Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry

1 Data reduction

A full description of the principles of the Matlab code used to produce the images is given below.

1. Read in all csv files
   (a) Read laser log files (which always contain the word *log* in the file name) in as text
   (b) Read Agilent data files (which never contain the word *log* in the file name) as matrices
   (c) Read the date and time from the first data line of the Agilent csv files
2. Find analyses using the laser-log files
   (a) Read the date and time from the first data line of the Geostar log file
   (b) Compare the start time of all csv files and match them into log file-data file pairs
3. Produce an analysis sequence
   (a) Identify standards based on analyses labelled in Geostar as containing all or part of their name (e.g. '610', 'NIST612' etc.)
   (b) Samples are identified using a sample identifier (requires user input)
4. Split data into standards, samples and background
   (a) Read stage coordinates from the Geostar log files
   (b) Find the start time of each path from the Geostar log files
   (c) Convert all dates to serial date number
   (d) Define the LA-ICPMS computer time difference
      i. The first analysis is defined as being the first point in the ICPMS data file which is greater than 1.5× the mean of the first background segment, provided this is also the case for the subsequent 20 data points (in order to avoid errors due to outliers)
      ii. The difference between the time stamp of this data point and the time given in the Geostar log defines the time offset between the two computers
      iii. Correct all data points for this offset
   (e) Each analysis track is separated into an individual matrix based on the start and end times of the Geostar log files
5. Data manipulation
   (a) Background segments are identified as being all lines of data more than 5 seconds away from analyses start and end points
   (b) Outliers are removed from each background segment (±3 SD from the mean)
   (c) Background intensities are subtracted from each analysis, based on the mean of the two adjacent background segments; in this way background drift is accounted for
   (d) Sample intensities are summed for each ICPMS sweep to calculate the total ion beam intensity
   (e) element/Ca ratios are calculated for all analyses

(f) Outliers are removed from the standards (±2 SD from the mean)

(g) Mean standard X/Ca ratios are calculated

(h) Every datapoint is assigned coordinates based on the Geostar log file

(i) Where images were collected twice to improve resolution, the datasets are combined

(j) Analysed isotopes are read from the header of the Agilent csv and molar ratios for each element are calculated for each standard used

(k) User input is required to define which available standard should be used to standardise each analysed isotope

(l) Raw sample element/Ca ratios are standardised using the relationship defined by *Longerich et al.* [1996]:

$$\frac{i^{STD}_{measured}}{c^{STD}_{reported}} = \frac{i^{SAMP}_{measured}}{c^{SAMP}_{actual}}$$

Where i denotes the background-corrected raw intensity ratio and c denotes the X/Ca molar ratio

(m) All sample data is output to an $m \times n$ matrix where m is the total number of data points and n is the number of isotopes analysed, plus the total ion beam and stage coordinates

(n) Standards not used for sample standardisation are treated as samples and output in the same way

6. Image production

(a) The length of the image in the x-axis direction is defined based on the maximum and minimum Geostar x-coordinates

(b) x-axis coordinates are replaced with integers in order to produce consistent values between rows

(c) The dataset is re-distributed into an $m \times n \times p$ matrix where m is the number of laser tracks, n is approximately equal to the number of data points in the longest track (analysis time/dwell time) and p is the number of isotopes analysed plus the total ion beam

(d) A user-defined cut-off point removes all data associated with a total ion beam intensity less than a specified value (e.g. 5×10^6 cps)

(e) The matrix is re-sampled to double the original dimensions; each new component is filled with the mean of all components with which it shares an edge or corner

(f) The above step is repeated three times in order to create an image eight times the raw pixel dimensions, large enough for pixels to be smaller than visible (typically around 16 megapixel)

2 Rationale for data exclusion

Although the resins used were clean (all analysed isotopes were below the limit of detection with the exception of ^{11}B, m/z=24 (^{24}Mg, ?$^{12}C_2$) and ^{66}Zn), chambers not filled with resin were analysable. Furthermore, subtracting the mean background intensity from all analyses inevitably leaves 50% of gas-blank data points and therefore ∼25% (0.5×0.5) of gas-blank data points may be given an X/Ca ratio (Figure 1a), assuming independence of X and Ca.

An image with no total ion beam data exclusion is shown in Figure 1b. Whilst the shape of the foraminifera is evident, it is confusing and contains much data which are of no interest.

Because it is not possible to standardise data from chambers that were not filled with resin (because the calcite in these locations is far below the focal point of the laser) and because data points that only relate to resin contain no useful information, we exclude these areas of the analysis using the total ion beam intensity.

3 Comparative standard maps

In order to demonstrate that (1) condensate from the previous ablation track (minimised by using a low fluence of ~3 J cm^{-2}) does not affect data acquired from the adjacent track, and (2) that overlapping previous tracks (where samples were analysed twice to improve resolution) does not affect the data, the same techniques were applied to the pressed powder carbonate standard MACS-3 (figure 2).

The standard was analysed in the same way as a small foraminifera, i.e. the image was acquired twice with the second set of tracks offset by half the track spacing in order to double y-axis resolution. The evolution of the sample/standard surface topography is shown in the upper left corner of figure 2. Crater depth is not exaggerated and is based on the assumption that each laser pulse removes a ~0.1 μm-thick layer of material from the surface. A third set of images (right side of figure 2) were produced by subtracting the first and second maps, shown as a percentage of the USGS information values for this standard. The fact that these images all average within 3% of 0 simultaneously demonstrates that (1) standardisation of carbonates using NIST and GOR glasses produces accurate data, (2) there is no significant offset as a result of the irregular sample surface following the acquisition of the first image (figure 2) and (3) the ablation blanket of the adjacent track does not contribute significantly to subsequent analyses. The random distribution of non-zero values in these images strongly implies that this noise is the result of heterogeneity in the standard, which has raw intensity RSDs ~5% higher than NIST610 at an equivalent spot size, and the relatively small spot size itself (20 μm). Furthermore, note that these images are not repeat analyses of the same tracks. Although we subtract the two acquisitions in figure 2 (in order to demonstrate no significant offset from zero) they are derived from different (adjacent) material which is likely to explain much of the fine-scale difference.

4 References

Longerich, H., S. Jackson, and D. Günther (1996), Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation, *Journal of Analytical Atomic Spectrometry*, *11*(9), 899–904.

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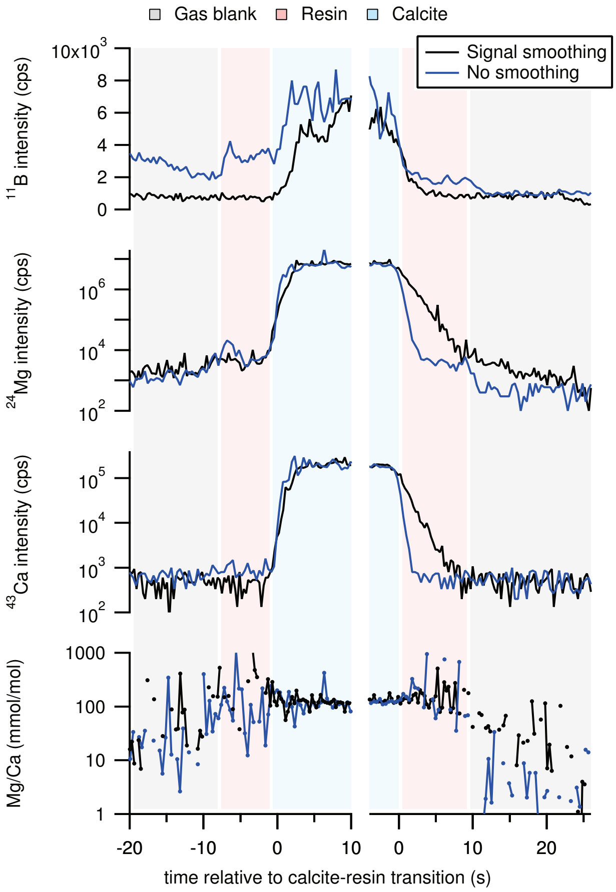
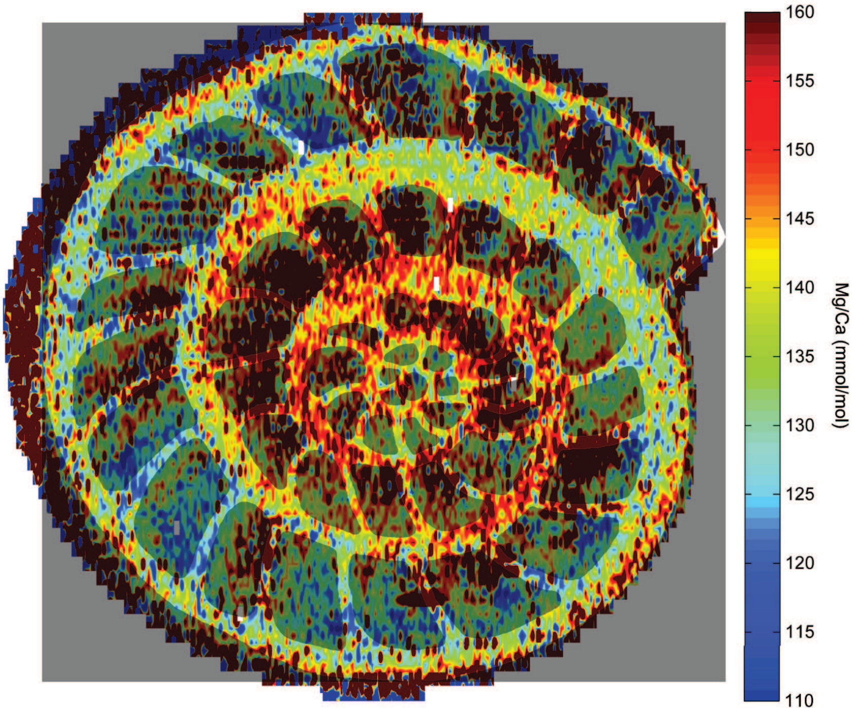


(a) Gas-blank, resin and sample analyses showing wash-in/out times for data collected with and without the squid signal smoothing device. Note that it is possible to produce Mg/Ca ratios for the gas-blank and resin, despite Mg and Ca intensity lower than the LOD, as a consequence of mean background subtraction removing only 50% of the gas-blank values.



(b) An image with no data exclusion based on the total ion beam intensity, Mg/Ca shown as an example. The shaded area shows the approximate position of the excluded data.

Figure 1: Rationale for data-exclusion based on the total ion beam intensity. Element/Ca ratios exist for resin and gas blank producing distracting and meaningless data.

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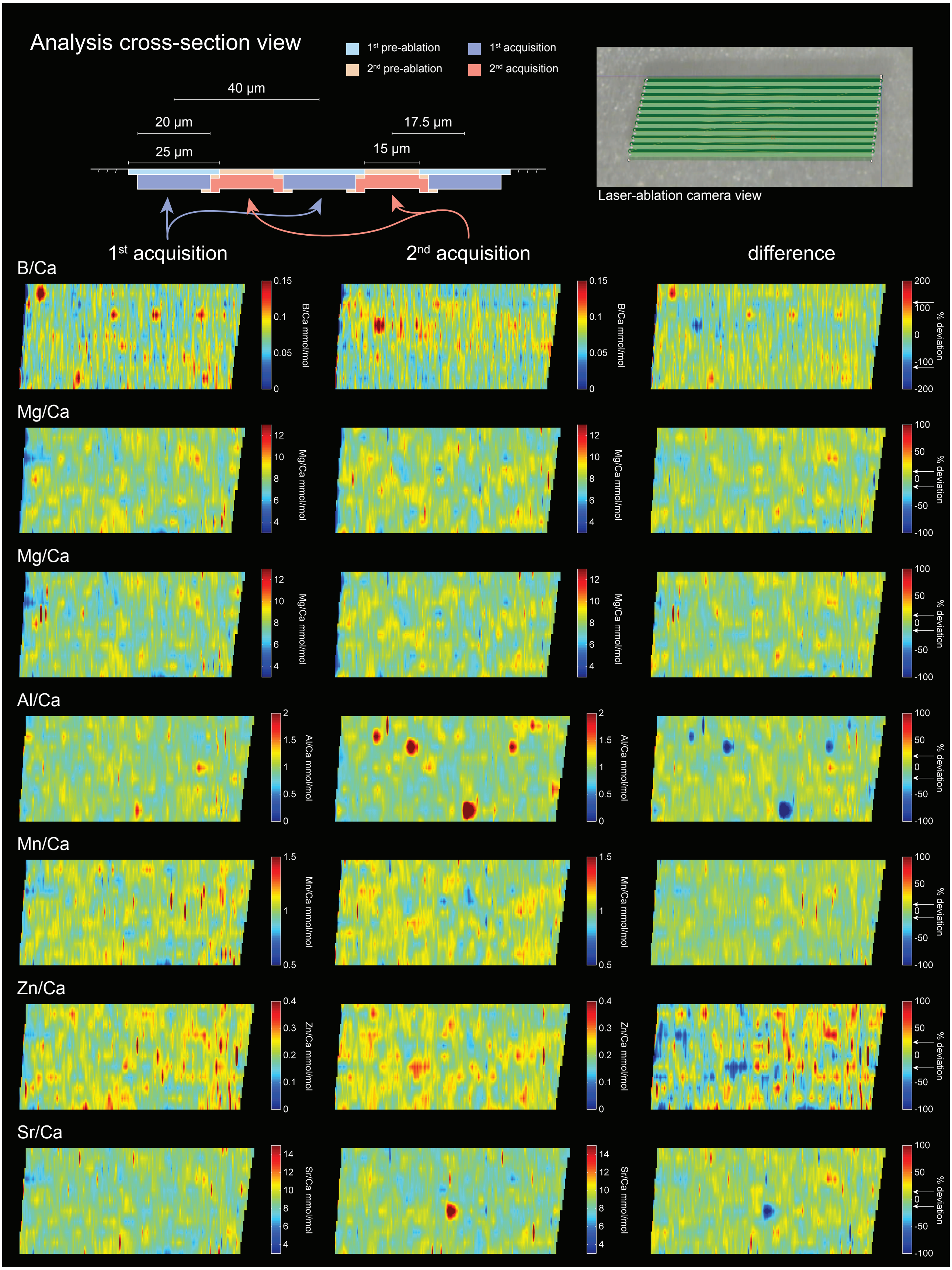

Figure 2: Trace element maps of the carbonate standard MACS-3. The maps were collected twice to mimick the analytical imaging procedure for small samples (left and center panels; see text). A cross-section view through five ablation tracks is shown to illustrate topographic changes during analysis. The set of images on the right shows the difference between these two acquisitions, expressed as a percentage of the MACS-3 information value. Arrows on these scale bars show the position of ±1SD. There is no discernable difference between the images related to the ablation procedure. Mg data derived from both ^{24}Mg (above) and ^{25}Mg (below) are shown.