TACS University E-learning Webinar Series:

Laser Ablation 102: The Evolution of LA-ICP-MS Through Collaborative Science

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VP Technology & PLM Laser Ablation
Who am I?

• I am the person responsible for the Development of Teledyne Photon Machines laser ablation systems
• My background is geology (degree) and geochemistry (PhD)
• After academia I worked for a UK Atomic Energy Lab working on trace metal analysis
• Several years as an ICP-MS product specialist with PerkinElmer
• Worked for laser ablation companies for over 17 years
Content

• What is Collaborative Science?
• Brief history of LA-ICP-MS
• Evolution of sample chamber designs
• Development of Cobalt Cell / Iridia / HDIP
• Development of high speed elemental mapping technology
• Q&A
What is Collaborative Science?

*Commercial / Academic initiatives designed to advance scientific understanding*

• Funded Research
  • PhD projects, Master’s projects, research group funding, workshops & conference support

• Collaborative research – ‘Support in kind’
  • Close relationship developing applications, hardware and software
  • Recognize that key academic labs are the application experts, not the laser companies
  • Provide application and engineering support to advance science and understanding
A Brief History of Laser Ablation

1985 - Alan Gray (Uni. Surrey, UK) first demonstrates LA-ICP-MS

35 Years old in 2020

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
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<tbody>
<tr>
<td>1985</td>
<td>Alan Gray (Uni. Surrey, UK) first demonstrates LA-ICP-MS</td>
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<tr>
<td>1987</td>
<td>Arrowsmith publishes using 1064 nm IR LA-ICP-MS</td>
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</table>
| 1993-1995 | VG Elemental launch the Microprobe LA system (a 1064 nm laser)  
CETAC Technologies launch the LSX-100, then LSX-200; Merchantek launch the LUV-266 |
| 1997   | Jeffries and Günther show fractionation performance improvement with 213 and 193 nm sources                                                |
| 1997   | John Roy - New Wave (formerly Merchantek) launch the LUV-213                                                                            |
| 1998   | Eggins, et al, move from argon to helium sweep gas                                                                                       |
| 1999   | CETAC Technologies introduce the LSX-213                                                                                                 |
| 2002   | Russo, et al, describe use of ultra-fast (femtosecond) pulse width lasers                                                               |
| 2005   | Eggins, et al, describe a two-volume helium excimer (“HelEx”) cell                                                                       |
| 2009   | Coherent/CETAC introduce the Geolas 193 excimer laser  
John Roy establishes Photon Machines Inc. Analyte 193 introduced with HelEx cell technology. |
| 2013-2015 | Wang, et al, describe a tube cell for rapid, high resolution imaging  
Douglas describes a dual concentric injection system for rapid, high resolution imaging  
Van Malderen, et al, describe a low-dispersion add-on for the HelEx (ARIS) |
| 2017   | Teledyne Photon Machines release ‘Pharos’ femtosecond laser                                                                            |
| 2018   | Teledyne Photon Machines release HDIP data reduction & imaging software                                                                 |
| 2019   | Teledyne Photon Machines launch Iridia 193 Excimer with Cobalt cell                                                                      |
Evolution of Sample Chambers

- Early sample stages were simple gas tight boxes
  - single volume
  - allows various sized samples to be analyzed
Evolution of Sample Chambers

- Single volume design suffers from poor gas flow dynamics
- Washout is typically 10s of seconds

Evolution of Sample Chambers

• Specialist cells developed to minimize volume and improve analytical data...
• ...but limited sample size

From: Jan Kosler & Mike Tubrett, Short course from Winter Conference on Plasma Spectrochemistry, 2004

NIGL Zircon Cell
(Horstwood et al, 2003, after design principles of Bleiner & Gunther 2001)
Two-Volume Type Designs


Credit: Benjamin Fricker, ETH PhD thesis, 2012
HelEx II Sample Chamber

- Evolution of Steve Eggins original ANU design
- Interchangeable cup design

**GeoChron Reproducibility**

<table>
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<th>3</th>
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<tr>
<td>A</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>561.1 ± 2.5</td>
<td>563.6 ± 2.9</td>
<td>562.9 ± 3.1</td>
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<tr>
<td>B</td>
<td>4</td>
<td>SLD standards</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>560.5 ± 3.5</td>
<td>564.3 ± 1.9</td>
<td>564.4 ± 2.9</td>
</tr>
<tr>
<td>C</td>
<td>11</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>559.4 ± 3.4</td>
<td>563.0 ± 3.0</td>
<td>562.9 ± 2.4</td>
</tr>
</tbody>
</table>

Results of test where all ages overlap with known age including uncertainty

6/8 age should be ~563.5 Ma

Note: these ages **do not** have all of the systematic errors added in yet.

Thanks to Prof Gehrels, Univ. Arizona
Washout Speed – Does it Matter?

• Recent developments centered on designing faster washout speeds, mostly driven by elemental imaging applications

• How fast do we need to go?
  • Application dependent
    • Slow (100s of ms) – long transients but may be needed for low sensitivity applications
    • Fast (1ms) – can observe individual pulses but may be too fast for quad dwell times
    • BUT – may want to observe individual pulses for rapid elemental imaging

• HelEx II is tunable from around 20 ms to over 700 ms to suit most applications but how to improve the performance further for imaging applications?
Cobalt Cell – Engineered by Science
Cobalt Cell – Engineered by Science

Gen I (2012)

Gen II (2013)

Gen III (2013)

Gen IV (2014)

Dr Stijn Van Malderen, PhD Project
Cobalt Cell – Engineered by Science

Gen V (2015)

Gen VI (2016)

<30 ms transient peaks

Dr Stijn Van Malderen, PhD Project
Zircon Geochronology

Chew et al,

Agilent 7900 ICP-MS
TDY PMI Analyte Excite with HelEx
Spot size: 7um
Scan speed: 20um/s
Rep Rate: 45Hz

“With an acquisition time of less than 10 minutes per map (which can be decreased even further), there are few reasons to perform spot analyses on complex polyphase zircons other than when sensitivity is needed.”
Sample Chamber Performance
Increased speed = Increased sensitivity

Uranium – Short Pulse

- Thermo Scientific NEPTUNE Plus
- Photon Machines Analyte G2
- HelEx II Cell vs. ARIS
- NIST SRM610
  - 20μm circle spot size
  - 100 Hz repetition rate
  - 5 shots
  - 7.68 J cm⁻² fluence
- ARIS
  - 400 mL min⁻¹ He, outer cell
  - 200 mL min⁻¹ He, inner cell
  - 6 mL min⁻¹ N₂
  - 1.05 L min⁻¹ Ar sample gas
- Jet sampler cone, X skimmer cone
- N = 10

4 x sensitivity with ARIS

Doubling Sensitivity in Multicollector ICPMS Using High-Efficiency, Rapid Response Laser Ablation Technology
Grant Craig, Amy J. Managh, Ciprian Stremtan, Nicholas S. Lloyd, and Matthew S. A. Horstwood
Analytical Chemistry 2018 90 (19), 11564-11571. DOI: 10.1021/acs.analchem.8b02896
Cobalt Cell – Engineered by Science

Gen VII (2017)


Sub-μm nanosecond LA-ICP-MS imaging at pixel acquisition rates above 250 Hz via a low-dispersion setup

Stijn J. M. Van Malderen, Thibaut Van Acker, and Frank Vanhaecke

Anal. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.analchem.9b05056 • Publication Date (Web): 23 Mar 2020
Cobalt Cell – Engineered by Science

- Dynamic Z, for constant distance between sample surface and aperture in Tube Cell (patent pending)
- <10 µm accuracy
- Controlled by Chromium
Cobalt – Too Fast?

• Long Pulse Module
• Based on proven HelEx cup design
  • 100’s of ms performance
  • Analytical testing well underway
Configurable Sample Holder

- Highest sample load to weight ratio
- Highly space-efficient
- Extremely customizable
- Three-point anchoring for improved reproducibility
- Higher transmitted light coverage for slides
Cobalt Cell Evolution

• Extensive field testing
  • Improved stage design
    • Specs ≠ Performance
  • Reversible gas flows
  • Single-handed operation, fully interlocked door with half twist for full seal
• Patented ‘tube cell’ design
• Dynamic Z
• Fast ‘tube cell’ module for <1ms performance
• ‘Long Pulse’ module for 100’s of ms performance
Cobalt – Ultrafast Signals

- Ablation of Gelatin
  - $^{115}$In
  - 3 µm Spot
  - 100Hz
  - 0.5 Jcm$^2$
  - 300 µm/sec

- Ablation of Zircon
  - $^{238}$U
  - 5 µm Spot
  - 100Hz
  - 4.0 Jcm$^2$
  - 500 µm/sec
Iridia Development

A purpose built laser ablation system for high speed imaging applications that integrates the Cobalt cell

• Which laser to use?
  • 266nm, 213nm or 193nm?
  • All the significant bio-imaging publications use 193nm lasers

Why 193nm lasers are preferred by laser ablation scientists:

• 193nm lasers generate smaller particles and have a smaller range of particle sizes than higher wavelengths

• The laser wavelength determines the amount of elemental fractionation
  • 193 better than 213 better than 266nm

• Analytical data is significantly improved using 193nm laser compared to a 213nm or 266nm laser
Iridia Development – reference papers

- 193nm lasers generate smaller particles and have a smaller range of particle sizes. This results in better ionization by the ICP, and therefore better analytical data

- The larger particles generated by 266nm ablation are not completely ionized by the plasma. They are therefore not completely analyzed so the data quality will be poor

- The laser wavelength determines the amount of elemental fractionation. Using 266nm lasers the results are biased with more light elements ionized and fewer heavy elements giving the wrong results. This is not seen with 193nm lasers

- Analytical data is significantly improved using 193nm laser compared to a 213nm or 266nm laser
Iridia - Development

• “The ideal situation for highly spatially resolved analysis of biochemical samples would be the use of consecutive small square laser induced craters, with a flat bottom and no redeposition.”

• For imaging applications a 193nm Excimer is **proven** to be the best option
  - Flat craters with no significant edge redeposition
  - <1µm to over 300µm spots
  - 1-300Hz & 1-500Hz options (1000Hz in test)
  - Easy to control and only ablate material of interest
  - Best analytical performance on hard and soft sample types
Controlled Ablation at 193nm

Cortical kidney tissue mounted on glass slide
• Section imaged using Si and Ca as a proxy for glass ablation
• Glass ablation slide occurs 1 - 1.5 J cm\(^{-2}\)
• Tissue ablation threshold < 0.3 J cm\(^{-2}\)
• Full ablation of tissue section only
• NO GLASS ABLATION

JAAS 2019: Selective ablation of biological tissue and single cells on a glass substrate by controlling the laser energy density of nanosecond 193 nm laser radiation
Thibaut Van Acker, Stijn J. M. Van Malderen, Legna Colina-Vegas, Ranjith K. Ramachandran, and Frank Vanhaecke
Iridia - designed for high rep rate analysis

• 2 Billion shot guarantee (4 Billion typical)

• 500Hz operation:
  • 1 min = 500 x 60 = 30k shots
  • 1 hour = 30k x 60 = 1.8m shots
  • 2 hours = 3.6m shots
  • 5 days x 2 hours = 18m shots
  • 1 month = 4 x 18m = 72m shots
  • 12 months = 12 x 72m = 864m shots

• 2 Billion shots = 2 years of operation, firing at 500Hz **constantly** for 2 hours per day, **every** day, **all** year.

• 500 million shots on resonator optics would take around 1 year under these conditions
  • (50 million shots could be used up in a month)

<table>
<thead>
<tr>
<th>Specification / Typical Data</th>
<th>Excimer Laser 193nm</th>
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<tbody>
<tr>
<td>Active Gas lifetime</td>
<td>Stabilised 4 mJ</td>
</tr>
<tr>
<td></td>
<td>50 Mio</td>
</tr>
<tr>
<td></td>
<td>80 Mio</td>
</tr>
<tr>
<td>Passive Gas Lifetime</td>
<td>Stabilised 6 mJ</td>
</tr>
<tr>
<td></td>
<td>30 Mio</td>
</tr>
<tr>
<td></td>
<td>50 Mio</td>
</tr>
<tr>
<td>Optics Lifetime</td>
<td>1 month 50%</td>
</tr>
<tr>
<td></td>
<td>3 month 50%</td>
</tr>
<tr>
<td>Tube Life</td>
<td>Stabilised 6 mJ</td>
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<tr>
<td></td>
<td>500 Mio</td>
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<td></td>
<td>1000 Mio</td>
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<tr>
<td></td>
<td>2000 Mio</td>
</tr>
<tr>
<td></td>
<td>4000 Mio</td>
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</table>
Iridia – Optimized Beam Path

• ‘Multi use’ optics giving 5 x lifetime for high fluence mirrors

• Full CLASS 1 (Eye Safe) operation, alignment and maintenance

• Pressurised purge (MFC controlled with interlocks) with N$_2$ Generator option
Iridia – The Evolution of Laser Ablation

• Purpose design for high speed imaging

• Dual Attenuation enables stable low energy for bio-imaging applications

• Dual software controlled polarizers for geo-imaging applications

• Cobalt sample chamber for ultimate performance & flexibility
  • <1ms to 100’s of millisecond transient peaks
Iridia – Laser specs

• 300Hz air-cooled, 500Hz water-cooled laser, custom optimized for Teledyne Photon Machines to give ultimate reliability and performance with a 2 billion shot guarantee. 1 kHz laser in test.

• Lifetime expectation of 500m shots on resonator optics (10 x current industry standard)

• Integrated gas cabinet contains all necessary excimer premix and helium gas bottles
Iridia - Application Flexibility

• Dual Attenuation enables stable low energy for bio-imaging applications (<0.2J/cm²)

• Dual software controlled polarizers for geo-imaging applications

• eQC energy measurement at the point of ablation in the sample chamber.

• Demag optics to increase spot size range
Zn in Mouse Small Intestine

- Deparaffinized 5 µm sections of mouse small intestine villi
- Pixel size of this image is 1 x 1 µm
- Total image size 350 x 300 µm,
- Spot size 1 µm,
- Laser rep rate 150 Hz,
- Energy density 0.44 J cm⁻²
- Pixel acquisition rate 50 pixels/sec (limited by ICP-MS software)
- 35 minutes to acquire data

Thanks to Dr Thibaut Van Acker & Dr Stijn Van Malderen, Ghent University
• Magmatic zircon from the Eastern Carpathians, Romania
• Sample courtesy of Dr Gavril Sabau, Geological Institute of Romania
• 2 µm resolution
• 300 Hz
• 1 pulse/pixel
• Imaging time = 9 min
• ‘Beta’ Cobalt cell
• HDIP Software
Olivine phenocrysts from an IODP Boninite sample. Sample courtesy of Dr. Jeff Ryan (USF) and Dr. John Shervais (USU).

- 5 µm resolution
- 50 Hz
- 1 pulse/pixel
- <1 hour acquisition time
- ‘Beta’ Cobalt cell
Our laser webinar series continues!

Laser Ablation 201: Applications of Laser Ablation & Data Reduction Strategies

Dr. Ciprian Stremtan (and Muffin) – Product Specialist