Iolite: Freeware for the visualisation and processing of mass spectrometric data†

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Iolite is a non-commercial software package developed to aid in the processing of inorganic mass spectrometric data, with a strong emphasis on visualisation versus time of acquisition. The goal of the software is to provide a powerful framework for data processing and interpretation, while giving users the ability to implement their own data reduction protocols. It is intended to be highly interactive, providing the user with a complete overview of the data at all stages of processing, and allowing the freedom to change parameters and reprocess data at any point. The program presents a variety of windows for the selection and viewing of data versus time, as well as features for the generation of X-Y plots, summary reports and export of data. In addition, it is capable of generating X-Y images from laser ablation rasters, and combining information from up to four separate elemental concentrations (intensities of red, green and blue, and the z-axis) in a false-colour three-dimensional image. By virtue of its underlying computing environment—Igor Pro—Iolite is capable of processing very large datasets (i.e., millions of timeslices) rapidly, and is thus ideal for the interrogation of multi-hour sessions of laser ablation data that can not be easily manipulated in conventional spreadsheet applications, for example. It is also well suited to multi-day sessions of solution-mode inductively-coupled plasma mass spectrometer (ICPMS) or thermal ionisation mass spectrometer (TIMS) data. A strong emphasis is placed on the interpolation of parameters that vary with time by a variety of user selectable methods including smoothed cubic splines. Data are processed on a timeslice-by-timeslice basis, allowing outlier rejection and calculation of statistics to be employed directly on calculated results. This approach can reduce the risk of processing biases associated with the manipulation of integrated datasets, while also allowing the implementation of more complex data reduction methods.

1 Introduction

Advances in mass spectrometry allow analysts to acquire increasingly large bodies of analytical data—a feature that can be both an asset and a curse. In the case of laser ablation ICPMS (LA-ICPMS), the difficulties associated with manipulating sizeable datasets are compounded by the need to treat parameters such as baseline intensities, isobaric interferences and elemental fractionation for every spot analysis individually, often with comparison to reference material analyses located in separate files. As a consequence, the process of data reduction is a burden that often requires considerably more time than the data acquisition itself.

Mass spectrometric data are typically manipulated in the form of data tables, either using an existing spreadsheet package such as MS Excel (e.g. LAMDATE1) or with Matlab (SILLS2), IDL (GLITTER3,4), LOTUS 1-2-3 (LAMTRACE5), or as a stand-alone package (AMS,6 compiled versions of SILLS). These deconvolution solutions typically incorporate some level of data visualisation, but this is often limited in scope to single analyses, which can make it difficult for the analyst to detect long-term temporal variations in the dataset. In addition, existing software packages are usually specialised for particular data reduction methodologies or instrumentation and are only rarely open to modification by the end user.

Here we present Iolite, a non-commercial freeware package for the reduction of data obtained by mass spectrometry (but also potentially applicable to any analytical method producing time-resolved output). In Iolite data are viewed, edited and interpreted predominantly in graphical form as plots versus time. Although originally developed to relieve the significant processing burden of laser ablation analyses,7 its capabilities have now been
extended to such a degree that it is also an advantageous tool for the processing of both solution-mode ICP-MS and TIMS data. The application grew out of the realisation that simultaneous visualisation and processing of an entire analytical session of data could not only reduce the processing load, but also greatly improve the consistency and reliability of data reduction.

Iolite is implemented as a self-contained package for Igor Pro, a scientific data processing and graphing application from WaveMetrics Incorporated. The Igor Pro host environment was chosen for its emphasis on time series, image analysis and curve fitting, and comes with its own programming language. In addition it includes powerful 3D graphing capabilities utilising an OpenGL visualisation tool. The Iolite package is non-commercial, and is available for free download from the website (http://www.iolite.org.au/), which also has links to the online manual, discussion forum, and blog.

Iolite’s critical distinguishing feature is the consistent visual display versus time at all stages of data processing, of all available raw and processed data over the course of an entire analytical session (regardless of the number of individual time-resolved files involved, or the length of time that they encompass). Although the underlying framework is closed, its data reduction algorithms are entirely open-source and can be of any level of complexity, meaning that users have complete control over how to process their data and calculate appropriate output parameters. In addition, all functions used to calculate statistics are unencrypted, and are grouped into a single file for easy access by users that wish to view the programming code. Once time-resolved data processing has been completed the data may be further interrogated on screen (for example by viewing the effects in real-time of varying interference parameters) or exported in a number of ways including as 2- or 3-dimensional spatially resolved data.

Such individually indexed time-series are, however, not straightforward to compare or process. Therefore, as the first stage of data reduction the selected input channels are translated onto a common index time-series. Because each input channel has an array storing the absolute acquisition time of each of its timeslices, this can be achieved by linear interpolation (see Fig. 1 for an illustration). After translation to a common time-series, the datapoints of any channels can be compared directly without interpolation (Fig. 1c). This approach allows for straightforward comparison of isotope intensities versus time and simplifies the calculation of more complex results. Any further calculations, for example a 206Pb/238U ratio, are also stored as additional channels in their own array, and results are calculated individually for each data point in the relevant array. Such timeslice-by-timeslice data treatment has the significant advantage of producing results that are time-resolved, which provides the user with much more information than a simple average of a selected time period. For example, a user could easily construct a test to determine whether data from a selected time period are normally distributed, and thus whether the use of parametric statistics is appropriate, or calculate error correlations from the individual data points in such a time period. It should be noted however, that the ratios of very low or noisy signals can produce extreme results for individual timeslices (e.g. a negative ratio if one of the channels has a negative intensity after baseline-subtraction), and can thus produce unexpected results when averaged. In such cases, a data reduction scheme employing appropriate pre-smoothing of the data can be beneficial.

2 Treatment of data in Iolite

The software parses mass spectrometer data files individually, retrieving measurements from the original files and storing them as one-dimensional arrays (referred to both here and within Iolite as ‘channels’). During the data import process, every imported time-resolved channel (be it a mass or isotope recorded by a single-collector instrument, or a mass-collector pair from a multi-collector instrument) is paired with a second identical array containing the absolute acquisition time of each timeslice‡ in the file. This is a flexible approach which makes no assumptions about the nature of any stored data except that they are time series, allowing for instance the combination of data sets containing different numbers of measured masses over the course of one or more days, or of simultaneously acquired data where more than one instrument is coupled to a single laser, or indeed any ion source.

‡ Note that we use the term “timeslice” throughout the manuscript to refer to a single measurement reported by a mass spectrometer. We intend “timeslice” (also referred to as a point, datum, cycle, replicate, or measurement) to mean a single value (typically an intensity) representing a period of time usually reflecting the time taken to sequentially measure all masses once in the case of a single-collector instrument, or the smallest interval of measurement on a multi-collector instrument.

Fig. 1 Example of the interpolation of input data acquired at different times (a,b) onto a common ‘Index Time’ wave (c). Here, the higher sampling rate and even spacing of the data in panel (a) make it an obvious choice as a template for the Index Time wave. Linear interpolation is used to calculate values of the input wave (b) for each point in the Index Time wave, resulting in interpolated waves where the same points in any two waves represent exactly the same absolute time (c), and can thus be compared directly.
In addition to measurement data, Iolite also collects metadata from source data files during import, which are stored in a flexible matrix that allows for the inclusion of varying quantities and types of information. Such metadata might typically include information about the version of Iolite and Igor Pro used during data reduction, details of the source of the original data file, and machine parameters such as laser repetition rate, spot size, etc. Collected metadata are preserved during data processing, and are exported together with output data.

In order to accommodate variations in format and contents, data are imported using modules specifically designed for each mass spectrometer’s output file format. These import modules convert the data into a generic internal format (refer to Appendix 1 for details of the data structure). Iolite is capable of importing data from files containing either single or multiple analyses, and can also conduct batch imports on all data files within a folder, making it convenient to import large numbers of analyses. In cases where each datum of the mass spectrometer data file is not individually time-stamped, a fixed time-spacing for data acquisition is assumed and the user is prompted for the required information.

3 Illustration using example datasets

In order to better illustrate Iolite’s features we employ two contrasting datasets as examples throughout this manuscript:

3.1 Case 1: in situ Sr-isotope measurement in kimberlitic perovskite by laser ablation

This dataset represents approximately one hour of continual acquisition using a Nu Plasma MC-ICPMS coupled to a 193 nm Excimer ‘Helex’ laser ablation system at The University of Melbourne. The analytical session contains a number of spot analyses of perovskite grains from a thin section of kimberlite, obtained using a 55 μm diameter spot. A full description of the analytical method employed is available in Paton et al.,10 but the following points are of interest here:

– To obtain useful Sr-isotope measurements, analyses must be corrected for Rb and doubly-charged REE interferences.
– Variable Kr backgrounds require rigorous monitoring of gas blanks and appropriate interpolation of changes in background intensities with time.
– Perovskite is high in Sr and very low in Rb, making it ideally suited to these analyses, but the grains are small, often contain fractures, and are surrounded by groundmass material high in Rb.

The above considerations make this a particularly demanding application, as many analyses are compromised to some degree by the ablation of groundmass material or fractures. In such a situation the capability to interrogate each analysis in detail and identify only the most reliable regions of data is essential.

3.2 Case 2: High-precision Mg-isotope measurements by solution mode MC-ICPMS

In contrast to the laser ablation session of Case 1, this dataset represents approximately 60 h of uninterrupted data acquisition under extremely stable operating conditions. Data were acquired in solution mode using a Neptune MC-ICPMS at The Centre for Star and Planet Formation, University of Copenhagen. A full description of the analytical methods employed is available in Bizzarro et al.,11 but the following points are of interest here:

– A calibrator-sample-calibrator bracketing approach is used, with each sample measured a total of ten times, bracketed by eleven measurements of the reference material solution (where each measurement is 28 min in duration).
– The Mg-isotope measurements have an external reproducibility of <3 ppm (i.e. 0.0003%), meaning that even small drifts in machine conditions with time (e.g. one hundred ppm per day) can significantly affect results. As such, selection of an appropriate interpolation method for the correction of instrumental drift is particularly important.
– By acquiring ten separate measurements for each sample, population based statistics and measures of data quality (e.g. MSWD) can be used.

Unlike Case 1, the stable and reproducible conditions of this method mean that careful interrogation of each individual analysis is less critical. However, the large number of reference material analyses in the dataset allow the use of Iolite’s uncertainty propagation protocols (the algorithms of which are described in detail in Paton et al.10), while the ten separate measurements of each sample are useful in illustrating population-level statistics in the Report Window.

4 Visualisation and selection of data

A strong emphasis is placed on the visualisation of data in Iolite, and although the underlying numerical information is always accessible to users, interaction with data is almost entirely achieved visually. As a natural consequence of this method of data processing, entire acquisition sessions are typically processed as a single entity. The processing of such large batches of data has a number of benefits, foremost of which is the improved treatment of factors that vary with time, such as baseline correction and reference-material normalisation. Additionally, the availability of a sizeable population of reference material analyses often allows the user to employ complex approaches to data reduction and uncertainty estimation that are not feasible with fewer analyses.

In addition to viewing multiple analyses at once, the software has been structured in a way that allows the user to view any combination of channels simultaneously, whether ‘raw’ input intensities, simple ratios, partially reduced data, or the results of more complex treatments (a simple illustration is provided in Fig. 2a). The ability to visually compare time-resolved calculations from different stages of data reduction in this way gives the user the ability to rapidly identify potential problems with analyses and/or data reduction protocols that might otherwise compromise results (e.g. Fig. 2b).

In order to define the segments of data to be used in computing results (e.g. analyses of a reference material, the user defines “integration periods” for relevant “integration types” (e.g. the NIST-612 certified reference material). To store these integration periods, a 3-dimensional matrix is generated for each integration type, and is populated with the start and end times of selected integration periods (see Appendix 1 for details). These time periods are then used to calculate averages and associated uncertainties for each channel using any of several available...
statistical methods (see Section 6). This storage approach allows the user to select any number of integration periods, which may vary in size, and are free to overlap. It also allows the user to generate any number of integration types, and to retain selections while reprocessing the data, switching between data reduction schemes (see Section 5), or changing the statistical method used.

As with all data in Iolite, integration periods are displayed visually, and are illustrated as a box encompassing the selected time period (on the $x$-axis) and a 95% confidence window for the average value (on the $y$-axis; e.g. Fig. 2b).

There are three windows (see Section 7) in which the selection and interrogation of data can be conducted, each with different capabilities. Common to these windows is the plotting of information versus time on the horizontal axis, with several options available to the user to allow convenient navigation of their data. For example, by zooming in on a particular time period, the user can view individual datapoints, finely tune their selections of integration periods, and interrogate the data on a timeslice-by-timeslice basis (e.g. Fig. 2b). Conversely, zooming out allows individual analyses to be viewed in the context of an entire session of data acquisition (or even multiple days of measurement if desired), revealing longer-term patterns in the variability. This ability to smoothly adjust the timescale at which data are viewed provides a perspective that is not readily obtainable in any other way, and allows for the rapid selection of suitable integration periods.

The selection and modification of integration periods can be achieved manually using the mouse. The horizontal sides of the

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**Fig. 2** (a) The entire session of data from Case 1, displayed using the Traces Window with $^{88}$Sr signal intensity (red, left axis) and corrected $^{87}$Sr/$^{86}$Sr ratio (blue, right axis) plotted simultaneously. Note that the latter has been automatically masked in regions of low signal intensity to avoid the plotting of extremely noisy ratios. b) A detailed view of a single spot analysis from Case 1 (16th analysis; approximately 11:11 am). In addition to $^{88}$Sr signal (red) and corrected $^{87}$Sr/$^{86}$Sr ratio (blue, left axis), Rb interference (green, right axis) has been added, and is quoted as contribution in ppm to the measured $^{88}$Sr signal. Despite most of the analysis being compromised by unacceptably high Rb levels, the early portion of the analysis is typical of perovskite, with high Sr signal and very low Rb levels, and contains useful information for the corrected $^{87}$Sr/$^{86}$Sr ratio (black box).
integration period box (representing the mean and its uncertainty) are updated in real time during editing, providing immediate feedback to the user on the impact of any changes. Similarly, any splines (see Section 8) associated with the integration type are also updated live (Fig. 3). This approach can be used on any channel, regardless of whether it is an input or a more complex calculation, and while viewing any combination of channels on screen.

In addition to manual selection of integration periods, there are also tools for selecting time periods automatically. This is useful when dealing with very large datasets, or when selection of integration periods needs to be kept uniform. These tools can use information from the original raw data files, from log files produced by a laser ablation system, or from thresholds in the intensity of input channels. In this way users can rapidly process tens or even hundreds of individual analyses and then graphically check the results.

5 Data reduction in Iolite

One of the primary goals of Iolite is to provide a powerful platform for data reduction, while keeping limitations on how such processing is conducted to a bare minimum. For this reason a plug-in approach is employed, with each method (referred to as a Data Reduction Scheme, or DRS) stored in a discrete file. These DRS files can be readily viewed and modified by the user and are by nature open source. Although there are some rules about how the DRS interacts with the underlying platform there are very few restraints placed on how the user processes their data, and methods can be anything from a simple subtraction of baselines to a complex package such as the “UPb_Geochronology” DRS, which contains numerous discrete functions, and interacts heavily with the user via customised windows generated within the DRS.

Although data reduction schemes may vary considerably, according to their author or requirements, the majority follow a workflow that can be generalised as follows:

1. A DRS will typically begin by taking input channels (which each have their own associated time index) and translating them onto a common index time array. This is usually combined with the subtraction of baselines if this is to be performed within Iolite.

2. These baseline-subtracted intensities are then most often used to calculate isotope ratios, or the ratio of elements to a selected internal standard element (for internally normalised trace element abundance calculation).

3. These raw ratios can be further manipulated, for example by calculating and correcting for mass fractionation effects and/or isobaric interferences. There is no restriction on the nature or number of such calculations, and any number of extra channels can be produced if desired.

4. If available, analyses of a reference material can be integrated into the data reduction protocol. Information from the reference material can be used in a number of ways, examples of which include correcting for instrumental drift, interpolating mass bias (e.g. for Pb-isotope analyses where two isotopes are unavailable for internal corrections), or calculating semi-quantitative trace element abundances.

5. In many cases, analyses of the reference material can also be used to estimate method uncertainties using the “pseudo-secondary standard” approach described in Paton et al.

6. Finally, the DRS can participate during export of data, for instance by calculation of an error correlation between specified output channels.

In each of these steps, a new channel is created to store the results, allowing the analyst to see the effect of each stage of data processing, while leaving the input data unaltered (for additional details of channel wave formats, etc., we refer the reader to Appendix 1).

Data reduction schemes can exploit the full range of Igor Pro commands, as well as a number of support functions specifically developed to support data reduction schemes, such as the subtraction of baseline intensities, or the interpolation of reference material values.

6 Statistics

Iolite calculates statistics separately for every input channel, intermediate channel and output channel available, and for each individual integration period selected by the user. This information is stored in a separate 3-dimensional data matrix for each integration type, and can be thought of as floating on top of the underlying raw data, which is not modified during the process. The results are calculated live whenever a change is made to the start or end time of an integration period, and are independent of the DRS employed.
Statistical methods for calculation of both the mean (for data with a Gaussian distribution) and median (useful for non-Gaussian datasets) are provided. The uncertainty of the median is quoted as two standard errors (2 s.e.), while the uncertainty of the median is quoted using the MAD (mean of the absolute deviation), converted to an approximation of a 2 s.e. based on the observation that for a normally distributed dataset the MAD is 1.4826 times the standard deviation. Although this relationship is not valid for non-Gaussian datasets, using a MAD-based uncertainty nevertheless provides a robust estimate that is comparable to the standard deviation notation. The statistics are calculated using the individual timeslices within an integration period, with the exception of undefined datapoints (i.e., timeslices where no value exists), which are ignored. Because each timeslice contains only a value (i.e., without an uncertainty assigned), no form of weighting is applied.

Outlier rejection is available in both mean and median methods, and can be set to a threshold of 2 or 3 standard deviations (or the MAD equivalent). To determine outliers, a preliminary average and uncertainty are calculated using all timeslices in the integration period. These preliminary statistics are used to identify any points that lie outside the threshold, and these are removed from the population; the final outlier-rejected statistics are then calculated using the remaining data.

In addition to assigning an uncertainty based on the scatter between individual timeslices (i.e., an internal precision), Iolite can also propagate an external precision for each integration period using a pseudo-secondary standard approach. This method uses multiple measurements of a reference material to assess whether the internal precisions assigned to each integration period are sufficient to explain the degree of scatter in the population. If not, the degree of excess scatter is assumed to represent a source of constant excess uncertainty, which is combined in quadrature with the internal precision of each integration period to generate an external precision. For a detailed description of this approach, we refer the reader to Paton et al.12

Features are also built into Iolite for calculating and visualising population-level statistics for a group of integration periods. In addition to the mean and median based approaches described above, these functions also contain additional options that take advantage of the uncertainties assigned to each integration period. These include the ability to calculate a weighted mean, and additional statistical measures such as the MSWD (mean square of weighted deviates) and probability of fit. In addition to calculating a mean weighted by the inverse of the internal precision, an option is provided for weighting by the relative number of ions detected in each integration period (i.e., the intensity multiplied by the duration). This approach can be useful in instances where one or more analyte isotopes vary significantly in intensity between integration periods, or the durations of integration periods vary significantly. Population level statistics can be viewed in the Report Window both numerically and graphically, and can be exported as a PDF report or data table.

Although the bulk of Iolite’s framework is encrypted, functions used to calculate statistics for both individual integration periods and populations statistics in the Report Window are unencrypted. In addition, the functions used to interpolate data, including the automatically smoothed spline (see Section 8), and functions for propagation of uncertainties and calculation of uncertainty correlations are not encrypted. These functions are all stored within the “Statistical uncertainties” procedure file in Iolite’s “Global Procedures” folder.

7 Features of the interface

To provide flexibility in the visualisation of data, Iolite has three separate windows in which the user can view, select and modify data:

- The Main Control Window is Iolite’s primary window, and is the main interface for actions such as import of data, selection of a data reduction scheme, data export, etc. (Fig. 5a).
- The Log Window is specifically designed for viewing datasets containing a large number of inputs (e.g. trace element analyses), and contains a plot of all input channels, viewed on a logarithmic scale (Fig. 4b).
- The Traces Window is the most useful interface for interpreting, selecting or modifying data. It is capable of displaying a minimum of nine (the actual number will vary depending on display resolution) different channels simultaneously, with the options of individually scaling each, and of viewing channels using a mixture of linear and logarithmic scales (Fig. 4c).

In addition to these windows, there are also a number of other features for interpreting and presenting data:

- The simplest of these features is the export of data as a “.csv” data table suitable for use in other programs (e.g. Microsoft Excel). In addition to the export of statistics for integration periods, it is also possible to export time-resolved data from any stage of data processing.
- The “Generate Report” feature allows users to view population level statistics for their data, such as for example a weighted average for all analyses of a particular sample (Fig. 5a).
- The X-Y Plot Window allows users to plot any two channels against each other, and provides a means for interpreting results more thoroughly without first exporting data (Fig. 5b).
- Perhaps the most powerful and unique feature of the software is its ability to generate XY images from laser data using Igor Pro’s “Gizmo” OpenGL visualisation tool. Images can be 2 or 3 dimensional, and can be used to view up to four channels simultaneously (Fig. 5c). Images can be automatically generated from a series of data produced by laser-rastering, or can be produced manually for more complex situations.

8 Key concepts of data treatment in Iolite

The software has two main concepts that distinguish it from other data reduction packages: the focus placed in Iolite on the interpolation of data that vary with time using “splines”; and the reduction of data on a timeslice-by-timeslice basis.

There are many parameters in mass spectrometry that can vary with time, such as detector sensitivity, levels of background noise and instrumentally induced mass bias. Despite the potentially large impact that variations in such parameters can have on reduced data, they are almost universally treated by simple bracketing methods, either by measuring the parameter prior to analysis of a sample, or by averaging measurements acquired...
Fig. 4 Illustrations of the three main interface windows of Iolite, each of which can be used for data selection and interpretation. a) The Main Control Window, displaying in this example the $^{87}\text{Sr}$ signal intensity for analyses of perovskite from Case 1. The screen is split to allow scaling of the entire signal range (top) and of baseline-level signals (bottom). Selected periods of gas blank are displayed (black boxes), as well as the calculated spline used for baseline subtraction (green line). Controls on the bottom and left sides of the window allow navigation and scaling of the X and Y axes, respectively, while the grey pane at the top of the window contains all of Iolite’s main controls and settings. b) The Log Plot Window allows the simultaneous display of a large number of inputs, and is particularly useful for trace element data. Data are plotted on a logarithmic scale, and can be navigated using the same controls as the Main Control Window. In this case data for eleven measured elements are displayed, where the laser was used to ablate a radial traverse of a speleothem. c) The Traces Window, which can display a minimum of nine (more with increasing screen resolution) different traces simultaneously. In this example the entire 60 h of Mg-isotope data from Case 2 are plotted, showing $^{25}\text{Mg}$ signal intensity (red, right axis), measured $^{25}\text{Mg}/^{24}\text{Mg}$ ratio (dark blue), mass bias corrected $^{25}\text{Mg}/^{24}\text{Mg}$ ratio (light blue, left axis) and drift-corrected $^{25}\text{Mg}/^{24}\text{Mg}$ ratio (green). In this case, integration periods of the DSM-3 Mg reference standard are displayed (black boxes), as well as the spline used for drift correction (green line).
Fig. 5  Illustrations of the main features of data interpretation available within Iolite. a) The Report Window, showing results from Case 2, expressed as deviation from the reference standard in ppm for mass bias corrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios. The table contains information for the population level statistics of each sample, and Sample 4 has been selected for viewing graphically. In the plot individual analyses are shown with both measured (black) and propagated (grey) uncertainty bars, while the horizontal black line and shaded grey band represent the weighted average and 2 se uncertainty of all Sample 4 analyses. b) The X-Y Plot Window is useful for investigating the relationship between traces. In this example a subset of the Mg-isotope data from Case 2 is plotted as measured $^{26}\text{Mg}/^{24}\text{Mg}$ on the $x$-axis versus mass bias corrected $^{26}\text{Mg}/^{24}\text{Mg}$ on the $y$-axis, with error bars representing the measured 2 se uncertainty in each case. Analyses of the reference standard are shown in black, and those of Sample 2 in blue. c) Iolite’s image interface can generate 3-D false colour images from laser ablation data acquired by rastering an area. The interface allows users to plot either a single trace, or three separate traces as red, green and blue intensities of the image. A fourth trace can be represented by the vertical scale if desired. This example shows a trace element image of a zircon grain, with internal-standard normalised concentrations of Y, Lu, Ta and Th as red, green, blue and depth, respectively.
both before and after sample analysis. In Iolite, a more complex approach is adopted in which an entire population of measurements, often distributed unevenly over a large time period, are used to model changes in a parameter with time. Interpolation is achieved by fitting a "spline" through the measurements, which can then be used to estimate the value of the parameter at any point in time (Fig. 6).

A number of interpolation methods are provided, varying from simple approaches such as an average or linear fit of all measurements (Fig. 6c), to complex approaches employing cubic splines and smoothed cubic splines. In addition, interpolation methods emulating traditional bracketing approaches are included for easy comparison with the results of other software (Fig. 6b), a feature which we believe to be unique. Splines are generated individually for each channel, and are created for channels at all levels of data reduction. To generate smoothed cubic splines the software utilises Igor Pro’s `interpolate2` function, which is based on the work of Reinsch. It incorporates measured uncertainties in the fit, and is capable of fitting in cases

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Fig. 6  Example of splines calculated using different methods of interpolation, again using a long (ca. 40 h) session of Mg-isotope analyses for illustration. Calculated mass bias corrected $^{26}\text{Mg}/^{24}\text{Mg}$ ratios are plotted in grey, with the black boxes representing the time range and 2 se of each analysis of the reference standard, and calculated splines shown in green. a) Iolite’s “Smooth Spline Auto” option, in which a smoothed cubic spline is used, with a degree of smoothing calculated automatically using a cross-validation algorithm and incorporating analytical uncertainties. Note that the spline follows broad trends in the data, but partially ignores individual analyses that deviate from the general trend (e.g. analyses 15 and 24). b) linear interpolation, in which drift is assumed to vary linearly between each analysis of the standard. Clearly this approach assumes that all analyses are of equal value, and does not take the calculated uncertainty of each analysis into account. c) A linear fit to all analyses of the reference standard, this method captures the broad trend of the data, but does not detect any finer subtleties.

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$\S$ The term ‘spline’ has a specific mathematical connotation that describes the more complex interpolation methods used by Iolite, and those that we would advocate for use with large data sets. On occasion, somewhat simpler methods of interpolation may be advantageous and the software includes the ability for users to employ such methods, and compare the results with more complex algorithms. For the sake of simplicity here, however, we retain the use of the term ‘spline’ as a generic descriptor of Iolite’s interpolation process.
where measurements of the parameter of interest are unevenly spaced. The smoothing is allowed to flatten the spline as much as possible, while maintaining the variance of individual measurements to the calculated spline below a threshold based on the smoothing factor (Fig. 6a). In addition to the manual selection of smoothing factors, an option for automatically selecting an optimum smoothing factor has been developed. This feature uses a cross-validation approach based on Craven and Wahba, where measurements are removed from the population one at a time and used to assess the validity of a spline based on all remaining measurements. A large range of smoothing factors are tested in this way, and that which minimises scatter in the cross-validation test is selected (see Fig. 3b for an example).

The second key concept of Iolite is the reduction of data on a timeslice-by-timeslice basis, to produce time-resolved results at each stage of data processing. This can be advantageous over methods which use averages generated at an early stage of data reduction to produce more complex values (e.g. the “ratio of the means” method), which can risk biasing results in cases where the data used are not normally distributed. A useful example of this is laser ablation “spot” analyses, where measured intensities tend to decrease systematically with ablation hole depth (Fig. 7a). Consequently, a group of datapoints from a single analysis will not be normally distributed (Fig. 7b), and the use of Gaussian statistics to calculate an average and uncertainty may produce biased results. However, an isotope ratio derived from two such measured intensities can remain unaffected, and thus may be normally distributed (Fig. 7c). By calculating data on a timeslice-by-timeslice basis, it is possible to test whether data are normally distributed, and to choose a statistical method accordingly.

The generation of time-resolved results allows the user to visualise their processed data, to compare them with input data, and to explore relationships between parameters that vary with time. In addition, it allows users to employ methods of data reduction that are not possible without time-resolved information (e.g. the down-hole elemental fractionation modelling of Paton et al.\textsuperscript{12}). In short, this approach provides fully calculated results without sacrificing the temporal (and therefore spatial) resolution of the data.

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