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LAtools: A data analysis package for the reproducible reduction of LA-ICPMS data

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ABSTRACT

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) is an increasingly popular analytical technique, that is able to provide spatially resolved, minimally destructive analyses of heterogeneous materials. The data produced by this technique are inherently complex, and require extensive processing and subjective expert interpretation to produce useful compositional data. At present, laboratories employ diverse protocols for data processing, and the reporting of these protocols is usually insufficient to allow data processing to be independently replicated, rendering the resulting data untraceable. Importantly, different expert users can obtain significantly different results from the same raw data using nominally identical processing workflows, depending on how 'contaminants' are identified and excluded, and which regions of signal are selected as representative of the composition of the sample. The irreproducibility of LA-ICPMS is a significant problem for the technique, but the complexity of the raw data has been a major hindrance to developing traceable data processing workflows. Here, we present LAtools – a free, open-source Python package for LA-ICPMS data processing designed with reproducibility at its core. The software performs basic data processing with similar efficacy to existing software, and brings a number of new data selection algorithms to facilitate reproducible reduction of LA-ICPMS data. We discuss the key advances of *LAtools*, and compare its output to trace metal analysis of marine $CaCO_3$ (foraminifera) processed both manually and with Iolite, and to manually processed trace element data from zircon grains.

1. Introduction

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) has become an increasingly available and valuable tool for extracting geochemical information from geological materials. Researchers are able to perform minimally destructive, micron-scale spatially-resolved trace chemical and isotopic analyses on solid samples, often with negligible sample preparation compared to more conventional solution-based techniques. The spatial resolution of LA-ICPMS allows the targeted analysis of specific regions within a sample, and its minimally-destructive nature preserves the majority of the bulk sample, facilitating coupled analyses of a sample by different techniques (e.g. combined trace element and stable isotope analyses; Vetter et al., 2017). These capabilities have made LA-ICPMS popular across the Earth and Environmental Sciences, from geochemistry (Jackson et al., 2004; Burnham and Berry, 2017) to archaeology (Gratuze, 1999), biomineralization (Eggins et al., 2004; Spero et al., 2015) and paleoclimate research (Müller and Fietzke, 2016; Gothmann et al., 2015; Jochum et al., 2012).

The development and adoption of LA-ICPMS has proceeded rapidly over the last two decades, and has been transformative in a number of fields. However, LA-ICPMS has developed without common and universally accepted 'best practices' for the reporting of data collection parameters, and data processing and evaluation protocols. This has led to several troubling trends in the literature:

1. Studies rarely report analytical parameters in sufficient detail to allow the data collection procedure to be understood, or repeat analyses to be conducted under similar conditions.
2. Data processing and reduction protocols tend to be highly variable

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Table 1
Analytical parameters that should be included alongside LA-ICPMS data. For examples of completed tables, see tables provided with the analysis of example data in the electronic supplement. We recognize that many of these analytical parameters will vary day-to-day in laboratories, but each can have important implications on how the raw data are interpreted so should be included.

	Parameter	Significance
LASER	Instrument type / Beam optics description (manufacturer & model may suffice, if not substantively modified, or a custom-built instrument)	Ablation characteristics can vary significantly, depending on the specifics of laser focus, wavelength, energy and pulse length, and can alter the form of the resulting raw data. Knowing these parameters is therefore essential to correctly interpreting raw data. Additionally, elemental and isotopic fractionation can be introduced by insufficient energy transfer to the sample. Regular calibrations of laser focus and energy at ablation point are necessary to report these parameters accurately.
	Laser Wavelength (λ)	
	Laser pulse length (time)	
	Calibrated Laser Energy at Ablation Site (J cm^{-2})	
	Laser Repetition Rate (Hz)	The repetition rate of the laser can influence signal intensity and patterns in the raw profiles. For example, if repetition rate is too low, it can introduce a periodic aliasing signal in the raw data.
	Ablation Spot Size (um, geometry)	Determines the degree to which spatial information should be interpreted, and the strength of measured signals.
	Calibrated Ablation Rate (distance $pulse^{-1}$)	Only strictly necessary in depth-profiling studies where spatial information is interpreted. Highly material-specific, and should be calibrated against microscopy measurements.
INTERFACE	Extraction Cell Type	This determines the washout characteristics of the signal, and is important context for interpreting patterns in the raw data (e.g. Helex 2-volume cell).
	Gas Flows (l min^{-1})	The types of gasses used to carry sample from the laser to the ICP-MS, and their flow rates. This determines sample transfer rates and ICP-MS analytical characteristics.
	Gas Flow Setup	E.g. use of a 'Squid', or direct connection. This will influence the shape of the raw profiles, and allow better interpretation of patterns and trends in the data.
MASS SPEC	Mass Spectrometer Parameters	The exact parameters here will vary depending on instrument type, but sufficient detail should be provided to allow the analytical conditions to be understood, and potentially replicated. In particular, dwell time for each mass and total cycle time are essential, as interaction between laser repetition rate and cycle time can lead to aliasing and spectral skew in the data.

Table 2
Available software for processing LA-ICPMS data.

Software	Platform	Cost	Link/reference
Iolite	Igor Pro	1740 AUD	https://iolite-software.com
Glitter	Windows	4400 USD	http://www.glitter-gemoc.com/
SILLS	Matlab	Free	Guillong et al., 2008
AMS	Windows	Free	Mutchler et al., 2008
Pepita	Windows	Free	http://www.sediment.uni-goettingen.de/staff/dunkl/software/pepita.html
LARS-C	Excel	Free	http://www.immr.tu-clausthal.de/geoch/labs/icp-ms/laplot/lars-c.shtml
ComPbCorr	Excel	Free	http://gemoc.mq.edu.au/comPbcorrect/practical.htm
LamDate	Excel	Free	https://web.natur.cuni.cz/ugmnz/icplab/lamd1.html
TERMITE	R	Free	Mischel et al., 2017
LAtools	Python	Free	This paper

and subjective, and are generally not reported in sufficient detail to allow them to be quantitatively reproduced by an independent researcher.

3. Researchers rarely provide the raw data required to assess data processing methods, which is vital given the subjectivity inherent in data processing.

These trends are particularly problematic, given that many samples are chemically heterogeneous at the scale of laser ablation analyses, and the specifics of analysis, data processing and the extraction of average compositional data can have a profound influence on reported sample composition. Equally important, the current state of LA-ICPMS data processing and reporting is insufficient to allow reviewers and readers to adequately evaluate the quality of data presented in the literature. These issues must be addressed, if LA-ICPMS data is to persist as an accepted method for routine analyses of geological materials.

The reporting of instrument operational parameters may be accomplished by inclusion of a table in the main manuscript or supplement (e.g. Table 1), and is relatively straightforward. The idiosyncrasies of IC-PMS will prevent an external user exactly reproducing the analytical conditions, but these parameters provide important context for the treatment and interpretation of data during processing, and allow an external user to attempt analyses under similar conditions. Reporting data processing and reduction procedures is more complex, and will be the main focus of this paper. Various software packages and approaches currently exist for reducing LA-ICPMS data (Table 2), most of which involve a degree of subjectivity that is difficult to completely describe in publications. Here, we introduce *LAtools*, a Python module that provides a platform for the semi-automated, reproducible reduction of complex LA-ICPMS data sets, and describe its new quantitative

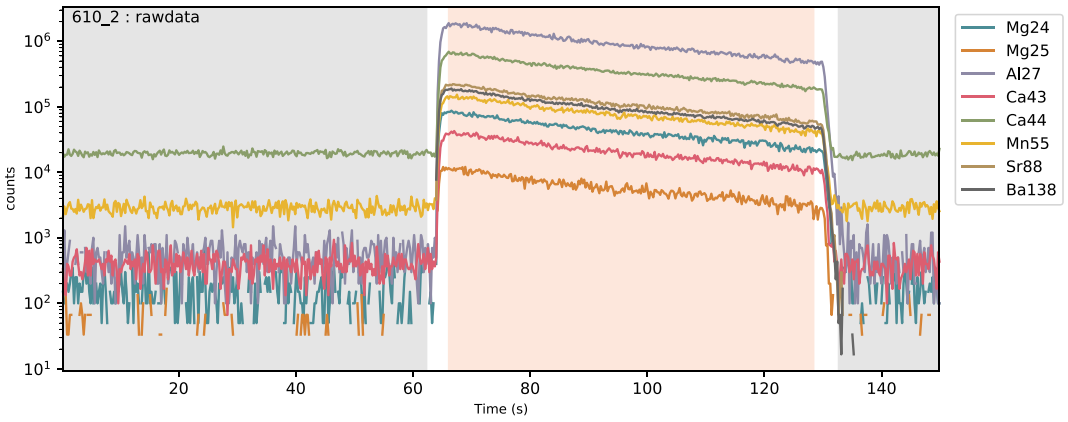


Fig. 1. An example LA-ICPMS depth profile, collected from a NIST610 standard reference glass, and produced by the *LAtools* 'trace_plots' command. Gray regions contain instrumental background (laser off), pink region contains the measured signal (laser on). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

data selection capabilities. We show that *LAtools* performs similarly to more established data reduction methods, and allows a user to exactly reproduce and evaluate the processing methodologies applied to a data set.

2. LA-ICPMS data reduction

Raw LA-ICPMS data are time-resolved measurements of specified analytes while the laser is toggled on and off. Normal operation produces an alternation between background (laser-off) and signal (laser-on) regions in the resulting time series (Fig. 1). The ablation beam may be rastered across a sample surface to produce horizontally resolved analyses, or remain in the same location for an extended period, ablating into the sample surface to produce a vertically resolved analysis (depth profile). The resulting data may be used to investigate surface or sub-surface chemical heterogeneity, or can be integrated to provide average chemical compositions of a sample, or regions of a sample. In the former, heterogeneity in the sample is the target of the analysis and spatially resolved data are presented. In the case of integrated data, the analysis is reduced to a single data point representing the average composition of a sample, with an error estimate reflecting either the sample heterogeneity, or the variability between repeat measurements. Data reduction can be divided into 'basic processing', which must be applied to all LA-ICPMS data to convert the laser-on regions of the profiles to calibrated compositional profiles, and 'selection and integration' stages, required to extract integrated compositional data.

2.1. Basic processing

Basic data processing steps typically include:

1. 'Despiking' to remove instrumental artifacts from the data, for example excluding detector errors that return physically impossible low or high values at single time points.
2. Data separation to identify 'signal' (laser-on) and 'background' (laser-off) regions within the profiles and exclude the 'transition' regions between these states. The 'background' region corresponds to the baseline detector signal at a particular mass, and the 'signal' region contains the additional counts from the ablated sample material.
3. Background correction, where identified 'background' regions are interpolated and subtracted from the 'signal' regions, to provide a baseline-corrected signal.
4. Standardization to an internally homogeneous element (e.g. Ca in the case of carbonate minerals) to account for variations in ablation efficiency both within samples, and between standards and samples.
5. Conversion of count ratios to compositional ratios by calibration to one or more external standards including drift correction of calibration parameters, particularly if the data were collected over an extended period. Commonly NIST glasses are used as reference materials, although matrix-matched standards with well-documented, homogeneous compositions can improve accuracy (Garbe-Schönberg and Müller, 2014; Jochum et al., 2016; Evans and Müller, 2018).

These steps are relatively straightforward, are well-described (e.g. Longerich et al., 1996), and are accomplished equally well by the majority of existing data processing packages (e.g. Iolite™, GLITTER™), although the ability to calibrate against multiple reference materials is absent from the most widely used commercial packages.

2.2. Selection and integration

In samples that are homogeneous on the scale of LA-ICPMS analyses, the entire 'signal' (laser on) region of the data can be integrated to calculate a robust compositional value. In heterogeneous samples the choice of region over which to calculate the integral is more complex and subjective, and can vary significantly depending on the type of samples under consideration. In many materials, heterogeneity is attributable to micro-domains of a contaminant phase, a secondary non-target material, or even the region of interest itself. In heterogeneous samples, subsections of the ablation profile that are characteristic of the material of interest must be identified to attain a representative integrated composition. The criteria used to select or remove regions from integration must be based on knowledge of the sample and the compositions of likely contaminant phases. Some materials have known, systematic heterogeneities which should be included in the data processing (e.g. Mg in foraminifera shells; Eggins et al., 2004). In such cases, the analyst must be sure that the laser analysis has collected sufficient data to yield a robust 'bulk' compositional estimate, despite the heterogeneity.

The method by which contaminant regions are identified and removed, or regions of interest are identified and selected, can have a significant effect on the integrated composition of a heterogeneous sample (Fig. 2; Section 4). At present, data selection and integration approaches range from fully manual (i.e. spreadsheets) to more sophisticated semi-automated scripts (AMS, SILLS, TERMITE; Table 2) and software packages (Iolite™, GLITTER™). There are also a range of in-house, unpublished data processing scripts employed by various laboratories. Fully manual approaches have the benefit of intimately involving the analyst with all steps of data processing, but are inherently slow, non-systematic, and create significant problems in reporting data

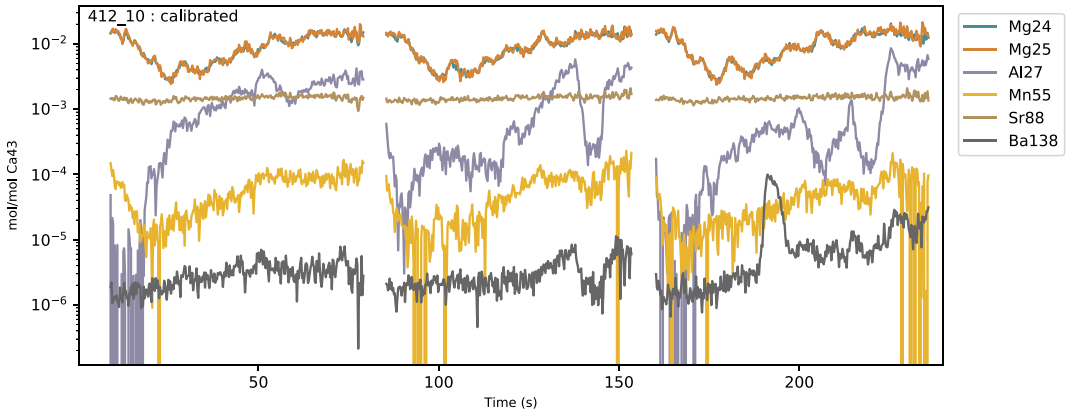


Fig. 2. An example LA-ICPMS analysis containing three depth profiles collected from the $CaCO_3$ test of the planktic foraminifera *Orbulina universa* taken from marine sediments. This plot is generated by the 'trace_plots' function of *LAtools*, after applying all basic processing and calibration steps (Section 2.1). In these samples Al, Mn and Ba are prone to contamination by clay minerals, regions where they are enriched should be excluded from integrations. However, these elements are highly heterogeneous, and the precise criteria selected to remove 'contaminated' data could have a significant influence on which specific regions are selected. In heterogeneous specimens like these, it is vital to have a record of data selection choices that completely describes the regions used to calculate integrated compositions. *LAtools* is designed to provide this capability, and makes data selection traceable.

processing procedures. Semi-automated techniques save time and are more systematic, but distance the analyst from the raw data, thereby increasing the risks of inappropriate processing, particularly in complex heterogeneous samples. In all existing software packages, data selection for integration is either conducted manually, or via simple threshold- or time-based selection criteria. The former is difficult to report, and the latter tends to be inadequate for processing complex materials. For materials where concentration thresholds are insufficient, no existing method offers a robust, traceable and reproducible approach to reducing data that can be quantitatively reported and evaluated by an independent user.

3. The *LAtools* software

LAtools is an open-source, cross-platform Python module, designed to address shortfalls in the traceability of LA-ICPMS data reduction. It is an open-source project hosted on GitHub (https://github.com/oscarbranson/latools), with a substantial body of online documentation (http://latools.readthedocs.io). Because it is open source, it the software can be examined and modified by its users, and can evolve with the needs of the community and the development of LA-ICPMS techniques (e.g. the incorporation of 2D imaging capabilities). For this reason, minimal explanations of the specific capabilities of *LAtools* are provided in this manuscript, as they are likely to evolve in future. To find out more about the capabilities of the current version of *LAtools*, and examples of their use, we direct the reader to the online manual (http://latools.readthedocs.io). To assist a new user in trying *LAtools*, we highlight key sections of the online manual in Box 1.

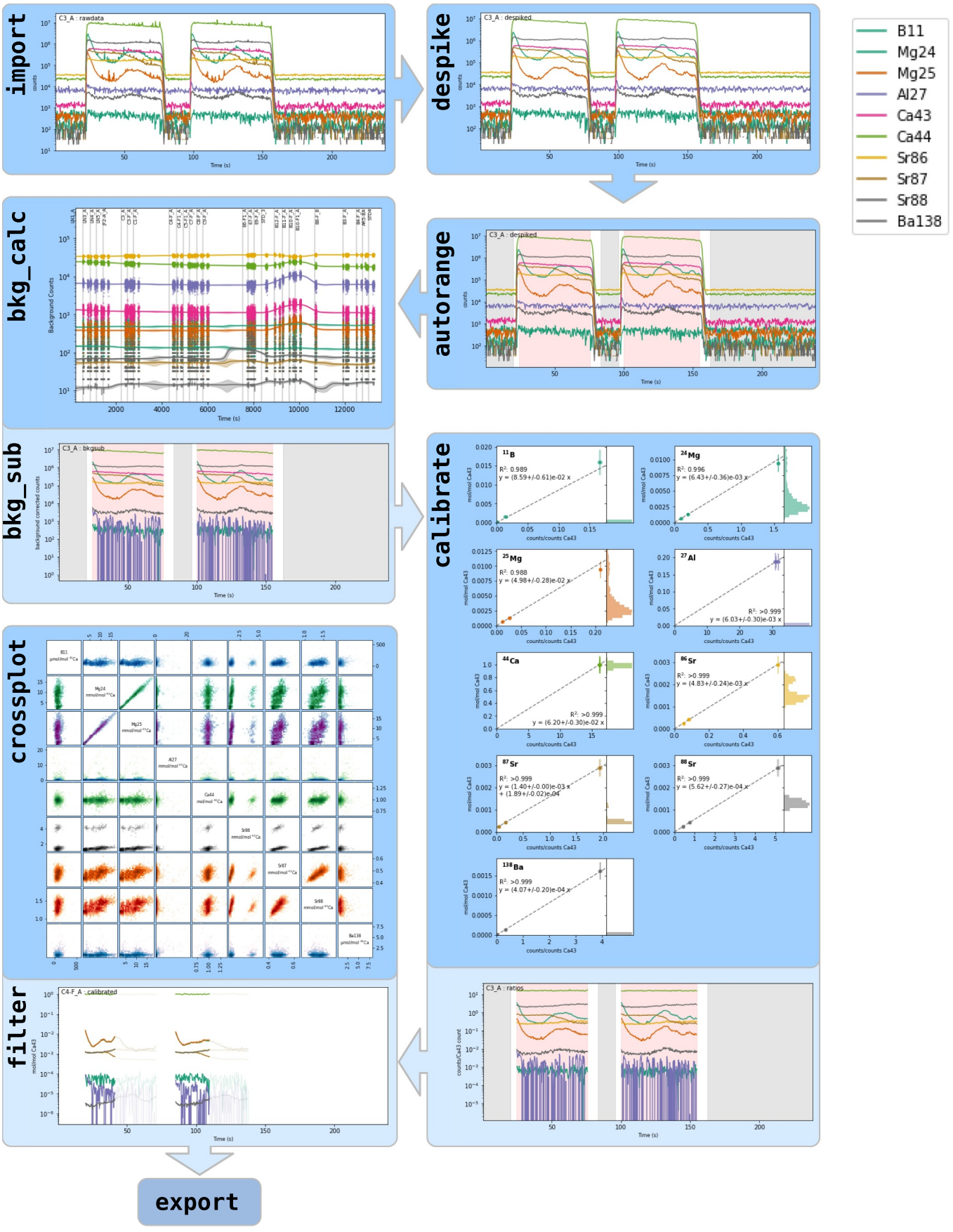
Data processing in *LAtools* is handled semi-automatically, where the analyst must review the results of each processing step, and adjust reduction parameters to achieve the desired result. An example *LAtools* workflow, showing plots produced at each stage of analysis is shown in Fig. 3. Basic data processing tasks (despiking, signal and background detection, background correction, interference corrections, internal standardization and calibration, drift-correction) are handled similarly to other software packages, with the addition of the ability to calibrate samples against multiple reference materials. GeoREM compositions for NIST610, 612 and 614 glasses (Jochum et al., 2011) are included in the default reference database, which can be expanded by the user to include additional standards. The use of multiple reference materials provides better statistics in calibrations, and offers resilience against problems that might arise from individual SRM measurements, such as heterogeneity, contamination, or matrix effects. The most significant advance over existing software is a comprehensive 'data selection' toolbox, which allows the quantifiable and reproducible integration of data.

Data selection tools (Box 2) include concentration, gradient and correlation threshold filters, multi-element Naïve Clustering algorithms (meanshift and k-means) available through the scikit-learn Python library (Pedregosa et al., 2011), and algorithms for identifying and excluding inclusions within homogeneous samples. Full technical details and example usage of these filters is available in the online manual

Box 1

Try *LAtools*. *LAtools* is accompanied by extensive online documentation. Here, we highlight key sections of the documentation that will be particularly useful for getting up and running.

Installation	https://latools.readthedocs.io/en/latest/users/installing.html Some basic instructions for installing Python and *LAtools* on your computer.
First steps	https://latools.readthedocs.io/en/latest/users/beginners/index.html The 'Beginners Guide' covers all the basics you'll need to start *LAtools*, followed by a step-by-step walk-through analysis of some example data.
Filtering	https://latools.readthedocs.io/en/latest/users/filters/index.html The 'Filtering' section contains an in-depth explanation of how filters work, and the tools you can use to help design them effectively for your data.
Example work-flows	https://latools.readthedocs.io/en/latest/users/examples.html Once you've come to grips with the basics, there are four example work-flows, which we used to process the data presented in the comparison examples presented below. This will provide some insight into using *LAtools* beyond the basics, and for different types of data.
Configuration	https://latools.readthedocs.io/en/latest/users/configuration/index.html If you want to use *LAtools* regularly, it's worth spending a little time configuring it for your specific system. This section contains some advice on defining data formats, editing the SRM database, and more.



(caption on next page)

Fig. 3. A schematic of an *LAtools* workflow, showing plots produced for a single sample after each stage of processing. After import, data are 'despiked', before 'autorange' is applied to separate signal and background regions. The background is then calculated ('bkg_calc') for the entire dataset, and subtracted from each sample ('bkg_sub'). The data are then normalised to an internal standard (^{43}Ca) and calibrated against reference materials. Filtering is conducted on the calibrated data, using visualisations like the 'crossplot' to help aid filter design and selection. After filtering, integrated data can be exported, alongside all raw data and a record of every action performed on the data during processing, which can be used to quantitatively reproduce the analysis. All plots shown are created directly by *LAtools* using one-line commands. This example is taken from fossil foraminifera dataset #1, and the workflow can be viewed in its entirety in the online examples (https://latools.readthedocs.io/en/latest/users/examples.htmlhttps://nbviewer.jupyter.org/github/oscarbranson/latools/blob/master/Supplement/fossil_foram_manual.ipynb).

(https://latools.readthedocs.io/en/latest/users/filters/index.html). Once created, filters can be turned on or off independently for subsets of samples and individual analytes, to facilitate fine control over data selection. As with the manual selection of integration regions, the choice and application of data filters remains subjective, and should be accomplished with in-depth knowledge of the samples. However, filters offer a significant advantage over manual integration as the parameters used to identify the filtered data can be recorded and reported, thereby permitting another researcher to obtain identical results from the same raw data set.

After data processing is complete, the parameters used in the *LAtools* analysis can be exported to a file, along with the raw data for all analytes required to reproduce the analysis, as well as the SRM concentration values used for calibration. These data are designed to be included with publications, thereby allowing other researchers and reviewers to examine the raw data and reduction methods used to produce the published data set.

A full description of *LAtools* with application examples is available in the online manual (http://latools.readthedocs.io).

4. Comparison of processing methods

To highlight the current problems in the reproducible reduction of LA-ICPMS data, and demonstrate the capabilities of *LAtools*, we compare four separate datasets collected from complex, heterogeneous materials, that were processed using multiple methods by different expert users in our research groups. We compare three separate sets of analyses of foraminifera ($CaCO_3$) from both sediment cores and live culture, and one set of Hadean zircon analyses. The raw data, alongside the full *LAtools* workflows applied to the data can be examined in the 'Example Analyses' section of the online documentation (https://latools.readthedocs.io/en/latest/users/examples.html).

In each comparison reduced compositional data from the different processing techniques are compared graphically and statistically.

Table 3
The 1 s.d. inter-replicate reproducibility of LA-ICPMS measurements for different types of sample, determined by fitting a half-Cauchy distribution to all unique pairs of replicate measurements in the reference dataset. Statistics are calculated from the reduced data produced either manually, or by Iolite.

mmol/mol	Manual (spreadsheet)		IoLite
	Cultured foraminifera	Fossil foraminifera (#1)	Fossil foraminifera (#2)
Mg/Ca	0.19	0.23	0.29
Sr/Ca	3.0×10^{-2}	1.7×10^{-2}	3.7×10^{-2}
Ba/Ca	1.8×10^{-4}	1.0×10^{-4}	3.7×10^{-2}
Al/Ca	1.0×10^{-2}	5.1×10^{-2}	5.7×10^{-2}
Mn/Ca		3.2×10^{-2}	4.1×10^{-3}
Fe/Ca			2.4×10^{-2}
Cu/Ca			5.6×10^{-3}
Zn/Ca			8.1×10^{-3}
B/Ca			5.4×10^{-3}

Comparisons are made in context of estimates of the reproducibility of LA-ICPMS analyses for different types of samples (Table 3). Reproducibility is assessed by computing the difference between all unique pairs of repeat analyses within the entire data set, which are described by a half-Cauchy distribution. Fitting the distribution to the data allows the IQR (equivalent to 1 standard deviation) to be precisely characterized. This 'reproducibility' metric incorporates uncertainties arising from both sample heterogeneity and the analytical technique, and provides an overall estimate of the inter-replicate variability associated with an LA-ICPMS measurement for a specific type of sample. This will be larger than estimates of uncertainty derived from repeat measurements of compositionally homogeneous reference materials, which is often reported as 'analytical precision'. However, as the subject here is the variance introduced by data reduction methods applied to heterogeneous samples, this estimate of the intra-population variability

Box 2
Data selection methods currently available in *LAtools*. For full explanations and example uses, see online manual (https://latools.readthedocs.io/en/latest/users/filters/index.html).

Thresholds	Identify data regions where the concentration or local gradient of a specific analyte is above or below a threshold value. 'Correlation'-thresholds may also be used to remove regions where two analytes correlate, for example regions where Al and Mn co-vary in sedimentary carbonates are often contaminated by Al-Mn-rich clays. Appropriate thresholds may be determined from prior knowledge of the samples, or by examining whole-analysis level cross-plots of the concentration or local gradients of all pairs of analytes, which reveal relationships within all the ablations, allowing distinct contaminant compositions to be identified and removed.
Clustering algorithms	Identify distinct compositional regions within the samples, using clustering analysis of the concentrations of one or more analytes. This method identifies distinct compositional regions (clusters) within the data, by defining either the number of expected distinct compositions in the data (kmeans), or parameters defining the degree of difference between clusters for them to be considered distinct (meanshift). Once calculated, clusters can be applied to identify regions in the raw data that belong to different compositionally distinct materials. These algorithms can be applied on a per-sample, per-subset or per-analysis basis.
'Signal optimization' algorithm	Identifies the longest contiguous region in the raw data where both the concentration and standard deviation of one or more analytes are minimised. This is particularly useful for relatively homogeneous materials containing inclusions of a known contaminant.
Defragmentation	Can be used to either include or exclude selected data regions that are below a threshold size. For example, if an analyte oscillates around a threshold value used for filtering, this will result in a 'fragmented' filter. Defragmentation consolidates the selection.
Down-hole exclusion.	Excludes all data after the first region excluded by other filters. This is relevant to integrating depth-profile data, where there is a degree of signal mixing from material from above the bottom of the ablation pit. Once a contaminant is encountered, it will be present as a minor component in all subsequently collected data during an ablation. Depending on the composition of the contaminant, data down-hole of the contaminant may need to be excluded.
Trimming/expansion	Filters may be made more or less conservative by 'trimming' or 'expanding' the selected data regions.

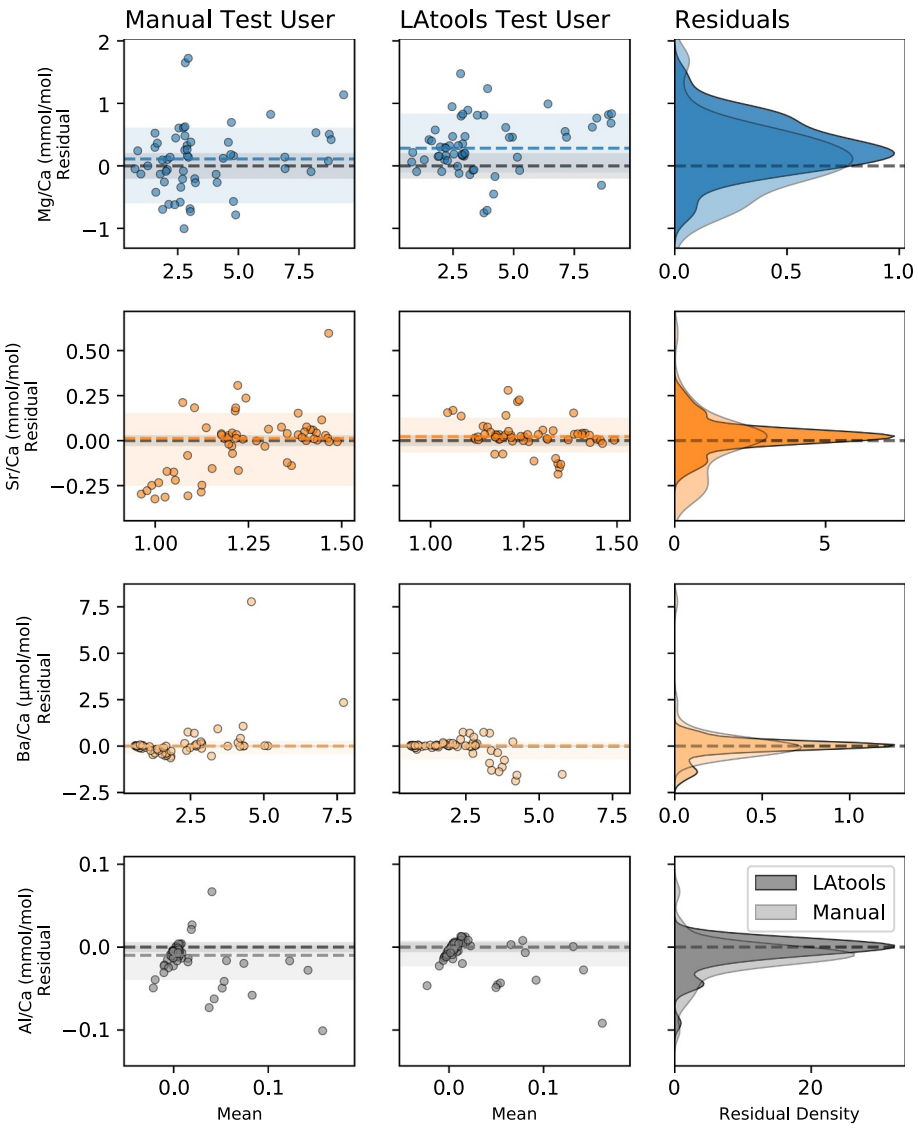


Fig. 4. Bland-Altman plots comparing data from cultured foraminifera reduced manually and using *LAtools*. Residuals (reference minus alternate) are plotted against mean (reference and alternate) ratios, providing a way of visualizing the similarity of two techniques, without requiring one to be an absolute reference. The similarity of the techniques can be visually assessed as scatter in the residual (y axis). If the techniques give identical results, all points should fall along the zero (dashed) line. On both sides of the zero line, a gray shaded region shows the 1 s.d. inter-replicate reproducibility for each analyte (Table 2). In the case of Sr/Ca and Ba/Ca, this envelope is much smaller than the scatter in the data, and is almost invisible. The residual median and IQR are shown as a colored dashed line and shaded envelope, respectively. For all elements, the residual median is within the inter-replicate reproducibility, but the residual IQR is considerably larger than inter-replicate reproducibility. This indicates that while the population mean is independent of data reduction method, considerable inter-replicate variability is introduced by data reduction choices. The kernel density plots on the right show the distribution of the residuals for each element (darker = LAtools, lighter = Test User). Note that Al/Ca values below zero are observed in these data, relating to problems with Al/Ca background subtraction. This issue does not preclude analysis of the data, as Al/Ca is used as a qualitative contaminant indicator in these samples.

provides a more useful comparison point.

The population-level similarity of data produced by different reduction methods is assessed using a 2-sample Kolmogorov-Smirnov test, which evaluates whether the data produced by the reduction techniques are distinguishable, given their variance. Additional insights can be gained by considering the median and inter-quartile range (IQR) of the residual between the two reduction methods (Method A–Method B). The IQR provides a metric to assess the variance introduced by data reduction methods. If the residual IQR is greater than the 1 s.d. inter-replicate reproducibility of the technique (Table 3), the choice of data reduction methods introduces more uncertainty than is inherent in the analytical technique for that type of sample. The mean and IQR of the residuals may be considered in tandem to assess whether differences between reduction methods would be detectable under normal operating conditions. If the median residual is greater than the 1 s.d. inter-replicate reproducibility, this suggests that the choice of reduction method can cause a significant shift in the population composition. However, if the difference between the median residual and the 1 s.d. reproducibility is less than the residual IQR, the variance introduced by data reduction methods renders the population-level difference undetectable, and the reduction methods may be treated as substantively identical.

Within-population pair-wise differences between the data resulting from different reduction methods are presented using Bland-Altman plots (Altman and Bland, 1983) and assessed by regression analyses of the residuals. Bland-Altman plots are designed to compare reduction methods where both contain a degree of uncertainty, by plotting the residual (Data A–Data B) against the mean of (Data A, Data B) pairs. Thus, differences in the results of the techniques may be gauged as scatter in the y-axis, while not having to make assumptions about the 'true' composition of the sample. In regression analyses, slope and intercept significance is assessed by one-sample *t*-tests. Significant slopes in the residuals imply a systematic bias between the two reduction methods, which will introduce trends within the data. All statistical analyses are conducted in Python 3.6, using the 'stats' module of SciPy (0.19.1; Jones et al., 2001) for Kolmogorov-Smirnov tests, and the OLS module of statsmodels (0.8.0; Seabold and Perktold, 2010) for regression analysis.

4.1. Comparison of manual reduction and LAtools

Two data sets were collected from the individually analyzed $CaCO_3$ tests of cultured (33 specimens) and fossil (fossil foraminifera dataset #1, 53 specimens) planktic foraminifera. The cultured dataset contains two species of foraminifera, *Orbulina universa* and *Neogloboquadrina dutertrei* cultured on Santa Catalina Island, CA USA. The fossil dataset

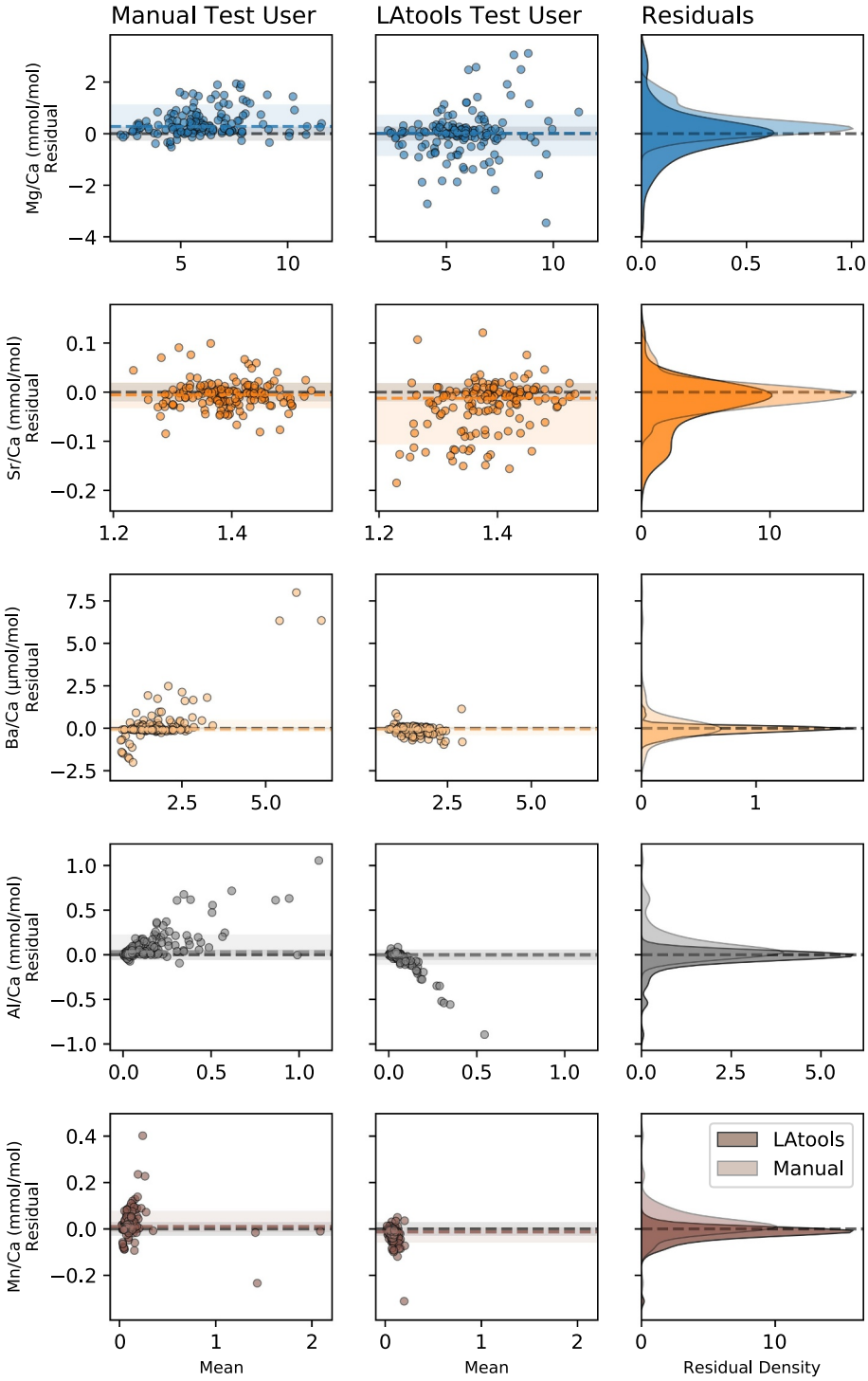


Fig. 5. Bland-Altman plots comparing data from fossil foraminifera (#1) reduced manually and using *LAtools*. For interpretation of the plot and annotations, see Fig. 3. There are numerous significant differences between both techniques and the reference data (Table 5). In general, the choice of processing technique has a greater influence on the compositional data in these fossil samples than in the cultured foraminifera data (Fig. 4). The marked trend in the Al/Ca residuals is attributable to the use of Al/Ca as a contaminant indicator when filtering the data in *LAtools*, leading to the exclusion of high Al/Ca regions.

from Vetter et al. (2017), and contains solely *O. universa*. Before analysis both sets of cultured specimens were oxidatively cleaned to remove residual organic material, and the fossil foraminifera were reductively cleaned to remove sedimentary contaminants, following standard protocols (e.g. Vetter et al., 2017). Data were collected from test fragments, ablating from the inside to the outside of the test. In the LA-ICPM-MS analysis of foraminifera it is common practice to generate multiple ablation pits through the chamber wall of the same specimen, and combine them to attain an average bulk composition. Thus, the similarity of multiple ablations from the same specimen (Table 3) provides an estimate of the precision of the technique, incorporating both analytical and sample heterogeneity factors. The variance introduced by data reduction techniques will be assessed relative to this estimate of analytical precision.

Data were reduced independently by three expert users: two manually using custom spreadsheets, and one using *LAtools*. For each

Table 4
Comparison of LA-ICPMS data from cultured foraminifera processed manually and with LAtools. In the Residual Summary, bold values are greater than the inter-replicate reproducibility (1 s.d.) determined from the reference data. In the Residual Regression and Kolmogorov Smirnov sections, bold values are significant at the $p < 0.05$ level. All units are mmol/mol, except Ba/Ca which is μmol/mol. N refers to the number of pair-wise ablation comparisons, and varies between techniques because of differences in criteria applied to exclude analyses. Statistical quantities: LQ = lower quartile, UQ = upper quartile, regression t/p = t statistic and significance level of one-sample *t*-test.

		Residual Summary					Residual Regression						Kolmogorov-Smirnov	
		N	Median	LQ	IQR	UQ	Slope	Slope t	Slope p	Intercept	Intercept t	Intercept p	KS	p
Manual test user	Mg/Ca	58	0.11	−0.21	**0.59**	0.38	0.03	0.76	0.45	0.01	0.05	0.96	0.138	0.61
	Sr/Ca	58	0.01	−0.13	**0.19**	0.06	−0.01	−0.06	0.95	0.00	−0.01	0.99	0.190	0.22
	Ba/Ca	58	0.00	−0.17	**0.24**	0.06	0.04	0.36	0.72	0.05	0.19	0.85	0.138	0.61
	Al/Ca	58	−0.01	−0.02	**0.01**	−0.01	**−0.35**	**−6.10**	**< 0.01**	**−0.01**	**−2.25**	**0.03**	**0.517**	**0.00**
LAtools test user	Mg/Ca	59	0.11	−0.11	**0.38**	0.27	**−0.07**	**−2.67**	**0.01**	**0.32**	**3.17**	**0.00**	0.136	0.62
	Sr/Ca	59	0.02	0.00	**0.04**	0.04	**−0.35**	**−5.74**	**< 0.01**	**0.47**	**6.11**	**0.00**	0.220	0.10
	Ba/Ca	59	0.03	−0.04	0.14	0.10	**−0.19**	**−5.47**	**< 0.01**	**0.38**	**4.23**	**0.00**	0.119	0.77
	Al/Ca	59	0.00	−0.01	**0.01**	0.00	**−0.48**	**−12.0**	**< 0.01**	0.00	0.33	0.74	0.237	0.06

Table 5
Comparison of LA-ICPMS data from fossil foraminifera (#1) processed manually and with LAtools. In the Residual Summary, bold values are greater than the inter-replicate reproducibility (1 s.d.) determined from the reference data. In the Residual Regression and Kolmogorov Smirnov sections, bold values are significant at the $p < 0.05$ level. All units are mmol/mol, except Ba/Ca which is μmol/mol. Note that the N refers to the number of pair-wise ablation comparisons, and varies between techniques because of differences in criteria applied to exclude analyses. In the *LAtools* case N also varies between elements, as different critera were applied to contaminant-prone (Ba/Ca, Mn/Ca, Al/Ca) and contaminant-resistant (Mg/Ca, Sr/Ca) elements. Statistical quantities: LQ = lower quartile, UQ = upper quartile, regression t/p = t statistic and significance level of one-sample t-test.

		Residual Summary					Residual Regression						Kolmogorov-Smirnov	
		N	Median	LQ	IQR	UQ	Slope	Slope t	Slope p	Intercept	Intercept t	Intercept p	KS	p
Manual test user	Mg/Ca	149	**0.28**	0.09	**0.50**	0.59	0.03	1.20	0.23	**0.26**	**1.88**	**0.06**	**0.17**	**0.03**
	Sr/Ca	149	−0.01	−0.02	**0.03**	0.01	**−0.12**	**−3.39**	**< 0.01**	**0.16**	**3.28**	**< 0.01**	0.13	0.16
	Ba/Ca	149	−0.07	−0.11	**0.19**	0.08	0.38	2.07	0.04	−0.47	−1.50	0.14	0.09	0.51
	Al/Ca	149	0.03	0.01	**0.11**	0.12	**0.41**	**4.55**	**< 0.01**	**0.06**	**3.41**	**< 0.01**	**0.25**	**< 0.01**
	Mn/Ca	149	0.01	0.00	**0.04**	0.04	**−0.06**	**−3.14**	**< 0.01**	**0.03**	**5.34**	**< 0.01**	**0.23**	**< 0.01**
LAtools test user	Mg/Ca	140	**0.04**	−0.27	**0.55**	0.28	**−0.07**	**−1.61**	**0.11**	**0.43**	**1.55**	**0.12**	**0.05**	**0.99**
	Sr/Ca	140	−0.01	−0.04	**0.05**	0.00	−0.07	−1.07	0.29	0.07	0.78	0.43	0.19	0.01
	Ba/Ca	122	−0.05	−0.26	0.30	0.04	−0.25	−5.20	< 0.01	**0.28**	**3.54**	**< 0.01**	0.14	0.17
	Al/Ca	133	0.00	−0.04	**0.04**	0.01	**−0.89**	**−58.0**	**< 0.01**	**0.04**	**14.0**	**< 0.01**	**0.23**	**< 0.01**
	Mn/Ca	133	−0.01	−0.03	0.03	0.00	**−0.57**	**−12.2**	**< 0.01**	**0.03**	**6.08**	**< 0.01**	**0.28**	**< 0.01**

data set, a 'reference' user with intimate knowledge of the samples and analyses reduced the data manually, and passed the raw LA-ICPMS data and a publication-style description of the data reduction methods to two independent expert 'test' users, one who reduced the data manually and one who used *LAtools*. The reduced compositional values produced by the test-manual and test-*LAtools* users are compared to the data produced by the reference user (Figs. 4 and 5, Tables 4 and 5). For elemental ratio analyses of foraminifera $CaCO_3$ shells, ratios of Mg/Ca, Sr/Ca, and Ba/Ca are of interest as proxies for environmental conditions whereas Al/Ca ratios are typically interpreted as an indicator of a contaminated or altered domain. In the fossil foraminifera, we expect Ba/Ca, Al/Ca and Mn/Ca to be prone to contamination by marine clay, whereas Mg/Ca and Sr/Ca should be more resistant to such contamination.

In the cultured samples (Fig. 4, Table 4), the median residual was within the 1 s.d. reproducibility of the reference data for all analytes. However, the IQR of the residuals was substantially larger than the 1 s.d. reproducibility for all except Ba/Ca in the *LAtools* case, indicating that considerable variance is introduced by choice of reduction method. The residual IQR in the Test User case was always larger than the *LAtools* case by up to a factor of ~6, indicating the *LAtools* values diverged less from the reference data than the test-manual values. Regression analyses revealed no significant slopes or intercepts in the residuals of the Test User data, but showed numerous significant trends in the *LAtools* residuals. This likely reflects the use of an Al/Ca concentration threshold in *LAtools* processing to remove sections of the raw data where the underlying Al-rich carbon tape was being ablated. In the clean, live-cultured foraminifera that comprise this dataset, high Al/Ca is unlikely to represent contamination from sedimentary processes. The application of the Al concentration filter in *LAtools* appears to have removed regions that were also high in other elements. This suggests that manual processing in which these high Al/Ca regions were not removed may be including contaminant-rich regions within the compositional data. At the population level, only Al/Ca data were significantly different from the reference data in both the Test User and *LAtools* cases, as indicated by Kolmogorov-Smirnov tests. This suggests that population-level statistics of paleoceanographic relevant elemental ratios should be relatively insensitive to the data reduction method, whereas intra-population trends may be more affected.

In fossil samples (Fig. 5, Table 5), the median residual was within the 1 s.d. reproducibility of the reference data for all analytes except Mg/Ca in both the Test User and *LAtools* cases. In both cases, the residual IQR was considerably larger than inter-replicate reproducibility for multiple analytes, with no clear difference in magnitude between the Test User and *LAtools* cases. There were also significant differences in both the slope and intercept of residuals in both the Test User and *LAtools* cases across multiple analytes, suggesting that choice of data reduction methods will introduce significant systematic variance at the intra-population level. At the population level, all analytes except Sr/Ca and Ba/Ca were significantly different from the reference data in both the manual and *LAtools* comparison cases. In general, there were many more significant differences between the data reduction techniques in the fossil samples than with the live-cultured foraminifera. This reflects the relative chemical complexity in fossil shells that arises from depositional and sedimentary processes, where these complex contaminant phases are removed to varying degrees by different processing

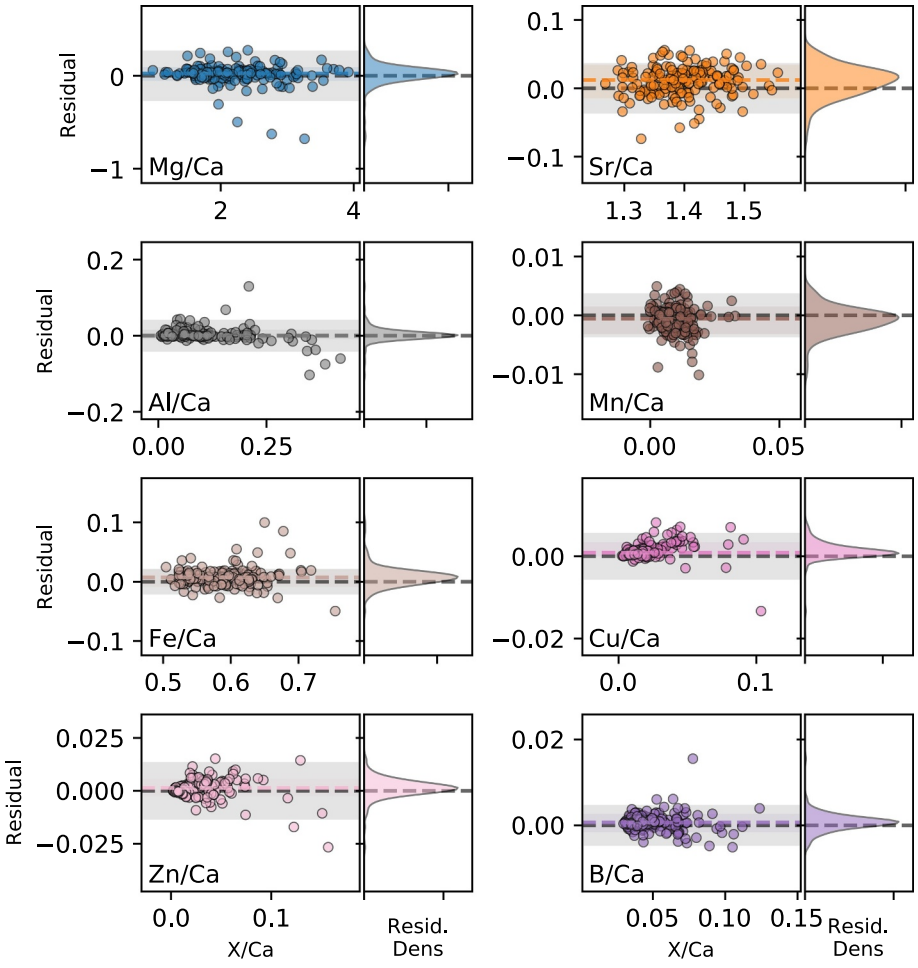


Fig. 6. Bland-Altman plots comparing data from fossil foraminifera reduced using Iolite and *LAtools*. Overall layout is modified from Figs. 3 and 4 because only two reduction techniques are compared, but the information presented is similar. Each axis contains a Bland-Altman plot (annotated after Fig. 4) for a different analyte, with a conjoined residual density plot (arbitrary units). The key features of these plots are that both the median concentration (colored line) and IQR (colored band) are within the inter-replicate reproducibility for all analytes. Thus, data reduced by Iolite and *LAtools* are similar within the inter-replicate reproducibility of the technique for all elements considered. All units are mmol/mol Ca.

Table 6
Comparison of LA-ICPMS data from down-core foraminifera processed with Iolite and LAtools. In the Residual Summary, bold values are greater than the inter-replicate reproducibility (1 s.d.) determined from the reference data. N refers to the number of pair-wise ablation comparisons, not the number of foraminifera. In the Residual Regression and Kolmogorov Smirnov sections, bold values are significant at the $p < 0.05$ level. All units are mmol/mol. Statistical quantities: LQ = lower quartile, UQ = upper quartile, regression t/p = t statistic and significance level of one-sample *t*-test.

	Residual Summary					Residual Regression						Kolmogorov-Smirnov	
	N	Median	LQ	IQR	UQ	Slope	Slope t	Slope p	Intercept	Intercept t	Intercept p	KS	p
Mg/Ca	162	0.024	−0.012	0.068	0.056	−0.01	−0.91	0.36	0.04	1.33	0.18	0.14	0.09
Sr/Ca	162	0.007	−0.006	0.024	0.018	−0.03	−1.22	0.22	0.05	1.39	0.17	0.07	0.75
Al/Ca	162	0.000	−0.003	0.005	0.003	**−0.09**	**−6.27**	**< 0.01**	**0.01**	**4.65**	**< 0.01**	0.12	0.20
Mn/Ca	162	−0.001	−0.002	0.003	0.001	**−0.10**	**−3.52**	**< 0.01**	0.00	0.59	0.55	0.10	0.39
Fe/Ca	162	0.005	−0.003	0.014	0.012	**−0.07**	**−2.63**	**0.01**	**0.05**	**2.97**	**< 0.01**	0.10	0.39
Cu/Ca	162	0.001	0.000	0.002	0.002	0.01	1.62	0.11	**< 0.01**	**3.51**	**< 0.01**	0.07	0.83
Zn/Ca	162	0.001	−0.001	0.003	0.003	**−0.04**	**−2.65**	**0.01**	**< 0.01**	**3.74**	**< 0.01**	0.07	0.75
B/Ca	162	0.001	0.000	0.002	0.001	0.00	−0.58	0.56	**< 0.01**	**2.16**	**0.03**	0.07	0.75

techniques. This shows that data reduction choices in complex samples from sedimentary environments can have significant impacts on both population-level compositions and intra-population trends. This is fundamental to all applications of LA-ICPMS to fossil foraminifera seeking to create paleoceanographic reconstructions, and highlights the necessity of improving user reporting of data reduction methods in this field.

4.2. Comparison of Iolite and LAtools

Data from a second set of fossil foraminifera tests (fossil foraminifera dataset #2, 89 specimens) of the species *Globigerina bulloides* were processed using Iolite and *LAtools* (Fig. 6, Table 6). In Iolite, data were processed using the 'trace element' data reduction scheme, with ^{43}Ca as an internal standard. Regions for signal integration were selected manually, because the complexity of the data rendered the use of threshold selection criteria insufficient. These data are from a test of reductive cleaning methods, and contain samples with a variety of levels of contamination. Samples were ablated in a range of orientations. As in the manual comparison, the influence of data reduction techniques is assessed relative to the inter-ablation precision of analyses (Table 3). In all cases, the median and IQR of the residual was within the inter-replicate reproducibility (1 s.d.) of the reference (Iolite) data. At the population level, the compositions calculated by Iolite and

Table 7
Comparison of LA-ICPMS data from zircons processed manually (Burnham and Berry, 2017) and with LAtools. In the Residual Regression and Kolmogorov Smirnov sections, bold values are significant at the $p < 0.05$ level. N refers to the number of pair-wise ablation comparisons. All units are ppm, except Al which is in wt%. Statistical quantities: LQ = lower quartile, UQ = upper quartile, regression t/p = t statistic and significance level of one-sample *t*-test.

	Residual Summary					Residual Regression						Kolmogorov-Smirnov	
	N	Median	LQ	IQR	UQ	Slope	Slope t	Slope p	Intercept	Intercept t	Intercept p	KS	p
Li	24	0.17	−0.01	0.45	0.44	0.04	1.09	0.29	−0.48	−0.97	0.34	0.08	1.00
Mg	13	0.83	−0.33	2.69	2.36	**0.08**	**41.0**	**< 0.01**	0.06	0.20	0.85	0.15	0.99
Al	26	0.00	0.00	0.00	0.00	**0.05**	**4.81**	**< 0.01**	0.00	0.20	0.84	0.08	1.00
P	26	−22.9	−62.7	86.5	23.8	−0.02	−0.81	0.43	7.94	0.18	0.86	0.08	1.00
Ti	26	−0.43	−1.05	1.43	0.38	0.00	−0.05	0.96	−0.32	−0.81	0.42	0.12	0.99
Y	26	14.3	−92.2	193	100	0.02	0.43	0.67	−48.5	−0.31	0.76	0.08	1.00
La	24	−0.01	−0.04	0.05	0.00	−0.08	−1.93	0.07	−0.03	−0.42	0.68	0.13	0.99
Ce	26	0.07	−0.18	0.40	0.22	**−0.04**	**−3.01**	**0.01**	0.28	1.79	0.09	0.12	0.99
Pr	26	0.00	−0.03	0.04	0.02	−0.07	−1.65	0.11	−0.01	−0.16	0.88	0.12	0.99
Nd	26	0.00	−0.22	0.35	0.12	−0.07	−1.63	0.12	0.05	0.12	0.91	0.15	0.89
Sm	26	0.09	−0.27	0.50	0.23	−0.02	−0.45	0.65	0.17	0.37	0.72	0.12	0.99
Eu	26	−0.02	−0.04	0.07	0.03	−0.06	−1.65	0.11	0.01	0.36	0.72	0.12	0.99
Gd	26	0.13	−0.85	1.99	1.14	0.01	0.15	0.88	−0.03	−0.01	0.99	0.08	1.00
Tb	26	0.08	−0.59	0.94	0.35	0.02	0.34	0.74	−0.26	−0.23	0.82	0.12	0.99
Dy	26	1.12	−7.00	14.60	7.60	0.02	0.56	0.58	−4.09	−0.32	0.75	0.08	1.00
Ho	26	0.83	−2.64	5.56	2.92	0.02	0.45	0.66	−1.56	−0.30	0.76	0.12	0.99
Er	26	5.45	−7.40	21.81	14.41	0.02	0.36	0.72	−4.33	−0.16	0.87	0.12	0.99
Tm	26	0.68	−2.82	5.87	3.05	0.00	0.06	0.95	0.64	0.12	0.91	0.12	0.99
Yb	26	7.07	−20.1	45.7	25.6	0.01	0.24	0.82	−0.28	0.00	1.00	0.12	0.99
Lu	26	0.51	−3.94	9.91	5.98	0.00	−0.14	0.89	2.25	0.25	0.80	0.12	0.99
Hf	26	6.75	−249	491	242	0.01	0.97	0.34	−259	−0.96	0.35	0.12	0.99
Pb	26	0.77	0.06	1.59	1.65	0.02	1.60	0.12	−0.23	−0.24	0.81	0.08	1.00
Th	26	1.46	−1.97	8.68	6.71	0.03	0.83	0.41	1.98	0.24	0.81	0.08	1.00
U	26	9.25	−1.46	22.69	21.23	0.04	1.69	0.10	−20.0	−0.79	0.44	0.08	1.00

LAtools were statistically indistinguishable (Kolmogorov-Smirnov tests). There were a number of slight but significant non-zero slopes and intercepts in the residuals, although these were all less than the inter-replicate reproducibility. Data processed using Iolite and *LAtools* gave equivalent results, to within the reproducibility of LA-ICPMS for these samples (Table 2). This is consistent with the more systematic nature of the processing methods applied to these samples, where elemental concentration thresholds were applied to all samples, rather than manually selecting integration regions in individual samples.

For elements of interest in these samples, *LAtools* is able to produce quantitatively similar results to Iolite, with the key difference that the results produced by *LAtools* are fully traceable. The complexity of these data precluded the use of systematic data selection tools available in Iolite, but through the combined use of clustering filters, gradient threshold filters and our 'signal optimisation' algorithm (Box 2), *LAtools* is able to systematically identify 'uncontaminated' signal regions with similar efficacy as an expert user.

4.3. Comparison of zircon data reduction

Data from Hadean zircons (26 grains) was reduced manually (Burnham and Berry, 2017) and using *LAtools* (Table 7, Fig. 7). Replicate analyses of the same grains were unavailable, so it was not possible to estimate the inter-replicate reproducibility in these samples. As with foraminiferal samples, zircon ablation depth profiles exhibit numerous heterogeneities, many of which are attributable to inclusions of foreign mineral phases, which must be excluded from analysis. For all analytes, compositional values produced by *LAtools* were identical at the population level to manually reduced data. There were small but significant trends in the residuals, particularly in elements known to be associated with contaminant phases (Mg, Al). Overall, *LAtools* produces compositional values that are much closer to the manually reduced zircon data than the manually reduced foraminiferal data. This is because data reduction in zircons focuses on identifying compositionally homogeneous regions within the sample, whereas foraminifera exhibit systematic chemical heterogeneity that is intrinsic to the sample and cannot be excluded. Thus, the data reduction methodology applied to zircons will inherently lead to more reproducible compositional values, which are less sensitive to data reduction methods.

4.4. Influence of choice of processing methodology

The examples above highlight that the choice of data processing technique can be of varying importance depending on the specifics of sample type and the reduction method. There is a general trend for simpler samples with easily identifiable contaminants (e.g. zircons) to yield more reproducible results between manual and automated processing than for more complex, heterogeneous materials (e.g. foraminifera). In heterogeneous samples, processing techniques that apply selection criteria at the population level (e.g. application of an elemental concentration threshold to all samples) will yield more reproducible results than manually selecting data from individual samples. These general patterns in reproducibility are intuitive, but it is impossible to quantify the uncertainty associated with choice of reduction technique for a given type of sample without reducing the data in different ways, and assessing the variability of the reduced values. *LAtools* brings two key advances in this regard: (1) allowing multiple processing approaches to be rapidly applied and compared, and (2) facilitating the quantitative reporting and reproduction of data processing methods. This allows the straightforward assessment of uncertainty associated with data reduction methodology, the examination of data processing routines by external users, and the application of data processing protocols to new sets of samples.

5. Advantages of LAtools

LAtools offers the first LA-ICPMS data processing package designed to focus on the traceability of analyses. It allows the fully reproducible reduction of data from complex, heterogeneous samples, increasing the transparency and reliability of LA-ICPMS data. At the end of analysis, *LAtools* allows the export of all raw data and analytical parameters required to quantitatively reproduce the integrated compositional data.

Beyond traceability, *LAtools* is fast and flexible, and facilitates the rapid evaluation of the influence of multiple filtering regimes on LA-

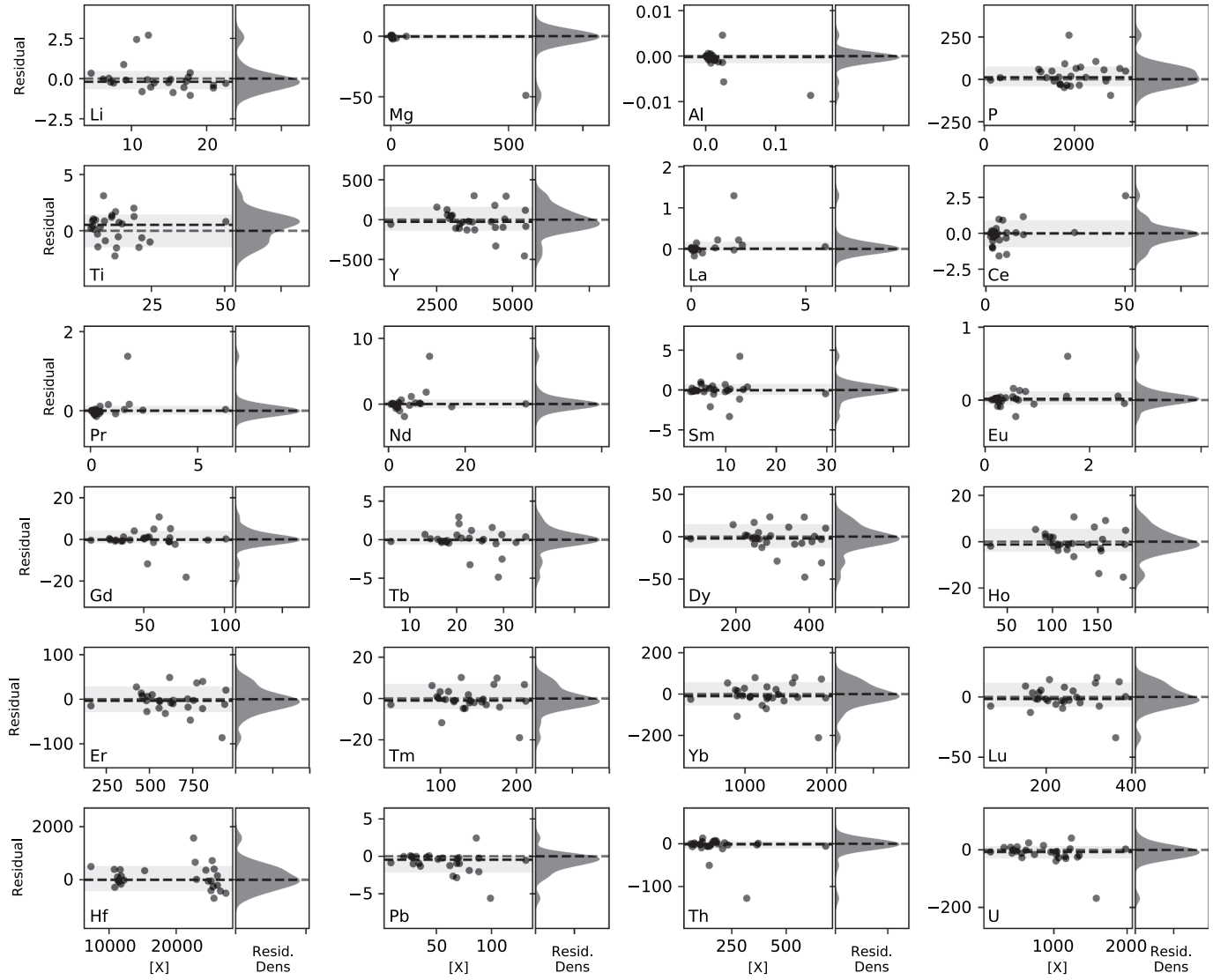


Fig. 7. Bland-Altman plots comparing data from zircons reduced manually and using *LAtools*. Layout as in Fig. 5. It was not possible to estimate the inter-replicate reproducibility in these samples, owing to a lack of replicate measurements. However, for all analytes the population residuals were statistically indistinguishable from zero, indicating good overall agreement between the techniques. There is some scatter in individual values, although there are no clear patterns in the residuals.

ICPMS data. For typical samples, hundreds of ablations may be processed (raw data to filtered integrated compositions) in around half an hour, where the majority of this time is dedicated to exploring the influence of different filters on reduced compositional data. The filtering process is non-destructive, enabling the rapid exploration of multiple filter types without re-processing data. At any point, filters may be cleared, and a new filter set created. This allows the influence of data filtering choices to be easily assessed. Once optimal filters are identified, total processing time for hundreds of ablations will be on the order of 1–5 min, depending on the complexity of chosen filters. With experience, users may establish sets of processing 'rules' for different types of samples, reducing the time required to design filters for a dataset.

6. Conclusions

LA-ICPMS offers transformative analytical capabilities across the natural sciences, but the current reporting of data reduction methods is inadequate, particularly for heterogeneous samples. Our inter-comparison of data reduction methods shows that different users can obtain significantly different results from the same raw data, following nominally similar data processing workflows. Some types of sample and reduction methods fared better than others, but the inability of any two methods to produce quantitatively identical results demonstrate that current LA-ICPMS data analysis workflows affect the results presented in publications, and cannot be replicated due to un-traceable user specific choices made during sample processing. We call on LA-ICPMS users, journal reviewers and editors to drive improvements in the reporting of LA-ICPMS data collection and processing, to keep pace with the rigorous reproducibility and traceablility standards that are emerging in modern science. Data reporting and traceability may be significantly improved through the use of systematic and clearly defined data reduction schemes in existing software, although existing software offers a limited range of data selection tools which are often insufficient when working with complex heterogeneous samples. The *LAtools* LA-ICPMS data reduction toolkit we present here is designed to make the processing and reduction of complex, heterogeneous samples quantitatively reproducible and traceable. At the end of a processing session, *LAtools* allows the export of all data and analytical parameters required to reproduce an analysis, which should accompany reduced compositional values presented in publications. As an open source project, *LAtools* provides a robust platform from which to develop new data

processing capabilities to keep pace with developments in new technologies and applications of LA-ICPMS. The capabilities of the software can be easily expanded by the community to meet the future needs of its users.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2018.10.029.

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Online resources

LAtools User Manual: http://latools.readthedocs.io.

LAtools Github Project Page: http://github.com/oscarbranson/latools.

Data Reduction Examples (comparisons presented in manuscript): https://latools.readthedocs.io/en/latest/users/examples.html.