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2D mapping of LA-ICPMS trace element distributions using R

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ABSTRACT

A new add-on package (*LAICPMS*) for the R language for statistical computing is presented, which greatly facilitates data reduction and visualisation (single tracks and 2D element maps) of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) data. The package determines many input parameters automatically and is easy to use. We present major and trace element distribution maps of natural calcite samples, processed using *LAICPMS*. Data processing from raw data to presented graphics takes only a few minutes. The empirical cumulative density function (ECDF) is used for optimised colour coding of the maps rather than linear or logarithmic scale, making a maximum of element-specific detail visible. For preprocessing, several different smoothing algorithms were evaluated and can be chosen by the user; for the presented data, a simple running median/running average was chosen. Typical data analysis is performed via short, easy-to-understand script files, and results can be used for further analyses within R. Owing to other R add-on packages utilised, the results can be output either numerically or as high-quality graphics in a wide range of file formats. Inheriting from its host environment R, the package is open-source software and freely available for all major computer platforms.

1. Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) facilitates elemental and isotopic analysis of solid samples at spatial resolutions typically in the range of 10–100 μm.

Developed in the mid-1980s (Arrowsmith and Hughes, 1988; Gray, 1985) and greatly improved throughout the 1990s (e.g., Fryer et al., 1995; Günther et al., 1997; Jeffries et al., 1998), this technique is now routinely and widely employed as a rapid and relatively inexpensive microanalysis method that requires little sample preparation (e.g., Durrant, 1999; Günther and Hattendorf, 2005).

Short (ns), high-power (GW/cm^2) laser pulses, focused as micrometre-sized small spots onto the solid sample surface, break the bonds in the uppermost sample surface (0.1–0.2 μm) quasi-instantaneously. The resulting plasma condenses into nanometre-sized aerosol particles that are taken up by an inert gas flow (typically He; Eggins et al., 1998). In the plasma torch of the mass spectrometer, the particles are broken down into their elemental constituents, ionised, and extracted into the mass analyser and collector of the mass spectrometer. Besides single-spot and line analysis, the technique is increasingly used for mapping the element distribution in samples (Koenig et al., 2009; Treble et al., 2005; Ulrich et al., 2009; Woodhead et al., 2007).

The signals from the mass spectrometer are recorded as a continuous data stream in fixed time intervals (“sweep”). We typically record background, standard, and sample signal intensities together in one file, but collection in separate data files is also common practise (equally well handled by the software; see below). By moving the sample using a computer-controlled *x*–*y* stage while ablating, information about different areas of the sample is obtained. For mapping, these time-resolved raw signal intensities from different localities need to be converted and remapped into spatial concentration information. A short system response time and sample washout of the ablation system to prevent mixing the signals from subsequent sampling spots along the ablation track are crucial for the obtainable spatial resolution (Müller et al., 2009; Woodhead et al., 2007).

Routine data acquisition and analysis software supplied with mass spectrometers does not offer the functionality of converting signals into the spatial domain. Traditionally, data processing (“data reduction”) is done using spreadsheet programs, a tedious and error-prone process. This yields good results for single (1D) ablation tracks, which can be manually correlated to the position of the ablated track on the sample. Yet, the spreadsheet approach reaches its limits in usability and performance when processing nonstraight tracks or arrays of tracks covering an area of the sample.

Here, we present a new software package for data handling and processing, called *LAICPMS*, based on the R language for statistical computing (R Development Core Team, 2010). This platform has

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rapidly gained popularity in the (Earth) Sciences in recent years for its powerful data analysis functionality and the fact that it is freely available as open-source software. Individual functions for specific repetitive tasks during processing of LA-ICPMS data greatly simplify and speed up data processing, and can be combined in scripts for more complex analyses and visualisation.

We have applied our software to create trace element maps of a sample containing multiple generations of calcite cements (Fig. 1), grown in the cavities of a tectonic scarp breccia from the central Northern Calcareous Alps (Austria). These cements grew from solutions circulating along ~N–S trending normal faults of presumed Oligocene age, which are linked to sinistral movement along the Inntal fault, and formation of the Inneralpine Molasse basin. The different cement generations are interpreted to have formed during increasing influence of meteoric waters, as the local sediment basin was filled (Ortner, 2003).

2. Analytical methods

We used a Resonetics excimer (193 nm) laser ablation system (RESOlution M-50 prototype) with a Laurin Technic two-volume ablation cell. For a compilation of the main instrumental parameters used in this study, see Table 1. The instrumental setup is shown schematically in Fig. 2. The laser illuminates a mask, whose demagnified image is focused onto the sample, determining size and shape of the ablation spot. A computer-controlled *x–y* stage moves the ablation cell under the stationary, pulsed laser beam, to remove material from different areas of the sample. Ablation takes place in a small, funnel-shaped upper volume within the main cell, which results in rapid signal washout (99% washout in less than 2 s) and uniform signal response anywhere in the LA cell (for details, see Müller et al., 2009). The carrier gas transporting the aerosol to the mass spectrometer is He, with the potential addition of a small amount of N_2 or H_2 downstream from the cell to enhance sensitivity. The present study was conducted utilising an Agilent 7500ce quadrupole ICPMS. A ~10,000 K hot Ar plasma maintained by a RF electromagnetic field at atmospheric pressure volatilises the nanometre-sized particles and ionises the resulting atoms. The ions, while being transferred into high vacuum, are accelerated and focused into a tight beam by electrostatic fields and then separated based on mass and ionic charge by a quadrupole mass analyser. This way, at any given time only ions of one specific mass/charge ratio (ideally just one atomic species) reach the collector and are counted for several milliseconds each ("dwell time"). The quadrupole mass analyser scans through the spectrum of all masses of interest ("sweep") several times per second.

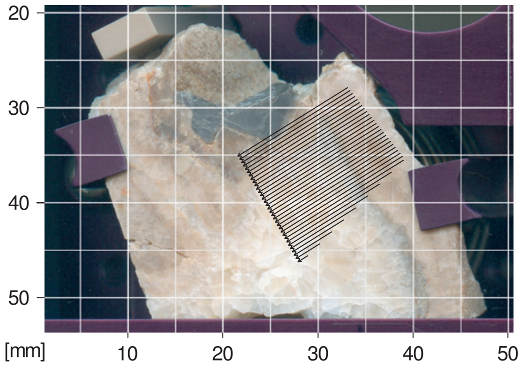

Fig. 1. Ablation site overview. Sample of multigeneration calcite cements mounted in the laser ablation sample holder, with indication of ablation tracks generated by GeoStar to fill the chosen area (arrows indicate ablation direction). Spacing between tracks is 400 μm.

Table 1
Main instrumental parameters used in this study.

Laser parameters	
Laser type	ArF excimer
Wavelength	193 nm
Pulse duration	20 ns
Ablation parameters	
Energy density	~4 J/cm^2
Ablation spot size	74 μm
Pulse repetition rate	20 Hz
Sample stage speed	67 μm/s
Track spacing	400 μm
ICPMS parameters	
RF power	1220 W
He gas flow	850 ml/min
N_2 gas flow	6 ml/min
Ar carrier gas flow	470 ml/min
Sweep time	0.49 s
Dwell time	10–40 ms

masses (m/z) analysed: 25, 27, 29, 43, 55, 57, 85, 88, 138, 140, 153, 172, 206, 207, 208, 232, 238

We used a laser repetition rate of 20 Hz and stage scan speed of 67 μm/s; see Table 1. The sample stage in our setup features constant velocity linear movement in every direction and also when changing scan direction. This is important to accurately relate the time of measurement to a calculated position. The *x–y* range of stage movement is 50 × 50 mm^2 (Müller et al., 2009).

The ablation process is controlled by Resonetics' purpose-built software GeoStar. Via a user-friendly, image-controlled graphical user interface (GUI), the software allows flexible programming of ablation points, tracks, or areas (being automatically filled with tracks), and all relevant parameters of sample stage position, speed, gas flow handling, laser parameters, and ablation spot size.

This information is stored in XML files, which are easily readable with other software to retrieve analysis parameters. In version 5.8 of GeoStar (at the time of writing), *x–y* coordinate information of the individual tracks making up an automatically filled area is not stored in these files. However, the start and end coordinates can be retrieved from the log files (.csv, .log) written during each analysis. This is done automatically by the software presented here.

Output from Agilent's ChemStation, on the mass spectrometer control computer, contains time-stamped raw intensities in counts per second (cps) for the chosen mass/charge (m/z) ratios. The data are typically exported as time-resolved "comma separated values" (.csv) files from the mass spectrometer computer. From these values, actual concentrations in the sample need to be calculated—as described below.

In our setup, the two computers are not connected electronically, so the different information about the same analysis is correlated afterward. Currently, connecting the two computers only allows the initiation of data recording at a given time. More sophisticated synchronisation of, e.g., individual ablation tracks in separate data files or recording of a synchronisation signal along with the data is not possible with GeoStar/ChemStation—thus use of the feature was not pursued further.

3. Data processing

The following workflow is the standard data reduction currently implemented in our new software, *LAICPMS*. Most calculation parameters are user-settable, and scripts for different calculations, based on the functions of *LAICPMS*, can be written.