Principles of LA-ICP-MS high-precision analysis of trace element abundances and isotope ratios in minerals and fluids

Thomas Pettke

[Image of laboratory equipment and computer interface]
We measure major to trace elements and isotope ratios "in anything" in situ, down to mg/t for a 100 µm beam diameter.

Instrumental considerations
What LA-ICP-MS can analyze and what not
Data quantification strategies

Forensic sciences: Car crash

Depth profiles for two green car paint samples (samples D and E), obtained with ICP-SF-MS: Intensity (log scale, cps) versus time.
(CC: clear coat; BC: base coat; PS: primer surfacer; FP: first primer)

Deconinck et al. 2006
Materials sciences

Characteristic element concentrations (here: Car windows) determine materials properties (flexibility, breaking resistance, colour, ....).

The analysis of small splinters may thus provide diagnostic element signatures, and can be used in forensic sciences, too.

Watling et al. (1997)

Otolith chemistry to track fish migration

Otoliths are mm-sized ear bones which grow throughout the life of an organism, displaying annual growth rings

Selected trace element signatures are a proxy for temperature and water type (sea vs. freshwater).

Migration of salmon can thus be tracked!

Otolithe of fossil fish can provide information about paleo-climate

(Miller, 2006)
Recent literature

Two LA-ICP-MS chapters by Pettke, focusing on the analysis of heterogeneous inclusions in minerals

We can measure "all" trace elements in one analytical point

Kaeser et al., 2006, 2007, 2009
Heterogeneous phases

Unmixing:
OPx lamellae in CPx

Reconstruction of homogeneous phase composition at formation conditions, i.e., high P and T!
Also essential in metallurgy

The unique possibility

- Analyze polyphase inclusions of confined volume
- Obtain bulk chemical composition of the inclusion trapped as one phase
Recall: We analyze a sample VOLUME; thus, danger of zonation with depth! (or: Potential for depth profiling)

Diffusion profiles analyzed in line-scan mode away from melt-olivine interface (data, points; lines, fits): Determination of diffusion coefficients at experimental P, T, X.

Spandler et al., 2007
Typical LA-ICP-MS instrument

Laser

Light Amplification by Stimulated Emission of Radiation

produce coherent, collimated, monochromatic radiation, in free-running or Q-switched mode

Solid source
- Nd-YAG (Nd-doped Y-Al garnet; 1064 nm), quadrupled or quintupled (266 or 213 nm).
- OPO lasers (Ti-Sapphire): down to <200 nm (Optical Parametric Oscillator)

Gas source
- Excimer = Excited dimer (noble gas – halogenides; e.g., ArF)
  down to 157 nm with F₂, gas source lasers (also named Exiplex)
Mass spectrometers
Quadrupole, Magnetic sector, Multiple collector, Time of flight

Fundamental principle of mass spectrometry
The analytes we measure are always mass-filtered according to their MASS / CHARGE RATIO

\[
\begin{align*}
90\text{Zr}^{++} &= 45\text{Sc}^+ \\
28\text{Si}^+ &= 56\text{Fe}^{++}
\end{align*}
\]

Mass spectrometers

<table>
<thead>
<tr>
<th>Type</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole</td>
<td>Robust, fast scanning, sensitive, low mass resolution (interferences)</td>
</tr>
<tr>
<td>Time of flight</td>
<td>&quot;Simultaneous&quot; measurement, moderate sensitivity and backgrounds</td>
</tr>
<tr>
<td>Magnetic sector</td>
<td>Highly sensitive, moderate scanning speed, High mass resolution (loss of sensitivity)</td>
</tr>
<tr>
<td>Multiple collector</td>
<td>Simultaneous analyte measurements, limited number of isotopes (i.e., mass range), high to moderate sensitivity</td>
</tr>
</tbody>
</table>
Magnetic sector mass spectrometry is based on the principle that moving charged species are deflected in a magnetic field.

Quadrupole mass spectrometry is based on the principle that moving charged species are (mass/charge)-filtered in an electrostatic field (between the rods). Only the ion of the mass-to-charge ratio we want to analyze can get through the mass filter (= resonant ion), all the other ions are lost.
Solid Sample Introduction by Laser Ablation for Inductively Coupled Plasma Source Mass Spectrometry

Alan L. Gray
Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, UK

The results are described of a preliminary study of the mass spectrometry of solid samples using a ruby laser to ablate the sample into an inductively coupled plasma (ICP) source mass spectrometer. Standard rock samples were used, pelleted with a binder into the form of a disc. Some 200 ablation pits could be accommodated on each sample. Laser pulse energies of 0.3-1 J were used in the fixed Q mode and the ablated material transferred from the ablation cell into the plasma torch by means of the plasma injector gas flow. The mass spectrometer was used in the fixed ion mode using mean ion current detection to evaluate the reproducibility of successive pulses on major constituents and in the scanning mode at the rate of 10 scans s\(^{-1}\) to produce spectra using mean current detection for major elements and pulse counting detection for traces. Problems were experienced with saturation of the detection system in both the mean current and pulse counting modes owing to the transient nature of the sample pulse from the laser, when attempting to quantify major elements, but except where a major peak was saturated, reasonably uniform sensitivity for most elements across the mass range from 7 to 238 m/z was obtained. Isotope ratio measurements were made on lead at 29 pg g\(^{-1}\) and detection limits for the elements examined appear to be 10 ng g\(^{-1}\) or less.

Keywords: Solid samples; inductively coupled plasma source mass spectrometry; laser ablation

First LA-ICP-MS paper in 1985

Comparison of LA-ICP-MS between

1985
- 700 µm deep and wide craters
- 40 shots = 200 µg per spot
- LOD's in the 1000 - 0.1 µg/g range

2008
- 0.05 - 200 µm deep and 5 - 350 µm wide craters
- 300 shots = 0.X µg per spot
- LOD’s in the 10 - 0.0005 µg/g range

This is the SIGNIFICANT detection of one apple in 2'000'000'000 potatoes !!!
Characteristics of LA-ICP-MS

- All the matrix all the time
- Ablation rates not known a priori
- Ablation rates may vary with time
- Sample volume is analyzed → heterogeneity ?!
- Occurrence of large particles
- Elemental analysis between 100 and 0.000'000'05 wt-% concentration possible from one spot

Interactive PARAMETERS in LA-ICP-MS

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>LASER</th>
<th>AEROSOL TRANSP.</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorptivity of laser light</td>
<td>Wavelength</td>
<td>Ablation and carrier gas</td>
<td>Power, gas flows</td>
</tr>
<tr>
<td>Material robustness</td>
<td>Energy</td>
<td>Cell and tube volume</td>
<td>Torch position</td>
</tr>
<tr>
<td></td>
<td>Pulse width</td>
<td>Cell flushing efficiency</td>
<td>Ion extraction</td>
</tr>
<tr>
<td></td>
<td>Beam energy profile</td>
<td></td>
<td>Isotopes, dwell time</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dual detector</td>
</tr>
</tbody>
</table>
### Interactive PROCESSES in LA-ICP-MS

<table>
<thead>
<tr>
<th>ABLATION</th>
<th>TRANSPORT</th>
<th>IONIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Responsible for:</td>
<td>Responsible for:</td>
<td>Responsible for:</td>
</tr>
<tr>
<td>Material removal</td>
<td>Aerosol transport</td>
<td>Ion production</td>
</tr>
<tr>
<td>Particle production</td>
<td>Aerosol dispersion</td>
<td>Signal intensities</td>
</tr>
<tr>
<td>Condensation</td>
<td></td>
<td>Signal stability</td>
</tr>
<tr>
<td>Particle agglomeration</td>
<td>Particle agglomeration</td>
<td>Mass bias</td>
</tr>
<tr>
<td>Material loss</td>
<td>Material loss</td>
<td>Material loss</td>
</tr>
</tbody>
</table>

### LA-ICP-MS

**KEY ADVANTAGE:**
Optimize aerosol generation and ion production independently!

- Air-tight plastic tube
Advantages of LA-ICP-MS

- In situ analysis (i.e., texturally controlled)
- Bulk mixtures
- Micro (≥5 µm spot size)
- From major to trace elements and isotopes
- High sensitivity
- Low backgrounds notably in high mass range
- Low limits of detection (LOD)
- "Easy" spectra (→ interferences)
- Chemists claim low sample prep:
  YES for actually producing numbers
  No for understanding and interpreting geoscientific data

Typical LOD achieved on in-house LA-ICP-MS

One order of pit size increase results in two orders of magnitude lower LOD!
LA-ICP-MS Instrumentation

Hot spots:
- Ablation site laser - sample interaction
- Aerosol transport 100 %
- Aerosol ionization 100 %
- Signal recording 100 %

.. wishful thinking ..
Laser ablation

- Produces sample aerosol with characteristic particle size and size distribution → shorter wavelength, smaller particles and narrower size distribution (at least for silicates)
- Absorbance of monochromatic light → Energy density in excited sample volume: irradiance
- Ablation energy threshold → "evaporation" (shattering)

Laser-sample interaction

Produce the smallest possible particles by:

- maximizing laser light absorbance
- thus maximizing sample irradiance
- unhindered expansion of ablation plume above spot (He-gas)
Laser ablation modes:
Single spot
versus
rastering or line scan

Rastering produces more large particles
Surface contamination always present
→ All the dirt all the time ...

Jeffries et al. (1998)

Light absorbance of calcite
Jeffries et al., 1998: LA in fluorite with 266 nm (a) and 213 nm (b)

Guillong et al., 2002: 266 nm energy-homogenized LA in quartz (A) and SRM610 glass (B)

Our system, 2006: 193 nm energy-homogenized LA in SRM610 glass, several pit sizes superposed


Argon Helium

Same scales

Use He gas in the ablation chamber

Günther and Heinrich (1999), JAAS

Ablation chamber gas
Terms in LA-ICP-MS

- Irradiance: Energy density in excited sample volume
- Laser fluence: Total energy per area (W/cm²)
- Laser light pulse duration
- Ablation energy threshold
- Laser light absorbance

Irradiance increases with decreasing pulse duration for a given laser fluence.
Irradiance increases with increasing absorbance.

Laser aerosol particles from silicates

Filtered aerosol of NIST SRM 610 glass after 100 ablation pulses.

Note that with 193nm wavelength, no spherical particles are larger than 200 nm. The pores of the filter are visible in the images as dark areas.

Kuhn & Günther, 2005
Different particle size fractions show variable chemical composition at least for some elements

266 nm, scanning ablation; SRM610 glass (i.e., conditions to maximize the production of large particles!)

Aerosol transport

- Should be quantitative — but it is not ...
- Laser ablation particles all chemically identical? — unfortunately not (Kuhn & Gunther, 2004)...
- Mass fraction of lost particles matters

Get as much small particles to the plasma as possible
Aerosol transport efficiency

- The ablation chamber gas flow geometries dominate the aerosol dispersion

- Ablation chamber and transport tube volume has no influence on the amount of aerosol reaching the plasma (but: gas flow geometries)

- The smaller the particles, the "easier" the transport → particle size depends on sample irradiation (wavelength, matrix, ......)

- Particle loss must be minimized because of variable particle composition

Ion production in the ICP-MS

Incomplete ionization: large particles survive transition through plasma

Elemental fractionation likely .....
Elemental fractionation:
Analyte ratios evolve with time

Elemental fractionation
• Collectively refers to changes in element responses (i.e., element sensitivity ratios) with changing LA-ICP-MS analytical conditions
• Occurs at the ablation site, during aerosol transport, and in the ICP
• Extent of element fractionation also matrix dependent
• Eliminate (minimize) element fractionation → achieve matrix independence
Two types of elemental fractionation

\[ \frac{^{238}\text{U}}{^{232}\text{Th}}: \text{monitors incomplete ionization in the ICP} \]

\[ \frac{^{208}\text{Pb}}{^{238}\text{U}}: \text{monitors fractionation at LA-site} \]

Fractionation at LA-site minimized ...

... by not drilling too deeply!!

depth / diameter < 1

Eggins et al. (1998)
Fractionation index F: \[ \frac{\text{El/Ca}_{(2\text{nd-hs})}}{\text{El/Ca}_{(1\text{st-hs})}} \]

(hs = half of signal)
is another expression for element response ratios that evolve with progressive ablation time (Fryer et al., 1995)

Elemental fractionation

Plasma processes

- ICP temperature and plasma temperature structure
  - higher rf-power \(\rightarrow\) higher plasma temperature
  - lower gas flow rates \(\rightarrow\) higher plasma temperature

- Gas composition affects energy transfer to aerosol (e.g., \(\text{H}_2\) promotes ionization)

- Sampling depth (i.e., position of sampler cone tip): Lower depth has higher temperature

- Ionization efficiency depends on
  - ionization energies
  - plasma temperatures
  - particle residence time in the plasma
For accurate results: Easiest approach

- Standards and samples should be matrix-matched
- Instrument parameters invariable between standard and sample analyses
- Ablation conditions should be selected to minimize the formation of large particles
- The first 5 seconds of the signal interval of a single spot ablation should be discarded

Do we really want this?!?

Ion production in the ICP-MS
Complete ionization approached for:

- Small particles
- Narrow size distribution
- Optimized combination matrix – wavelength – pulse width
- Strong plasma (plasma load ...)
- ROBUST PLASMA analytical conditions
Robust plasma conditions

- Tune (ThO)+ production rate to values < 0.5%
- Tune ICP-MS to maximum sensitivity

U and Th:
Elements with "equal" first ionization energies but different "volatility".
SRM 610: [U] = [Th]
Tune U/Th sensitivity ratio to 1

→ MINIMIZE FRACTIONATION EFFECTS resulting from incomplete ionization
Principles of signal quantification

1) Variations in signal intensity are generated exclusively by variable analyte concentrations

![Graph showing signal intensities for different concentrations](image)

→ External standardization alone quantifies the sample

2) Signal intensities change in response to variables other than analyte concentrations (e.g., beam size)

![Graph showing signal intensities for different spot sizes](image)

→ External standardization alone fails to quantify the sample
2a) Signal intensities vary at Constant Signal Intensity Ratios (blue case) → Combined internal and external standardization quantifies the sample (define SENSITIVITY FACTOR)

Key:
Element sensitivity ratios remain invariable!
→ ONE sensitivity factor for all analytes

2b) Red case:
Signal intensities and Signal Sensitivity Ratios are variable → cannot be quantified! → must be eliminated!

Commonly done by using identical analytical conditions and matrix matching

Impracticable for inclusion analysis by LA-ICP-MS
Analytical accuracy

**Basalt glass**

External standard:
SRM 610 (NIST)

Matrix glass
100 wt-% El-Ox = IS

LA - ICPMS (n = 20)

EMP / SIMS (n = 20 / 7)

100 wt-% El-Ox = IS

**Ti-pargasite (BF-219)**

Clinopyroxene (BF-7)


Spinel (BF-219)

Trace elements on XRF pellets

RGM-1 rhyolite standard, Li2B4O7-pellet

But: 27Al is missing ?!?
→ 11B16O interference ...

Analytical accuracy

Even for sulfides!
(pyrrhotite, chalcopyrite and millerite)

Halter et al., 2004
Limitations on analytical accuracy

- Knowledge of external standards used, including most used SRM 610 and 612 from NIST (see Spandler et al., in review).
  - notably for "uncommon" elements, e.g., Be, Cl, Ge, Se, Mo, Sb, Nb, Ta, W, Au, ....

- Variability in ion production in ICP-MS as a function of elemental fractionation
  - Robust plasma conditions
  - Plasma aerosol load
  - Particle size and size distribution
  - Laser ablation conditions
  - ......

Interferences

- Plasma-based gas interferences are, in principle, accounted for by background subtraction
- Isobaric interferences (e.g., $^{87}\text{Rb}$ on $^{87}\text{Sr}$) avoided by proper analyte selection
- Polyatomic interferences are dangerous, e.g.,
  - matrix-gas-based: $(^{40}\text{Ar}^{16}\text{O})$ on $^{56}\text{Fe}^{+}$ in silicates
  - matrix-gas-based: Metal-argides on, e.g., $^{105}\text{Pd}^{+}$
  - matrix-based: $(^{44}\text{Ca}^{16}\text{O})$ on $^{60}\text{Ni}^{+}$ in carbonates, or $(^{16}\text{O}^{16}\text{O})$ on $^{32}\text{S}^{+}$ and $(^{16}\text{O}^{18}\text{O})$ on $^{34}\text{S}^{+}$ in silicates
- Doubly charged ions, e.g., $^{90}\text{Zr}^{++}$ on $^{45}\text{Sc}^{+}$ (recall: ions are measured as mass/charge ratio)

PAY ATTENTION IN ANALYSTE SELECTION
ICP-MS: Dynamic range and background

Major elements essential for quantification by internal standardisation

Some ICP-MS instruments allow for band passing

Measurement routine on a single collector instrument

Total analysis time per sweep: 88 ms

Total analysis time per sample:
Limited by homogeneous signal section or - not seldom - by section thickness !!!

Key: measure each analyte often enough to obtain a statistically significant number of individual measurements (i.e., sweeps) per analysis

Duty cycle: This is the net measurement time per isotope in one sweep, e.g., for Ca = 11.4%, for Rb = 22.7%
Representative recording of short, transient signals

Net count rate: 106830 cps

Net count rate: 23840 cps

78% of the signal missed!!

Pettke et al. (2000) JAAS

Representative recording of short, transient signals

Net count rate: 106830 cps

Net count rate: 207692 cps

95% excess signal!!

Pettke et al. (2000) JAAS
Matrix independent analytical conditions can be approached

Matrix independent calibration strategies can provide accurate results

*In-situ* analysis of "any" materials possible (solid and even liquid)
Since the LOD is 3\times \text{stderr}(bkg) / S, the variability of the background measurement matters most!
The LOD "signal" corresponds to a signal of \( \text{average(bkg)} + 3\times\text{stderr}(\text{bkg}) \) (green line)

... divide this by the element-specific sensitivity and you obtain the LOD in concentration units

A significant signal is thus ...

... everything which exceeds \( 3\times\text{stderr}(\text{bkg}) \), here shown in blue
One order of pit size increase results in two orders of magnitude lower LOD!
Signal variability in heterogeneous MI

Second constraint necessary: "internal standard"

Chem. Geol.
Second constraint:
Concentration of one element or an element ratio at MI entrapment known independently to determine MI-specific mass ratio, e.g., whole rock data.
This mass ratio is then used to calculate the element concentrations of this MI

Limitations on analytical accuracy

- Knowledge of external standards used, including most used SRM 610 and 612 from NIST (see Spandler et al., in review).
  - notably for "uncommon" elements, e.g., Be, Cl, Ge, Se, Mo, Sb, Nb, Ta, W, Au, ....

- Elemental fractionation during LA-ICP-MS analysis
  → The analyst should know what he/she is doing.....
Some more essential considerations

Interferences

• Plasma-based gas interferences are, in principle, accounted for by background subtraction
• Isobaric interferences (e.g., $^{87}\text{Rb}$ on $^{87}\text{Sr}$) avoided by proper analyte selection
• Polyatomic interferences are dangerous, e.g.,
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ICP-MS: Dynamic range and background

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Some ICP-MS instruments allow for band passing

Matrix independent analytical conditions can be approached

Matrix independent calibration strategies can provide accurate results

*In-situ* analysis of heterogeneous samples in the Earth Sciences