UNIVERSITY OF
NOTRE DAME

JUNE 5-9, 2023

PROGRAM VOLUME

WELCOME to NAWLA2023!

Subsequent postponement of our 2021 meeting, several of us wondered if there was general interest to resurrect NAWLA, or was it to become distant memories of past, highly productive, and well attended meetings? In particular, given that the venue moved from the University of Texas (Austin) to here at the University of Notre Dame in South Bend, Indiana. Well, given the positive response to various advertisements via social media accounts, distribution of flyers, and cajoling by committee members about our meeting at various conferences, our fears were put to rest as we accepted 73 total abstracts (43 oral, 30 poster) from participants stemming from all corners of the globe. We will be hosting attendees (>120 total) from countries as distant as Australia, India, China, and South Africa, and strong delegations from both Europe (Austria, Germany, Ireland, the Netherlands, Norway, Slovenia, Spain, Sweden, UK) and North America (Canada, Mexico, USA)!

NAWLA2023 features a different format compared to previous meetings in that five workshops are integrated within the scientific program and not scheduled as pre-meeting activities. Our workshops are meant to provide a platform in which world leaders in their respective LA-ICP-MS-based research fields can convey their expertise and knowledge in a more informal and interactive setting with participants. The five workshops cover topics that consist of both well-established fields, such as U-Pb geochronology, developing strategies for reference standards and materials, and data processing methodologies, to burgeoning research themes such as bioimaging. Also, as a first, our meeting will feature seven "vendor talks" in which sponsors will have the opportunity to transmit information in relation to their latest instrument developments, technologies, and/or protocols meant to elevate and transform our future LA-ICP-MS research endeavors.

Naturally, this meeting would not be possible without the tremendous support of our 14 vendor partners! Attendees will have the opportunity to interact with our sponsors in the exhibitor booth area, which is located adjacent to the main lecture hall in the McKenna Conference Center; for participants' convenience, all meeting-related activities will be held within this newly constructed conference center.

This meeting could not have taken place without the assistance and invaluable contributions from organizing and scientific committee members and Harriet Baldwin, conference coordinator (*Emerita*) at Notre Dame. Harriet's extensive expertise and knowledge of the "ins-and-outs" of conference planning at Notre Dame greatly facilitated our endeavor!

We wish everyone an enjoyable and highly productive meeting and hopefully, you will have time to relish and admire the beauty of our wonderful campus and Midwestern hospitality. Who knows, you may even come across a leprechaun…….
GO IRISH!

Warm regards,

Tony Simonetti, *Chair, Organizing Committee*

Paul Sylvester, *Chair, Scientific Committee*

ABLATE LIKE A CHAMPION TODAY

Scientific Committee

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Organizing Committee

Antonio Simonetti – *Chair*, conference organization

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Mike Laughery – *Ligero Technical Services* - Sponsor coordinator, meeting promotion, logistics

Ciaran O'Connor – *Elemental Scientific Lasers* - Sponsor coordinator, meeting promotion, logistics

Paul Sylvester – Meeting promotion, logistics

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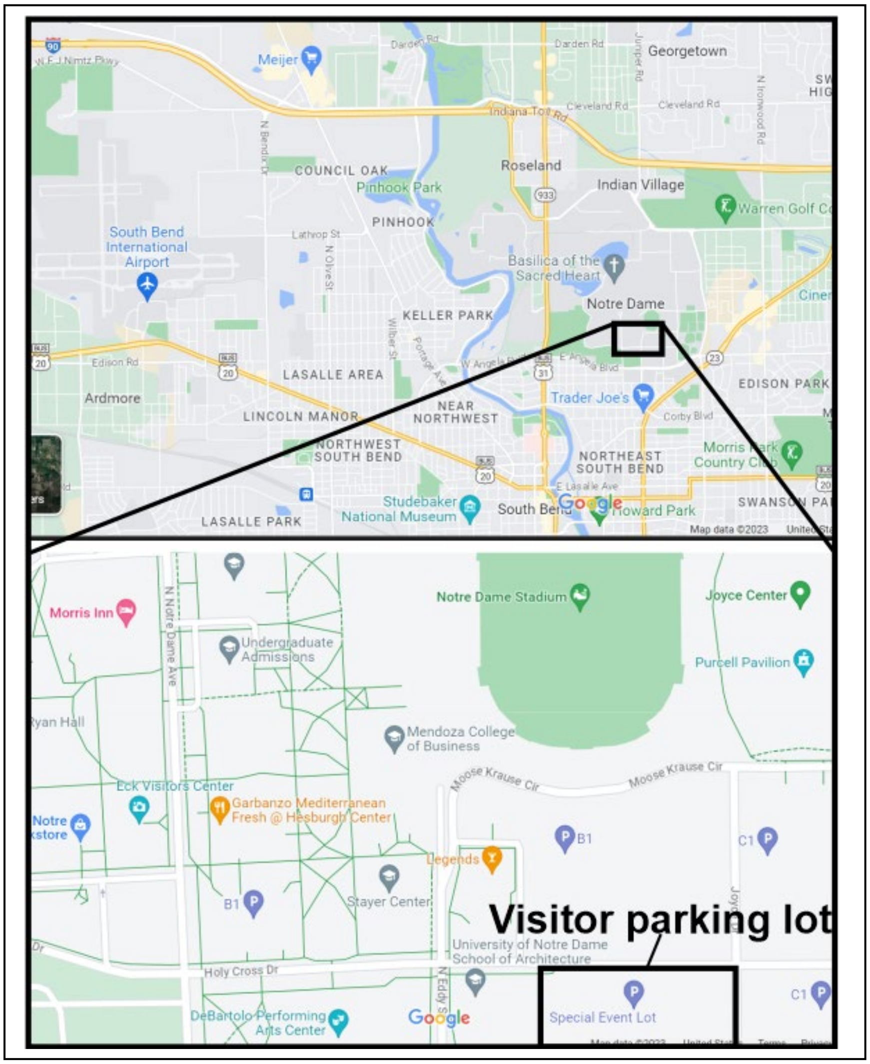
UNIVERSITY OF NOTRE DAME – Area Map & Parking

The campus of the University of Notre Dame is located east of South Bend International Airport, approximately 15 minutes' drive.

If you are arriving by car, you have several options to park your vehicle.

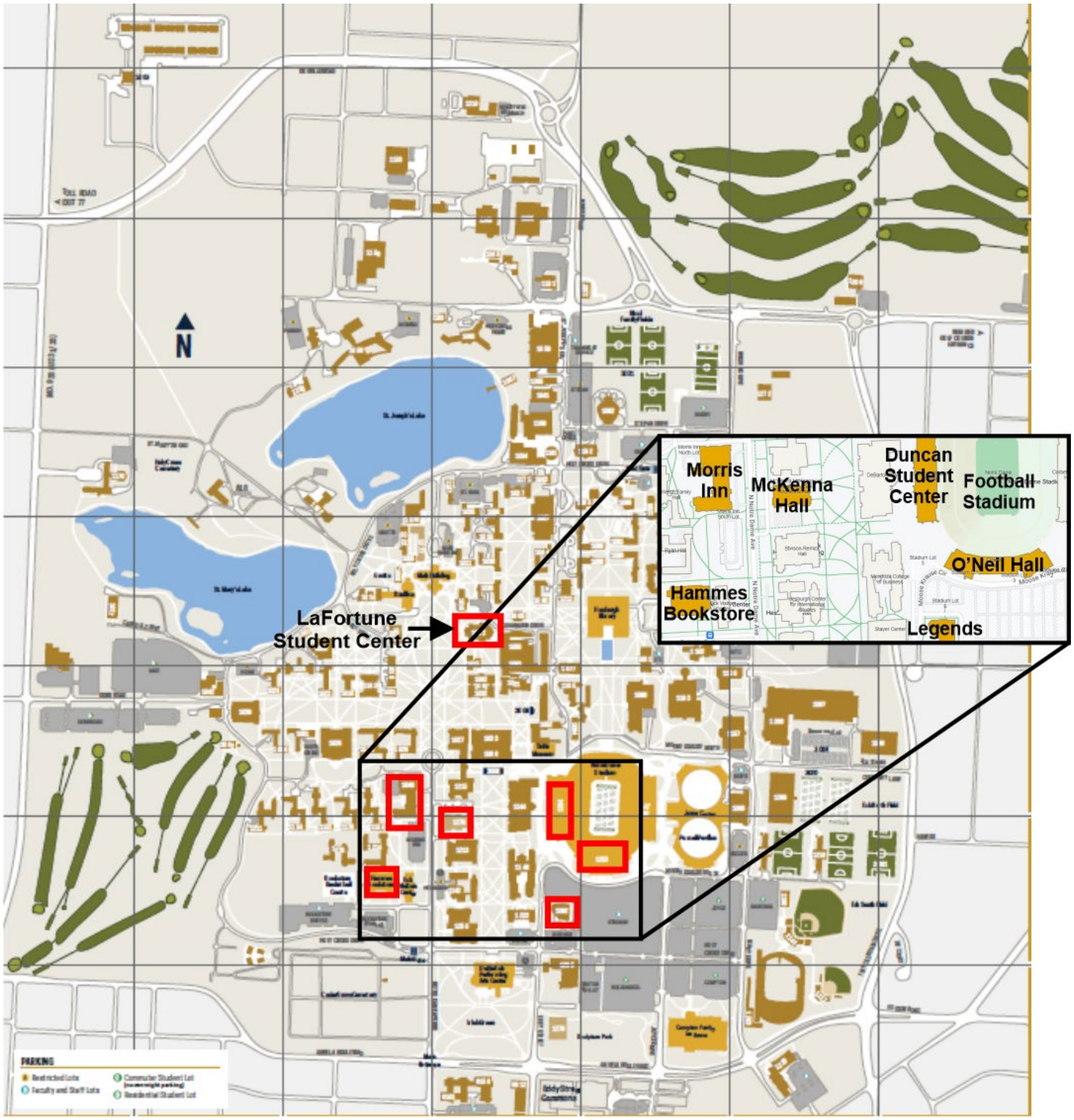
If you are staying at the ***Morris Inn***, then $15 self-parking is available at the ***Morris Inn lot*** (on a first come, first served basis).



If your accommodations are off campus, then you can park your vehicle in a ***visitor lot*** on the south side of campus (see bottom map for location). The primary visitor lot is ***Walsh Visitor lot***, and visitor parking is also available in ***Compton, Walsh Architecture, and Baseball lots***. These lots are ***pay-to-park*** with free one hour parking (you will see pay stations where you will need to enter your license plate number).

The campus map (and inset) on the following page outlines the locations of meeting-related venues, including the ***Morris Inn***, and the ***McKenna Conference Center*** (relative to the iconic football stadium), and the ***Duncan Student Center*** and ***O'Neil Hall***, which will host the Wednesday and Thursday evening sponsored suppers, respectively. Also shown are the locations of several campus eateries and the ***Hammes Bookstore*** should you wish to purchase Notre Dame memorabilia!

UNIVERSITY OF NOTRE DAME - CAMPUS MAP

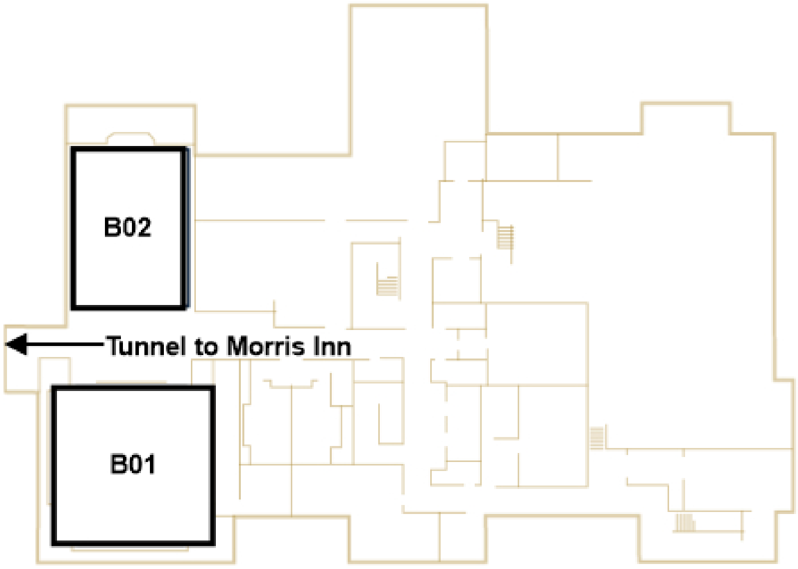


McKenna Hall – Venue for NAWLA2023
Morris Inn Hotel – Rohr's Tavern & Bistro
Duncan Student Center – 7th floor – **Dahnke Ballroom**, location of Wednesday evening dinner
Duncan Student Center – location of eateries (Haggerty Family Café, Modern Market, Chick-fil-A)
O'Neil Hall – **Foley's Club** – location of Thursday's evening dinner
Hammes Bookstore – location of The Gilded Bean Café & gift shop
Legends – Restaurant & pub
LaFortune Student Center – Starbucks, Flip Kitchen, Smashburger
All locations are within 5 to 10 minutes walking distance from the Morris Inn Hotel.
https://map.nd.edu/#/placemarks//zoom/15/lat/41.69773021194584/lon/-86.23629510771595

MEETING VENUE – MCKENNA HALL CONFERENCE CENTER

Except for the two sponsored evening dinners on Wednesday and Thursday, all meeting-related activities will take place within the 2nd **floor** and **lower level** of the **McKenna Conference Center** (floor plans displayed below). The main entrance to the conference center is located on the ground floor, west-facing doors (facing Morris Inn), and the second floor may be accessed via stairs or an elevator. Attendees will be asked to register and pick-up their conference bag (and materials) at the registration desk on the second floor, which is proximal to the staircase/elevator area, on the morning of Tuesday, June 6th area. **Rooms B01** and **B02** in the **lower level** will be used for distribution of **lunch meals**.

MCKENNA HALL // SECOND FLOOR



MCKENNA HALL // LOWER LEVEL

NAWLA2023 Scientific Program at-a-glance

TUESDAY, JUNE 6th

7:30-7:50 am	Coffee & refreshments	Coffee & refreshments
7:50 - 8:00 am	Opening of Workshop & Welcome Address	Opening of Workshop & Welcome Address
	U-Pb WORKSHOP - Rm# 215/216	**BIO-IMAGING WORKSHOP - Rm# 202**
8:00 - 8:20 am	Dr. Michael Wiedenbeck- Proficiency G-chron	Dr. Brian Jackson talk
8:20 - 8:40 am		
8:40 - 9:00 am	Dr. Matthew Horstwood talk	Dr. Keith MacRenaris talk
9:00 - 9:30 am		
9:30 - 9:50 am	Break	Break
9:50 - 10:10 am	Panel Discussion	Panel Discussion
10:10 - 10:30 am		
10:30 -11:00 am	Break	Break
	U-Pb Geochronology Oral Session	
11:00 - 11:20 am	*Jackson et al. - Pb-U fractionation*	
11:20 - 11:40 am	*Hourigan & Seymour - U-Pb depth profiling*	
11:40 - 12:00 noon	*Horstwood - long-term uncertainties*	
12:00 - 1:00 pm	Lunch Break	
1:00 - 1:15 pm	***Jhanis Gonzalez - Applied Spectra***	
1:15 - 1:30 pm	***Craig Jones - Agilent***	
1:30 - 1:50 pm	*Cottle et al. Petrochronology*	
1:50 - 2:10 pm	*Courtney-Davies et al. - U-Pb hematite*	
2:10 - 2:30 pm	Break	
2:30 - 2:50 pm	*Moller & Pell- U-Pb minerals*	
2:50 - 3:10 pm	*Garber et al. trace element & U-Pb fluorapatite*	
3:10 - 3:30 pm	*Dev & Tomson U-Pb minerals*	
3:30 - 4:00 pm	Break	
	Applications Biology Oral Session	
4:00 - 4:20 pm	*Minaeva et al. LA-ICPMS neuroimaging*	
4:20 - 4:40 pm	*Clance et al. LA-ICPMS dolphin skin*	
4:40 - 5:00 pm	*Chavrez-Ambriz(Bernal)- in situ Sr shark teeth*	
5:00 - 7:00 pm	**ICE BREAKER - EXHIBITOR AREA**	

NAWLA2023 Scientific Program at-a-glance

WEDNESDAY, JUNE 7th

7:30 - 8:00 am	**Coffee & refreshments**
	LA-ICP-MS/MS (SC/MC) Workshop- Rm 215/216
8:00 - 8:30 am	**Nuts & Volts (Dr. Jamie Lewis)**
8:30 - 8:40 am	**Q & A**
8:40 - 9:10 am	**Reaction Kinetics (Dr. Mark Kelinski)**
9:10 - 9:20 am	**Q & A**
9:20 - 9:50 am	**Break**
9:50 - 10:20 am	**Geochronology Applications (Dr. Sarah Gilbert, KEYNOTE)**
10:20 - 10:30 am	**Q & A**
10:30 - 10:50 am	**Panel Discussion**
10:50 -11:00 am	**Break**
	Isotope Applications Oral Session
11:00 - 11:20 am	*Cruz-Uribe et al. Rb-Sr dating*
11:20 - 11:40 am	*Petts et al. Rb-Sr in-situ dating*
11:40 - 12:00 noon	*Telouk et al. hyphenated LA-MC-ICPMS*
12:00 - 1:00 pm	**Lunch Break**
1:00 - 1:15 pm	***Phil Shaw - Nu Instruments LA-TOF-ICP-MS***
1:15 - 1:30 pm	***Nicholas West - Norris Scientific***
1:30 - 1:50 pm	*Thompson & Souders Lu-Hf & U-Pb dating*
1:50 - 2:10 pm	*Oalmann et al. - ICP-TOF-MS - elemental mapping & Lu-Hf dating*
2:10 - 2:30 pm	*Chen & Lu Mg isotopes*
2:30 - 2:50 pm	**Break**
2:50 - 3:10 pm	*Pucas et al. LA-IRMS d13C (presented by Ciprian Stremtan)*
	New Instrumentation/Methods Oral Session
3:10 - 3:30 pm	*Pisonero et al. LA-TOFMS challenging samples*
3:30 - 3:50 pm	*Sala et al. LA-ICP-TOFMS bio-imaging (presented by Kristina Mervič)*
3:50 - 4:10 pm	*Billimoria et al. LA-ICP-TOFMS cells imaging*
4:10 - 4:30 pm	*Savard et al. LA-ICP-TOF-MS imaging melt inclusions*
4:30 - 5:00 pm	**Break**
5:00 - 6:30 pm	**POSTER SESSION**
6:30 - 7:00 pm	**Break**
7:00 - 9:00 pm	**DINNER @ DAHNKE BALLROOM**

NAWLA2023 Scientific Program at-a-glance

THURSDAY, JUNE 8th

7:30 - 8:00 am	**Coffee & refreshments**
	REFERENCE MATERIALS/STANDARDS WORKSHOP - Rm 215/216
8:00 - 8:20 am	**Workshop activities led by Drs. Paul Sylvester, Kate Souders & Jay Thompson; Overview of ref. materials for LA-ICP-MS and lecture by Dr. Nicholas Sharp**
8:20 - 8:40 am	
8:40 - 9:00 am	
9:00 - 9:20 am	
9:20 - 9:40 am	**Break**
9:40 - 10:00 am	**PANEL DISCUSSION**
10:00 - 10:20 am	
10:20 - 10:50 am	
10:50 -11:00 am	**Break**
	New Instrumentation/Methods Oral Session (cont'd)
11:00 - 11:20 am	*Gibbs et al. Instr/Methods Dev*
11:20 - 11:40 am	*Hourigan et al. Cross-calibration SEMs*
11:40 - 12:00 noon	*Williams et al. (EXUM) - Non-laser resonant ionization*
12:00 - 1:00 pm	**Lunch Break**
1:00 - 1:15 pm	***Jonathan Putman - Exum***
1:15 - 1:30 pm	***Derrick Quarles - ESL***
	LIBS Tandem / Laser are Rad / Laser Fund. Oral Sessions
1:30 - 1:50 pm	*Limbeck et al. INVITED LIBS microplastics*
1:50 - 2:10 pm	*Martinez - LIBS environmental medicine*
2:10 - 2:30 pm	*Martinez-Lopez et al. LA-ICP-MS analysis of multivitamins*
2:30 - 2:50 pm	**Break**
2:50 - 3:10 pm	*Andrews INVITED LIBS nuclear reactor develop.*
3:10 - 3:30 pm	*Quarles et al. INVITED LIBS & TOF-ICPMS nuclear*
3:30 - 3:50 pm	*Chiniros et al. INVITED nuclear*
3:50 - 4:10 pm	*Hull et al. INVITED nuclear*
4:10 - 4:30 pm	*Metarapi et al. laser fund.*
4:30 - 5:00 pm	**BREAK**
5:00 -6:30 pm	**POSTER SESSION**
6:30 - 7:00 pm	**BREAK**
7:00 - 9:00 pm	**DINNER @ FOLEY'S CLUB**

NAWLA2023 Scientific Program at-a-glance

FRIDAY, JUNE 9th

7:30 - 8:00 am	**Coffee & refreshments**
	DATA PROCESSING WORKSHOP - Rm 215/216
8:00 - 8:20 am	**Workshop activities led by Drs. Alan Koenig & Leonid Danyushevsky**
8:20 - 8:40 am	
8:40 - 9:00 am	
9:00 - 9:30 am	
9:30 - 9:50 am	**Break**
9:50 - 10:10 am	
10:10 - 10:30 am	
10:30 -10:45 am	***Aaron Hineman - Perkin Elmer***
10:45 - 11:00 am	**Break**
	Applications Geochem. Oral Session
11:00 - 11:20 am	*Danyushevsky & Norris, Uncertainty in Mineral Analysis*
11:20 - 11:40 am	*Page et al. Trace element garnet*
11:40 - 12:00 noon	*Yang et al. Reference Materials*
	Concluding Remarks/address
	END OF CONFERENCE

NAWLA2023 Scientific Program

All meeting events take place in the McKenna Hall Conference Center

TUESDAY, JUNE 6th

7:30 - 7:50 Registration, Coffee & Refreshments……………………..…....… **Exhibitor area**
7:50 - 8:00 Welcome Address………………………………………..………………**Rm 215/216**

8:00 – 9:30 **U-Pb Geochronology Workshop……………………...………...…. Rm 215/216**
Co-convenors: Matthew Horstwood, Michael Wiedenbeck, & Paul Sylvester
8:00 – 8:20 **Michael Wiedenbeck**
Observations from the G-Chron U-Th-Pb Proficiency Testing Program
8:20 – 9:30 **Matthew Horstwood** & Paul Sylvester
LA-ICP-MS U-Pb age determination: a review of recent performance in PT schemes

8:00 – 9:30 **Bioimaging Workshop……………………………………….......…..….. Rm 202**
Co-convenors: Keith MacRenaris & Brian Jackson
8:00 – 8:30 **Brian Jackson** & Tracy Punshon
Biomedical Elemental Imaging as a User Resource
8:30 – 9:00 **Keith MacRenaris**
Systematic approaches for standardization and quantification via LA-ICP-TOF-MS

9:00 - 9:30 Panel Discussion

9:30 – 9:50 **BREAK**

U-Pb Geochronology Workshop (cont'd)……………………...… Rm 215/216
9:50 – 10:30 Panel Discussion

Bioimaging Workshop (cont'd) ……………………………..…...…. Rm 202
9:50 - 10:30 Panel Discussion

10:30 - 11:00 **BREAK**

ORAL SESSION 1: U-Pb GEOCHRONOLOGY……………………………... Room 215/216

Moderated by: Luigi Solari

11:00 **Simon Jackson**, D. Petts, W. Davis, M. Horstwood, & S. Tapster
Mitigation of Pb-U fractionation effects in LA-ICP-MS zircon U-Pb dating

11:20 **Jeremy Hourigan** & N. Seymour
Cycle-by-Cycle Processing of LA-ICP-MS U-Pb Depth-Profile Data

11:40 **Matthew Horstwood**
Long-term Uncertainty Estimation and its Role in the Quantification of U-Pb Age Uncertainties

12:00 – 13:00 **LUNCH BREAK (RM B01, B02)**

VENDOR TALKS SESSION -1………………………………………………….. Room 215/216

Moderated by: Tony Simonetti

13:00 **Jhanis Gonzalez**, C. Sisson, C. Liu, S. Shuttleworth, J. Yoo, & R.E. Russo, ***Applied Spectra***
Advances in Tandem LA – LIBS Technology and Data Analysis

13:15 **Craig Jones**, ***Agilent Technologies***
Unique Capabilites of ICP-MS/MS Single Unit Mass Resolution Technology for Laser Ablation

ORAL SESSION 1: U-Pb GEOCHRONOLOGY…………………………..…… Room 215/216

Moderated by: Dirk Frei

13:30 **John Cottle**, A.R.C. Kylander-Clark, C. O'Connor, R.W. Hutchinson, L. Schlatt, & P. Shaw
High Spatial Resolution Petrochronology by LA- ICP-TOF-MS

13:50 **Liam Courtney-Davies**, R. Flowers, M. Danišík, S. Kainz, & J. Metcalf
Laser Ablation U-Pb Dating and He Mapping of Hematite: Latest Progress and Examples

14:10 – 14:30: **BREAK**

14:30 **Andreas Möller** & D.A. Pell
U-Pb dating of unusual minerals of the Magnet Cove Intrusive Complex: analytical strategy and suitability as reference materials

14:50 **Joshua Garber**, K.V. Lau, G. Felker, & M. Marshall
U-Pb and trace-element analyses of carbonate fluor-apatite (CFA): chemostratigraphy of the Phosphoria Rock Complex, USA

15:10 **J. Amal Dev** & J.K. Tomson
LA-ICPMS zircon-monazite- titanite-rutile-apatite chronology: A robust tool to understand t-T evolution of long-lived orogens

15:30 – 16:00 **BREAK**

ORAL SESSION 2: APPLICATIONS in BIOLOGY………………………… Room 215/216

Moderated by: Olga Minaeva

16:00 **Olga Minaeva**, N. Hua, N. Lupoli, M. Uretsky, V.E. Alvarez, J.A. Moncaster, & L.E. Goldstein
LA-ICP-MS in Neuroimaging

16:20 Lauren Clance, C. Cloyed, T. Bouveroux, C. Sinclair, K. Barry, K. Mullin, & **Ruth H. Carmichael**
First use of LA-ICPMS to analyze trace metals in dolphin skin: informing movement ecology and contaminant exposure risk

16:40 J. Chávez-Ambriz, **Juan Pablo Bernal**, B. Weber, C. Ortega-Obregón, L.Corona-Martínez, & Ó. Carranza-Castañeda
Accurate ^{87}*Sr/*^{86}*Sr analysis in bioapatite by LA-MC-ICP-MS; constraining Rb-mass bias using modern shark teeth*

17:00 – 19:00 **ICEBREAKER EVENT – EXHIBITOR HALL**

WEDNESDAY, JUNE 7th

7:30 - 7:50 Registration, Coffee & Refreshments…………………………......... **Exhibitor area**

8:00 – 10:50 **Laser Ablation Tandem Mass Spectrometry Workshop……..….. Rm 215/216**
Co-conveners: Alicia Cruz-Uribe, Sarah Gilbert, & Jamie Lewis

8:00 – 8:30 **Jamie Lewis**, C.D. Coath, & T. Elliott
The nuts and volts of building an LA-(MC)-ICPMS/MS
8:30 – 8:40 Questions & Answers
8:40 – 9:10 **Mark Kelinske**
Reaction Gas Fundamentals and Considerations on Tandem ICP-MS/MS System
9:10 – 9:20 Questions & Answers

9:20 – 9:50 **BREAK**

9:50 - 10:20 **Sarah E. Gilbert**, A. Simpson, S. Glorie, J.C. Lloyd, M. Hand, J. Farkas, & T. Zack
The dating of everything: beta-decay geochronometry by LA-ICP-MS/MS
9:10 – 9:20 Questions & Answers

10:30 - 11:00 **BREAK**

ORAL SESSION 3: ISOTOPE APPLICATIONS…………………………….. Room 215/216
Moderated by: Simon Jackson
11:00 **Alicia Cruz-Uribe**, G. Craig, J.M. Garber, B. Paul, Cemil Arkula, & C. Bouman
Single spot Rb-Sr isochron dating of micas by LA-MC-ICP-MS/MS
11:20 **Duane Petts**, William J. Davis, S.E. Jackson, Y. Amelin, & B.A. Kjarsgaard
Considerations for the application of in situ Rb-Sr dating using ICP-MS/MS
11:40 **Philippe Telouk**, E. Albalat, F. Albarède, B. Bourdon, & V. Balter
New developments in hyphenated laser ablation MC-ICP-MS equipped with the MS/MS technology

12:00 – 13:00 **LUNCH BREAK (RM B01, B02)**

VENDOR TALKS SESSION -2…………………………………………………. Room 215/216
Moderated by: Tony Simonetti
13:00 **Phil Shaw**, L. Schlatt, & P. Warburton, ***Nu Instruments***
Advances in time-of-flight LA-ICP-MS using up to 1kHz ablation rates and novel techniques to increase sensitivity and remove interferences when imaging biological matrices

13:15 C. Ash Norris & **Nicholas West**, ***Norris Scientific***

Elimination of Aliasing by use of Aligned LA–ICP–MS

ORAL SESSION 3: ISOTOPE APPLICATIONS (cont'd)……………........ Room 215/216

Moderated by: Tyler Spano

13:30 **Jay M. Thompson** & Kate Souders

It's Complicated: LA-ICP-MS/MS double-dating of apatite for Lu-Hf and U-Pb dates allow for new age constraints in terranes with protracted histories.

13:50 **Jeffrey Oalmann**, P. Olin, I. Belousov, & M. Morissette

Combining Laser Ablation ICP-ToF-MS Elemental Mapping with ICP-MS/MS Lu-Hf Dating of Garnet

14:10 **Wei Chen** & Jue Lu

Water-assisted laser ablation Mg isotope analysis of carbonates

14:30 – 14:50 **BREAK**

14:50 M. Puscas, **Ciprian Stremtan**, G. Armstrong, E. Sahlstedt

LA IRMS – a cost-efficient, minimally destructive alternative for in-situ single/repeat/sequential δ^{13}*C analyses of solid or liquid matrices*

ORAL SESSION 4: NEW INSTRUMENTATION/METHODS……………. Room 215/216

Moderated by: John Cottle

15:10 **Jorge Pisonero**, C. Soto, A. Mendez, C. Mendez, A. Calon, J. Linare, E. Avigliano, A. Cepedal, I. Garcia, J. Orejas, & N. Bordel

Critical evaluation of UV-fs-LA-TOFMS for fast, sensitive and high spatially resolved elemental mapping of challenging samples

15:30 Martin Šala, D. Metarapi, A. Schweikert, A. Jeršei, M. Schaier, J.T. Van Elteren, G. Koellensperger, & S. Theiner (presented by **Kristina Mervič**)

Semiquantitative analysis for high-speed mapping applications using LA-ICP-TOFMS

15:50 **Kharmen Billimoria**, S. Strekopytov, & H. Goenaga-Infante

Novel internal standard strategy to improve multi element quantitative bioimaging in cell samples

16:10 **Dany Savard**, S. Dare, P. Bédard, J. Petrus

Progress Towards µm-3D Analysis Using a fs-LA-ICP-TOF-MS System

16:30 – 17:00 **BREAK**

17:00 – 18:30 **POSTER SESSION**

18:30 – 19:00 **BREAK**

19:00 – 21:00 **DINNER @ DAHNKE BALLROOM**

THURSDAY, JUNE 8th

7:30 - 7:50 Registration, Coffee & Refreshments…………………….….…...... **Exhibitor area**

8:00 – 10:50 **Reference Materials/Standards Workshop……………………….…. Rm 215/216**
Co-conveners: Paul Sylvester, Kate Souders, & Jay Thompson

8:00 – 9:00 **Nicholas Sharp**, J. Weaver, R. Corzo, & M. Isabel Vega Martinez
Overview of NIST SRM Creation and Certification

9:20 – 9:40 **BREAK**

9:40 - 10:50 PANEL DISCUSSION

10:50 - 11:00 **BREAK**

ORAL SESSION 4: NEW INSTRUMENTATION/METHODS (cont'd)….... Room 215/216

Moderated by: Wei Chen

11:00 **David Gibbs**, J. Frank, & A. Limbeck
A novel approach for the assessment of the water content in thin film polymers

11:20 **Jeremy Hourigan**, M.T. Brandon, & R.P. Franks
A Novel Algorithm for Cross-Calibration of Multi-Mode SEM Detectors

11:40 **Jeffrey Williams**, J.C. Putman, & P. Willis
Coupling Laser Ablation with Non-resonant Laser Ionization

12:00 – 13:00 **LUNCH BREAK (RM B01, B02)**

VENDOR TALKS SESSION -3………………………………………………… Room 215/216

Moderated by: Tony Simonetti

13:00 **Jonathan C. Putman**, P. Willis, & J. Williams, ***Exum Instruments***
Simplifying Solid Material Characterization with the Massbox

13:15 **C. Derrick Quarles Jr**., C. Wolf, K. Sommer, U. Karst, L. Brunnbauer, B. Achleitner, & A. Limbeck, ***Elemental Scientific Lasers***
High-Speed Imaging for Biological and Geological Applications

ORAL SESSION 5: LIBS TANDEM / LASERS ARE RAD / LASER FUNDAMENTALS Room 215/216

Moderated by: Ben Manard

13:30 (*INVITED*) **Andreas Limbeck**, C.D. Quarles Jr., L. Brunnbauer
Spatially resolved analysis of microplastics using a combined LIBS and LA-ICP-MS approach

13:50 **Mauro Martinez**, G.J. Harry, E.N. Haynes, PI-I.D. Lin, E. Oken, M.K. Horton, R.O. Wright, M. Arora, C. Austin
Use of molecular emission by laser induced breakdown spectroscopy (LIBS) for fluoride imaging in environmental medicine
14:10 **Claudia Martinez-Lopez** & T.I. Todorovi
Development and Validation of a LA-ICP-MS Method for the Analysis of Multivitamins

14:30 – 14:50 **BREAK**

14:50 (*INVITED*) **Hunter B. Andrews**
Laser-Induced Breakdown Spectroscopy to Support Advanced Nuclear Reactor Development
15:10 (*INVITED*) **C. Derrick Quarles Jr.**, B.T. Manard, H.B. Andrews, T.L. Spano, J.A. Petrus, B. Paul, C.R. Hexel
Expanding the Elemental Coverage by Combining LIBS with ICP-TOF-MS for High-Speed Imaging
15:30 (*INVITED*) J. Chirinos, X. Mao, M. Park, C. Kim, Z. Alvidrez, B. Zhang, & **Vassilia Zorba**
Emerging Ultrafast Laser Ablation Technologies for Remote Elemental and Isotopic Analysis
15:50 (*INVITED*) **Gregory Hull**
LA-ICP-MS mapping of uranium absorption within living tissue
16:10 **Dino Metarapi**, J.T. Van Elteren, K. Mervič, & M. Šala
Enhancing LA-ICP-MS Image Quality through Ablation Grid Optimization

16:30 – 17:00 **BREAK**

17:00 – 18:30 **POSTER SESSION**

18:30 – 19:00 **BREAK**

19:00 – 21:00 **DINNER @ FOLEY'S CLUB**

FRIDAY, JUNE 9th

7:30 - 7:50 Registration, Coffee & Refreshments…………………….…........ **Exhibitor area**

8:00 – 10:30 **Data Processing Workshop……………………..……………..…. Rm 215/216**
Co-conveners: Alan Koenig & Leonid Danyushevsky

9:30 – 9:50 **BREAK**

VENDOR TALKS SESSION -4…………………………………………………. Room 215/216

Moderated by: Tony Simonetti

10:30 R. Merrifield, S. Clemons, J. Ferencz, R. Wolf, R. Hutchinson, **Aaron Hineman,** ***Perkin Elmer***
Automated High Throughput Analysis of Rare Earth Elements in Large Batches of Mining Discovery Samples by LA-ICP-MS

10:45 - 11:00 **BREAK**

ORAL SESSION 6: APPLICATIONS to GEOCHEMISTRY……………..…. Room 215/216

Moderated by: Elisabeth Widom

11:00 **Leonid Danyushevsky** & C. Ash Norris
Characterising and minimising analytical uncertainty of multi-element mineral analyses by LA-ICP-MS

11:20 **F. Zeb Page**, A. Cruz-Uribe, A. Goltz, & W. F. Hoover
Mapping fluid and metamorphic events with trace elements in eclogite garnet

11:40 **Zhaoping Yang**, S.E. Jackson, C.J.M. Lawley, B. Kjarsgaard, M. Polivchuk, P. Pelchat, A. Grenier
Development of a matrix-matched reference material for quantitative multi-element determination of sphalerite using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

12:00 (noon) **CONCLUDING REMARKS / ADDRESS**

END OF NAWLA2023 MEETING

ORAL PRESENTATIONS

ABSTRACTS

Bioimaging Workshop

Tuesday, June 6th

Biomedical Elemental Imaging as a User Resource

JACKSON, BRIAN P[1,2], TRACY PUNSHON[1,3]

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In 2021 the Dartmouth Trace Element Core received funding from National Institute of General Medical Sciences (NIGMS) to establish the Biomedical National Elemental Imaging Resource (BNEIR) to provide access to and training in elemental imaging and to reach out to the biomedical community and promote the technology. Over the first two years BNEIR has provided 2600 hours of imaging and grown its userbase to 17 users across 8 academic institutions. Sample types range from biominerals such as teeth to soft tissue organoids, mouse organs (brain, liver, kidney) and human tissues (spinal column, liver) and sample preparations include from flash frozen, OCT embedded and paraffin embedded. The userbase covers a wide range of disciplines including cancer research and drug delivery, Wilson's disease, essential element homeostasis and environmental metal exposures in ALS and neurocognitive decline. I will discuss details of providing elemental imaging as a resource, including approaches to calibration and validation, access to software for occasional users, data processing and statistical approaches for multi-element data and use of elemental tags/labels for multiplex imaging.

U-Pb Geochronology Workshop & Oral Session

Tuesday, June 6th

LA-ICP-MS U-Pb age determination: a review of recent performance in PT schemes

HORSTWOOD, M[1], SYLVESTER P[2]
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In 2016 the LA-ICP-MS U-(Th-)Pb community published a set of standards for uncertainty propagation, age interpretation and data reporting, derived from a series of workshops and other communications spanning several years, involving more than 100 researchers across the globe[1]. These standards recognised the importance of 1) random vs systematic uncertainties in the uncertainty propagation and age interpretation process, 2) the use of valid reference values for normalisation, 3) the role of validation materials in the propagation of long-term uncertainty, 4) the comparison of data at appropriate uncertainty levels and 5) the appropriate reporting of data, amongst other factors, in the accurate quantification of U-Pb ages and their assigned uncertainties.

Since 2019, a proficiency testing (PT) program for zircon U-Pb age determinations has been available, the results of which are reported in this workshop. A number of observations are highlighted from the results of these PT rounds, querying the veracity of application of these standards across the U-Pb community.

We will analyse the results and observations from the PT program, looking at the requirements of the PT scheme, the data distribution assumptions therein and their relevance to LA-ICP-MS U-Pb data, the potential cause of some of the resulting observations and take a renewed look at the community-derived standards and their application 7 years after their definition. Through this discussion we will learn relevant lessons, construct any feedback for the PT scheme operators, and determine pathways to improved LA-ICP-MS U-Pb performance in PT schemes.

([1]Horstwood et al 2016, GGR, https://doi.org/10.1111/j.1751-908X.2016.00379.x)

Observations form the G-Chron U-Th-Pb Proficiency Testing Program

Wiedenbeck, Michael[1], Webb P[2], Glodny J[3], Meisel TC[4]

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[2]formerly of the Open University, Milton Keynes, UK <peterwebb@macace.net>
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Since 2019 the International Association of Geoanalysts has operated the G-Chron proficiency testing scheme (http://www.gchron.info/) devoted to U-Th-Pb zircon geochronology. To date, two rounds of this PT scheme have been completed: Round#1 based on the Permian Rak-17 zircon from Norway and Round#2 based on the late Archaean Kara-18 zircon from Western Australia. The ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb target ages for these materials were established by Isotope Dilution Thermal Ionisation Mass Spectrometry conducted in multiple, independent laboratories. For those laboratories participating in the actual proficiency test it was required that both their determined ^{206}Pb/^{238}U and their ^{207}Pb/^{206}Pb ages should be reported. The following table provides some key parameters from these first two rounds of the G-Chron proficiency test scheme:

Sample Name	^{206}Pb/^{238}U target age (Ma)	number of labs reporting data	youngest reported ^{206}Pb/^{238}U Age (Ma)	oldest reported ^{206}Pb/^{238}U Age (Ma)
Rak-17	295.6	63	283.0	305.7
Kara-18	2628.4	50	2556.4	2761.3

Several significant insights can be gained based on the age data reported by the participating laboratories. (1) The ^{206}Pb/^{238}U system produced non-Gaussian data sets with no clear consensus ages, whereas the reported ^{207}Pb/^{206}Pb data sets yielded much better-defined age plateaus within their ranked distribution plots. (2) LA-ICP-MS facilities dominated the data sets, where in general those labs using quadrupole MS systems reported smaller ^{206}Pb/^{238}U uncertainty estimates than was the case for the sector-field-based facilities. In the case of the ^{207}Pb/^{206}Pb geochronometer the two types of instruments reported similar uncertainty estimates for the Archean Kara-18 zircon. (3) Both G-Chron data sets show only modest correlations between the reported measurement uncertainties and the bias of the reported age results relative to the TIMS-defined target ages. (4) For both G-Chron rounds over a quarter of the laboratories produced data deemed to be unfit-for-purpose. According to the design of the G-Chron programme, a result is fit-for-purpose when the age bias relative to the target age is less than ± 2 times the median of the reported measurement uncertainties for the given instrument class. Sample distribution for the next round of the G-Chron scheme is planned for late 2023.

Mitigation of Pb-U fractionation effects in LA-ICP-MS zircon U-Pb dating

JACKSON, SIMON[1], DUANE PETTS[1], WILLIAM DAVIS[1], MATTHEW HORSTWOOD[2] AND SIMON TAPSTER[2]

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Inter-element fractionation during LA-ICP-MS analysis of geological samples can seriously limit the precision and accuracy of elemental and inter-elemental isotopic analyses (e.g., U-Pb) because the degree of fractionation is sensitive to laser operating conditions and sample matrix. This makes accurate non-matrix-matched calibration challenging, and generally requires the use of well-calibrated matrix-matched reference materials. However, approaches, including femtosecond ablation[1] and water vapour-assisted ablation[2], have been reported to mitigate elemental fractionation effects, allowing non-matrix-matched U-Pb zircon dating using glass standards. In this study, we evaluated procedures for mitigating fractionation-related biases in U-Pb dating, including water vapour-assisted ablation and a major element normalisation correction.

As part of our evaluation, we discovered inaccuracies in the calculated Pb/U isotopic compositions of the NIST 610 glass[1,3] used in several LA-ICP-MS studies. Recalculation based on published elemental and isotopic values yields an atomic ^{206}Pb/^{238}U ratio 13% higher than the previously used values. The recalculated value is confirmed by published[4] and new ^{206}Pb/^{238}U isotope dilution data. Using this value, we could not demonstrate that water vapour-assisted ablation mitigates matrix-related Pb/U fractionation differences between zircon and glass. Other demonstrations of apparently successful approaches for non-matrix matched zircon U-Pb dating (e.g., “active focusing”, “soft ablation”, line scan ablation, chemically assisted ablation, femtosecond ablation) may be similarly affected by adoption of an inaccurate ^{206}Pb/^{238}U ratio for NIST610.

The major element normalisation method uses the sensitivity ratio of two mutually fractionating major elements (Si/Zr in zircon) to normalise inter analysis Pb/U signal intensity ratios. We show that this method provides significant improvements in precision and accuracy of zircon U-Pb analyses but a full evaluation is hampered by biases induced by operating variables (especially laser focus and sample location/time-variable ablation gas contaminants) that are not corrected by the normalisation method.

1. Horn, I. and von Blanckenburg, F. (2007) Spectrochim. Acta, **62B**, 410-422. 2. Luo, T. et al. (2018) Anal. Chem., **90**, 9016–9024. 3. Hirata, T. and Nesbitt, R.W. (1995) Geochim. Cosmochim Acta, **59**, 2491-2500. 4. Stern, R.A. and Amelin, Y. (2003) Chem. Geol., **197**, 111-142.

Cycle-by-Cycle Processing of LA-ICP-MS U-Pb Depth-Profile Data

HOURIGAN, JEREMY K.[1], NIKKI M. SEYMOUR[1,2]

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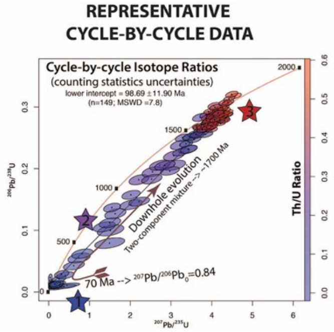
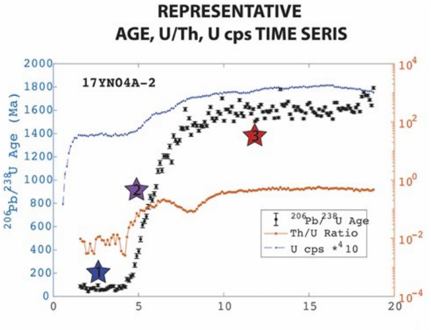
Many minerals preserve a record of their petrogenetic milieu in the form of chemically or isotopically distinct growth zones that are parallel to external crystal faces. Zircons are particularly prodigious in their ability to record multiple generations of growth in a single crystal. Often such zones are too narrow to analyze with typical laser spots sizes in polished grain mount without overlapping adjacent zones. In these cases, depth-profile analysis of whole, unpolished grains affords the high spatial resolution required to isolate the geochemical characteristics of individual growth zones. Additionally, minerals such as apatite, titanite, and rutile may preserve elemental concentration profiles related to thermally-activated volume diffusion which may be recovered by depth-profile analysis.

All laser ablation data must be corrected for downhole elemental fractionation. For depth profile analysis, the downhole fractionation correction (DHF) algorithm must be able to produce corrected elemental or isotopic ratios for each analytical cycle (e.g. Patton et al., 2010). Following DHF correction, typical treatment of isotopically heterogeneous depth-profile data involves manually windowing and averaging relatively homogeneous subsets of the profiled data. A common-Pb correction is then applied to the averaged data to calculate a concordia age for the domain.

In this contribution, we detail an alternative approach that leverages the distribution of individual cycle data on concordia. With the Python API in Iolite 4, we have developed plug-ins and ancillary modules to process U-Pb data with relevant DHF at a cycle-by-cycle scale, apply a series of objective tests to differentiate growth zones, and directly access the plotting functionality in IsoplotR (Vermeesch, 2018) to ultimately calculate the ages of individual domains using concordia model ages.





Paton,C., Woodhead, J. D., Hellstrom, J. C., Hergt, J. M., Greig, A., and Maas, R. (2010), doi:10.1029/2009GC002618; Vermeesch, P., 2018, doi: 10.1016/j.gsf.2018.04.001

Long-term uncertainty estimation and its role in the quantification of U-Pb age uncertainties

HORSTWOOD, M

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Long-term uncertainty estimation is the mainstay of accurate age representation in LA-ICP-MS U-Pb dating. Non-random, analytical session-related systematic biases cause differential inaccuracies of validation reference materials between sessions, resulting in an underestimation of the required U-Pb uncertainty for sample materials if only the session-related uncertainty is calculated. The scale of the required propagation for single collector, sector field-based ICP-MS instrumentation was recently quantified over a 6-year period using 7 zircon reference materials[1]. Typical measurement precision of 1.4-2.6% (2σ) required no intra-session propagation but required 0.6-1.7% (2σ) inter-session propagation, highlighting a minimum 2% (2σ) uncertainty (after propagation) for each sample data set.

Basic uncertainty propagation and how it can be performed for U-Pb data, will be highlighted in this presentation with a simple walk-through calculation. In addition, available tools to interrogate and quantify excess variance (random and systematic) and how this can be used in age uncertainty quantification, will be discussed, highlighting impact on interpreted age difference.

[1] Sliwinski et al 2022, GGR, doi: 10.1111/ggr.12442

High Spatial Resolution Petrochronology by LA- ICP-TOF-MS

Cottle, J.M.[1], A.R.C. Kylander-Clark[1], C. O'Connor[2], R.W. Hutchinson[2], L. Schlatt[3], P. Shaw[3]

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Recent advances in laser ablation systems and mass spectrometers have enabled the high-speed acquisition of high spatial resolution 2-D and 3-D 'images' of elemental and isotopic variations in a range of materials. With some notable exceptions, most applications of this potentially transformative technique have been in the field of biological imaging, and have not yet found widespread application in the field of earth science. Here we combine two recently developed technological advances to demonstrate the ability of this technique to produce petrochronologic data at the micron-scale on accessory minerals (e.g., U/Pb on zircon, monazite, titanite), and rock-forming minerals (e.g., Rb/Sr on mica) and assess the potential applications of these methods. Analytical instrumentation consists of a newly developed "TwoVol3" laser ablation chamber installed on an NWR193 laser ablation system (Elemental Scientific Lasers) connected to a "Vitesse" time-of-flight inductively coupled plasma mass spectrometer (Nu Instruments). In Laser-based imaging applications, there is a key balance between the speed of acquisition and the required spatial resolution that places practical limits on the area that can be mapped and/or the spatial resolution with which differences in elemental concentrations can be detected. We present data demonstrating that the ultrafast washout (~1 ms), nm-scale stage precision, and the across-chamber <1% elemental reproducibility of the "TwoVol3" cell coupled with the ultrafast acquisition rate of the "Vitesse" increases the limits by which high-resolution, multi-element/isotopic maps can be generated in a given period of time. Together, these instrument attributes enable the routine production of petrochronology images at a rate of up to 1000 pixels per second at detection limits in the ppm range.

Laser Ablation U-Pb Dating and He Mapping of Hematite: Latest Progress and Examples

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[2] John de Laeter Centre, Curtin University, Perth, Australia

Laser ablation-ICP-MS U-Pb dating of hematite is gaining user traction, with numerous existing and potential applications in environments spanning ore deposits to Martian regolith. Furthermore, coupling hematite U-Pb geochronology with parallel fields such as thermochronology and paleomagnatism presents an exciting new means to more accuratly calibrate Earth history. Hematite has proven to be a valuable mineral geochronometer because; (1) it can incorperate up to wt.% concentartions of U into its structure during primary crystallization; (2) it does not appear to accumulate radiation damage; (3) it can retain its radioactive decay products over geologic timescales, and; (4) hematite has yielded reproducable isotope dilution-thermal ionization mass spectrometry ages at up to 0.05% uncertainty (^{207}Pb/^{206}Pb) on 1590 Ma samples, a testament to the minerals robust U-Pb systematics.

Here we demonstrate latest advances and capabilities in hematite LA-ICP-MS U-Pb geochronology using case studies which tackle hotly debated questions in geoscience, e.g., bracketing the formation of the great unconformities and redefining the timing of worldwide banded iron formation mineralization. Secondly, we will discuss initial results from combined laser ablation noble gas microsampling and trace element analysis by time-of-flight secondary ion mass spectrometry, providing the first two-dimensional, grain-scale hematite He "maps". The element maps illustrate the relative homogeneity of U and Th and their decay products Pb and He, further highlighting the suitability of hematite to both thermo- and geochronology.

U-Pb dating of unusual minerals of the Magnet Cove Intrusive Complex: analytical strategy and suitability as reference materials

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The Magnet Cove Intrusive Complex (MCIC), AR, is a Cretaceous alkaline ring complex with jacupirangite, ijolite, phonolite, nepheline syenite and carbonatite units [e.g. 1]. Some of these are well known for hosting a variety of unique or rare minerals, including some potentially suitable for U-Pb geochronology, such as perovskite, Ti-rich (schorlomite) and Zr-rich (kimzeyite) garnet. Many of these can be found in mineral collections around the world, but there has been little academic interest since about 2009, until recently. Earlier geochronological studies used K/Ar, Ar/Ar, Rb-Sr and fission track dating [data compilations found in 2, 3], attested an age of 94-100 Ma for intrusion and fast cooling, with individual uncertainties of ca. 5 Ma or more on the individual dates. Recently, laser ablation U-Pb dating on MCIC schorlomite gave a consistent and quite precise age of 96.4 ± 1.8 Ma [4].

Based on a collection of MCIC samples collected by M. Bickford and R. van Schmus in the 1960's and M. Howard's generously shared specimen we are investigating the potential for U-Pb dating of the Ca-Ti-Zr minerals listed above and their suitability as primary or secondary reference material. With the recent explosion of applications for laser ablation U-Pb dating of non-traditional minerals comes the need for more, and reliable, reference materials (RMs).

Our initial results on perovskite yielded rather uniform U-Pb systematics and clustering of data in large (several mm diameter perovskite crystals from the carbonatite). The data are discordant and do not form a long linear array, not suitable as a primary RM. But they have potential as a secondary, validation RM with a suitable comPb composition to be established from analysis of cogenetic calcite. With multiple cogenetic datable minerals from separate MCIC rocks units, we are testing the possibility of using matrix-matched fractionation corrected data for multi-mineral discordia lines to obtain precise data. This will be permissible given relatively fast cooling and the similar and high Pb closure temperature for most target minerals. The by-product will be an improved timeline for the MCIC intrusive event(s).

[1] Erickson & Blade 1963, USGS Prof. Paper v. 425, pp. 94; [2] Zartman et al. 1967, Am. J. Sci. v. 265; p. 848-870 [3] Eby & Vasconcelos 2009, J. Geol. v. 117, p. 615-626; [4] Yang et al., 2019, JAAS, v. 33, p. 231-239.

U-Pb and trace-element analyses of carbonate fluor-apatite (CFA): chemostratigraphy of the Phosphoria Rock Complex, USA

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[2]Department of Earth and Environment, Albion College

Phosphorites – P-rich sedimentary rocks – form from the confluence of unique oceanographic conditions. Understanding these conditions in modern to ancient phosphorite deposits is important for reconstructing the composition and redox state of ancient oceans, as well as characterizing modern phosphorus, uranium, and rare-earth element resources. The Phosphoria Rock Complex (PRC) in the western USA has been intensely investigated for its rich stratigraphic record of environmental conditions during phosphorite deposition. However, much of the paleoenvironmental information gleaned from this complex is from whole-rock analyses; how much of these signals represent "primary" depositional conditions vs. subsequent diagenetic to late alteration is poorly known. Here, we performed LA-ICPMS split-stream (U-Pb + trace element) analyses on ten phosphorite samples from three PRC exposures that exhibit varying forms of carbonate fluor-apatite (CFA), including numerous phosphatic fossils (fish bones/teeth, brachiopods, conodonts), coated grains, and peloids. For U-Pb analyses, we used recently-published gem-quality apatite standards (Apen et al., 2022); for trace elements we used NIST612 silicate glass and STDP-5 phosphate glass, with Ca as an internal standard.

The results from these analyses show several distinct signals. Some population of each sample lies along an "errorchron" with a ~250–245 Ma U-Pb date, which is younger than the published stratigraphic date for the PRC (≥260 Ma; Wardlaw, 2015; Davydov et al., 2018). This offset may relate to systematic matrix differences between CFA and the igneous apatite standards, or otherwise suggests "early" diagenetic disturbances to U-Pb systematics over the entire PRC. Other analyses clearly plot off these errorchrons due to "late" post-crystallization U and/or Pb gain. Those analyses with strongly disturbed U-Pb age spectra typically include biogenic apatite – particularly fish, conodonts, and brachiopods – although other trace elements like REE are similar between these fossils and other non-biogenic apatites in the same stratigraphic layers. Indeed, there are few systematic REE differences between any feature types within a single sample, particularly between brachiopods, coated grains, and peloids. Instead, the dominant elemental variations within individual thin sections are stratigraphic. Although the errorchron ages are similar between outcrops, individual localities exhibit distinct ^{207}Pb/^{206}Pb upper intercepts; likewise, there are regional differences in trace-element patterns even in the same beds. These combined U-Pb + trace-element measurements are thus effective for understanding phosphorite deposition, diagenesis, and subsequent alteration in the PRC, with potential applications to other phosphorite deposits globally.

LA-ICPMS zircon-monazite- titanite-rutile-apatite chronology: A robust tool to understand t-T evolution of long-lived orogens

DEV, J. AMAL AND J.K TOMSON

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The use of microprobe investigations has garnered attention in the past decades owing to its potential to characterize the different magmatic, metamorphic and deformation stages of a terrane, discerned from potential U-Pb bearing accessory phases in rocks. Also, the recent advancements in the LA-ICPMS techniques have greatly enhanced its capabilities to extract elemental and age information from texturally controlled domains in a rock or mineral with enhanced precision, accuracy and fast data acquisition. In addition to its application in resolving a wide range of geological problems, in situ LA-ICPMS studies on multiple accessory phases have been highly explored in unravelling the tectonothermal evolution of polydeformed high- (HT) to ultrahigh-temperature (UHT) granulite terranes. This is because individual accessory phases may not be effective in fingerprinting discrete magmatic/metamorphic/cooling records of a polydeformed terrane due to their variable response to physio-chemical conditions prevalent during a long-lived orogeny. This study demonstrates the application of in-situ LA-ICPMS based geochronometry to untangle the time-temperature evolution (t-T) of the Kambam UHT belt, one the largest ultrahigh-temperature metamorphic belt in the world. The Kambam UHT belt is located at the central part of the Precambrian Southern Granulite Terrane (SGT), which is considered to be the nuclei of the East Gondwana supercontinent with a crustal evolutionary history ranging from late-Archean to Neoproterozoic. The application of texturally controlled LA-ICPMS U-Pb dating in multiple accessory phases such as zircon, monazite, titanite, rutile, and apatite from a suite of rocks provides U-Pb age spectra pointing to the polydeformed nature of the terrane with variable cooling records. The assessment of zircon and monazite ages constrains the timing of UHT metamorphism in the region between 590-530 Ma, peaking at 550 Ma, designating a 40 Ma duration for this orogeny. Titanite, rutile, and apatite ages cluster around ~520 Ma ~460-430 Ma, and ~390 Ma respectively, suggesting their formation in the retrograde cooling path, subsequent to the peak metamorphism. Combining these ages with the available P-T records, Zr-in-rutile temperatures, and closure temperatures of these accessories, a differential cooling pattern is proposed for the terrane with an initial slow cooling profile followed by ultra-slow cooling patterns. The new U-Pb ages from these accessory phases reveal the post-Gondwanan cooling history of SGT which was not previously constrained and signifies the application of accessory mineral geochronology using LA-ICPMS technique in deciphering the tectonothermal evolution of polydeformed granulitic terranes.

Applications to Biology, Health, Food, Archaeology, Climate Change Oral Session

Tuesday, June 6th

LA-ICP-MS in Neuroimaging

Minaeva, Olga[1,2,3], Ning Hua[1,2], Nicola Lupoli[2], Madeline Uretsky[2], Victor E. Alvarez[2,4], Juliet A. Moncaster[1,2,3], Lee E. Goldstein[1,2,3,5] *email: ominaeva@bu.edu*

[1] Department of Radiology, Boston University School of Medicine, Boston, MA, USA; [2] BU Alzheimer's Disease Center, Boston University School of Medicine, Boston, MA, USA; [3] Boston University Photonics Center, Boston, MA, USA
[4] VA Boston Healthcare System, Jamaica Plain, MA, USA; [5] Boston University College of Engineering, Boston, MA, USA

LA-ICP-MS imaging is gaining recognition as a powerful new tool for neuroscience research. This technique enables precise anatomical localization and ultra-trace elemental quantitation. Here we present applications of LA-ICP-MS in brain imaging. We studied regional accumulation, distribution, and retention of gadolinium in rat and human brains after exposure to intravenous Gd-based contrast agents (GBCAs). The goal for the rat study was to investigate whether quantitative MRI R1 mapping accurately reflects gadolinium retention and distribution in the brain by comparing it to gadolinium retention in rat forebrain measured with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) imaging after GBCAs administration. In human case series we are comparing retention of Gd in the brain acute (within first 2 years) and long-term (more than 5 years) after GBCA administration.

In these studies we used the laser ablation system (LSX-213 or Analyte Excite+, Teledyne CETAC Technologies, Omaha, NE) coupled to a quadrupole inductively-coupled plasma mass spectrometer (iCAP-Q, Thermo Fisher Scientific, Waltham, Massachusetts). Analytical calibrations were performed with 10% gelatin standards doped with Gd as a matrix-matched material. Iron, phosphorus, zinc and other biologically relevant maps were generated in the same scan. Phosphorus is highly abundant in the brain, with greatest relative enrichment in gray matter with high cellular density of small neurons. Therefore, phosphorus is an ideal element for differentiating gray and white matter and provides detailed structural information. ^{31}P map can be used for co-registration between LA-ICP-MS maps and other type of images (MRI, histology, etc). In rat brain study we showed that gadolinium retention in the brain measured by MRI R1 mapping and LA-ICP mass spectrometry yielded different results, indicating that some forms of retained metal may escape detection by MRI. In human brain study we observed prolonged gadolinium retention in human brains that lasts years after GBCA injection for all investigated GBCAs (gadodiamide, gadopentetate dimeglumine, and gadobutrol). Concentration of retained gadolinium did not correlate with time after GBCA administration but rather reflected the brain pathology at the time of GBCA administration.

First use of LA-ICPMS to analyze trace metals in dolphin skin: informing movement ecology and contaminant exposure risk

Clance, Lauren[1,2], Carl Cloyed[1,2], Thibaut Bouveroux[1,2], Carrie Sinclair[3], Kevin Barry[3], Keith Mullin[3], Ruth H. Carmichael*[1,2]

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We investigated seasonal patterns of site fidelity for resident bottlenose dolphins (*Tursiops truncatus*) in Mobile Bay, Alabama, Eastern Mississippi Sound (EMSS), and nearshore waters of the northern Gulf of Mexico (Gulf), areas highly influenced by freshwater discharge and anthropogenic sources of trace metals. We determined trace metal concentrations (As, Ba, Cd, Co, Cr, Cu, Fe, Pb, Sr) in dried, intact skin from remotely biopsied dolphins using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Elemental concentrations were corroborated with traditional photo-identification data. We found that dolphins acquired some location-specific elements indicative of site fidelity, with the greatest differences at geographic extremes (As, Co) and relative to salinity (Fe, Pb, Cu, Sr). Highest concentrations of trace metals were found in winter (particularly Fe, Pb, Cd), consistent with periods of higher riverine discharge. Photo-identification data supported fidelity patterns indicated by elements in tissues, showing higher connectivity within Mobile Bay than between Mobile Bay and EMSS or the Gulf. This study demonstrates that trace metals can be analyzed in skin with minimal pre-processing and have application as indicators of space use and potential for susceptibility to contaminant exposure even in highly mobile aquatic megafauna.

Accurate ^{87}Sr/^{86}Sr analysis in bioapatite by LA-MC-ICP-MS; constraining Rb-mass bias using modern shark teeth

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Several factors hamper the acquisition of accurate data during *in-situ* ^{87}Sr/^{86}Sr analysis in bioapatite using LA-MC-ICP-MS: isobaric interferences, elemental and isotopic fractionation of Rb and Sr, and the lack of standard reference materials to characterize such processes. Here we assess teeth from modern specimens of *Carcharinus leucas* (Bull shark) as a potential matrix-matched material to constrain the Rb-mass bias during the *in-situ* analysis of ^{87}Sr/^{86}Sr in bioapatite. We show that, assumption of equal Sr and Rb mass-bias can lead to systematically high ^{87}Sr/^{88}Sr compositions, even for samples with low Rb/Sr, hence, independent estimation of Rb mass-bias is essential to obtain accurate data. By bracketing the analysis of unknown samples with the shark teeth, we obtain ^{87}Sr/^{86}Sr compositions that are within +/- 40 ppm of expected values.

Frontiers in laser ablation tandem mass spectrometry (LA-ICP-MS/MS) Workshop & Oral Session

Wednesday, June 7th

The nuts and volts of building an LA-(MC)-ICPMS/MS

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The recent development of laser ablation inductively coupled plasma tandem mass spectrometry (LA-(MC)-ICPMS/MS) techniques has made a step change in approaches to elemental and isotopic analyses in the earth sciences, as well as other fields of research. The power of the LA-(MC)-ICPMS/MS is that it provides enormous flexibility in the types of analyses that can be undertaken but also offers potent specificity in analyte targeting and interference removal for *in situ* analyses. LA-(MC)-ICPMS/MS techniques have enabled novel measurements which have never been attempted before but has also rejuvenated more traditional techniques and enabled them to be applied to new types of samples. The number and complexity of different types of ICPMS/MS available from instrument manufacturers continues to grow as does the range of collision-reaction gases which users are introducing into their collision cells and this represents a rapidly growing and exciting field of endeavour.

This talk aims to give a broad introduction to the LA-(MC)-ICPMS/MS technology as a basis for the rest of the workshop and will be accessible to those people who may be new to LA-(MC)-ICPMS/MS. The talk will focus on the design concepts and fundamental hardware involved in the construction of tandem and hybrid ICP mass spectrometers. In detail this will consider how several types of mass analysers namely, quadrupoles, magnetic sectors and time-of-flight analysers can be combined with collision-reaction cells and configured into single and multiple collector designs. The merits and functionality of these different designs, particularly as pre-collision cell mass filters, and how they lend themselves to different applications will be discussed.

Reaction Gas Fundamentals and Considerations on Tandem ICP-MS/MS System

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In the early adoption of LA-ICP-MS, users often sacrificed sensitivity, specificity, or both, when selecting masses during analytical method setup. This was typically due to unmitigated spectral interferences or high isotopic abundance of the sample material. The use of reaction cell gases did not provide much relief on single quad ICP-MS system due to the potential formation of interfering product ions on other target analytes. Tandem ICP-MS/MS systems use a mass filtering quadrupole before the collision/reaction cell which gives the user more precise control of precursor ion introduction and subsequent product ion formation. This even enables the separation of isobaric isotopes leveraging differences in reactivity without the need for HR-ICP-MS techniques. In this session we will discuss reaction gas fundamentals, method development considerations, and explore real world examples of appropriate use of reaction gases on tandem ICP-MS/MS platforms to include both on-mass and mass-shift applications.

The dating of everything: beta-decay geochronometry by LA-ICP-MS/MS

Gilbert, Sarah E.[1], Alexander Simpson[2], Stijn Glorie[2], Jarred C. Lloyd[2], Martin Hand[2], Juraj Farkas[2], Thomas Zack[3]

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The development of in-situ laser ablation tandem mass spectrometry (LA-ICP-MS/MS) has made a new range of geochronometers readily accessible to geologists: Rb-Sr, Lu-Hf, K-Ca, and Re-Os. In these beta-decay systems the parent-daughter isotopes have the same atomic mass (e.g. ^{87}Rb and ^{87}Sr) which are not resolvable with single-quadrupole ICP-MS and some are difficult or impossible to resolve with high resolution MC-ICP-MS/MS. Analysis of these geochronometers now enables direct dating of a wide range of geological processes in sedimentary and igneous settings, metamorphic terrains and ore deposit systems. These isotopic systems also highlight the versatility of LA-ICP-MS/MS which utilise a range of reaction gases to effectively resolve the isobaric interferences.

Rb-Sr dating of micas and feldspars has gained recent popularity, where Sr readily reacts with N_2O or SF_6 while Rb is unreactive.[1,2,3] K-Ca isotopes in feldspars and K-bearing micas can be separated from the additional ^{40}Ar isobaric interference using a combination of SF_6 and H_2 gases.[1] This has the potential for simultaneous analysis of both Rb-Sr and K-Ca from the same laser spot. Lu-Hf dating of garnet, apatite and calcite uses NH_3 to efficiently separate Lu from Hf as they form large cluster ions with different isotopic masses.[4] Combining U-Pb and Lu-Hf dating of apatite can be used to differentiate the high-temperature crystallisation age by Lu-Hf from subsequent lower temperature overprinting by U-Pb.[5,6] Finally, Re-Os isotopes can be measured in molybdenite in ore deposits using CH_4 as the reaction gas with the addition of He to supress the Re reaction.[7]

A brief overview of each isotopic system will be presented with emphasis on the analytical approach, potential pitfalls, and future directions.

[1] Hogmalm et al., 2017, JAAS, v.32, p.305; [2] Bevan et al., 2021, JAAS, v.36, p.917; [3] Redaa et al., 2021, JAAS, v.36, p.322; [4] Simpson et al., 2021, Chemical Geology, v.577, p.120299; [5] Glorie et al. 2022, Tera Nova, v.34, p.201; [6]Glorie et al., 2023, Geological Society Publications, v537; [7] Hogmalm et al., Mineralium Deposita, 2019, v.54, p.821

Single spot Rb-Sr isochron dating of micas by LA-MC-ICP-MS/MS

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Laser ablation coupled with tandem mass spectrometry is a burgeoning field for the measurement of in situ Rb-Sr geochronology. The addition of Wien-style pre-cell mass filters on the Thermo Scientific™ Neoma MS/MS MC-ICP-MS enables simultaneous collection of on-mass and mass-shifted isotopes of Rb and Sr, with vastly improved precision over dynamic quadrupole-based instruments. Simultaneous isotope ratios of ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr in metamorphic biotite from western Maine were determined using an ESL™ imageGEO™193 excimer laser-ablation system coupled to the Neoma. Measurements were made on Faraday cups with 10^{11} or 10^{13} ohm resistors, with Rb measured at mass 87; Sr isotopes were reacted with SF_6 gas in a hexapole collision cell and measured as SrF on masses 103, 105, 106, and 107. Twenty-two laser spots in pelitic schist sample Ra-D72 give a "traditional" Rb-Sr isochron date of 289 ± 8 Ma. However, individual integrations reveal significant zoning in ^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr within single spot analyses, which were used to construct single spot isochrons. Many of these laser spots contain multiple populations that define multiple isochrons within a single spot analysis; some spots contain up to three distinct Rb-Sr isochron dates that are entirely decoupled from variations in Rb/Sr ratio. Thirty-five isochron dates were determined using this "sub-spot" approach, and two-point isochrons were calculated for each individual integration (n=780) based on the single-spot ^{87}Sr/^{86}Sr intercepts, the latter of which systematically vary with Rb-Sr date. Both methods yield three age peaks for the sample, at 303, 270, and 240 Ma. These data suggest that the Rb-Sr system has the potential to record multiple heating, cooling, or fluid-alteration events spanning ~100 m.y. within small domains in single biotite crystals.

Considerations for the application of in situ Rb-Sr dating using ICP-MS/MS

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Aliasing can significantly affect the precision of isotope ratios acquired by laser ablation analyses on a single collector-ICP-MS/MS instrument. We assess potential sources of noise in Rb-Sr geochronological studies using LA-ICP-MS/MS, with a particular focus on evaluating the effects of aliasing on the precision of ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr measurements. Additional geological factors, such as alteration and the occurrence of secondary carbonate interlayers within mica, and their impact on measurement precision, are also evaluated.

Optimization experiments were undertaken on NIST glass to evaluate potential sources of signal noise and variation during Rb-Sr analyses. Notably, these experiments indicate that aliasing, i.e., desynchronization between the laser pulse rate and ICP-MS sampling periods (dwell and/or sweep times), results in significant additional uncertainty in the ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr ratios beyond those expected based on counting statistic considerations. Precision can be improved by optimizing the timing of the laser pulse rate with the ICP-MS total sweep time, such that measurement of specific Rb and Sr isotopes occurs within similar time periods during successive sweeps (e.g., 10 Hz laser pulse rate with a total sweep time of 100 ms). The efficiency of signal smoothing methods (e.g., different types of in-line smoothing devices) mitigates this effect to varying degrees, but does not entirely eliminate it. Utilizing optimized instrument parameters, an isochron age of 90.5 ± 0.6 Ma (Initial ^{87}Sr/^{86}Sr of 0.7114 ± 0.0009; MSWD 0.83) was obtained for combined analyses of hornblende and mica from a sample of the Tombstone intrusive suite (Yukon, Canada), within uncertainty of a TIMS Rb-Sr isochron age for mica.

Precise dating of phlogopite macrocrysts from kimberlite can be affected by secondary carbonate within the interlayers of individual phlogopite crystals. This produces significant short wavelength spikes in Sr signals, which are difficult to eliminate by selective integration of specific time windows in the analyte signal. Dilute HCl leaching techniques, as commonly used in bulk grain TIMS analysis, were utilized to reduce this effect. Analyses on leached phlogopite from Cretaceous kimberlites (Ontario, Canada) and Tombstone biotite showed an overall improvement in measurement precision of 25-40% compared to analyses on non-leached fractions of the phlogopite and biotite samples. This improvement in measurement precision due to leaching should be an important consideration for high precision LA-ICP-MS/MS measurements of mica, particularly, development of mica reference materials and measurements on altered mica.

New developments in hyphenated laser ablation MC-ICP-MS equipped with the MS/MS technology

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In this presentation, we will present the advantages of an MC-ICP-MS/MS coupled with a laser ablation system for isotopic analyses. The double Wien filter capability of the Neoma MS/MS (ThermoFisher) will be presented and the use of SF_6, SF_6 + He and SF_6 + N_2O as reaction gas in the collision cell will be discussed. Laser ablation analyses for a series of ten certified reference materials or in-house standards was performed with the NWR 193 (ESI) laser ablation system and the results were compared to solution analysis. Using identified best settings, we performed Sr (SrF form) radiogenic isotopes mapping thanks to the fast acquisition electronics installed on the instrument. The results are compared with Sr single profiling analyses previously obtained on a Neptune plus (ThermoFisher) on same samples.

It's Complicated: LA-ICP-MS/MS double-dating of apatite for Lu-Hf and U-Pb dates allow for new age constraints in terranes with protracted histories.

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LA-ICP-MS is widely used in geoscience to obtain U-Th-Pb isotopic compositions from rocks to calculate crystallization ages for minerals. This age determination is based on the decay of ^{238}U to ^{206}Pb, ^{235}U to ^{207}Pb, and ^{232}Th to ^{208}Pb. The U-Pb system is the most widely used decay system in geoscience due to the ability to assess concordance of the ^{238}U and ^{235}U decay systems and the availibility of well-characterized mineral reference materials (e.g. zircon). The use of LA-ICP-MS for rapid U-Th-Pb geochronology analyses with precision and accuracy of ~ 1-2% (2s) has resulted in a substantial increase in the amount of geochronological data available to the geoscience community in the last ~15 years. However, a limitation of the U-Pb system for any mineral chronometer is that it records the last time the mineral cooled through the U-Pb closure temperature; unique to that mineral. This could represent a crystallization age, secondary mineral growth, or (partial) resetting of the U-Pb system within a mineral by thermal or hydrothermal events. In high-grade metamorphic terranes it is often difficult to obtain protolith crystallization ages or peak metamorphism using minerals with high closure temperatures (e.g. zircon) due to partial resetting of the U-Pb system, Pb loss, and inheritance. In these complicated terranes, the U-Pb decay system in minerals with lower closure temperatures, such as apatite, can provide useful insight into the timing of late-stage metamorphism or deformation.

The availibility of ICP-MS/MS, where two mass filters are sandwiched between a collision / reaction cell, has allowed for the analysis of beta decay systems (e.g. Lu-Hf [1]) using in-situ laser ablation. In this study we present a new variation on LA-ICP-MS/MS analysis by using NH_3 reaction gas in the collision cell of an Agilent 8900 ICP-MS/MS. We are able to measure Lu-Hf isotopes, U-Th-Pb isotopes, and selected isotopes for elemental compositions in the mineral apatite in a single analysis at a 50 µm laser spot. Combining the apatite Lu-Hf isochron age with the apatite U-Pb age provides a 'double-dating' method well-suited for complex metamorphic terranes where determining U-Pb zircon ages has proven difficult. A geological example from the late Archean Great Lakes Tectonic Zone (GLTZ), Upper Peninsula, Michigan, will be presented. The GLTZ separates the Wawa-Abitibi Subprovince to the north and the Minnesota River Valley Subprovince to the south [2]. Apatite from a granitic dike, cross-cutting the GLTZ was analysed by the Lu-Hf/U-Pb double-dating method and results show a 2560 Ma U-Pb age and a 2725 Ma Lu-Hf age. The discrepancy between these two ages is interpreted to be related to differences in the closure temperatures between these two decay systems with the Lu-Hf system likely recording apatite crystallization age and the U-Pb system recording late-stage cooling below the apatite U-Pb closure temperature (i.e. exhumation). This study will also present U-Pb and Lu-Hf ages on a number of apatite refence materials to demonstrate accuracy of both U-Pb and Lu-Hf ages using this methdology.

1. Simpson, A., et al., *In-situ Lu–Hf geochronology of garnet, apatite and xenotime by LA ICP MS/MS.* Chemical Geology, 2021. **577**: p. 120299.
2. Sims, P.K., et al., *The Great Lakes tectonic zone — A major crustal structure in central North America.* GSA Bulletin, 1980. **91**(12): p. 690-698.

Combining Laser Ablation ICP-ToF-MS Elemental Mapping with ICP-MS/MS Lu-Hf Dating of Garnet

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Beta decay geochronometers, such as Rb-Sr, Lu-Hf, and Re-Os, have been widely used in geosciences and can be applied to a vast range of minerals and rock types. These systems are useful in dating a variety of different geologic processes such as magma crystallisation, metamoprhism, exhumation, deformation, ore deposition, and volcanic eruptions. However, the fundamental aspect in which the parent and daughter isotopes have the same atomic mass necessitates chemical separation prior to isotope ratio measurements. Recent advances in ICP-MS/MS technology provide a means to chemically separate the parent and daughter ions using a reaction cell sandwiched between two quadrupole mass analysers. Either the parent or daughter isotope is shifted to a higher mass by reacting with the gas to form a polyatomic ion in the reaction cell. This allows for *in situ* dating of a wide variety of minerals using a laser ablation microprobe with minimal sample preparation.

Garnet occurs in a wide variety of geological settings, and its composition can be used to estimate conditions of formation such as pressure and temperature as well as the post-crysallisation thermal history. Garnet is well suited for Lu-Hf dating because of its high affinity for heavy rare earth elements and low affinity for high field strength elements. Therefore, combining garnet dating with petrological studies can be used to directly date geologic events, including regional metamorphism and ore deposition.

Here we propose a protocol in which garnet crystals are chemically mapped by LA-ICP-ToF-MS prior to Lu-Hf dating by LA-ICP-MS/MS. Laser ablation ICP-ToF-MS allows for rapid mapping of the distributrions of nearly all major, minor, and trace cations in garnet at high spatial resultion. The maps are used to identify crystals or zones within crystals that have a spread in Lu-Hf elemental ratios. The isotopic ratios measured by LA-ICP-MS/MS from crystals or zones with different parent-daughter ratios can be used to calculate an isochron age, or if the initial ^{176}Hf/^{177}Hf of the garnet is known or can be surmised, a Lu-Hf date can be obtained from each spot analysis. Linking the dates to the geologic conditions inferred from the elemental concentrations and distributions can be used to directly date geological processes. Combining elemental mapping with *in situ* beta decay geochronology is a powerful tool that can potentially be applied to many geologic settings using a wide range of radiometric dating systems.

Water-assisted laser ablation Mg isotope analysis of carbonates

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Micron-scale magnesium isotope compositions of carbonates play an important role in tracing geological and biological processes. Matrix effects of carbonates with distinct chemical and physical properties are the main factors affecting the accurate and precise determination of Mg isotopes by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). This study investigates Mg isotope microanalysis of magnesite, dolomite and siderite under wet and dry conditions. The results demonstrated that the main isobaric interference of $^{48}\mathrm{Ca}^{2+}$ on $^{24}\mathrm{Mg}^{+}$ in carbonate with high Ca/Mg ratios (up to 6.79) can be significantly suppressed and downhole isotopic fractionation can be reduced with the addition of water vapor before the ablation cell (e.g., wet condition). MGS-3, DOL-8, DOL-9 and SD-5 show homogeneous in situ Mg isotope compositions with intermediate precision better than 0.14‰ and 0.15‰ for δ^{26}Mg and δ^{25}Mg, and are adopted as in-house standards. The obtained in situ δ^{26}Mg and δ^{25}Mg values of matrix-matched samples were consistent with those determined by solution nebulization (SN)-MC-ICP-MS with uncertainties of 0.16-0.27‰ and 0.12-0.25‰ (2SD) under dry condition and 0.15-0.18‰ and 0.06-0.10‰ (2SD) under wet condition. This further indicates that water-assisted laser ablation analyses improved the analytical precision of Mg isotope determinations by 1.1 to 2.5 times. Inaccurate Mg isotope data were obtained under dry condition when carbonate samples were measured against a physical property and/or chemical composition different standard, such deviation can be largely improved in wet-laser analyses.

LA IRMS – a cost-efficient, minimally destructive alternative for in-situ single/repeat/sequential δ^{13}C analyses of solid or liquid matrices

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For decades elemental analyzers (EA) have been the go-to sample introduction instrument for IRMS analyses of solid materials. Sample preparation is labor intensive and time consuming while sample recovery is impossible in case of malfunctioning. It might be time to search for an alternative to EA IRMS. One that offers minimal to no sample preparation, allowing for minimally destructive measurements, repeat measurements even on minute sample amounts, even in situ sequential sampling. LA IRMS (laser ablation hyphened with an isotope ratio mass spectrometer) is a thrilling alternative to EA IRMS, opening a world of possibilities!

We tested LA IRMS on a variety of organic materials: pollen, wood, bone collagen, whole bone, tooth, chitin (hair -human and animal, fingernail, and horn), sugars and sweeteners, vegetable oils, bee honey and wax, airborne particulate matter, whole blood, and many more. For some of these we also present EA data, to show method equivalency.

Depending on matrix, we carried out these tests using two instrumental set-ups. The front end was either an LSX 213 G2+ laser or a Fusions CO2 laser (both Teledyne Photon Machines, Bozeman MT, USA). The back end in all testing was an HS2022 IRMS via a CryoFlex sample preparation module (both Sercon, Crewe, UK). An isoScell Δ100 (Terra Analitic, Alba Iulia, Romania) sample chamber, specifically designed for LA IRMS, was utilized for all analyses. The EA IRMS used for inter-instrument comparison is also Sercon.

Establishing the optimal laser parameters is a two-step process; the first one is fine tuning the laser energy to ensure the sample is ablated efficiently. The next step requires finding the optimal spot size and ablation time necessary for producing sufficient aerosol to be converted into CO2 in the combustion furnace. For all the matrices we tested with our current setup, this process translated into two or three measurements, meaning 15 – 30 minutes for optimizing the matrix-dependent laser parameters.

Samples where spatial resolution is crucial (e.g., wood, hair, fingernail, tooth) can be ablated sequentially at intervals of down to 20 µm (matrix and laser-type dependent). As each ablation removes a minute amount of sample, replicate analysis will not be an issue for homogenous matrices. An important additional aspect (both financially and for ease of use) is the fact that with LA there is no need to matrix-match the reference material to the unknown sample, which is an aspect discussed in this contribution.

New Instrumentation/Methods Oral Sessions

Wednesday & Thursday, June 7th & 8th

Critical evaluation of UV-fs-LA-TOFMS for fast, sensitive and high spatially resolved elemental mapping of challenging samples.

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Laser Ablation Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) is rapidly evolving into a well-established technique for direct, highly sensitive and high lateral resolution analysis in numerous fields such as geology, biology, metallurgy, or environmental sciences [1]. Significant research and advances continue to thrive for achieving the fastest, most accurate and efficient analysis, such as those focused on improvements such as low dispersion setups and cell geometries for the finest control of aerosol trajectories [2]. Additionally, ultra-short pulsed lasers, such as femtosecond laser ablation, are employed to reduce melting effects around the ablated area as well as fractionation effects. Therefore, the combination of a fast-response femtosecond laser ablation-based units and novel ICP-TOFMS technology provides one of the top-most interesting analytical methods for high spatial resolution determination -mapping- in samples of different matrices and nature.

In the present work, the analytical capabilities of a NWRfemto laser coupled to a Nu Vitesse ICP-TOFMS, which includes a collision/reaction cell and a controlled ion beam attenuation, are critically evaluated for high spatially resolved analysis of challenging samples, including:

- Determination of multielemental diffusion in metallurgical samples after welding processes and after interaction with aggressive environments.
- Determination of multielemental distribution in cancer cells after chemotherapeutic treatments with Pt-based compounds.

[1] J. Pisonero, D. Bouzas-Ramos, H. Traub, B. Cappella, C. Alvarez-Llamas, S. Richter, J. C. Mayo, J. M. Costa-Fernandez, N. Bordel, N. Jakubowski, J. Anal. At. Spectrom., 34, 655-663 (2019).

[2] C. Neff, P. Becker, D. Günther, J. Anal. At. Spectrom., 37, 3, 677 – 683 (2022).

Semiquantitative analysis for high speed mapping applications using LA-ICP-TOFMS

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Laser ablation inductively coupled plasma time-of-flight mass spectrometry (LaA-ICP-TOFMS) enables monitoring of elements from the entire mass range, regardless of the isotopes of interest for a certain application. As such it provides non-targeted multi-element imaging capabilities and the unique opportunity to screen for elements that were initially not expected in the samples, for example emerging conatminants. We have prepared a series of highly multiplexed calibration standards for (bio-)imaging by LA-ICPMS and used it for the costruction of response factor library.With this we have developed a workflow for semiquantitative analysis by LA-ICP-TOFMS based on these multi-element gelatine micro-droplet standards. The method was evaluated in two steps, (i) on prepared gelatine samples with known elemental concentrations and (ii) on real-world samples including examples of bioimaging (mouse tumor and spleen). The semiquantification approach using approximately 10 elements as calibration standards can determine 136 nuclides of 63 elements, with errors below 25% and for half of the nuclides below 10%. An application for quantification and semiquantification of LA-ICPMS was also developed and can be accessed by any ures free of charge.

Novel internal standard strategy to improve multi element quantitative bioimaging in cell samples

BILLIMORIA, KHARMEN *, STANISLAV STREKOPYTOV AND HEIDI GOENAGA-INFANTE

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In vitro testing of cell models is a major component of clinical testing as an initial step before investing in larger animal or patient trials. Bulk measurements of cell populations do not provide a sufficient representation of individual cell responses and, therefore, methods that can provide information at the intracellular level are increasingly being used. Lanthanide-based immunochemical tags are commonly used in flow/mass cytometry to assist diagnosis and assess novel treatments. LA-ICP-MS methodology is thought to be a powerful tool to underpin these measurements[1].

Advances in LA-ICP-ToF-MS instrumentation have improved the speed and sensitivity of imaging analysis making it possible to map both endogenous and externally tagged elements at intracellular resolution. In-line with technological advancements new strategies for quantification are also being developed. Gelatin is now widely used as biological matrix to prepare calibration standards[2]. One remaining challenge for spatially resolved elemental quantification in biological samples is the lack of a suitable internal standard (IS) that can be reliably measured in both gelatin calibration standards and samples.

In this work, methodology based on multi-element quantitative intracellular imaging of cells tagged with lanthanide nanoparticles using a novel IS strategy is described. Assessment of how data processing and interpretation impact the quality of the imaging data is also discussed. To achieve this, an internal standard layer is deposited onto microscope slides containing either gelatin calibration standards or cell samples. This IS layer contains both gallium and indium. Monitoring either IS element individually showed variations in signal between slides, which is indicative of the difficulties in producing a homogenous film at intracellular resolution. However, normalisation of the lanthanide signal to the ratio of the IS elements helped improve the calibration correlation coefficients from 0.9885 to 0.9971 and 0.9805 to 0.9980 for Eu and Ho, respectively; whilst also providing a consistent signal to monitor the ablation behaviour between standards and samples. By measuring an independent quality control sample, it was observed that without normalisation there was an overestimation of the Eu and Ho concentration by approximately 20%. This overestimation was also observed in the lanthanide concentration distribution of the samples.

1. D. Clases and R Gonzalez de Vega, *Anal. Bioanal. Chem.*, **volume 414**, 7363–7386 (2022)
2. M. Martinez, M. Baudelet, *Anal. Bioanal. Chem.*, **volume 412**, 27–36 (2020).

Progress Towards µm-3D Analysis Using a fs-LA-ICP-TOF-MS System

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A femtosecond laser ablation system (Applied Spectra) coupled to an ICP-TOF-MS (TOFWERK) was used to produce a novel approach for fully quantitative 3D analysis. A glassy melt inclusion (MI) (Fig. 1-A) from Hawaiian olivine was targeted by successive series of 28 maps in decreasing size, forming at the end, a crater of about 500x800µm wide and 130µm depth, comparable in shape to an open-pit mine (Fig. 1-B). The beam size used was 20µm and 10µm for the 22 first top layers and was reduced to 5µm when approaching the target melt inclusion, which was embedded at a depth of about 60-100µm below the surface. Major and trace elements from each map were converted to quantitative analysis using the new “3D Trace Elements" data reduction scheme recently released for IOLITE software [1-3]. Quantitative maps were achieved by combining multiple calibration material and normalization, then tabulated to EXCEL charts, converted and merged into a single file using a house-made Python script. LeapFrog software (SEEQUENT), a visual software commonly used in geological mining industry, was used to produce 3D images of the MI (Fig. 1-C). Major and trace elements concentration of the MI were in good agreement with literature [4] (Fig. 1-D). The aim of this project intends to open the door to LA-ICP-MS analysis of more complex 3D features.

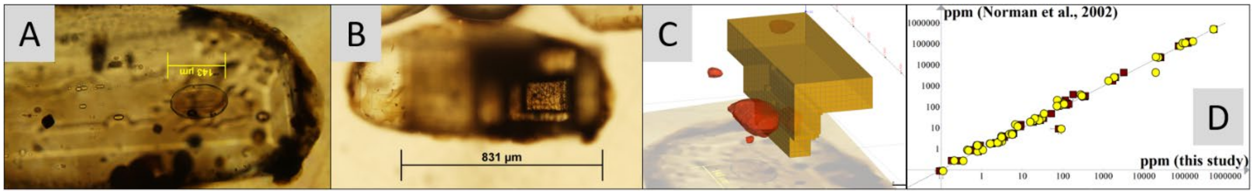

Figure 1. A) embedded glassy melt inclusion in Hawaiian olivine prior analysis. B) Ablation pit after analysis. C) 3D chemical image (Al_2O_3) highlighting the MI shape. D) Good agreement of major and trace elements when compared to data of similar MI from Hawaiian olivine [4].

[1] Savard et al. (accepted, 2023). *J. of Geost. Geoanal. Res.* [2] Paul et al. (submitted 2023) [3] Savard et al. (2022). *In Christie AB (ed.) Proceeding of the 16th SGA Biennial Meeting* [4] Norman et al. (2002). *Chemical Geology*, *183*(1-4), 143-168.

A novel approach for the assesment of the water content in thin film polymers

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Polymers are nowadays used in a large variety of industries and products. Applications cover relatively trivial uses like packaging materials for consumer goods and construction materials, but polymers are also utilized in more demanding fields, such as the electronic and semiconductor industries. There, polymers are often employed as an encapsulation material or protective layer to prevent devices from the influence of light and surrounding atmosphere. However, in the course of the component's use degradation of the coating/encapsulation material occurs, which in extreme cases can lead to device failure. Since the presence of moisture is known to promote the degradation of polymers, there is an increasing interest to measure the water absorption of polymers.

Water content of solid materials is mostly analyzed using thermo-gravimetric analysis, differential thermal analysis, or dynamic vapor sorption [1]. Although well established, these techniques are connected with severe drawbacks, such as the limitation to bulk investigations or the relatively large quantities of material required for analysis. The presented work aims to study the feasibility of measuring the water uptake of polymers by means of LA-ICP-MS. In order to overcome the difficulties related to the analysis of hydrogen with ICP-MS the polyatomic $^{40}Ar^{2}D^{+}$ ion is monitored as a proxy for Deuterium [2].

The developed procedure is based on the preliminary treatment of a dried polymer thin film with Deuterium enriched water (D_2O), and the subsequent LA-ICP-MS analysis of the Deuterium content in the polymer, enabling a reliable determination of the water uptake. For the conducted LA-ICP-MS investigations, a special ablation chamber containing a cryostage has been constructed, which allowed to measure the samples in frozen state. Polymer thin film standards containing defined supplements of deuterated organic compounds have been prepared using a drop casting procedure. LA-ICP-MS analysis revealed a linear correlation between the measured $^{40}Ar^{2}D^{+}$ signal and the Deuterium content of the standards, enabling spatially resolved measurements of Deuterium in polymers down to the permille range. Finally, applicability of the proposed procedure has been demonstrated by the analysis of polymer samples exposed to atmospheres containing heavy water.

[1] Bley O., J. Siepmann and R. Bodmeier. J. Pharm Sci. 2009 (98), 651-664. Characterization of moisture-protective polymer coatings using differential scanning calorimetry and dynamic vapor sorption

[2] Galbacs et al., Analytica Chimica Acta 1104 (2020) 28-37. Deuterium analysis by inductively coupled plasma mass spectrometry using polyatomic species: An experimental study supported by plasma chemistry modeling.

A Novel Algorithm for Cross-Calibration of Multi-Mode SEM Detectors

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Multi-mode SEM detectors on modern ICP-MSs feature both analog and pulse detectors which allow signal intensities with up to 11 orders of magnitude dynamic range. Over a limited signal range, high-signal-to-noise-ratio analog signals and pulse signals are simultaneously measured permitting estimation of a linear analog-to-count factor (ACF). The product of the analog signal and ACF is used to extrapolate signals when the pulse counter has tripped off at high count rates. The treatment of time and mass dependency in ACF estimation is variable between instrument types and instrument manufacturers. We will show real-world data from a quadrupole ICP-MS (Thermo X-Series II) and a magnetic-sector ICP-MS (Thermo ElementXR) to facilitate a discussion of standard cross-calibration practice. Furthermore, we will utilize these data to demonstrate time, mass and count-rate dependency in real-world data that are undercorrected in these instruments' software (*e.g.* Pullen et al., 2018, G-Cubed). These observations motivate development of a novel algorithm to model and correct for all of these dependencies.

We will derive an expression which forms the basis for a linear least squares inverse problem using raw (i.e., no deadtime correction) pulse P_{ij} and analog A_{ij} signal data :

$$\frac{1}{P_{ij}} = \tau_j + a_{1j}\frac{1}{A_{ij}} + a_{2j}\frac{t_i}{A_{ij}} . \qquad \text{(eq. 1)}$$

Here, the subscripts *i* and *j* are cycle and isotope, and t_i is cycle time. The fitted parameters τ_j, a_{1j}, a_{2j} are "pseudo-deadtime", reciprocal starting ACF and reciprocal ACF drift, respectively. Parameter estimates (denoted by the 'hat' operator) are used to post-process raw data to create revised signal intensities, I_i:

$$I_i = \begin{cases} \frac{1}{\hat{a}_1 + \hat{a}_2 t_i} A_i & P_i \geq P_{cutoff} \\ \frac{P_i}{1 - P_i \hat{\tau}} & P_i < P_{cutoff} \end{cases} \qquad \text{(eq. 2)}$$

These calculations are made discretely for each isotope, j, during post-processing. This algorithm simultaneously corrects for cross-calbration drift and non-linear detector response, τ, which includes pulse detector deadtime.

We will demonstrate open-source Python software that implements this algorithm for Thermo Element binary data files. The software: (1) reads Thermo Element binary data files, (2) performs least squares estimation of the cross-calibration parameters (eq. 1), and (3) exports post-processed data (eq. 2) as Thermo chromatogram text (*.FIN2) for use with third-party data reduction software. The code is fully object-oriented and can be extended to import raw data, where accessible, from other instruments.

Coupling Laser Ablation with Non-resonant Laser Ionization

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The concept of Laser Ionization is by no means new. For the past several decades variations of laser ionization have been researched with a heavy emphasis on resonant ionization, while non-resonant, multiphoton ionization was neglected due to constraints of laser technology, size and instrument complexity. Non-resonant ionization provides a largely universal solution for ionization across the period table, and thus couples well with Time-of-Flight Mass Spectrometry (TOF-MS). We will be specifically focusing on the 2-photon multiphoton ionization regime (MPI). Some early works that coupled non-resonant ionization with SIMS achieved large improvements to matrix effects, quantitative abilities, and detection limits. However, studies utilizing non-resonant ionization in combination with laser ablation were limited in both scope and frequency. In recent years, improvements in technology and our understanding of both laser ablation and laser sources in general have made Laser Ablation Laser Ionization (LALI) a viable and practical solution for a new suite of instruments. We will discuss the advantages LALI has over traditional laser ablation techniques. Further, we will explore the variables and optimization space which must be considered in instrument design (i.e., primary laser pulse width, plasma rejection, neutral formation, MPI saturation, and beam formation and others). Finally, results will be presented from a new commercial LALI instrument to demonstrate the abilities this technique can provide to a large application space.

Reference Materials/Standards Workshop

Thursday, June 8th

Workshop on Reference Materials for LA-ICP-MS

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The goals of this workshop are to (1) provide a brief introduction to reference materials (RMs) for Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS), (2) identify the current RMs used most widely for trace element analysis, isotope ratios and geochronology by LA-ICP-MS, and (3) discuss and identify current/future RM needs for the LA-ICP-MS community.

RMs for LA-ICP-MS are needed for external calibration, method validation (QA/QC), and corrections for instrumental mass bias, instrument drift, and laser-induced elemental fractionation (LIEF). Characteristics of 'good' RMs are well-determined reference values traceable to known calibrants, wide availability, documented heterogeneities restricted to specific elements or domains, and few spectral interferences that compromise measurements. RMs are produced and characterized by government agencies (NIST, IRMM, etc.) and professional societies (IAG) following rigorous guidelines such as those of the International Organization for Standardization (Geneva) compared to RMs developed by individual research groups. The main types of RMs available for geoscience applications are synthetic and natural composition glasses, pressed powder pellets, including those using nano-powders (Weber et al., 2020), and natural minerals. For imaging biological tissues, gelatin micro-droplet standards spiked with multi-element standard solutions have been developed recently (Schweikert et al., 2022).

Recent requests for information from the GeoReM database (Ulrike et al., 2022) about microanalytical RMs is led by NIST SRM synthetic glasses (610, 612, 614), USGS natural composition (BCR-2G, BHVO-2G, BIR-1G) and synthetic (GSD-1G, GSE-1G) rock glasses, MPI-DING natural composition glasses (ATHO-G, KL2-G, GOR132-G, GOR128-G, T1-G), USGS pressed powder pellets (MACS-3, MASS-1) and the 91500 zircon. Supplies of most of these RMs are depleted or no longer in distribution, providing the LA-ICP-MS community with an opportunity to develop a new generation of RMs appropriate for 21st century research.

Schweikert, A., Theiner, S., Wernitznig, D., Schoeberl, A., Schaier, M., Neumayer, S., Keppler, B.K. and Koellensperger, G., 2022. *Analytical and Bioanalytical Chemistry*, *414*(1), pp.485-495.

Weber, M., Lugli, F., Hattendorf, B., Scholz, D., Mertz-Kraus, R., Guinoiseau, D. and Jochum, K.P., 2020. *Geostandards and Geoanalytical Research*, 44(1), pp.69-83.

Weis U., Stoll B., Hell K., Winkes, E. and Jochum K.P. (2022) *Geostandards and Geoanalytical Research*, 46 (4), 753–759.

Overview of NIST SRM Creation and Certification

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The National Institute of Standards and Technology (NIST) produces Standard Reference Materials® (SRMs) for use in quality assurance, regulatory requirements, and for improving measurement capabilities. As the nation's metrology institute, NIST conducts an exhaustive analysis of potential SRM materials to determine if they meet the requirements to be SRMs and what aspects of their composition or physical properties can be certified. The requirements for an SRM vary depending on the measurement need being addressed. A certified value in an SRM is traceable to the International System of Units (SI) which make them incredibly important for quality assurance programs. This presentation will show how an SRM is produced and the processes involved in assigning a value a "certified" or "non-certified" value. The entire lifetime of an SRM from proposal to renewal will be covered. Additionally there will be some discussion of the historical characteristics of the SRM 61x series along with thoughts on potentially new SRMs designed with the micro-analysis community in mind.

LIBS Tandem/ Lasers are Rad / Laser Fundamentals Oral Session

Thursday, June 8th

Spatially resolved analysis of microplastics using a combined LIBS and LA-ICP-MS approach

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Today, industries across many sectors use synthetic polymers at some point during production or include plastics in their final products due to its great versatility. Even though efforts to implement proper recycling strategies have increased in the last years, a significant amount of discarded plastic ends up in the environment. There, it undergoes alteration and degradation, resulting in the formation of microplastics. Due to their high persistence, microplastics can be transported over long distances and finally accumulate in various environmental compartments.

Exposure to such sub-micron and nanosized plastics can lead to adverse health effects within humans. Moreover, the release of additives as well as the adsorption of trace elements from the environment, may also cause potential health effects. Due to microplastics' immense impact on our ecosystems, a better understanding of their fate in the environment and characterization of their changing properties is becoming of significant interest.

In literature, various procedures for the characterization of microplastics are reported, but only some provide information about the elemental composition. In the last few years, the use of sp-ICP-MS to assess particle size has become very popular. With this approach concurrently, the occurrence of inorganic additives or contaminations could be determined. However, information about the distribution of the prevailing elements within the microplastic particles is not accessible with this technique. For this purpose, the application of solid sampling techniques is mandatory.

In this contribution, a wide range of commonly used polymers (e.g., PET, PP, PS, PVC) are analyzed using a combined LIBS and LA-ICP-MS procedure. The collection of broadband LIBS spectra provides information about polymer-specific signals (e.g., C, H, O, C2, CN), enabling the identification of the polymer type, whereas LA-ICP-MS was used for the quantitative assessment of inorganic sample constituents. The developed procedure is applied to analyze native but also aged polymer samples. Isolated particles were analyzed before and after treatment with artificial seawater containing defined amounts of heavy metals. Imaging and depth profiling experiments allowed us to investigate changes in the elemental composition of individual particles, indicating the release of additives and the uptake of trace metals during treatment with artificial seawater.

Use of molecular emission by laser induced breakdown spectroscopy (LIBS) for fluoride imaging in environmental medicine

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ROBERT O. WRIGHT[1], MANISH ARORA[1] AND CHRISTINE AUSTIN[1]

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Timing of environmental exposures is an important determinant of associated health outcomes. Tissues that grow incrementally, teeth, hairs and nails, archive snapshots of what is circulating in the blood and can provide sub-daily to monthly exposure histories when sampled at fine resolution. Fluoride, an exposure associated with neuro and renal toxicity, is a challenging environmental exposure to measure in tissue due to high detection limits for most imaging methods and the lack of suitable standards. Teeth are an excellent matrix to study fluoride exposure due to its high affinity with calcium. We developed a method to quantify fluoride in teeth using CaF molecular emission by laser induced breakdown spectroscopy (LIBS). The method was validated using novel matrix-matched hydroxyapatite standard material to quantify and measure the fluoride distribution in teeth. Doped sintered pellets were optimized to match the chemical composition, crystalline structure, mineral hardness, laser-surface response and other properties of teeth. We applied this method to quantify fluoride in teeth from rats exposed to fluoride at different levels and compare this results to that obtained by ion selective electrode analysis. Finally, we applied this method to human teeth to demonstrate utility for epidemiological study of health effects associated with fluoride exposure during early life.

Development and Validation of a LA-ICP-MS Method for the Analysis of Multivitamins

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Monitoring nutritional and toxic elements present in food, dietary supplements, and cosmetics is part of the United States Food and Drug Administration's mission to protect and promote public health. The analysis of toxic elements in multivitamins typically involves nitric acid digestion followed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) analysis. However, acid digestion is time consuming, has known health and safety concerns, and generates hazardous waste.

Laser Ablation (LA) ICP-MS offers quick, automated sample analysis without corrosive acids or extensive sample preparation while reducing hazardous waste and carryover contamination. Additionally, LA-ICP-MS is suitable for evaluating the total elemental composition of products that are resistant to nitric acid digestion and require the use of hydrofluoric and/or perchloric acids. A method for the LA-ICP-MS analysis of multivitamins was previously developed by our group. We now describe the initial steps towards the single-laboratory validation of the analytical method by reporting recoveries, limits of detection, precision, and linearity.

Multivitamin samples were quantified by LA-ICP-MS using cellulose and matrix-matched calibration standards. A set of 10 multivitamins and 3 reference materials were fortified with As, B, Co, Cr, Cu, Fe, Mg, Ni, Na, Pb, S, Zn by the addition of a cellulose multielement powder in the appropriate mass fractions. Multivitamin tablets, calibrants, and reference materials were digested using hydrofluoric/nitric acid, analyzed by solution ICP-MS, and compared to the laser ablation results. All samples were ablated using a UV excimer laser followed by ICP-MS analysis. Instrumental parameters were optimized to obtain the best signal while reducing fractionation and the variability between replicate measurements. Data on recoveries, precision, and calibration linearity of the method will be reported.

Laser-Induced Breakdown Spectroscopy to Support Advanced Nuclear Reactor Development

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Laser-induced breakdown spectroscopy (LIBS) offers a great degree of flexibility in its applications because it can be performed remotely through fiber optics, and it is able to monitor nearly the entire periodic table regardless of sample form. At Oak Ridge National Laboratory, LIBS is being used to support research on advanced nuclear reactor designs, particularly molten salt reactors. These reactors use liquid salts as the reactor coolant or as both the coolant and the fuel. As nuclear fission occurs, in which atoms are split to generate energy, new elements are produced and called *fission products*. Some fission products will form aerosols or gases and leave the reactor core through the off-gas system, where the products are captured with a variety of filter systems. A LIBS system is being developed at Oak Ridge National Laboratory to monitor molten salt reactor off-gas systems and help evaluate filter systems. Additionally, LIBS is used to support other advanced reactor research projects, such as investigating the interaction between salts and graphite, evaluating the hydration of salts before thermophysical property testing, and mapping advanced fuel forms for potential quality control purposes.

Expanding the Elemental Coverage by Combining LIBS with ICP-TOF-MS for High-Speed Imaging

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The use of laser ablation-inductively coupled plasma-time of flight-mass spectrometry (LA-ICP-TOF-MS) has become an intriguing option for the analysis of materials due to the ability to capture the entire mass spectrum with each laser pulse. However, a few hurdles still exist: the speed of analysis must be precisely synced with the laser ablation system, the difficulty of measuring light elements with a TOF, and the data treatment of very large data sets when performing large mapping experiments, to name a few. The work presented here will discuss some of these hurdles while providing pathways to address them.

The speed of analysis, including the syncing of the LA system (TOF sync) will be displayed using a two-volume laser ablation chamber (TwoVol3) in combination with a dual concentric injector (DCI) to provide ultra-fast washouts with speeds up to 1,000 Hz (in this example the max laser repetition rate was set to 200 Hz). To address the difficulty of detecting light elements, laser-induced breakdown spectroscopy (LIBS) is coupled to the LA system to provide coverage to elements such as Li, Be, C, Na, Mg, K, and Ca that may be difficult or impossible with the TOF-MS. LIBS also provides the unique ability to measure H, N, O, and F at the same time when the LA chamber is purged with a inert gas, which is the case when performing LA experiments (e.g. helium is almost always used). Lastly, the entire data processing of the TOF and LIBS data will be conducted in iolite V4, providing a complete, single software platform capable of handling large data sets.

In this work, a sample of finchite and carnotite, strontium and potassium uranyl vanadate minerals, respectively, are analyzed using LIBS and LA-ICP-TOF-MS to better understand the isotopic and chemical composition. Of interest is the isotopic ratio of ^{235}U/ ^{238}U and ^{206}Pb/^{207}Pb, and the distribution of U and O within the mineral. As finchite and carnotite are alteration phases of primary uranium ores, with their limited solubility making them important immobilization species for environmental U(VI), understanding the paragenesis of these phases in the context of spatially resolved isotopic information is essential towards understanding the environmental behavior of uranium. Further, this effort provides valuable insight into the potential of analyzing radiological material with high spatial resolution for other environmental, mineralogical, and nuclear nonproliferation applications.

Emerging Ultrafast Laser Ablation Technologies for Remote Elemental and Isotopic Analysis

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The ability to detect and quantify nuclear material at remote distances remains a continuing challenge in nuclear security and non-proliferation applications. Challenges associated with such remote detection schemes include suppressing diffraction for remote laser plasma generation, and the development of all-optical means for isotopic detection from solid materials in air at atmospheric pressure. In this talk, we will discuss emerging ultrafast laser sampling techniques that enable long-range beam propagation, as well as the development on new optical emission spectroscopy techniques for the detection and quantification of isotopes. Technologies include femtosecond laser filamentation for long-range propagation, filament-induced plasmas for optical emission spectroscopies, and the development of novel GHz bursts of femtosecond pulses as means to improve sampling and solid-target coupling for isotopic analysis. These findings underline the importance of understanding and controlling femotsecond filament -matter interactions for improving plasma formation and the corresponding elemental and isotopic signatures at remote locations.

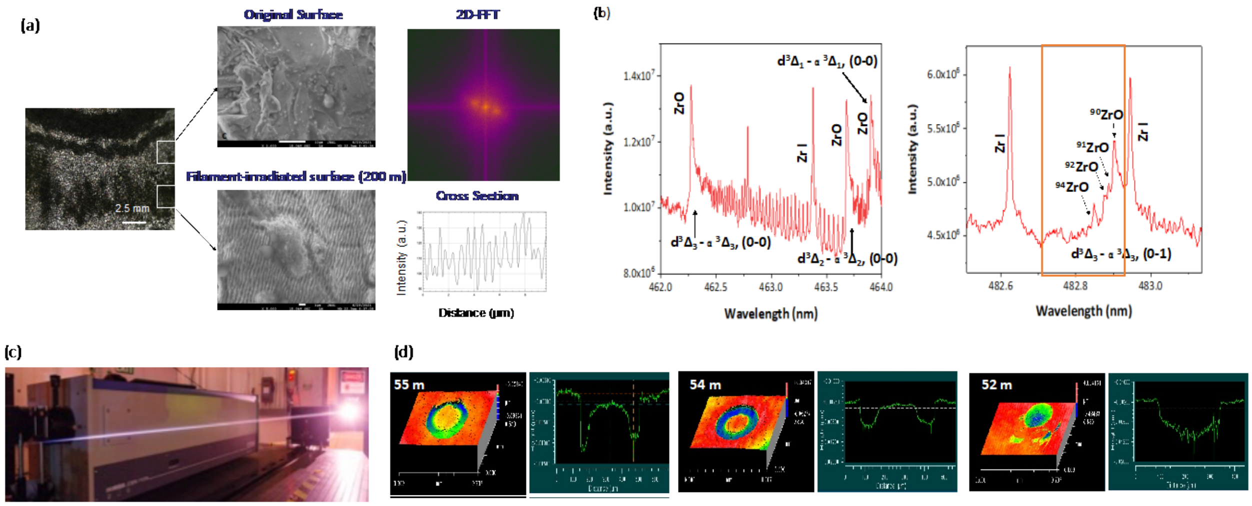

Figure 1. a) Filament-matter interaction at 200 m and corresponding surface topographies. b) Isotope detection from plasmas formed 110 m via filamentation. c) Filament propagation in air under long-exposure photography. d) Femtosecond filaments formed at 52 – 55 m propagation, showing crater charactristics and abalted volume as a function of distance.

LA-ICP-MS mapping of uranium absorption within living tissue

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The LANL *in-vitro* bioassay program currently monitors workers from across the lab at occupational risk of radionuclide exposure to plutonium, uranium, americium and tritium. The in-vitro bioassay program is largely based upon monitoring urinary excretion levels which requires an understanding of the solubility and absorption of the radionuclide by the worker and its subsequent excretion. Of particular concern are acute exposures that can occur during serious incidents such as glovebox breaches (leading to inhalation of uranium or plutonium particles) or puncture injuries which can pierce laboratory gloves and skin and embed particles in tissue directly. In these cases, little is still known about the mechanisms and levels of radionuclide absorption in the localized trauma region.

In order to investigate the absorption of radionuclides at a trauma site, we have exposed a set of living human tissue samples to aqueous and solid uranium contamination. Using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), we are investigating whether the migration of uranium can be tracked as the cells multiply and the tissue grows. 3D visualization can be achieved by exploiting the cratering of a sample surface which is inherent in the analytical method, allowing layer-by-layer elemental mapping into the sample. Tracking uranium migration from a puncture site may provide a better understanding of injuries caused by the handling of dangerous metals and how to limit the extent of tissue damage from such injuries.

Enhancing LA-ICP-MS Image Quality through Ablation Grid Optimization

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In this study, we investigate the potential benefits of adapting the ablating grid in two-dimensional (2D) and threedimensional (3D) laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in single pulse mapping mode. We show that by carefully contracting the ablation grid and controlling 2D overlapping of ablation spots, it is possible to control the depth of ablation while still producing a smooth surface, resulting in significant improvements in post-ablation surface smoothness, spatial resolution, and control of the ablation layer depth. To achieve this, we used a computational approach using geometrical modeling to compound square or round experimentally obtained 3D crater profiles on variable orthogonal or hexagonal ablation grids. The optimized grids were then used to simulate the post-ablation surface and related image quality. Our findings indicate that arranging the ablation grid in a hexagonal pattern can increase pixel density by 15 %, and further gains can be achieved by closer packing of "soft shell" spots to reduce the post-ablation surface roughness, depending on the crater profile. Although blurring could be addressed through deconvolution, the relatively high noise in LA-ICP-MS mapping typically results in poor quality deconvolved maps. Our study recommends using symmetrical contraction to moderate levels, such as a maximum of 2×2 crater overlaps, to prevent depth related distribution differences and reduce the risk of blurring. Overall, our results provide insights into how to optimize LA-ICP-MS mapping for accurate surface sampling of element distributions, improving control of depth-related sampling, and increasing image quality. An online application to experiment with contracting/expanding orthogonal and hexagonal ablation grids for generic 3D super-Gaussian laser crater profiles will be demonstrated to showcase the resulting post-ablation surface layer roughness and depth.

Applications to Geochemistry Oral Session

Friday, June 9th

Characterising and minimising analytical uncertainty of multi-element mineral analyses by LA-ICP-MS

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Characterisation of analytical uncertainty of LA-ICP-MS analyses has been a focus of many studies (e.g., [1][2][3]). Currently, consensus is emerging with regards to uncertainty estimation and reporting for LA-ICP-MS U-Pb dating applications [4], however complete uncertainty budgets for LA-ICP-MS multi-element mineral analysis are not well constrained, largely due to complexities with characterising uncertainty contributions from matrix effects and other sources of elemental fractionation.

In this contribution, we will describe various sources of uncertainty in LA-ICP-MS multi-element mineral analysis and discuss approaches to developing quantitative analytical methods that allow for characterisation and minimisation of uncertainty. Random sources of uncertainty that contribute to precision can be assessed by comparing the results of multiple successive analyses of a homogeneous sample. In addition to counting statistics, precision is affected by physical processes that occur during analytical sessions, such as variations to laser fluence and differences in the geometry and rate of gas flow in different locations within the ablation cell, both affecting aerosol formation and transport processes.

Characterisation and minimisation of systematic sources of uncertainty that contribute to accuracy is linked to consistency in instrumentation performance and the design of analytical methods. Consistency of laser fluence at the sample, aerosol digestion efficiency in the ICP and the amount of air and moisture in the ablation cell and interface tubing [5] between and during analytical sessions allow for significant decrease in intra-laboratory uncertainty (between-session reproducibility).

Maintaining low intra-laboratory uncertainty is essential for developing robust approaches to quantification that are based on using non-matrix matched reference materials (RMs). A single calibration RM is selected to minimise measurement uncertainty. Secondary RMs are measured using the established settings required for accurate quantification of the unknowns. Results from the secondary RMs are used for quality control and to estimate correction coefficient values for each set of laser conditions required for assessing external reproducibility accurate quantification of the unknowns.

[1] Luo et al. (2007) JAAS 22, 122-130. [2] Gilbert et al. (2013) GGR 37, 51-64. [3] Ulianov and Muntener JAAS 29, 934-940. [4] Horstwood et al. (2016) GGR 40, 311-332. [5] Thompson et al. (2018) JAAS 33, 221–230. [6] Danyushevsky et al. (2011) GEEA 11, 51-60.

Mapping fluid and metamorphic events with trace elements in eclogite garnet

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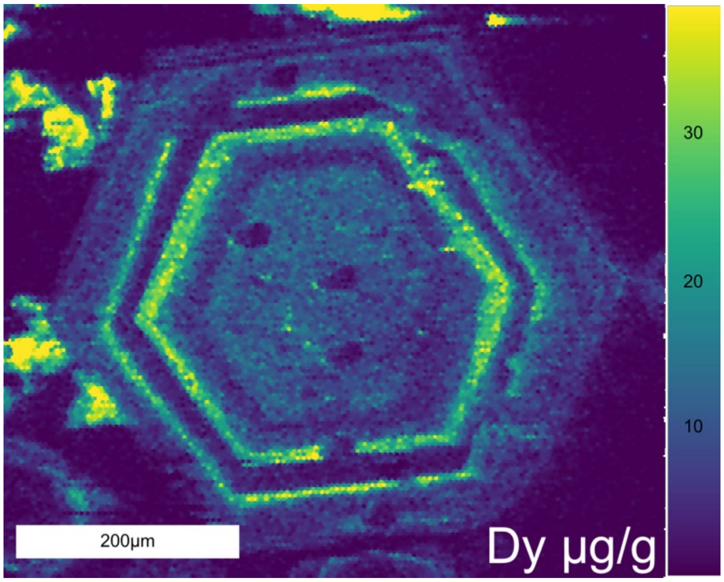
Eclogite and related garnet-bearing rocks can be used as probes into fossil subduction zones to reconstruct pressure-temperature-time-fluid (*P*-*T*-*t*-f) histories. Garnet, with its slow rates of intracrystalline diffusion and utility in thermobarometry, makes a robust archive of trace-element and stable isotope information that can be tied to *P*-*T*-*t*-f histories. Trace element zoning in garnet is a complex phenomenon controlled by metamorphic reactions and external metasomatic fluids, as well as variable diffusion rates through the rock, and even changing porosity. In many cases, major and trace element zoning features are too small and irregular to be adequately characterized using a traditional spot traverse approach.

Trace elements (Sc, Cr, Co, Y, Dy, Er, Yb) were mapped by LA-ICP-MS using a 3x3 µm spot in garnets from three samples of eclogite from the Franciscan Complex of California. Many of these elements are zoned at the sub-10 µm scale. All three samples have a clear core-rim zonation visible in major and trace elements. REE (Dy, Er, Yb) and Y are generally elevated in garnet cores with multiple annuli in garnet rims. Inner annuli are richer in MREE (Dy) than HREE (Yb). In the outermost rims of two samples with oxygen isotope evidence of external fluid infiltration, elevated HREE (Er, Yb) and Y are correlated with the fluid infiltration. Figure 1 (at right) shows a Dy map of a single garnet from one eclogite sample. Multiple annuli of decreasing Dy concentration are present in the garnet rim, including one truncated by resorption.



Transition elements offer a different record. Cr zoning is generally patchy, likely controlled by pre-existing mineralogy, but in some cases displays oscillations that match REE zoning. The garnets are zoned in Co, with zoning patterns most similar to Mg. Sc is generally anti-correlated with Co and is most similar to Ca, but contains more oscillations and is elevated in rims in samples with evidence of fluid infiltration.

Development of a matrix-matched reference material for quantitative multi-element determination of sphalerite using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

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The advent of LA-ICP-MS allows rapid, in situ, quantitative determination of multi-element concentrations and resolving potential paragenetic differences in element composition in zoned sphalerites. However, the calibration reference material Mass-1 commonly used in analysis of sphalerite contains significant amount of water (13.6 Wt.%) that results in substantial sulphur and ioxide interferences on ^{70}Ge and ^{72}Ge, and iron-oxide interferences on ^{73}Ge and ^{74}Ge, and consequently biased measurement of Ge concentration in sphalerites. Moreover, the other commonly used calibration reference material STDGL2b2 does not report a preferred Ge concentration. As a result, the lack of well-characterized matrix-matched calibration standard limits application of LA-ICP-MS for in situ analysis of sphalerite. In this contribution, we present a new method to produce a ZnS calibration material for quantitative multi-element analysis by LA-ICP-MS. The single element (e.g., V, Cr, Ti, Ge, and Te) and metal-sulphide standard reference materials (e.g., MnS, FeS, CoS, NiS, CuS, ZnS, Ga_2S_3, As_2S_5, SeS_2, MoS_2, Ag_2S, CdS, In_2S_3, SnS, Sb_2S_3, WS_2, PbS, Bi_2S_3) from Alfa Acesar and Sigma-Aldrich Inc. were used to prepare the new ZnS calibration reference material. In order to cover a wide range of natural sphalerite compositions, the major, minor and trace element contents of the reference material were adjusted to achieve the target element concentrations of ~400 µg/g V, Ti, Ni, Ga, As, Se, Mo, Ag, Sb, Te, W, Bi, Mn, Co, ~2000 to ~3000 µg/g Cu, Ge, Cd, In, Sn, Pb, ~2.72 Wt.% Fe, ~32.83 Wt.% S and ~62.27 Wt.% Zn. The resulting final dry powder reference material was prepared through grinding the mixture of 23 standard reference materials using a planetary micro-mill, followed by drying the material slurry using a freeze dryer. The particle size distribution of the dried ZnS reference material determined using a laser particle size analyzer shows 96% of particles are in the size range of between 0.084 and 2.011 µm, and 4% of particles in the rage of between 2.011 and 2.92 µm. This result is consistent with the particle size of <3.0 µm determined by SEM. The reference material nanopowder was then pressed into pellets. The pellets will be sintered using a furnace at a temperature of 400 ± 5 °C over a period of 100 hours. The study will also present statistical results for the homogeneity of major and trace element distributions in the sintered ZnS calibration reference material measured using EPMA, ICP-OES, solution nebulization and laser ablation triple quadrupole ICP-MS. Finally, the homogeneity of grain size distribution and its impact on laser ablation behaviour of the calibration material will be discussed to evaluate the suitability of future applications of this ZnS reference material.

VENDOR / SPONSOR TALKS

Advances in Tandem LA – LIBS Technology and Data Analysis

GONZALEZ JHANIS J[1], CHARLES SISSON[1], CHUNYI LIU[1], STEVE SHUTTLEWORTH[1], JONG YOO[1], AND RICHARD E. RUSSO[1].

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Since 2012, for more than a decade, Applied Spectra has led both introduction and advancement of tandem LA-LIBS instrumentation. This technology combines LIBS and LA-ICP capabilities to address the needs of the scientific community to analyze heterogeneous materials with higher productivity, superior sensitivity and enhanced precision, while delivering the maximum chemical information with each laser sampling. Applied Spectra continues to evolve this technology to exploit some unique advantages of LIBS and LA-ICP in the analysis of solid samples. This presentation highlights the advantages of the system capable of utilizing multiple LIBS sensors that operate simultaneously, sample chambers for effective simultaneous LA and LIBS operation and new data analysis software (ClarityNeXt™) that processes, fuses, and provides chemical maps of both LIBS, LA-ICP, and Tandem data.

Unique Capabilites of ICP-MS/MS Single Unit Mass Resolution Technology for Laser Ablation

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Utilizing the unique capabilities of ICP-MS/MS with true single unit mass resolution solves many issues that are not possible with single quad ICP-MS and in some cases HR-ICPMS. This discussion will demonstrate the capabilities of a high sensitivity ICP-MS/MS, using mass shift technology to remove interferences, both from sample matrices and associated isobaric interferences. In addition, the low abundance sensitivity of MS/MS mode assure there is no tailing of adjacent masses on the element of interest, increasing the accuracy of the resulting laser ablation data.

Advances in time-of-flight LA-ICP-MS using up to 1kHz ablation rates and novel techniques to increase sensitivity and remove interferences when imaging biological matrices

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In situ techniques based on Laser Ablation and Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) have been widely used, rapidly evolving into well-established, powerful tools for direct analysis of solid samples.

Recent advances in laser ablation have allowed for particulate plumes from each laser shot to be efficiently transported to the detection system with minimal diffusion, enabling a clear differentiation of each shot at very high ablation rates up to 1000Hz.

Fully leveraging these advances requires a new type of mass spectrometer. Sequential scanning mass spectrometers are unable to measure more than one or two ions during such rapid events, and efforts to do so result in aliasing effects and pixel lag that cannot be resolved through data reduction. A TOF mass analyser solves these issues by detecting virtually the entire mass spectrum quasi-simultaneously at spectral accumulation times in the sub-millisecond timeframe. Data will be shown which demonstrates high speed LA-ICP-TOF-MS at high lateral resolution with full elemental coverage.

We also demonstrate that the previously reported issues of limited dynamic range and poor abundance sensitivity of a TOF-ICP-MS can be resolved using multiple shots per pixel and closed loop triggering of stage movements to enable a novel technique which can create images showing elements between per cent and sub-ppm levels in one image.

Other applications will show the increased sensitivity available with an increase of the TOF duty cycle when reducing the mass range covered and the specialist interference removal capabilities that allow access to more abundant isotopes not normally used in the laser ablation of biological matrices.

Elimination of Aliasing by use of Aligned LA–ICP–MS

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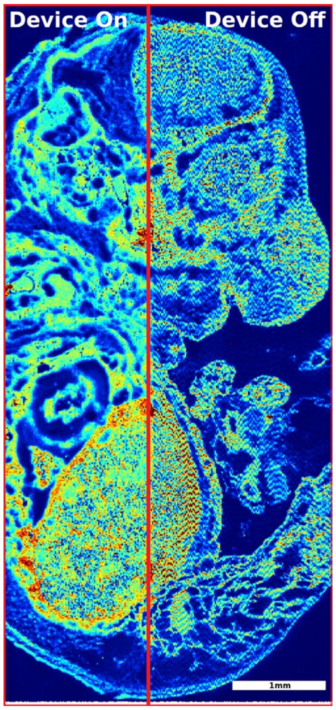
Using a fast-washout ablation cell (“fast cells” for short, defined as washout time to 1% < 50 ms) for LA–ICP–MS improves spatial resolution of images, reduces the time required for measurement, and raises the peak signal intensity – which in some cases may bring signals above detection. The primary motivation to develop fast cells has been for imaging, which is a powerful and useful technique with a wide range of applications in the earth, material, and biological sciences[1]. Other applications of fast cells include high throughput analysis and whenever high spatial resolution in the down-hole signal is required, such as ablation of heterogeneous materials.



When using fast cells with a sequential mass spectrometer, such as a quadrupole, it is necessary to avoid certain conditions otherwise images will be marred by artefacts caused by aliasing. One way to eliminate aliasing is to lengthen the response time of the ablation cell, but doing so is fundamentally at odds with the objective of collecting images that contain millions of pixels[2].

Our new approach[3] is to align firing of the pulsed laser with the sweep time of the single-detector mass spectrometer. We call this aligned LA–ICP–MS and the technique can be implemented by way of an external circuit that monitors the mass filter position of the mass spectrometer in real time and fires the laser as required.

To demonstrate the effectiveness of this technique we have collected a series of images from biological and mineral samples which demonstrate that aligned LA–ICP–MS is an effective approach to imaging and makes it feasible to use fast cells with quadrupole mass spectrometers. We will also demonstrate further applications of the technique, such as the ability to selectively increase or decrease the signal intensity for individual masses within the sweep.

[1] Doble, Philip A., et al. *Chemical Reviews* 121.19 (2021): 11769-11822.

[2] Marillo-Sialer, Estephany, et al. *Journal of Analytical Atomic Spectrometry* 35.4 (2020): 671-678.

[3] Norris, C. Ashley, et al. *Journal of Analytical Atomic Spectrometry* 36.4 (2021): 733-739.

Simplifying Solid Material Characterization with the Massbox

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Exum developed world’s first Laser Ablation Laser Ionization Time of Flight Mass Spectrometer (LALI-TOF-MS), the Massbox, to address many challenges and limitations of existing analytical instruments for solid sample characterization. The Massbox combines Exum’s patented dual-laser ionization source with a TOF mass analyzer for rapid, high-sensitivity elemental and/or chemical characterization of any solid sample. This work showcases the Massbox’s quantitative and qualitative capabilities with a variety of sample types. Exum’s Massbox is capable of quantifying both trace and major elements, as well as many interstitial elements like carbon, nitrogen, and oxygen. Additionally, the Massbox has an adjustable laser spot size and accommodates chemical/elemental mapping with a spatial resolution that ranges from 5-200 um, and results reveal spatial distributions and/or depth profiles for elements of interest. In addition to the analytical advantages, the hardware innovations of the Massbox also enable a unique user interface and many software automations. Users navigate through the automation sequence with an integrated touchscreen interface that provides an experience reminiscent of modern smart-phones. Within minutes brand new users have high-quality mass spectral data for their samples of interest. There are so few interferences and overlaps in the mass spectra that much of the data processing is also automated. At the end of the day, the Massbox brings powerful analytical capabilities into the hands of users that have never had access such technology without the assistance of highly-trained chemists.

High-Speed Imaging for Biological and Geological Applications

Quarles, C Derrick Jr.[1], Carina Wolf,[2] Karolin Sommer,[2] Uwe Karst,[2] Lukas Brunnbauer,[3] Birgit Achleitner,[3] Andreas Limbeck[3]

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2 University of Münster, Institute of Inorganic and Analytical Chemistry, Münster, Germany
3 TU Wien, Institute of Chemical Technologies and Analytics, Vienna, Austria

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has become a popular tool for measuring and determining elemental distributions within a given sample. Recent advancements in technology have led to improvements in detection limits, spatial resolution, and speed of analysis. The laser ablation cell is one of the key technological advancements that is responsible for these improvements.

Here we present two different platforms, imageBIO and imageGEO^{LIBS}, which are dedicated LA systems designed for biological and geological applications, respectively. Important to both platforms is the TwoVol3 (two-volume chamber), which enables superior washout and contains high-precision stages which are important for high-speed, high-resolution imaging. New to the TwoVol3 is the ability to add laser-induced breakdown spectroscopy (LIBS) which allows for simultaneous LIBS-ICPMS. To demonstrate these capabilities, three different imaging applications will be highlighted: 1) LA-ICP-MS to measure the uptake of free Gd^{3+}, linear GBCAs, and macrocyclic GBCAs in Arabidopsis Thaliana, 2) LIBS-ICPMS to measure tattoo pigments in skin samples, and 3) LIBS-ICPMS to measure trace and major elements in various minerals.

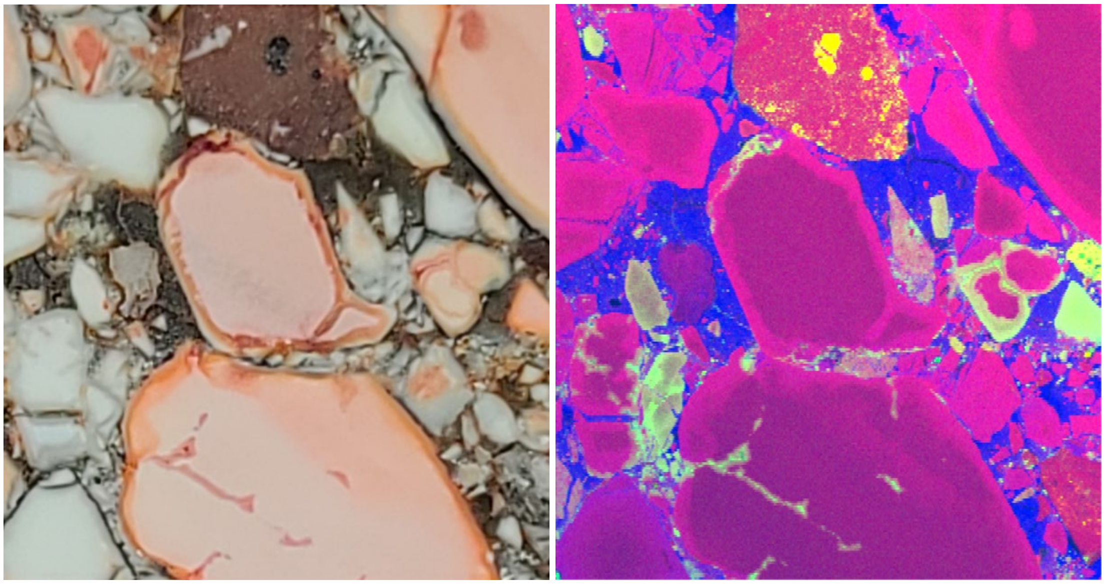

Figure 1. Left) Microscope image of the minerals in application 3 and **Right)** Mg-C-Si overlay using iolite V4 (R-B-G scale, Mg = red, C = blue, Si = green).

Automated High Throughput Analysis of Rare Earth Elements in Large Batches of Mining Discovery Samples by LA-ICP-MS

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[2] PerkinElmer Inc., Shelton, CT, USA
[3] Elemental Scientific Europe Ltd., Huntingdon, UK

Identifying deposits of rare earth elements (REE) that are economically viable to extract has become increasingly important. Providing rapid and cost-effective means to screen discovery samples for REE content would allow greater resolution and/or greater survey area coverage but would necessitate the analysis of hundreds, if not thousands of samples per day. Acid digestion may require several different approaches, depending on rock/mineral composition and has time and safety implications.

Direct analysis of solid samples via LA-ICP-MS in a high throughput environment has been made possible by synchronising the NexION 5000 ICP-MS (PerkinElmer) with the sample handling/ablation capabilities of LaserTRAX (Elemental Scientific Lasers) into a single workflow. This work demonstrates the NexION 5000 Multi-Quadrupole ICP-MS as sensitive and robust detector suitable for the routine quantification of ultra-trace impurities and major components in solid matrices.

Here we present, short and long-term performance data, of discovery samples in the determination of major and trace elements. Fused Li-tetraborate bead samples were analysed by XRF before being transferred to the LaserTRAX/NexION 5000 instrument. Automated data reduction was performed in Xceleri (Elemental Scientific Lasers) synchronised sample ID's with quantitative data, regularly calibrated and performed quality control checks.

POSTER PRESENTATIONS
GROUPED BY THEME

GEOCHRONOLOGY
POSTER PRESENTATIONS

Cryptic geologic events revealed by single spot Rb-Sr dating of biotite by LA-MC-ICP-MS/MS

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[2]The Pennsylvania State University, Department of Geosciences, University Park, PA 16803, USA
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Metamorphic micas preserve a rich record of tectonism, thermal perturbations, and fluid interactions, but are challenging to date in situ, and often exhibit complex Ar/Ar and Rb-Sr age spectra. Recent developments in tandem mass spectrometry enable precise in situ Rb-Sr mica geochronology, and potentially permit deconvolving individual (re)crystallization events. Here we measured simultaneous isotope ratios of ^{87}Sr/ ^{86}Sr and ^{87}Rb/ ^{86}Sr in metamorphic micas from the contact aureole of the Mooselookmeguntic pluton in western Maine, USA, using an ESL™ image GEO™193 excimer laser-ablation system coupled to a Thermo Scientific™ Neoma MS/MS MC-ICP-MS. These mica-bearing metasediments were subject to regional metamorphism during the Acadian Orogeny (ca. 400 Ma) followed by thermal metamorphism during post-orogenic plutonism, including the Mooselookmeguntic pluton (ca. 370 Ma). Fully integrating the data from each biotite spot analysis yields sample isochrons with average Rb-Sr dates of ~290 Ma; however, single spot Rb-Sr isochrons constructed from individual integrations within each spot reveal peaks at 303, 270, and 240 Ma (see also Cruz-Uribe et al., this session). These individual Rb/Sr dates are apparently independent of Rb/Sr ratio, suggesting decoupling between biotite elemental compositions and isotopic ages. Previous amphibole Ar-Ar plateau ages from the Mooselookmeguntic pluton range from 370–305 Ma [1,2], consistent with our oldest Rb-Sr dates and indicative of lengthy Carboniferous metamorphism in Maine. Slightly discordant U-Pb dates for the nearby Mt. Mica pegmatite ca. 270 Ma [3] indicate a possible intrusive heat source in western Maine during the final stages of the Alleghanian orogeny. Biotite Ar-Ar cooling ages in the Mooselookmeguntic and adjacent plutons range from 229–249 Ma [2], consistent with our youngest Rb-Sr single-spot isochron dates. The punctuated nature of events recorded by Rb-Sr in biotite suggests the ability for micas to record complicated heating, cooling, and fluid histories of rocks, and may elucidate cryptic metamorphic events in western Maine associated with the Alleghanian orogeny and subsequent breakup of Pangea.

[1] Lux & Guidotti (1985). Geology, 13, 696–700.

[2] DeYoreo et al. (1989), Studies in Maine geology: igneous and metamorphic geology 3, 19–34.

[3] Bradley et al. (2016), The Canadian Mineralogist 54, 945–969

Small volume (multi-shot) approach to U-Pb dating of uraninite by LA-ICP-MS for nuclear forensic applications

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Laser induced elemental fractionation (LIEF) remains an obstacle in achieving the analytical precision and accuracy associated with other in-situ U-Pb dating techniques. LIEF typically results in non-stoichiometric sampling of the target analyte, and has previously been minimized using different approaches: adopting a short (157 or 193 nm) laser wavelength[1], maintaining focus above the material surface[2], careful tuning of carrier gas flow and composition[3] and avoiding melting or particle re-deposition over the sample surface by utilizing shorter pulse widths[4]. However, LIEF can also be minimised by ensuring craters are of a critical aspect ratio (depth/diameter)<1[5]. Previous studies have demonstrated the utility and potential of a singleshot approach to laser ablation for minimising sample destruction by integrating discrete ion signal peaks generated by consecutive single laser pulses[6]. This multi-shot approach results in much shallower depths than a conventional laser analysis (up to 96.5%), which demonstrably minimises U-Pb 'downhole' fractionation[7]. A recent study applied a small volume, multishot LA-ICP-MS approach to various zircon standards and samples dated by IDTIMS, which produced weighted mean age determinations largely reproducible to ≤1% (2σ) on small sample volumes (as low as 704 ±23 μm^3) with a 40 μm diameter spot[7].

This study reports U-Pb age results using a multi-shot approach in an investigation of previously dated, natural uraninites from various deposits[8] using spot sizes between 8 and 15 μm. Employing such small spot diameters for the dating of uraninite is advantageous due to the inherent difficulties associated with open system behavior that involve either uranium and/or lead loss or gain[8]. The U-Pb dating results obtained here overlap reported ages for previously investigated uraninites[8]. Obtaining meaningful age determinations with minimal sample preparation in a timely fashion help to discriminate geochemical signatures (e.g., chondrite normalized REE patterns) for natural uranium ores, and may assist to potentially restrict geographical areas for provenance consideration for nuclear forensic applications.

[1]- Jackson, S.E. et al. 2004. *Chem. Geol.* 211 (1–2), 47–69; [2]- Marillo-Sialer, E. et al. 2016. *Chem. Geol*. 438, 11–24; [3]- Kroslakova, I., Günther, D., 2007. *J. Anal. At. Spectrom*. 22, 51–62; [4]- Shaheen, M.E. et al. 2012. *Chem. Geol*. 330-331, 260–273; [5]- Mank, A.J.G., Mason, P.R.D., 2001. *J. Anal. At. Spectrom.* 16, 1381–1388; [6]- Cottle, J.M. et al. 2009. *J. Anal. At. Spectrom.* 24, 1355–1363; [7]- Corbett, E.P. et al. 2020. *Chem. Geol*. 544: 119568; [8] Corcoran, L., Simonetti, A. 2020. *Minerals* 10, 205.

Detrital zircon ages from Silurian strata in the Central Maine Basin: Implications for the existence of the Messalonskee Lake thrust

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The Central Maine Basin is composed of metamorphosed marine sedimentary rocks deposited in Late Ordovician to Early Devonian time. Metasedimentary sequences span across inland Maine, increasing in grade to the southwest. Repeated deformation obfuscates the stratigraphy and has led to varied interpretations of Maine's tectonic history. The Messalonskee Lake thrust has been proposed to divide the Central Maine Basin into western and eastern sections, separating two formations of similar age and lithologic character, the Sangerville in the western lower plate and formations in the Vassalboro Group in the eastern upper plate. Graptolite fossils in the Vassalboro Group formation constrain deposition to about 430 Ma, and relative dating places formation of the Sangerville younger than the Vassalboro Group. The Messalonskee Lake thrust was first proposed to explain inverted sequences and stratigraphic discrepancies, however, no direct field evidence for faulting exists, classifying the Messalonskee Lake thrust as a conceptual fault. The Maine Geological Survey is remapping the bedrock geology of Maine, and the existence of the Messalonskee Lake thrust is called into question as it is portrayed as a major structure in south-central Maine.

Detrital zircon U-Pb dates will be determined by LA-ICP-MS to further constrain depositional ages and sediment provenance of units currently mapped on either side of the proposed location of the Messalonskee Lake thrust. Significant differences in detrital age populations would be consistent with existence of a fault, whereas similarities would call into question as to whether a fault is necessary. Either outcome would impact interpretations of the bedrock geology in the area between Waterville and Lewiston. Confirmation of the fault solidifies the current stratigraphic formations and tectonic history and leads to more questions of the details of the fault. Similar ages could lead to a reclassification of the Sangerville and Vassalboro Group formations and influence the tectonic history in the Central Maine Basin.

Development of apatite dating in ms/ms mode by LA-QQQ-ICP-MS and application to ore deposit research

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The LabMaTer laboratory, located at the University of Quebec in Chicoutimi (UQAC), is currently developing its analytical capabilities by the recent acquisition of a LA-QQQ-ICP-MS. This study is part of a larger plan to develop applications to ore deposit research at LabMaTer. One of the outstanding outcomes of the use of a LA-QQQ-ICP-MS is the ability to add reactive gases that would remove selected interferences in a batch of measured isotopes. Specifically, adding NH_3 has proved to be an excellent reactant to form complexes with Hg and therefore allow to measure ^{204}Pb with better precision, a crucial isotope in dating applications. A precise measurement of the ^{204}Pb isotope is crucial when dating minerals that are prone to remobilization and common lead integration, such as apatite.

Apatite is a very common mineral in ore deposits but also in multiple geological settings whether it is mineralized or not. Apatite is also a very good mineral to trace processes and environments because its mineralogical structure allows substitution with elements from its environment. Finally, apatite is rich in phosphorus and variably rich in REE which also makes it an economically interesting mineral.

Preliminary results of U-Pb dating of apatite at LabMater on multiple apatite reference material from the literature (MAD, Durango, Fish Canyon Tuff, McClure and Slyudyanka) are very promising and emphasize the ability of NH_3 to remove the Hg interference and allow more precise dating results for this type of ^{204}Pb-rich mineral. Our measurements show perfect agreement with the ages published in the literature and as good precision as early studies with similar protocoles.

We have started to analyze samples from Fe-Ti-P mineralisation from Québec where apatites are highly abundant but also quite homogeneous, potentially suitable for new dating reference material. Specifically, the Lac A Paul Fe-Ti-P deposit in Québec could potentially provide an apatite reference material in the age range of 1 Ga, which is rather rare. Dating apatite from the ca. 565 Ma Sept Iles Ìntrusive Suite could bring insight into multiple pulses forming a mafic layered intrusion and its Fe-Ti-P mineralisation (Kieffer et al., 2023). Further work will follow towards developing new standards for dating but also for trace element work. The results are currently in an early stage but we encourage discussion about collaborative projects to develop new standards and analytical protocoles.

Kieffer, M. et al., 2023. The use of trace elements in apatite to trace differentiation of a ferrobasaltic melt in the Sept-Iles Intrusive Suite, Quebec, Canada: Implications for provenance discrimination. Geochimica et Cosmochimica Acta, 342, 169-197.

Protocol Development and Application of Young (≤10Ma) U-Pb Zircon Dating by LA-Quadrupole-ICP-MS

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Zircon U-Pb age spectra provide important constraints on the behaviour of volcanic systems and the magma processes that lead up to eruptions. Although much of this work has traditionally been done by ion microprobe, laser ablation offers an alternative approach to more rapidly characterize the U-Pb age systematics of young volcanic systems. We have developed an in-house methodology for dating young (≤10 Ma) volcanic zircons by LA-Quadrupole-ICP-MS involving optimizing ablation, mass spectrometry and data processing approaches. Results from round robin experiments on common zircon reference materials and zircons from an ~3 Ma ignimbrite from Cerro Chaxas of the Central Volcanic Zone of the Andes show that ow laser pulse rates (5 Hz) and long ablation periods (40 secs) are imperative for producing quality data in this age range. Distinguishing between real age zoning and U-Pb interelement fractionation is ambiguous with higher pulse rates. Increasing the number of channels and dwell times on peaks of key radiogenic daughter isotopes (^{206}Pb,^{207}Pb) also dramatically improves accuracy and precision for young zircons and reference materials. With these optimized ablation and mass spectrometry approaches produce fully propagated errors of individual analyses from Andean zircons as low as 5% (2σ).

Cerro Chaxas (8.35-2.16Ma; ^{40}Ar/^{39}Ar in biotite) in the Altiplano-Puna Volcanic Complex (APVC) of the Central Andes was targeted as a long-lived volcanic centre that may have recorded a significant arc magma flare-up that occurred between 1 and 10 Ma. Application of our methodology shows that prior ^{40}Ar/^{39}Ar age data for this unit may be incorrect, and that *Cerro* Chaxas was in fact a zone of focused volcanism between 1- 4.5 Ma. Updated stratigraphy and a preliminary geologic map of *Cerro* Chaxas are presented here. A continuous-time Markov chain (CTMC) applied to zircon age data can help to make predictions on the tendency for Chaxas' prolific flare-up reservoir to remain supra-solidus via high flux. Predictions from the CTMC can be compared with zircon ages from small volume systems emplaced in low flux conditions to examine the influence of magmatic flux in the development of volcano-plutonic systems.

Geochronology and Geochemistry of the Maple-Hovey Manganese Deposit, Northern Maine

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The Aroostook County Manganese District in Northern Maine consists of northern, central, and southern sub-districts of Silurian age. Collectively, they represent the largest manganese reserve in the United States. This study focuses on the central sub-district where the largest known deposit, the Maple-Hovey Fe-Mn deposit, is located. Detailed mapping, geochemical, petrographic, and mineralogic analyses have been conducted to characterize the lithogeochemistry, chemostratigraphy, and mineralogy in the deposit to better constrain its metallogenesis. Field observations show that the deposit is presented as a continuous but pinch-and-swell layer, and the primary ore zone consists of thinly laminated, very fine-grained manganese ironstone. The ore and surrounding host rocks are dominated by a layered sequence with varying mineralogy. Petrographic and mineralogic observations reveal a chlorite-rich host rock, Fe-rich layers largely consisting of hematite with lesser magnetite and pyrite, Mn-rich layers of varying compositions of Mn-silicates, oxides, and carbonates, and P-rich layers occurring in the primary Mn ore zone. Cross-cutting veinlets containing Mn-silicate (possibly rhodonite, $MnSiO_3$), albite, and other minerals indicate minor hydrothermal activity. These observations support the interpretation that the Maple-Hovey deposit represents a sedimentary origin similar to the well-characterized Silurian Woodstock Fe-Mn deposits in New Brunswick, Canada, and other Fe-Mn deposits worldwide. However, the geochronology of the Maple-Hovey deposit is not well-constrained. Recent bedrock mapping efforts reveal that the Maple-Hovey deposit is hosted in a volcanic basin, differing from the other Mn sub-districts in the area. Palynology and megafossils confirm a post-Homerian Silurian age for the deposit. Zircon U-Pb dating of the volcanic formations conformably underlying the formation that hosts the Maple-Hovey deposit will constrain the absolute timing, allowing for an improved understanding of the role of the volcanics in the basin and the time frame of Mn deposition. Detrital and igneous zircon U-Pb dates will be determined by LA-ICP-MS.

Building upon laser ablation split stream depth profiling for granitic zircons: developing LASS raster-profiling

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Granitoids are a major constituent of continental crust. Despite their prevalence, the formation of granitoid rocks remains poorly understood. One challenge is that granitoids may take several million years to cool after emplacement, during which time they may experience many post-emplacement effects such as fluid alteration, additional magma intrusion, and/or volcanic eruption. These effects make interpretation of primary features difficult by altering whole-rock chemistry and field textures. Zircon ($ZrSiO_4$) is resistant to many of these secondary processes, and is therefore frequently used to study granitoid magmatism. As zircon grows in a granitic melt, it sequesters key trace elements (U, Ti, REE) from the melt that may be useful for constraining the magmatic history. For example, U (and Pb) yield age information, Ti concentration is a thermometer, and REE can provide information about co-crystallizing phases or melt compositions.

Laser ablation-split stream-inductively coupled plasma-mass spectrometry (LASS) allows for simultaneous measurement of all these variables within a single analysis, revealing significant detail about zircon growth histories. The growth history of zircon is typically measure by spot analysis, but a spot on the surface of grains averages the chemistry of the grain and excludes significant detail. In efforts to decrease mixing and increase spatial resolution, we have recently employed laser-ablation depth profiling to recover near-rim magmatic evolution trends. While depth profiling yields more detailed geochemical trends than spot analyses, there are significant trade-offs, particularly the higher uncertainties per integration due to the smaller volume per integration compared to a spot analysis. To address these issues, we are developing a method of "raster profiling", in which we perform multiple, progressively deeper transects across the same lines and integrate across their lengths. This method yields larger volumes of ablated material per integration and reduces the uncertainties inherent to depth-profiling analyses. However, many variables remain to be optimized, including laser energies, scan rates, and progressive downhole focusing of the laser. This presentation will present the current work and limitations on the development of this technique.

U-Pb geochronology and Hf isotopes of Grenvillian units in Santiago Coatepec, Puebla: deciphering the pre-Rodinian scenario of southern Mexico

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Oaxaquia, a Mesoproterozoic microcontinent located in Mexico and constituting a significant portion of the Grenville orogen, is constituted by several inliers of lower-crust rocks. The Oaxacan Complex is the largest outcrop of ortho and metasedimentary units, made up of mostly 1.0-1.3 Ga protoliths, affected by local migmatization (ca. 1.1 Ga) and granulite facies metamorphism at ca. 0.98 Ga. Several samples were studied in this work, including both in situ and clasts recovered from the latest Paleozoic Matzitzi Formation, a fluvial unit mostly sourced by Grenvillian rocks. Those samples were interpreted as representative of the northernmost exposures of the Oaxacan Complex.

U-Pb geochronology and Lu-Hf isotopic determinations in zircon by LA-(MC)-ICP-MS were conducted, trying to sample localities that were eroded and are not currently exposed. Most of the studied clasts have a unimodal zircon U-Pb age distribution, recording a crystallization event at ca. 1.2-1.27 Ga. Scarce inherited zircon cores between ca. 1.4-1.6 Ga were found, with only one sample with a wider age distribution, suggestive of a detrital protolith with zircon cores as old as ca. 1.8 and 2.4 Ga. Almost no zircon overgrowths indicative of granulite metamorphism were documented. Furthermore, all the studied metaigneous samples show discordant zircon ages, produced by Pb loss events barely constrained between latest Paleozoic to the Mesozoic.

Hf isotopes reveal that zircon crystals from clasts have a range of $\varepsilon\mathrm{Hf}_{(1.25\ \mathrm{Ga})} \approx +1$ to +5 and yield Hf model ages from 1.7 to 1.9 Ga. On the other hand, the in-situ basement samples also record the ca. 1.2 and 1.02 Ga crystallization events, however, they lack the > 1.3 Ga components. The zircon Hf isotopes of one analyzed basement sample reveal a higher range of $\varepsilon\mathrm{Hf}_{(1.25\ \mathrm{Ga})} \approx +7$ to +9 and Hf model ages from 1.5 to 1.6 Ga.

Both ≈1.2 Ga and 1.02 Ga events are consistent with magmatic ages previously documented elsewhere in Oaxaquia, interpreted as indicating portions of the NW Amazonia-Oaxaquia arc system with cratonic influence or to slices of Baltica thrusted over Oaxaquia during the Grenville orogeny. However, the absence of granulite facies indicators, such as zircon metamorphic ages and/or granulite paragenesis (typically, in other Oaxaquia samples, orthopyroxene and garnet) are interpreted as prime evidence that the studied samples didn't undergo such high grade of metamorphism. They must belong to a source that has the influence of an older continental crust and can be tentatively found in the central basement of the Maya block, currently exposed farther to SE in Chiapas.

Alteration in Ultramafic Lamprophyres and its Control on REE Distribution in the Illinois-Kentucky Fluorspar District

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Carbonate-rich alkaline igneous rocks in the Illinois–Kentucky Fluorspar District (IKFD) have been recognized as a potential source of rare earth elements (REEs), a group of critical minerals used in clean energy technologies. The origin of the carbonate content and its effect on the distribution of REEs within the dikes is not well understood. The goal of this research is to identify the origin of the carbonates in the dikes via establishing a carbonate alteration and mineral paragenesis for the IKFD, and to characterize how the REE content varies with carbonate content and its genetic type in the dikes. Fifty thin sections have already been selected out of ca. 500 available through on-going and previous USGS EarthMRI projects, to evaluate cross-cutting relationships, growth zonation in carbonates, and to characterize carbonate pseudomorphs to determine the relative timing of distinct alteration episodes in the dikes. Whole-rock geochemistry data, also available through EarthMRI projects, were found to have a maximum REE concentration of 603.7 ppm and minimum of 8.88 ppm within the selected sample set, suggesting a variable fluid evolution. LA-ICP-MS will be used to gather in-situ data of trace-metals within fluid inclusions and within their host minerals to further characterize changes in mineralizing fluid chemistry and spatially correlate it with growth zones, replacement minerals, and individual generations of veining. U/Pb isotope ages will be collected with LA-ICP-MS to establish absolute ages of the various alteration features so that the fluid evolution may be put into a broader tectonic context.

GEOCHEMICAL APPLICATIONS
POSTER PRESENTATIONS

LA-ICP-MS analysis of teeth: A comparison of discrete spot analysis using Q-ICP-MS and imaging analysis by ICPTOF

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Deciduous teeth begin growing in utero before the 2nd trimester and are shed starting from age 6. Various elements, both essential and toxic that are present in blood during tooth growth co-precipitate in the hydroxyapatite matrix. Stable temporal signals can be measured in dentine, which contains collagen and where mineralization is immediate. Spatially resolved elemental analysis of teeth can reveal changes in nutritional status or exposure to trace elements during sensitive windows of fetal development, which have health consequences later in life. There are very few, if any, comparable biomarkers that provide time-resolved elemental status during this stage of gestation, and none that are collected non-invasively. Teeth are accretionary biominerals; elemental concentrations can be ‘dated’ relative to the date of birth using a visible stress line in the tooth cross section that is formed at birth called the neonatal line. The conventional method involves (1) 50 µm spot ablation of teeth from cusp to root following the enamel-dentine junction (EDJ) using an NWR 213 laser coupled to an Agilent 7900 ICP-MS, (2) calibration using a pressed pellet of a bonemeal standard (NIST 1486) and (3) offline ablation point dating calculated from the distance between the EDJ the neonatal line along the prism path. 50 µm corresponds to approximately 14 d growth. An alternative approach, made tractable by fast laser-ICPTOF is to image the whole labial side of a sectioned tooth, encompassing both enamel and dentine. This allows for analysis of all elements in an equivalent time, and potentially allows an almost daily exposure resolution. Furthermore, our preliminary data suggest strontium (Sr88) may have potential use in showing stress lines such as the neonatal line, obviating the need for a time-consuming microscopy stage, applicable to approximately 75% of specimens. The drawback of the ICPTOF approach may be a lack of sensitivity for some trace elements, such as Hg and Sn. We will present data collected from teeth sections from three distinct cohorts; an historic US cohort (1958-1970), a contemporary rural US cohort (2009-) and a contemporary African cohort and evaluate the relative merits of spot analysis compared to the imaging approach.

In-situ determination of silver nanoparticles by Laser Ablation - Single Particle - Inductively Coupled Plasma - Mass Spectrometry (LA-SP-ICP-MS)

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Nanoparticles are used in commercial products such as sunscreens, paints, and textiles due to their beneficial optical and antimicrobial properties. As the production and utilisation of nanoparticles has increased significantly over the last decade, so too has our need for a clear understanding of their potential behaviour and impacts once released to the environment. Quantifying nanoparticle size, morphology and chemical form requires a combination of analytical techniques. Electron imaging techniques (SEM/ TEM) can provide valuable information; however, SEM is limited in its ability to resolve smaller particles, i.e. <50nm, and TEM can be both prohibitively expensive and tedious to prepare specimens for. The development of SP-ICP-MS [1] has provided improved sensitivity for both the size and abundance of nanoparticles but requires nanoparticles to be suspended in solution. Nanoparticles must therefore be extracted from a solid sample, with the possibility of alteration, before they can be quantified using this technique. More recently, LA-SP-ICP-MS has been developed [2] to allow the in-situ determination of nanoparticles in various matrices. In this study we use LA-SP-ICP-MS to investigate the characteristics of Ag nanoparticles incorporated into textiles as antimicrobial agents and compare these results to analysis of the same nanoparticles extracted from the textile and analysed via SP-ICP-MS. Experiments were performed using a 193nm laser coupled to an Agilent 8900 with dedicated nanoparticle analysis software. Accurate in-situ characterisation of the Ag nanoparticles by LA-SP-ICP-MS was achieved and the results were confirmed by analysis of a range of reference Ag nanoparticles of varying size. In addition, the potential for spatially resolved imaging of Ag nanoparticles in-situ was demonstrated.

1. Laborda, F., E. Bolea, and J. Jiménez-Lamana, *Single Particle Inductively Coupled Plasma Mass Spectrometry: A Powerful Tool for Nanoanalysis.* Analytical Chemistry, 2014. **86**(5): p. 2270-2278.
2. Metarapi, D., et al., *Nanoparticle Analysis in Biomaterials Using Laser Ablation−Single Particle−Inductively Coupled Plasma Mass Spectrometry.* Analytical Chemistry, 2019. **91**(9): p. 6200-6205.

Multistage deformation and metasomatism of c. 1.9 Ga eclogitic garnet revealed by laser ablation trace-element and electron backscattered diffraction maps

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Bulk grain Lu-Hf dating of garnet is a well-established chronometry technique that provides key constraints on the timing of metamorphism. Of particular importance in assessing the significance of garnet dates, is studying the preserved chemical zoning of its major (Mn, Ca, Fe, Mg) and trace-elements (e.g., Cr, Sc, V, Y, REE). These commonly form zonations that enable garnet growth, or portions therein, to be linked to specific mineral reactions. Recent advances in laser ablation instrumentation allow for the routine acquisition of fully quantitative high resolution chemical maps, which provide unparalleled insight into the development of chemical zoning in garnet, and other associated metamorphic minerals, and their influence on the interpretation of geochronology data.

An underexplored aspect in the interpretation of bulk garnet ages is the role of deformation in overprinting chemical zoning and its potential to disturb chronometer systematics. To investigate the interplay between garnet chronometer systematics, chemical zoning, and deformation we couple bulk grain Lu-Hf garnet geochronology, with major- and trace-element mapping by LA-ICP-MS, and electron back-scattered diffraction (EBSD) analyses on three highly-strained eclogite samples from the east Athabasca mylonite triangle in Saskatchewan, Canada. The area was affected by intense deformation and mylonitization, coeval with protracted granulite to eclogite-facies metamorphism, the timing of which has been long been debated.

The three samples yield broadly similar Lu-Hf garnet ages that are within 10 Myr of each other – precluding in situ analysis using novel MS/MS-based techniques. The samples are retrogressed, with garnet showing varying degrees of fracturing, disagregation, and resorbtion, factors that could affect the interpretation of geochronology data and explain the observed variations. Chemical maps preserve diffuse major-element zoning typical of rocks that experienced high temperatures. In contrast, trace elements Cr and the heavy rare early elements (HREE) show well-defined oscillatory zoning, which is a primary growth feature, and this corresponds to areas showing a low degree of internal grain deformation as indicated by EBSD. The growth zoning is truncated by fracture networks coincident with a high density of internal grain deformation, and these correspond to areas with low Ca, V, Ti, Mn, HREE, and locally Cr contents and elevated Zr; suggesting infiltration and/or scavenging of select elements during deformation of the rock. Some grain boundaries are irregular and cuspate, with Mn-Y-HREE-rich rims—features commonly associated with resorption—while other grain boundaries are straight and oriented parallel to a finer-scaled intra-grain fracture network that show enrichments in large ion lithophile and and LREEs.

The combination of observations from high resolution trace-element maps and EBSD data allow us to establish a timeline for the growth and modification of garnet involving initial growth at eclogite facies conditions, at least two deformation and fracturing events, each associated with metasomatic overprinting at suprasolidus conditions, and final resorption and re-enrichment of the HREE. While the infiltration and scavenging of trace-elements has minimal effect on the chronometer systematics, the final resorption and re-enrichment of HREE can explain the variations in ages observed between the samples.

Geochemical mapping using LA-ICP-MS

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Laser ablation-ICP-MS has become a widely-used technique for mapping trace element distributions within mineral grains to provide insights into the evolution of igneous and metamorphic rocks, along with later (e.g. hydrothermal) processes that may have modified their primary chemistry. Recent instrumentation advances include the i) development of low-dispersion cells which reduce wash-in / wash-out times thus minimizing signal smearing and enhancing the spatial resolution of LA-ICP-MS maps, and ii) the ability to run at high-repetition rates (up to 500 Hz with water cooling). Employing high repetition rates is advantageous when using modern low dispersion LA cells. It minimizes both temporal variations in signal intensity caused by pulsing of the laser and imaging artefacts (spectral skew) caused by interaction between the laser repetition rate and the total sweep cycle time, particularly when using a sequential Q-ICP-MS analyser.

This presentation highlights a series of mapping experiments on a variety of geomaterials, with an emphasis on both rapid data acquisition (i.e., short total experiment times) by employing rapid scan speeds and high (> 100 Hz) repetition rates, and high spatial resolution (short total sweep cycles). One such map (>1 cm^2) was acquired on Slyudyanka apatite, a potential U-Pb dating reference material, and shows complex fluid infiltration along fractures modifying primary oscillatory zoning and was acquired in less than 3 hours (35µm square spot size, 200 Hz repetition rate, scan speed of 700 µm/s). Other mapping experiments presented herein include a sphalerite crystal enriched in energy critical elements and zoned metamorphic garnets.

TACtool: A Targeting and Co-ordination tool for spatially resolved data

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LA-ICP-MS is one of many spatially resolved methods (e.g. SIMS, EPMA, LIBS) which target discrete areas of a sample for analysis. In order for these analyses to be performed on spatially constrained areas in a time-efficient manner, and to enable traceability of the data back to the material analysed, prior imaging of the sample material to target areas of interest and record the areas analysed, is required. Systems to let you do this quickly and simply are required for efficient workflows.

TACtool is a simple new 'Targeting And Co-ordination' software tool that enables prior imagery (e.g. from a SEM or optical microsope) to be imported and analysis locations placed in context, recording the sites of analyses undertaken at the time of analysis. Alternatively, TACtool can be used to prepare for analysis sessions by generating and exporting analysis position co-ordinates along with the image. These can be easily imported into analysis systems, populating them with predefined lists of analysis locations, saving large amounts of laboratory preparation time. Our development of this tool has been focussed on applying it to LA-ICP-MS applications but as generic software, it can be applied to other systems and co-ordinates are exported in a GIS-friendly format.

TACtool will be demonstrated at this workshop. It is written in Python and will be freely available on the BGS GitHub home page (https://github.com/BritishGeologicalSurvey) as a community tool for use. Uptake by, and feedback from, users is actively encouraged through the GitHub site.

Benefits of a large format 2-volume laser cell for *in situ* analysis of speleothem calcite formed monthly on 10x10cm monitoring plates

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Stalagmites are cave mineral deposits that accrete vertically through time below drip sites and under favorable circumstances can record seasonal variations in growth fabrics that proxy aspects of paleoclimate. Such is the case for central Texas caves of the Edwards Plateau that undergo seasonal ventilation, with a strong cool month bias toward calcite accumulation, and stalagmite records spanning the last 70 ka. Monitoring studies demonstrate that growth follows drip rate, which is linked to recharge storage volume in the overlying limestone (epikarst). Because epikarst water volume should fluctuate between wetter and drier periods, stalagmite growth records should be sensitive recorders of hydroclimate. Recent high-resolution 2D mapping of last deglacial (~19-11 ka) stalagmite intervals demonstrate that variations in trace element concentrations (esp. Mg, Sr, Ba) directly correspond with independently resolved seasonal growth fabrics. The cause of these trace element variations is unknown but could originate from (1) seasonal variations in drip water compositions related to epikarst processes and/or hydroclimate; (2) seasonal variations in in-cave processes that affect calcite growth; or (3) combinations of these factors. Monitoring studies of paired drip water and plate (i.e., modern) calcite provide a means of assessing these potential origins. Solution mode ICP-MS is a practical means for determining drip water compositions but is challenging for finite (<10s of mg) plate calcite due to concerns about obtaining spatially representative sampling while also preserving calcite for other geochemical analyses. Here we take advantage of LA-ICP-MS featuring a large format 2-volume (LF2V) laser cell to quantify trace element compositions of calcite formed *in situ* on standard 10x10cm glass monitoring plates. The large number of plate samples (n=96) requires an efficient and systematic analytical approach, with the goal of characterizing spatial calcite compositions away from the central drip impact point that may have had differing water film thicknesses and saturation gradients that could affect precipitation rate. The LF2V laser cell uniquely facilitates rapid calcite analysis across monitoring plates, allowing for comparisons with corresponding drip waters.

Applications of LA-ICP-MS in Archaeological Chemistry at the MURR Archaeometry Lab

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Understanding the evolution of social networks, technological innovations, and adaptations to environments throughout human history are topics at the forefront of archaeological inquiry. Key evidence needed to interpret aspects of human behavior in the past often requires determining the elemental compositions of complex materials at high sensitivity and spatial resolution. Laser ablation ICP-MS is a highly effective tool for this and is frequently used to analyze materials derived from archaeological contexts, such as ceramics, glazes, historic glass, and mineral pigments. These efforts typically require procedural development and the evaluation of matrix-specific calibrations that are needed to mitigate the effects of interferences and laser-material incompatibilities. Here, we present highlights from several recent collaborative projects that illustrate the utility of LA-ICP-MS for materials characterization of glass and ceramic glaze technologies, taphonomic impacts on ceramics, and the provenance of artist's pigments to understand ancient mineral resource provisioning and use.

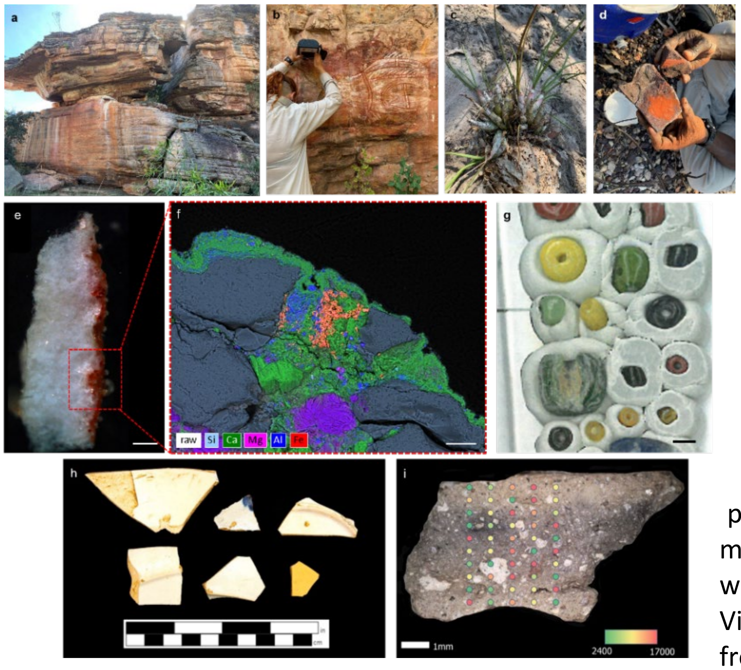

Figure (a) Sandstone rock shelter with paintings, Australia (b) portable Raman analysis of pigments, Madjedbebe rock shelter, Australia; (c) tea tree orchid (*Dendrobium canaliculatum*) juice was used as a binding agent, (d) iron-rich rocks used to produce powdered hematite; (e) a pictograph fragment, scale = 500 µm. (f) EDS map of a paint particle, (g) glass beads from western Africa; (h) lead-glazed pottery from Virginia; (i) barium-contaminated ceramics from Soconusco, Mexico.

Ablation Volume-Aided Calibration in 2D LA-ICP-MS Mapping to Correct for Differences in Ablated Mass

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Despite the rapid development of the laser ablation inductively plasma mass spectrometry (LA-ICP-MS) technique, quantification of elements in 2D LA-ICP-MS mapping is still a challenge. The measured signal is often not fully representative of the sample composition due to problems with elemental fractionation issues (non-stoichiometric effects during vaporization, transport of ablated particles, atomization, and ionization in the plasma), and matrix-dependent ablation rates that lead to differences in ablated mass.[1, 2] To overcome such problems, quantification in LA-ICP-MS mapping typically requires matrix-matched standards combined with internal standardization. However, the availability of matrix-matched standards is limited, and the requirement for a homogeneously distributed internal standard is rarely met. Therefore, we focused on correcting for the differences in ablation rate in samples and standards by normalizing the elemental maps using the accompanying ablation volume per pixel measured via optical interferometry. We applied the volume-corrected calibration approach to the LA-ICP-MS quantification of elemental concentrations of eight major, minor, and trace elements in a decorative glass (Murrina) using SRM NIST610 and 612 as standards. The approach was validated using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM /EDXS) and laser ablation with sum normalization calibration.[3] We have shown that ablation volume-aided calibration leads to more reliable quantification of elemental concentrations in 2D LA-ICP-MS maps.

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Mpx/hr ICP-TOFMS mapping of multiphase rock sections

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LA-ICP-MS mapping is moving towards ever higher ablation rates, at higher spatial resolution, looking at more analytes in lower concentrations. Each one of these points is a field of active technological development. Here, we present current advancements in LA-ICPMS mapping capabilities of an ICP-TOFMS (icpTOF by TOFWERK AG, Switzerland) coupled to an 193 nm excimer laser ablation system (imageGEO by ESL, USA) with a low-dispersion, fast wash-out ablation cell.

In a pilot study, a natural rock section was mapped at 2 µm spatial resolution at an ablation rate of 500 Hz. The entire 10 Mpx image took over 9 hours to acquire, resulting in an acquisition rate of > 1 Mpx/hr. Ultra-fast wash-out of the ablation cell guarantees no signal carry-over between pixels, while the data acquisition rates of the ICP-TOFMS provide full-elemental information on every pixel, without compromises in data quality. A specific dry-plasma sampler cone in the sampling interface of the ICP significantly increases sensitivity.

In the presented examples of data processing, we apply clustering and segmentation algorithms to the resulting highly multiplexed data set, which allows specific data reduction for individual mineral classes.

Comprehensive atmospheric particulate matter analysis via laser ablation ICP MS and IRMS

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Around the world hundres of government environmental agencies are actively monitoring atmosperic particulate matter (PM) due to the significat health hazards they impose on the human population and livestock. Understanding the chemical composition and physical properties of PM is critical for designing better ways to monitor them and mitigate the potential environmental risks associated with PM.

Traditionally, the elemental composition of PM particulates is measured via inductively coupled plasma mass spectrometry (ICP MS). where particles deposited on cellulose or quartz fiber filters are subjected to microwave assisted digestion by a combination of reagents and the resulting solution is then analyzed. The main advantage of this approach is that the methodology has been standardized (*e.g.*, EN14902:2005). However, sample digestion is a tedious task, often reulting in incomplete digestion of PMs which in turns may yield inconsistend results. The stable isotope composition of PMs has long been neglected as the traditional way of measuring solids (*e.g.,* via combustion) is very time consuming and offers little to no spatial information.

In this contribution we present a novel approach to measuring both elemental as well as stable isotope composition for PM. The method uses laser abaltion (LA) as a reliable sample introduction technique. The advantages of this approach for elemental compositions have been clearly presented by Ogrizek *et al.*(2021)[1]. Stable isotope measurements on the other hand, are a new addition to the tool box and they allow for a much more accurate fingerprinting of the potential pollution sources, especially when used in conjunction with elemental analysis.The method developed by Terra Analitic allows users to accurately measure δ^{14}C values via LA IRMS.

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Investigating REE Mineralization at High-Spatial Resolution Within Fenite Alteration Zones Using LA-ICP-MS

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Rare earth elements (REEs) play a critical role in the expansion of clean energy technology. These elements form key components of batteries for electric vehicles and other energy storage devices, but their overall low concentrations within Earth's crust requires inefficient, energy-intensive extraction processes. In the last few decades, carbonatites have been shown to host the most abundant REE deposits on Earth. Carbonatite complexes have been studied extensively, but little attention has been given to the adjacent country rocks that are chemically altered by the intrusion of carbonatite magma. These rocks, known as fenites, show a similar REE enrichment and represent an untapped reservoir of key elements and minerals that can help to accelerate the transition to a clean energy future.

In this study, we investigate the mobility and concentration of REEs in three carbonatite complexes from China (Miaoya, Maonuiping-Dagudao, and Bayan Obo) and their spatially associated fenite alteration zones. Bulk rock, solution mode Sr isotopic ratios obtained by MC-ICP-MS for both carbonatite and associated fenite samples yield overlapping values, and therefore confirm a petrogenetic link between both rock types at the Maonuiping-Dagudao deposit. This finding alone supports the hypothesis that intrusion of carbonate-rich magma is responsible for metasomatic alteration of the country (surrounding) rock and plays an important role in the observed REE enrichment.

Bulk rock analysis of fenite samples from the Maonuiping-Dagudao deposit has revealed extreme REE enrichment in the fenites relative to the carbonatite. Certain areas of the fenite alteration zone were found to exhibit nearly sevenfold enrichment, as measured by total REE concentration, compared to the carbonatite intrusion. The bulk rock trace element results also validate analogous data obtained by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for individual minerals (calcite, amphibole, clinopyroxene) investigated within the fenite samples, which provide insight into the partitioning behavior of the REEs during the metasomatic alteration event. Calcite and amphibole control the mass budget of the light REEs, whereas amphibole and clinopyroxene dictate to a certain degree the distribution of the middle-to-heavy REEs. Future work will involve obtaining in-situ Sr and Pb isotope ratios by LA-MC-ICP-MS of the different minerals to better constrain the nature of the metasomatic fluids and processes involved in fenite formation. Through the juxtaposition of in-situ and bulk trace element analyses, we will gain an improved understanding of the distribution of REEs between the carbonatites and the associated fenites, thus providing valuable insights into the future use of the latter as reservoirs of economically and technologically critical elements.

Major element composition determination of thin films on silicon wafers

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Engineered thin films have a wide array of applications. They are present in many electronic devices as magnetic storage media, batteries, and micro-sensors. They have utility in clean energy research as components of photovoltaic cells and catalysts in chemical reactions. Their versatility is due in part to their ability to exhibit a wide range of physical properties based on composition. Small changes in the major element chemistry, oxidation states and atom to atom interactions can cause major changes in hardness, magnetism, conductivity, and other useful properties. Many compositional characterization techniques provide limited information on the bulk stoichiometry of thin films or lack the precision to resolve compositional differences of a few weight percent. Some techniques (XPS) provide composition determinations on just the first 5 nm of material. Samples that have formed surface oxide layers or undergone changes during annealing or post-depositional processing may not have a bulk composition represented by the uppermost 5 nm of the thin film. Alternative analytical techniques that provide bulk compositional determinations with minimal sample processing can expedite the fabrication and quality control of research-grade thin films.

Femtosecond laser ICP-MS (fs-LA-ICP-MS) has been used to characterize thin film compositions by spot analysis, compositional mapping, and depth profiling [1,2]. The short laser pulse time has the advantage of causing minimal interaction between the laser beam and the ablated material reducing elemental fractionation effects during ablation. Nanosecond laser ablation systems (ns-LA) have longer pulse times and require careful attention to potential thermal effects, and correction for elemental fractionation. ns-LA-ICP-MS systems are widely available in many research settings and could be a valuable screening tool for thin film compositions.

We use ns-LA-ICPMS to explore stoichiometric variations in $Nb_xCo_ySn_z$ thin films sputtered on to silicon wafer substrates. We test both spot analyses and transects to determine a method for rapid characterization of the bulk composition of the thin film material.

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Major and Trace Element Concentrations Measured in olivine crystals from Apollo 15 Olivine-Normative Mare Basalts

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Previous studies of Apollo 15 olivine-normative mare basalt samples (ONBs) have suggested closed-system fractional crystallization based on whole rock geochemistry and quantitatively examined the texture of olivine crystals present in the samples. Major and trace element concentrations have previously been measured in olivine crystals from Apollo 12, 14. and 17 basalts and impact melts and used to show distinct chemical variation among the groups. This study conducts similar major and trace element analyses on olivine crystals within nine Apollo 15 olivine-normative mare basalt thin sections (15529,15, 15545,2, 15547,7, 15555,250, 15557,94, 15622,20, 15647,7, 15676,14, and 15678,7). These samples were selected because they span the range of Apollo 15 ONB whole rock compositions. Element maps of the thin sections were made using a Cameca SX100 Electron Microprobe (EMP). The elements mapped included Si, Al, Fe, Mg, Ca, K, P, Ti, Na, and Cr. Major element compositions of olivine crystals in each sample were also acquired via EMP. The elements measured were Fe, Mg, Ca, Al, Ti, Cr, Na, Si, O, and Mn. Trace elements (Ca, Sc, Ti, V, Cr, Mn, Co, and Ni) were measured in olivine crystals using a New Wave UP-213 laser ablation system and Nu Plasma Attom High Resolution Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) at the University of Notre Dame's Midwest Isotope and Trace Element Research Analytical Center (MITERAC). Forsterite percentages within the Apollo 15 olivine crystals ranged from 17% to 71%, which is lower than most of the olivine crystals previously analyzed and represents a broad range of geochemical evolution. Some elements, such as Mn, form a linear trend consistent with fractional crystallization in a closed system. Data for other elements, such as Cr, show significant scatter. Evolution of the equilibrium liquid calculated for the most forsteritic olivine measured was not able to recreate the compositions of the other olivines in these samples via fractional crystallization of olivine alone. A crystallizing assemblage of 80% olivine and 20% spinel was able to recreate the olivine compositions measured over a range of ~20% fractional crystallization. Further work will involve detailed evaluation of the olivine data from samples that were identified as texturally similar to impact melts (15557,94 and 15676,14). If they are consistent with closed-system fractional crystallization it will support the assertion that cooling rate, rather than formation mechanism, may be controlling the texture of these samples.

Monitoring Mass Filter Position For The Purpose Of Aligned LA-ICP-MS

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Imaging of elemental and isotope ratio distributions by LA-ICP-MS has shown great utility in a range of fields[1][2] due to its high sensitivity, spatial resolution and wide dynamic range, though imaging at high spatial resolution comes with a significant time penalty[3]. Fast-response ablation cells (e.g “S155 Fast Funnel”, “ARIS”, “TwoVol”, “Cobalt”, etc…) have been developed to reduce washout times (to 1%) down to < 50 ms and in some cases down to 1–2 ms. With many modern laser systems capable of firing at hundreds of Hz, scan speed is limited by washout time, therefore a faster washout will allow for faster scanning and consequently faster imaging.

However, with the rise in popularity of these fast-response cells, the issue of aliasing, or “beats”, in images collected by LA–ICP–MS becomes problematic[4]. Increasing the washout time will resolve this issue, but negates all the benefits of the fast-response cell, because ablated material reaches the ICP in overlapping waves instead of discrete pulses, resulting in “blurring” of the final image or map.

When using aligned LA–ICP–MS[5] the firing of the laser is aligned with the scan/sweep cycle of the mass spectrometer so that the arrival of the ablated aerosol reaches the detector at the same moment of every sweep. This synchronisation is performed for each sweep of the mass filter, so the two instruments remain aligned continuously, even during very long analyses.

Our alignment circuit (called ”QuadLock”) uses a voltage divider to measure the DC component of the superimposed AC and DC mass filter voltages. The voltage divider has a very high impedance which prevents it interfering with the normal operation of the quadrupole. Because QuadLock directly measure the DC voltage on the quadrupole, it is not limited to any specific instrument family or manufacturer. For instruments with multiple quadrupoles (e.g “triple quad” or “MS–MS” instruments) we have found it sufficient to measure the mass filter position of the second quadrupole.

QuadLock can also interface with single collector magnetic sector field mass spectrometers (e.g. Thermo Scientific “Element” or Nu Instruments “Attom”) by measuring the DC voltage applied to the electrostatic analyser, with the additional challenge that the ESA typically floats at the acceleration potential of the instrument (typically around −10 kV).

Here we describe how the mass filter position is sampled in real-time without affecting the performance of the instrument, and how QuadLock is physically interfaced with a range of mass spectrometer hardware from various manufacturers.

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REFERENCE MATERIALS

POSTER PRESENTATIONS

Development of a matrix-matched standard for human hair for laser-ablation-based analysis

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Chemical analysis of human hair by laser ablation poses challenges in forensic and medical applications due to a lack of standards that are matrix-matched. In comparison to bodily fluids, hair provides a minimally invasive sample collection and are highly temperature stable. Hair can also provide a sensitive approach as it holds higher concentration of analytes, especially when evaluating past and present exposure of metals and metalloids. Thus, this makes hair useful to keep a biological temporal record of organic and inorganic components in the body.

Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been established as a powerful analytical tool for determining the concentration and distribution of trace metals within hair samples. Utilizing this technique eliminates the need for sample modification prior to analysis. It is nonetheless imperative for a calibration material to show similarity to the chemical, physical, and optical properties of its matrix. However, there is a lack of certified reference materials that meet these criteria all at once for chemical hair analysis. As a result, strategies that are not chemically sound are being relied upon by current industry and research. In this study, the use of a matrix-matched standard reference material will allow for the correction of sample matrix effects. The reference materials utilized for quantitative hair analysis include hair powder, dogfish liver powder, and glass. While posing similar chemical species to hair, these standards do not accurately emulate its physical and optical properties. Thus, the development of a hair reference standard suitable for laser ablation is crucial.

We have developed a method for a new calibration material using keratin film as a matrix-matched reference standard for LA-ICP-MS. Keratin matrix-matched standards allow for the use of single hair analysis to evaluate the quantitative chronological record of potential environmental exposure, health conditions, and drug exposure in an individual. This study employs a keratin film doped with analytes of interest as a calibration material for LA-ICP-MS analysis. Keratin was extracted from human hair using the "Shindai method", purified, spiked, and cross-linked to obtain a thin film. Characterization of the physical properties including physical and chemical homogeneity, stability, and dimensions of the film were studied. The reference material demonstrates comparable dimensions to a single hair strand. These results pave the way for a new set of standards for internal medicine, forensic toxicology, and anthropology.

Trials & Tribulations in Synthesizing a Sulfide Standard

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Well-characterized sulfide reference materials that can serve as matrix-matched calibrants for *in-situ* trace element analyses via laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) remain elusive. Here, we describe the creation an in-house sulfide standard at NASA JSC that will be used to measure siderophile and chalcophile trace elements in low pressure experimental products, specifically pentlandite ($[FeNi]_9S_8$) and pyrrhotite ($[FeNi]_{1-x}S$), as well as natural sulfides in terrestrial and meteoritic mineral assemblages. Recent methods in creating a homogenous sulfide standard include pressed pellets, synthesized chips, or fused glass [e.g. 1-3]. Other studies, however, have had success in forming homogenous FeS standards via synthesization methods [e.g. 4-6]. We present a variation of the method described in [4], in which we create a pyrrhotite standard doped with a variety of trace elements (Zn, As, Se, Mo, Ru, Rh, Pd, Sn, Sb, Te, W, Os, Ir, Pt, Au) at ~10-40 ppm and Cu at ~200 ppm.

Sulfide compositions were constructed using Fe and Ni metal and elemental sulfur powders. Trace elements were added to elemental sulfur from Atomic Absorption Spectroscopy (AAS) elemental standards as either nitrate or chloride solutions to prevent oxidation of the metal powders. The dried sulfur mixture was mixed with Fe and Ni powders and mechanically mixed before two aliquots were placed in separate SiO_2 tubes. Each tube was held under vacuum for ~30 minutes, sealed under vacuum, and then heated at 800°C for 48 hours. Like [4], the synthesis products were composed of pourous sulfide crystals. Major element analyses of both experimental aliquots, collected using an Electron Probe Microanalyser (EPMA), yield indistinguishable major element compositions (uncertainties in 2SE & 2RSE[%]), with an average of 57.90 ± 0.09 (0.16 %), 4.95 ± 0.03 (0.55 %), and 39.70 ± 0.14 (0.34 %), for Fe, Ni, and S, respectively. Trace element data were measured using a Photon Machines 193nm laser ablation system coupled to a Thermo-Scientific Element-XR ICP-MS. Spot sizes were limited to 50 µm due to the porous nature of the sulfide target material. Trace element abundances, normalized to Fe as an internal standard, were also found to be homogenous between the two aliquots, with weighted mean 2RSE (%) values of <3.0 for all trace elements.

Synthesized products were re-powdered and absolute concentrations measured via solution ICP-MS. Although the sulfide appears to be homogenous, sintering experiments will be performed to more closely match the standard density to natural sulfides and minimize differences in ablation behavior. Improved density also allows for higher sensitivy (i.e. more compact target material) and larger spot sizes or traverses, as void space is eliminated. Additional major and trace element analyses on the products of the sintering experiments will be undertaken.

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LIBS / TANDEM APPLICATIONS

POSTER PRESENTATIONS

Investigating the corrosion of copper in H_2S containing atmosphere using LIBS

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Understanding corrosion mechanisms is an important requirement to ensure the reliability of many produced goods. This is especially true in the field of microelectronics, where devices are often exposed to harmful environments during application. The negative influence of humidity but also reactive gases promotes degradation of used materials, causing changes in the material properties and sometimes even leading to product failure.

In the semiconductor industry copper is commonly used as a metallization to provide electrical contact between electronic devices. To assure reliable application of these products even in harsh environments (e.g. automotive industries), it is essential to study the resistivity of the metallization material to prevent device failure. Here, especially environments containing elevated temperatures, humidity and gaseous sulphur species are of concern. Combined with an applied bias typically present in electronic devices, these conditions can significantly influence the lifetime of a device due to corrosion of the delicate connections.

Recently we have presented a custom-built weathering chamber, which enabes the controlled exposure of materials to a defined atmosphere containing H_2S, SO_2, and humidity [1]. In this work the sulfur uptake in weathered polymer samples has been assessed using LA-ICP-MS, which allows sensitive and depth-resolved analysis of the element sulfur, but information about the elements oxygen and hydrogen was not accessible with this technique.

In this contribution, LIBS is used for elemental analysis of weathered copper metallizations, which enables the simultaneous measurement of the elements copper, sulfur, oxygen and hydrogen. To overcome the negative effect of the Ar emission line at 922.4 nm, which hampers analysis of the sulfur lines in the wavelength region from 920-923 nm, all measurements are performed using He atmosphere. Depth profiling of the weathered samples is used to investigate the composition of the corrosion layers in relation to the depth whereas imaging is used for assessing the homogeneity of the formed corrosion products. Besides the expected uptake of sulfur also significantly increased signals for hydrogen and oxygen are found, which points to the formation of oxides and hydroxides during the weathering process.

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Laser Ablation-Based Tandem Approach to the Analysis of Solid Samples: The Road Towards Successful Implementation

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Laser Ablation-Based techniques for direct solid material analysis have become routinely used in research labs and industry alike due to their capability to provide a wide range of chemical information, from elemental and molecular data to isotopic information. However, the traditional individual implementation of these laser ablation-based approaches still suffer from some of the same limitations of other analytical techniques. For example, constraints associated with lack of sensitivity below certain concentration levels (i.e., LIBS with LOD's on the 100's ppm for certain elements) or the inability to detect specific elements or species (i.e., ICP-MS inability or/and difficulty detecting elements such as H, He, F, Halogens, and others). In 2014 Applied Spectra, Inc. published the first paper [1] on the use of these tandem approaches (simultaneous LIBS and LA-ICP-MS) and since then, increasing number of articles have been published on various analytical topics. The unparallel advantage of these laser ablation-based approaches is the ability to perform both measurements simultaneously and from the same ablation event. This, however, required engineering and analytical solutions related to hardware synchronization, experimental conditions optimization, data reduction and processing of the large amount of data obtained. In this presentation, we will demonstrate some of the advantages of this simultaneous tandem approach to laser ablation and discuss some of the most recent advances in its implementation from the hardware and software for data processing point of view. We will also introduce our new advanced software platform for laser ablation-based data porcessing ClarityNeXt^{TM} and demonstrate its capabilities.

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Time-resolved investigation of oxidation resistance for technologically relevant materials in their working environments by in-situ LIBS measurements

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Technologically relevant materials, especially used in the machining or aerospace industry, are often exposed to elevated temperatures in corrosive or oxidizing atmosphere. This can cause diffusion or even an alteration of stoichiometry, like oxidation. Both mechanisms impair the function of the material and can lead to the device's failure. To predict the performance of those materials simulating the operating conditions is a crucial task to avoid early malfunction. However, estimating the impact of the working conditions on the material properties and their lifespan can be challenging and time-consuming. Considering the ageing and subsequent measurements are often separated, additional changes in the sample induced by cooling to room temperature can't be controlled.

To overcome this potential drawback, an in-house built heating stage, which can be placed inside the ablation chamber of a 266 nm LIBS system, is utilized. This stage allows the aging of samples at temperatures up to 1000°C in various atmospheres (e.g., synthetic air, Ar, He, gas mixtures, etc.) while offering the possibility of making in-situ LIBS measurements. In this way, time-resolved studies of elevated temperatures' impact on technologically relevant materials can be conducted in oxidizing environments.

However, to gain more insights about the diffusion processes the oxidized samples were also analyzed using a 193 nm ArF-laser ablation system equipped with a broadband spectrometer and an additional ICCD-detector for monitoring the emitted radiation. In this way, the depth resolution can be enhanced below 100 nm, leading to a better understanding of the oxidation behavior inside the sample.

Using laser dosage to generating high resolution LIBS images

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Over the past few years, laser induced breakdown spectroscopy (LIBS) has become an increasingly popular technique for imaging geologic samples due to the decreased time it takes to run an experiment and versatility of which elements can be monitored. To obtain emission spectra with the highest overall signal intensities, we utilized a large spot size with a high laser fluence which results in high laser energy ablation. However, this increased spot size results in lower resolution images. One strategy to increase resolution without decreasing emission spectra intensity is to increase the laser dosage, which is defined as the number of laser pulses per unit area. Using a high laser dosage has been demonstrated as a viable technique for increasing image quality for LA-ICP-MS imaging (1). Therefore, applying this technique to LIBS can allow imaging with a large spot size which will maximize the emission spectra intensity, resulting in increased image resolution.

In this work, we will explore two different LIBS imaging techniques. The first technique, considered the current standard, uses a low laser dosage, while the second technique utilizes a higher laser dosage, in which high spatial resolution is achieved by small XY stage movements. These experiments were conducted using a 193 nm ns excimer laser in combination with a multi-channel CMOS detector. LIBS images collected with a high laser dosage generated higher resolution images that would not normally be achievable when running at a lower laser dosage.

(1) van Elteren et al., J. Anal. At. Spectrom., 2019, 34, p. 1919-1931

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