

A grayscale microscopic image of a mineral surface, showing a grid of small, dark, rectangular features. The grid is oriented diagonally across the frame. The background is a lighter, textured surface with some small, dark spots.

North American Workshop on Laser Ablation 2017

MAY 25-27, AUSTIN

Jackson School of Geosciences
UNIVERSITY OF TEXAS AT AUSTIN | AUSTIN, TX

Foreword

We are pleased to present the Abstract Book for the 2nd North American Workshop on Laser Ablation (NAWLA'17). NAWLA is a new biennial meeting with the mission to transfer laser ablation knowledge between specialists and promote a sense of community among laser ablation users. The inaugural 2015 workshop lasted two days and had 110 participants. NAWLA'17 now expands to 2.5 days and brings together 130 scientists and vendors from 12 countries. Once again, the Jackson School of Geosciences hosts NAWLA at the University of Texas at Austin.

NAWLA'17 covers the latest progress in laser-based microanalytical instrumentation, methods and applications, and provides opportunities for informal interaction among attendees. We accepted 66 abstracts (34 oral, including 8 plenary talks, 32 poster presentations), contributing to eight thematic sessions – most concluding with a moderated Q&A period. Eminent guest speakers, Professors Sam Houk (USA) and Henry Longerich (Canada) initiate a theme session on the Foundations of LA-ICP-MS including a moderated discussion with all participants. NAWLA'17 introduces a laser ablation image competition, with a grand prize and people's choice award. We have built ample time into the poster sessions to allow for extended discussions, and the social events continue into the evening with vendor-sponsored dinners on Thursday and Friday.

Pulling off NAWLA'17 has been a group effort. This abstract book constitutes a “snap shot” of laser ablation research in 2017, illustrating the diverse research activities of the authors of the presentations. The Scientific and Organizing committees met often to develop the theme sessions, coordinate logistics, and interface with prospective speakers and attendees. We are grateful for the support of nine vendor partners who helped sponsor the workshop, and Jackson School of Geosciences personnel who provided key assistance (Erin Negron, Elsa Jimenez, Julie, Lake, Brian, Zavala, Sean McKeever, Steffi Wafforn, Federico Galster).

We hope you will have an engaging workshop and enjoy your stay in Austin.

On behalf of the Scientific and Organizing committees,

Nathan Miller

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Table of Contents

Program Overview	4
Scientific Program	5
Talk Abstracts	9
Vendor Affiliated Talks	47
Poster Abstracts	58
Vendor Affiliated Posters.....	86
Partners	97
List of Participants	99
Author List.....	106
Map of venue, parking and diinner locations	109
City bus information/map to Rattle Inn.....	110

Program Overview

Thursday 25th May

08:00-08:45	Registration, West entrance foyer, Jackson School of Geosciences
08:45-9:00	Welcome and introduction
09:00-10:30	Session 1 – LA-ICP-MS Fundamentals & Parameters (I)
10:00-10:30	Group workshop activity 1
10:30-10:50	Coffee break
10:50-12:00	Session 1 – LA-ICP-MS Fundamentals & Parameters (II)
12:00-13:30	Lunch, vendor talks, poster preview
13:30-15:30	Session 2 – Instrumentation Developments
15:30-18:00	Poster session 1 + beverages (sponsored by TOFWERK)
19:00-22:00	Dinner (sponsored by ESI)

Friday 26th May

08:50-09:00	Welcome and introduction
09:00-10:00	Session 3 – Data Quality and Analytical Improvements
10:20-10:40	Coffee break
10:40-12:00	Session 4 – Imaging
12:00-13:15	Lunch, vendor talks, poster preview
13:15-14:00	Group workshop activity 2
14:00-15:45	Session 5 – Geo/Thermochronology
15:45-18:00	Poster session 2 + beverages (sponsored by Teledyne CETAC)
19:00-22:00	Dinner (sponsored by Perkin Elmer)

Saturday 27th May

08:50-09:00	Welcome and introduction
09:00-10:10	Session 6 – Forensic and Industry Applications
10:10-10:30	Coffee break
10:30-12:00	Breakout session options
	Session 7 – Bio and Paleoclimate Applications
	Session 8 – Earth Science Applications
12:00-13:10	Lunch, vendor talks, final wrap-up

Scientific program

Thursday 25th May

08:00	Registration – Jackson School of Geosciences, West entrance foyer
08:45	Opening of NAWLA2017 - Welcome and introduction
09:00-12:00	Session 1 – LA-ICP-MS Fundamentals & Parameters (A. Koenig, Session Chairperson)
09:00	Plenary – Sam Houk: The ICP-MS Part of LA-ICP-MS
09:30	Plenary – Henry Longerich: LA-ICP-MS – a history and personal odyssey
10:00	Moderated Discussion with Houk and Longerich (Koenig moderator)
10:30-10:50	Coffee break
10:50	Plenary – <u>Marcel Burger</u> , Debora Käser, Hale Ceren Yilmaz, Alexander Gundlach-Graham, Gunnar Schwarz, Emanuel Billeter, Jérôme Käslin, Joachim Koch, Bodo Hattendorf, Daniela Rubatto, Paolo S. Garofalo & Detlef Günther: From fundamentals to applications
11:20	Simon Jackson: Correction of matrix effects in LA-ICP-MS analysis of minerals
11:40	Session Q & A and Introduction to Friday's workshop activity
12:00-13:30	Lunch / vendor presentations / poster preview / (H. Spero, Session Chairperson)
12:15	<u>Grant Craig</u> , Matthew S. A. Horstwood, Nicholas Lloyd, Claudia Bouman & Johannes Schwieters: 10^{13} Ω Amplifier Technology for LA-MC-ICP-MS of Uranium Particles: Can we Measure Depleted and Highly Enriched Compositions in a Single Analysis? [Thermo Fisher]
12:30	<u>Ariane Donard</u> , Phil Shaw: AttoM HR-ICP-MS an instrument of choice for laser ablation ICP-MS [Nu Instruments]
12:45	Ashley Norris: RESolution-SE – Key features for exceptional LA-ICP-MS [ASI]
13:30-15:30	Session 2 – Instrumentation Developments (P. Sylvester, Session Chairperson)
13:30	Plenary – Davide Bleiner: Extreme UV LA
14:00	Plenary – Leonid Danyushevsky, J. Thompson, O. Borovinskaya, M. Tanner, M. Cubosin, J.M. Shelley, & A. Norris: Geological Applications of LA-ICP-TOFS
14:30	<u>Daniel F. Stockli</u> , Margo Odlum, & Desmond Patterson: UV laser ablation in ultra-high vacuum: plasma shields & popcorn
14:50	<u>Matthijs C. van Soest</u> , Kip V. Hodges, Alyssa J. Anderson, Alexandra M. Horne, Christopher S. McDonald, & Cameron M. Mercer: UV laser ablation applications in noble gas analysis
15:10	Session Q & A
15:30-18:00	Poster session 1 – Beverages (sponsored by TOFWERK)
19:00-22:00	Dinner (Sholtz Garten, sponsored by Perkin Elmer)

Friday 26th May

08:50	Welcome and introduction to the day
09:00-10:00	Session 3 – Data Quality and Analytical Improvements (H. Spero Chairperson)
09:00	Jhanis J. González: Laser Ablation-Based Techniques: An ideal toolbox for direct chemical analysis of solids
09:20	Jared Wesley Singer: Routine inter-calibration of LA-ICPMS with EPMA: Creating secondary reference materials for elemental analysis
09:40	Xin-Yuan Zheng, <u>Brian L Beard</u> & Clark M. Johnson: Matrix affects associated with Fe isotope analysis of iron oxides and sulphides by ns- and fs-LA
10:00	<u>Zhaoping Yang</u> , S.E. Jackson, L.J. Cabri, P. Wee, H.P. Longerich & M. Pawlak: Determination of ppb level Rh and Pd in Cu Minerals by LA-ICP-MS
10:20-10:40	Coffee break
10:40-12:00	Session 4 – Imaging (A. Koenig, Session Chairperson)
10:40	Plenary - <u>Simon Jackson</u> & Zhaoping Yang: Chemical Imaging by LA-ICP-MS: a “how to” guide
11:10	<u>Stijn J.M. Van Malderen</u> , Brecht Laforce, Thibaut Van Acker, Maarten De Rijcke, Luc Van Hoorebeke, Olga Borovinskaya, Laszlo Vincze, & Frank Vanhaecke: Low-Dispersion LA Aerosol Transport Systems and CT-based Registration Approaches: Advanced 3D and High-Resolution Imaging
11:30	Bence Paul, Jay R. Black, Estephany Marillo-Sialer, Kai Kysenius, Peter Crouch, Dominic Hare, Janet M. Hergt and <u>Jon D. Woodhead</u> : Elemental tomography: coupling 3D LA-ICP-MS and X-Ray-Tomography reconstructions of a mouse embryo
11:50	<u>Session Q & A</u>
12:00-13:15	Lunch / vendor presentations / poster preview / (N. Miller, Session Chairperson)
12:10	<u>Lauren Amable</u> , Eric Shide, Andrew Breglio, Aaron Rusheen, Katharine Fernandez, Katherine McLauchlin, and Lisa Cunningham: Imaging cisplatin-induced ototoxicity using LA-ICP-MS [ESI-affiliated application talk]
12:25	<u>Michael Colucci</u> , Jhanis González, and Jong Yoo: Applied Spectra Inc: Company Overview, Laser Ablation Technology, and Applications Served [Applied Spectra Inc]
12:40	Ruth Wolf: NexION 2000 - the Next Generation ICP-MS from PerkinElmer [PerkinElmer]
13:15-14:00	Group workshop activity

14:00-15:45

**Session 5 – Geo/Thermochronology
(P. Sylvester, Session Chairperson)**

14:00 **Plenary** – Noah McLean: ET_Redux_U-Pb geochron data reduction
14:30 Stephanie Wafforn, D.F. Stockli, S. Seman, J.R. Kyle, M. Cloos & L.D. Stockli: Andradite Garnet U-Pb Geochronology by LA-ICP-MS: Procedures, Standardization, and Mineral Exploration Case Studies
14:50 Yan Luo, Chris M Fisher, Chiranjeeb Sarkar, Qiao Shu, Henry Longerich, Graham Pearson: Laser Ablation Split Stream (LASS) or Single Instrument Stream (LASIS)? A critical evaluation for zircon U-Pb dating and Hf isotope analysis
15:10 Leonid Neymark, Chris Holm-Denoma & Richard Moscati: Cassiterite LA-ICPMS U-Pb Geochronology: No Need for Independently Dated Matrix-Matched Standard
15:30 Session Q & A

15:45-18:00

Poster session 2 – Beverages (sponsored by Teledyne CETAC)
Dinner (Rattle Inn, sponsored by ESI)

Saturday 27th May

08:50 Welcome and introduction to the day

09:00-10:00

**Session 6 – Forensic and Industry Applications
(N. Miller, Session Chairperson)**

09:00 **Plenary** – Jose Almirall: LA-ICP-MS Analysis and Characterization of Adhesive Tape as Forensic Evidence
09:30 Michelle Kelvin, Joe Petrus, Matthew Leybourne & Vongani Nkuna: Application of LA-ICP-MS Analysis to Process Mineralogy: Ga and Ge Recovery at Kipushi Deposit (tentative replacement of poster)
09:50 Todor Todorov: Challenges and advancements in the LA-ICP-MS analysis of food samples
10:10-10:30 Coffee break
10:30-12:00 Breakout session options

**Session 7 – Bio and Paleoclimate Applications
(N. Miller, Session Chairperson)**

10:30 Helen Atkinson & Neil Loader: Stable Isotopes in Tree Rings by Laser-Ablation - Combustion - GC- IRMS
10:50 Malte Willmes, James A. Hobbs, Levi S. Lewis, Kirsten Sellheim, Justin J. G. Glessner: Unravelling the life history and origin of fish using strontium isotope laser ablation analysis
11:10 DaCosta, K.P. & Carmichael, R.H.: Analysis of manatee periotic bone chemistry as a tool to track West Indian manatee migrations in the northcentral Gulf of Mexico
11:30 Lael Vetter & Howard Spero: Reconstructing Laurentide Ice Sheet Meltwater Geochemistry using Combined LA-ICP-MS and Oxygen Isotope Measurements on Individual Foraminifera
11:50 Session Q & A

Session 8 – Earth Science Applications
(P. Sylvester, Session Chairperson)

- 10:30 Herrmann, A.D., Haynes, J., & Leslie, S.: Cryptic crustal events during the Taconic Orogeny elucidated through LA-ICPMS studies of volcanic zircons, southern Appalachians, Alabama
- 10:50 Céline Martin, Sarah Penniston-Dorland, George Harlow, Emmanuel Ponzevera: Lithium Isotope Measurements in Spodumene, Lithiophilite, Tourmaline, Petalite, and Beryl by LA-MC-ICP-MS
- 11:10 Ian Szumila, Dustin Trail & Lisa Danielson: Diffusivities of Redox-Sensitive Elements in Basalt vs. oxygen fugacity determined by LA-ICP-MS
- 11:30 Session Q & A
- 12:00-13:10 **Lunch, vendor talks, final wrap-up**
(H. Spero, Session Chairperson)
- 12:15-12:30 Ciprian Stremtan, Stijn van Malderen, Balz Kamber, Johannes van Elteren & Olga Borovinskaya: Examples of Collaborative Research & Development Producing Meaningful Analytical Innovation [Teledyne-CETAC]

TALK ABSTRACTS

LA-ICP-MS Fundamentals & Parameters

The ICP-MS Part of LA-ICP-MS

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This talk will describe historical background and operating principles of the ICP, ion extraction, and mass spectrometer. Characteristics of an "ideal" ICP specifically for the larger solid particles created by LA will be discussed. Can we even get there from here?

LASER ABLATION-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: A HISTORY AND PERSONAL ODYSSEY

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I have published several reminiscences (Longerich, 1995, 2001, 2004, 2012) of my scientific life following my personal “discovery”, in 1983, of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), nearly three decades ago. These stories were named “Odysseys” after Homer's classic story of Odysseus and his “ten years of wandering in the wilderness” as “wandering” described the first years of ICP-MS, and later years after we interfaced LA (Laser Ablation) sampling to our ICP-MS. This lecture will review these years, noting the tremendous effect that ICP-MS has had on geoanalytical elemental analysis. And in the first days of ICP-MS it was noted that isotopic analysis was possible with ICP-MS which we also noted in our first ICP-MS publication (Strong and Longerich, 1985). In 1988, we started an investigation of Laser Ablation (LA) sample introduction, which Alan Grey (1985) first reported. We configured a system from components since at that time there were no commercially available LA systems. Especially important was the incorporation of petrographic quality microscope optics, an essential capability not appreciated by the instrument companies. Our land mark paper (Jackson, et al., 1992) demonstrated the tremendous power of the technique for quantitative geological micro analysis, along with several weaknesses which we later minimised. A later paper (Longerich, et al., 1996) is a JAAS “most cited” paper which deals with LA analyte concentration calculation. This talk will also emphasise the fun and satisfaction of these early days of research and development of ICP-MS. And I will try to encourage the audience to “go for” the next new analytical elemental tool.

Gray, A. L., *Analyst*, volume 110, page 551-556, 1985. Jackson, S. E., et al., *Canadian Mineralogist*, volume 30, page 1049-1064, 1992. Longerich, H. P., *ICP Information Newsletter*, volume 20, number 10, page 703-705, 1995. Longerich, H. P., et. al., *Journal of Analytical Atomic Spectrometry*, volume 11, page 899-904, 1996. Longerich, H. P., *Newsletter of the Mineralogical Association of Canada*, volume 65, page 1-6, 2001. Longerich, H. P., *ICP Newsletter*, volume 30, page 501-507, 2004. Longerich, H. P., *Journal of Analytical Atomic Spectrometry*, volume 27, page 1181-1184, 2012. Strong, D. F. and Longerich, H. P., *Geoscience Canada*, volume 12, page 72-75, 1985.

From Fundamentals to Applications – The Use of Laser Ablation in Inductively Coupled Plasma Mass Spectrometry

Marcel Burger¹, Debora Käser¹, Hale Ceren Yilmaz¹, Alexander Gundlach-Graham¹, Gunnar Schwarz¹, Emanuel Billeter¹, Jérôme Käslin¹, Joachim Koch¹, Bodo Hattendorf¹, Daniela Rubatto², Paolo S. Garofalo³ & Detlef Günther¹

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Ever since its introduction in 1985, a lot of effort has been made to turn LA-ICPMS into an off-the-shelf technique for the analysis of major, minor, and trace element concentrations in various types of samples. Studies have been targeted towards understanding fundamental processes or implementation of real life applications in diverse research fields such as geology, material sciences, biology and medicine. Although nanosecond (ns) laser ablation systems are predominantly used, in recent years the feasibility of femtosecond (fs) laser sources has been studied to increase the accuracy and precision of LA-ICPMS analyses, and, thus extend the range of application. Specifically, the suitability of fs laser ablation for non-matrix-matched quantification in LA-ICPMS analyses has been investigated. Beam delivery via two-stage Fourier transform (TSFT) optical processing has turned out to be a very promising approach for homogenization of fs laser radiation. This increased depth resolution for elemental depth profiling. Here, we present surface morphology studies carried out on metals and insulators revealing the formation of well-shaped craters with flat bottoms and steep walls. Depth profile analyses on a sample consisting of alternating Cr/Ni layers showed up-take rates below 10 nm/pulse. LA in combination with a low dispersive aerosol transport system and an ICP-time-of-flight-mass spectrometer (ICP-TOFMS) has emerged into the only technique providing high-speed, high-resolution imaging with comprehensive elemental coverage. Practically any type of samples including geological specimens and biological thin sections have been studied. Most recent ICP-TOFMS instrumentation also features collision/reaction cell technology that expands the setup's flexibility regarding isotope selection. While the instrumentation for acquisition of high-pixel-density, multi-elemental images matured, data processing, image evaluation and interpretation remains largely unexplored. Here, we also discuss several LA-ICP-TOFMS imaging case studies to illustrate aspects of data handling and image analysis.

Correction of Matrix Effects in LA-ICP-MS Analysis of Minerals

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There is a widely held belief that matrix matching is a pre-requisite for accurate LA-ICP-MS analyses. Matrix effects in LA-ICP-MS are of two types: (1) ablation yield, which is a function largely of the absorptivity of the sample to laser radiation and is very effectively corrected by internal standardisation; (2) matrix-dependent laser-induced elemental fractionation (LIEF), which compromises accuracy when the fractionation index [1] of the analyte does not closely match that of the internal standard used, and is rarely corrected. To minimise LIEF-related matrix effects, considerable research effort has been expended on the development of matrix-matched standards and fs laser ablation systems; yet, remarkably little effort has been devoted to the development of computational algorithms that correct LIEF effects, despite their manageable size. The three algorithms proposed to correct LIEF biases [2-4] are rarely applied. This presentation evaluates these algorithms and a newly developed algorithm for correction of LIEF effects ("FMEN"). The FMEN correction utilises the linear relationship generated between $\ln(\text{analyte/internal standard signal intensity ratio})$ versus $\ln(\text{sensitivity ratio of two mutually fractionating major elements})$ in the sample (e.g., Si and Al). This relationship has a near constant slope, regardless of matrix composition, allowing the analyte/internal standard signal intensity ratios of the sample and standard to be compared at the same sensitivity ratio of the mutually fractionating major elements (i.e., zero relative fractionation).

The four LIEF correction algorithms have been tested by analysis of well characterised igneous silicate glass reference materials calibrated using a non-matrix-matched standard. The FMEN correction uniquely produced both accurate and highly precise data. This development removes the need for matrix-matched standards or fs lasers for accurate LA-ICP-MS analysis of applicable matrices. The FMEN approach is transferrable to the important application of Pb/U zircon dating.

[1] B.J. Fryer, S.E. Jackson and H.P. Longerich, 1995, *Canadian Mineral.*, 33, 303-312. [2] P.J. Sylvester and M. Ghaderi, 1997, *Chem. Geol.*, 141, 49-65. [3] Z. Chen, 1999, *J. Anal. At. Spectrom.*, 14, 1823-1828. [4] S.E. Jackson, 2008, *Mineral. Assoc. Canada Short Course Series*, 40, 169-188.

INSTRUMENTATION DEVELOPMENT

Extreme UV Laser Ablation for Enhanced Spatial Resolution and Stoichiometric Microanalysis

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Laser action in the extreme ultraviolet and soft X-ray has been demonstrated [1-3] using laser-produced and discharge-produced hot/dense plasmas as single-pass high-gain media. In the time of large accelerator-based X-ray lasers, e.g. LCLS, fundamental and applied research on compact plasma-driven X-ray laser carries the promise of bridging the gap between the user and the tools. This demands contributions in (i) better quantitative understanding of the parameters effect on plasma-lasing, (ii) performing proof-of-principle ablation experiments on “real world” samples.

Experiments were run using the newly installed system at the Empa Laboratories. A 0.2ps Nd:glass oscillator feeds a chirped-pulse amplification stage to deliver Terawatt pulses on a target for plasma lasing. A parametric study is presented.

Nano-analytics were indeed performed on reference materials as well as catalysts. Focusing was performed using a self-developed Schwarzschild microscope. The short wavelength of about 10 nm permitted real quasi-non-destructive analysis. Preliminary results will be shared, as well as an outlook on future work.

1. Arbelo, Y, F. Barbato, D. Bleiner (2017) He-doped pseudospark as a home-lab XUV source beyond the beamtime bottleneck, Plasma Sources Sci. Technol., in press
2. Bleiner, D., Arbelo-Pena, Y., Masoudnia, L., & Ruiz-Lopez, M. (2014). Table-top X-ray lasers using a plasma gain-medium: Limits and potentials. Physica Scripta, 2014(T162), 014050.
3. Staub, F., Imesch, C., Bleiner, D., & Balmer, J. E. (2012). Soft-X-ray lasing in nickel-like barium at 9.2 nm using the grazing-incidence scheme. Optics Communications, 285(8), 2118-2121.

Geological Applications of LA-ICP-TOFS

L. Danyushevsky^{1,2}, J. Thompson¹, O. Borovinskaya³, M. Tanner³, M. Cubosin³, J.M. Shelley⁴, A. Norris⁵.

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This presentation highlights the benefits of simultaneous detection (the entire mass spectrum is acquired in 33 μ sec), ultra-fast data acquisition and high mass resolution offered by ICP-TOFMS^[1], for mineral chemical characterisation and measurement of isotopic compositions using laser ablation microprobes. The main focus will be on: 1) the approach to data acquisition and processing, as compared to other types of ICPMS, including developing matrix-independent baseline definitions, derivation of detection limits and their dependence on data integration times, and accounting for polyatomic and doubly charged interferences; 2) the impact of simultaneous detection on improving precision of isotopic ratio measurements in samples with high concentration gradients, such as analysis of Pb isotopic compositions in pyrites and U/Pb dating of complexly zoned minerals; and 3) characterisation of the performance of fast-washout, low-aerosol dispersion sample cells^[2], which are required for the utilisation of the ultra-fast data acquisition as a means to significantly minimise time for imaging applications. Boost in sensitivity delivered by fast-wash-out cells enables single-shot integration on ICP-TOFMS, resulting in significantly increased scanning rates during imaging^[3, 4]. We will discuss the impact of this approach to detection limits, using custom modifications to the large-format, constant-geometry S-155 laser ablation cell installed on a RESolution laser ablation microprobe.

[1] M. Harlaux et al., J. Anal. At. Spectrom., 2015, 30, 1945-1969.

[2] S.J.M. Van Malderen et al., Analytical Chemistry, 2017, DOI: 10.1021/acs.analchem.7b00111.

[3] A. Gundlach-Graham et al., Analytical Chemistry, 2015, 87, 8250-8258.

[4] M. Burger et al., Analytical Chemistry, 2015, 87, 8259-8267.

UV Laser Ablation in Ultra-High Vacuum: Plasma Shields & Popcorn

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UV laser ablation is widely used for micro-analytical investigations of industrial, geological, or biological materials, for micromachining and photolithography, or for surgery and dermatologic treatments. The UV laser interaction disrupts atomic bonds without heating, leading to controlled near-surface disintegration and generation of a plume of ablated particles and plasma shield from the aerosol incoming UV laser beam interaction. For micro-analytical techniques either the aerosol itself is analyzed by mass-spectroscopy or the in-situ plasma is analyzed by atomic emission spectroscopy. For elemental or isotopic analysis of solid geological materials, the aerosol is removed from the ablation site by He carrier gas and transported to an ICP-MS. In contrast, UV laser ablation of geological materials for noble gas geochemistry occurs in an ultra-high vacuum (UHV) environment without the aerosol being removed by a carrier gas and remaining as a particle cloud above the ablation volume. UV laser ablation has been widely used for $^{40}\text{Ar}/^{39}\text{Ar}$ dating and recently for He concentration measurements for in-situ (U-Th)/He dating. These concentration measurements critically depend on ablation rate and clean ablation pit geometry for precise determinations of ablation volumes by interferometric or atomic force microscopy. It has become evident that plasma shielding from aerosol and UV laser interaction leads to diminished ablation rates and in-situ formation of refractory condensates. This condensation results in the formation and deposition of refractory compounds in the ablation pit with a granular popcorn-like texture, making precise ablation volume measurements difficult. We investigated both the role of target material and the influence of laser energy and pulse frequency on “popcorn” formation. The data suggest that popcorn formation is most extreme in zircon and less important in apatite or rutile due to the formation of refractory ZrO_2 condensates within the plasma shield, suggesting a significant influence of chemical composition on plasma shield processes. The formation of popcorn-textured condensates seems to be accentuated at high laser energy and higher ablation frequencies, likely caused by more intense plasma shielding. The effect is less pronounced at <5 Hz laser pulse frequency and appears negligible in shallow ablation pits (<3-5 microns), while becoming dramatically more pronounced with increasing ablation depth. While He appears to be completely released/degassed during laser ablation, plasma shielding leads to a diminished ablation rate and dramatic deterioration of the pit geometry amid popcorn-textured refractory condensates in some minerals. It remains unclear whether radiogenic or stable isotope measurement could potentially be isotopically fractionated in the in-situ plasma at high or ultra-high vacuum. In summary, while fine-tuning of laser energy and ablation frequency can minimize the plasma shielding effect, it can represent a significant obstacle for in-situ UHV measurements.

UV Laser Ablation Applications in Noble Gas Analysis

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Laser ablation (LA) microprobes have remained relatively under-utilized for noble gas (NG) geochronology and geochemistry despite first being adapted for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology around the time LA-ICP-MS applications became widespread¹. This is surprising because LA gas extraction offers several obvious advantages over more traditional gas extraction techniques that employ IR lasers or vacuum furnaces, especially the spatially precise sampling of material in petrographic context, and a capacity to explore intracrystalline zoning in NG concentrations. Early adopters of LA methods faced substantial criticism because the smaller sample volumes they analysed yielded results with substantially lower precision than conventional methods. However, as LA systems and NG mass spectrometers have improved over the last two decades, LA is enjoying a renaissance in $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology², NG diffusion^(e.g. 3,4) studies, NG partitioning studies^(e.g. 5), (U-Th)/He thermochronology^{6,7}, synchronized U/Pb and (U-Th)/He LA “double” dating^{8,9}, 4He mapping in complexly zoned and radiation damaged zircons¹⁰, and NG isotope geochemistry^(e.g. 11, 12).

Over the last decade, ASU’s Group 18 Laboratories has been active in the development and application of a wide array of LA methodologies for NG analysis. The laboratory houses two Teledyne/Photon Machines (Analyte G2 and Excite) excimer LA systems shared between three NG mass spectrometers (GVi Helix SFT, Nu Noblesse, and ASI Alphachron), and a quadrupole ICP-MS (Thermo iCapQ). In the presentation, LA analytical protocols and their associated challenges will be discussed, and LA NG applications will be illustrated with recent research results.

¹Kelley et al. (1994) *Geochim. et Cosmochim. Acta* (GCA) 58, 3519-3525; ²Mercer et al. (2015) *Science Advances* (Sci. Adv.) 1, 8p.; ³Wartho et al. (1999) *Earth and Planet. Sci. Let.* 170, 141-153; ⁴van Soest et al. (2011) *GCA* 75, 2409-2419; ⁵Brooker et al. (2003) *Nature* 423, 738-741; ⁶Boyce et al. (2006) *GCA* 70, 3031-3039; ⁷Tripathy-Lang et al. (2013) *J. of Geophys. Res.: Earth Surface* 118, 1-9; ⁸Evans et al. (2015) *J. of Anal. Atomic Spec.* 30, 1636-1645; ⁹Horne et al. (2016) *GCA* 178, 106-123; ¹⁰Danisik et al. (2017) *Sci. Adv.* 3, 9p.; ¹¹Heber et al. (2009) *GCA* 73, 7414-7432; ¹²Vogel et al. (2011) *GCA* 75, 3057-3071.

Data Quality and Analytical Improvements

Laser Ablation-Based Techniques: An ideal toolbox for direct chemical analysis of solids

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Laser ablation is a major technology for direct sampling in analytical chemistry. The advantages of laser ablation chemical analysis include direct characterization of solids, liquid or gases, no chemical procedures for dissolution, reduced risk of contamination or sample loss, analysis of very small samples not separable for solution analysis and, in the case of solid samples, determination of spatial distributions of elemental composition. The use of Laser Ablation as a sampling tool for Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Inductively Coupled Plasma Spectrometry (LA-ICP-MS), direct spectroscopic analysis of the elemental emission of laser-induced plasmas, known as Laser Induced Breakdown Spectroscopy (LIBS), and finally the recently introduced spectroscopic analysis of molecular emission for isotopic determination, known as Laser Ablation Molecular Isotopic Spectrometry (LAMIS). This presentation will describe several applications that involved the combination of two or more of these Laser Ablation-Based approaches to chemical analysis of solid samples.

Routine Inter-Calibration of LA-ICPMS with EPMA: Creating Secondary Reference Materials for Elemental Analysis

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) and Electron Probe Micro Analysis (EPMA) are synergistic microanalytical techniques sharing ranges of sensitivity and spatial resolution. This study reports the method of maximum overlap for LA-ICPMS/EPMA inter-calibration including all major, minor, and select trace elements in a variety of inorganic materials. Accuracy is limited for some stand-alone LA-ICPMS systems by matrix mismatch of sample and standard; EPMA offers a matrix correction scheme resulting in accuracy ~1 to 5% relative without matrix matching standards. In practice the LA-ICPMS analyst may select materials that bracket the composition space of interest, inter-calibrate by EPMA, identify systematic differences (slope, intercept), and apply post hoc accuracy corrections to LA-ICPMS datasets based on the secondary references.

Results of inter-calibration are highly linear with slopes on the order of 1. The slope of inter-calibration often ranges ~20% for various combinations of element-matrix-internal standard. Sound justification for EPMA's accuracy is essential, and a significant electron dose is required to achieve precise trace elements by EPMA. When properly implemented the propagated error of linear inter-calibration gives a total uncertainty around ~1 to 5% relative. The 'fractionation index' associated with depth-dependent ablation processes does not wholly predict the observed systematic errors, although predictive correction schemes should emerge with more strict control of ablation, aerosol transport, ICP digestion, and interferences. The combined method provides routine confirmation of LA-ICPMS accuracy, and sidesteps the daunting task of large-scale distribution of matrix-matching trace element standards.

Matrix effects associated with Fe isotope analysis of iron oxides and sulphides by ns- and fs-LA

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We have made a comparative study of the accuracy and precision of Fe isotope analysis of magnetite (Fe_3O_4), pyrite (FeS_2) and pyrrhotite (FeS) by laser ablation using a laser with a ~4 nanosecond pulse width and a laser with a ~150 femtosecond pulse width. The same type of HelEx ablation cell and the same multi-collector ICP-MS (Nu Plasma II) were used for the comparisons. The test consisted of Fe isotope LA analyses using phase-matched and non-phase-matched sample-standard bracketing to correct for instrumental mass bias. For phase-matched analyses a suite of magnetites (Fe_3O_4 concentrations between 100 and 85%) were used. The purest magnetite was used as the bracketing standard. The ns-LA analyses of magnetite samples had a precision of ± 0.3 ‰ in $^{56}\text{Fe}/^{54}\text{Fe}$ and overlapped the true isotope composition as determined by solution nebulization analysis. The fs-LA analyses were precise to ± 0.07 ‰ and with this improved precision it was possible to identify small deviations (0.1-0.2‰) in accuracy for magnetite samples with the most impure compositions. For non-phase-matched analysis of magnetite and pyrrhotite using pyrite as the bracketing standard, ns- and fs-LA yielded inaccurate results (up to 2‰). However, accurate non-phase-matched fs-LA analyses can be obtained if water is added during ablation, as has been applied in previous work [1,2]. In detail, fs-LA analyses are not truly “matrix-free” but require water addition to minimize matrix effects. Although use of a “moist” aerosol is effective in minimizing matrix effects it decreases ion signals by ~50% which limits spatial resolution. In contrast, water addition did not significantly improve the accuracy or precision of ns-LA analyses, thus careful matrix matching is always required for ns-LA, posing a challenge for ns-LA analyses of Fe isotopes in addition to the potential non-stoichiometric sampling of substrates [3].

[1] Shuessler & von Blanckenburg (2014) Spectro. Acta B 98:1.

[2] Horn et al. (2006) GCA 70:3677.

[3] Zheng et al. (2017) Chem. Geol. 450:235.

Determination of ppb level Rh and Pd in Cu Minerals by LA-ICP-MS

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Quantitative determination of platinum-group element (PGE) contents in ore minerals is critical for understanding the genesis of magmatic Ni-Cu-PGE deposits and optimising mineral processing methods. However, determination of the light PGE (Ru, Rh and Pd) in transition metal sulphide minerals using LA-ICP-MS is severely compromised by large spectroscopic interferences, notably Co-Ni-Cu-Zn argides, Cd⁺ isobars and ²⁰⁶Pb²⁺. Thus, determination of the typical concentrations (up to 10's ppb) of Ru, Rh and Pd in these minerals has been a formidable challenge. This study presents figures of merit achievable using LA-ICP-MS determination of Rh and Pd in Cu minerals using collision/reaction cell technology. Three synthetic Cu-Fe sulphides, seven natural chalcopyrite, and two bornite samples, containing 24-63% Cu, < 10 ppb Rh, and up to 250 ppb Pd, were analyzed using LA sampling with an Agilent single quadrupole (7700x) ICP-MS, using He collision gas, and a triple quadrupole (8900x QQQ) ICP-MS, using a blend of NH₃/He (10%/90%) reaction gas. Results are compared to values obtained from digested separates of the same minerals analyzed using an Agilent 8800x ICP-QQQ in NH₃/He reaction mode. Using LA-ICP-QQQ at an optimized NH₃/He flow rate, the CuAr contributions to ¹⁰³Rh and ¹⁰⁵Pd were reduced by more than two orders of magnitude, and the method LOD obtained for ¹⁰³Rh (1.7 ppb) and ¹⁰⁵Pd (7.0 ppb) were approximately an order of magnitude lower, than those obtained using single quadrupole LA-ICP-MS (16 ppb for Rh, 48 ppb for Pd) at an optimized He flow rate. The achievable accuracy and precision for measurement of a few ppb Rh and Pd in Cu-rich minerals were in the range of 0.5-19% and 19%-31% respectively. This opens up the potential for LA-ICP-QQQ to be widely applied in quantitative determination of the trace level contents of Ru, Rh and Pd in transition metal sulphide minerals.

IMAGING

Chemical imaging by LA-ICP-MS: a “how to” guide

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This presentation will review procedures used for 2-D and 3-D chemical and isotopic imaging by LA-ICP-MS, and highlight important applications of the technique, with particular reference to geological materials.

Two laser sampling protocols are in common use: continuous line scans and lines of multiple discrete spots. Line scan ablation is faster but suffers from degradation of resolution through aerosol mixing. Spot sampling allows spot size-limited resolution and pre-ablation of each point immediately prior to data collection. The ICP-MS data are presented as maps of signal intensities or concentrations derived by calibrating signals against a standard(s), using internal standardisation to correct for variable ablation yield. For multi-phase mineral maps, an algorithm that identifies mineral phases and assigns internal standard values accordingly[1], or normalisation to 100% total concentration[2] is used. Normalisation to 100% total requires no prior knowledge of the sample's mineral chemistry and best handles grain edge effects. The benefits of different scaling functions and the ability to interrogate maps will be discussed.

Geological minerals grow by incremental crystallisation or precipitation, and thus record the chemical history of the environment in which they grew (e.g., magmatic, hydrothermal), together with post-crystallisation modification processes. Examples of how LA-ICP-MS element mapping can elegantly unravel processes in hydrothermal gold deposit formation, identify age domains in zircon and monazite, explain anomalous $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratios in zircon and identify multiple hydrothermal events via fracture mapping will be presented. These highlight the extraordinary wealth of genetic information that can be derived from LA-ICP-MS imaging that is rarely apparent from multiple spot analyses alone. The future of the technique, including recent developments in high-speed and high-resolution imaging using rapid cell washout systems and advanced deconvolution algorithms, will be discussed.

[1] B. Paul, J.D. Woodhead, C. Paton, J.M. Hergt, J. Hellstrom, and C.A. Norris, 2014, *Geostand. Geoanal. Res.*, 38, 253-263.

[2] L. Halicz, and D. Günther, 2004, *J. Anal. At. Spectrom.*, 19, 1539-1545.

Low-Dispersion LA Aerosol Transport Systems and CT-based Registration Approaches: Advanced 3D and High-Resolution Imaging

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This work demonstrates a workflow for profiling the 3D elemental distribution in a freshwater crustacean approximately 300x300x500 μm^3 in size [1]. A specimen, exposed to Zn, Cu and Ni under controlled conditions, underwent fixation, staining, and embedding. The specimen was sectioned using a microtome, and every second 5 μm thick section was imaged with a spot 5x5 μm^2 in size and a scan speed of 100 $\mu\text{m}/\text{s}$ using a 193 nm ArF* LA system (Analyte G2, Teledyne Photon Machines, Bozeman, MT, USA), equipped with the ARIS (Aerosol rapid introduction system) for the HELEX 2 cell, coupled to an icpTOF (TOFWERK AG, Thun, Switzerland) ICP – time-of-flight (TOF) – MS unit. The ARIS, in combination with the ICP-TOFMS enables a pixel acquisition rate up to 2 orders of magnitude higher than conventional systems. For scanning MS, artefacts in the image, such as aliasing, blurring and undersampling effects as a result of faster pixel acquisition rates can be avoided by harmonising the MS cycle timing, the laser repetition rate and the scan speed through a calculation based on the single-pulse peak width and by adopting other good practices specific to low-dispersion systems. External calibration was performed based on gelatin droplets spiked with a multi-element standard. The information on the curvature of the sample object along its boundary orthogonal to the cutting plane is lost in the microtomy process. 3D LA-ICP-MS approaches based on the registration of neighbouring slices failed to correctly reconstruct the 3D volume as the tilt of the sample could not be mimicked and a high amount of structural variability was present between sequential slices. Alignment of the set of 59 LA-ICP-TOFMS 2D slices relative to the corresponding slices of a high-resolution X-ray absorption computed tomography (μ -CT) image of the sample (with a voxel size of 1.5x1.5x1.5 μm^3) recorded a priori permitted the accurate reconstruction of the 3D LA-ICP-MS-based elemental distribution. Data fusion approaches were then applied on the registered multiplexed data to improve the lateral resolution and decrease noise levels. Segmentation of the data allowed to estimate the concentration levels in individual biological structures. The synergy of ICP-TOFMS instrumentation and fast LA cells is also discussed, and an outlook is provided elaborating on the potential of future low-dispersion LA cells.

[1] Van Malderen, S.J., et al., Three-dimensional Reconstruction of the Tissue-specific Multielemental Distribution within *Ceriodaphnia dubia* via Multimodal Registration Using Laser Ablation ICP-Mass Spectrometry and X-ray Spectroscopic Techniques. *Anal Chem*, 2017, DOI:10.1021/acs.analchem.7b00111

‘Elemental tomography’: coupling 3D LA-ICP-MS and X-Ray Tomography reconstructions of a Mouse Embryo

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Mapping elemental distributions in 3D using LA-ICP-MS can provide insights into the biological function of elements, such as metal utilization by enzymes [1]. Here we register LA-ICP-MS data to a micro-CT image for a mouse embryo at the gestational age of two weeks, providing a means of imaging elemental distributions during development. The embryo was frozen in Tissue-Tek® OCT compound to perform a 10 minute micro-CT scan at 13.33 μm resolution. It was then cryostatically-sectioned in c. 20 μm thick slices in the same x-y plane as the micro-CT data for LA-ICP-MS analysis. High-resolution elemental maps, including those for Na, Mg, P, K, Ca, Fe, Cu, Zn, Rb, were obtained by rastering a 48 x 48 μm^2 beam of a 193 nm ArF excimer laser over the sample. LA data were exported as 16-bit grayscale images and registered to the micro-CT data using Avizo software (FEI). Figure 1 compares the micro-CT (Fig. 1A and C) to the phosphorus LA-ICP-MS map (Fig. 1B and D).

Registering laser ablation data to micro-CT data in this way reduces the effects of the sectioning process (e.g. tearing and shearing of sliced material) as the CT data are collected pre-sectioning. The co-registered compositional and density 3D datasets, allow us to examine the metal distribution in the developing embryo, providing insights into fundamental aspects of biology such as embryo development.

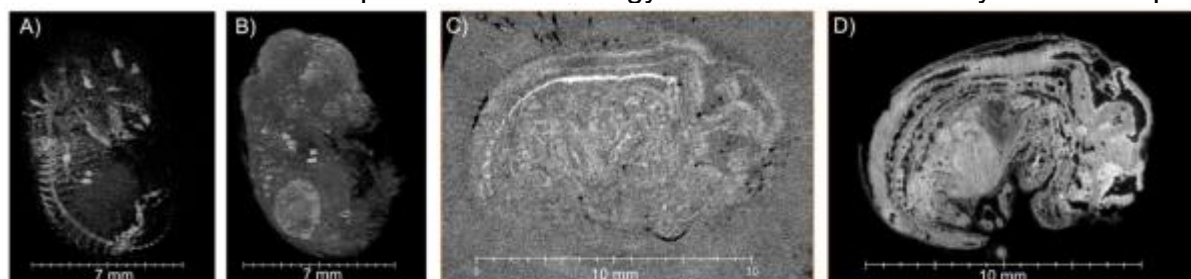


Figure 1. 3D rendering of micro-CT data (A) and P data from LA-ICP-MS (B); 2D slice through mid-section of sample: micro-CT data (C); P data from LA-ICP-MS (D). Brighter shades represent denser materials (micro-CT) and areas of higher P concentration (LA-ICP-MS)

[1] Paul, B., et al. (2015). *Chem. Sci.*, **6**, pp. 5383-5393.

GEO/THERMOCHRONOLOGY

U-Pb Geochronology Data Reduction: ET_Redux

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U-Pb geochronology measurements by LA-ICPMS are revolutionizing large segments of Earth Science research, from detrital zircon analyses that utilize the technique's high throughput to illuminate the provenance of clastic sedimentary rocks, to in-situ investigations of metamorphic accessory minerals that utilize the technique's high spatial resolution to untangle complex mountain-building processes. Because LA-ICPMS data interpretations play such an important role in modern geology, it is critical that those data be as accurate and precise as possible, and because those measurements are of such broad utility, it is critical that they be as accessible as possible. The U-Pb geochronology data reduction and uncertainty propagation software package ET_Redux [1] provides a free, open-source, platform-independent solution that also produces interactive, publication-quality visualizations and (relatively) easy integration into existing laboratory workflows. This talk will present several of the underlying statistical principles ET_Redux employs with examples and discussion, demonstrating what can go wrong for instance when sample/standard bracketing or analyzing the relative abundances of isotopes in your sample. Failure on these fronts generally results in inaccurate data with underestimated uncertainties, though the damage depends on both the value of the measurements (e.g., isotopic ratios or dates) and their relative uncertainties.

[1]: McLean, N.M., Bowring, J.F., and Gehrels, G. (2016) *Geochemistry, Geophysics, Geosystems*, doi:10.1002/2015GC006097.

Andradite Garnet U-Pb by LA-ICP-MS: Procedures, Standardization, and Mineral Exploration Case Studies

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U-Pb dating of accessory minerals has long been of importance for providing critical constraints on timing, durations, and rates of geological processes. While high U concentration accessory minerals, such as zircon or rutile, have provided invaluable insights into Earth's history, many geological processes remain inaccessible to isotopic geochronology. One of these processes is the formation of skarns. The UTChron research group has developed procedures and standards for andradite garnet U-Pb LA-ICP-MS geochronology. 110-micron spot size and 4 mJ energy were chosen to attain <2% precision for individual spots. Down-hole fractionation and element fractionation were corrected using both a matrix-matched Willsboro garnet and GJ1 zircon. There were no discernible differences between the primary standards; however, propagation of isotopic ratio uncertainties favors GJ1, which has considerably more precise TIMS calibration.

We applied this methodology in a case study to the Big Gossan skarn, located in the prolific Ertsberg-Grasberg mining district, to test standardization, inter-session reproducibility, precision, and accuracy of garnet U-Pb LA-ICP-MS dating. The high-grade ore body (71 million tonnes at 2.4 wt% Cu and 0.9 ppm Au) was emplaced adjacent to the 3.0-2.7 Ma Ertsberg diorite. U-Pb analyses of 8 garnet samples from the Big Gossan skarn yielded ages of 2.9-2.7 Ma. Inter-session comparison (3 months apart) produced overlapping Tera-Wasserburg intercept ages of 2.75 ± 0.03 Ma (n=150 spots) and 2.73 ± 0.06 Ma (n=50 spots). High analytical precision was achievable due to the high U contents (10-100 ppm), homogenous U distribution, and consistent common Pb composition. The garnet U-Pb ages are compatible with district-wide zircon U-Pb and phlogopite $^{40}\text{Ar}/^{39}\text{Ar}$ ages, and show that the maximum duration of Big Gossan skarn formation was <200 kyr. This case study shows the applicability of andradite U-Pb chronometry as a robust dating technique for constraining the timing and duration of skarn-forming hydrothermal systems.

Laser Ablation Split Stream (LASS) or Single Instrument Stream (LASIS)? A critical evaluation for zircon U-Pb dating and Hf isotope analysis

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Laser Ablation Split Stream has evolved into a powerful tool for the simultaneous analysis of LA aerosols for mineral scale isotope analyses and in particular for zircon U-Pb and Hf isotopes [1-2]. However, the analytical uncertainty of this technique has not been rigorously quantified [3]. This study systematically evaluates and compares the uncertainty associated with LA single stream and split stream for zircon U-Pb dating and Hf isotope analysis, using a large set of data acquired on the same instrumentation, to examine the compromises in accuracy and precision that occur when using LASS analysis. Analytical uncertainty, sensitivity, data accuracy, and precision were evaluated for an instrumental set-up using a RESOLUTION M50 ArF 193 nm excimer laser system, a Thermo Element XR2 SF-ICPMS, and a Thermo Neptune plus MC-ICPMS. The Plesovice zircon reference material, with near homogenous Hf concentration, was chosen for the Hf isotope study. The 91500 and GJ1 zircon reference materials, with homogeneous U, were chosen for the comparison of U-Pb dating. This study was carried out using spot sizes of 23, 33, 40, and 50 microns. Four methods were investigated (1) U-Pb isotopes determined using SF-ICP-MS at a high fluence of 6.5 J/cm²; (2) U-Pb isotopes determined using SF-ICP-MS at a low fluence 2 J/cm²; (3) Hf isotopes using MC-ICP-MS at a fluence of 6.5 J/cm²; (4) Hf and U-Pb isotopes simultaneously using MC-ICP-MS and SF-ICP-MS at a fluence 6.5 J/cm². In addition, this study explores a minimum spot size for useful LASS U-Pb+Hf measurement by comparing data taken using a 23-micron laser spot size. Comparative data for “unknowns” will also be presented. This report will present quantitative estimates of differences in accuracy and precision obtained using LASS versus LASIS that allow the user to evaluate which method is best suitable for purpose.

[1] Yuan HL, et al. 2008, Chem. Geol. 247: 100-118 2.

[2] Fisher CF, et al. 2014, Chem. Geol. 15: 121-139 3.

[3] Sylvester P, et al. 2015, North American laser ablation workshop 2015, Abstracts: P10

Cassiterite LA-ICPMS U-Pb Geochronology: No Need for Independently Dated Matrix-Matched Standard

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The paradigm of the LA-ICPMS U-Pb dating is to analyze a matrix-matched mineral previously precisely dated by a reliable technique (e.g., ID-TIMS) and use it as a bracketing standard for analyses of unknowns. This approach is difficult to implement for the mineral cassiterite (SnO_2) because it is extremely difficult to digest completely^{1,2} in order to obtain accurate ID-TIMS results. Precise and accurate dating of cassiterite is useful for direct age determinations of tin mineralization. Our new approach is based on unique geochemical properties of rutile group minerals (including cassiterite). These minerals typically are extremely low in Th and, therefore, measured ^{208}Pb in cassiterite is almost entirely of non-radiogenic origin (i.e. does not contain appreciable amounts of radiogenic ^{208}Pb from in situ ^{232}Th decay). Hence, we applied an isochron approach based on measured ^{208}Pb as a common-Pb proxy, which allows cassiterite U-Pb dating without any assumptions about the isotopic composition of initial common Pb. LA-ICPMS system (Photon Machines Excite-Analyte™ 193 nm excimer laser + NU Instruments SC-ICPMS Attom™, 135 μm spot diameter) was used to acquire U-Th-Pb data using NIST 612 glass as a primary non-matrix-matched standard and Lolite™ for data reduction. Our analyses of cassiterite from tin deposits in Spain, Saudi Arabia, Siberia, Russian Karelia, and Brazil (age range of ~300 to ~1,900 Ma) yield ages that are in good agreement with the published geochronology of rocks associated with these tin deposits.

1 Gulson, B.L. and Jones, M.T. *Geology*, 1992, v. 20, 355-358.

2 Yamazaki, E. et al. *Geochem. J.*, 2013, v. 47, 21-35.

Forensic and Industry Applications

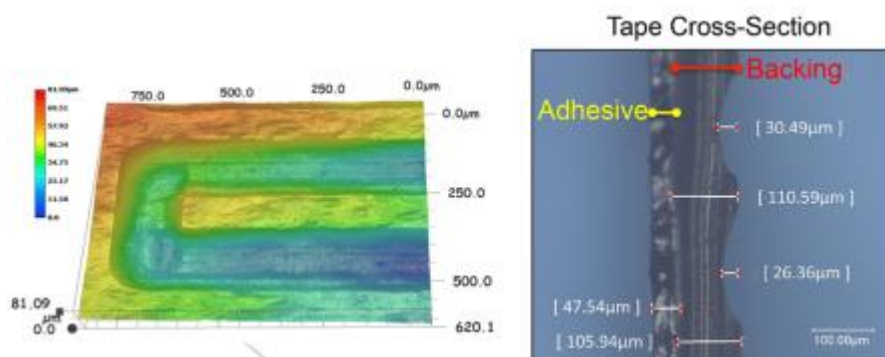
LA-ICP-MS Analysis and Characterization of Adhesive Tapes as Forensic Evidence

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Adhesive tapes are commonly found as physical evidence in cases involving violent crimes and national security threats. LA-ICP-MS was used for the characterization of chemical signatures of electrical tapes for forensic comparison and provenance purposes. The backings of 90 black electrical tapes, previously characterized by microscopical examination, Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS), Fourier Transform Infrared Spectroscopy (FTIR) and Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) were analyzed by LA-ICP-MS to evaluate the ability of the technique to discriminate samples originating from different sources and to associate pieces of tapes originating from the same roll. The results showed that LA-ICP-MS is a useful tool that complements current protocols for the organic and inorganic characterization and comparison of electrical tapes and results in improved discrimination and superior characterization. The developed LA-ICP-MS method alone provided 94% correct discrimination of the tapes known to originate from different rolls and 100% correct association of the tapes known to originate from the same roll. Moreover, LA-ICP-MS captured a large amount of compositional information, as the use of elemental profiles alone provide similar discrimination and classification capabilities as all the conventional methods together. The analytical sensitivity of LA-ICP-MS provides a means for the classification of tapes to support investigations as well as the potential for database searching capabilities in the future.



Microscopical images of an electrical tape after being ablated using a raster pattern with the selected optimal parameters. Left: 3D image of the ablation pattern. Right: Cross-section of the tape.

Application of LA-ICP-MS Analysis to Process Mineralogy: Ga and Ge Recovery at Kipushi Deposit

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LA-ICP-MS offers a unique facet to process mineralogy. Many economic metals are present at ultra-low levels in mineral deposits and require complex recovery techniques to separate them from the bulk ore. Understanding metal occurrence is necessary for implementing the proper recovery strategies. LA-ICP-MS is a cost-effective and versatile method for measuring precious-metals and other economic trace-elements in solid solution in various types of mineral phases while achieving low detection limits. The results can help calculate accurate plant metal-balances, diagnose reasons for lower than expected recoveries in a concentrator, or when included in larger geometallurgical programs, can define areas of an orebody that may require different processing routes. To demonstrate the practical uses of LA-ICP-MS to process mineralogy, data collected from a sulphide-rich heavy liquid separation and shaking table concentrate from the Kipushi Cu-Zn deposit, Katanga, DRC is presented. The objective was to determine the proportion of Ge and Ga present in solid solution in sulphides and in discrete mineral phases. GSD-1G reference glass was the most appropriate material available for calibration, and produced reasonable reconciliation. The results indicate that sphalerite carries significant amounts of Ga (42.5ppm, representing 54% of the Ga) and chalcopyrite hosts moderate proportions of Ge (2462ppm, representing 21% of the Ge). Discrete phases host the remaining portions. The deportment information was used to guide flowsheet development in order to optimize Ge and Ga recovery. This case study also emphasizes the demand for a suitable sulphide reference material that can accommodate a large suite of trace-elements.

Challenges and Advancements in the LA-ICP-MS Analysis of Food Samples

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LA-ICP-MS offers direct chemical and isotopic analysis in a variety of solid matrices ranging from a single micron to submillimeter resolutions. Although initially geared towards geological and chemical applications, in the past decade interest in applying the technique to biological samples has increased due to its capability of providing elemental distribution information. However, the ablation process, sample transport and plasma dynamics are still poorly understood for biological samples. In this study we focus on the optimization of both the laser ablation and the ICP-MS systems in an attempt to provide quantification with and without matrix matching. As an example, the elemental content of rice samples is determined using in-house prepared mixed food standards, a rice SRM, spiked cellulose powder material and NIST 612 glass SRM. The use and choice of internal standard is evaluated based on the elements, samples of interest (individual grains or homogenized pressed pellet powders), and the standard materials used for quantification.

Bio and Paleoclimate Applications

Stable Isotopes in Tree Rings by Laser-Ablation - Combustion - GC- IRMS

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Studying stable isotope ratios of carbon in tree rings allow us to understand changes in plant physiological and metabolic processes when responding to a changing climate¹. In order to fully understand the processes occurring, it is desirable to study the intra-annual variability of $\delta^{13}\text{C}$.

The high temporal resolution necessary for this may be obtained using a laser ablation device, coupled to an isotope ratio mass spectrometer via a combustion furnace and cryogenic trap. Sercon, an IRMS company based in the UK, and Swansea University have together successfully built a system on which the analysis of $\delta^{13}\text{C}$ on tree samples has been possible.

The potential of extending this analysis to other sample matrices is now available, for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$.

1. Danny McCarroll, Neil J. Loader, Stable isotopes in tree rings, Quaternary Science Reviews, Volume 23, Issues 7–8, April 2004, Pages 771-801

Unravelling the Life History and Origin of Fish using Strontium Isotope Laser Ablation Analysis

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Laser ablation analysis of strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of otolith (fish ear bones) is a powerful and well-established tool to determine life history patterns and origins of fish. Other calcified fish tissues such as scales, spines, and fin rays can also be used to extract valuable chemical information and are useful as a non-lethal alternative for endangered or threatened fish species. However, unlike otoliths that are predominantly aragonite, these tissues are comprised of biological apatite. Analyses of biological apatite using in situ laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) is complicated by polyatomic interferences on mass 87, which can cause inaccurate $^{87}\text{Sr}/^{86}\text{Sr}$ measurements.

We tested the effect of these interferences on a variety of samples including pectoral fin rays of green sturgeon (*Acipenser medirostris*) and white sturgeon (*Acipenser transmontanus*), a salmon shark (*Lamna ditropis*) tooth, and otolith, scales and spines collected from freshwater walleye (*Sander vitreus*). We observed elevated $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in the bioapatite samples, likely related to a polyatomic interference ($^{40}\text{Ca}^{31}\text{P}^{16}\text{O}$ or $^{40}\text{Ar}^{31}\text{P}^{16}\text{O}$). Instrument conditions that either reduce oxide production levels, or switching the instrument to medium resolution (~7500) mode, successfully removed the effect of the polyatomic interference, and resulted in consistent $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values across all sample types.

This provides fish ecologists with a powerful new tool to reconstruct life histories and origins for threatened or endangered fish species where otolith extraction is not a viable option. Furthermore, our findings are also applicable to other bioapatite samples such as teeth and bones for archaeological and forensic applications.

Analysis of manatee periotic bone chemistry as a tool to track West Indian manatee migrations in the northcentral Gulf of Mexico

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Migration and habitat use of the threatened West Indian manatee in the northcentral Gulf of Mexico (nGOM) is minimally studied and critical for determining manatee population connectivity and conservation needs. Estimates of migration and habitat use have been made using satellite/GPS tags, photo identification of individuals, and opportunistic sighting reports, but these samples are spatially and temporally limited and rely on seeing and documenting animals. Chemical analysis of inert tissues with annual growth (i.e. otoliths, baleen, hair) of marine taxa has enabled inference about migration pathways, habitat use, and population connectivity in a variety of species. This approach has potential to aid in determining manatee migrations via analysis of chemical constituents (trace elements and stable isotopes) in their periotic bone. Manatee periotic bones display annual growth layers similar to those found in fish otoliths or mollusc shells and chemical analysis of transects across these structures can reveal age-specific information about migrations. To examine these chemical variations, manatee periotic bones were collected from necropsied animals along the nGOM coast from Mississippi to the western Florida Panhandle. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) was used to analyze trace elements within growth layers of periotic bones. Preliminary analysis of Sr:Ca and Ba:Ca ratios indicated approximately annual variation in use of saltwater versus freshwater habitats through time. Fluctuations in other elements of interest (e.g.; Mn, Zn) could indicate use of urbanized or industrialized waters. Use of these techniques will increase understanding of lifetime manatee habitat use in the nGOM and when coupled with stable isotope ratios will define diet during migrations.

Reconstructing Laurentide Ice Sheet Meltwater Geochemistry using Combined LA-ICP-MS and Oxygen Isotope Measurements on Individual Foraminifera

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The $^{18}\text{O}/^{16}\text{O}$ of continental ice varies with latitude and elevation due to Rayleigh fractionation during ice sheet evolution. Modern continental ice sheets exhibit dynamic processes that produce variable melting, producing meltwater that is isotopically heterogeneous depending on its melt source. Knowledge of the history of past meltwater oxygen isotope variability during a melting event could yield novel insight on the behavior of ice sheet melting during glacial terminations. In this study, we present a record of reconstructed Laurentide Ice Sheet (LIS) meltwater geochemistry from the Gulf of Mexico during Termination I (18–11 ka) using a novel combination of LA-ICP-MS and IRMS techniques. To reconstruct Mississippi River deglacial melt geochemistry, we perform LA-ICP-MS analyses (Mg/Ca, Ba/Ca) on individual specimens of the planktonic foraminifera *Orbulina universa* from a number of intervals in an Orca Basin, Gulf of Mexico core. Data assessment protocols for LA-ICP-MS on individual foraminifera shells include monitoring 1) the heterogeneity of intra-shell Ba/Ca ratios 2) covariation of Mg/Ca and Ba/Ca, both of which could indicate diagenetic overprinting, and 3) Al/Ca, which monitors sedimentary clay contamination. Following data reduction, we pair these single-shell trace element measurements with $\delta^{18}\text{O}$ data from fragments of the same shells to reconstruct coupled $\delta^{18}\text{O}$ seawater and salinity pairs for each specimen. In each core interval, we reconstruct $\delta^{18}\text{O}$ seawater-salinity relationships from populations of data to generate instantaneous meltwater $\delta^{18}\text{O}$ values (y-intercept from regressions). During the Bølling-Allerød (15.5–13 ka), our reconstructions of LIS meltwater $\delta^{18}\text{O}$ values range from -20‰ to -49‰ (VSMOW). This range suggests a dynamic melting history for the LIS, including contributions from both the low-elevation southern margin and high-elevation, high-latitude interior domes, alternating on decadal timescales. Prior to Bølling-Allerød warming, the $\delta^{18}\text{O}$ value of Mississippi River outflow reflects either regional precipitation, LIS meltwater with an isotopic value indistinguishable from precipitation, or a mixture of the two. After ~13 ka (Younger Dryas and Holocene), our data show no evidence of Mississippi River outflow above the site of the core.

Earth Science Applications

Cryptic crustal events during the Taconic Orogeny elucidated through LA-ICPMS studies of volcanic zircons, southern Appalachians, Alabama

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Despite a long history of stratigraphic work, many questions remain about the tectonic setting of the Taconic orogeny during the early late Ordovician. Several different global paleogeographic hypotheses exist about the driving force that led to this orogeny. While some studies suggest that the closing of the Iapetus ocean was caused by the collision of the North American and South American plates, most studies suggest that island arc systems collided with the passive continental margin of North America. Nevertheless, disagreement exists on how to explain the stratigraphic architecture of the siliciclastic sequences representing the erosion of the Taconic Highlands in an island arc setting. Some studies suggest the collision was analogous to the modern Banda Arc system with the development of a foreland basin and a sedimentary wedge, while other studies call for the presence of a back arc basin. Here we present U-Pb results of volcanic zircons that are associated with the magmatic activity during this time. Previous studies focused on slender zircons for age dating. However, in this study we analyzed several large zircons from close to the volcanic center in Alabama that have inherited cores in order to test for the presence of geochemical evidence for multiple crustal events.

While the rims have ages consistent with the Taconic Orogeny (~450 my), the cores have much older ages (~1000 my). Our results support the hypothesis that during the closing of the Iapetus ocean, Precambrian and Cambrian sediments from the passive continental margin were subducted and incorporated into the volcanic system. This led to the inclusion of Precambrian zircons into melts associated with the Taconic Orogeny. Overall, our study supports the presence of subduction of preexisting sedimentary rocks and potentially the presence of a sedimentary wedge.

Lithium Isotope Measurements in Spodumene, Lithiophilite, Tourmaline, Petalite, and Beryl by LA-MC-ICP-MS

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Lithium is a highly fluid-mobile element with two isotopes that are useful in studying how hydrous fluids transfer components from a subducting slab into the mantle wedge. Most of the Li isotopic data available from subduction-related rocks are from whole-rock analyses, and only few in-situ data were acquired by SIMS. A new in-situ method to obtain isotopes analyses faster than by SIMS, coupling an excimer laser-ablation microscope with a MC-ICP-MS has been developed. Lithium content and isotope measurements were conducted on 13 Li-bearing minerals from the American Museum of Natural History and Harvard Museum of Natural History, e.g., lithiophilite, elbaite, schorl. Lithium isotopes were measured in-situ by LA-MC-ICP-MS in both low and medium resolution (LR and MR) to test possible interferences on ^6Li or ^7Li . Lithium isotopes were also measured by MC-ICP-MS on bulk minerals, after digestion and separation of Li on ion-exchange columns. Li concentrations were acquired by LA-ICP-MS. The Li contents range from ~ 20,000 ppm in lithiophilite to ~ 200 ppm in schorl, which ensures measurements over a wide range of Li concentrations. The $\delta^7\text{Li}$ values of the minerals measured in this study using an ESI New Wave UP-193-FX ArF* (193 nm) LA microscope coupled to a Neptune Plus (Thermo Scientific) MC-ICP-MS display significant offsets between LR and MR analyses and also between different sessions of analyses. For example, elbaite H-98144 ([Li] ~ 2000 ppm) yielded a $\delta^7\text{Li}$ ranging from $+27.3 \pm 0.9 \text{ ‰}$ to $+32.1 \pm 2.3 \text{ ‰}$ in LR, over 3 different sessions of analyses. The same elbaite measured in MR yielded $\delta^7\text{Li}$ of $+20.7 \pm 0.3 \text{ ‰}$ ($n = 3$), and $+13.0 \pm 5.8 \text{ ‰}$ ($n = 11$). The $\delta^7\text{Li}$ of H-98144 measured by SIMS was $+7.3 \pm 0.6 \text{ ‰}$. Similar offsets have been observed for all the other minerals studied. The careful observation of Li peaks in both LR and MR does not show any interference that could explain such discrepancies. The comparison of these results with measurements by MC-ICP-MS on the same samples shows that in-situ and bulk values do not match. For example, lithiophilite H134825 has a $\delta^7\text{Li}$ of $+28.4 \pm 2.5 \text{ ‰}$ in LR and $+17.7 \pm 1.0 \text{ ‰}$ in MR, when measured in-situ by LA-MC-ICP-MS, and a $\delta^7\text{Li}$ of $+2.4 \pm 0.2 \text{ ‰}$ when measured in bulk by MC-ICP-MS. There is no explanation yet to explain such discrepancies, but until the issue is resolved, the use of LA-MC-ICP-MS to measure Li isotopes must be discontinued.

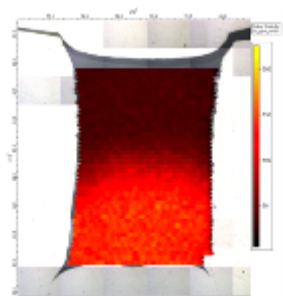
Diffusivities of Redox-Sensitive Elements in Basalt vs. oxygen fugacity determined by LA-ICP-MS.

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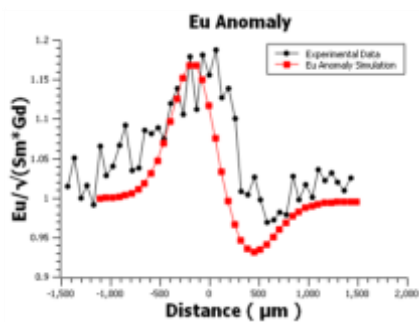
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Several diffusion experiments were conducted in a piston cylinder device across a range of oxygen fugacities (FMQ-3 FMQ-1.2, FMQ+6) at 1 GPa and 1300 C. This was done to explore the effects of oxygen fugacity (fO_2) on diffusivity of redox sensitive trace elements. This allows investigation of how these elements diffuse across the fO_2 range encountered in different reservoirs on planets and moons in our solar system. The University of Rochester LA-ICP-MS system was used for analysis of samples. Analyses were conducted using an Agilent 7900 quadrupole mass spectrometer connected to a Photon Machines 193 nm G2 laser ablation (LA) system equipped with a HelEx 2-volume sample chamber. Spots used were 35 μm circles spaced at 65 μm intervals. Laser fluence was 7.81 J/cm² with a rep rate of 10 Hz. The Iolite software package was used to reduce data collected from laser ablation analysis of experiments with Si-29 used as the internal standard isotope. Iolite's global fit module was used to simultaneously fit elements' diffusivities in each experiment while keeping the Matano interface constant. Elements analysed include V, Nb, W, Mo, La, Ce, Pr, Sm, Eu, Gd, Ta, and W.



same run as analyzed



Figures 1 (left) and 2 (right): Figure 1 is a laser ablation generated map of Gadolinium concentration in a diffusion experiment run for 80 minutes with an oxygen fugacity buffered at FMQ-3. Figure 2 is a simulated Europium anomaly (red line) using the diffusivities acquired from a 40 minute molybdenum capsule experiment. The black line is the experimental Europium anomaly from the by a LA-ICP-MS spot traverse.

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VENDOR AFFILIATED TALKS

THURSDAY

10¹³ Ω Amplifier Technology for LA-MC-ICP-MS of Uranium Particles: Can we Measure Depleted and Highly Enriched Compositions in a Single Analysis?

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The possible application of laser ablation (LA-) multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) to the isotopic characterisation of single particles for nuclear safeguard purposes is under investigation^[1]. Developments have focused on natural and lightly enriched uranium isotopic compositions, achieving the best precision collecting ²³⁵U on an ion counter^[2]. However, a true nuclear safeguard sample may contain particles highly enriched in ²³⁵U, ablation of which would result in count rates greater than the operating range of an ion counter.

Faraday detectors incorporating 10¹³ Ω amplifier technology have only recently been applied to LA-MC-ICP-MS^[3]. Here we will report on the application of LA-MC-ICP-MS with 10¹³ Ω amplifiers to the analysis of sub-micron uranium oxide particles. For particles of natural and lightly enriched uranium composition the performance of the 10¹³ Ω amplifiers was comparable or better than the same analysis with an ion counter. The 10¹³ Ω amplifier was subsequently tested for highly enriched uranium compositions (>50% ²³⁵U) and demonstrated improved performance with increasing ²³⁵U signals.

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AttoM HR-ICP-MS an instrument of choice for laser ablation ICP-MS.

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The AttoM HR-ICP-MS is a double-focusing single-collector instrument of forward Nier-Johnson geometry which features the unique FastScan Ion Optics. The instrument is entirely purpose designed and built to provide the best performance and reliability coupled with flexibility and ease-of-use for precise and accurate elemental and isotope ratio analysis. The instrument can also be used to rapidly scan/jump between isotopes of interest over a 40% relative mass range without the necessity to change the magnetic field or acceleration voltage. For this mode, the magnet is parked in the middle of the mass range of selected isotopes (known as 'park mass'). Acceleration voltage, ESA voltage and ion optics used for beam focusing are kept constant during the acquisition. Only the FastScan Ion Optics located at the entrance and exit of the magnet are varied, being used to rapidly deflect the selected isotopes sequentially onto the magnet park mass for data acquisition. Several applications regarding laser ablation with an AttoM will be presented.

RESOLution-SE - Key features for exceptional LA-ICP-MS

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RESOLution laser ablation systems (manufactured by Australian Scientific Instruments) provide an optimum configuration for ICPMS analyses. Since its release onto the market in 2008, these 193nm excimer laser systems have a long-standing reputation in the LA-ICPMS community, incorporating the industry leading Laurin Technic sample cells and unique GeoStar operating software. Learn more about the RESOLution- SE system and its key features for LA-ICPMS applications including U/Pb Geochronology, split stream and ice core analysis.

FRIDAY

Imaging cisplatin-induced ototoxicity using LA-ICP-MS

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Cisplatin is a platinum metal-based chemotherapy drug used in the treatment of a variety of cancers. Cisplatin treatment has several side effects including peripheral neuropathy, nephrotoxicity, and ototoxicity. Hearing loss occurs in a significant proportion of patients undergoing cisplatin therapy. As the population of cancer survivors grows, so does the importance of addressing the long-term consequences of therapy. Cisplatin is toxic to several cell types in the inner ear, including sensory hair cells and supporting cells. Since uptake and clearance of cisplatin from the inner ear are poorly understood, we developed a mouse model of cisplatin ototoxicity to study repeated cycles of cisplatin administration followed by intervals of recovery, resonant of clinical cisplatin administration. Cisplatin uptake and clearance from the cochlea and other tissues were characterized in this mouse model using traditional ICP-MS. Unlike other analyzed organs, the cochlea abnormally accumulated cisplatin and displayed no removal of cisplatin during any point in the experiment. Increased levels of cisplatin were also observed in cisplatin treated patient samples; however, the location(s) of cisplatin accumulation in the inner ear remain unknown. Molecular biology techniques have been unsuccessful in characterizing the localization of cisplatin in the inner ear. We utilized laser ablation ICP-MS to characterize the localization of platinum in the cochlea. Laser ablation scans were performed on mouse and human inner ear tissue sections using the platinum 195 isotope to determine cisplatin localization. Calcium 43 served as the background isotope to control for drift. The images were normalized and merged using the Iolite software. In both mice and human samples, levels of platinum accumulated in several areas of the inner ear; some accumulation of cisplatin was observed in bone but the highest levels were observed in the auditory nerve, stria vascularis, and organ of Corti. No platinum was observed in control specimens. Our experiments demonstrate that cisplatin clearance from the cochlea is inefficient, resulting in the accumulation of cisplatin in the inner ear. These technologies have given new insight into the mechanisms of cisplatin induced ototoxicity. Future studies will allow for the development of new therapies to prevent accumulation and ototoxicity.

Applied Spectra, Inc: Company overview, technology and applications

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Spectra Inc. (ASI) is a provider of laser solutions for analytical chemistry.

Founded in 2004, ASI manufactures a suite of laser ablation systems for LA-ICP-MS and LIBS (Laser Induced Breakdown Spectroscopy) instruments serving a wide range of applications. LIBS is essentially an optical spectrometer that is integrated into the body of a Laser Ablation system that measures the optical spectra from the laser induced plasma at the sample surface. LIBS has the ability to measure elements that are impossible and/or difficult by traditional LA-ICP-MS methods such as H, O, N, C, F, halogens, etc. down to ppm levels. LIBS has full periodic table coverage but is particularly good at analyzing the light elements (H, B, Be, Li). ASI manufactures a very unique laser ablation system that combines both LA for ICP-MS and LIBS in one instrument, the J200 “Tandem” system. When these technologies are combined in “Tandem”, the elemental coverage and dynamic range of the laser ablation experiment is expanded as LIBS can also measure major elements at percent levels simultaneously with trace elements by both LA-ICP-MS and LIBS. We have applied this laser solution to both nanosecond and femtosecond laser ablation instrumentation. Applications served by our technology includes, but is not limited to, geochemistry, forensic sciences, life sciences, metallurgy, and various industrial applications.

NexION 2000 - The Next Generation ICP-MS from PerkinElmer

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This presentation will go over the key features of the new NexION 2000 ICPMS and benefits to the laser ablation community. The technical innovations of the NexION 2000 offer unique benefits to laboratories, both large and small. The NexION 2000's second-generation Universal Cell Technology™ features three modes of operation (Standard, Collision, Reaction) and all systems come with three gas channels for unsurpassed flexibility and performance. The NexION 2000 is configurable with a variety of sample introduction systems to suit specific applications. The matrix tolerance of the NexION 2000 is further enhanced by a new 34 MHz solid-state, free-running RF generator designed to deliver superior plasma power and stability. The revolutionary LumiCoil RF coil requires no cooling or maintenance and is guaranteed for life. The patented combination of the Triple Cone Interface and Quadrupole Ion Deflector on the NexION 2000 controls and focuses the ion beam so effectively that the NexION 2000 is the only ICP-MS with a cell that is designed to never need cleaning or replacing. The Simultaneous Dual Mode Detector delivers the fastest data acquisition rates on the market (100,000 data points/sec) providing superior analysis times and single particle ICP-MS capability. The Universal Cell Technology on the NexION 2000 also provides the unique capability of performing electronic dilution of selected analyte signals using Extended Dynamic Range mode, so both high concentration elements and low concentration elements can be analyzed together in the same method without increasing acquisition time or requiring the use of a collision/reaction gas. These features combined with the flexibility of the new Syngistix software offer the laser ablation user an unrivaled set of tools for their application.

SATURDAY

Examples of Collaborative Research & Development Producing Meaningful Analytical Innovation

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It is often argued that the era of the “lone scientist” is long gone^[1] and that collaborative research is the true way forward in today’s scientific world. The data available on scientific research databases make a strong point in favor of co-authorship, showing that the most referenced publications are the result of collaborative work^[1].

Teledyne CETAC Technologies has embraced the model of collaborative research as the durable way for enabling technological innovations in science. We have long recognized the true value of the research carried out by multidisciplinary teams and have diligently cultivated mutually beneficial projects. We have often turned to academia to validate our findings as well as supported academic endeavors.

In this contribution, we present the latest technological innovations as well as the cutting-edge applications developed by our scientists in collaboration with well-established research groups and institutions, including University of Ghent (Belgium), Trinity College Dublin (Ireland), National Institute of Chemistry (Slovenia), and TOFWERK AG (Switzerland).

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POSTER ABSTRACTS

BIO APPLICATIONS

Mapping the elemental distribution in brown and polished rice using laser ablation ICP-MS

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Rice is one of the most consumed grains in the world. Therefore, consumers will be affected not only by nutrients (carbohydrates, protein, copper, zinc etc.) but also toxic elements (arsenic, cadmium etc.) present in the rice. Those elements are primarily distributed in the outermost layer of a rice grain, the bran. Thus, elemental concentrations are impacted by polishing of the rice. In this study, we evaluated four degrees of milling and determined the elemental content (C, K, P, S, Cd, Mn, Na, As, Fe, Zn) using microwave assisted sample decomposition followed by inductively coupled plasma mass spectrometry (ICP-MS). Additionally, rice grains were embedded in epoxy blocks and sliced using a microtome followed by laser ablation ICP-MS analysis. The spatial elemental information was mapped in cross-sections of the rice grains. As the elemental contents are concentrated in the bran layer, polishing to a higher degree decreases the amount of toxic elements in rice.

Zn- and Cd-protein Identification in Proteomic Samples Using LA-ICP-MS: Current Status

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Zinc is an essential metal in all life forms. From protein folding and stability to enzyme catalysis, zinc is used widely to support many functions inside the cell. The collection of proteins within the cell commonly known as the proteome contains as many as 2800 Zn-Proteins. Most of these Zinc proteins have not been characterized. The problem are the missing methods to isolate and identify Zn-proteins at the proteomic level. Potentially, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can act as a powerful and sensitive microanalytical technique to detect metals bound to proteins.¹ Native methods for the determination of such proteins has been lacking until recently. The new method of native sodium dodecyl sulfate polyacrylamide gel electrophoresis (NSDS-PAGE) solves this issue.² The present work involves LA-ICP-MS of Zn- and Cd- proteins from LLC-PK¹ cell supernatant that have been separated by DEAE-HPLC and then NSDS-PAGE. Repetitions of LA-ICP-MS resolve reproducible patterns of peaks of Zn and Cd qualitatively but not quantitatively. Proteins can be visualized by silver staining and correlated to corresponding gel runs. Special Zn-protein staining is under investigation. Pre-electrophoresis with EDTA reduces the background level of Zn in the gel. Isotopically labelling cells with ⁷⁰Zn to distinguish ⁷⁰Zn-proteins from background spikes fails due to in-gel exchange with adventitious Zn. Proteomic Zn also exchanges with Cd²⁺. Exchange has been confirmed at the individual protein level with many bands of Zn in control lanes transformed into bands containing both metals in proteome samples exposed to Cd. Some have lost all of their Zn. Problems and prospects for this methodology will be described. Supported by NIH grant ES-024509 and a Research Growth Initiative grant from the University of Wisconsin-Milwaukee.

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Exploring natural chemical tracers in shark vertebrae to assess migration patterns

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Characterizing long-distance migrations by large pelagic sharks typically involves conventional or electronic tagging that requires capturing and handling individuals, high expense, and low reporting rates. Natural chemical tags such as trace elements and stable isotopes contained in chronologically formed band pairs of shark vertebrae, may increase our understanding of individual migration patterns and population connectivity. The highly mobile nature of pelagic sharks that migrate across international boundaries necessitates information on the movement of sharks across national boundaries and management jurisdictions. In this study, trace element profiles (^7Li , ^{23}Na , ^{25}Mg , ^{55}Mn , ^{63}Cu , ^{66}Zn , ^{88}Sr , ^{138}Ba) were quantified by laser ablation ICP MS in vertebrae of common thresher (n=10), shortfin mako (n=9), and blue sharks (n=7) with known tag and recapture locations between the US and Mexico. These sharks were all injected with oxytetracycline (OTC) when they were initially captured and released allowing for identification of the vertebral band associated with their initial location. Movements included both latitudinal and longitudinal patterns that ranged from <10 km to > 600 km. Individuals exhibited time at liberty from 215 to 1385 days. Patterns in vertebrae elemental chemistry profiles between known capture/tagging (OTC band) and recapture (outer margin of vertebrae) will be explored as potential natural tracers of movement in both north-south and east-west directions. Ultimately, the goal is to correlate shifts in elemental profiles with known migration distances and direction, to further explore the potential of natural chemical tracers to record shark migration patterns.

DATA HANDLING

U-Pb measurement in zircon by using single shot method with HR-ICP-MS AttoM coupled to NWR213 laser ablation: reduction of fractionation effect and automated data treatment.

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High spatial resolution measurement by laser ablation ICP-MS has continuously improved in recent years addressing challenges in depth and lateral resolution. However, there are still significant challenges for samples that require precise isotope ratio measurements. The ultimate spatial resolution is to evaluate isotope ratios from a single laser shot, applications of this technique include lead uranium/lead isotope ratios of zircons and single particle analysis for uranium ratios.

This work will describe the latest performance available with Nu AttoM ES and improvements obtained using the data processing technique outlined by Cottle, Horstwood and Parrish (1) in 2009, highlighting the signal compression and fast washout of the latest ESI laser ablation cells and fast peak jumping capability of the Nu AttoM single collector ICP-MS. It will also describe how NuQuant can be used to have an automated data processing method to improve ease of use when obtaining isotope ratios from integrated transient peaks compared to the manual processing of data through spreadsheets. This work will also present results that show how using single shot method instead of conventional spot ablation in zircon reduce the fractionation effect for Pb/U ratio without external calibration.

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Towards a Robust Laser-Ablation Whole-Rock Data Reduction Routine: Time-Varying Calibration Curves and Uncertainty Propagation

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Whole-rock trace element data are widely used in the geological sciences, but methods for their measurement by laser ablation are heterogeneous. Some workers use a single rock standard for calibration, yielding data that can be of questionable accuracy, especially if the chemical composition of unknowns deviates significantly from the standard. Even those laboratories that utilize multi-point calibration curves often do not consider time-varying instrumental drift, uncertainties in the standard composition, or regression errors. We are developing a combined Lolite™ and Matlab™ data reduction routine to calculate multi-point, three-dimensional calibration curves for every measured element, account for non-linear instrumental drift, and propagate uncertainties from the calibration curve regression. Standard analyses reduced using a preliminary version of this method yield precise and demonstrably accurate trace-element data, and laser line traverses across whole-rock glasses yield data that are of equal or better accuracy than static spot analyses. On-going and future tasks include i) testing different approaches for regression and uncertainty propagation, ii) analyzing whole-rock glasses of uncommon composition to test for matrix effects, and iii) making these tools available to the laser ablation community.

A New Approach to Laser Ablation ICP-MS Using the Flexible Map Interrogation Tool ‘Monocle’

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We present a flexible new interrogation tool for 2-dimensional chemical and isotope maps obtained by LA-ICP-MS. The tool, called Monocle, works with Iolite, a popular LA-ICP-MS data processing software package (www.iolite-software.com; [1]), to enhance and simplify one's ability to define and extract data from regions of interest (ROI) on a map. Initially, a customizable loupe is panned over the map while 'inspectors' (e.g., histogram, kernel density estimate, rare earth element, or U-Pb concordia diagrams) update continuously to provide a sense of the variation within the map that is not always apparent when looking at elements/isotopes individually. From this initial assessment, ROIs can be defined using four different strategies: 1) from the loupe itself; 2) by drawing polygons, ellipses, rectangles, etc.; 3) by 'growing a seed'; or 4) from a list of criteria. Drawing a ROI can be useful to pool data for irregular zones of apparently similar chemistry thereby improving the accuracy and precision. Growing a ROI from a seed works by adding adjacent 'pixels' to the seed ROI if they satisfy some statistical boundary set by the user (e.g., 1 SD of the original seed. Lastly, for cases in which too few adjacent pixels exist to grow a ROI from a seed, multiple criteria can be set (e.g., element A > 1 ppm and $^{206}\text{Pb}/^{238}\text{U}$ age < 1500 Ma) to determine which pixels to include in a ROI.

The tool and its various features are illustrated with four examples, including a Mn crust from behind the Mariana Arc, a garnet from a serpentinised Iherzolite, zoned augite from Mt. Etna, and a zircon with complex core-rim structures. These examples show that the extraction of data from 2-dimensional maps that are less than < 1 μm deep avoids many of the limitations/complications of conventional LA-ICP-MS analyses that rely on typically larger and deeper pits. In combination with fast aerosol transfer systems that permit high repetition rate mapping (up to ~ 80 Hz), the extraction of quantitative data with Monocle heralds a new era of *in situ* chemical and isotopic analysis.

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Using Discordant Data: Potential Methods and Applications

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Laser ablation U-Pb dating of various minerals often produces a dataset that contains analyses varying from concordant to very discordant. This discordance can be caused by many factors, including mixing of multiple age domains by the laser spot, true Pb-loss from the mineral structure, and inheritance of common Pb. Conventional methods typically apply a concordance cut off, and ignore any data that are more discordant than this filter. However, these discordant data contain useful information about the history of the sample, information that is lost using traditional methods. We recently developed a modeling procedure to extract upper and lower intercept age information from discordant U-Pb data in Wetherill Concordia space (Reimink et al. 2016) and have recently completed a version for Tera-Wasserburg Concordia space. Using our procedure we are able to model U-Pb resetting events such as fluid flow through sedimentary basins, metamorphic resetting, and zircon inheritance, using lower intercept ages from discordant data. We are also able to reconstruct primary age spectra from upper intercept ages of discordant data. Here we show select case studies where the utility of this modeling procedure is highlighted. For example, we are able to recalculate upper intercept ages for discordant analyses from detrital zircons, calculate the ages of fluid flow in sedimentary basins from lower intercept ages, and distinguish the sedimentary source rocks of granites with a significant inherited zircon component.

Reimink, J. R., Davies, J. H. F. L., Waldron, J. W. F., & Rojas, X. (2016). Dealing with discordance: a novel approach for analysing U–Pb detrital zircon datasets. *Journal of the Geological Society*, 2015–114.

EARTH SCIENCE APPLICATIONS

Downhole Fractionation in Natural and Pre-treated Zircon by LA-ICPMS

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Among the most significant challenges of LA-ICP-MS U-Pb zircon geochronology is accurately correcting for downhole fractionation, the time-dependent evolution of Pb/U during ablation. Downhole fractionation is commonly quantified in a reference material and a correction factor is then applied to correct for the increasing Pb/U over ablation time, assuming similar fractionation behaviour between the reference and unknowns. To test this assumption, we examined the downhole fractionation patterns in three common zircon reference materials (Plešovice, Temora-2, 91500) and in three low-U zircons from mafic intrusions (Laramie, Bushveld, Stillwater) ranging from the Mesoproterozoic to the Neoproterozoic that were treated as unknowns. Aliquots of all the analyzed zircon, including reference materials, were subjected to pre-treatment protocols, including annealing and chemical abrasion (leaching). Using exponential downhole correction models based on the zircon reference materials, the respective correction factors were applied to the unknowns and time-resolved Pb/U and final ages were compared. The reference materials exhibited distinct downhole fractionation, which resulted in variable success in correcting downhole fractionation and reproducing CA-TIMS ages in the unknowns. Annealing zircon grains prior to LA-ICP-MS analysis generally lessened the magnitude of U-Pb mass fractionation by 0.1-3.5%; leaching did not improve this effect. This indicates that crystallinity is an important factor for the reduction and normalization of downhole effects and needs to be considered when selecting reference materials.

Fused bulk rock powder major and trace element analysis by LA-ICP-MS: a comparative study of 213 nm and 193 nm laser performance

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Fusion of rock powders in $\text{Li}_2\text{B}_4\text{O}_7$ flux and analysis by LA-ICP-MS is a cost- and time-effective alternative to traditional acid digestion and sample dilution methods and analysis by solution-mode ICP-OES or ICP-MS. This study compares the effectiveness of 213 nm and 193 nm laser ablation systems in these matrices. Two Teledyne Photon Machines laser ablation systems were used for testing, an LSX-213 G2+ Nd:YAG laser and an Analyte G2 193 nm excimer, both equipped with HelEx II 2-volume laser ablation cells. The lasers were coupled to a Thermo-Scientific ICAP Q ICP-MS and surface scans on fused powders of standard reference materials of discrete compositions (including basalt, peridotite, andesite, latite, syenite and rhyolite) were performed. Laser ablation parameters for both systems were set to be similar: fluence of $\sim 4 \text{ J.cm}^{-2}$, 10Hz, scanning speed of $10 \text{ }\mu\text{m/s}$ with a 100-110 μm beam diameter. Flux and powders were mixed in a 3:1 proportion and fused following the protocols of Rooney et al. (2011), with the exception of rhyolite powder RGM-1, mixed in a 9:1 proportion. Data were processed using Thermo-Scientific Qtegra software. With the 213 nm laser, internal (within-run) signal precision of surface scans varies within $\sim 5\text{-}20\%$ (RSD) for most major and trace elements in basalt and syenite powders and geochemically compatible elements in peridotite. Duplicate scans generally reproduce within 3% (RSD) or better, unless trace elements concentrations are below $\sim 0.5 \text{ }\mu\text{g/g}$. Internal signal quality degrades to $\sim 20\text{-}50\%$ for most differentiated rock powders, particularly on RGM-1, with reproducibility generally ranging between 5-10%. This performance loss originates from significantly lower ablation rates and unsteady ablation in the most felsic matrices. The excimer laser produces signals with $\sim 5\text{-}10\%$ internal precision on most major and trace elements. Data reproducibility is within 2-3% (RSD) or better in most trace elements with concentrations higher than $\sim 100 \text{ ng/g}$. A negligible drop in ablation rate, signal internal precision, and reproducibility occurs for the felsic matrices compared to basalts.

Rooney T.O. et al., 2011, Contrib Mineral Petrol (2011) 161:373–388

LA-ICP-MS Analysis of Hydrothermal Dolomites: Revisiting Cement Microstratigraphy in Carbonate Breccias

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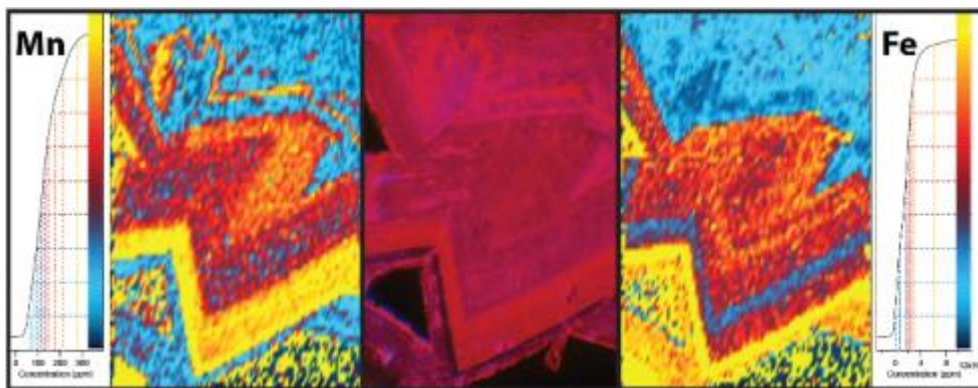
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Mines and former exploration programs provide samples of extensive solution-collapse breccia networks in Knox Group carbonates in Tennessee-Kentucky. These breccia bodies are broadly similar over a >50,000 km² area, including cementation dominantly by coarse hydrothermal dolomite. However, the cement assemblage, sequence of pore filling, and remaining porosity vary considerably, suggesting spatial and temporal variation in basinal brine systems and cementation histories.

Cathodoluminescence variation in dolomite cements has been used to define local or regional cement microstratigraphy. These studies have shown that CL response of dolomite is largely due to the variation of trace elements, particularly the Mn and Fe contents. We report initial results of LA-ICP-MS analysis that show potential to examine a diverse group of trace elements, that may be useful to define detailed microstratigraphy, and thus to constrain the evolution of local and regional breccia cementation with attendant effects on porosity. The initial research will analyze dolomite cements in individual drill cores with a large vertical range of dolomite-cemented fractures to attempt to constrain the history of fracture development. Does the microstratigraphy capture (1) the progressive development of the breccia body, in general from the base upwards in collapse (and cementation) events over time, or (2) breccia formation resulting from a single collapse event and thus all fractures were available for brine circulation and dolomite precipitation?

Comparison of LA-ICP-MS 2D-chemical maps to CL image (center) of hydrothermal dolomite cements reveals timing of Mn- and Fe-bearing basinal brines. The brightest CL zones typically are high Mn with

relatively low Fe. Maps acquired using a 20 x 20µm square aperture with a scan rate of 25µm per second. Map area is 1 mm wide by 1.5 mm tall.



Isotope and trace element analysis of zircons by LA-MC-ICPMS and LA-ICPMS, Mass Spectrometry Lab, CEGA-UChile

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Laser ablation techniques coupled with mass spectrometers have become an essential tool for zircons analyses. U-Pb analyses, Hf isotopes and trace elements concentrations are carried out at the Mass Spectrometry Laboratory of the Andean Geothermal Center of Excellence (CEGA), Universidad de Chile. The equipment used is an ArF excimer laser 193nm (Photon Machine Analyte G2) coupled with a Neptune Plus MC-ICP-MS (ThermoFisher) or an ICPMS iCAP Q (ThermoFisher). These two techniques have been used to determine U-Pb on four different reference zircons: Plešovice, 91500, Temora-2 and Sri Lanka SL2 zircons. A comparison of the accuracy and precision obtained for the different isotopic ratios have been carried out. Ages obtained by LA-ICPMS and LA-MC-ICPMS for the different zircons are consistent with published ages but some differences can be noted between the two techniques. For example, the propagated uncertainties are generally lower for LAMC-ICPMS than for LA-ICPMS analysis.

Hafnium isotopes have also been determined using LA-MC-ICPMS. Analysis of the Plešovice standard, yielded a corrected $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 0.282495 ± 0.000018 , consistent with published data.

Trace elements analyses, specially Ti which is a crystallization thermometer and the rare earth elements which can record the magmatic oxidation state have also been developed in our lab.

Trace Element Variation and CL Zoning of Volcanic Apatites from Dominica, Central Antilles

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Detailed textural characterization with CL or elemental maps of individual apatites is required to interpret subtle variation in trace element chemistry determined using LA-ICPMS. Apatites from ignimbrite deposits in the Roseau Valley of Dominica were analyzed to evaluate the generation of chemically homogeneous andesitic-dacitic ignimbrites from a single large batholith, as postulated by Howe et al. 2014.

Laser ablation analyses were performed on 150 apatite grains using a Cetac LSX-213 and an Elan 6100 DRC quadrupole mass spectrometer, fired for 300 pulses at 10 Hz with a 50 μm spot size using He as a carrier gas. Analyses were standardized on NIST glasses 610 and 612, and checked for precision and accuracy with a series of natural apatite standards, including the Durango apatite, the Peach Springs Tuff and a carbonatite from Bancroft, ON. Elements measured included Ca (as internal standard), Sr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Yb, Lu, Pb, Th and U.

Some ignimbrites have chemically homogeneous apatite populations, whereas others vary within a limited range. The CL textures of homogeneous populations are dominated by oscillatory zoning, while those with a larger spread contain different populations of grains with dark or bright CL cores. Further examination reveals that dark CL cores are enriched in LREE and depleted in HREE. Two deposits with nearly identical whole rock chemistry and zircon age populations have very distinctive apatite chemistry (and textures), suggesting that although the eruptive units share a common history, they experienced different magmatic conditions prior to eruption. The uniqueness of each eruptive unit is further shown by halogen zonation (Cl rich cores) in some samples and by variable U concentrations (a tetravalent cation) in others. LA-ICPMS is a powerful tool for discriminating between different eruptive units within a single volcanic deposit which are otherwise chemically and mineralogically homogeneous, but must be used in tandem with detailed microanalytical imaging techniques.

Surface Formation of Carbon Isolation from Sedimentary Rock by Basalt during Volcanic Shock Wave Events in Yamaguchi, Japan

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Introduction: High-pressure rock-minerals are formed at stable condition at Earth's deep interior or surface plate tectonic metamorphism. However, dynamic highpressure by shock-wave events of volcano and meteoritic impact might be formed at Earth's surface and checked by experiments by laser beam run on sedimentary rocks.

Surface evidences by dynamic volcanic compression and quenching: Phologopite crystals in volcanic basalt in the Mutsurejima, Yamaguchi, Japan [1] have been investigated microscopically to be formed carbon and carbon-bearing carbonate from shallow-layered Akiyoshi Palaeozoic limestone which is mixed with basalt to form micro-diamond, graphite and calcite on micas [2-4]. Carbon element can be obtained by the analytical FE-SEM method and by the micro-Raman method.

Surface evidences by dynamic impact compression and quenching: Carbon from impact layer sediment has been obtained in the Barringer crater, Arizona, USA .

Synthetic production by carbon separation from carbonates by laser beam: High-pressure carbon micro-diamonds and carbon separation from sedimentary carbonates have been obtained by laser-beam focussing method in laboratory [2-4].

Shocked grains on shallow origin: Shallow origin of high-pressure micro-grains has been obtained in shocked grains naturally and laboratory samples in this study.

Application of carbon origin: The present study suggests that diamond grain can be produced on shallow surface by shocked process on carbon bearing sediments. Experimental shocked process formed high-pressure form is required careful interpretation on the grain formation of shallow or deep interior origin [2-4].

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Research Activities in the Laser Ablation Geochemistry Laboratory at the University of Ottawa

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Equipped with a Photon Machines 193nm Excimer laser and an Agilent 7700x ICP-MS, the Laser Ablation Geochemistry Laboratory at the University of Ottawa has recently started to welcome users interested in high-spatial resolution trace element geochemistry and U-Pb geochronology. With applications that span a wide range of Earth Science fields, the facility is a new addition to Canada's capital geoscience research network.

A major pole of activity is the analysis of trace element composition of iron, titanium oxides and apatite from magmatic and hydrothermal ore deposits. Investigation into the common use of NIST610/612 as the calibration standard for Fe-rich minerals, compared to other widely available Fe-rich glasses such as GSE-1G, is being assessed using in-house magnetite (BC28) standard.

Other areas of research include trace element analysis of zircon from porphyry Cu-Au related granitic rocks. Ce and Eu anomalies in zircon are used to evaluate the fertility of porphyry intrusions for mineralization. Recent internal developments in U-Pb analysis of zircon (using 91500 and Plešovice) have allowed us to date zircon as part of a tectonic/exhumation rate study.

A final research component involves the trace element analysis of calcite. These projects are using this data to determine the source(s) and timing of fluid migration associated with calcite vein formation in low-permeability Ordovician limestones in southern Ontario. The development of in-house calcite standards and optimization of the data reduction routine (i.e. use of NIST612 vs MACS3) have been valuable areas of this research.

Determination of trace element zoning in mineral and biological samples using LA-ICPMS transect line profiling

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Transverse profile analysis on minerals and biological samples has been developed in the Mass Spectrometry Laboratory of the Andean Geothermal Center of Excellence (CEGA), Universidad de Chile. The equipment used in all the analyses is an ArF 193nm laser Analyte G2 ablation system coupled to an ICP-MS iCAP Q.

We have successfully performed transverse profiles in different silicate minerals such as olivine, pyroxene and plagioclase from the southern Chilean volcanic arc. Different reference materials, such as NIST 610 and BHVO-2G, have been analyzed to calibrate and validate the analytical procedure. Variations of trace element concentrations in these minerals are used to have a better understanding of the magmatic reservoir evolution.

Transverse profile analysis was also applied on magnetite grains from several orebodies from Kiruna-type deposits in northern Chile. Concentrations of rare earth elements and critical geochemical tracers such as V, Al, Ti, Cr and Mg were determined in zoned magnetite grains. Preliminary data shows a distribution which is consistent with an early magmatic stage of crystal growth and a possible later hydrothermal rim.

Marine biology applications have also been developed in our lab. Specifically, we have performed trace element transects on sagittal otoliths from Catfish *Genidens barbus*. Using the MACS-3 standard, transects of Sr:Ca and Ba:Ca ratios were measured. These measurements are a powerful tool for stock identification and to determine the annual migratory patterns between different fluvio-marine environments such as freshwater, estuarine and marine waters.

Monazite and Xenotime Pb/U dating by LA-ICP-MS: Importance of Operating conditions for accurate analysis.

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Analysis of monazite by LA-ICP-MS is well established ^{1,2} as an accurate technique for obtaining Pb/U ages for geological applications, however LA-ICP-MS Pb/U dating of xenotime has been less studied. This study investigates the prospect of using monazite to calibrate xenotime Pb/U ages as the latter have very few well characterized standards. Previous work by Liu et al ³ shows that xenotime Pb/U ages are only accurate when calibrated on a xenotime of known age, and not on monazite, however previous analyses on the Trimouns xenotime⁴ at the University of Tasmania suggest use of monazite calibration gives accurate Pb/U age for xenotime.

This study utilizes a large crystal of xenotime from Novo Horizonte, Brazil and an in-house monazite megacryst with ID-MC-ICP-MS age. LA-ICP-MS analyses are conducted using an ArF excimer laser coupled to an Agilent 7900 ICP-MS. To better understand difference in ablation between these two minerals, a series of tests were conducted at different spot sizes, laser fluences and ICP-MS residence times (controlled by the distance of the load coil to the sample cone). Results presented will show the effects of these variables on Pb/U ages for xenotime calibrated on monazite. These results suggest laser fluence is an important parameter in controlling the Pb/U fraction and matrix effects between these two minerals and that other effects, such as plasma conditions are relatively minor. This suggests the Pb/U fractionation is predominately a laser ablation phenomenon for these two minerals.

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Is Sphene ‘Recycled’ in the Tuolumne Intrusive Complex?

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High-precision U-Pb zircon ages from the Tuolumne Intrusive Complex (TIC) indicate that zircons from older, outer units are commonly recycled into younger, inner units [1]. Intracrystalline trace element zoning patterns and textures of sphene were investigated to assess whether these crystals are also recycled. If recycling of sphene is prevalent in the TIC, then the cores of some sphene from interior units should be compositionally and texturally distinct from their rims and similar to sphene from the older, outer units.

Sphene trace element compositions were collected by LA-ICP-MS from the outer Kuna Crest unit and two interior units: equigranular Half Dome and porphyritic Half Dome. BSE imaging commonly shows oscillatory, sector, and patchy zoning. In any given sample, the larger, more euhedral sphene typically has the highest REE and Y abundances, negative Eu anomalies, and the highest temperatures of crystallization [2]. Smaller, anhedral, and interstitial sphene is instead characterized by lower REE and Y, positive Eu anomalies, and lower crystallization temperatures [2]. Sphene from a given sample is typically normally zoned, with linear compositional trends in compatible vs compatible element plots (e.g. Y vs Sm). Sphene from each TIC unit displays a distinctive trend; however, intra-unit trends generally overlap, with only subtle differences between intra-unit samples. Thus, if recycling of sphene occurred in the TIC, it was restricted to intra-unit recycling.

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Correlating Cu-Fe Sulfides and Au Mineralization in the Ertsberg-Grasberg District of Papua, Indonesia using LA-ICP-MS: Comparing Bornite, Chalcopyrite, and Native Gold Trace Element Variation

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The Ertsberg-Grasberg District in Papua, Indonesia, hosts two of the largest intrusion-related Cu-Au deposits in the world: the Ertsberg Intrusive System, a hybrid porphyry-skarn deposit and the Grasberg Igneous Complex, a high-grade porphyry deposit. Cu mineralization within the Grasberg porphyry and Ertsberg skarn systems consists primarily of bornite and chalcopyrite, whereas native gold grains occur as inclusions within, or along boundaries of, these minerals (Rubin and Kyle, 1997). At hydrothermal ore-forming temperatures (~300° - 700° C) bornite and chalcopyrite can host up to 1800 ppm Au within the sulfide lattice or as nano-inclusions (Kesler et al., 2002; Fraley and Frank, 2014). Upon retrograde cooling of the hydrothermal system, the capacity of the Cu-Fe sulfides to host Au decreases significantly to ~10 ppm, suggesting that the Au would become unstable within the Cu-Fe sulfide matrix and could passively migrate out of the sulfides and coalesce to form native gold grains. The traditional model for native gold deposition in large-scale porphyry and skarn systems relies primarily on fluid pulses and does not consider gold contributions from gold within Cu-Fe sulfides. We are using LA-ICP-MS to assess and compare trace element geochemical variation within the Cu-Fe sulfides in the porphyry and skarn deposits in the district. Using LA-ICP-MS, we will also compare the trace element geochemistry between skarn- and vein-hosted bornite and chalcopyrite. Additionally, trace element variation of native gold in the high-grade porphyry stockwork will be determined using small (<10 µm) spot analyses. These geochemical data will be used to better constrain the geochemical variance between the primary sulfide minerals within the district, and potentially to refine the mineralization mechanisms for Cu-Fe sulfides and native gold grains.

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GENERAL ISSUES

Improved Spatial Resolution of LA-ICP-MS Trace Element Analysis in Plagioclase

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Many naturally occurring materials such as crystals, otoliths and speleothems have chemical variations that record important information on the conditions of their formation. In many cases, the spatial variation in composition records temporal changes in the environment in which these materials form. In order to interpret this information, we must extract it at a spatial scale sufficient to resolve the chemical changes with both precision and accuracy. Here we report high spatial resolution trace element analyses of plagioclase crystals by LA-ICP-MS using an XY-Theta aperture mask. Analyses were performed as line of spot transects using a 5 x 50 μm rectangle and a 5 μm step length, resulting in discrete analyses with no overlap and no space between spots. This approach results in 5 μm spatial resolution in the direction of the analytical traverse, but also maintains higher count rates to improve precision and signal/noise ratio. The 5 x 50 μm spot is equivalent in area to a circular spot of $\sim 18 \mu\text{m}$ diameter, resulting in greater than a factor of 3 improvement in spatial resolution at similar precision. Likewise the 5 x 50 μm spot has an area that is ~ 12 times greater than a 5 μm circular spot, resulting in precision that is ~ 3.5 times improved. Analytical uncertainties (2 SE) for individual plagioclase analyses are $< 10\%$ for most trace elements. Most trace elements are also within 10% of the accepted values for repeat analyses of the ATHO-G standard. For cases where the orientation of chemical variations in a material is known, these rectangular spots can greatly improve spatial resolution without loss of precision.

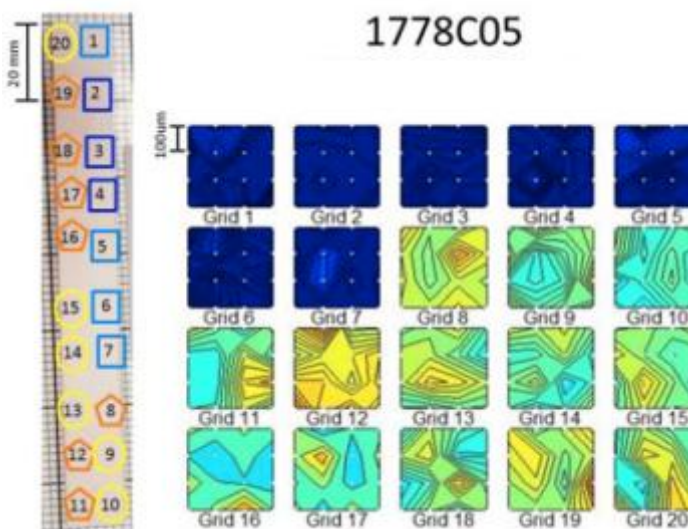
In Praise of Plasmas: The Quantagenetics® Approach to Material Classification

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Emission spectra from LIBS (Laser Induced Breakdown Spectrometry) plasmas contain useful information on the concentrations of all elements, some isotopic ratios, and the electronic structure of ions prior to ablation. Quantagenetics® uses multivariate analysis of the plethora of information in LIBS spectra to classify materials with information that uniquely represents their compositions and history. This work presents three examples of the Quantagenetics® method. In the first study, 64 spectra were acquired from each of 510 emeralds from 18 Colombian mines. Using a multivariate leave-one-out method based on the Euclidian distance between spectra, spectra were assigned to mines, establishing a reference database. Individual samples compared with that database matched specific mines with accuracy of 98% to 100%. In a second study, a single bar of 17-4 steel was cut into 90 coupons. No treatment was applied to 30 coupons; the other two groups of 30 were heat treated by different methods. Each coupon was analysed in 64 spots; 97.8% of the spectra were correctly classified to the correct treatment. The composition of the three groups is essentially the same, but the structure may differ. The third study involves heterogeneities of ceramic test coupons. Compositional maps were constructed that compare the spectrum from each point in a 4X4 grid to the most common spectrum for the material. Blue colors indicate similarity; warm colors indicate differences. In the example here, Grids 1-7 are the most homogeneous and similar to the norm, while Grids 8-20 are heterogeneous with compositions different from the norm. Inspection of individual spectra can uncover the compositional or structural causes of the heterogeneities. The Quantagenetics® method is rapid, accurate, and classifies materials without using human judgement.



Enriched Stable Isotope Target Preparation at the Oak Ridge National Laboratory

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Since the 1960s, the U.S. Department of Energy (DOE) Isotope Program, through the Stable Isotope Group at the Oak Ridge National Laboratory, has been developing and supplying enriched stable isotope targets for nuclear, medical, academic, and industrial research around the world. This group also maintains and distributes the DOE inventory of enriched stable isotopes. Chemical and pyrochemical techniques are used to prepare enriched stable isotopes from this inventory in the desired chemical and physical form. Metallurgical, ceramic, or vacuum processing methods are then used to prepare the isotopes in a wide range of physical forms—from thin films, foils, and coatings to large fabricated shapes—to meet the needs of experimenters. Significant characterization capabilities are also available to assist in the preparation and evaluation of these custom materials. This work is part of the DOE Isotope Program, Office of Nuclear Physics within the DOE Office of Science. A goal of this program is to enable research and development. This presentation will focus on the custom preparation of enriched stable isotope targets and other research materials.

LA-ICP FUNDAMENTALS AND PARAMETERS

Spectral and Non-spectral Matrix Effects during High Precision Isotope Ratio Measurements by Laser Ablation MC-ICP-MS

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Analytical advances have resulted in the ability to perform high precision *in situ* measurements of S, Sr and Pb isotope ratios by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) in environmental and geological samples. Much of the previous work reported for LA-MC-ICP-MS isotope analyses has been conducted in a relatively narrow range of sample matrices with the effects of polyatomic interferences, isobaric interferences, and plasma dynamics still poorly understood for a great many matrices. The extent of matrix effects both spectral and non-spectral on the precision and accuracy of isotope ratio measurements need to be evaluated for sample matrices. For example, sulfate sulfur (barite, anhydrite, jarosite), sulfide sulfur (pyrite, chalcocite, sphalerite) and sulfide sulfur in mid-oceanic ridge basalts are comprised in different matrices as well as sulfur in varying oxidation states which results in non-spectral matrix and plasma dynamic effects resulting in inaccurate isotope ratios. Another example is the possible formation of a polyatomic interference or the presence of phosphate during *in situ* $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of bio-apatite materials (i.e. fish fins, scales and teeth) resulting in variable $^{87}\text{Sr}/^{86}\text{Sr}$ values as a function of phosphate concentration. Lastly, *in situ* Pb isotope ratios were determined to vary as a function of laser scan speed caused by plasma loading when TI from an independent introduction system was used to correct for mass fractionation. Here we report on non-spectral and spectral interferences using dual system introduction (desolvation nebulizer with laser ablation) and reverse split flow (dual laser ablation systems) LA-MC-ICP-MS. We conclude the need for continued development of *in situ* isotope reference materials in which the element of interest has a known isotopic value but variable matrix composition that can assist in precise and accurate measurements of *in situ* isotope ratios for a wide range of matrices. The development of matrix matched isotopic reference materials is critical in identifying and correcting spectral and non-spectral matrix effects.

VENDOR AFFILIATED POSTERS

Analysis and Advanced Interference Removal by QQQ-ICP-MS for Elemental Analysis

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The analysis of trace elements by single quad ICP-MS has continuously improved providing greater sensitivity and interference removal using collision/reaction cell technology. The introduction of the 8800/8900 QQQ ICP-MS/MS with unit mass resolution provides analysis of elements at much lower levels of detection with superior interference removal. Controlling Q1 to a unit mass resolution allows for accurate mass shift of either the analyte or interfering molecule providing a more accurate and precise analysis of complex matrices. The techniques and benefits of the Agilent QQQ ICP-MS will be discussed.

Towards Real-Time Multi-element Imaging of Solid Samples with Laser Ablation Inductively Coupled Plasma Time-of-Flight Mass Spectrometry (LA-ICP-TOFMS)

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LA-ICP-MS trace element imaging of solid samples at the micro-scale has become an important tool in geological, biological, and medical studies. Recent advances in laser ablation setups, including fast ablation cells and sample introduction systems, have paved the way for rapid, high-resolution imaging [1, 2]. These imaging methods are especially efficient when coupled to fast time-of-flight mass spectrometers (TOFMS) that allow for the detection of single laser pulses while recording the full mass spectrum simultaneously [3].

However, a limitation of such imaging experiments is that they are often recorded “blindly” because the images only become visible after elaborate offline data processing has been performed. This may pose the risk of losing valuable analytical time and/or precious sample material.

Here, we present recent developments in software design for the icpTOF (TOFWERK AG, Thun, Switzerland), a relatively new, commercially available time-of-flight mass spectrometer (<http://www.tofwerk.com/icp/>). We introduce an integrated icpTOF control software –TOFpilot – which, in addition to greatly simplifying the workflow for the end-user, can construct multi-element, high-resolution images during the data acquisition process (online). We demonstrate the functionality of this software on a zoned garnet sample. The semi-quantitative multi-element images can be refined and quantified during post-processing (offline), using third-party software, such as lolite^[4].

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Gold deportment using LA-ICP-MS for high-resolution elemental microscopy

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Understanding the distribution of gold in an ore body is essential for making practical decisions about resource economics, mining methodologies, economic feasibility, milling and metallurgy. Gold found in silicate minerals requires a different milling procedure than native gold or gold occurring in sulfides. Ore that has toxic co-products requires specific environmental management techniques, and may result in penalties at the smelter.

Recent developments in laser ablation ICP-MS allow the rapid generation of high-resolution elemental maps for use in gold deportment. Example thin sections and concentrates are mapped to demonstrate the technique.

LA icpTOF: the Ultimate Tool for Rapid Elemental Screening of Carbonates

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Elemental mapping of geologic materials is rapidly becoming routine in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The speed and high spatial resolution it offers makes this analytical technique highly time- and cost-effective.

We present new data describing a fast and accurate screening procedure for spelean carbonates. Speleothems are outstanding proxies of past climate information, as well as robust candidates for U-series geochronology. In this respect it is critical to identify samples (and intra-sample areas) that can negatively impact data quality for U-series investigations (*i.e.*, high detrital Th) and stable isotope and/or elemental measurements. High-resolution, rapid elemental imaging by means of LA icpTOF was used to resolve growth increments < 40μm that show chemical fingerprints of detrital input (*e.g.*, high ²³²Th and selected REE, low ²³⁸U/²³²Th ratio). Furthermore, the method allows to differentiate individual crystals within a single growth zone. Coupling of the highly sensitive, simultaneous, and fast TOFWERK's icpTOF with the Teledyne CETAC's Aerosol Rapid Introduction System (ARIS) allows for much faster acquisition of data necessary for paleoclimate reconstructions.

Rapid imaging of stalagmites by means of LA icpTOF dramatically decreases sampling uncertainty and increases the accuracy and precision of the data used in paleoclimate research. The screening procedure is very fast, consequently saving valuable analytical time and resources. The method is easily adaptable to other types of samples that are relevant to paleoclimate studies (*e.g.*, corals, ice cores, etc.).

High-Resolution, High-Speed, Multi-Element Imaging of Garnet using LA-ICP-TOFMS – A Direct Comparison to Conventional EPMA Imaging

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Garnets are well known for their chemical zoning which can be used to recognize thermo-tectonic events that affected the host rock. Traditionally, the electron probe microanalyzer (EPMA) was the technique of choice for unveiling such complex zonalities. However, while EPMA imaging yields high-resolution results for major and some minor elements, it is often a resource-consuming technique.

Recent developments in laser ablation (LA) instrumentation, such as fast-washout ablation cells and low dispersion sample transport technologies, have transformed this technique into a time-effective, high-resolution alternative to EPMA imaging. When coupled to a fast time-of-flight mass-spectrometer (TOFMS), LA imaging becomes an extremely powerful imaging tool, allowing for micron-scale spatial resolution to be achieved using single laser pulse analysis. The analytical setup used for this contribution comprises a Teledyne Photon Machines Analyte G2 LA system, coupled via the Aerosol Rapid Introduction System (ARIS) to a TOFWERK icpTOF mass spectrometer.

Large (> 5 mm) garnet porphyroblasts from medium-grade metamorphic rocks from the South Carpathians (Romania) were imaged in less than 60 minutes and data compared to previously acquired EPMA images. The resolution of the LA icpTOF images matches the EPMA resolution, while the wealth of data for major, minor, and trace elements allows for much more detailed information to be extracted, such as identification of trace element zoning, including highly detailed REE patterns, highlighting elemental correlations and chemical substitutions mechanisms, and revealing inherited structural features (i.e., foliations) that were not observed on EPMA images.

Advanced Techniques for Overcoming Interferences in Laser Ablation-Based Bioimaging

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In the last couple of years, an increasing number of interesting studies in the field of Life Sciences – especially Metallomics – have been published that employ different imaging techniques to, for example, understand the fundamental principles of cancer growth or illuminate the importance of the availability or absence of different (trace) elements in crop production. For trace and ultra-trace elemental analysis, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become one of the methods of choice due to its high sensitivity, linearity over several orders of magnitude and the possibility for quantitation. One of the major challenges, however, is the presence of isobaric and polyatomic interferences leading to false positive results. This is especially important for the transient signals produced by LA-ICP-MS, where it is hard to predict if the signal is affected by interferences.

In the work presented in this poster, chemical resolution, i.e. the utilization of selective mass shift reactions performed on the analyte or plasma-based interferences using triple quadrupole ICP-MS, was used to improve analytical figures of merit for difficult elements such as iron, selenium, phosphorus and others. This is of particular importance for bioimaging samples, which often consist of thin sections and need to be analyzed at high spatial resolution, leading to only minute amounts of sample being introduced into the plasma per laser shot.

Investigation into Using Laser Ablation ICP-MS as an Industrial Forensics Tool

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Industrial manufacturers need a fast way to tell if two products are different from one another in order to figure out why one product may fail or has significantly different characteristics than the other. The product types needing testing may include plastics, films, coatings, coating substrates, etc. Methodologies currently in use to perform this type of “industrial forensics” analysis include microscopy, FTIR, SEM, Thermal Desorption, and micro EDXRF. However, the need to determine very low levels of different elements in these types of substrates currently exceeds the detection capabilities of these technologies. This talk will present several case studies performed to see if Laser Ablation ICP-MS can offer a fast and easy to use solution for these types of industrial forensics studies in terms of detection limits achievable, minimal spot size for distinct feature analysis and mapping of elemental content and differences.

Accurate and Precise U-Pb Age and Hf Isotope Composition Determination using the Laser-Ablation Split-Stream Technique

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Most traditional geochronology studies have been conducted to measure dates in one analytical session and elemental composition in another session. This requires a large area for analyses, also the isotopic and elemental information are not extracted from the same volume of material [1]. In order to overcome these disadvantages, the laser-ablation split-stream (LASS) technique was first introduced by Yuan et al. [2], utilizing a laser to ablate the same sample volume and split the aerosol stream into an MC-ICP-MS for Hf isotope analyses, and a Quadrupole or high-resolution ICP-MS for U–Pb age determination. The LASS technique has a number of technical advantages comparing to the traditional analytical techniques, and is becoming a powerful tool for concurrent determination of U-Pb age and Hf isotope composition of zircon [3].

This work describes the analytical setup using a NWR213 laser system coupled to a Nu AttoM High Resolution ICP-MS and a Plasma 3 MC-ICP-MS. Precise and accurate measurements of 6 reference zircons with well-characterized ages and Hf isotopic compositions are being demonstrated. Results show the capability of the LASS technique in significantly improving the analytical precision and reducing the volume of ablated material.

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Analysis of nutrients in plants leaves using Laser Ablation-Inductively Coupled Plasma Optical Emission Spectrometry with Carbon as an Internal Standard

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The essential nutrient elements in plants can be classified into two groups: macronutrients at percentage concentrations such as N, P, K, Mg, Ca, S, and micronutrients, at mg kg⁻¹ levels such as Fe, Mn, Zn, Cu, Ni, B, Mo, and Cl. The determination of these elements is important as changes in concentration could compromise essential functions in plant metabolism. Laser Ablation Inductively Coupled Plasma Optical Emission Spectroscopy (LA-ICPOES) is not as widely used for quantitative analyses of plant materials compared to LIBS and LA-ICP-MS, even though LA-ICP-OES offers simultaneous multi-element detection capability, with low limit of detection high spectral selectivity by using high-resolution spectrometers modern instruments with dual view technology offer an increased dynamic range of concentration (from low ppm level to major (%) elements present in samples). The primarily goal of this study was to explore the benefits of the synchronous vertical dual view mode (SVDV) ICP-OES for determination of essential elements in plants using laser ablation as a sampling tool. In this study were also addressed two different matrix effects: a “natural matrix effect” which is related to the natural differences between the samples, and a “synthetic matrix effect” which is generated when a binder is added to the sample

Environmental Forensics of Contaminated Plant Samples Using a Tandem Laser Ablation (LA) and Laser Induced Breakdown Spectroscopy (LIBS) Instrument

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The J200 Tandem LA – LIBS instrument from Applied Spectra, Inc. provides the unique capability of combining the analytical benefits of both LA-ICP-MS (Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry) and LIBS (Laser Induced Breakdown Spectroscopy). Specifically, LIBS can be used for the analysis of H – Pu, which includes non-metals such as H, N, O, and halogens (e.g. F) that are difficult or impossible by conventional ICP-MS systems. When coupled with an ICPMS instrument, the J200 can perform LA-ICP-MS measurements focusing on trace elemental and isotopic ratio compositions. This tandem instrument, in combination with an ICP-MS (Analytik Jena Plasma Quant Elite ICP-MS), expands the dynamic range of analysis from sub-ppb levels (or the absolute detection limits of the ICPMS), to % levels with LIBS.

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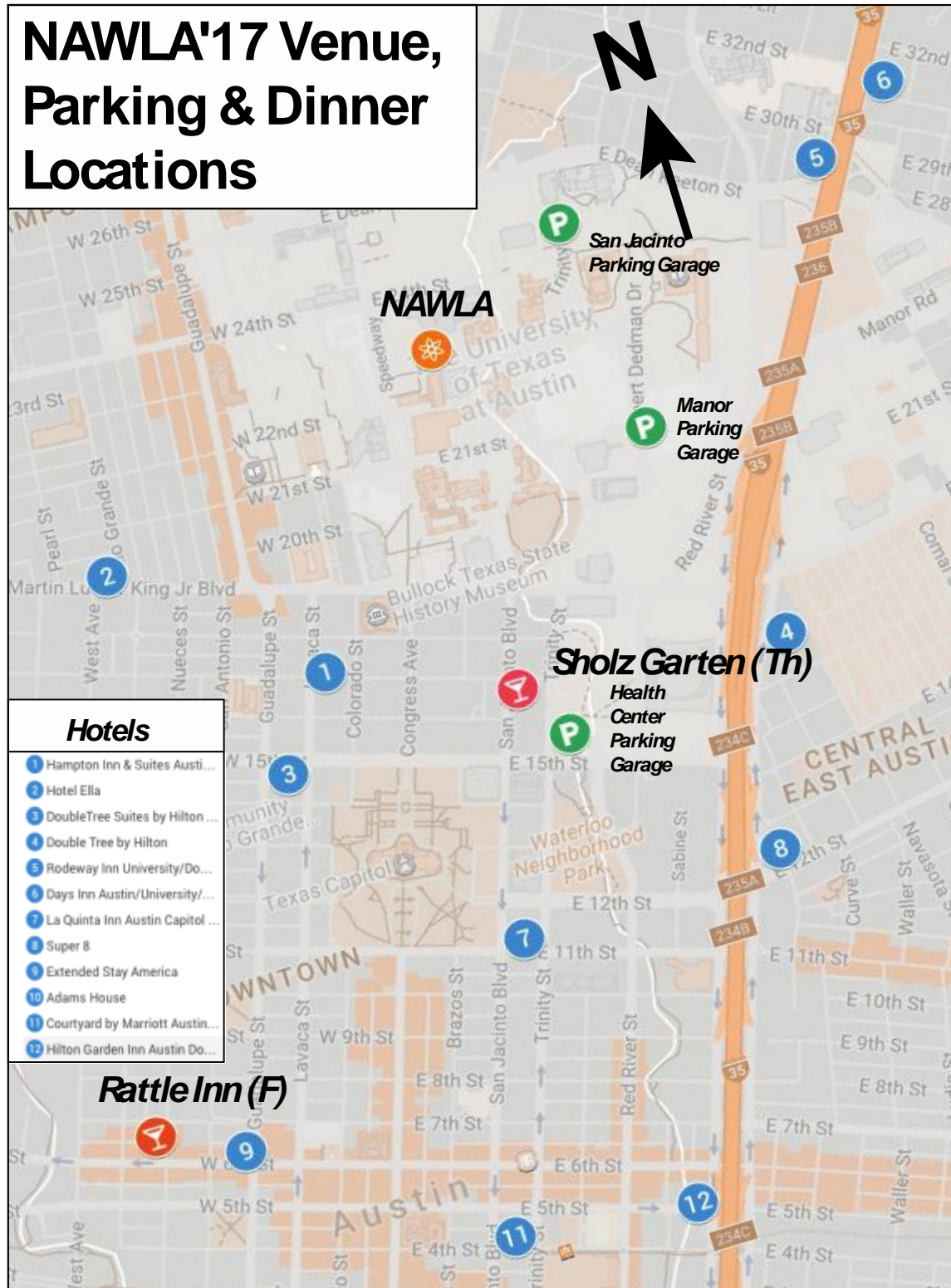
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Atkinson, H.	39	Hattendorf, B.	13
Ausmus, C.	83	Hattori, K.	75
Avigliano, E.	76	Haynes, J.	44
Barnes, C.G.	78	Hergt, J.M.	28
Barra, F.	72, 76	Herrmann, A.D.	44
Beard, B.L.	23	Herzka, S.S.	62
Billeter, E.	13	Hickman, E.	83
Black, J.R.	28	Hobbs, J.A.	40
Bleiner, D.	16	Hodges, K.V.	19
Borovinskaya, O.	17, 27	Holm-Denoma, C.	33
	57, 83	Horne, A.	19
	90, 91	Horstwood, M.S.A.	49
Bouman, C.	49	Houk, S.	11
Bradshaw, R.W.	81	Hutchinson, R.	89
Breglio, A.	53	Jackson, S.	14, 24, 26
Burger, M.	13	Jo, G.	60
Bussweiler, Y.	88, 91	Johnson, C.M	23
Cabri, L.J.	24	Jones, L.C	87
Carmichael, R.H.	41	Kamber, B.	57, 66
Chew, D.	66	Karst, U.	92
Chirinos, J.	95	Käser, D.	13
Cloos, M.	31	Käslin, J.	13
Colucci, M.T.	54, 95, 96	Kelvin, M.	36
Cottle, J.	65	Kent, A.J.R.	81
Craig, G.	49	Kimmel, J.	88
Crouch, P.	28	Kinney, M.	62
Cubosin, M.	17	Kiseeva, E.S.	85
Cunningham, L.	53	Koch, J.	13
DaCosta, K.P.	41	Koenig, A.E.	85
Danielson, L.	46	Kohin, S.	62
Danyushevsky, L.	17, 77	Kyle, J.R.	31, 71, 79
Dare, S.	75	Kysenius, K.	28
Davies, J.H.F.L.	67	Laforce, B.	27
De Rijcke, M.	27	Leisen, M.	72, 76
Dewar, H.	62	Leslie, L.S.	44
Disch, B.	64	Lewis, L.S.	40
Donard, A.	50, 64, 94	Leybourne, M.	36, 66
Drăgușin, V.	90	Lloyd, N.	49
Fernandez, K.	53	Loader, N.	39
Fisher, C.M.	32	Longerich, H. P.	12, 24, 32
Frey, H.M.	73	Lund, E.	61
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Garofalo, P.S.	13	Manon, M.R.	73
Girard, G.	70	Marillo-Sialer, E.	28
Glessner, J.G.	40	Martin, C.	45
González, J.J.	21, 54,	McDonald, C.S.	19
	95, 96	McLachlin, K.	89

McLean, N.	30	Sosa-Nishizaki, O.	62
McManus, C.E.	82	Sperling, M.	92
McMillan, N.J.	82	Spero, H.	42
Meffre, S.	77	Spetzler, T.	88
Memeti, V.	78	Stockli, D.F.	18, 31
Mercer, C.M.	19	Stockli, L.D.	31
Miller, N.R.	62, 71, 79	Stremtan, C.	57, 70, 90, 91
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Morata, D.	72, 76	Takatori, Y.	74
Morfin, S.	75	Tanner, M.	17, 88
Moscatti, R.	33	Tatum, A.	83
Neymark, L.	33	Thomas, C.L.	93
Nkuna, W.	36	Thompson, J.	17, 77
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O'Connor, C.	89	Todorov, T.I.	37, 60
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