	-	-	-	0.102	0.143	-	0.061	0.282	-	-	0.101	0.077	0.096	0.070	0.070	0.086	0.083	-	0.267
	GOR132-G	0.088	0.116	0.079	0.069	0.077	0.030	0.077	0.059	0.240	0.088	-	0.058	0.057	0.118	0.251	0.148	0.198	0.068	-	0.371
	GOR128-G	0.058	0.131	0.080	0.067	0.073	0.035	-	0.065	0.246	0.130	-	0.049	0.056	0.091	0.279	0.123	0.137	-	-	0.626
20–25	GOR128-G	-	-	-	-	-	-	0.178	-	0.254	-	-	0.060	0.059	0.198	0.377	0.213	0.221	-	-	-
Tracks																					
74–96	NIST SRM 610	-	-	-	-	0.064	0.017	-	0.040	0.144	-	0.039	0.024	0.041	0.037	0.032	0.039	-	0.059	0.047	0.089
	MACS-3	-	-	-	-	0.219	0.165	-	0.109	-	-	-	0.086	-	0.151	-	0.082	-	0.242	-	0.139
44–57	NIST SRM 610	0.044	0.213	0.016	0.103	0.044	0.023	-	0.033	0.201	0.242	0.037	0.036	0.037	0.040	0.033	0.041	0.036	0.060	0.069	0.052
	MACS-3	0.119	-	-	0.165	0.153	0.186	-	0.064	-	0.384	-	0.091	0.109	0.082	0.090	0.119	0.093	0.250	-	0.249
	GOR132-G	-	0.276	0.106	0.097	0.115	0.060	-	0.093	-	0.396	0.117	0.059	0.087	0.186	0.145	0.104	-	0.125	-	0.126
	GOR128-G	-	0.210	0.112	0.105	0.114	0.058	-	0.100	-	0.318	-	0.060	0.075	0.164	0.119	0.079	-	-	-	0.233
	KL2-G	-	0.226	0.035	0.076	0.208	0.031	-	0.041	-	0.203	0.056	0.034	0.063	0.025	0.038	0.050	-	0.326	-	0.141
	STDP3-150	-	-	-	-	0.064	0.041	-	-	-	-	0.086	0.026	0.054	0.044	-	0.032	0.148	0.086	-	0.063
	STDP3-1500	-	-	-	-	0.083	0.029	-	-	-	-	-	0.042	0.059	0.048	-	0.043	0.137	0.068	-	0.053
	STDP5	-	-	-	-	-	-	-	-	-	-	0.081	0.060	0.059	0.072	-	0.068	-	0.102	-	0.090
20–25	NIST SRM 610	0.041	0.106	-	0.056	0.048	0.036	-	0.026	-	0.289	-	0.022	0.038	0.027	0.026	0.021	-	-	-	0.055
	MACS-3	0.123	-	-	0.177	0.176	-	-	0.095	-	0.358	-	0.146	0.173	0.119	0.134	0.140	-	-	-	0.330
	GOR132-G	-	0.129	-	0.074	0.060	0.032	-	0.100	-	0.535	-	0.042	0.077	0.160	-	0.101	-	-	-	-
	GOR128-G	0.097	-	-	0.093	0.063	0.045	-	0.045	-	0.264	-	0.026	0.054	0.138	0.188	0.071	-	-	-	-

Table 5.

Ablation parameter and reference material-specific accuracy, based on primary calibration to NIST SRM 610. See Table 3 caption

Spot size / Spots		^{7}Li	^{11}B	^{23}Na	^{24}Mg	^{25}Mg	^{27}Al	^{29}Si	^{55}Mn	^{57}Fe	^{66}Zn	^{85}Rb	^{88}Sr	^{89}Y	^{138}Ba	^{139}La	^{140}Ce	^{146}Nd	^{208}Pb	^{232}Th	^{238}U
74–96	NIST SRM 612	1.008	1.071	1.006	0.846	0.831	1.012	-	0.977	-	1.008	1.013	1.001	1.006	1.01	0.991	0.994	1.02	1.005	0.995	1.002
	GOR132-G	1.172	1.157	1.072	0.918	0.932	1.05	-	1.003	-	0.977	-	0.986	1.008	1.107	-	-	-	-	-	-
44–57	NIST SRM 612	-	-	-	0.928	0.942	1.053	-	1.017	-	-	-	1.002	0.995	0.96	-	-	-	-	-	-
	MACS-3	1.013	1.074	1.01	0.856	0.829	1.013	1.015	0.994	-	1.013	1.027	1.017	1.026	1.021	1.017	1.017	1.009	1.025	1.032	1.017
	GOR132-G	1.184	1.171	1.078	0.928	0.93	1.041	-	1.016	0.842	0.963	-	0.99	0.991	1.085	0.86	1.025	0.895	1.048	-	0.775
	GOR128-G	1.12	1.06	1.1	0.937	0.939	1.044	-	1.031	0.861	1.062	-	1.014	0.993	0.951	0.818	0.875	0.86	-	-	0.721
20–25	GOR128-G																				
Tracks		-	-	-	-	0.854	1.022	-	0.994	-	-	1.017	1.012	1.015	1.011	1.009	1.009	-	1.013	1.009	1.009
74–96	NIST SRM 612	1.002	1.181	1.01	0.85	0.843	1.015	-	0.984	-	1.136	1.014	1.003	1.01	1.009	1.005	1.001	1.016	1.016	0.99	1.001
	MACS-3	1.033	-	-	0.845	0.856	1.015	-	0.942	-	1.177	-	0.923	0.923	0.94	-	0.958	0.935	1.141	-	0.842
44–57	NIST SRM 612	-	1.182	0.916	0.899	0.933	1.052	-	0.994	-	1.113	0.875	0.992	0.982	1.178	0.973	1.076	-	1.03	-	0.889
	MACS-3	-	1.054	0.926	0.899	0.933	1.051	-	1.002	-	1.169	-	1.003	0.974	1.019	0.908	0.906	-	-	-	-
	GOR132-G	-	-	0.879	0.879	0.91	1.035	-	1.006	-	1.03	0.87	0.989	0.924	0.956	0.968	0.977	-	1.058	-	0.95
	GOR128-G	-	-	-	-	0.889	1.023	-	-	-	-	0.923	1.048	1.073	0.98	-	0.988	0.853	0.944	-	0.994
	KL2-G	-	-	-	-	0.857	0.992	-	-	-	-	-	0.984	1.02	0.97	-	0.927	0.956	0.901	-	0.973
	STDP3-150	-	-	-	-	-	-	-	-	-	-	0.982	1.041	1.023	1.065	-	0.997	-	1.089	-	1.086
	STDP3-1500	1.021	1.088	-	0.885	0.85	1.013	-	1	-	1.13	-	1.017	1.011	1.02	1.013	1.018	-	-	-	1.016
	STDP5	1.125	-	-	0.97	0.969	-	-	0.977	-	1.207	-	1.05	0.865	0.983	0.966	0.905	-	-	-	0.63
20–25	NIST SRM 612	-	-	-	0.928	0.943	1.059	-	1.022	-	-	-	1.003	0.954	1.222	-	1.089	-	-	-	-
	MACS-3	1.115	-	-	0.963	0.971	1.064	-	1.054	-	1.234	-	1.024	0.935	1.009	0.869	0.918	-	-	-	-
	GOR132-G	1.008	1.071	1.006	0.846	0.831	1.012	-	0.977	-	1.008	1.013	1.001	1.006	1.01	0.991	0.994	1.02	1.005	0.995	1.002
	GOR128-G	1.172	1.157	1.072	0.918	0.932	1.05	-	1.003	-	0.977	-	0.986	1.008	1.107	-	-	-	-	-	-

Table 6.

Ablation parameter and reference material-specific precision, based on primary calibration to NIST SRM 610. See Table 4 caption

Spot size Spots		^{7}Li	^{11}B	^{23}Na	^{24}Mg	^{25}Mg	^{27}Al	^{29}Si	^{55}Mn	^{57}Fe	^{66}Zn	^{85}Rb	^{88}Sr	^{89}Y	^{138}Ba	^{139}La	^{140}Ce	^{146}Nd	^{208}Pb	^{232}Th	^{238}U
74–96	NIST SRM 612	0.022	0.27	0.021	0.049	0.025	0.022	-	0.047	-	0.063	0.04	0.051	0.053	0.051	0.05	0.046	0.031	0.061	0.059	0.064
	GOR132-G	0.086	0.312	0.084	0.059	0.061	0.039	-	0.035	-	0.374	-	0.048	0.039	0.073	-	-	-	-	-	-
44–57	NIST SRM 612	-	-	-	0.063	0.065	0.057	-	0.033	-	-	-	0.045	0.054	0.076	-	-	-	-	-	-
	MACS-3	0.036	0.183	0.024	0.041	0.039	0.023	0.023	0.033	-	0.062	0.036	0.03	0.036	0.034	0.033	0.038	0.042	0.039	0.026	0.059
	GOR132-G	0.083	0.227	0.078	0.055	0.058	0.029	-	0.04	0.217	0.09	-	0.046	0.061	0.115	0.193	0.118	0.185	0.049	-	0.352
	GOR128-G	0.062	0.162	0.082	0.05	0.053	0.032	-	0.043	0.208	0.083	-	0.045	0.056	0.097	0.22	0.134	0.139	-	-	0.701
20–25 Tracks	GOR128-G	-	-	-	-	0.05	0.018	-	0.039	-	-	0.04	0.026	0.035	0.036	0.031	0.037	-	0.06	0.055	0.097
74–96	NIST SRM 612	0.043	0.348	0.014	0.085	0.04	0.023	-	0.03	-	0.315	0.036	0.034	0.036	0.036	0.03	0.037	0.032	0.059	0.069	0.054
	MACS-3	0.092	-	-	0.104	0.115	0.173	-	0.047	-	0.228	-	0.064	0.098	0.071	-	0.102	0.085	0.211	-	0.226
44–57	NIST SRM 612	-	0.326	0.094	0.063	0.082	0.053	-	0.07	-	0.371	0.096	0.062	0.095	0.182	0.133	0.101	-	0.176	-	0.145
	MACS-3	-	0.197	0.058	0.048	0.061	0.056	-	0.062	-	0.392	-	0.046	0.085	0.186	0.119	0.064	-	-	-	-
	GOR132-G	-	-	0.03	0.046	0.04	0.026	-	0.037	-	0.128	0.075	0.033	0.07	0.032	0.039	0.057	-	0.348	-	0.119
	GOR128-G	-	-	-	-	0.025	0.029	-	-	-	-	0.103	0.035	0.036	0.055	-	0.044	0.136	0.11	-	0.075
	KL2-G	-	-	-	-	0.019	0.022	-	-	-	-	-	0.023	0.055	0.029	-	0.024	0.114	0.059	-	0.05
	STDP3-150	-	-	-	-	-	-	-	-	-	-	0.071	0.023	0.026	0.036	-	0.027	-	0.058	-	0.054
	STDP3-1500	0.044	0.123	-	0.041	0.037	0.037	-	0.032	-	0.232	-	0.023	0.039	0.027	0.024	0.022	-	-	-	0.053
	STDP5	0.103	-	-	0.142	0.14	-	-	0.053	-	0.181	-	0.083	0.169	0.116	0.13	0.141	-	-	-	0.306
20–25	NIST SRM 612	-	-	-	0.044	0.043	0.022	-	0.048	-	-	-	0.055	0.102	0.125	-	0.115	-	-	-	-
	MACS-3	0.083	-	-	0.056	0.05	0.039	-	0.046	-	0.349	-	0.027	0.054	0.152	0.21	0.073	-	-	-	-
	GOR132-G	0.022	0.27	0.021	0.049	0.025	0.022	-	0.047	-	0.063	0.04	0.051	0.053	0.051	0.05	0.046	0.031	0.061	0.059	0.064
	GOR128-G	0.086	0.312	0.084	0.059	0.061	0.039	-	0.035	-	0.374	-	0.048	0.039	0.073	-	-	-	-	-	-

NIST SRM 612-calibrated ^{25}Mg

NIST SRM 612-calibrated ^{66}Zn

NIST SRM 612-calibrated ^{88}Sr

NIST SRM 612-calibrated ^{208}Pb

NIST SRM 612-calibrated ^{238}U

N₂ accuracy 0.871 ± 0.008

H₂ accuracy 0.951 ± 0.015

Panel (a): NIST SRM 610 calibrated using NIST SRM 612

Panel (b): GOR132-G calibrated using NIST SRM 612

Panel (c): NIST SRM 610 calibrated using NIST SRM 612

Panel (d): GOR132-G calibrated using NIST SRM 612