North American Workshop on Laser Ablation 2019

May 28, 29-31, Austin

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

FOREWARD

Welcome to Austin and the 3rd North American Workshop on Laser Ablation (NAWLA). NAWLA covers the latest progress in laser-based microanalytical instrumentation, methods and applications, and provides opportunities for informal interaction among attendees. NAWLA is run by and for the user community with the mission to ***facilitate laser ablation knowledge transfer and promote community among laser ablation users.*** This abstract book constitutes a “snap shot” of laser ablation research in 2019, portraying the diverse research activities of the laser ablation community. A total of 77 abstracts (36 oral, 41 poster) were accepted, which contribute to 12 thematic sessions spread over three days. A noteworthy focus for NAWLA’19 is a special plenary session dedicated to latest advances in laser ablation data processing software. It should not be forgotten that NAWLA is a ***workshop***, and thus endeavors to provide engaging opportunities for peer-to-peer learning. Group learning activities for NAWLA’19 include a day of pre-meeting workshop options, and a special workshop within the scientific program devoted to LA-ICP-MS reference materials. As with past workshops, scientific program sessions conclude each day with refreshments and informal time to visit the poster presentations and vendor exhibits, and talk among attendees.

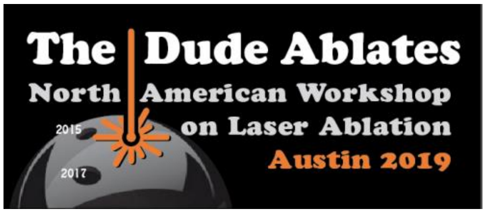
2019 marks the third time for NAWLA to be held in the Jackson School of Geosciences. The workshop has grown each biennium, beginning with the inaugural 2-day 2015 meeting with 110 participants. At the conclusion of that workshop, attendees were asked *en masse* if they wanted to do “this” again and the overwhelming answer was “yes!”. When asked where, the unexpected response was “Austin” (it is remarkably easy to convince Canadians and upper mid-westerners to come to Austin in May). Following the 2.5 day 2017 meeting with 130 participants, NAWLA’19 now convenes for a full three-day scientific program, with 145 participants. The original intent for NAWLA (should it survive the inaugural trial) was, after establishing a solid organizational infrastructure, for it to move each biennium to a new host institution. We are happy to report that that infrastructure is now in-place and ready to be passed on to successive organizers. From analogy with the “Dude Ablates” bumper sticker, we have completed drilling of the final hole; **NAWLA workshops are ready to roll**!

Pulling off a NAWLA workshop is always a group effort, and 2019 is no exception. The Scientific and Organizing committees developed the thematic sessions, coordinated logistics, and interfaced with prospective speakers and attendees. Several Jackson School of Geosciences personnel provided key assistance (Camille Barraza, Brian Zavala, Javier Valadez, Chris Stella). We are particularly grateful for the support of 10 vendor partners who helped sponsor the workshop. Obtaining this support early during the organizing process is essential for planning. This is the first year for having vendor exhibition booths at NAWLA, so we encourage attendees to visit them all and see what is new.

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

On behalf of the Scientific and Organizing committees,

Nathan Miller



NAWLA

North American Workshop on Laser Ablation

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12:00-13:00	Lunch
13:00-17:00	Pre-meeting workshops Session 3
17:00-19:00	NAWLA Ice Breaker Ceremony

Wednesday, May 29th

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08:25	Welcome and Introduction – Nate Miller and Paul Sylvester
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12:00-13:00	Lunch + Vendor Exhibits
13:00-14:30	Session 3: Reference Materials for LA-ICP-MS
14:30-15:30	Session 4: Workshop Activity Group Meetings
15:30-17:30	Session 5: Posters/Vendor Exhibits/Beer
19:00	Dinner

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Friday, May 31st

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13:00-15:55	Session 13A: U/Pb Age, Isotopic and Trace Element Analysis for Geology Session 13B: Trace Element Analysis and Imaging for Paleo-Environmental Research, Health Science, Food Safety, Artefacts
15:55	Adjournment

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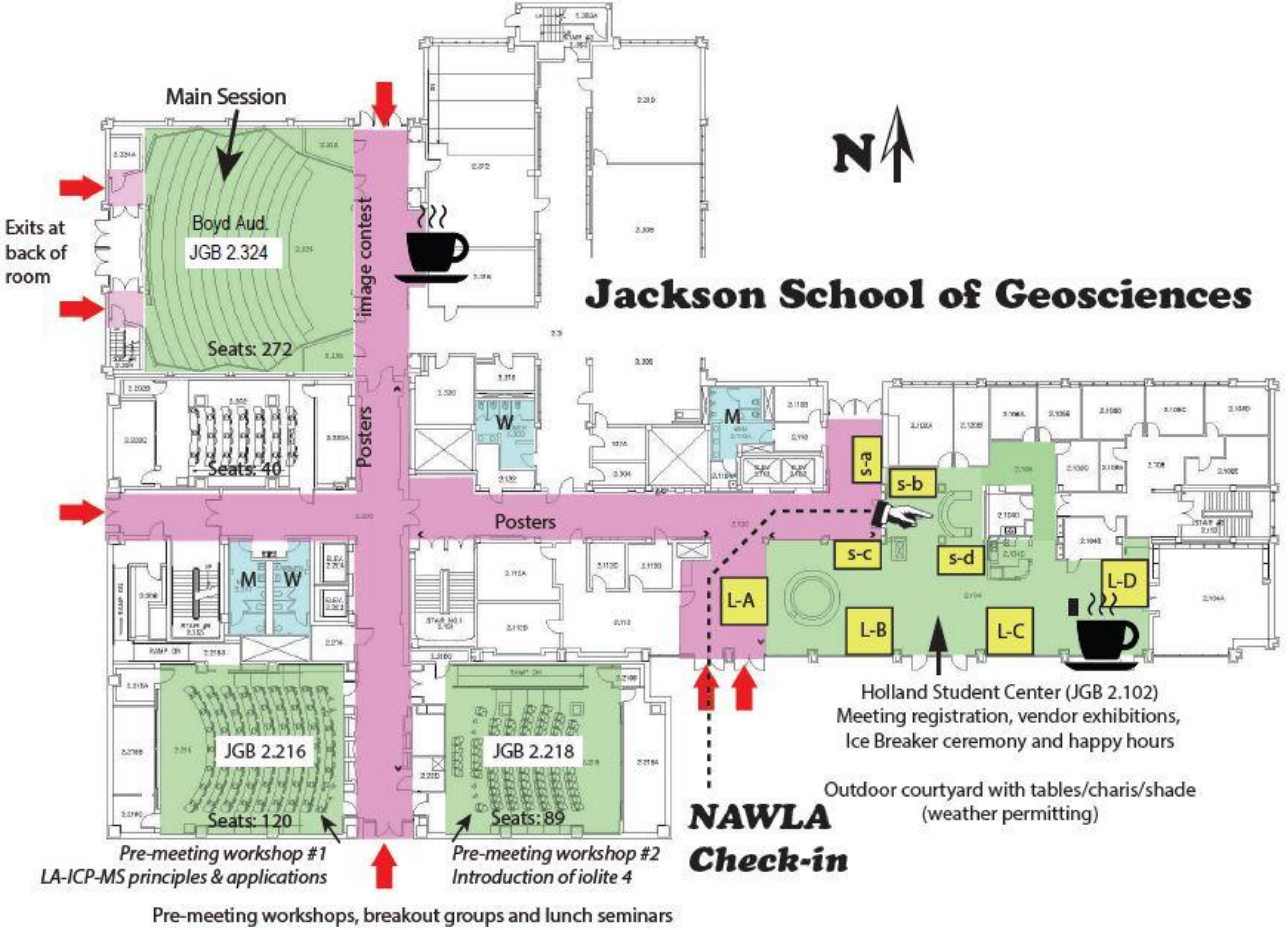

NAWLA ’19 Scientific Program

Tuesday, May 28th

08:00 Registration, Pre-meeting workshop check-in, and Coffee…………Holland Student Center
09:00 Pre-meeting workshops Session 1
LA-ICPMS Principles and Applications ……………………..……….... JGB 2.216
Introduction to Data Processing with Iolite 4 ……………………….. JGB 2.218
10:30 Coffee break
10:50 Pre-meeting workshops Session 2
12:00 Lunch ………………………………………………………………………..……Holland Student Center
13:00- Pre-meeting workshops Session 3 (4 hours)
17:00 NAWLA Ice Breaker Ceremony (2 hours) ………………………………Holland Student Center

Wednesday, May 29th

07:30 Registration and Coffee ……………………………………………….…..…Holland Student Center
08:25 Welcome and Workshop Logistics – Nate Miller ………………………….. Boyd Aud., JGB 2.324
08:35 Possible Special Issue of Geostandards and Geoanalytical Research - Paul Sylvester

Session 1: LA-ICP-MS Foundations and Fundamentals……………………….. Boyd Aud., JGB 2.324
Moderator: Paul Sylvester
08:40 Jan Fietzke (Keynote)
Influence of plasma conditions on elemental behavior during LA-ICP-MS
09:15 Matt Horstwood (Keynote)
Uncertainties and resolution of variation in LA-ICP-MS
09:50 Tao Luo, Zhaochu Hu, Wen Zhang, Yongsheng Liu, Xiaodong Deng, Jianwei Li (Keynote)
Water vapor-assisted “universal” non-matrix-matched analytical method for the in situ U-Pb dating of zircon, monazite, titanite, xenotime and wolframite

10:25 **Coffee break**

Session 2: Isotopic Analysis by LA-MC-ICP-MS ………………………..………. Boyd Aud., JGB 2.324
Moderator: Matt Horstwood
10:50 Malte Willmes, Levi S. Lewis, James A. Hobbs (Keynote)
Rocks, Bones, and Teeth: New frontiers and old problems in strontium isotope analysis in ecology and archaeology
11:25 Wei Chen, Jue Lu, Antonio Simonetti (Keynote)
In-situ sulfur isotope measurements by LA-MC-ICP-MS: sulfate standards and matrix effects

12:00 **Lunch + Vendor Exhibits** ………………………………………………..…..Holland Student Center

Session 3: Reference Materials for LA-ICP-MS…………………….……….…… Boyd Aud., JGB 2.324
Moderator: Alan Koenig
13:00 Dieter Garbe-Schönberg, Samuel Müller, Maxim Portnyagin, Axel Renno (Keynote)
Nano-particulate pressed powder pellets (not only) for LA-ICP-MS
13:35 Leonid Danyushevsky, Jay Thompson, C. Ashley Norris (Keynote)
Accurate LA-ICP-MS analysis of minerals using non-matrix matched reference materials

14:10 Introduction of Workshop Activity on Reference Materials - Kate Souders, Todor Todorov & Alan Koenig

Session 4: Workshop Activity Group Meetings………………………………… Boyd Aud., JGB 2.324
Moderator: Todor Todorov
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Session 5: Posters/Vendor Exhibits/Beer……………………………………Holland Student Center
15:30-17:30

19:00 **Workshop Dinner at Scholz Garten (Hosted by Teledyne CETAC Technologies)**

Thursday, May 30th

08:00 Coffee ………………………………………………………………………………Holland Student Center
08:30 <u>Regina Mertz-Kraus</u> …………………………………………………………… Boyd Aud., JGB 2.324
Announcement of G-Chron: A proficiency testing programme for zircon geochronology

Session 6: Data Processing Software for LA-ICP-MS……………………………Boyd Aud., JGB 2.324
Moderator: Simon Jackson
08:40 <u>Yongsheng Liu</u>
ICPMSDataCal: An accurate, simple, convenient and friendly ICP-MS data calculation software
09:00 <u>Regina Mertz-Kraus</u>, Dennis Rupprecht, Simon Mischel, Alexander Budsky, Klaus Peter Jochum, Denis Scholz
TERMITE 2.0: An R script for data reduction of LA-ICP-MS trace element data
09:20 <u>Ashley Norris</u>, Leonid Danyushevsky
LADR: Comprehensive software for data reduction of LA-ICP-MS data sets
09:40 <u>Bence Paul</u>, Joseph Petrus, E. Marillo-Sialer, Jon Woodhead, Janet Hergt and Linus Maas
Iolite version 4: A proven solution for efficient and robust processing of LA-ICP-MS data
10:00 <u>Stijn J. M. Van Malderen</u>, Laszlo Vincze , Frank Vanhaecke
HDIP: powerful LA-ICP-MS data reduction software with extensive data interrogation tools

10:20 **Coffee break**

Session 7: Data Processing Software Discussion…………………………………Boyd Aud., JGB 2.324
Moderator: Simon Jackson
10:45 <u>Simon Jackson</u>
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12:00 **Lunch + Vendor Exhibits**……………………………………………………Holland Student Center

Session 8: Instrumentation/Method Development……………………………..Boyd Aud., JGB 2.324
Moderators: Chris McFarlane, Joe Petrus
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Overview and preliminary results of the promising fs-LA-LIBS-ICP-TOF-MS system
13:35 <u>Thomas Zack</u> (Keynote)
Recent findings of in-situ beta-decay geochronology: Rb-Sr dating of glauconite and Re-Os dating of molybdenite

14:10 Ariane Donard, Leon Eldridge, Chantal Peiffert, Marie Christine Boiron, Julien Mercadier, Phil Shaw
Combining high sensitivity and fast full mass range scanning capability for imaging by laser ablation ICP-MS: performance of the High resolution ICP-MS AttoM
14:35 Tobias Fusswinkel (Invited)
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15:00 Nancy McMillan (Invited)
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19:00 **Workshop Dinner at Stubb's BBQ (Hosted by Elemental Scientific Lasers)**

Friday, May 31st

08:00 Coffee ……………………………………………………………………………….Holland Student Center

Session 10: Novel Applications of LA-ICP-MS………………………………………Boyd Aud., JGB 2.324
Moderator: Tony Simonetti
08:30 Amy J. Managh, Calum J. Greenhalgh, Ellie Karekla, J. Howard Pringle (Keynote)
High Resolution Imaging of Explant Tissue in Anti-cancer Therapy
09:05 Mark Golitko (Keynote)
Laser Ablation-ICP-MS in Archaeology

Session 11: Summary of Workshop Activity on Reference Materials……..Boyd Aud., JGB 2.324
Moderator: Kate Souders
09:40 Working Group Presentations and Discussion

10:35 **Coffee break**

Session 12: New Data Collection and Processing Techniques for LA-ICP
Moderator: Tony Simonetti ………………………………………………………………Boyd Aud., JGB 2.324
11:00 Joe Petrus, David Chew, Bence Paul, Jeffrey Marsh, and Jon Woodhead
Systematic error associated with sequential detector LA-ICP-MS measurements in zoned minerals with implications for U-Th-Pb geochronology
11:25 Bence Paul, Peter Rayner, Estephany Marillo-Sialer, Joe Petrus, Jon Woodhead, Janet Hergt and Michael Shelley
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11:55 Announcement of NAWLA2021 at University of Notre Dame -Tony Simonetti

12:00 Lunch + Vendor Exhibits………………………………………………………Holland Student Center

Session 13A: U/Pb Age, Isotopic and Trace Element Analysis for Geology
Moderator: Luigi Solari…………………………………………………………………………………. JGB 2.216
13:00 Jeffrey Marsh, T.R.C. Jorgensen , J.A. Petrus, M.A. Hamilton and D.R. Mole
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13:25 Yan Luo, D. Graham Pearson, James Scott, Marshall Palmer, Chris M Fisher, Chiranjeeb Sarkar, Adrien Vezinet, Pilar Lecumberri-Sanchez
Simultaneous In situ Analysis of Sm-Nd isotopes and Trace Elements in Scheelite by Laser Ablation Split Stream ICP-MS: Challenges and Emerging Approaches

13:50 Duane Petts, William J. Davis, Simon E. Jackson and Isabelle Girard
U-Pb dating of Paleoproterozoic travertine using LA-Q-ICP-MS and LA-SF-ICP-MS

14:15 Chris McFarlane and Brandon Boucher
In situ U-Pb geochronology of simple and complex oxides

14:40 Margaret Odlum, Eirini Poulaki, Megan Flansburg, Daniel Stockli
Dating exhumation and fluid-fault interactions in fault systems using apatite U-Pb and trace element LA-ICP-MS analysis

15:05 Eoghan Corbett, A. Simonetti, P. Shaw, Q.G. Crowley, L. Corcoran
Eliminating U-Pb 'Downhole' Elemental Fractionation and Achieving Nanometer (nm) depth resolution in zircon by low volume single-shot LA-ICP-MS.

15:30 Staci Loewy, Aaron Satkoski, John Lassiter and Jay Banner
MC-ICP-MS Isotope Measurements using Multiple Daly Detectors

Session 13B: Trace Element Analysis and Imaging for Paleo-Environmental Research, Health Science, Food Safety, Artefacts……………………………………………………………….Boyd Aud., JGB 2.324
Moderator: Nate Miller

13:00 Hehe Jiang and Cin-Ty Lee
Reconstructing paleo-hydrologic history with LA-ICPMS U-Pb dating and trace element analyses on agates

13:25 Jhanis Gonzalez
Chemical Analysis using Tandem LIBS and LA-ICP-MS/OES

13:50 Eszter Sendula, Benjamin C. Gill, Tim K. Lowenstein, Javier Garcia-Veigas, Robert J. Bodnar
Measurements of redox-sensitive trace elements in individual fluid inclusions in halite – a record of paleoseawater redox conditions?

14:15 Stijn Van Malderen, Thibaut Van Acker, Michiel De Bruyne, Riet de Rycke , Laszlo Vincze Frank Vanhaecke
Leveraging the low-dispersion COBALT/ARIS ablation system for multi-megapixel 3D images of single cells.

14:40 Theodora J. Stewart, Philip Blower, Wolfgang Maret
London Metallomics Facility: An Emerging Scientific Platform for Multidimensional Metallomics

15:05 Todor Todorov
Evaluating the accumulation of toxic and nutrient elements in rice grains using 3D bioimaging by means of laser ablation ICP-MS

15:30 Vid Simon Šelih, Martin Šala, Johannes T. van Elteren, Thibaut Van Acker, Frank Vanhaecke
Evaluation of the state-of-the-art LA-ICP-(q)MS systems for elemental imaging of decorative glass object

15:55 **Adjourn**

TALK ABSTRACTS

Influence of plasma conditions on elemental behavior during LA-ICP-MS

JAN FIETZKE[1]

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Matrix effects are one of the frequently observed and discussed issues challenging the accuracy of LA-ICP-MS results. The complex interactions between the three principal components (LA, ICP and MS) complicate attempts to experimentally determine specific causes for analytical biases related to different sample matrices.

In particular the role of the ICP as a source of elemental fractionation seems not fully understood. While some potential problems e.g. isobaric interferences like poly-atomic clusters or multiply-charged ions may be relatively easy to identify, some other more subtle ones may not. The later include e.g. changes in ionization efficiency, mass fractionation or background intensity in the presence of differing matrix compositions and loads.

We carried out experiments using six internationally available reference materials (five silicates, one carbonate) measured under different plasma conditions. To focus the experiments solely on effects happening in the plasma the experimental conditions did not include any changes for the laser side (constant laser settings and cell gas flow). Additionally, the optimization of the mass spec's ion optics had been done tuning for maximum transmission of the $^{36}Ar^{+}$ ions.

The thermal/energetic state of the plasma was estimated based on the ratio of $^{38}Ar^{+}$ and $^{40}Ar^{2+}$ ions. This ratio (defined here as NAI - "normalized Argon index") should be one a robust parameter to estimate the Ar plasma energy density, with higher NAI representing more energetic ("hotter") conditions at the site where the ions are sampled from the plasma.

We observed a highly systematic common behavior for all standards used in the experiment: element specific behavior (volatile vs. refractory) dominates at cool but vanishes under hot plasma conditions. For robust (hot) plasma conditions matrix-tolerance seems to have been achieved. Additionally, we address the problem of matrix-load with respect to the plasma conditions. We discuss practical limits for the amount of matrix which can be introduced into the ICP without significantly changing the plasma conditions. The results of the experiments provide insight into the systematics of mass bias, too.

Finally, practical guidelines for the instrumental tuning can be obtained from the experimental results which can help to establish a more reproducible long-term performance of the instrumentation used.

Uncertainties and resolution of variation in LA-ICP-MS

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In 2016 the LA-ICP-MS U-Pb community published new accepted guidelines on uncertainty propagation for U-Pb dating. When used appropriately, these allow resolution within and between data sets at relative and absolute scales. This uncertainty propagation philosophy is widely applicable to isotope data gathered by ICP-MS (and other mass spectrometry platforms), characterising analytical repeatability (within session) and reproducibility (between sessions) and providing quantified constraints and limits on geological interpretations.

With this better understanding and quantification of analytical variation, resolution of compositional difference (or lack there-of) can be interrogated and interpreted with greater confidence. Examples using Sr-Nd-Hf and U-Pb isotope data will be considered, detailing their components of uncertainty, when they are required in the interpretation and what are their true resolution.

Considering these factors for all produced and published data will improve data quality and interpretations in the scientific literature and enable a more detailed understanding of processes and events.

Water vapor-assisted “universal” non-matrix-matched analytical method for the in situ U-Pb dating of zircon, monazite, titanite, xenotime and wolframite by LA-ICP-MS

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The U-Pb geochronologic analysis of accessory minerals has played an important role in Earth and solar system science in constraining the ages of a wide variety of rocks and minerals. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is one of the most popular techniques for U-Pb geochronologic analysis. Currently, the significant matrix effects observed between different accessory minerals and the lack of high-quality standards for many minerals of interest are the major limitations of its geochronological applications. In this study, we investigated the effects of the addition of oxygen, nitrogen and water vapor before and after the ablation cell on the accuracy of the U-Pb dating of different minerals (e.g., zircon, monazite, titanite, xenotime and wolframite) by LA-ICP-MS. We found that the addition of water vapor, unlike that of oxygen and nitrogen, before the ablation cell can significantly suppress the matrix effects on U-Pb dating. The deviations of the measured 206Pb/238U ratios in zircon (91500 and GJ-1), monazite (44069), xenotime (BS-1 and MG-1), titanite (Khan, OLT-1) were significantly reduced from 10-24% to less than 1-2% when using NIST 610 glass as an external standard. This can be attributed to the suppression of elemental fractionation in both the laser ablation and ICP ionization processes by the presence of water vapor. The developed water vapor-assisted LA-ICP-MS U-Pb dating method has been successfully applied to the analysis of zircon, monazite, xenotime and titanite with NIST 610 glass as a reference material in both the 193 nm excimer laser and 213 nm Nd: YAG laser ablation systems. In addition, the obtained wolframite lower intercept ages were approximately 12% younger than their isotope dilution thermal ionization mass spectrometry (ID-TIMS) ages using zircon 91500 as the external standard in ns-LA-ICP-MS. By adding water vapor before the ablation cell, the measured lower intercept ages of wolframite samples show excellent agreement with the ID-TIMS ages. This simple and effective non-matrix-matched analytical method shows great potential for the U-Pb dating of different accessory minerals.

Rocks, Bones, and Teeth: New frontiers and old problems in strontium isotope analysis in ecology and archaeology

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[1]Wildlife, Fish, and Conservation Biology, University of California Davis, California, USA.

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Strontium isotope ratios ($^{87}Sr/^{86}Sr$) are an incredibly useful tracer in archaeological and ecological research to assess the geographic origin and movement of humans, animals, and materials across geologically distinct areas. Laser ablation enables rapid and minimally-destructive analysis of a large range of different sample materials for the determination of strontium isotope ratios. As this technique is being applied to new sample materials, additional analytical interferences need to be considered. This can be problematic if no standard materials have been characterised or if data reduction and data analysis have not been experimentally validated. One prominent example that has caused significant scientific discourse is the potential interference of polyatomic compounds ($^{40}Ca^{31}P^{16}O$ and/or $^{40}Ar^{31}P^{16}O$), when analysing strontium isotopes in bioapatite samples such as teeth, bones, spines, and fish scales. Here I present on the past and current method development for strontium isotope analysis via laser ablation and their application in archaeology and ecological research. I will highlight some particularly promising sample materials, discuss typical problems that occur when working with previously uncharacterized samples, and compare the different approaches laboratories world-wide have taken to produce accurate data from complex biominerals. Last, I will detail the work we have done at UC Davis to use strontium isotope ratios in both modern and archaeological fisheries research and how laser ablation can play a pivotal role in the conservation of threatened and endangered species.

In-situ sulfur isotope measurements by LA-MC-ICP-MS: sulfate standards and matrix effects

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Sulfate minerals are widely distributed in nature and their sulfur isotope signatures offer a largely untapped source of potential information for improving our understanding of magmatic, hydrothermal and sedimentary processes. In this study, we describe an analytical procedure for measuring sulfur isotope compositions for natural sulfate-bearing samples using a LA-MC-ICP-MS technique. YF-2 barite (BaSO4) from the Yongfu hydrothermal deposit yields a δ^{34}S value of 18.1 ± 0.4‰ (n = 11, 2s) obtained by elemental-analyzer isotope-ratio mass spectrometer (EA-IRMS), and has been adopted as the reference material for sulfur isotopic determination in this study. We validate the sulfur isotopic ratios of NIST SRM 8557 and IAEA-06 barium sulfate by using YF-2 pressed powder tablet as reference material. The result yielded good consistency with the recommended values. The measured δ^{34}S values obtained here for YF-1, GTS and DGD barites are similar to those recorded by EA-IRMS for these samples. WC barite displays highly variable sulfur isotopic compositions although the average δ^{34}S value for WC barite is similar to that obtained by EA-IRMS. Sulfates in barite-celestine solid solution series and anhydrite were analyzed to determine the isotopic fractionation with varied matrices using both the RESOlution and GeoLasHD laser ablation systems. Results suggest minimal sulfur isotope fractionation between barite and other S-bearing matrices for analyses using both laser systems. Sulfur isotope measurements conducted with the GeoLasHD laser system did not produce fractionation while using varying laser parameters, whereas optimizing laser parameters such as beam size, frequency and energy was required in order to minimize matrix-related fractionation using the RESOlution laser system.

Nano-particulate pressed powder pellets (not only) for LA-ICP-MS

Dieter Garbe-Schönberg[1], Samuel Müller[1], Maxim Portnyagin[2], Axel renno[3]

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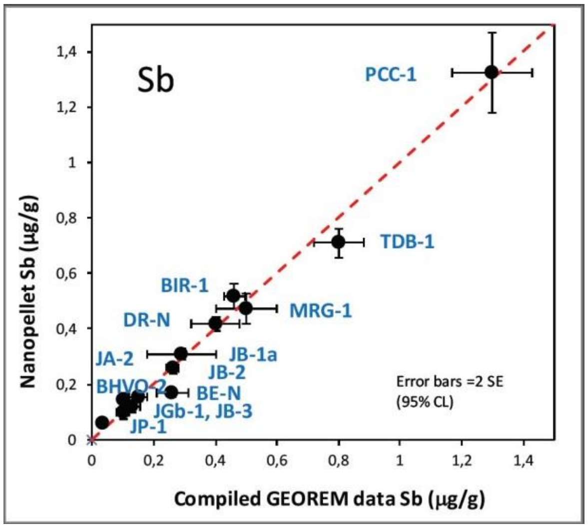
While *in-situ* analytical instrumentation for the direct elemental and isotopic analysis of solid materials has undergone continuous and significant improvement over recent years, development of well-characterized and homogeneous microanalytical reference materials (MRM) for calibration and validation of analytical data is lagging behind. Ideally, MRM must be homogeneous down to the single micrometer scale for major, minor, trace, and ultra-trace elements and isotopes, withstand high-vacuum and impact of high-energy electron, ion, and photon beams, stable in its physical and chemical properties over time and under various environmental conditions, certified following ISO guidelines, and available for a wide variety of materials.

We developed a method for manufacturing undiluted, binder-free pressed powder pellets[1] with particle grain size down to the nanometer range (D_{50} <170 nm), extremely low roughness of pellet surface (R_A <50 nm), and excellent within and between pellet homogeneity. This technique has been applied so far to a wide range of very different sample types: biogenic carbonates (foraminifera, clam shells, red algae, corals), speleothem, silicate rocks, iron ores and banded iron formation, manganese nodules, sulphides UQAC-FeS, (refractory) minerals, plutonic and volcanic rocks, fly ash, bone-apatite, minerals for Rb/Sr age-dating[2] etc.. We successfully blended different materials opening new ways for producing e.g., series of elemental and isotopic calibration standards. These "nanopellets" have been successfully used with LA-ICP-MS, LIBS, µ-XRF, handheld-XRF instruments, and with EPMA, PIXE, SIMS. Hence, nanopellets proved to be a new and, possibly, more universal matrix-matched MRM for many custom solid materials to be used with different *in situ* analytical techniques.

In addition, this way of sample preparation bears the potential of completely replacing conventional tedious and time-consuming wet-chemistry procedures for bulk analysis, and this holds true in particular for refractory samples like ceramics, granites, ultramafic rocks, and samples with volatile or easy-to-contaminate components (e.g., B). Here we give an overview of the present state of development of new MRM and their characterization in terms of grain size distribution, surface topography, porosity, homogeneity, and accuracy of analytical results for both elemental (major, minor, trace and ultra-trace elements) and isotopic (Sr, Li, B, O) composition.

[1] Garbe-Schönberg D & Müller S, *JAAS,* 29, 990 (2014); [2] Hogmalm KJ et al., *JAAS*, 32, 305 (2017)



Development of accurate methods for LA-ICP-MS analysis of minerals using non-matrix matched reference materials

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The contribution of matrix effects and other elemental fractionation to the uncertainty of mineral analysis by LA-ICP-MS is well documented [1][2][3]. Management of the issues remains an outstanding challenge, especially when high accuracy of the results, approaching that of electron beam-based techniques is required. Use of matrix-matched calibration reference materials (RM) [4] and identical ablation conditions on the RM and unknowns is largely limited to LA-ICPMS U/Pb dating applications. We present an approach which enables analysing different minerals in a single analytical session. The approach builds on previous work [5] and involves using mineral stoichiometry as a criterium for establishing the appropriate analytical conditions for mineral analysis using non-matrix matched calibrations and secondary RMs. Quantification [6] is performed using normalisation to a specified total. A single calibration RM is analysed throughout the session under fixed laser conditions, selected to minimise measurement uncertainty. During the same analysis session, secondary RMs are measured using the established laser conditions (e.g. beam diameter, fluence, ablation mode: spot or line) required for accurate quantification of the unknowns. Results from the secondary RMs are used for quality control and to estimate separate correction coefficient values for each set of laser conditions required for accurate quantification of the unknowns. Measurement of multiple secondary RMs under the same conditions allows the uncertainty in the corrections to be estimated. When variations in laser parameters on the available secondary RMs and the unknowns are insufficient to achieve accurate results on the unknowns, an additional matrix correction coefficient for each element can be determined and added to the quantification procedure. This coefficient can be quantified once and subsequently reused, provided all analytical conditions remain unchanged between analytical sessions. We will present the results of LA-ICPMS analyses of major and trace elements in olivine ($Fe_{0.2}$,$Mg_{1.8}SiO_4$), plagioclase ($Na_{0.4}$,$Ca_{0.6}Al_{1.6}$,$Si_{2.4}O_8$) and ilmenite ($FeTiO_3$) using the above approach. To facilitate adoption of this protocol, new software has been written for reduction of LA-ICP-MS data. The software package “LADR” (pronounced “ladder”) is available for download from the authors' website [7] and performs all necessary calculations, including estimation of a “bottom up” [8] uncertainty budget.

[1] Fryer et al. (1995) Can Mineral 33.2, 303-312. [2] Eggins et al. (1998) Appl Surf Sci. 127, 278-286. [3] Kroslakova and Günther (2007) J. Anal. At. Spectrom. 22.1, 51-62. [4] Wilson et al. (2002) J. Anal. At. Spectrom. 17.4,406-409. [5] Danyushevsky et al. (2011) Geochem-Explor. Env. A 11.1, 51-60. [6] Longerich et al. (1996) JAAS 11.9, 899-904. [7] http://norris.org.au/ladr/ “LADR” (Mar 2018). [8] Luo et al. (2007) JAAS 22.2, 122-130.

ICPMSDataCal: An accurate, simple, convenient and friendly ICP-MS data calculation software

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Data reduction software ICPMSDataCal was written in the Visual Basic programming language and works on the Microsoft Excel. This software integrates all the calculation and correction methods for the LA-(MC)-ICP-MS analysis of elemental and isotopic compositions. It gives users a unique analytical environment, based on the interactive selection of background and sample intervals from the time-resolved signals provided by LA-(MC)-ICP-MS. It provides real-time and on-line data reduction for the LA-(MC)-ICP-MS analysis, and features linked graphics and analysis tables, greatly improving both productivity and the flexibility of analysis. At present, data analyzed by LA-(MC)-ICP-MS of Agilent, Thermo X and Neptune plus, Elan, Varian, Nu Plasma and Attom can be directly calculated by the software without any additional adjustment. In order to guide the users to use the data reduction software, a detailed manual (Guide book for ICPMSDataCal) including the specific operations of different applications (*e.g.,* U-Pb dating of zircon, trace element analysis of mineral and melt/fluid inclusion, and isotope analysis of Li, Sr, Nd, Hf, Os, Pb) is provided. In addition, the software is upgrading and modifying based on the users' requirements.

The functions and features of ICPMSDataCal mainly include:

- It integrates the calibration and correction methods for trace element analysis of silicate mineral, carbonate, metal oxide, sulfide minerals and single melt/fluid inclusion by LA-ICP-MS;
- The isotopic ratios of Li, Sr, Nd, Hf, Os and Pb measured by LA-MC-ICP-MS can be calibrated；
- Data reduction of zircon U-Pb dating and trace element analysis can be quickly done at one time;
- The time-dependent sensitivity drift in the analysis can be corrected by the measurement of quality control reference materials, which can be easily chosen by user;
- The used external standards can be automatically identified and easily changed (replace, add and delete) by the user;
- The unfinished data reduction can be processed continually as long as the relevant "data summery file" was saved.

TERMITE 2.0: An R script for data reduction of LA-ICP-MS trace element data

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) can generate huge quantities of high spatial-resolution trace element data within a short time frame. Several hundreds of single spot analyses or several line scans can be performed easily during a single analytical session. The reduction of such large data sets, however, can be time-consuming and tiresome. Thus, fast and efficient data reduction is required. For evaluation of LA-ICP-MS trace element data, commercial programs [1,2] and non-commercial software packages, e.g., [3], are available, each having their individual strengths and weaknesses.

Recently, Mischel et al. [4] introduced TERMITE, an R script that is capable to perform data reduction of both spot and line scan measurements. We now included a graphical user interface (GUI) in version 2.0 to simplify the application of the algorithm. As a result, no previous knowledge of R is necessary to apply the algorithm. Data visualization within the algorithm by several tables and plots simplifies the selection of integration intervals for further processing. All features from the previous version are still included.

The main features of TERMITE 2.0 are that it (1) is open-source software for the reduction of trace element LA-ICP-MS data, (2) has a GUI allowing parameters to be adjusted without prior knowledge of R, (3) can process both spot and line scan analyses, (4) is extremely fast once all required parameters have been defined, (5) can use multiple reference materials at the same time for calibration, and (6) is particularly useful for large datasets from samples that are homogeneous with respect to their major element composition.

TERMITE 2.0 is available free from https://www.blogs.uni-mainz.de/fb09-geosciences/termite/.

[1] Griffin, W.L. et al. (2008), Mineral. Assoc. Canada Short Course series 40, 308-311. [2] Hellstrom, J.C. et al. (2008), Mineral. Assoc. Canada Short Course series 40, 343-348. [3] Guillong, M. et al. (2008), Mineral. Assoc. Canada Short Course series 40, 328-333. [4] Mischel, S. et al. (2017), Rapid Commun. Mass Spectrom., 31, 1079–1087.

LADR: Comprehensive software for data reduction of LA-ICP-MS data sets

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In addition to solving the basic Longerich equation[1], successful data reduction of LA-ICP-MS data sets requires a comprehensive approach that includes: identification and removal of transient spikes; corrections for interferences; modelling of variations in background intensity; synchronisation with laser firing time; modelling and correction for down hole fractionation; modelling of calibration drift; assessment of secondary standards and correction for matrix effects; addition of unmeasured elements by stoichiometry; quantification to a total concentration without using an internal standard concentration; support for mixed quantification types within a data set, including changes to internal standard and calibration SRMs; and most importantly, correct and robust error propagation from all sources of uncertainty.

Here we present an overview of a new software package "LADR" (**L**aser **A**blation **D**ata **R**eduction, pronounced "ladder') designed to perform all of these functions while remaining tractable to most analysts. To assist the user's comprehension of data quality the software displays graphics for visualisation of time-dependent values such as background variation, calibration drift, and downhole fractionation curves. LADR is able to load data files from most commercially available ICP-MS instruments and it can compute results for trace element analysis, ages for U/Pb dating, and quantify arbitrarily defined ratios of any two masses.

Interpretation of LA-ICP-MS measurements is improved if the analyst is presented with a comprehensive uncertainty budget. As well as enabling judicious application of the results, an uncertainty budget rapidly guides the analyst in method optimisation and appraisal of external constraints. Recent workers [2] have highlighted the need for robust error propagation, which we believe can be addressed by the "bottom up" approach of the EURACHEM/CITAC-Guide [3] as applied to LA-ICP-MS [4][5]. Our LADR software accounts for all sources of uncertainty, the values of which are combined for final output, but also shown in an expanded view for assessment by the analyst. A significant benefit of determining and quantifying all of the factors contributing to the complete uncertainty is the ability to purposefully resolve parts of the budget relating to precision and accuracy components. To facilitate the interpretation of measurement uncertainty we introduce the concept of *levels* of uncertainty as a useful practical tool to assist the analyst. The levels we define are descriptively named "Signal Precision", "Quantification Precision", "Within-Run Analytical Precision", "Full Within-Lab Analytical Precision", and "Full Analytical Uncertainty". The software allows the analyst to choose whether to report at the uncertainty level appropriate to a specific intra-run, intra-laboratory, or inter-laboratory comparison.

The software package LADR is available for download from the author's website [6].

[1] Longerich et al. (1996) *JAAS* **11.9**, 899-904. [2] Horstwood et al. (2016) *Geostand. Geoanalytical Res.* **40.3**, 311-332. [3] Ellison & Williams (2012) Eurachem/CITAC guide, ISBN 978-0-948926-30-3. [4] Luo et al. (2007) *JAAS* **22.2**, 122-130. [5] Gilbert et al. (2013) *Geostand. Geoanalytical Res.* **37.1**, 51-64. [6] http://norsci.com/ladr/ "LADR" (May 2019).

Iolite version 4: A proven solution for efficient and robust processing of LA-ICP-MS data

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Iolite development began in 2003 to provide a flexible platform for the processing of time-resolved mass spectrometry data. Initially released as free-ware to the analytical community, a series of peer-reviewed publications resulted in a dramatic increase in iolite's userbase and iolite v3 was commercialised in 2014.

Iolite v4, the next generation implementation, has been developed in C++ and python to run natively on Windows and Mac. Version 4 provides major speed improvements (up to 10 times faster than v3) while still using the same peer-reviewed and trusted algorithms as v3, with significant improvements to the user interface (UI).

A key new feature is the ability to write scripts in python. These allow the user to call import functions; create, move and delete selections based on data criteria; run Data Reduction Schemes; and to export data in custom formats. Python was chosen for its ubiquitous use in scientific computing and for the availability of many powerful add-ons, many of which can be used with iolite v4. Uniquely, Python scripts produced for iolite v4 are entirely open and can be shared amongst the analytical community.

The latest version builds upon iolite's previous visualisation paradigm: intermediate data are viewable at all stages of processing and can be examined on a variety of levels from the individual data points, to the mean of each selection, and the mean of each group of selections. This approach provides full data confidence and complete transparency.

Iolite v4 also brings powerful new imaging capabilities and includes advanced image 'inspectors' which provide visualisation of pixel values within regions of interest. Iolite v3 was the first package to offer full automation in the form of "Processing Templates", which are essentially processing macros. These have been expanded and further developed in v4 for fast, unbiased processing of large datasets in a reproducible fashion. Iolite's latest release continues its history of innovation, offering users a combination of flexibility and power. Backed by a large community of long-term users and continual innovation based around peer-reviewed publications, iolite continues to provide one of the best data processing platforms available for LA-ICP-MS.

HDIP: powerful LA-ICP-MS data reduction software with extensive data interogation tools

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In recent years, the volume of data in mass spectrometry imaging (MSI) methods has been steadily increasing, as well as the time required by the user to process MSI data, as a result of advances in lateral resolution, increases in the dimensionality and the emergence of multiplexed, complex data sets. Efforts within the community have given rise to numerous data reduction software packages, notably the Iolite project, GLITTER and LADR to resolve the data reduction problem. HDIP is an advanced software platform for processing transient mass spectrometry signals, with a specific emphasis on laser ablation-inductively coupled plasma-mass spectrometry imaging, focused on going beyond the limitations of the current software packages, and with a strong focus on imaging applications. HDIP is based around the HDF5 file-type for full metadata retention and its ability to deal with large files. In contrast to many closed file-formats from the current software packages, this file-type is readily accessible by many other pieces of software, permitting a higher level of flexibility and transparency. HDIP is currently operational at more than a dozen laboratories, and aims to become an important player in LA-ICP-MS data processing software in the next years, through continued development and deployment cycles of the software to incorporate increasingly advanced features. Raw detector data can be imported from a broad range of ICP-MS instrument manufacturers and other microscopy techniques, whilst the laser log data captured in Chromium can be directly imported. HDIP uses an advanced algorithm that can reconstruct an image from any lasing approach, i.e. the reconstruction does not require an image to consist of line scans. Background correction and drift correction can be performed using a multi-spline higher-order degree fitting curve through selected sections of the signal, thus compensating for instrumental drift during a measurement. Convolution, deconvolution and denoising filters can be applied to improve the spatial resolution of the reconstructed images. Advanced multivariate analysis tools are also present; for example, collections of voxels within the image can be selected and clustered, and statistical analysis can be performed on the group of clusters. Multi-standard external calibration with internal standardization is possible, allowing for better calibration curves to be constructed. Many other features are present, which will be highlighted in this talk.

Overview and preliminary results of the promising *fs-LA-LIBS-ICP-TOF-MS* system

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Most LA-ICP-MS systems today couple a nanosecond (10^{-9} s) pulsed laser (ArF-excimer 193nm or solid-state 213nm Nd:YAG) to a quadrupole mass spectrometer (Q-ICP-MS). Equipped with a double-volume ablation cell, such systems are used in many fields of science. However, a limitation of the nanosecond-LA system is the known matrix-dependence of the interaction of the laser with the sample. The femtosecond laser (10^{-15} s) mitigates thermal-induced chemical fractionation and thus makes the technique less dependent of matrix-matched calibration materials. A limitation of Q-ICP-MS is the number of analytes that can be measured simultaneously due to the sequential acquisition of the quadrupole mass filter. The time-of-flight mass spectrometer (ICP-TOF-MS) can detect entire mass spectra of inorganic analytes at the tremendous speed of 33,000 times per second, allowing the study of "whole" inorganic composition of nanoparticles. Another limitation of the ICP-MS is the difficulty to detect and quantify elements such as H, O, C, Cl and F. The electromagnetic spectrum (UV, visible, IR) generated from the micro-plasma at the laser impact site is a function of the chemical composition of the sample. Laser-induced breakdown spectroscopy (LIBS) is the technology of monitoring the electromagnetic spectra at the ablation site, and allows the detection of those elements. The promising system coupling femtosecond-LA equipped with LIBS (Tandem J200, Applied Spectra) and attached to a time-of-flight inductively coupled mass spectrometer (icpTOF R, TOFWERK) was installed in January 2019 at the LabMaTer-UQAC (Chicoutimi, Canada). With the potential abilities to circumvent limitations stated above, this state-of the-art *fs-LA-LIBS-ICP-TOF-MS* system would be able to provide nearly complete high quality *in-situ* elemental and isotopic chemical information. Preliminary results demonstrating: 1) the performance of the system, including some advantage of using a femtosecond laser; 2) the potential of simultaneous LIBS/TOF-MS for assessing water content in minerals; 3) some examples of the high-speed and space resolution acquisition capacities of the system and, 4) weakness, limitations and improvement/modifications required to the actual system to reach its maximize potential; will be presented.

Recent findings of in-situ beta-decay geochronology: Rb-Sr dating of glauconite and Re-Os dating of molybdenite

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The advent of ICP's with reaction cells sandwiched between two quadrupoles allows significant reduction, if not elimnation of many notorious interferences. An exciting development for geosciences is the realization that monoatomic isobaric interferences can be dealt with that are inherent to beta decay systems (e.g., ^{40}K-^{40}Ca, ^{87}Rb-^{87}Sr, ^{176}Lu-^{176}Hf, ^{187}Re-^{187}Os). Continuing progress appears to be guaranteed by carefully investigating more gases that may interact selectively with ions in the reaction cell. Each parent-daughter couple at this stage of knowledge has its specific set of gas (mixes), e.g., N_2O for Rb-Sr, SF_6+H_2 for K-Ca and CH_4 for Re-Os. In this contribution I want to highlight two recent geologic applications:

Rubidium-Sr dating of glauconite. In-situ Rb-Sr dating of glauconites from stratigraphically well-calibrated sections give geologic reasonable ages. Combining in-situ dating with microtextural information (in the spirit of petrochronology) allows to distinguish detrital components that give older ages as well as alteration products that give younger ages. This allows reliable dating of sedimentary sequences lacking index fossils and/or zircon-bearing ash layers, e.g., in many Precambrian sedimentary basins.

Rhenium-Os dating of molybdenite. It has recently been shown (Hogmalm et al., in press) that fully quantifyable in-situ Re-Os molybdenite ages from six different localities are consistent with published ages. Surprinsingly, no "decoupling" of Re from Os is observed, in contrast to previous studies. Possible explanations will be discussed.

LA-ICP-MS microanalysis of fluid inclusions

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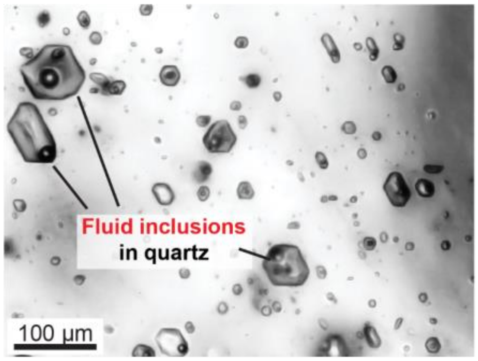
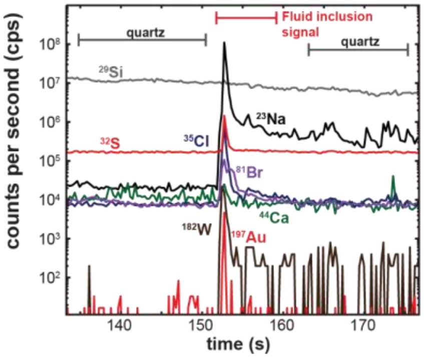
Aqueous hydrothermal fluids are a key driver of mass transfer processes in the Earth's crust, the hydrosphere and the atmosphere. Knowledge of the composition of crustal fluids has been crucial to our understanding of magmatic, volcanic, metamorphic, and ore forming processes. Since hydrothermal fluid activity typically occurs at great depths and cannot be investigated directly, most of the information we possess about fluids deep in the Earth's crust comes from the study of fluid inclusions. Fluid inclusions are microscopic, liquid-filled cavities in host minerals such as quartz, fluorite and carbonates. They preserve pristine aliquots of hydrothermal crustal fluids over millions or even billions of years, and so provide unique windows into the geological past.

The development of LA-ICP-MS fluid inclusion microanalytical techniques has made it possible to directly sample individual inclusions even within highly complex textural contexts. This key innovation was the driver for many breakthroughs in our understanding of fluid-rock interaction, the sources and transport mechanisms of crustal hydrothermal fluids and the formation of ore deposits, as well as our ability to quantitatively address all of these processes. Using state-of-the-art 193 nm UV laser ablation systems and high sensitivity mass spectrometers (commonly quadrupole or magnetic sector instruments), it is possible to reliably sample fluid inclusions as small as 15-20 µm, located up to 200 µm below the surface of their host mineral, and determine the concentrations of major and trace elements down to limits of detection in the ng/g range. Adaptation of the method to multi-collector ICP-MS systems even allows the determination of Pb and Sr isotope ratios from individual fluid inclusions. Laser ablation systems for fluid inclusion analysis must meet demanding performance criteria, especially with regard to beam homogeneity, beam energy and visual observation capabilities, to enable reliable sampling of target inclusions. The sampling of small volumes of liquids during ablation of the solid host mineral leads to highly transient signals with a very characteristic peak shape, requiring careful data reduction procedures and mass spectrometers with very good time resolution.

LA-ICP-MS microanalysis of fluid inclusion is a highly efficient method for the multi-element analysis of crustal fluids. Recent method development efforts have focussed on expanding analytical capabilities to allow for reliable quantification of halogens (e.g. Cl, Br, I) and ultra-trace concentrations of rare metals in fluid inclusions, as well as novel standardization and quantification techniques. Improvements in mass spectrometer design, sensitivities and time resolution will further extend the ranges of application and promise to lead to novel insights into fluid flow processes within the Earth's crust.





Hand-held Laser-Induced Breakdown Spectroscopy (LIBS) Instruments and Applications

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LIBS is an optical emission spectroscopic technique that diffracts and records photons emitted by excited atoms, ions, and molecules during cooling of laser ablation plasmas. Off-the-shelf instruments are available in both benchtop and hand-held models. Some hand-held models permit analysis in an Ar atmosphere which increases signal-to-noise by exciting more analyte at the expense of high-excitation energy Ar atoms. Hand-held models have two disadvantages in comparison with benchtop models. Analysis parameters such as the Q-switch delay time and gate width are typically pre-set and not variable in hand-held instruments, eliminating the possibility of optimizing parameters for specific materials. In addition, optical imaging of the analysis area is limited or impossible because the instruments are designed for tasks such as identification of scrap metal. Analysis of LIBS spectra must consider two main issues. First, LIBS spectra are highly matrix dependent, requiring many standards for quantitative analysis. Second, there is a high amount of shot-to-shot variation in peak intensities, the result of hardware variations such as the energy of each laser shot and the degree of coupling between the laser and material as well as heterogeneity of geologic materials. These issues are minimized by averaging many spectra, normalization of intensities to the mean intensity, using log-transformed spectra, and filtering out poor quality spectra. Most hand-held LIBS spectrometers use univariate analysis to determine concentrations of elements; software performs background correction. Multivariate techniques such as PLSR are useful for material identification problems such as sorting scrap metal by comparing a spectrum of unknown material to a spectral database. Hand-held LIBS instruments are excellent options for screening samples. One possible application is analysis of many samples of fine-grained rocks to determine which represent the norm and which are compositional outliers; the researcher would be able to make informed decisions about samples to collect for lab analysis. In addition, because LIBS spectra contain information on most elements, multivariate analysis yields information on which elements are the most variable between samples. This is a valuable guide for further analysis using traditional techniques.

High Resolution Imaging of Explant Tissue in Anti-cancer Therapy

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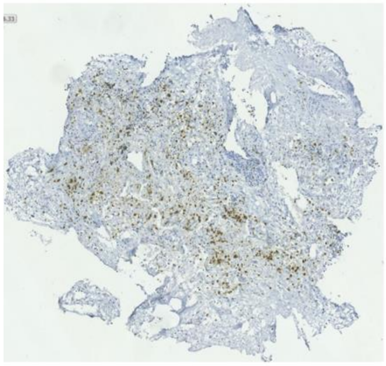
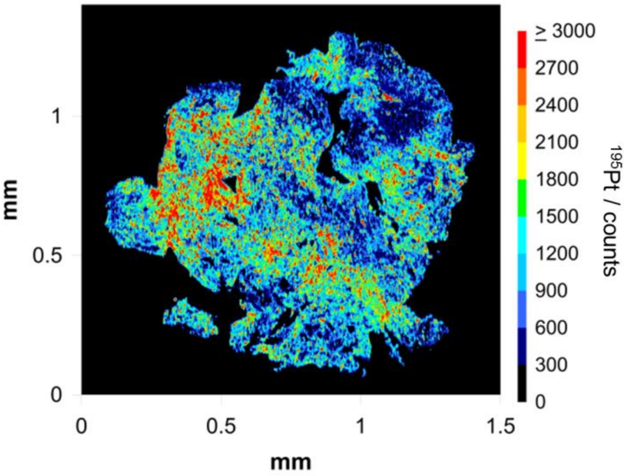
Models of patient response are required to improve understanding of the mechanisms of drug action in oncology. Such models can predict the chemotherapeutic benefits of emerging therapies, as well as facilitating more targeted use of existing drugs, to provide improved clinical outcomes. Karekla *et al*. recently reported the development of an 'explant' model of non-small cell lung cancer.[1] Patient derived lung tumour biopsies were grown on *in vitro* and dosed with cisplatin. Histological staining was subsequently used to classify the tumours as either cisplatin sensitive or cisplatin resistant at each of the doses studied (1 μm, 10 μm and 50 μm).

Laser ablation – inductively coupled plasma - mass spectrometry (LA-ICP-MS) offers a high resolution approach to image metal containing drugs in tissue explant samples. Recent developments in the core technology have provided dramatic improvements in the analytical throughput, spatial resolution and absolute sensitivity of the technique, therefore improving its potential for integration into the clinical workflow.[2] In this work a low-dispersion laser ablation system was applied to image explant tissue from the aforementioned Karekla study. The LA-ICP-MS images were correlated to histological images (H&E, cPARP and Ki67) of consecutive sections, which highlighted association of platinum with tumorous regions and areas of cell proliferation and cell death. It was demonstrated that tumours classified as cisplatin resistant exhibit a different platinum distribution pattern compared to tumours classified as sensitive. The resolution of the system also revealed information regarding the association of platinum with extracellular deposits in the tissue. These findings will be explored further during the workshop.

[1] E. Karekla *et al.*, *Cancer Research*, 2017, 77, 2029-2039.

[2] S.J.M. Van Malderen *et al.*, *Journal of Analytical Atomic Spectrometry*, 2016, 31, 423-439.





Laser Ablation-ICP-MS in Archaeology

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Laser Ablation-ICP-MS has been applied to archaeological materials since the late 1990s. The technique quickly gained in popularity due to its relatively low cost of analysis, and perhaps most importantly, minimal requirements of sample preparation or destruction. While early applications reproduced analyses previously carried out by other means (XRF, INAA), by the mid-2000s, the technique was being increasingly employed to analyze particular phases within complex cultural materials. This talk will review some of these applications, including depth-profiling of ancient coinage, multi-phase analysis of glasses, and identification of post-depositional chemical alteration of ceramics. The particular challenges of analyzing heterogeneous materials with no modern analogues, standardization for "atypical" materials, and interpretation of multi-phase data will be reviewed using case studies from multiple world regions and periods of pre- and early-history.

Systematic error associated with sequential detector LA-ICP-MS measurements in zoned minerals with implications for U-Th-Pb geochronology

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Laser ablation quadrupole ICP-MS (LA-Q-ICP-MS) instrumentation is widely available and routinely used for trace element characterization and geochronology. Its widespread adoption has encouraged a significant body of research into ways to improve measurement precision and accuracy, e.g., thermal annealing (Solari et al., 2015), chemical abrasion (Crowley et al., 2014), studying matrix effects (Marillo-Sialer et al., 2014), down-hole fractionation (Paton et al., 2010) and alpha-dose (Sliwinski et al., 2017) corrections, software (Petrus et al., 2017), etc., in addition to on-going improvements in laser and ICP-MS technology. Geochronology is an application that benefits significantly from these advances. However, one basic aspect of LA-Q-ICP-MS is often overlooked when processing data that can significantly influence the results, namely, the dwell times.

When using a sequential detector, U, Th and Pb isotopes are measured at different times, however, these measurements are commonly recorded in data files as if they were measured at the same time and treated as such in data processing. Geochronology reference materials are often relatively homogeneous (e.g., 91500) in U, Th and Pb content, so when secondary reference materials are reproduced as expected, analyses of unknown samples are expected to yield the 'correct' data as well. However, U-Th-Pb mapping and detrital zircon data, e.g., clearly show that U and Th can be strongly zoned by orders of magnitude within a single crystal. This is not a problem if the concentrations are relatively homogeneous, but if significant zoning exists, the derived ratios and ages are systematically biased depending on the rate of change of the analytes, whether it is increasing or decreasing, and the time between measurements.

Here we explore how dwell times and U-Th zoning affect U-Th-Pb geochronology through numerical simulations and real data from the Tardree zircon (Ganerød et al., 2011). We show that by shifting the data to its 'true' time and interpolating the analytes on to the same 'index time', much of the systematic error can be removed.

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An inversion approach to processing LA-ICP-MS imaging data from fast washout cells

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Hardware advances in laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) promise improvements in sensitivity and resolution in imaging applications. In particular, fast washout cells are one of the most significant developments in recent years. However, with decreasing washout times, current data processing approaches are no longer necessarily applicable as the ability to resolve individual laser pulses in the mass spectrometer become feasible within reasonable experiment times.

Here we present preliminary findings from a new approach to processing data from fast washout cells using a combination of inversion and synthetic aperture techniques typically used in remote sensing and geophysical applications. In contrast to previous attempts to use inversion approaches, we construct the Jacobian used in the inversion from empirical data. We also use a matrix-free approach to speed up the time taken for processing. The inversion is positive-definite, to the limit the inversion results to positive values only. While these factors improve the physical model underpinning the inversion, it does introduce the problem of analytical uncertainty in the Jacobian, and non-linear inversion.

Initial testing of the technique included synthetic tests with known structures before analysing results from a prototype cell from Laurin Technic. We use this approach to correct data collected along a line scan to examine how well the “smearing” effect of high-concentration pulses overlapping with subsequent pulses can be corrected.

As we approach the limits of what can be collected by a laser/quadrupole combination we discuss the factors that must be taken into consideration when performing high-speed imaging experiments, including the ultimate trade-off between resolution and time for a given application.

Combining high sensitivity and fast full mass range scanning capability for imaging by laser ablation ICP-MS: performance of the High resolution ICP-MS AttoM ES

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For the past decades, interest in performing imaging with by laser ablation coupled with ICP-MS has grown in several area such as geology, bio medical, pharmacology… Recent improvements to laser ablation sample cells have prompted requests for even faster data acquisition for wide if not full mass spectra. Although high resolution magnetic sector ICP-MS has become the favoured instrument for many laser ablation applications due to the high sensitivities seen in dry aerosol sampling and the flat-topped peak, it still hasn't been widely used for imaging purposes due to slower wide mass range scanning capability compared to quad ICP-MS. Recent changes to the Nu AttoM ES have improved the speed for the closed loop control and a more powerful 200V power supply provides a faster hysteresis loop of 400-800ms. It has also been possible to increase the magnetic field ramping and fall-back speeds of the "linkedscan" mode to obtain spectra up to uranium in 102ms leading to an acquisition rate of 9.5Hz. Combining the stable cycling magnet field with fast deflector scanning provides the ability to track the ions with deflectors in the OPPOSITE direction of the changing magnetic field and thus remain on the peak top for longer and improve the measurement duty cycle. The cycle time doesn't vary depending of the number of isotopes measured so if many isotopes are selected the scanning capability can be faster than a quad ICP-MS one.

In this work the interest of using this fast analysis mode for imaging purposes will be demonstrated on several geological material such as Sphalerite and Biotite.

MC-ICP-MS Isotope Measurements using Multiple Daly Detectors

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One of the latest developments in multi-collector ICP mass spectrometry (MC-ICP-MS) is the augmentation of the collector assemblage to include, as many as, six high-sensitivity Daly detectors among a suite of Faraday detectors. The dynamic range of the ubiquitous Faraday detector is 10^4-10^{10} counts per second (cps). The Daly detector range of 10^0-10^6 cps overlaps that of the Faraday detector but extends to much lower signal intensities. Pairing Daly and Faraday detectors enables simultaneous measurement of isotopes with orders of magnitude differences in abundance. The incorporation of multiple Daly detectors enables the simultaneous measurement of multiple low abundance isotopes, in addition to higher abundance isotopes in Faraday detectors. The ability to measure multiple low abundance isotopes facilitates: 1) analysis of smaller sample sizes; 2) more precise measurement and, therefore, correction of isobaric interferences; 3) use of less spike and better spike to sample isotope ratios; and 4) laser ablation isotope analyses of lower concentration elements.

The Jackson School of Geosciences at The University of Texas at Austin has one of the first Nu Plasma 3D MC-ICP-MS with 6 Dalys and 16 Faradays. The collector housing is custom designed to facilitate use of multiple Dalys in Pb and Li isotopic analyses, U-Th geochronology, and simultaneous measurement of U and Pb. We are currently developing analytical techniques for low abundance Pb and Li isotope measurements by solution for analysis of mineral grains in sample-limited xenoliths and meteorites. For many of these samples, we anticipate using laser ablation (LA) to analyse Pb and Li isotopes using Daly detectors. Greater sensitivity enabled by multi-Daly analysis may allow some samples to be analysed, in-house, by LA-MC-ICP-MS, rather than, externally, by more complicated secondary ion mass spectrometry (SIMS). For U-Th geochronology, better ^{229}Th (spike)/^{230}Th (sample) ratios can be achieved by measuring both masses in Daly detectors, rather than one Daly and one Faraday, and the large dynamic range of the Daly detectors allows measurement of the ^{232}Th signal, whose intensity can vary greatly from one sample to another.

In this presentation, we will describe the current state of our progress in developing isotopic analytical techniques employing multiple high-sensitivity Daly detectors.

Simultaneous *In situ* Analysis of Sm-Nd isotopes and Trace Elements in Scheelite by Laser Ablation Split Stream ICP-MS: Challenges and Emerging Approaches

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Scheelite ($CaWO_4$) is a widespread accessory mineral in skarns, aplite and pegmatite dikes, metamorphic stratabound and hydrothermal vein ore deposits. [1] It is a principle ore of W and has potential to be an important indicator that constrains the age of gold mineralization, ore genesis and the pathways of mineralizing fluids. [2, 3]

In situ LA-MC-ICP-MS has been used as a powerful tool for a variety of a LREE-rich accessory minerals (titanite, monazite, apatite and allanite etc) as an isotopic tracer to investigate grain scale Nd isotope heterogeneities and date their formation [4]. However, scheelite remains one of the least studied minerals for testing in situ Sm-Nd isotopic systematics because of the relatively lower mass fractions of Sm and Nd, and the lack of good scheelite reference materials. Due to the complex elemental zonation often present in scheelite, simultaneous *in-situ* and Sm-Nd isotope and trace element analyses in the same growth zone is greatly preferable but rarely reported in the current literature. This study attempts to develop protocols for simultaneous in situ analysis of scheelite for Sm-Nd isotopes (Nd>150 ppm) and trace elements using the Laser Ablation Split Stream (LASS) method. The experiments were carried out using a RESOlution M-50 (Resonetics) 193 nm ArF Excimer (CompexPro 102, Coherent) laser ablation system coupled to a Thermo Element XR2 ICP-MS and a Thermo Neptune Plus MC-ICPMS in the Arctic Resources laboratory at the University of Alberta. Using a fluence of ~5 J/cm^2 and a 193 µm spot at 7 Hz we were able to obtain less than 1.5 epsilon unit precision for $^{143}Nd/^{144}Nd$ at ~300 ug/g Nd in scheelite samples. The analytical challenges and emerging approaches will be addressed in a few aspects: (1) the effect enhancing Nd signals by adjusting the relative proportion of sample aerosol in each of the split streams; (2) the sample matrix effect on Sm-Nd by calibration against a titanite standard (Bear Lake) and apatite standard (Bancroft), and comparing results to in-house scheelite reference material analyzed by ID-TIMS; (3) dealing with scheelite with elevated Sm/Nd ratios. We also evaluate the data quality for split stream vs. single stream ablation. We will present an example of an in situ Sm-Nd isochron for scheelite, which illustrates its potential as a gechronometer, and discuss the trace element diversity in this mineral.

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U-Pb dating of Paleoproterozoic travertine using LA-Q-ICP-MS and LA-SF-ICP-MS

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Calcite is a common mineral in sedimentary rocks that often forms along vein and fracture systems during low-temperature fluid movements. Despite its typically very low U content, calcite has become an important U-Pb geochronometer for dating fluid movements in sedimentary basins and along fault structures. At the Geological Survey of Canada, the technique has also been used to date gold mineralization in a Carlin-type deposit, Yukon, Canada.

Here we report U-Pb age data for a ca. 1.8 Ga travertine (a form of limestone deposited by mineral springs) sample (z5601) from the Baker Lake region, Nunavut, Canada, with the purpose of characterizing this sample as an in-house reference material for calcite dating studies. U-Pb data were acquired using a Photon Machines Analyte G2 laser coupled to an Agilent 7700x ICP-MS. Laser ablation conditions were varied throughout the analytical sessions, including spot diameters of 160 and 216 µm, a fluence of ~5-6 J/cm^2, repetition rates of 10 and 12 Hz and addition of 1.2 mL/min of N_2 to the carrier gas stream (160 µm session only). Using this instrument setup, the sensitivity of ^{238}U in NIST-614 ranged from 85,200 cps/ppm to 109,000 cps/ppm. For data calibration, NIST-614 was used to correct for instrument drift and to calculate ^{207}Pb/^{206}Pb in the calcite reference materials and unknowns. Utilizing the x-intercept correction method, ^{238}U/^{206}Pb were calibrated using a matrix-matched calcite reference material, WC-1 (254 Ma). Throughout five analytical sessions, the calculated age of z5601 varied between 1729 ± 37 and 1791 ± 43 Ma (2σ), comparable to the published TIMS age of ca. 1785 ± 3 Ma.

LA-ICP-MS mapping of the travertine sample (using a 10 µm spot) reveals complex elemental zoning, including 10x higher U in optically darker bands of the sample (~ 10 ppm in dark bands and ~ 1 ppm in light bands). Within the high U bands, micro-clusters (commonly only 50-150 µm in diameter) of high U and Pb (with up to ~ 96 ppm U) occur within the interior of individual calcite crystals.

In order to target these high U zones with higher spatial accuracy, while maintaining adequate sensitivity, U-Pb age measurements were also conducted using an Element XR SF-ICP-MS. Utilizing a 110 µm spot and similar laser conditions to the settings outlined above, the sensitivity of ^{238}U in NIST-614 was 147,400 cps/ppm. By extrapolation, this equates to a sensitivity increase of ~ 7x compared to the U-Pb measurements made using the Agilent 7700x ICP-MS. While both instrument configurations are fully capable of undertaking U-Pb dating of calcite, our results indicate that SF-ICP-MS is ideally suited to complex carbonate samples where high spatial resolution is required.

In situ U-Pb geochronology of simple and complex oxides

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The goal of this study is to gauge the feasibility of 193nm LA-ICPMS geochronology of simple and complex oxides that can occur in peralkaline igneous rocks, Sn-W granites, evolved LCT and NYF pegmatites, kimberlites, uranium deposits, and carbonatites. Although zircon, monazite, and apatite can occur in these rocks facilitating more routine dating methods, these accessory phases are often xenocrystic or altered by late-stage magmatic-hydrothermal fluids. In such cases alternative mineral groups such as U-bearing oxides might be targeted and unambiguously related to crystallization from fractionated late-stage liquids or hydrothermal fluids. These include the pyrochlore group, uraninite, fergusonite, euxenite, zirconolite, columbite-group-minerals (CGM), and cassiterite. These minerals are normally considered 'leaky' to Pb-loss owing to high actinide concentrations and, thus, high amorphous fractions. Details of their isotopic robustness are, however, generally lacking. Our approach has been to empirically test these minerals for isotopic homogeneity and robustness. Candidate minerals drawn from archival collections are mounted and polished and subjected to compositional mapping by micro-XRF and SEM-BSE imaging. The time-dependent behavior during ablation at different laser fluence and pulse rate is assessed, as is common-Pb content and optimal crater sizes for intrinsic U and Th concentrations and age. Once these conditions are established, the material is 'dated' using NIST610 glass as an external standard. This step establishes whether the material is isotopically homogeneous. In some cases (e.g., uraninite, fergusonite, CGM) standardization against NIST610 yields concordant data within error of the assumed age of the material. Minerals with high and variable common-Pb such as cassiterite define inverse-concordia arrays with lower and upper intercepts that overlap the known age and common-Pb composition of the material respectively. Demonstrating primary external standardization using NIST610 relieves us of finding an additional natural material to act as a secondary standard. The results so far emphasize that each mineral has a unique set of ablation conditions and tuning parameters (e.g. gas flows) that yields useable U-Pb data. We also believe that routine U-Pb LA-ICPMS geochronology of these phases is possible once a set of well-characterized mineral standards has been established.

Dating exhumation and fluid-fault interactions in fault systems using apatite U-Pb and trace element LA-ICP-MS analysis

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Apatite U-Pb depth-profiling and trace and rare earth element (TREE) LA-ICP-MS analyses in combination with detailed imaging have the power to recover the spatial age and chemical information that reveal the thermal history and fluid-rock interactions along crustal-scale faults in of the middle and lower crust, and to distinguish between different thermal scenarios and isotopic/elemental resetting mechanisms. These scenarios include diffusive processes during rapid or slow monotonic cooling, protracted residence in the partial retention zone, or reheating and complex growth or recrystallization during metamorphism or deformation. Detailed apatite depth profiling LA-ICP-MS U-Pb analysis allows the recovery of spatial age profiles and evaluate the topology in terms of diffusive loss or non-Fickian processes with sub-micron resolution and recover quantitative thermal history information. Distinguishing between these is critical for interpreting apatite U-Pb ages and geologic and tectonic histories. This study presents a detailed workflow for apatite U-Pb depth-profile LA-ICP-MS analysis to understand U-Pb age topology, microtextural analysis by cathodolumiescence, TREE analysis, and data intepreation from two significantly different tectonic settings. Unpolished apatite grains were tape-mounted and depth-profiled with an excimer laser using a 40µm spot at 4mJ for 30sec. Data were corrected for depth-dependent and elemental fractionation. Integrated bulk apatite ages were used to constrain both upper and lower Tera-Wasserburg concordia intercepts to determine Pb_c composition and bulk age. Subsequently, U-Pb ages were calculated for individual 3-sec (~2µm) depth intervals using a ^{207}Pb correction. Depth-profiled, Pb_c-corrected increment ages were plotted as apatite U-Pb age spectra (age vs. depth) and categorized according to age topologies. Selected apatite grains with representative U-Pb age profiles were flipped 90°, embedded in epoxy, polished to expose grain-internal sections, and imaged by cathodoluminescene scanning electron microscope (CL-SEM) to reveal zoning, deformation (e.g. fracturing, crack and seal), or growth/recrystallization microtextures. Apatite grains were then analyzed by LA-ICP-MS for TREE to understand the petrologic conditions of growth and recrystallization during deformation and fluid-rock interactions. This methodology was applied and tested on mid- to lower-crustal granulitic basement rocks in the Pyrenees, France and exhumed subduction zone rocks in the Cyclades, Greece. Results demonstrate the power of this intergrated approach of U-Pb geochronology and TREE analysis by LA-ICP-MS coupled with microtextural analysis in distinguishing between processes affecting apatite U-Pb ages, directly dating deforamtion near the brittle-ductile transistion, and providing ages and constraints on the petrologic and geochemical conditions of (re)crystallization and fluid-rock interaction at middle to lower crustal depth.

Eliminating U-Pb 'Downhole' Elemental Fractionation and Achieving Nanometer (nm) depth resolution in zircon by low volume single-shot LA-ICP-MS.

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The interaction between incident laser radiation and sample substrate is difficult to predict. Natural zircon is often both structurally and chemically heterogeneous in 3-dimensional space. Encountering growth-related structural micro-heterogeneities, inclusions and chemical complexities, is almost inevitable during a static ablation of several tens of seconds. A single-shot approach to laser ablation implements a minimal sample exposure time to incident laser radiation for each integration; thus, reducing sample consumption, the probability of thermally induced effects (e.g. substrate melting), and the potential for signal mixing with depth.

Single-shot laser ablation analyses were conducted using a Nu Instruments Attom HR-ICP-MS coupled to a UP213 laser ablation system, a set-up requiring no modification of existing instrumentation or specialised equipment (e.g. low volume sample cell). The acquired data, are processed using NuQuant software, which integrates and collates short-lived signal peaks produced by multiple (x30) individual laser shots, as opposed to the broad signal peak produced by a continuously pulsing laser. This analytical protocol routinely produces age determinations reproducible to <1% (2s) on a small sample volume (~1530 μm^3) with a 40μm diameter spot. The single-shot laser ablation protocol employed here effectively eliminates 'downhole' fractionation as the resultant pit depths are shallow (average of ~1.2 μm) and maintain an aspect ratio of <<1. Pit depths of this magnitude are equivalent if not shallower than those produced during conventional SIMS analysis, and the iterative integration of each laser shot allows for depth resolution on the order of ~40nm $pulse^{-1}$. The single-shot method outlined here is validated with results obtained on zircon standards and samples dated using benchmark ID-TIMS. Calculated ages are associated with external reproducibilities (for 91500) of 6% and 8% (2SD) for the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ratios, respectively.

U-Pb, trace element, and hafnium isotope composition of the Maniitsoq zircon: A potential new Archean zircon reference material

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The U-Pb, trace element, and Hf isotope composition of zircon megacrysts from a late magmatic vein related to Mesoarchean gabbronorite from the Maniitsoq region of West Greenland have been extensively characterized by LA-ICPMS and TIMS analysis. The crystals are typically euhedral, 1-5 mm in diameter, and exhibit heterogeneous internal zoning, cut locally by thin, CL-bright veinlets. Chemical abrasion ID-TIMS U-Pb analysis of three fragments yield uniform, concordant results and a ^{207}Pb/^{206}Pb weighted average age of 3008.70 ± 0.72 Ma (MSWD = 0.9). LASS-MC-ICPMS U-Pb analyses, normalized to OGC zircon, exhibit slight normal discordance, with <2% discordant spots yielding an identical ^{207}Pb/^{206}Pb weighted average age of 3008.8 ± 2.2 Ma (n = 94; MSWD = 0.36). Uranium and Th concentrations average 141 ± 39 and 154 ± 77 ppm, respectively, with Th/U = 1.07. REE compositions are relatively uniform, with average total REE = 602 ± 186 ppm, positive Ce-anomaly (Ce/Ce* = 142) and negative Eu-anomaly (Eu/Eu* = 0.16), and moderate HREE enrichment (Yb/Gd = 5.6). Hf concentrations are moderate, averaging 10849 ± 630 ppm, with ^{176}Yb/^{177}Hf (0.015 ± 0.006) and ^{176}Lu/^{177}Hf (0.0005 ± 0.0001), close to the average for natural zircon. In comparison with common zircon reference materials, ^{176}Yb/^{177}Hf and ^{176}Lu/^{177}Hf are similar to that of Temora2, and greater than Mud Tank, 91500, and Plesovice zircon, making Maniitsoq well-suited for verifying the ^{176}Yb+Lu interference correction on ^{176}Hf/^{177}Hf. The average interference-corrected ^{176}Hf/^{177}Hf value determined by LASS-MC-ICPMS is 0.280862 ± 21, with an age-corrected ^{176}Hf/^{177}Hf$_i$ value of 0.280833 ± 20, corresponding to a slightly negative average εHf value of -0.38 ± 0.70. The large crystal size, abundance, and largely homogeneous chemical and isotopic composition of the Maniitsoq zircon makes it a useful reference material for verifying the accuracy of U-Pb, trace element, and Hf isotope analyses by LA-ICPMS. Further characterization is in progress, and crystals will be distributed by the first author upon request.

Reconstructing paleo-hydrologic history with LA-ICPMS U-Pb dating and trace element analyses on agates

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Subsurface fluid systems are important for chemical weathering, ore formation and thermal evolution of the crust. Changes in the dynamics of distribution of subsurface fluid flow systems are controlled by changes in global and regional terrestrial climate, tectonic, and elevation. However, direct dating of water-rock interaction is challenging because of the lack of appropriate materials to date and the more open and complex behaviors of subsurface flow regimes. Here, we explore the prospects of using U-Pb dating of petrified (silicified) wood as means of quantifying ancient continental hydrology. Oxidizing fluids, often of meteoric origin, tend to leach and mobilize U from the country rock, but when such waters contact organic-rich material, U can become reduced and immobilized, resulting in U-rich silicified wood. We present in situ laser ablation ICPMS analyses of U-Pb isotopes and trace elements in petrified wood from the Upper Triassic Chinle Formation (225-208 Myr) in the Petrified Forest National Park in Arizona (USA), establishing a generalized workflow for making meaningful paleo-hydrologic interpretations of the U-Pb systematics of silicified wood. Wood characterized by brownish colors and preservation of cellular structure have low Fe contents and positive Ce anomalies, indicating silicification in reducing environments and isolation in relatively reduced conditions since silicification, resulting in closed system behavior of U and Pb. Woods characterized by vivid colors (orange, red, etc.) and little to no preservation of cellular structure are much higher in Fe and exhibit negative Ce anomalies, indicating influence by more oxidized fluid flows. The brownish samples yield U-Pb ages clustered between 250-200 Ma with a peak coinciding with the time of deposition (~220 Ma), which indicates that fossilization largely takes place almost immediately after deposition and that U-Pb in quartz faithfully retains the time of such fossilization. In contrast, the orangish-reddish-whitish samples yield younger U-Pb ages, defining distinct errorchron peaks, which reflect subsequent generations of quartz crystallization. Distinct younger age peaks appear to correlate with the timing of regional unconformities associated with tectonic or epeirogenic uplift. We suggest that uplift and exhumation may initiate the onset of oxidizing fluid systems, resulting in leaching and transport of U from the surroundings, followed by subsequent generations of quartz precipitation. In summary, U-Pb dating of petrified wood, or silicified organic material, have high potential for dating paleo-hydrologic events. However, due to complexities in terrestrial hydrologic systems, interpretations of U-Pb systematics must be informed by accompanying geochemical and textural observations.

Chemical Analysis using Tandem LIBS and LA-ICP-MS/OES

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Bulk and micro analysis especially mapping heterogeneities and species distribution within solid samples is critical for understanding materials behavior, transport, and migration processes within those samples. Some of the most common examples are studies of corrosion on metals alloys, metal distribution inside plastics, distribution of species within rocks, and elemental distribution within biological tissues, etc. For analysis of lateral and depth heterogeneities, laser ablation with a combination of LAICP-MS, LAICPOES, and LIBS offers the ability to measure every element/isotope with high spatial resolution. In this presentation, Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS/-OES) is used simultaneously chemically analyzed and spatially resolved mapping of major and trace elements and isotopes for a wide range of sample matrices. The combination of the two techniques provides complementary measurements for elements that are separately unattainable due to low sensitivity and strong interferences. Two-dimensional (2D) layer-by-layer mapping, 2D cross-sectional imaging and three-dimensional (3D) volume rendering of elements and isotopes from these samples are presented. These results pave the way for improved bulk analysis and 3D elemental imaging through simultaneously acquired LIBS and LA-ICP-MS measurements.

Measurements of redox-sensitive trace elements in individual fluid inclusions in halite – a record of paleoseawater redox conditions?

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Oceanic Anoxic Events (OAE) were partially responsible for mass extinction events during Earth's history, and are therefore a phenomenon of major geologic significance. Minor and trace elements that show variations of valence state, solubility and isotope fractionation as a function of redox conditions are extensively used as paleo-redox proxies for seawater by the scientific community studying OAEs. The concentrations of trace elements in sedimentary rocks, however, are indirect indicators of the redox state of seawater and can be subject to changes due to post-depositional remobilization during diagenesis. Analysis of primary fluid inclusions trapped in evaporite minerals that precipitate from evaporating seawater can provide direct information about the chemical composition of seawater and have been used to document changes in major ion concentration of paleo-seawater during the Phanerozoic. Our goal in this study is to explore the potential for redox-sensitive trace elements in primary fluid inclusions in halite to provide direct information about the redox state of seawater.

In this study, we develop a methodology to quantify minor and trace elements (Rb, Sr, Mo, Ba, Li, B, V, U, Fe, Mn, Cu) and their ratios in seawater based on LA-ICP-MS analysis of individual fluid inclusions in primary marine halites, and evaluate whether the element ratios may be related to redox conditions. Preliminary measurements of fluid inclusions in laboratory-grown halite crystals using LA-ICP-MS were able to reproduce concentrations reported for corresponding seawater samples for most of these minor and trace elements.

In order to test our hypothesis, we studied natural samples from the Late Permian Zechstein Evaporite Formation from Poland. Previous study of fluid inclusion samples from this formation suggests that the major ion chemistry of the seawater changed from sulfate-rich brines, similar in composition to modern evaporated seawater, to sulfate-depleted (calcium-rich) brines during the latest Permian (Garcia-Veigas et al., 2011). This change was interpreted to be the result of overturn of anoxic sulfidic deep-waters from the Panthalassa stratified superocean coinciding in time with the Permian–Triassic mass extinction event. In this study, we compare ratios of redox-sensitive trace elements that show different solubilities as a function redox state of the water to observe changes in redox conditions troughout the studied section. For instance, iron is more soluble in its reduced Fe^{2+} (ferrous) form than in its oxidized Fe^{3+} (ferric) form, while uranium shows the opposite behavior.

Data from individual fluid inclusions in Zechstein halite show significantly higher ratios of Fe/U, Mn/U, Fe/V, Mn/V, Fe/Mo and Mn/Mo in halite samples with sulfate-depleted (calcium-rich) brines compared to samples with sulfate-rich brines, which supports the previous interpretation of a transition from relatively oxic (sulfate rich) to anoxic (sulfate-depleted) conditions. At the top of the section where the major ion chemistry returns to sulfate-rich brines, we observe increasing ratios against Mn, while ratios against Fe stay relatively constant. This may be explained by a gradual shift to relatively more reducing water compositions within the redox range where iron is still sequestered in a solid phase as ferric iron (Fe^{3+}).

Leveraging the low-dispersion COBALT/ARIS ablation system for multi-megapixel 3D images of single cells.

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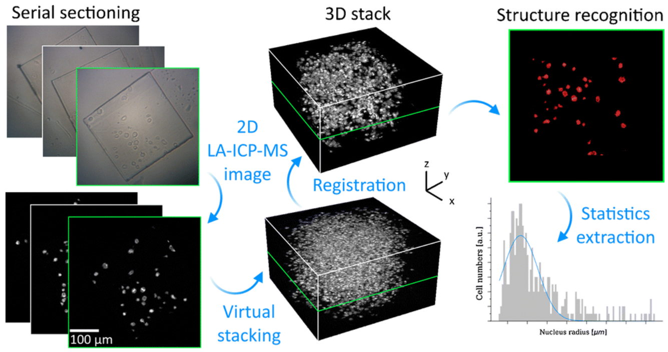
The Atomic & Mass Spectrometry (A&MS) Research Unit at Ghent University, Belgium, has, through funding of the Research Foundation – Flanders (FWO), invested in the development of a low-dispersion high-throughput LA-ICP-MS ablation system, consisting of the COBALT ablation chamber and the ARIS laminar flow aerosol transport system, which permits visualization of the distribution of endogenous trace elements and bioconjugated metal tags (e.g., secondary antibodies labelled with lanthanides) at the sub-cellular level. One of the limitations of the single-cell LA-ICPMS imaging approaches applied thus far is the limited axial resolution: signals originating from different cell compartments are confounded, as the laser beam penetrates through the entire cell. The discrimination of signals from different cell organelles is highly desirable, as quantification of the metal content of each organelle would provide information to unravel mechanisms behind metal transport through the cell. In this talk a methodology is presented towards the reconstruction of the 3D elemental distribution profile within human cervical carcinoma cells (HeLa), at a spatial resolution down to 1 µm. The suspended cells underwent a series of fixation/embedding protocols, and were stained with uranyl acetate and an Ir-based DNA-intercalator. A priori, laboratory-based absorption micro-computed tomography (µ-CT) was applied to acquire a reference frame of the spatial distribution of cells and their morphology before sectioning. After CT-analysis, a trimmed 300×300×300 μm^3 block was sectioned into a sequential series of 132 sections with a 2 µm thickness and subjected to LA-ICP-MS imaging. A pixel acquisition rate of 250 pixels s^{-1} was achieved through a bidirectional scanning strategy. The volume was reconstructed using multiple registration approaches. The reconstructed volume encompasses data from 29 million spatial positions, which is, to our knowledge, the largest amount of sampling positions ever recorded for a single dataset in this field. Registration using the section outline itself as a fiducial marker resulted into a volume, which was in good agreement with the morphology visualized in the µ-CT volume. Hence, the 3D µ-CT volume could be registered to the LA-ICP-MS volume, yet, the µ-CT dataset is no longer required in the approach presented here to correctly reconstruct the volume. The average distance from the centre to the surface of the nucleus could be calculated from a density histogram build using cell recognition software; a distance of 6.7±1.7 µm was found to be within the expected range based on existing literature. These findings open the pathway to routine 3D single-cell imaging using LA-ICP-MS.



London Metallomics Facility: An Emerging Scientific Platform for Multidimensional Metallomics

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Metallomics takes an integrated approach to understand the metallobiochemistry of cells and organisms in health and disease, utilising analytical tools to decipher the biological roles of metals in both space and time. Identification of characteristic metal profiles within the life span of individual cells and tissues, in vitro and in vivo, has significant value for fundamental scientific questions relating to determination of cell fate and health, trace element metabolism, and for translational science in diagnosis, prognosis, and therapy in a range of human diseases including cancer, neurodegeneration and metabolic diseases. Just as metabolomics is a rapidly growing field explored by molecular mass spectrometry, metallomics is an emerging field explored by elemental mass spectrometry and other techniques. Laser ablation ICP-MS has developed into a cornerstone metallomic bioimaging technique as a result of several key advances in both hardware and software. The development of fast washout technology (Teledyne CETAC ARIS and Cobalt Ablation Cell) coupled with powerful image generation software capable of quantitative analytics (HDIP) now opens the potential for higher throughput applications in academic, clinical, and industrial fields. The London Metallomics Facility (LMF) is a new Wellcome Trust and King's College London supported core facility, whose aim is to be a centralised hub for comprehensive multi-institutional integration of state-of-the-art metallomic analytics and correlative bioimaging, establishing direct interaction between leading research groups, commercial partners, and industry, whilst driving educational outreach and public engagement strategies. Current instrumental analytical techniques include ICP-MS, LC-ICP-MS, LA-ICP-MS/MS, TXRF, Oxygen Ion Plasma SIMS, and microwave sample digestion for high-throughput applications. With its links to the School of Biomedical Engineering and Imaging Sciences at King's, it also has access to a range of radionuclides of trace metals suitable for radiotracer imaging studies and PET metallomics in vivo, in animals and humans. This presentation will focus on recent analytical developments within the LMF, specifically illustrating the application of laser ablation ICP-MS and highlighting recent bioimaging work conducted using the Analyte Excite 193 Excimer laser and HDIP software within the context of metals in human health and disease.

Evaluating the accumulation of toxic and nutrient elements in rice grains using 3D bioimaging by means of laser ablation ICP-MS

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Rice is one of the most consumed grains and is a large part of the diet in many countries. It is grown under flooded conditions and it absorbs both nutrient and toxic elements that have been mobilized from the soil. The rice grain is composed from an outer bran layer which surrounds the endosperm and embryo. The concentrations of trace elements vary greatly between the different parts of the grain. Recent advances in LA-ICP-MS have resulted in the development of rapid elemental imaging, allowing for the generation of 3D images in a reasonable amount of time. For this work, rice grains were embedded in epoxy and a series of cross-sections were prepared using a microtome. Each section was mapped using LA-ICP-MS to produce images of toxic and nutrient elements, including As, P, K, Fe, Cu and Zn. Following image registration, a 3D volume reconstruct was generated for each element. The calibration was performed using a rice flour reference material in the form of pressed pellets. Nutrient elements, such as P, K and Fe, were present at higher concentrations in the bran layer and in the embryo, while Cu and Zn were also accumulated in the endosperm. Arsenic was mainly absorbed in the bran layer, but also present in the outer layers of the endosperm.

Evaluation of the state-of-the-art LA-ICP-(q)MS systems for elemental imaging of decorative glass object

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In this contribution we present elemental images of highly decorated glass artefact – murina glass piece – that was imaged at three LA-ICP-(q)MS setups, featuring different state-of-the-art cells and aerosol delivery systems (HelEx, HelEx with ARIS, Cobalt with tube cell) interfaced to the same (q)ICP-MS instrument. Murina glass piece was used as model sample in this work, as it features highly detailed surface elemental distributions. The sample itself can be used numerous times due to the fact that the decoration pattern is not changed after subsequent grinding/polishing.

Experimental conditions for the systems were used under the assumption of the "best possible image quality" for specific setup. With this starting condition, we evaluated different modes of operation, e.g., continuous vs. single shot, different number of overlaps/dosages, different laser beam sizes, element contents (concentration), and number of elements measured in one run. The resulting elemental images will be analyzed for the image quality, (noise, contrast, resolution) and total analysis time. Considerations for most efficient use of elemental imaging with these setups will be also discussed.

POSTER ABSTRACTS BY TOPIC

BIO APPLICATIONS

Discriminating between groups of farmed Atlantic salmon by LA-ICP-MS analysis of scales

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In 2017, the produced quantity of farmed Atlantic salmon was 1.2 million tons in Norway alone, making up 57% of the global production. Farmed Atlantic salmon escapees have become an ecological problem by competing with the wild population for food and breeding ground. Recently, the Norwegian salmon industry has developed a tracking system for escaped fish involving element profiles in salmon scales.

As scales develop, elements from the surrounding environment are incorporated in the outer hydroxyapatite layer. This outer layer grows like the trunk of a tree, with rings that create a timeline of exposure to different water environments, like the transition from fresh water to seawater.

In this study we used different patterns and parameters for laser ablation to discriminate between groups of farmed salmon and track a simulated escape. We ablated several parts of the scale for information about different stages in the life of the salmon. Solid line patterns were ablated along specific circuli of the scale in the fresh water and seawater regions. To pinpoint the exact circulus to be ablated, a line of spots pattern from the center towards the edge of the scale was first used to determine the area for transition from fresh to seawater. A solid line pattern from the center to the edge of the scale included element concentrations from both regions.

We analyzed for 14 different elements to make profiles from the different ablation regions for the fish groups and the simulated escapees. Combined, these three profiles have been successfully used to discriminate between groups and track simulated escaped salmon back to the farm and net from which they escaped.

Using trace element ratios to track lifetime freshwater exposure in bottlenose dolphins (*Tursiops truncatus*)

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Prolonged freshwater exposure can have harmful effects on bottlenose dolphins (*Tursiops truncatus*), ranging from skin lesions and electrolyte abnormalities to organ failure and death. Determining if a dolphin has been exposed to freshwater for prolonged periods of time can be difficult without costly and labor-intensive direct observation. We tested the feasibility of reconstructing long-term freshwater exposure in bottlenose dolphins using trace element ratios in teeth, which are comprised of annual growth layer groups (GLGs) that assimilate elements reflective of environmental conditions throughout life. As a first step to test this approach, we collected a tooth from a dolphin carcass that stranded in Alabama in 2016 and had a known history of freshwater exposure. Our results show that there were differences in elemental composition between enamel and lifetime GLGs. Ontogenetic shifts were seen in some elemental ratios (Zn:Ca, Ba:Ca, Pb:Ca) between prenatal and postnatal GLGs, including interannual variation (spikes in Ba:Ca) in postnatal GLGs consistent with seasonal freshwater inputs to the system. Zn:Ca and Ba:Ca were tightly coupled in postnatal dentin while Pb:Ca and Ba:Ca showed similar trends throughout development. These data suggest Alabama resident bottlenose dolphins experience interannual variation in environmental conditions, particularly seasonal pulses of low-salinity that are traceable using elemental ratios in teeth. These results support the potential for trace elements in teeth to be used for assessment and historical tracing of habitat variation, including freshwater and associated contaminant exposure in bottlenose dolphins throughout their lifetime. In the future, teeth will be collected from Alabama dolphin carcasses that span multiple size- and age-classes to determine ontogenetic changes and habitat differences within this freshwater-dominated system.

Strontium Isotope Ratio determination using Laser Ablation Triple Quadrupole ICP-MS (LA-QQQ-ICP-MS)

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Preliminary results for Sr isotope ratios in anthropological samples were obtained by laser ablation – triple quadrupole inductively coupled plasma mass spectrometry (LA-QQQ-ICP-MS). Published values on commercially available reference materials were measured for their Sr isotope ratios. Modern bone and tooth matrices were analyzed to evaluate a matrix relationship and potentially show any detectable variation. The common isobaric interferences from 87Rb and associated polyatomic interferences on 87Sr and 86Sr were mitigated by the tripe quadrupole ICP-MS system utilizing a collision reaction cell in either "on-mass" or "mass-shift" mode. The precision and repeatability were determined for several lateral and longitudinal sections of bone and teeth.

A new high speed data collection system for multi-collector ICP-MS suitable for imaging biological samples by laser ablation ICP-MS with a very fast response sample cell

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Use of laser ablation and ICP-MS for elemental imaging of samples is a rapidly evolving technique. For some years commercially available laser ablation cells have produced single shot signal durations of less than half a second and the latest designs can now achieve routine durations of 10-30ms, depending on the matrix. Although most imaging work has concentrated on elemental mapping, in certain applications it is important to monitor the isotope ratios of a particular element. The highest precision isotope ratios are obtained with multi-collector ICP-MS, which typically uses an array of faraday or ion counting detectors. The standard minimum acquisition time for multi-collector ICP-MS is 100ms, which is limited by the response times of the faraday data collection electronics.

A new design of electronics is tested here whereby the data from multiple ion counting detectors can be collected simultaneously in as little as 10µs on all channels. This speed of data collection more closely matches the latest design of laser ablation cells and also permits more precise correction for dead-time, critical when considering the noisy signals derived from laser ablation. This work will demonstrate the operation of the fast data collection system, the artefacts that can be seen in the signals from the laser shots and the importance of the data processing technique in obtaining accurate and precise isotope ratios. This new technique opens up many possibilities for tracer studies in the field of biological research and examples of relevant applications will be used to demonstrate the feasibility of future studies.

The technique has been utilised to image two biological tissue types. The first example involved ablation of 5 µm thick sections of retina tissue. Retina samples were taken from a study on Long Evans rats that had received Zn supplementation through their drinking water over a period of 8 months. The second example involved the ablation of platinum in an in vitro model of platinum-drug response. These samples are important in the context of age related macular degeneration and cancer research respectively.

Trace Metals to Trace Movements: quantifying variation in the life history of Longfin Smelt

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The Longfin Smelt (*Spirinchus thaleichthys*) is an iconic sea-going forage fish that once thrived in the San Francisco Bay Estuary, California. In the last 50 years, the population has crashed to less than 1% of historic levels, suggesting the ecosystem has become unsuitable for this native species; however, little is known about the habitat characteristics required for successful spawning and rearing. We are using laser ablation IC-PMS line scans in otoliths (ear bones) to acquire continuous, life-long records of multiple geochemical tracers for individual fish. By combining mutliple chemistry profiles with microstructure analyses and time-series statistics, we aim to quantify patterns and variation in the life-history strategies of Longfin Smelt. Strontium isotopes can be used to reconstruct detailed movements within low salinity environments, oxygen isotopes enable us to reconstruct movements throughout higher-salinity regions of the bay and ocean, and multivariate trace element fingerprinting allows us to identify previous natal rearing habitats. We have validated otolith aging and growth reconstructions and are currently validating the temporal resolution of our geochemical techniques using manipulative experiments at the UC Davis Fish Conservation and Culture Lab. Results of this work could transform our understanding of the habitat requirements and population dynamics of this threatened species, thus enhancing the effectiveness of future management and conservation efforts.

Trace elements accrued in endangered freshwater bivalves in two North Carolina stream

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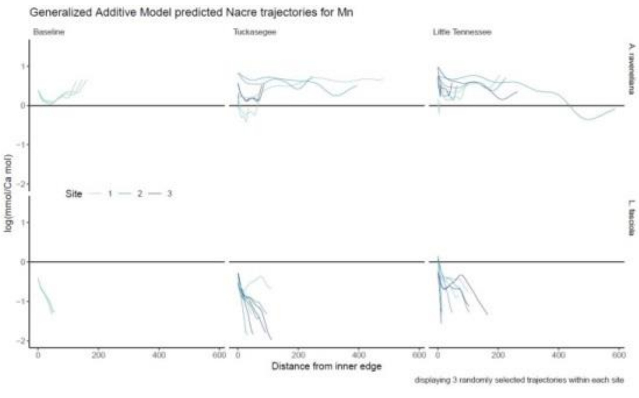
Precipitous declines in the Federally endangered Appalachian Elktoe (*Alasmidonta raveneliana*) have been observed since 2004 in the Little Tennessee River, but populations appear stable in the Tuckasegee River. To assess river-specific factors associated with health and physiological outcomes, we conducted a completely randomized experiment, assigning specimens to sites within each river. Here, we examine differences between sites in trace element concentrations accumulated in specimens' valves.

Eighty-two *A. raveneliana* were collected from a healthy population in the Tuckasegee River. For comparison, an equal number of hatchery-raised Wavy-Rayed Lampmussel (*Lampsilis fasciola)* were included. For each species, ten specimens were held out for baseline comparisons, and the remaining were equally allocated to three sites in each river. After follow-up, one valve of each specimen was cut and blocked in epoxy using standard techniques. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) transects that crossed the region of most recent growth within the nacre (innermost layer) were used for statistical comparisons. For each element, we tested the hypothesis that log(conc mol/ Ca mmol) trajectories within the nacre did not differ between any of the sites. Inference was drawn using the randomization distribution and a test statistic of the deviance between two nested Generalized Additive Mixed Models (GAMM): one including terms for experimental sites and one without.

Preliminary results revealed differences in nacre elemental trajectories of the experimental sites. In *A. raveneliana*, for example, trajectories of Mn differ in at least one experimental site (p-value = 0.002). Visual examination of the predicted values from a GAMM model show systematically higher levels in the region of most recent growth in Little Tennessee specimens. Results for the comparatively younger *L. fasciola* specimens show a similar though not as obvious pattern (p-value = 0.054).

Our analysis showed differences between the experimental sites in Mn concentrations accumulated during the study period. Manganese is an essential trace element with important roles in numerous enzymatic pathways that could have harmful effects on freshwater bivalves. The completely randomized design allows for robust, internally valid inference; however, further analyses with these data are needed to: 1) Examine other observed differences in elemental concentrations; 2) Rule out possible confounding such as seasonal and batch effects; and 3) Explore sources of these elements within the watersheds.



Rapid elemental screening in food using automated laser ablation sampling

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The U.S. Food and Drug Administration is tasked with ensuring the safety of the American food supply and monitors essential, non-essential, and potentially toxic elements in a wide variety of foods, and dietary supplements. LA-ICP-MS is an excellent alternative to conventional ICP-MS analysis as it not only eliminates time-consuming microwave assisted digestion techniques, but also provides a path for the analysis matrices that may be resistant to acid digestion such as multivitamins and dietary supplements. However, until recently, the technique lacked automation essential for a high-throughput laboratory. In this paper, we present an implementation of a fully automated laser ablation setup for food analysis. The ESI NWRauto system utilizes a selfseal micro-chamber in combination with a custom carousel. The advantages of the system are that (1) it allows a large number of samples to be analyzed unattended, (2) has an easy to clean micro-chamber and (3) has a small laser window (cost-effective compared to replacing a large format laser chamber window). Infant cereal samples were combined with several internal standards (premixed in a cellulose matrix modifier), pressed using a pellet press, and analyzed by LA-ICP-MS. Elemental quantification was performed using matrix matched standards (rice flour CRMs). This paper will look at the important aspects of the hardware as well as the analytical performance for nutritional and/or harmful elements present in food.

DATA HANDLING

Multivariate statistic treatments of LA-ICP-MS chemical mapping

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The last two decades, LA-ICP-MS emerges as a cost effective and time-efficient technique for quantitative elements distribution on wide range of geological material [1]. Those type of micro-scale mapping may also be considered as a big dataset (often>100ko) able to be statistically analysed and provide insight on numerous geological issue [2].

Although software for concentration maps building are more and more powerful (*e.g.* Iolite 4), statistical treatment are generally done manually with Excel spreadsheets and are very time consuming.

In this context, BRGM has developed an exploratory and predictive multivariate statistical tool able to:

- open a multichannel concentration map from LA-ICP-MS or EPMA analysis and filtered the low (<LOD) or high (inclusion?) concentrations in different ways;
- implement different types of conventional statistical treatment like discriminants diagrams, error ellipse plotting, Agglomerative Hierarchical Clustering (AHC), Principal Component Analysis (PCA), Multidimensional Scaling (MDS) and Linear Discriminant Analysis (LDA)

The complete method has been tested and validated on an already treated dataset of sulphur LA-ICP-MS maps of Algoma-Type BIF gold system [3], the results are in perfect agreement with those obtained through manual Excel Spreadsheet treatment. This approach has also been performed on isolated quartz grains and quartz in thin section, and provide statistical evidences of different mineralising events [2].

In addition to the BRGM capacities to performed LA-ICP-MS mapping on different minerals, this rapid and efficient integrative tool for multivariate statistical treatment(s) leads to raise the level of prospective exploration of elemental coupling/decoupling on geological sample.

[1]Woodhead et al. (2007), *Geostand. Goanalytical Res.*, **31**, 331-343.

[2]Monnier et al. (2018), *Lithos*, 355-377

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LACV: A computer vision approach to laser ablation sequence generation

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Laser ablation ICP-MS (LA-ICP-MS) systems have become fast and reliable to operate such that thousands of traditional spot analyses can be conducted in a single day. Simultaneously, there has been growing interest in 'big data' geoscience and studies that demand a large number of analyses. Therefore, there is the possibility and demand for very high throughput LA-ICP-MS analysis. However, manually setting up thousands of spots on, e.g., detrital zircon grains, can be time consuming such that it might take as long to setup a sequence of spots as it takes to run the analyses.

Here we present a software tool called 'LACV' to automate LA sequence generation to alleviate this bottleneck. The software takes as an input a 'coordinated' image that can be produced by most LA system software, analyzes the image to detect grain boundaries, applies a targeting strategy, and outputs a sequence file that can be imported into the LA system software. Two targeting strategies are implemented at present: core and rim. A range of adjustments are offered to more accurately define grain boundaries. LACV is an open source work in progress. Current source and binary releases can be obtained from https://github.com/japetrus/LACV.

Advances in the LA-ICP-MS U-Pb geochonology of common-Pb rich minerals in kimberlite, e.g., perovskite

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Along with laser ablation U-Pb geochronology of zircon, the in-situ LA-ICPMS technique has seen increased application on other accessory minerals including rutile, titanite, apatite, monazite and perovskite. However, the analyses of many of these accessory minerals possess more challenges because unlike zircon, they often contain significant amounts of common-Pb in their structure. Along with the laser induced Pb-U fractionation, correction for this non-radiogenic Pb induces the largest uncertainty on any resulting radiometric age, quite often expressed by ^{206}Pb/^{238}U ratio (particularly for samples those are Paleozoic or younger). Although common-Pb is generally considered to reflect average Pb isotopic composition of the host rock, it is not always possible to find a suitable syngenetic phase to determine this composition. Thus, the correction is quite often done assuming a common-Pb composition based on a terrestrial Pb evolution model e.g. Stacey and Kramers, 1975. There is no a priori reason to assume that this is correct/accurate.

Common-Pb correction using the ^{207}Pb/^{206}Pb ratio is perhaps a more suitable method for minerals like perovskite, which have low U content and high Th-U ratios. Two main approaches are commonly used for this correction. The first method involves projecting a line through data that are uncorrected for common-Pb, on a Tera-Wasserburg Concordia diagram, where the upper intercept gives the common ^{207}Pb/^{206}Pb composition while the lower intercept gives the age of the mineral without common-Pb. The uncertainty on the final age depends on the spread of the data points and their linearity, plus the disposition of the data relative to the lower intercept, which in turn reflects the fraction of common Pb in each analysis. Because of this, minerals containing a very high proportion of common-Pb (e.g. perovskite from kimberlites) without having enough linear spread in composition, often produce a lower intercept age with an uncertainty up to 20%. An alternative approach is to correct each data point individually for common-Pb (either using the ^{207}Pb/^{206}Pb from Stacey and Kramers, 1975 model or using the upper intercept obtained from the Tera-Wasserburg plot) and then to use the corrected ^{206}Pb/^{238}U ratios to get an age for each analysis and finally calculate a weighted mean to determine the final age. Although individual ages, following this approach, can be quite imprecise (due to the large magnitude of the common Pb correction and sometimes small signals), the apparent precision on the weighted average can be substantially improved (up to ca.10x times) by having a large number of data points (n) included in the weighted mean. Partly for this reason, the weighted average ages have often been preferred for a perovskite population representing the timing of a kimberlite intrusion.

Here we stress that this apparent improvement in precision is simply due to weighted mean statistics by virtue of the large number of data points. This over-precise data from a very high common-Pb rich mineral like perovskite may create undue confidence in a given kimberlite eruption age. Instead, we suggest that the lower intercept age, although less precise than weighted average age, is a better representation of the population. The final age uncertainty in this approach is not dependent on n, rather it is a true reflection of the magnitude of the common-Pb correction and the uncertainty of the upper intercept (the common Pb isotope composition). The final age precision can however be significantly improved if the upper intercept (common ^{207}Pb/^{206}Pb) is determined from a syngenetic phase or if the data points have a large linear spread in Tera-Wasserburg plot. We also suggest that the fraction of common-Pb correction for each data point should be reported as that is directly related to the final uncertainty of the lower intercept age.

EARTH SCIENCE APPLICATIONS

Geochronologic evidence for post-rift tectonic rejuvenation in the northeastern U.S.

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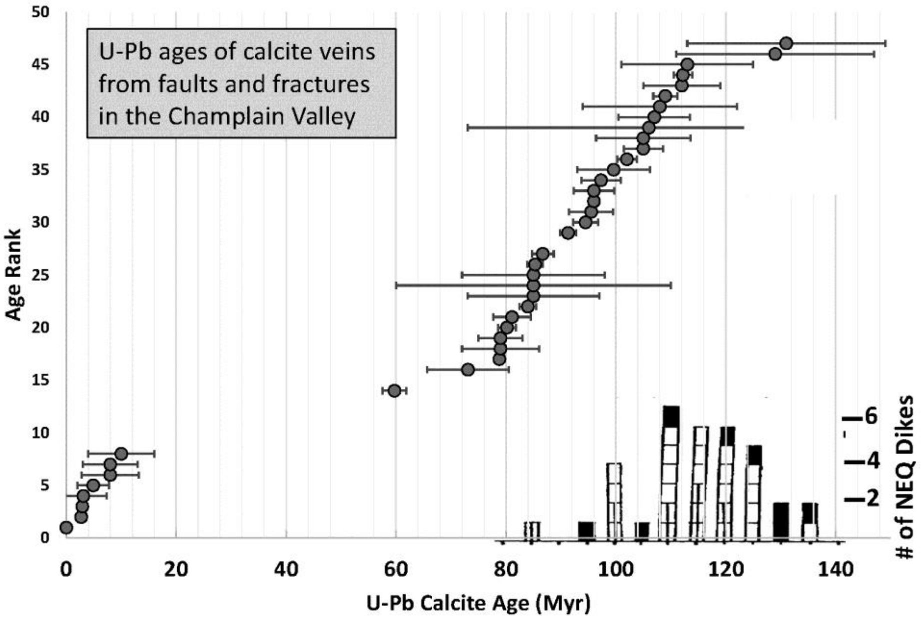
Although post-rift tectonic rejuvenation of Atlantic passive margins is increasingly recognized, driving mechanisms remain poorly understood despite their importance in understanding Cenozoic landscape evolution and offshore sedimentary architecture. This work presents geochronologic evidence that the northeastern US margin has experienced significant tectonic rejuvenation events during the Mid-Cretaceous, Late-Cretaceous, and Miocene periods. Low temperature thermochronology from deep drill cores suggests pulses of exhumation near 125-110 Ma and again at 85-65 Ma, synchronous with pulses of sedimentation to the Atlantic offshore. Additionally, U-Pb ages and trace-element mapping of vein calcite from faults and fractures in the Champlain Valley of New York and Vermont suggest significant brittle fracturing occurred during the latest Cretaceous (85-65 Ma) and document a third episode of tectonism during the Miocene. Although the kinematics of these rejuvenation events remain unclear, circumstantial evidence suggests that the Mid-Cretaceous event (125-110 Ma) was driven by regional upwelling associated with volcanism, and the latest Cretaceous event (85-65 Ma) was associated with compressional thrusting in response to a change in Atlantic spreading direction.



Dike ages from McHone and Butler, 1984

Trace elements in mollusc shells and benthic foraminifera

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Throughout the course of an organism's life, the chemical signatures of environment, food consumption, and weather are recorded into their carbonate structures; these signatures can be directly linked to a time-resolved lifespan. Here we present trace element data from benthic foraminifera and tropical molluscs determined using an ESI NWR193^{UC} excimer laser coupled with an Agilent 8900 triple quadrupole mass spectrometer in the MicroAnalytical Geochemistry and Isotope Characterization (MAGIC) Laboratory at the University of Maine. Benthic foraminifera are protists that live on the sea floor and produce calcite shells, progressively adding chambers. Changes in Mg/Ca in foraminifera are used as a proxy for ocean temperature. Laser ablation ICP-MS data for 18 trace elements were collected in individual growth chambers in foraminifera of the genus *Uvigerina* from the Bay of Plenty. Line scans were performed within thin (~10 μm) chamber walls using a spot size of 8 μm, beam energy density of 3 J/cm^2, repetition rate of 12 Hz, and scan speeds of 2-3 μm/s. Concentrations were determined relative to the NIST610 glass. Ratios of Mg/Ca and other trace elements record the same range of values as those determined via bulk wet chemistry analysis of ~10 foraminifera for a given population, which suggests that LA-ICP-MS may be a viable alternative to wet chemistry.

Trace element data were collected across shells of the warm-tropical mollusc species *Chione subrugosa* from the Ostra Base Camp area, Peru (78°37'22"W, 8°54'46"S). Previous studies of the area have suggested that a large climate transition occurred, transforming a warm water tropical bay into a desert surrounded by a coastal stand with cool waters. This area was occupied by humans at 6250-5450 radiocarbon years BP. This study examines *Chione subrugosa*, which were found in the living position at the fossilized Ostra Beach and are thought to have been the final living warm-tropical molluscs in the bay. Studies of modern molluscs have revealed that molluscs record massive climatic changes, such as El Niño, in their chemistry. Laser ablation provides a unique opportunity to examine chemical changes directly related to the changing coastal environment. Line scans transverse growth bands along the length of the shell, providing a high resolution record of daily variation in trace element chemistry over the lifespan of the mollusc. Eleven elements were analysed with a beam energy density of 2.4 J/cm^2, repetition rate of 15 Hz, spot size of 5 x 25 μm, and a scan speed of 5 μm/s. Preliminary data suggest the preservation of yearly oscillations in trace elements, with high concentrations of La, Ce, U, and Pb during early shell growth. Continued study will examine catastrophic mollusc life events in an effort to link these with environmental climate changes over daily timescales.

Happy Jack uraninite: a new reference material for high spatial resolution analysis of U-rich matrices

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There is currently a lack of well-characterized matrix-matched reference materials (RMs) for forensic analysis of U-rich materials at high spatial resolution. To address this deficit, we have characterized a uraninite (nominally UO_{2+x}) that can be used as a RM to validate chemical and isotopic signatures in nuclear materials for both the geochemical and nuclear forensics communities. To date, the chondrite normalized rare earth element (REE) signature has been identified as the most useful nuclear forensics tool for the purpose of determining the provenance of uraninite, the primary ore of uranium for nuclear material. The REE signature of uraninite is dependent on the geologic environment in which the ore formed, allowing for the assignment of a particular deposit type based on the chondrite normalized REE pattern. In this study, we demonstrated through a detailed geochemical investigation of uraninite from Happy Jack Mine (Utah, USA) that it can be used as a RM for determination of REE concentrations in nuclear materials. The chemical signature of this uraninite was investigated at the macro (cm)-scale with micro-X-ray fluorescence (μXRF) mapping, and at high-spatial resolution (10s of micron-scale) using electron microprobe analysis (EMPA) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses. Based on EPMA results, the uraninite is characterized by homogeneous UO_2 and CaO contents of 91.57 ± 1.49% m/m (2σ uncertainty) and 2.70 ± 0.38% m/m (2σ), respectively. Therefore, CaO abundances were used as the internal standard when conducting LA-ICP-MS analyses. The REEs are homogeneously distributed throughout the sample at abundances ~1300 times chondrite with the exception of La (~60 times chondrite). Overall, the major and REE compositions are homogeneous at both the centimeter and micron scales, allowing this material to be used as a RM for high spatial resolution analysis of U-rich samples.

Zircon trace elements as an indicator of amphibolite petrogenesis

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Amphibolites from the Rattlesnake Creek terrane in the Klamath Mountains (northern CA and southern OR) record evidence for high-grade metamorphism at 155 – 157 Ma (CA-ID-TIMS)1, including local migmatite generation. We use Ti-in-zircon thermometry2, trace element geochemistry, and rare earth element (REE) concentrations of zircon and whole rock to determine the petrogenesis of amphibolites from the Rattlesnake Creek terrane in the Klamath Mountains.

Titanium-in-zircon thermometry2 from migmatites in amphibolites of the Rattlesnake Creek terrane record average temperatures of between 606 and 649°C. These temperatures are below amphibolite dehydration melting temperatures of between 850 and 900°C3, leading to the conclusion that the amphibolites underwent water-present melting, at or near the water-saturated solidus. Using the Watson and Harrison calibration, zircon saturation thermometry4 indicates that zircon should be stable in the leucosomes at temperatures of~590°C. However, use of the Boehnke et al. calibration5, zircon saturation thermometry returns temperatures well below the wet solidus, with average temperatures of 504°C.

Rare earth element diagrams for zircon display a wide range in concentrations and patterns. Zircon from the southern sample area (Scott Bar) are LREE-poor and have normalized Lu concentrations that vary from 1x102 to 1x105 times chondrite. Where measurable, the Eu/Eu* anomaly for the Scott Bar zircon is less than 1 (~0.84), whereas the Ce/Ce* anomaly is greater than 1 (~14). Zircon from the northern sample area (Applegate River) record similar patterns as zircon from Gold Flat, but with higher LREE and a narrower range in normalized Lu concentrations (1x103 – 3x103 times chondrite). The Eu/Eu* anomaly for the Applegate River zircons is slightly less shallow (~0.63), whereas the Ce/Ce* anomaly is much larger (~60). The difference in zircon REE can be attributed to the presence of garnet in equilibrium with zircon in the Scott Bar samples, and the lack of garnet in the Applegate River samples. The larger Ce/Ce* and lower Eu/Eu* anomalies in the Applegate River samples is likely the result of a more oxidized melt, compared to the melt in the Scott Bar samples.

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Integrated provenance analysis of Upper Jurassic-Cretaceous strata of Sverdrup well (Kara Sea): implication for the Late Mesozoic history of High Arctic

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Present day Arctic ocean sediment budget are significantly controlled by influx of water and sediments by large continent –scale rivers as Yenisei, Ob', Lena and Kolyma. There are only 4 wells drilled within the offshore Russian part of Arctic basins to the east from the Barents Sea that are limited the precise reconstruction of paleogeography and provenance of the sediments across the significant part of Arctic. Furthermore, there is no any provenance study of available cores. Thus, here we present the first data on the provenance of clastic succession of the Sverdrup well – the only drilled in the Kara Sea north to Taimyr peninsula.

The combined U-Pb data on detrital zircons and rutiles, (U–Th)/He zircons thermochronologic analyses samples from Upper Jurassic Cretaceous strata provide the first glimpse on the Late Mesozoic paleogeography of Kara Sea and wider Arctic.

Our study reveals a major shift in the provenance of clastic sediment within Upper Jurassic-Cretaceous succession of Sverdrup well drilled in the Kara Sea. Furthermore all studied samples could be dividing on two groups sourced from the different crustal domains. The Group 2 comprises Late Jurassic – Hauterivian samples (sv1621, sv1475, sv1303) and Group 1 is represented Aptian-Albian strata (sv 707, sv840, sv953 and sv1078).

The Upper Jurassic – Hauterivian strata (Group 2) quite are immature composition of sandstones and point on the proximity of sedimentary source area. The U-Pb detrital zircon and rutile ages pointing that provenance area located within northern part of Taimyr. ZHe ages revealed that uplift of provenance are occurred in Late Triassic that matches with reported ages of uplift of Taimyr peninsula.

Samples from Group 1 (Albian-Aptian) are way more mature arkosic arenites with limited unstable lithic grains pointing on longer sedimentary transport and /or multiple reworking of grains. The U-Pb dating of detrital zircons and rutiles show that the source of clastic located within southern margin of Siberian continent. Furthermore the latest uplift revealed by available apatite fission track data from south-eastern Siberia indicate that cooling event starts in the Middle Jurassic and ends during the late Early Cretaceous, around 120–110 Ma that perfectly match with obtained ZHe ages. The comparison of distribution of detrital zircons ages reveals a strong similarity between detrital zircon populations within Aptian-Albian succession of Sverdrup well and modern sands of Yenisey and Ob'Rivers (Safonova et al, 2010). Thus, we propose that big continent –scale rivers started to evolve and carry clastic grains from the far located Siberian craton margins to Arctic Ocean since the Aptian. The results presented in this study provide new constraints on the paleogeographic evolution of the Russian High Arctic in Mesozoic.

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Coexisting and intersecting magma systems in and near Yellowstone caldera, Wyoming, USA.

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Since its last cataclysmic collapse 640 ka ago with the 1000-km^3 Lava Creek Tuff eruption, Yellowstone caldera has experienced a long history of rejuvenated volcanism, primarily consisting of rhyolite lava flow eruptions, the youngest of which occurred 70 ka ago. This study utilizes LA-ICP-MS (a Teledyne Analyte G2 excimer laser coupled to a Thermo-Scientific ICAP Q mass spectrometer) to investigate bulk rock, volcanic glass and mineral major and trace element compositions in these post-640-ka rhyolites to decipher their long-term magmatic evolution and the factors leading to their eruption. Among these lavas, the Gardner River lava flow, erupted 301 ka ago ~20 km to the North of the caldera brings a unique perspective to these questions. Geographically, it belongs to a group of small-volume lava flows and domes erupted outside of the caldera from ~480 ka to ~80 ka. Geochemically however, it resembles the most primitive and earliest erupted end-members of the intra-caldera lavas, the Upper Basin (UBM) and Central Plateau (CPM) members, which each become gradually more differentiated over time, forming two overlapping liquid lines of descent. By its mineralogy, the Gardner River lava also resembles these members, with plagioclase, sanidine, quartz, and pyroxene (>10% total crystallinity). By contrast, other extra-caldera lavas have <1% crystals of much smaller size, and trace element signatures distinct from UBM and CPM, suggesting that they belong to a separate magmatic system. Mineral compositions in the Gardner River lava are consistent with an intra-caldera origin, but some sanidine crystals contain Na-rich cores, which compositions are observed at Yellowstone only in extra-caldera lavas. Furthermore, the Gardner River lava contains cm- to m-sized inclusions of basaltic andesite. While host-enclave boundaries are sharp and glass compositions are homogeneous, transfer of crystals between the two magmas is widespread, with mafic magma minerals present in the rhyolitic glass, and vice-versa. These observations together suggest that the Gardner River magma migrated northward away from the caldera subsurface, likely utilizing regional faults. During its migration, it intersected extra-caldera rhyolite melts, scavenged some of their crystals, which continued growing in their new host melt until eruption. Finally, the input of a hot-spot-derived mafic magma in this recently established rhyolitic reservoir, or the intersection of the migrating rhyolitic sill with a differentiating mafic magma reservoir are two plausible trigger mechanisms for the eruption.

Applications in paleoceanography: Proxy calibration of cultured cold water corals and rapid U-Th age-screening

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The aragonitic ($CaCO_3$) skeletons of long-lived and globally-distributed cold water corals offer a promising archive of past oceanic conditions. The element ratios of P/Ca, Ba/Ca, and U/Ca have been shown to be proxies for seawater nutrient and carbonate concentrations but much work remains to improve the calibrations[1]. The relatively large scatter in the current field calibrations stems from uncertainties in the hydrographic data and the heterogeneous distribution of elements within the skeleton. To this end, we culture *Desmophyllum dianthus* in flow-through aquaria with systematically controlled seawater chemistry and properties, and add calcein (fluorescent dye) and Pb-isotopes to chemically mark each of the 6-month stages in the skeleton. Here we present preliminary laser confocal scanning microscopy images and LA-ICPMS depth profiles of septa (skeletal plates) that support their use as seawater proxies. Patterns of element variation highlight the complexities in the skeleton but also provide a constraint for understanding the biomineralization process. To further investigate the fine-scale structural and compositional variability, we propose to evaluate 2-D maps of element composition against high spatial resolution observations (e.g., helium ion microscopy, Raman spectroscopy) of coral microstructures. We also present U-Th ages of fossil corals collected near New Zealand determined using LA-MC-ICPMS. This promising method[2], while less precise than isotope dilution techniques, offers the ability to rapidly age-screen corals with age uncertainty <2ka for corals <30ka, and to investigate the incorporation mechanism and spatial relationships between U and Th within the skeletal microstructure.

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Geographic origin determination of ruby and sapphire using trace elements

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The geographic origin of gem corundum has emerged as one of the major factors affecting their sale on the market, in large part due to the prestige attributed to certain regions (e.g. rubies from Burma) but also because of political, environmental and ethical considerations.

Deposits of gem-quality corundum are well distributed all around the world and occur in various different geological settings, generated via several different petrogenetic processes. Trace element analysis is a powerful tool to investigate source characteristics, i.e. corundum-forming fluids and crystallization environments, and most gemological laboratories today use trace elements obtained by LA-ICP-MS combined with gemological observations (e.g., inclusion characteristics and growth features) to determine gem corundum provenance. To date, however, only a small number of trace elements can be determined accurately and the success of this approach is often limited to the determination of the type of geological deposit. Due to similar properties and features of rubies and sapphires from similar geological settings but different geographic regions, the determination of geographic origin remains a challenge. Here we aim to (1) refine the existing LA-ICP-MS method and expand the number of elements that can be accurately determined with this technique, and (2) explore the potential usefulness of radiogenic isotopes (Sr-Pb) for origin determination.

We analyzed rubies and sapphires from several different localities of geologically similar deposits – Rubies from amphibolite-type (Mozambique, Tanzania, Madagascar, Greenland), and marble-hosted deposits (Myanmar, Vietnam, Tanzania, Afghanistan), and metamorphic blue sapphires (Myanmar, Sri Lanka, Madagascar) – by LA-ICP-MS using a RESOlution M-50 (Resonetics) 193 nm ArF Excimer (CompexPro 102, Coherent) laser ablation system coupled to a Thermo Finnigan Element2 ICP-MS. Using a fluence of ~6.6 Jcm^2 and a 285 µm spot at 20 Hz we were able to obtain quantitative data (> LOQ @ 7σ bg) for up to 26 elements. In addition to those elements that can substitute for Al^{3+} in the crystal structure, seven elements were consistently >LOQ, while six were frequently quantifiable. Among this wider spectrum of quantitative data, three elements show potential for geographic origin determination: Ni for amphibolite-type ruby, Sn for marble-type ruby, and Cr for metamorphic blue sapphire. Sr and Pb isotope compositions were obtained using an off-line laser sampling technique followed by TIMS. For amphibolite-type ruby isotopic ratios for different localities plot into separate fields, for marble-hosted ruby and metamorphic blue sapphires, however, different geographic origins overlap. Our results re-emphasize the challenge of geographic origin determination of marble-hosted ruby and metamorphic blue sapphire and the need for a more powerful discriminatory tool.

Strontium Isotope Ratio determination using Laser Ablation Triple Quadrupole ICP-MS (LA-QQQ-ICP-MS)

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Preliminary results for Sr isotope ratios in anthropological samples were obtained by laser ablation – triple quadrupole inductively coupled plasma mass spectrometry (LA-QQQ-ICP-MS). Published values on commercially available reference materials were measured for their Sr isotope ratios. Modern bone and tooth matrices were analyzed to evaluate a matrix relationship and potentially show any detectable variation. The common isobaric interferences from 87Rb and associated polyatomic interferences on 87Sr and 86Sr were mitigated by the tripe quadrupole ICP-MS system utilizing a collision reaction cell in either "on-mass" or "mass-shift" mode. The precision and repeatability were determined for several lateral and longitudinal sections of bone and teeth.

Determination of foraminiferal TE/Ca in thin section by LA-ICP-MS

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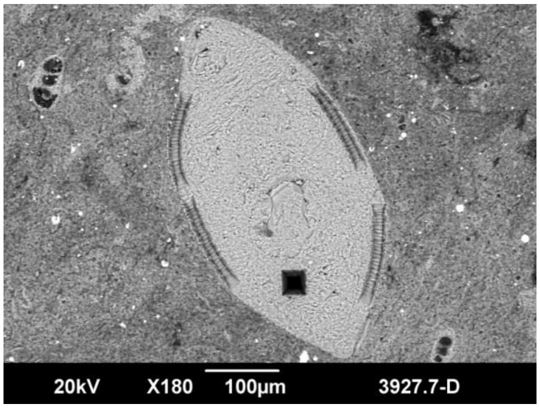
Trace element/Ca (TE/Ca) ratios derived from chemical analysis of well-preserved tests of calcareous foraminifera (early Paleozoic to present) are widely used in paleoceanographic studies as proxies of primary water mass characteristics (e.g., temperature via Mg/Ca). These proxies are typically measured from isolated and cleaned foraminifera, either as pooled multi-shell dissolutions or from LA-ICP-MS spot ablations of external or internal chamber surfaces. However, physical extraction, cleaning, and selection of optimal foraminifera specimens is not always possible or practical (e.g., from highly indurated lithologies). At the same time, visibly well-preserved foraminifera (e.g., with intact microstructure) are commonly observed in thin section. As previous foraminiferal LA-ICP-MS studies are almost exclusively based on geologically young (<20 ka) specimens, the extent to which primary water mass characteristics can be traced in deeper time remains largely untested. Here, we assess the potential for extracting primary TE/Ca values from foraminifera chamber walls (≥10µm) exposed in thin section by LA-ICP-MS. Using an ESI NWR193^{UC} excimer laser coupled with an Agilent 7500ce ICP-MS, we optimize analytical parameters from thin sections of pristine modern foraminifera (Ontong Java Plateau, California Margin) and foraminifera-bearing intervals of the Miocene Monterey Formation (offshore California). We find curvilinear square-aperture transects to be optimally suited for whole-test cross-sectional sampling, allowing multiple transects to be made from the same chamber. Screening of the resulting geochemical time-series enables altered (or otherwise contaminated) intervals to be excluded. The accuracy of derived TE/Ca transect averages for individual chambers is independently confirmed by EPMA traverses made over the same chambers. Similar to LA-ICP-MS studies based on physically isolated planktonic foraminifera, we find consistent TE/Ca among traverses made within the same chamber, but that different chambers of the same specimen can vary systematically. TE/Ca variations in tests of visibly well-preserved Monterey Formation foraminifera generally fall within expected ranges from literature, whereas elevated Mg, Mn and Ba and low Sr distinguish dolomitized foraminifera. Benthic foraminifera from the same thin section show very similar Mg/Ca regardless of whether chambers are open or filled by secondary spar (with highly variable Mg/Ca). These findings support the analytical feasibility of measuring primary TE/Ca in foram test cross-sections by LA-ICP-MS.



Split-Stream and 2D mapping U-Pb and trace elements depth profiling

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Zircon U-Pb dating is a widely used geochronologic technique to unravel complicated geological histories and constrain ages and rates of magmatic, metamorphic, and sedimentologic processes. Recent technological and methodological advances allow us to reveal a more detailed picture of the geologic adventure of a zircon grain, which is particularly useful to examine high-grade deformed rocks that have undergone multiple stages of magmatism and deformation. The signature of these geologic events is recorded not only in the age, but also in the trace element characteristics of a zircon, which evolve as the rock undergoes petrologic and metamorphic processes. Specifically, new attention is directed towards the rims on zircon grains, which were previously disregarded or even abraded away to expose the core. Here, we utilized a novel zircon U-Pb technique to show that zircon rims record recrystallization growth through both metamorphic and metasomatic events which provide valuable insight into the geologic evolution of complex metamorphic rocks.

We performed laser ablation split-stream (LA-SS)-ICP-MS depth-profiling and 2-D mapping techniques to reconstruct the entire history of metamorphic rocks from single zircon grains. We used a Photon Machine Analyte G.2 193nm Excimer laser with a 30 µm spot at 4 mJ with a 10 Hz repetition rate to simultaneously measure the U, Th and Pb isotopes as well as trace element and rare-earth element concentrations. Unpolished zircon grains were ablated from the metamorphic rims to the magmatic cores, which allowed us to distinguish the geochemical signature of the rims and exclude possible mixing ages. Depth profiling from single spots revealed the isotopic and chemical zonation of the zircon grains which can be used to assess whether the recrystallization of these zircon rims are related to either metamorphic or metasomatic growth. Lastly, 2-D mapping with 5 µm spots and 4 second ablation of polished zircon grains demonstrated the ability to delineate spatial isotopic and elemental distributions of different zircon zones.

We applied these techniques to zircon from metamorphic rocks in Sikinos and Ios, Greece, which record metamorphism and deformation associated with subduction and subsequent back-arc exhumation. We found multiple distinct zones of zircons rims, with metamorphic rims recorded at 50 Ma and metasomatic rims at ~26 Ma, suggesting that zircon recrystallized in several stages. 2-D ICP-MS mapping analyses indicate the specific chemical composition of these thin zones, thus providing important constrains on the metamorphic and fluid-flow history during subduction. These results illustrate the potential of future studies for constraining the temporal evolution of highly-deformed rocks that experienced subduction and exhumation processes.

Provenance of the Devonian–Carboniferous clastics of the Prikolyma terrane (Verkhoyansk–Kolyma orogen, northeast Asia) based on U–Pb dating of detrital zircons

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U–Pb dating of detrital zircons collected from the Middle–Upper Paleozoic strata of the Prikolyma terrane (Verkhoyansk–Kolyma orogen) provide the first insight into provenance areas and the Middle–Late Paleozoic geological history of the Russian Far East. Detrital zircon ages from the Lower–Middle Devonian sandstones form a prominent peak at 395–405 Ma (Emsian–Eifelian) and correlate well to trachyte of the Uvyazka zone and the Kedon Complex of the North Okhotsk active continental margin located on the Omolon terrane. Precambrian-aged zircons group around 1740–2080 and 2460–2800 Ma, suggesting possible sources within metamorphic rocks of the basement of the Omolon terrane or the Siberian Craton. The majority of the zircons from the Lower and Upper Carboniferous sandstones form a peak at 333–375 Ma, suggesting that the principle source of the clastics were volcanic rocks and comagmatic felsic intrusions of the Kedon Complex of the North Okhotsk active continental margin. Our new data allow us to evaluate and revise the available paleotectonic reconstructions of northeast Asia for the Devonian and Carboniferous.

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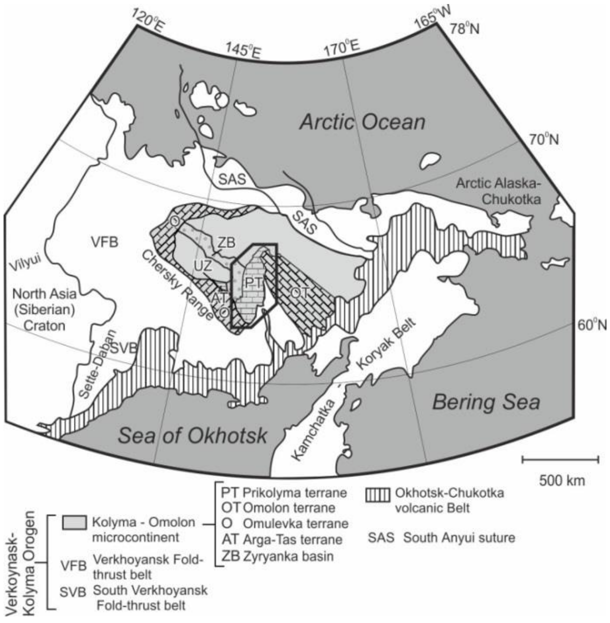

Figure 1. Main geological units of the northeast Asia and location of the study region.

Provenance analysis and AFT thermochronology of the Triassic Matzitzi Formation: implication for the tectonic reconstructions of southern Mexico during Pangea assembly

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The geological evolution of southern Mexico during the end of the Paleozoic and beginning of the Mesozoic was characterized by tectonic processes related to the last stages of the Pangea assembly. In this contribution integrated petrographic analysis, U-Pb detrital zircon geochronology, U-Pb detrital apatite thermochronology, geochemistry and fission track analyses were obtained in the late Paleozoic-Early Triassic sedimentary Matzitzi Formation, a continental detritic unit located in southern Mexico. Those data allow to constrain the provenance and tectono-thermal record of southern Mexico's geological history during the final amalgamation of Pangea. Sandstone samples belonging to the Matzitzi formation contain zircons belonging to a metamorphic Grenvillian main source, with a reduced Late Paleozoic, arc-related source. A main Early Neoproterozoic detrital apatite subpopulation shows a geochemistry signature similar to metamorphic rocks of the underlying granulite-facies Oaxacan Complex, which is locally dated at 1035±7.2 and 1237±6 Ma (U-Pb on zircons). Volcanic clasts contained in the Matzitzi basal conglomeratic members yield ages comprised between ca. 269 and ca. 285 Ma, whereas granitoid clasts are Grenvillian. Finally, quartz-litharenite clasts have detrital zircons spanning from Archean to lower Permian, with most abundant population yielding Grenvillian and Panafrican ages. U-Pb geochronological dates of the Atolotitlán stock, interbedded with the uppermost strata of the Matzitzi formation, suggest an upper depositional limit of the Middle Triassic. A Late Cretaceous – Paleocene exhumation pulse is recorded in sandstones of the Matzitzi Formation by AFT, which is correlated with Cretaceous-Eocene compressive deformational history in southern Mexico, coincident with the Laramide Orogeny.

These new results suggest a continental sedimentary accumulation during the late Permian to Early-Middle Triassic, controlled by basement blocks and Carboniferous-Permian magmatic arc roots exhumation/uplift, coincident with a waning arc activity during this period.

Creation of Matrix-Matched Corundum Standards

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The Gemological Institute of America (GIA) has created sets of highly accurate matrix-matched corundum standards for LA-ICP-MS analysis as an alternative to NIST SRM glasses. These standards cover applicable ranges of key trace elements Be, Mg, Ti, V, Cr, Fe, and Ga found in natural ruby and sapphire. The motivations to create matrix-matched standards for quantifying the most common trace elements in corundum were centered around improving accuracy: Having the same composition and structure between standards and samples will avoid dissimilar interferences and ablation characteristics that could negatively impact the quantification process; Minimizing the differences in ratios of matrix elements and trace elements of interest between standards and samples will reduce calibration errors; and possibly the most important consideration for moving away from NIST SRM glass standards for these trace elements was the fact that they simply are not certified for most of the elements of interest (Be, Mg, Ti, V, and Ga). To ensure the highest accuracy possible, we created and characterized individual ion implant standards for each trace element of interest in corundum, calibrated a Secondary Ion Mass Spectrometer (SIMS) with these implants, and then calibrated each individual corundum standard piece using SIMS. We turned to Czochralski-growth to produce large and highly uniform multi-doped crystals for three of the four of these standards. Each set of standards include an ultra-high purity synthetic sapphire “blank” with a combined total of less than 0.5 ppma of the key trace elements mentioned above; two multi-doped pieces of synthetic sapphire to capture relevant levels of Be, Mg, Ti, V, Cr, Fe, and Ga; and a highly uniform piece of Yogo sapphire to capture a higher level of Fe than we could generate synthetically. Each standard piece was screened to ensure high homogeneity. GIA has been using these standards for over a year in their own colored stones laboratories, and is working towards making these standards available outside of GIA. The adoption of these standards by other labs will help in creating industry-wide uniformity when it comes to reporting ruby and sapphire key trace element data.

Multi-stage mixing and mingling of boninitic melts captured by multielement LA ICP MS single pulse imaging

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The quality of LA ICP TOF MS generated elemental distribution maps is heavily dependent on the effects of aerosol dispersion in the ablation chamber and sample transport system. Long pulse response duration, gravitational settling of the aerosol particles, turbulent gas flows, coupled with unsuitable lasing and data acquisition parameters will likely create imaging artefacts which can blur or even obscure the features that are naturally present in the samples. The use of rapid-response technology enables the acquisition of full pulse signals of less than 3ms (FW0.1M). When coupled to a TOF mass spectrometer, such technologies allow images to be generated at higher laser repetition rate and scanning speed without compromising data quality. Due to the increased mass flux, sensitivity is also increased, allowing for a micron-scale lateral image resolution to be achieved using single pulse analysis mode. The analytical setup used for this contribution comprises a Teledyne Photon Machines Analyte G2 excimer laser equipped with a fast washout Cobalt cell, coupled to a TOFWERK icpTOF mass spectrometer.

Sample U1439C 25R2 18/19 is a boninite lava from the Izu-Bonin forearc, which was recovered during IODP Expedition 352. While boninites are typically of interest because of their unique mode of formation (fluxed melting of highly depleted mantle [1]) and their tectonic significance (forearc rift-related magmas, erupted in this case within the first 1.5 Myr after the initiation of IBM subduction [2]), the sample also shows evidence for complex mineralogical zoning, suggestive of multi-stage mixing and mingling of boninitic melts as they rose through the crust. Multi-element imaging via LA ICP TOF MS document this open-system history, showing clear zoning of Fe, Mn and especially Ni in Opx phenocrysts, reflecting contact with both more and less primitive melts. As well, the icpTOF maps document the evolution of vesicle-filling secondary assemblages, starting with vesicle-lining zeolites enriched in Na, K, and Rb, and followed by Sr-rich carbonate fluids that also mobilize Mn, Y and light rare earth elements.

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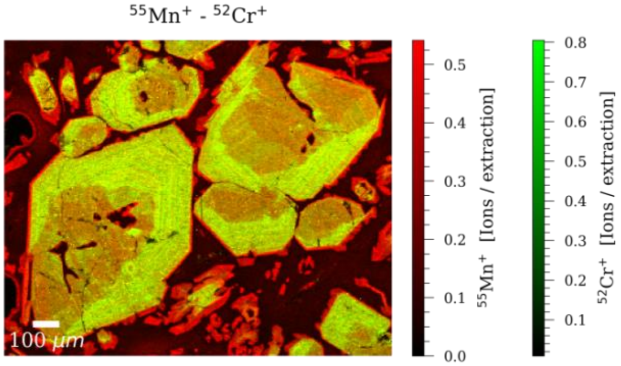

Simultaneous in situ U/Pb dating and Hf-isotope ratio determination of zircons with laser ablation ICP-MS

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Laser ablation ICP-MS has become a common method for U/Pb dating of zircons, especially when large numbers of grains have to be analyzed. The same is valid for laser ablation multi collector ICP-MS Hf isotope determination in zircons. These two measurements are normally done independently, leading to a potential mismatch of ages and Hf isotope ratios in heterogeneous grains. Recently, some laser ablation ICP-MS laboratories (e.g. Yuan et al. [1]) introduced a split stream approach, where the laser ablation aerosol is split into two parts. One part is used for U/Pb dating, normally on a single collector ICP-MS and the other part is used for Hf isotope determination on a multi-collector ICP-MS, allowing simultaneous in situ determination of both of them. This split stream approach has been implemented at Memorial University and the performance of the setting is presented here.

Using the 91500 zircon as primary standard for dating gave over a period of a few months average $^{206}Pb/^{238}U$ ages of 336.5 +/- 0.7 Ma for Plesovice (ID-TIMS: 337.13 +/- 0.37 Ma), 291 +/- 1 Ma for 02123 (ID-TIMS: 295 +/- 1 Ma) and 412.9 +/- 2.1 Ma for Temora-2 (ID-TIMS: 416.78 +/- 0.33 Ma) secondary zircon standards. The accuracy of mass interference and mass bias corrections applied to $^{176}Hf/^{177}Hf$ are validated by analyzing synthetic zircons doped with Lu and Yb, along with natural zircon standards. Recent results include $^{176}Hf/^{177}Hf$ = 0.282302 +/- 38 for 91500 (solution ICP-MS: 0.282308 +/- 6) and $^{176}Hf/^{177}Hf$ = 0.282757 +/- 45 for R33 (solution ICP-MS: 0.282764 +/- 14).

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Crystal Accumulation in Silicic Rocks and its Impact on Zircon Thermometry

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Hornblende (Hbl) from three calc-alkaline intrusive systems of intermediate composition (English Peak pluton, Wooley Creek batholith, and Tuolumne Intrusive Complex) show core to rim decreases in Zr, Hf, and Zr/Hf at temperatures above 800°C. Given that Zr and Hf are only slightly compatible in Hbl and are generally incompatible in other co-precipitating mineral phases (e.g. plagioclase, biotite, FeTi oxides), it's probable that zircon is responsible for these decreases. This interpretation is supported by the occurrence of zircon in Hbl cores and by Ti-in-zircon thermometry from each system. However, zircon saturation thermometry[1,2] indicates that zircon should not saturate in these systems until temperatures that are near or below the wet solidus are reached.

We use Hbl-melt Fe/Mg partioning[3], Hbl chemometry[4], and zircon saturation thermometry[1,2] to demonstrate that the bulk-rock compositions from these silicic plutonic systems are partial cumulates and that silicic and Zr-rich melts were removed. Bulk-rock compositions from each of these intrusions are variable, ranging from diorite to granite to leucogranite. However, Hbl chemometry[4] indicates that both the high and low temperature Hbl are in equilibrium with melts that are rhyolitic in composition. Melt Zr contents can be calculated using either partitioning relationships (e.g. Zr partitioning in Hbl) or by solving for melt Zr using zircon saturation thermometry equations, provided that a saturation temperature can be independently estimated and that the major element melt composition can be estimated (i.e. Hbl chemometry). For the silicic intrusive systems investigated in this study, we estimate zircon saturation occurred at ~ 825°C, which is the approximate temperature at which Zr/Hf decreases in Hbl and the temperature of some of the highest Ti-in-zircon thermometry values recorded by zircon from these rocks. Using these approaches we find that melt Zr contents are higher than bulk-rock Zr concentrations. Since zircon is the principal reservoir of Zr in these magmas, it's possible to estimate the amount of Zr lost from the bulk-rock using the equation: Zr deficit in rock = $Zr_{melt} - Zr_{rock}$. This approach indicates that at least 40% melt was removed from each system (which could produce voluminous rhyolitic eruptions) and that bulk-rocks are partial cumulates. Thus, saturation thermometry may be a useful tool for discerning crystal accumulation and melt loss in plutonic systems.

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GENERAL ISSUES

LA-ICP-MS a la carte

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The community of the LA-ICP-MS scientists encompasses users of many laser ablation systems interfaces with a multitude of the ICP-MS instruments.

We were fortunate to use few laser ablation systems and decided to create a wish list of the hardware and software configurations for an ideal LA-ICP-MS system.

Maybe in a future, a real Laser Ablation system will be able to include all the best features, which often are the application-specific, by mixing and matching some standard modules.

The list includes our best experiences with sample cells and cell inserts and discusses their geometries. We will examine interfacing of the laser's output into the torch, and signal smoothing devices. We will present the utilization of solid tune glasses (different than NIST 612 SRM).

Finally, we will discuss data reduction and data processing. The focus will be on quantitative analyses and graphical presentations of a line scan.

INSTRUMENTATION

ICP-MS TuneSim: A Software App to Simulate Tuning an ICP-MS

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In recent years there has been a rise in the use of simulated analytical experiments to support undergraduate learning. These virtual environments offer students the chance to familiarise themselves with laboratory instrumentation prior to practical classes and/or to gain additional skills that could not be taught effectively within the laboratory session. Tuning of analytical instruments is a skill that is often neglected in undergraduate laboratory experiments due to the limited availability of expensive instrumentation and the time constraints associated with scheduling of laboratory sessions. However, it is a skill that is vital for subsequent industrial and PhD research.

Here we present the development of a new and freely available software application, the 'ICPMS Tune Sim'. The app provides a virtual environment for students to tune a sector-field ICP-MS and to explore how issues with instrumental setup could influence experimental errors. The app allows students to adjust parameters, such as the torch position, gas flows, radio frequency power and guard electrode state, whilst observing the 'measured' signal in real time. The software has been used successfully with a group of second year undergraduate students, as part of an Atomic Spectrometry course at Loughborough University. Student feedback from this exercise will be reported, along with a demonstration of the key features of the software.

Potential and Pitfalls of Mercury Elimination with a "Triple-Quad" ICPMS

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Measurement of stable lead at mass 204 is inherently problematic for quadrupole instruments because of an isobaric interference from mercury which tends to be several times the signal of the low abundance lead at mass 204. As pointed out in an application note from Agilent (Woods, 2014) ammonia gas in the collision cell provides excellent removal of mercury at mass 204 by charge transfer reaction, however uranium is also affected by the ammonia gas in the cell. Unlike for liquid analyses, the time dependent nature of laser ablation does not allow any change in cell gas during the analysis, so a gas mode chosen to isolate one interference must work for all analytes.

Theoretically a triple quad instrument allows for hightly controlled reaction cell chemistry, because the mass filter before the cell allows only a single mass/charge into the cell, and the mass filter following the cell selects for only the target ion. Therefore when measuring at mass 204 after the collision cell, complex interferences introduced by, for example, REE + NH3 are not an issue, because only mass 204 enters the reaction cell. In a liquid mode test solution of 1 ppb Hg, Pb, and U, sensitivy of 202 Hg drops from ~20,000 to 27 cps at 10% ammonia flow. This removes all but half a percent of mercury from the analysis stream, and allows for interference-free measurement of stable 204 Pb. However, a significant tradeoff exists, because the measured intensity of U at mass 238 is also sensitive to the ammonia reaction gas. Sensitivity of U is more than halved, from 80,000 to 30,000 cps. By allowing 238 U through Q1, and scanning Q2 we find significant U+NH3 product ions at masses 253, 254 and 270.

We analyzed ~1 Ga zircons from the Southern Adirondacks, sampled from localities with known U-Pb zircon ages (Selleck et al. 2005 and Wong et al. 2011). Separated zircons are mounted in epothin epoxy at the center of 1" rounds and ablated with the 213 nm Nd-YAG Cetac laser ablation system at Union College, in a geomed barrel cell using 0.7 L/min He as carrier gas, subsequently mixed with 1 L/min Ar. All analyses were performed on an Agilent 8900 using both quadropoles as mass filters, and tests were done in both "no-gas" mode and under 9% flow rate of ammonia gas. As compared to no-gas mode, backgrounds at mass 204 drop from a consistent 126 to 1 cps, showing excellent interference removal. Analyses run in ammonia mode showed huge variation in measured 238 U 236 Pb ratios, compared to relatively fixed 236 Pb 237 Pb ratios, likely as a result of varying gas flow affecting the uranium which is measured at mass 238. Wildly discordant ages resulted from these tests, unless uranium reaction products were also measured (253, 254, 270) in which case ages calculated using the move back towards concordance. Pb/Pb ages obtained in both gas modes are of similar quality, affirming that Pb istopes are relatively unaffected by the ammonia. The clearest takeaway from this work so far is that gas flow must be tightly controlled, or else whatever benefit is gained from direct measurement of ^{204}Pb will be lost by uncertainties in measured ^{238}U.

Portable laser ablation analysis: archaeological science applications

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Trace element and isotopic analyses are both robust, widely utilized methods within archaeological sciences to determine, among many other applications, material provenance, migration patterns, and paleodieatary information. Micro-destructive techniques, such as laser-ablation, are employed to collect this information as they preserve material unblemished for future generations. However, traditional methods are limited to small objects which can fit into a laser ablation cell. Also, objects to be analysed must be removed from their current environment, whether that be at an archaeological site or within a museum collection, which is often a complex, time-consuming process. Portable laser ablation (pLA), first developed by Glaus et al., 2012, allows for the collection of ablated material outside of a lab environment. Deposited onto a filter, the sample can then be transported and subjected to traditional LA-ICP-MS analysis or to destructive, isotopic methods, such as radiogenic Sr or Pb isotopes. We present a series of case studies showing trace element and isotope data collected via pLA from archaeological materials, including ceramics, metals, glass, and bone.

Laser Ablation Split Stream Between Two Multicollector Inductively Coupled Plasma Mass Spectrometers for Determination of Reactor Neutron Fluence

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Reactor grade zircaloy, which is composed of 95% zirconium (Zr) with hafnium (Hf) concentrations of 100 ppm or less, is a common material used in nuclear reactors. The exposure of Zircaloy to the high neutron fluence of a reactor alters the isotopic composition of various elements via neutron capture; this allows the neutron fluence to be inferred from the change in the isotopic composition of elements in the Zircaloy at specific locations. As a proof of concept, simultaneous analyses of the isotopic compositions of both Hf and the Zr within the alloy was conducted using an ESI NWR213 Nd:YAG laser to ablate a raster on the Zircaloy sample with a 20μm diameter beam at 20Hz. The ablated material stream was split in two and directed into two Nu Instruments MC-ICP-MS instruments operating concurrently. Zirconium isotopes were analysed to within 0.1% of solution value by static multi-collection using $10^{11}\Omega$ resistor Faraday cups on a Nu Plasma HR, and Hf isotopes were analysed to within 1% of solution value for major isotopes by dynamic multi-collection on ion-counters using a Nu Plasma II. Further analyses were conducted to constrain sample usage to 20μm single spot sizes, with the goal of analyzing a 20μm x 20μm x 5μm Zircaloy chip. Data collected on 20μm spot sizes on the Zircaloy sample were comparable in precision and accuracy to ablation of conventional rasters used in the first half of the experiment. Final results demonstrate this as a valid method for simultaneous collection of high precision isotopic compositions of bulk and trace elements within a material with high spatial resolution for minimal consumption of limited mass samples.

Assessing spatial reproducibility of U-Pb zircon LA-ICP-MS analyses using a two-volume laser ablation chamber

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The transition from single-volume, open-design laser ablation cells to two-volume laser ablation chambers is thought to have reduced or eliminated the negative effects of gas circulation within the laser ablation cell (e.g. fractional transport of particles, signal tailing, and transport delay) by creating a uniform high-efficiency transport zone at all positions within an ablation chamber. In this experiment, we tested the spatial reproducibility of U-Pb zircon LA-ICP-MS measurements using a NWR193 laser ablation system with a TwoVol2 laser ablation chamber coupled to a Nu AttoM sector-field, single-collector ICP-MS. Nine different 25 mm epoxy round mounts, each containing a piece of 91500 zircon, were loaded into a 100 mm x 100 mm aluminum sample holder and placed into the TwoVol2 laser ablation chamber. Each 91500 zircon crystal was analyzed using a 20 µm spot, a fluence of 2 J/cm^2 and a repetition rate of 8 Hz. Data were collected to simulate a typical U-Pb zircon experiment with two primary reference standards analyzed before and after every nine unknowns. For this experiment the 91500 crystal in the center sample holder position was treated as the primary reference material and the 91500 zircon crystals located in each of the eight surrounding sample positions were analyzed as a standard 'unknown'. Data were reduced in Iolite using the VisualAge data reduction scheme [1]. Final ^{206}Pb/^{238}U were corrected for Pb-U downhole fractionation using an exponential function. The average variation of ^{206}Pb/^{238}U was less than 1% for all chamber positions (n = 9 at each position) relative to the center position (n = 20). The results suggest that placement of reference standards and sample unknowns at different positions within the laser ablation chamber contribute less than 1% to the variations in ^{206}Pb/^{238}U observed in this experiment.

Within position variation of ^{206}Pb/^{238}U was less than 2 % for all chamber positions. Offsets of individual analyses relative to the center position were up to 2%. These variations approach the 2% (SE) uncertainty commonly associated with U-Pb LA-ICP-MS zircon analyses [2], and are attributable to errors beyond chamber position effects. These include variations in laser-sample interaction between samples and standards due to differences in chemical and physical properties of different zircon grains, focus of the laser beam on the sample surface, and/or position misalignment of the small-volume inner cup.

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U-Pb dating of titanite by LA-ICP-QQQ-MS

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Titanite has the ability to incorporate significant amounts of common Pb, which leads to uncertainty when applying the U-Pb decay series for geochronology. The isobaric interference of ^{204}Hg on ^{204}Pb poses an additional complexity in applying common Pb corrections. Here we investigate the removal of ^{204}Hg interferences during titanite U-Pb dating using reaction cell gas chemistry via triple quadrupole mass spectrometry. U-Pb dates were determined for the natural titanite reference materials MKED-1 and BLR1 using an ESI NWR193^{UC} excimer laser coupled to an Agilent 8900 'triple quad' mass spectrometer. The 8900 is equipped with an octopole collision/reaction cell, which enables online interference removal. Two experiments were run, one in which we collected data in NoGas mode, and one in which NH_3 was used as a reaction cell gas in MS/MS mode, in order to assess the feasibility of determining U/Pb ratios with mass shifted isotopes.

In all experiments, a signal smoothing device was placed inline just before the ICP-MS interface, downstream from the addition of the Ar nebulizer gas to the He carrier gas stream. For the NoGas experiment, titanite was ablated using a 25 μm spot, with a beam energy density of 3 J/cm^2, and a pulse rate of 4 Hz. In NoGas mode, signal intensities for the isotopes ^{201}Hg, ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{232}Th, ^{235}U, and ^{238}U were counted. In MS/MS mode, titanite was ablated using a 40 μm spot, with a beam energy density of 5 J/cm^2, and a pulse rate of 4 Hz. A larger spot size in this experiment was used to counteract the decrease in signal intensity due to use of the reaction cell. In MS/MS mode, NH_3 was flowed through the reaction cell in order to enable a charge transfer reaction between NH_3 and Hg^+, effectively neutralizing Hg. The isotopes ^{201}Hg, ^{202}Hg, ^{204}Pb, ^{206}Pb, and ^{207}Pb were measured on-mass, as the isotopes of Pb are not affected by the NH_3 gas. Uranium and Th both exhibit partial reaction with NH_3 gas; therefore, the isotopes ^{232}Th, ^{235}U, and ^{238}U were measured mass-shifted up 15 mass units, at masses 247, 250, and 253 respectively.

Ratios of ^{207}Pb/^{235}U, ^{206}Pb/^{238}U, and ^{207}Pb/^{206}Pb were determined using the UPbGeochron4 DRS in Iolite (v.3.71) with MKED-1 as the primary reference material. Dates were calculated using IsoplotR by applying the Stacey-Kramers correction for common Pb. All isotopes of Hg were effectively neutralized by the NH_3 charge transfer reaction in MS/MS mode; zero counts were detected for Hg isotopes. Dates for the BLR-1 titanite were 1050.55 ± 2.72 (2σ, n=12) Ma in NoGas mode, and 1048 ± 1.88 (2σ, n=15) Ma in MS/MS mode. These dates are in excellent agreement with the TIMS ^{206}Pb/^{238}U date for the BLR-1 titanite of 1047.1 ± 0.4 Ma. This method has the potential to enable measurement of ^{204}Pb without needing to correct for Hg interferences.

Development of a new Laser Ablation Platform – the Iridia

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Teledyne Photon Machines has always made collaborative research a priority. We believe this to be the only durable way for empowering technological innovations in science. From developing applications that enable our users to make the most out of their instrumentation to developing new tools, both hardware and software, that allow the scientific community to further their research, we have long recognized the true value of the science driven innovation and have diligently cultivated mutually beneficial projects. We have often turned to academia to validate our findings, as well as being strong supporters of academic endeavours.

Laser ablation inductively coupled mass spectrometry (LA ICP MS) elemental mapping has recently changed from being a rather cumbersome and resource-consuming tool mainly used by the earth sciences community, to mainstream technique for analysing anything from biological samples to archaeological artefacts. In order to accommodate this pivotal change, new hardware was needed that would speed up the analytical process, but also yield uncompromised data quality [1]. Based largely on the feedback we received from our user base, we have developed a new, dedicated ablation system that offers unprecedented control over the speed, lateral resolution and analytical sensitivity. Built around the extensively tested Cobalt tube cell [2, 3] and with a completely new design evolved from many years of experience working with Analyte Excite and G2 platforms, the Iridia system is focused on offering the shortest pulse response duration (full pulse signal acquisition of less than 3 ms at FW0.1), the lowest maintenance costs, and the highest sensitivity [4] available.

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The Application of Triple Quadrupole Based Interference Correction to Laser Ablation ICP-MS

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Laser Ablation allows the direct determination of trace metals and isotopes in a wide variety of materials, from soft biological tissues to hard accessory minerals. The type of information desired from all sample types is different, but the basic principle of the technique is the same.

For bio-materials, the focus of LA-ICP-MS is with bio-imaging: visualizing both naturally occuring and artificially introduced trace elements; however, low concentrations and small sampling areas (required to achieve sufficiently high lateral resolution) challenge ICP-MS detection sensitivity (equivalent to image contrast) and stability over long analysis time. In addition, isobaric interferences on biologically relevant elements, such as phosphorous, sulfur and selenium, mask trace element signals and degrade acquired image fidelity.

In accessory minerals, one of the main applications for LA-ICP-MS is geochronology, which depends on the accurate determination of radiogenically formed isotopes, for example the U-Th-Pb, K-Ca and Rb-Sr systems. In each of these systems, isobaric overlaps present challenges to accurate isotope determination.

To be able to resolve isobaric overlaps, high resolution mass spectrometers could be used; however, most interferences require specialist instrumentation to achieve mass resolution above 30,000 ($m/\Delta m$), which is usually large and costly.

Collision/Reaction cells (CRCs) have been used in quadrupole mass spectrometers to remove polyatomic interferences by pressurizing the CRC with an inert gas to reject the (larger) polyatomic interferences. CRCs can also be pressurized with reactive gases to allow chemical reactions to occur within the ion beam. In this way, it is possible to use reactive gases, such as oxygen, ammonia and others to specifically react with certain elements to effect chemical separation from isobaric interferences.

Mass shift alone may shift the analyte mass to a region where another isobaric interference exists, for example $^{87}Sr^+$ can be shifted to $^{103}SrO^+$, but $^{103}Rh^+$ will now be an interference. For this reason, triple quadrupole (TQ) technology is required to filter out any existing 'mass shift interferences' and provide a clean background for analysis.

In this presentation, the benefits of using triple quadrupole ICP-MS for laser ablation imaging will be shown using different sample types and focusing on biologically relevant analytes. In addition, accurate age determinations made possible with a triple quadrupole ICP-MS system are also presented by demonstrating the use of mercury interference elimination for U-Pb geochronology.

LAICP Fundamentals and Parameters

Comparison of 193nm and 266nm Wavelengths for Elemental Bio-Imaging by Laser Ablation Inductively Coupled Plasma

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Producing accurate Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) images of biological tissues may be compromised by substrate contribution. In instances where the sample is completely ablated (tissue is easily ablated, thin tissue samples, max sensitivity required, etc.) laser coupling with the substrate can contribute elemental impurities. Substrate contribution is difficult to quantify given variability in 1) tissue samples, 2) standards, 3) substrate composition, 4) laser conditions, and 5) elements imaged. Here we investigate elemental (trace and major) impurities in a selection substrate material (glass slides) and evaluate conditions that control their contribution; 1) LA wavelength (193nm vs 266nm), 2) fluence, 3) crater profiles, and 4) depth profiles.

The central findings of this study are that 1) at fluences above 1.1 J/cm2,193nm LA systems will ablate the substrate, 2) 266nm systems will not ablate the substrate until the fluence is above 4.4 J/cm2, 2) similar sensitivity for elements of interest for both wavelengths, and 3) stability is similar over the appropriate fluence range for 193nm and 266nm lasers.

For bioimaging, comparable analytical performance can be obtained using a 193nm or 266 nm laser if fluence is appropriately controlled. The 266nm system, however, offers a larger fluence range, lower purchase price and lower cost of ownership.

High repetition lasers and fast washout for 1.8 Mpx/h LA-ICPMS imaging

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Traditionally, laser ablation inductively coupled mass spectrometry (LA-ICPMS) imaging of solid samples is considered to be an analytically slow technique. Even with the latest hardware and software developments, i.e., fast washout technologies and parameter modelling procedures, most of the mapping data published is obtained using conservative parameters as far as repetition rate, scanning speed and acquisition time are concerned.

While there is nothing inherently wrong with using traditional approaches in LA-ICPMS imaging, experiments can be unnecessarily long, wasting both time and valuable resources. Quality data, i.e., high spatial resolution, low noise, limited smear, etc., can be achieved not only by slowing down the imaging process, but rather by adapting the experiments to the latest refinements in hardware and software.

In this contribution we present data taking advantage of the fast aerosol transfer technologies (Aerosol Rapid Introduction System – ARIS, Teledyne CETAC Technologies) and the fastest repetition rate excimer laser, as well as the latest developments in modelling the imaging process for optimization of the LA-ICPMS parameters. Murrina glass sections were ablated at both high and low repetition rates (100 Hz to 500 Hz), and the resulting images were compared in terms of image quality. The advantage of using the highest repetition rate (500 Hz) is that the image quality is uncompromised, while the analysis time is greatly reduced, thus saving lab resources, e.g., Ar and He gases, and increase the throughput, which will be of great importance in applying this technique in the field of medicine.

STANDARDIZATION

Preliminary LA-ICP-MS Analyses of the INTAV Reference Glasses for Tephrochonology

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Tephrochronology employs the use of major and trace element concentrations of volcanic glass shards to correlate volcanic deposits to their source volcanoes. Researchers commonly attempt to correlate data collected in one lab with published data produced by other labs. Therefore, it is of paramount importance that these data be free of laboratory-based bias, such as those resulting from the use of different primary calibration standards and secondary reference materials. Furthermore, analyzing compositionally evolved glasses (rhyolites, phonolites) by LA-ICP-MS presents analytical challenges: (1) Because of low major element concentrations (e.g. <1.0 wt.% CaO) and the requirement of small spot sizes, Si is the commonly used internal standard. However, using Si results in >10% differences between measured and accepted values of most trace elements in evolved reference glasses (e.g. ATHO-G). (2) Anhydrous, synthetic glasses (e.g. NIST glasses) and glasses made by melting natural rocks (e.g. MPI-DING glasses) ablate differently than naturally hydrous, evolved glasses, resulting in different degrees of laser-induced element fractionation between standards and unknowns. Therefore, most of the commonly-used reference glasses do not make ideal calibration standards. In order to get trace element concentrations of secondary reference materials within 10% of accepted values, it is common practice in the tephrochronology community to perform a correction routine. This correction routine consists of analyzing 3 or more reference glasses (e.g. MPI-DING glasses) and determining correction factors (measured value/accepted value) for each element. These correction factors are then applied to all the analyses of the unknowns. This process introduces uncertainties that are not typically propagated and reported in publications.

In an attempt to identify and decrease laboratory biases and these analytical challenges, a set of natural glasses (INTAV glasses: 3 rhyolites and 1 phonolite) has been prepared and sent to various labs for interlaboratory comparison and better characterization. Here we present preliminary results obtained at the Earth Observatory of Singapore by LA-SF-ICP-MS point analyses at different spot sizes (10, 15, 20, and 50 µm) for these glasses. Data collected at spot sizes ≥15 µm, are reproducible (≤5% RSD), and there are not significant differences in internal precision between analyses performed with different spot sizes. Furthermore, the concentrations determined for the INTAV glasses, using the correction routine discussed above, are in good agreement with concentrations determined by solution ICP-MS where available. However, when a 10 µm spot size is used, internal precision decreases and the results deviate from those determined with other spot sizes.

These results raise several questions, which will hopefully be addressed by the interlaboratory comparison: (1) Do the INTAV reference materials make good calibration standards for trace element analyses of compositionally evolved glass? (2) Is the complex correction routine used in the tephrochronology community necessary, or will using calibration standards, which are more like the unknowns, eliminate the need for this routine? (3) How can we improve accuracy and precision at spot sizes ≤10µm? (4) What other steps can we take to ensure that miscorrelation of volcanic units does not result from laboratory biases?

Comparison of Multiple Reference Materials and Multi-Internal Standard Models using HALite—a Steady-State Calibration Software

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HALite is a development-stage software project for quantification of LA-ICPMS trace element data using multiple reference materials (RMs) and multiple internal standard (IS) elements—building on the widely used IS correction model of Longerich et al. (1996). Here we compare the multi-standard, multi-internal standard calibration results for several standard sets including XRF Li-borate fusions (from Hamilton Analytical Lab), synthetic doped glasses (from NIST, USGS, Corning Museum of Glass, and Smithsonian Microbeam Standards), and MPI-DING whole-rock fusions. An overview of the HALite calibration procedure is given here:

First, the raw data are integrated, baseline subtracted (gas blank), and long-term drift corrected using a doped glass (e.g. NIST610 or similar drift monitor). These preliminary processing steps may be accomplished in the mass spec software, other time-resolved software packages, or using HALite's built in drift correction. The intensity data should not have severe downhole fractionation over the periods of averaging and steady reproducibility over the duration of an analytical session after long-term drift correction is applied. The mean corrected intensity data, RM tables, and IS determinations are each input to HALite.

Generally an IS correction model is invoked to compensate for biases that affect elements proportionally (variable ablation yield, incomplete ionization, matrix-specific sensitivity). In the top display panel, HALite facilitates the inspection and selection of ideal IS elements using bi-variate sensitivity correlation plots derived from the RM population. The analyte-IS pairs whose sensitivity correlations are most precise (best R^2) will maintain their precision through the IS correction procedure. Currently HALite prioritizes IS selection lists based on the best R^2 coefficients of the sensitivity correlation. Importantly however, the ideal IS element also depends on availability of, and precision of, IS determinations (inherited from XRF or EPMA). For future developments the automatic prioritization of IS selections will combine the precision of the sensitivity correlation with the precision of IS determination. Sometimes poor sensitivity correlations may result from inclusion of low-concentration standards (e.g. NIST616), presence of spectral interferences, and accuracy of given RM values. Based on sensitivity correlations and/or intuition, users may select one or more IS elements per analyte.

In the bottom display panel, the sensitivity correlation fit is passed on to the Longerich equation to assemble the IS-corrected model. Modeled concentrations are calibrated to the known values (model vs. given ppm). The user can adjust the IS selections in the upper panel and simultaneously observe the impact to the calibration line's parameterization and precision below. Despite potential problems with sensitivity correlation fitting (esp. with blanks), HALite still recovers a correct calibration line when modelled concentrations are correlated to known values of appropriate RMs. If multiple IS elements are selected, the IS model is weighted by standard error of the sensitivity correlation fit. Often we find that the weighted average model using multiple IS can improve the overall calibration precision. HALite calibrations give robust results and comparison of diverse RMs can elucidate the matrix-dependent phenomenon that may be hidden in more simple calibration schemes.

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NAWLA ’19

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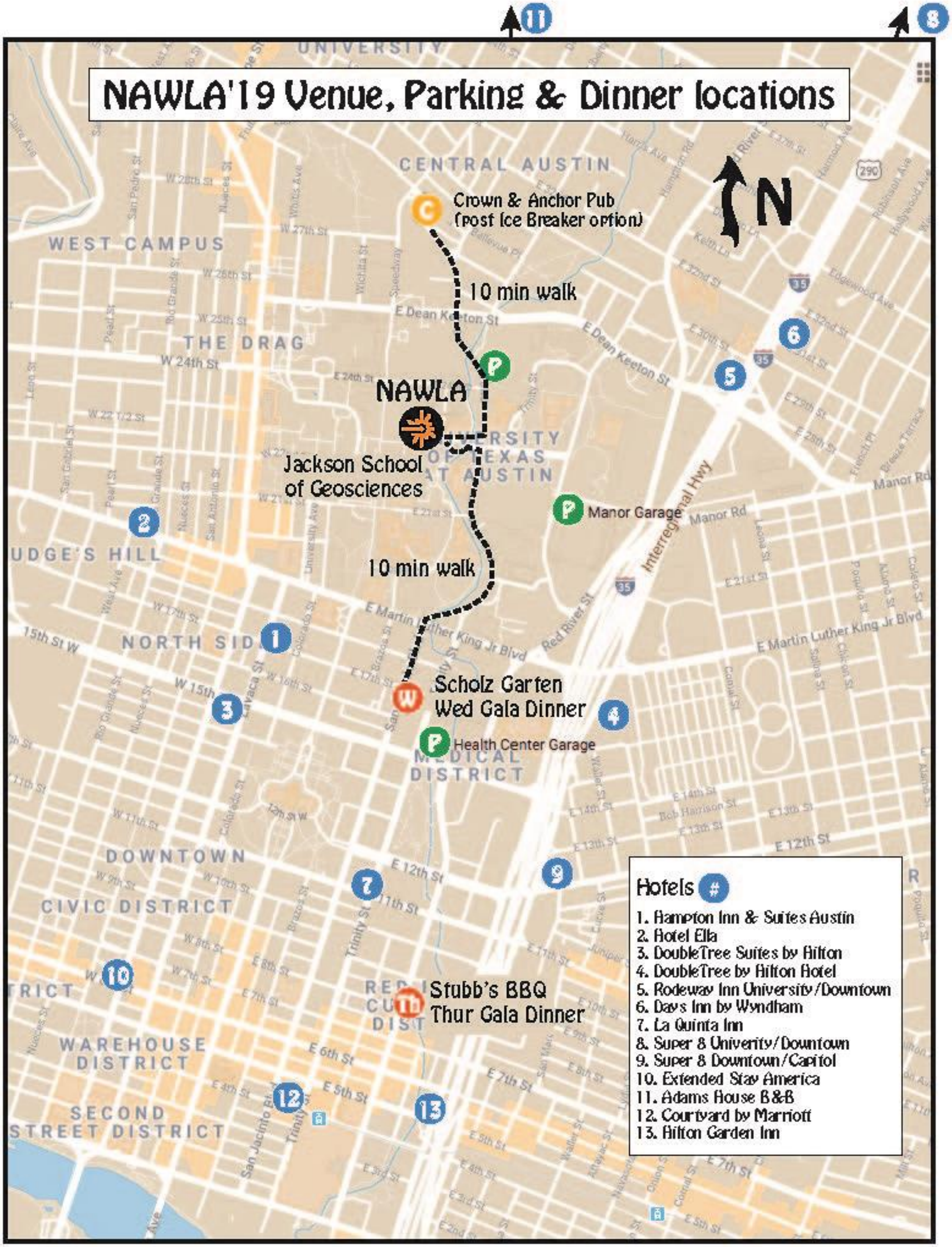

NAWLA'19 Venue, Parking & Dinner locations

Hotels #

1. Hampton Inn & Suites Austin
2. Hotel Ella
3. DoubleTree Suites by Hilton
4. DoubleTree by Hilton Hotel
5. Rodeway Inn University/Downtown
6. Days Inn by Wyndham
7. La Quinta Inn
8. Super 8 Univerity/Downtown
9. Super 8 Downtown/Capitol
10. Extended Stay America
11. Adams House B&B
12. Courtyard by Marriott
13. Hilton Garden Inn