EUROPEAN WORKSHOP ON LASER ABLATION

July 2nd-5th 2024, Ghent, Belgium

EWLA
EUROPEAN WORKSHOP ON LASER ABLATION

Book of abstracts of the 16th European Workshop on Laser Ablation
(EWLA2024)

GHENT UNIVERSITY

FACULTY OF SCIENCES

A&MS
Atomic and Mass Spectrometry

Book of abstracts of the 16th European Workshop on Laser Ablation (EWLA2024)

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Editors:

Thibaut Van Acker and Frank Vanhaecke

Ghent, July 2024

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Introduction

Dear laser ablation enthusiasts,

On behalf of the Local Organising Committee, we would like to warmly welcome you in Ghent, Belgium for the European Workshop on Laser Ablation EWLA2024.

We hope to be able to offer all of you – all 187 participants from universities, research institutes and companies located in 25 different countries – a stimulating environment to discuss fundamentals and applications of laser ablation in the analytical sciences.

For that very purpose, the Scientific Organizing Committee has aided us in setting up a scientific programme consisting of 7 invited (opening or keynote) lectures, 42 contributed lectures and 65 poster presentations. On the basis of the abstracts received, two of our younger colleagues were selected for an "upcoming talent oral presentation award" and also two excellent poster presentations will be awarded. Special thanks go to the *Journal of Analytical Atomic Spectrometry* and *TOFWERK* for sponsoring the upcoming talent and poster awards.

The scientific part of the conference will take place at Ghent University's Campus Coupure, home of the Faculty of Bioscience engineering. This campus is within 10 min of walking of the historic city centre. Ghent, the third largest city of Belgium, is often described as vibrant. To a considerable extent, this is due to the presence of many students, of which Ghent University alone already hosts almost 45,000. For our students, the exam period is concluded at the end of June, as a result of which you will find fewer of such specimens in the streets and bars than during the academic year. This situation definitely has advantages as well, not only to find a place on one of the many terraces, but also your safety should benefit as the majority of these students usually cycle at a speed and with a relentless determination that makes you think they are late for their own wedding, while most probably, they are only thirsty.

Next to an interesting conference with high-quality presentations, stimulating discussions and time for informal talks with your colleagues, perhaps leading to novel ideas and cooperations, we also would like you to have a good time.

That's why we start with an icebreaker reception on Tuesday evening to catch up with old friends and make new ones. On Wednesday evening, we'll go boating! A skipper will take you by motor boat to Ghent's Saint Peter's Abbey for a Belgian evening, where you will be invited to sample Belgian beers and try some Belgian food, including the so-called "French" fries. On Thursday evening, there will be a gala dinner and party located in the very centre of Ghent, in the old fish market, just across the Medieval castle. While we largely expect you to sit down during the lectures, in contrast, at the party, the DJ will attempt to get you up and moving, so wear your dancing shoes!

All of this has been made possible thanks to the financial support of many sponsors, several of which also participate with a booth. You are invited to visit them to discuss instrumentation, become aware of their latest innovations and inspire them by mentioning what you are still missing. Also look out for the lunch break seminars that some sponsors are offering.

We hope that at the end of the conference all of you will travel home with fond memories of the 2024 edition of the EWLA series and of the city of Ghent!

Frank Vanhaecke & Thibaut Van Acker   Ghent, July 2nd 2024

EWLA history

Since 1994, the European Workshop on Laser Ablation (EWLA) is a key international meeting focused on novel concepts and developments in laser ablation (LA) based micro-analytical techniques for elemental and isotopic analysis. Major topics dealing with fundamentals include laser-matter interaction, particle formation and transport phenomena, elemental and isotopic mapping, standardization, isotopic analysis, chemical depth profiling, simultaneous tandem and/or multi-sensor techniques, data processing and management. Applications cover a wide range of scientific fields, such as the Earth Sciences, Geology, Planetary Sciences, Biology, Medicine, Life Sciences, Archaeology, Forensics, Cultural Heritage, Material Sciences and Industrial applications.

2026	?	**2008**	Prague, Czech Republic
2024	Ghent, Belgium	**2006**	Zürich, Switzerland
2022	Bern, Switzerland	**2004**	Sheffield, UK
2020	COVID-19	**2002**	Utrecht, The Netherlands
2018	Pau, France	**2000**	Zürich, Switzerland
2016	Ljubljana, Slovenia	**1997**	Keyworth, UK
2014	London, UK	**1996**	Nancy, France
2012	Gijon, Spain	**1995**	Keyworth, UK
2010	Kiel, Germany	**1994**	Keyworth, UK

Committees

EWLA2024 Chairs

Thibaut Van Acker, Atomic & Mass Spectrometry (A&MS) research group, Ghent University

Postdoctoral Research Fellow of the Research Foundation of Flanders (FWO). His research focuses on unravelling fundamental aspects of LA-ICP-MS and boosting the analytical capabilities for quantitative high-resolution elemental mapping applications. © Photo EWCPS2023

Frank Vanhaecke, Atomic & Mass Spectrometry (A&MS) research group, Ghent University

Senior Full Professor in Analytical Chemistry, leading the A&MS research group that specialises in the determination, speciation and isotopic analysis of (ultra-)trace elements via ICP-mass spectrometry. His group studies fundamentally oriented aspects of the technique and develops methods for solving challenging scientific problems in interdisciplinary contexts. Currently, topics of research include elemental mapping by LA-ICP-MS, single-event ICP-MS and high-precision isotopic analysis using multi-collector ICP-MS.

Scientific Organising Committee (SOC)

David Chew, Trinity College, Dublin, Ireland

Steven Goderis, Vrije Universiteit Brussel, Belgium

Detlef Günther, ETH Zürich, Switzerland

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Andreas Riedo, University of Bern, Switzerland

Martin Šala, National Institute of Chemistry Ljubljana, Slovenia

Vassilia Zorba, Lawrence Berkeley National Laboratory, United States of America

Thibaut Van Acker, Ghent University, Belgium

Frank Vanhaecke, Ghent University, Belgium

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Rinus Dejonghe, PhD Student, Ghent University, Belgium

Iker Basabe Mendizabal, PhD Student, Ghent University, Belgium

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Laura Suarez-Criado, Postdoctoral Researcher, Ghent University, Belgium

Kaj Sullivan, Postdoctoral Researcher, Ghent University, Belgium

Thibaut Van Acker, Postdoctoral Researcher, Ghent University, Belgium

Tom Van Helden, PhD Student, Ghent University, Belgium

Mathias Vandermeiren, PhD Student, Ghent University, Belgium

Frank Vanhaecke, Senior Full Professor, Ghent University, Belgium

Sponsors

Platinum sponsor

Teledyne Photon Machines can make light work for you in many ways. The company specializes in advanced, laser-based, instrumentation with integrated detectors to gauge the presence and concentration of elements, end-points and isotope ratios in all types of solid samples. These markets include geological, environmental, biological pharmaceutical, academia, forensic, battery technologies and industrial quality control. Moreover, they have a broad selection of sample introduction systems for mass spectrometry.

Gold sponsor

Elemental Scientific Lasers has the analytical tools needed for higher resolution, faster analyses and greater automation for applications as diverse as biomedical, geochemical mineralogy or industrial quality control. With decades worth of combined expertise and a lineage tracing back to the very first commercially produced laser ablation systems, ESL has been at the forefront of laser ablation sampling for atomic spectroscopy since the very beginning. ESL laser ablation products are designed and developed with an emphasis on superior performance and benchmark analytical results, application flexibility, operating convenience and reliability.

Silver sponsor

Nu Instruments is a market leading designer and manufacturer of high-performance mass spectrometers. Our highly specialised instrumentation includes; Multi-Collector ICP-MS (MC-ICP-MS), Time-of-Flight ICP-MS (TOF-ICP-MS), High Resolution ICP-MS (HR-ICP-MS), Glow Discharge Mass Spectrometry (GD-MS), Isotope Ratio Mass Spectrometry (IRMS), Gas Analysis Mass Spectrometry, Thermal Ionisation Mass Spectrometry (TIMS).

Bronze sponsors

TOFWERK is making the world a cleaner place through innovative solutions for chemical analysis. Their time-of-flight mass spectrometers bring the speed and sensitivity of TOF to diverse application fields – allowing you to rethink existing analyses and accelerate your science in new directions.

Agilent Technologies supports scientists in cutting-edge life science research; patient diagnostics; and testing required to ensure the safety of water, food and pharmaceuticals. Our advanced instruments, software, consumables, and services enable our customers to produce the most reliable results. Together with our customers, we're bringing great science to life.

Applied Spectra provides LA and LIBS instruments that can meet and exceed your elemental and isotopic analysis needs. Our instruments can tackle the most challenging research project, be used for routine analysis, and come with a state-of-the-art software package and support from our world-class team of scientists. Transform the Way YOU do Chemistry!

International Association of Geoanalysts is an international society devoted to the advancement of geoanalytical science and promoting the interests and supporting the professional needs of those involved in the analysis of geological and environmental materials. They are supporting EWLA since the very beginning in 1994.

Thermo Fisher Scientific is a supplier of analytical instruments, life sciences solutions, specialty diagnostics, laboratory, pharmaceutical and biotechnology services. Thermo Scientific ICP-MS instruments are designed to meet the needs of all laboratories, from high-throughput laboratories performing applied testing to cutting-edge research facilities.

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The Iridia laser ablation system exists to simplify what is normally a complicated and technically challenging process – proven to generate the highest quality data quickly and easily

- The result of >5 years of collaborative academic research
- Quick, easy optimization for all types of solid sample analysis
    - HDIP software to automatically optimize the entire system, and to automatically process all resulting analytical data
        - Able to produce fully quantified elemental image maps in minutes
        - Publication quality images, plus high quality bulk analysis tools
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        - CryoCobalt option available offering the same analytical performance
- High resolution and high precision analytical data with rep rates from 1Hz to 1kHz
- Single Pulse Response (SPR) of <1ms to >1 second with simple configuration changes
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- Proprietary expanded objective array replacing the traditional style objective lenses
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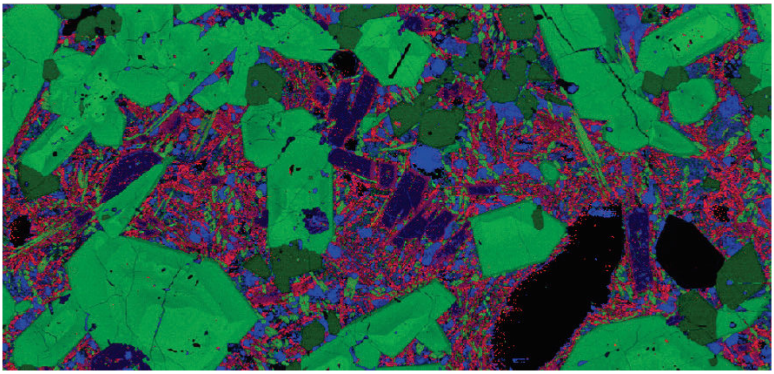
Fully field tested by globally renowned academic partners with analytical specification proven through peer reviewed and published data



1kHz ablation of Basalt using Nu Vitesse ICP-TOF-MS

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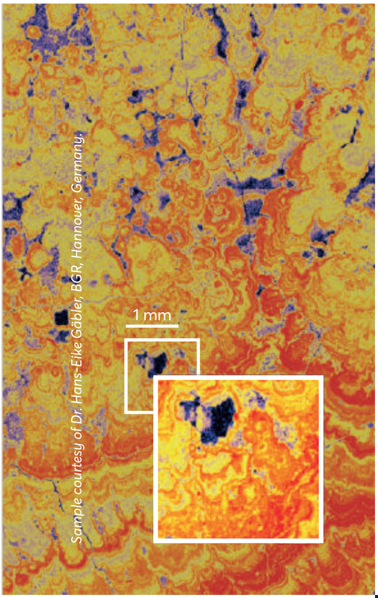
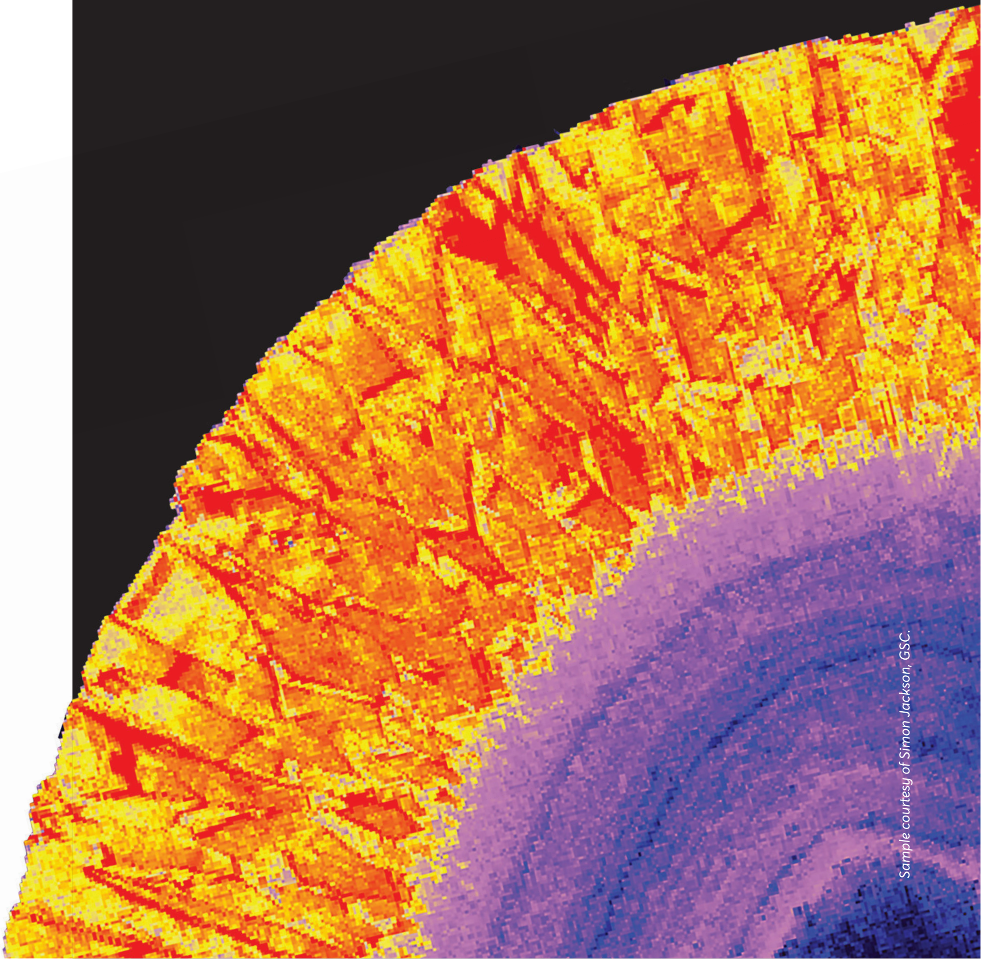


Sample courtesy of Dr. Hans-Eike Gäbler, BGR, Hannover, Germany.



Sample courtesy of Simon Jackson, GSC.

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imageBIO266

FAST (> 1 megapixel per hour), High-Resolution Bioimaging

- High frequency laser source enables pixel acquisition >1000 per second
- Lower fluence, better stability and superior sample transport for bioimaging
- Selective ablation of sample tissue optimizes experimental conditions
- Redesigned beam delivery system
  - Unrivaled reliability and robustness
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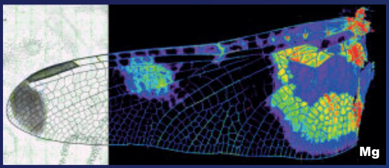
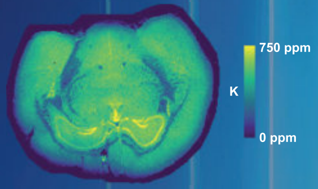


Dragonfly Wing



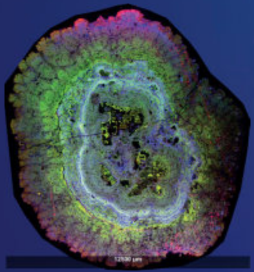
Mouse Brain – imageBIO + iLumen

imageGEO193

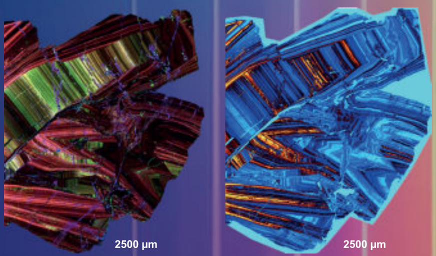
imageGEO193

FAST (> 1 megapixel per hour), High-Resolution Geoimaging

- Creates the highest resolution geochemical images at unprecedented speed
- A single system for FAST imaging and high precision isotope ratio determination
- LIBS compatible for simultaneous LIBS-ICPMS applications
- Compatible with DCI/TwoVol3



Deep Sea Nodule



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- Full spectra collection from 190-1100 nm
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**Requirements to add LIBS: TwoVol3 laser ablation chamber and iolite software.*

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Images of shark teeth courtesy of Ben Manard, Oak Ridge National Laboratory

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Upcoming talent awardees

The Scientific Organizing Committee selected Kristina Mervič (National Institute of Chemistry Ljubljana, Slovenia) and Dr. Sota Niki (Nagoya University, Japan) as winners of the 2 upcoming talent awards based on the quality of their oral abstracts and contributions to the field so far. They will present their work during 2 dedicated upcoming talent presentation slots on Wednesday July 3rd (16:10-16:30) and Thursday July 4th (16:10-16:30).

Kristina Mervič (National Institute of Chemistry Ljubljana, Slovenia) is a final year PhD student at the National Institute of Chemistry in Slovenia. After completing her MSc degree at Liverpool John Moores University, she worked at Unilever, where she published a patent. She then returned to academia and is currently pursuing a PhD in analytical chemistry, focusing on investigating the fundamentals of LA-ICP-MS, with an emphasis on aerosol formation during ablation and non-matrix-matched calibration approaches for quantitative analysis. Her research has led to the development of a novel calibration method based on volume correction that enables quantitative LA-ICP-MS analysis without matrix-matched standards.

Sota Niki (Nagoya University, Japan) is a postdoctoral researcher at the Institute for Space-Earth Environmental Research at Nagoya University, currently holding a postdoctoral fellowship from the Japan Society for the Promotion of Science (JSPS). He received his Doctor of Science degree from the University of Tokyo in March this year. From the onset of his doctoral research, he has been engaged in geochronology based on laser ablation ICP-mass spectrometry (LA-ICP-MS). His studies include the development and applications of dating methods for minerals containing trace abundances of descendent nuclides by utilising ICP-MS with multiple Daly detectors or with collision cell technology. Recently, his research focus has broadened to explore fundamental concepts in analytical chemistry, particularly investigating elemental fractionation during particle generation by femtosecond laser ablation. His upcoming presentation will unveil a novel system for online isotope ratio determination of individual particles generated via femtosecond laser ablation, shedding light on the mechanism of elemental fractionation.

JAAS – themed collection

It is our pleasure to invite you to submit your research to the *Journal of Analytical Atomic Spectrometry's* themed collection on the conference, celebrating work related to the development and application of laser ablation based techniques.

Guided by Chair Heidi Goenaga-Infante (LGC, UK) and supported by an international Editorial Board, *JAAS* is the home of premier fundamental discoveries in the analytical and bioanalytical sciences. *JAAS* is the central journal for innovative research on the fundamental theory and application of spectrometric techniques, as reflected by the composition of the Editorial and Advisory Board. More details about the journal, the full Editorial and Advisory Boards and the journal author guidelines are available on our website – https://www.rsc.org/jaas.

If you would like to submit a review or a research article, please contact JAAS with a short description.

We hope that you are able to accept our invitation. Please do not hesitate to contact us if you have any questions and we look forward to hearing from you.

With best wishes,

Frank Vanhaecke
Guest Editor
Chairman, EWLA

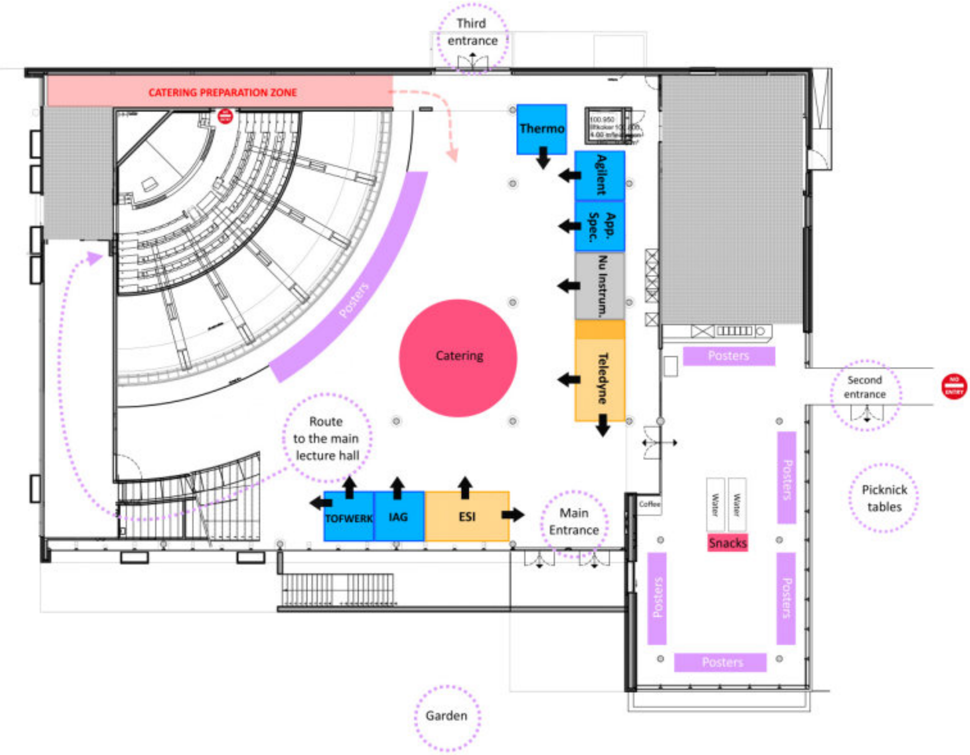
Thibaut Van Acker
Guest Editor
Co-chairman, EWLA

Alice Smallwood
Deputy Editor, JAAS
Royal Society of Chemistry

Conference site

The conference venue for EWLA2024 is Ghent University's Campus Coupure, home of the Faculty of Bioscience engineering, on the banks of the canal Coupure which is connecting the river Lys with the canal of Bruges. The historical city center of Ghent is a 15-minute walk away from the conference venue only. The entire building E is at our disposal:

- Auditorium Oehoe: all oral talks, opening and closing ceremony
- Foyer Agora: exhibition partner booths, coffee breaks, lunches and poster presentations
- Auditoria A and B (1st floor): lunch break seminars
- Campus garden: networking and relaxing


Third entrance
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Catering
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TOFWERK
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ESI
Main Entrance
Posters
Second entrance
NO ENTRY
Coffee
Water
Water
Snacks
Posters
Posters
Posters
Posters
Picknick tables
Garden

Social events

Icebreaker reception

Tuesday, 18:30-20:00 @ Garden Campus Coupure

On Tuesday evening after the opening ceremony and opening lectures, we will host an Icebreaker reception in the garden of the conference site accompanied by drinks and snacks. This will be an ideal opportunity to explore the conference venue and to start networking with old and new friends and colleagues.

Boat trip – Belgian evening

Wednesday, 18:00-19:00 @ Korenlei (boat trip)
Wednesday, 19:00-23:00 @St. Peter's Abbey (Belgian evening)

For the boat trip on Wednesday evening, we will gather at Korenlei, located in the middle of the city center. The boats will leave at 18:00 sharp, so make sure you are present 10 minutes in advance. The 60-minute boat trip will take us from Korenlei to the St. Peter's Abbey, navigating past the historic buildings of Ghent while having an aperitif with drinks and snacks. Upon arrival, you will be welcomed in the garden of the St. Peter's Abbey (Sint-Pietersabdij), a former Benedictine abbey, founded in the late 7th century and located on the Blandijnberg (the highest point of the city). You will be able to freely explore the beautiful abbey and enjoy fries and burgers from a food truck. A wide variety of Belgian beer and cheese is waiting for you all around the venue. A real Belgian evening!

Gala dinner

Thursday, 19:00-23:00 @ Old Fish Market (Oude Vismijn)

The Old Fish Market is one of the oldest fish markets in Belgium (1689) and it is characterized by a monumental gatehouse and open-air stables, located next to the Castle of the Counts (Gravensteen), the only remaining medieval castle in Flanders built in 1180. The Old Fish Market was renovated in 2007 and now serves as an event hall in which our gala dinner will take place. You will be welcomed on the large outdoor terrace with a view of the water and the city center for an aperitif. The dinner will take place in two charming rooms. After dessert, we will retire to the adjacent room, where the DJ will start a party and we will burn some calories.

Conference programme

Monday July 1st 2024

(13:30-16:00) **TOFWERK and Teledyne Photon Machines Joint LA Workshop** @UGent-A&MS lab, Campus Sterre, Krijgslaan 281 – building S12, 9000 Ghent, Belgium

Tuesday July 2nd 2024

(13:30-15:00) **Nu Instruments and Teledyne Photon Machines Lab Demo** @UGent-A&MS lab, Campus Sterre, Krijgslaan 281 – building S12, 9000 Ghent, Belgium

(16:00-17:00) **Official start on-site registration**

(17:00-17:30) **Opening ceremony by Prof. dr. Frank Vanhaecke and Dr. ir. Thibaut Van Acker**: Welcome to EWLA2024 in Ghent, Belgium

(17:30-18:00) **OL - Opening lecture by Prof. dr. Detlef Günther**: Revisiting our understanding of laser ablation-ICPMS

(18:00-18:30) **IL - Invited lecture by Prof. dr. Takafumi Hirata**: Laser ablation for molecular analysis

(18:30-20:00) **Ice Breaker reception**

Wednesday July 3rd 2024

(08:30-09:00) **KL1 - Keynote lecture 1 by Dr. Martin Šala**: Beyond conventional calibration: advancing LA-ICP-MS methodologies

<u>(09:00-10:00) **Session 1 chaired by Dr. Martin Šala – Fundamentals laser-matter interaction**:</u>

- (09:00-09:15) **OT1 - Wolfgang Müller** - Why go shorter? Design and Rationale of a Dual-Wavelength (157 & 193 nm) Cryo-LA-ICP-MS/MS System
- (09:15-09:30) **OT2 - Tobias Erhardt** - Initial Performance of a Dual-Wavelength (157 & 193 nm) Cryo–LA–ICP–MS/MS System
- (09:30-09:45) **OT3 - Pascal Bohleber** - Ablating the transparent: testing femtosecond laser ablation ICP-MS in the UV absorption dead zone of ice
- (09:45-10:00) **OT4 - Hideki Iwano** - Laser-induced heating onto solid materials through annealing of fossil fission tracks

(10:00-10:30) **Coffee break sponsored by Normec Servaco**

(10:30-12:00) **Session 2 chaired by Prof. dr. Detlef Günther – Fundamentals particle formation, transport phenomena & standardization:**

- (10:30-10:45) **OT5** - **Dylan Käser** - Ablation effects in nitrogen for LA-N_2-MICAP-MS
- (10:45-11:00) **OT6** - **Kanoko Kurihara** - Analysis of Mechanism for Generation of Ions and Particles via Laser Ablation in Liquid (LAL) Technique using ICP mass spectrometry
- (11:00-11:15) **OT7** - **Laura Kronlachner** - A novel sample preparation and calibration approach for nanoparticle analysis using laser ablation single particle-ICP MS
- (11:15-11:30) **OT8** - **Beatriz Fernández** - Quantitative protein bioimaging in individual cells by LA-ICP-MS; labelling with ruthenium red and metal nanoparticles
- (11:30-11:45) **OT9** - **Ana Lores Padín** - Advancing Quantitative Mapping of Biogenic Carbonate Matrices with LA-ICP-TOF-MS
- (11:45-12:00) **OT10** - **Mathias Schannor** - LA-MC-ICP-MS analysis of Cu isotopes in biological material

(12:00-13:30) **Lunch break:**

- (12:40-13:20) **Lunch break seminar 1 by TOFWERK** (Oehoe main lecture room): Demonstration of the Workflow for 1000 Hz Bioimaging: From Sampling to Data Processing

(13:30-14:00) **KL2** - **Keynote lecture 2 by Prof. dr. Gunda Koellensperger**: LA-ICP-TOF-MS - the essential tool for spatial single cell metallomics

(14:00-15:00) **Session 3 chaired by Prof. dr. Gunda Koellensperger – Applications in Biology, Medicine & Life Sciences (part A):**

- (14:00-14:15) **OT11** - **Martin Schaier** - Unraveling cobalt skin permeation and cellular interactions: Novel insights from LA-ICP-TOFMS imaging
- (14:15-14:30) **OT12** - **Alexander P. Morrell** - Can metallomic imaging of TNBC tissues help predict the NACT response?
- (14:30-14:45) **OT13** - **Heike Traub** - Laser ablation ICP-ToF-MS to investigate the interaction of MRI contrast agents the extracellular matrix components
- (14:45-15:00) **OT14** - **Michaela Kuchynka** - Nano-savers for Ischemic stroke? Investigation using a combination of CT and LA-ICP-MS

(15:00-16:05) **Poster session 1 + coffee break sponsored by Glass Expansion:**

- **PP1** - **Marcel Guillong** - Investigating Ablation Rates in Geological Materials: A Comparison of UV fs and ns Laser Ablation
- **PP2** - **Antea Hrepić** - Empirical Insights into Crater Geometry: Modeling for Enhanced Laser Ablation Inductively Coupled Plasma Mass Spectrometry Analysis

- **PP3 - Ciprian Stremtan** - Laser Ablation – Cavity Ringdown Spectrometry – A novel method for in situ measurement of light stable isotope ratios
- **PP4 - Guillaume Girard** - Elemental fractionation in LA-ICP-MS quantified
- **PP5 - Tom Van Helden** - Dual-phase formation during LA-ICP-MS analysis of biological tissue
- **PP6** - **Sarah Gilbert** - Sculpting the ablation plume - using QuadLock to enhance sensitivity for isotopic analyses
- **PP7 - Phil Shaw** - What's in a pixel?
- **PP8** - **Helmut Ernstberger** - Technological prerequisites for high quality isotope ratio measurements using quadrupole ICP-MS
- **PP9 - Julien Leger** - The more, the better: new practices for U/Pb data reduction based on multiple reference material standardization
- **PP10** - **Nathan Westwood** - Characterisation of nano-pellets as potential reference materials for Pb-Pb isotope analysis in ferromanganese crusts
- **PP11 - Nicholas West** - Real-time Measurement Of Mass Filter Position For Aligned LA–ICP–MS
- **PP12** - **Ashley Norris** - Ultra-Trace-Element Imaging Using Aligned LA–ICP–MS With a Magnetic-Sector Single-Collector Mass Spectrometer
- **PP13 - Lukas Schlatt** - What is dynamic range in LA-ICP-MS and how can it be extended?
- **PP14** - **George Cooper** - Femtosecond Laser Ablation for High-Speed Elemental Mapping
- **PP15** - **Matthew Horstwood** - TACtool: A Targeting and Co-ordination tool for LA-ICP-MS and other spatially resolved methods
- **PP16** - **Ethan Tonks** - Automated Selection of Sites for Chemical Microanalysis Using Image Segmentation
- **PP17** - **Stijn J.M. Van Malderen -** Hardware and software integration improvements in LA-ICP-TOF-MS for acquisition rates of 1000 resolved multichannel pixels per second
- **PP18** - **Martin Kutzschbach** - LA-ICP-MS/MS-based Rb-Sr isotope mapping for geochronology
- **PP19 - Jhanis Gonzalez** - High precision and spatial resolution chemical interrogation of planetary materials using fs-LA/LIBS in tandem with multi-collector ICP-MS
- **PP20** - **C. Derrick Quarles Jr.** - Exploring the benefits of combining LIBS and LA-ICPMS for geological based applications
- **PP21 - Max Frank** - Tracing thin water layers from the leaf surface into the plant: how the laser burns the doubt
- **PP22** - **Noémie Thiébaut** - Efficiency of foliar fertilization assessed by LA-ICP-MS
- **PP23** - **Daniel Pergament Persson** - Suberin restricts potassium leakage from plant roots
- **PP24** - **Lena Hiddeßen** - Quantitative bioimaging of boron-based contrast agents by means of LA-ICP-MS
- **PP25** - **Ana Justo-Vega** - Titanium imaging in fish tissues exposed to titanium dioxide nanoparticles by quantitative laser ablation-inductively coupled plasma-mass spectrometry
- **PP26** - **Paula Menero-Valdés** - Determination of target metals and proteins associated with neurodegeneration in tissue sections of a mouse model using LA-ICP-MS: Study of Zn supplementation

- **PP27** - **Olga Minaeva** - Imaging of environmental toxic metals distribution in the brain by LA-ICP-MS
- **PP28** - **Marie Novotná** - High-resolution LA-ICP-MS imaging of Pt-derivates in single cell and tumour tissue
- **PP29** - **Michaela Vašinová Galiová** - High-resolution LA-ICP-MS and tracing Ru-based metallocene in tumour cells
- **PP30** - **Lingna Zheng** - Mass spectrometry imaging of renal alternations in mice with cisplatin-induced acute kidney injury treated with CeO2 nanoparticle
- **PP31** - **Hunter Andrews** - Investigating the Use of Simultaneous Laser-Induced Breakdown Spectroscopy/Laser Ablation–Inductively Coupled Plasma–Time-of-Flight–Mass Spectrometry for the Analysis of Biological Materials
- **PP32 - Cinzia Chiurlia** - Platinum nanoparticles enhance LA-ICP-MS signal for trace element detection in serum spots
- **PP33** - **Alex Griffiths** - Metallomic imaging of microbial nutritional immunity

(16:05-16:30) **UT1** - **Upcoming talent award presentation 1 by Kristina Mervič**: Correcting Ablated Mass Differences in 2D LA-ICP-MS Mapping through Ablation Volume-Assisted Calibration

(16:30-17:00) **Session 4 chaired by Kristina Mervič – Applications in Biology, Medicine & Life Sciences (part B):**

- (16:30-16:45) **OT15** - **Johannes Schmeinck** - Laser ablation-atmospheric pressure chemical ionization-time of flight-mass spectrometry for molecular imaging
- (16:45-17:00) **OT16** - **Meng Wang** - Elemental and molecular Imaging of the boron drug BPA in the tissue sections of tumor bearing mice using LA-ICP-MS and DESI-MS

(18:00-19:00) **Boat trip starting** (Korenlei)

(19:00-23:00) **Belgian evening** (St. Peter's Abbey)

Thursday July 4th 2024

(08:30-09:00) **KL3** - **Keynote lecture 3 by Dr. Alicia Cruz-Uribe**: Prospects and challenges for in situ beta decay geochronology by MC-ICP-MS/MS

(09:00-10:00) **Session 5 chaired by Dr. Alicia Cruz-Uribe – Fundamentals isotopic analysis**:

- (09:00-09:15) **OT17** - **Michael J. Pribil** - Multiple Sulfur Isotope Ratios by LA MC-ICP-MS and LA MC-ICP-MS/MS: Unraveling Minerals at the Micron Scale
- (09:15-09:30) **OT18** - **Enrico Cannaò** - In-situ B and Ti isotopes in amphibole: a new potential geochemical tool
- (09:30-09:45) **OT19** - **Stijn Glorie** - In situ molybdenite and shale Re-Os geochronology: a comparison of reaction gasses
- (09:45-10:00) **OT20** - **Fabien Pointurier** - Implementation of laser ablation – ICPMS coupling for isotopic analysis of uranium micro-particles

(10:00-10:30) **Coffee break**

(10:30-12:00) **Session 6 chaired by Dr. Amy J. Managh – Fundamentals qualitative and quantitative elemental and isotopic mapping:**

- (10:30-10:45) **OT21** - **Nathan T. Westwood** - The application of LA-ICP-MC-MS for quantified, high spatial resolution imaging of Pb-Pb isotope ratios in ferromanganese crusts
- (10:45-11:00) **OT22** - **Dany Savard** - Advances on 3D-mapping by fs-LA-ICP-TOF-MS: quality assessment for the analysis of melt inclusions in Hawaiian olivine
- (11:00-11:15) **OT23** - **Yoshiaki Kon** - Mineral liberation analysis using LA-ICPMS
- (11:15-11:30) **OT24** - **Iker Basabe Mendizabal** - Towards 1,000 pixels/s acquisition rate for elemental mapping via LA-ICP-MS
- (11:30-11:45) **OT25** - **Kharmen Billimoria** - Improving calibration standards for LA-ICP-MS bioimaging
- (11:45-12:00) **OT26** - **Pascal Becker** - Fossilization of Leaves for Quantitative Bio-Imaging using LA-ICP-TOFMS

(12:00-13:30) **Lunch break:**

- (12:40-13:20) **Lunch break seminar 2 by Elemental Scientific Lasers** (lecture room A, 1st floor) Advancements from ESL in the field of super-fast elemental imaging by LA-ICP-MS, LIBS and LIBS-ICP-MS
- (12:40-13:20) **Lunch break seminar 3 by Teledyne Photon Machines** (lecture room B, 1st floor) Significant scientific advances made by the laser ablation community in the last year – a discussion of published examples

(13:30-14:00) **KL4** - **Keynote lecture 4 by Prof. dr. Jorge Pisonero**: Pros and Cons of LA-ICP-MS for fast, sensitive and high-spatially resolved elemental mapping of challenging samples

(14:00-15:00) **Session 7 chaired by Prof. dr. Jorge Pisonero – Applications in Geology, Archaeology, Earth & Planetary Sciences (part A)**

- (14:00-14:15) **OT27** - **Andreas Riedo** - Towards the flight design and concept of operations of the CLPS- LIMS systems for NASAs Artemis program
- (14:15-14:30) **OT28** - **Piers Larkman -** Effective data collection for large area mapping: insights from polar ice cores
- (14:30-14:45) **OT29** - **Ivan Belousov** - Deconvolution of mixed LA ICPMS signals and quantification of trace element compositions of microinclusions in minerals
- (14:45-15:00) **OT30** - **Markus Wälle** - Boron isotope ratio analysis of Cu-bearing tourmaline by LA-ICP-TOF-MS for origin determination

(15:00-16:05) **Poster session 2 + coffee break:**

- **PP34** - **Elisabeth Foels** - How to assess limits of detection for single-cell elemental bioimaging by LA-ICP-MS

- **PP35 - David Loibnegger** - LA-ICP-TOFMS imaging reveals Pt(IV)-drug bioaccumulation in tumor tissue at the single-cell level
- **PP36 - Hugo Louet** - Development of LA-ICP-MS analysis for quantitative elemental mapping in dendrochemistry
- **PP37 - Jeffrey Oalmann** - Comparing methods for quantifying elemental images obtained by quadrupole and time-of-flight LA-ICP-MS
- **PP38 - Daniel A. Frick** - Pseudo-Isotope Ratios by LA-ICP-OES for Sea Surface Temperature Reconstruction
- **PP39 - Stefan Wagner** - In situ mapping of elemental dissolution at ultra-trace levels during aqueous corrosion of Al alloys
- **PP40 - Jay Thompson** - False signals: quantification issues of trace Si in non-silicate minerals by LA-ICP-MS
- **PP41 - Adrien Vezinet** - Concurrent determination of Sr-isotope signature and trace elements contents of depleted glasses via laser ablation split stream: Pros and Cons Of Different Approaches
- **PP42 - Herbert Siegmund** - Analysis of ultra-fast transient signals by LA-MC-ICPMS – overcoming instrumental limitations
- **PP43 - Ciprian Stremtan** - In-situ, simultaneous measurement of oxygen and carbon isotope ratios via LA IRMS – study case on inorganic carbonates
- **PP44 - Ciprian Stremtan** - Laser ablation IRMS analysis of **δ**13C in creep affected Picea abies from Făgăraș Mountains, Romania
- **PP45 - Claire Aupart** - Trace elements in quartz: a tool for sediment provenance
- **PP46 - Fatima Zohra Bouhdayad** - Late Neogene ENSO variability in the SE Pacific recorded in bivalve shells through Laser Ablation ICP-MS
- **PP47 - Stepan Chernonozhkin** - Probing the evolution of primitive achondrite parent bodies: insights from LA-ICP-MS analysis of silicate minerals
- **PP48 - Helmut Ernstberger** - Automated High Throughput Analysis of Rare Earth Elements in Large Batches of Mining Discovery Samples by LA-ICP-MS
- **PP49 - Isabelle Genot** - Multi-element analyses of silicate glasses using a femtosecond laser ablation system coupled to an ICP-MS/MS
- **PP50 - Pamela Guttiérrez** - S isotopic analyses of S-bearing compounds using a femtosecond laser ablation system coupled to an ICP-MS/MS
- **PP51 - Youn-Joong Jeong** - Imaging of Geological sample by fs LA-ICP-MS with ARIS
- **PP52 - Nathan Miller** - Utility of LA-ICP-MS methods for reconstructing hydroclimate from stalagmite and cave monitoring archives
- **PP53 - Ségolène Rabin** - High-resolution in situ Fe isotope measurements of Belgian micrometeorites by femtosecond laser ablation MC-ICP-MS
- **PP54 - Lorenzo Tavazzani** - Synthesising homogeneous calcium carbonate reference materials for in situ determination of U–Pb and Sr isotopes
- **PP55 - Massimo Tiepolo** - Historical trends of metal pollution in the metropolitan area of Milano, Italy: a combined dendro-chemical, dendro-magnetic and dendro-XRD approach
- **PP56 - Maarten Van Brussel** - Advancements in Isotope Analysis for Geochronology: Integrating MS/MS and Laser Ablation
- **PP57 - Róbert Arató** - Graphite LIBS analysis: Opportunities for elemental mapping and multivariate classification
- **PP58 - Kengo Ito** - Ilmenite age determination using LA-ICP-MS technique

- **PP59** - **Remi Dallmayr** - New cryogenic ablation cell technology for high sample throughput impurity mapping in ice-cores with LA-ICP-MS
- **PP60- David Douglas** - SelfSeal technology-based open-cell laser ablation system for trace elements analysis of full-size archaeological artefacts: application on historical Chinese enamelled copperware
- **PP61** - **Ashlea Wainwright** - Comparing interference removal tools for in situ analysis of 87Sr/86Sr in bioapatite
- **PP62 - C. Derrick Quarles Jr. -** Understanding the Elemental Composition of SEI and CEI Layers in Li-Ion Batteries
- **PP63** - **Alban Moradell-Casellas** - Fast analysis of trace elements and lithium isotopy by LA-(MC)-ICP-MS for the traceability of lithium in the battery supply chain
- **PP64** - **Petr Rudolf** - Development of the LA-ICP-MS method for liquid analysis
- **PP65** - **Agnieszka Stoklosa** - LA-ICP-MS Calibration Strategy to Investigate the Ion Transport in Concrete

(16:05-16:30) **UT2 - Upcoming talent award presentation 2 by Dr. Sota Niki**: Online multiple-isotope analysis of individual nanoparticles generated through femtosecond laser ablation

(16:30-17:00) **Session 8 chaired by Dr. Sota Niki – Applications in Geology, Archaeology, Earth & Planetary Sciences (part B):**

- (16:30-16:45) **OT31** - **Pim Kaskes** - Blasting dinosaurs in Brussels: new µXRF and LA-ICP-MS setup to unravel the origin of fossil bonebeds
- (16:45-17:00) **OT32** - **Robert Anczkiewicz** - Deducing Upper Paleolithic woolly mammoth mobility patterns with high spatial resolution trace element, O and Sr isotope analyses

(19:00-…) **Gala dinner and laser party** (Old Fish Market, Rekelingestraat 5, 9000 Ghent)

Friday July 5th 2024

(09:00-9:30) **KL5 - Keynote lecture 5 by Dr. Vassilia Zorba**: Advancing Ultrafast Laser Ablation Sampling: From Femtosecond Filamentation to GHz Bursts of Ultrafast Laser Pulses.

(09:30-10:00) **Session 9 chaired by Dr. Vassilia Zorba – Fundamentals tandem multi-sensor techniques**:

- (09:30-09:45) **OT33** - **Jakob Willner** - Acquisition parameter optimization for single pulse resolved simultaneous LA-Q-ICP-MS multielement analysis
- (09:45-10:00) **OT34** - **Benjamin T. Manard** - Utilization of Laser-Based Sampling for High-Throughput Particle Analysis

(10:00-10:30) **Coffee break**

(10:30-12:00) **Session 10 chaired by Dr. ir. Thibaut Van Acker – Fundamentals data processing, standardization and applications in Material & Industrial Sciences:**

- (10:30-10:45) **OT35** - **Salome Gruchola** - Exploring On-Board Data Reduction Techniques for Improved Space Mission Returns
- (10:45-11:00) **OT36** - **Keith MacRenaris** - LA-ICP-TOF-MS Imaging in Reproductive Biology: Elemental Changes as a Marker for Fibrosis and Infertility in AIRE Deficient Male Mice
- (11:00-11:15) **OT37** - **Claude Molitor** - Introducing a general cell membrane marker for bioimaging with LA-ICP-(TOF)MS
- (11:15-11:30) **OT38** - **Lena Michaliszyn** - Improved Quantification of Solid Samples using LA-ICP-MS with Standard Addition and Isotope Dilution: A Promising New Technique
- (11:30-11:45) **OT39 - Yuan Shang -** Application of in-situ Laser Ablation ICP-MS analysis in developing geochemical fingerprints to trace cobalt and nickel along the battery value chain
- (11:45-12:00) **OT40** - **Christoph Walkner** - Two approaches for elucidating the origin of non-metallic inclusions in steels using LA-ICP-MS

(12:00-12:30) **Closing and award ceremony**

(12:30-13:30) **Farewell lunch**

	Monday	**Tuesday**	**Wednesday**	**Thursday**	**Friday**
8:00 – 8:30			Pick-up badges and conference bags	Pick-up badges and conference bags	
8:30 – 9:00			Keynote lecture Martin Šala	Keynote lecture Alicia Cruz-Uribe	
9:00 – 9:30			S1: Fundamentals laser-matter interaction	S5: Fundamentals isotopic analysis	Keynote lecture Vassilia Zorba
9:30 – 10:00					S9: Fund. multi-sens. techniques
10:00 – 10:30			Coffee break	Coffee break	Coffee break
10:30 – 11:00			S2: Fundamentals particle formation, transport phenomena and standardization	S6: Fundamentals qualitative and quantitative elemental/isotopic mapping	S10: Fund. data processing, standardization and Apps. Material & Industrial Sciences
11:00 – 11:30					
11:30 – 12:00					
12:00 – 12:30			Lunch break (12.00-13:30)	Lunch break (12.00-13:30)	Closing + award ceremony
12:30 – 13:00			Lunch break seminar TOFWERK (12:40-13:20)	Lunch break seminars ESL and Teledyne Photon Machines (12:40-13:20)	Farewell lunch
13:00 – 13:30					
13:30 – 14:00	TOFWERK + Teledyne workshop @A&MS (Campus Sterre, S12)	Nu Instruments Lab Demo @A&MS (Campus Sterre, S12)	Keynote lecture Gunda Koellensperger	Keynote lecture Jorge Pisonero	
14:00 – 14:30			S3: Applications Biology, Medicine, Life Sciences (A)	S7: Applications Geology, Archaeology, Earth & Planetary Sciences (A)	
14:30 – 15:00					
15:00 – 15:30			Poster session 1 + coffee break	Poster session 2 + coffee break	
15:30 – 16:00					
16:00 – 16:30		Pick-up badges and conference bags	S4: Applications Biology, Medicine, Life Sciences (B)	S8: Applications Geology, Archaeology, Earth & Planetary Sciences (B)	
16:30 – 17:00					
17:00 – 17:30		Opening ceremony			
17:30 – 18:00		Opening lecture Detlef Günther			
18:00 – 18:30		Invited lecture Takafumi Hirata	Boat trip (Korenlei)		
18:30 – 19:00		Ice breaker reception			
19:00+			Belgian evening (St. Peter's Abbey)	Gala diner (Old Fish Market)	

Revisiting our Understanding of Laser Ablation-ICPMS

Pascal Becker, Dylan Käser, Tobias Schoeberl, Gunnar Schwarz, Joachim Koch, Bodo Hattendorf, Detlef Günther*

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The prerequisites for accurate laser ablation sampling are well defined – 100% particle formation of the ablated material, 100 % aerosol transport at any given distance between ablation chamber and ICP, 100 % vaporization, atomization and ionization at a single point and no diffusion within the plasma, constant ion extraction, constant counting of ions on the detector. Some of the shortcomings in the processes above have been mentioned in the first paper by Gray in 1985 [1] and several fundamental aspects have been extensively studied ever since.

The literature contains information about laser wavelengths and their influence on particle size distribution, aerosol expansion, laser pulse duration and fluence requirements, the ablation cell geometry and size, suitable transport tube materials, the ICP plasma optimization and size limits for complete vaporization of laser-generated particles, various possible gas combinations and their influence on aerosol transport efficiency and recommendations for various available mass analyzers.

Are some of those results, observations, and assumption from the past still valid today? Our instrumentation has changed significantly and due to advanced technology, the capabilities of LA- ICP-MS improved.

Yet: Do we have a sufficient understanding of the relevant processes affecting the final outcome of LA-ICPMS analyses? How comparable are particle formation and transport processes for different materials (and LA-setups)? What governs the vaporization of the aerosol inside the ICP? How much differences do we observe for different aerosol transport systems?

Currently a vast majority of LA-ICPMS applications relies on a very limited set of calibration materials (NIST SRM 61X) while the breadth of current topics in LA-ICPMS certainly requires a better understanding of the aforementioned processes, also to assist in the development of calibration strategies.

Some of these aspects will be revisited and discussed in the presentation.

[1] A. Gray, *Analyst*, 1985, 110, 551-556

Laser Ablation for Molecular Analysis

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Laser ablation (LA) is emerging as a powerful method for the sampling of both elements and molecules. The LA technique is not only practical for solid sampling in a gaseous medium (*e.g.* elemental analysis by LA-ICP-MS), but also in liquids, *i.e.*, laser ablation in liquid (LAL) [1]. Recently, *in situ* and rapid analysis of organic compounds using a combination of LAL sampling and electrospray ionisation mass spectrometry (ESI-MS) was described [2]. LAL is a technique that allows laser ablation of a solid material which is immersed in liquids, allowing for organic compounds from the solid material to be extracted into the liquid medium. The resulting sample solution was directly introduced into ESI-MS to be analysed, without the need for any chromatographic separation. With LAL-ESI-MS, water-soluble and non-soluble compounds were successfully detected, which is one of the great advantages over the conventional liquid extraction surface analysis technique (LESA).

Another important application of the LA technique is the sensitive imaging analysis for both elements and molecules. The laser ablation sampling technique is typically combined to inductively coupled plasma mass spectrometry (ICP-MS), which is a sensitive and quantitative analytical tool for elemental mapping of various solids. Despite its advantages, the ICP is so powerful that no species information on the introduced molecules remains, which is a major drawback in environmental and biochemical studies. To overcome this, we are trying to develop a new ion source to couple with LA for organic mass spectrometry. For elemental analysis, "hard ionisation" using ICP ion sources is required to improve quantification; whereas for biomolecular analysis, "soft ionisation" is required to reduce fragmentation of the biomolecules. Our group developed a low-temperature plasma ion source utilising dielectric barrier discharge (DBDI). One main advantage of this ion source is that the plasma can accept and ionise components in the dry sample aerosols produced through LA. Through our preliminary results, we found that $[M–H]^+$ base peaks (the strongest ion signal in a mass spectrum) were obtained for most of amino acids and vitamins, indicating that molecules could be ionised with minimal fragmentation [3]. By combining ICP with the developed ion source, simultaneous imaging analysis of elements and biomolecules can be made from the identical ablation pits through a split-flow technique into the respective ion sources. LA was used for sampling, DBDI-MS and ICP-MS, in parallel with each other, were used for ion detection. In this presentation, basic principles of the laser ablation technique and several applications for the analysis of both elements and molecules will be demonstrated. The laser ablation is for lack of a better word, perfect.

[1] Okabayashi et al., *J. Anal. Atom. Spectrom.*, 2011, 26, 1393-1400.
[2] Hirata et al., *Mass Spectrometry*, 2023, 12, A0121.
[3] Khoo et al., *Metallom. Res.*, 2022, 1, 44-54.

Beyond Conventional Calibration: Advancing LA-ICP-MS Methodologies

Martin Šala[1], Kristina Mervič[1,2], Ana Jerše[1], Sarah Theiner[3], Andreas Schweikert[3], Gunda Köllensperger[3], Martin Schaier[3], Dino Metarapi[1], Johannes T. Van Elteren[1], Vid S. Šelih[1]

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In recent years, remarkable progress has been made in enhancing the throughput, sensitivity, and image quality of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Despite these advancements, precise quantification remains a challenge due to the reliance on matrix-matched standards, which are often difficult to procure. In response to this challenge, our laboratory has devised two novel approaches aimed at improving quantification in LA-ICP-MS analysis.

The emergence of Inductively Coupled Plasma Time-of-Flight Mass Spectrometry (ICP-TOFMS) systems enables simultaneous measurement of all nuclides, prompting the development of a semi-quantitative calibration protocol. This innovative approach facilitates the measurement of nuclides even in the absence of suitable standards with the certified values for the nuclides in question, thereby overcoming limitations associated with traditional calibration methods.

Essential for the accurate calibration in LA-ICP-MS is the matching of material ablated by the laser during analysis. Our alternative approach involves signal correction based on the volume ablated, as determined in a separate experiment. This method ensures precise quantification even in the absence of matrix-matched standards, provided that laser fluences are appropriately adjusted.

Both methodologies will be comprehensively discussed, highlighting their respective advantages and contributions towards addressing the challenges of quantification in LA-ICP-MS analysis.

We aim to demonstrate that these innovative approaches represent significant progress in advancing LA-ICP-MS methodologies, bringing us closer to achieving more robust and reliable analytical results.

[1] Analytical Chemistry, 2023, 95, 19, 7804–7812
[2] Talanta, Volume 269, 1 March 2024, 125379
[3] Talanta, Volume 271, 1 May 2024, 125712

Why go shorter? Design and Rationale of a Dual-Wavelength (157 & 193 nm) Cryo-LA-ICP-MS/MS System (1)

Wolfgang Müller[1,2,*], Tobias Erhardt[1,2], C. Ashley Norris[3], Michael Shelley[4], Linda Marko[1,2], Alexander Schmidt[1,2], Ruben Rittberger[1,2]

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Over the past ~30 years laser-ablation plasma mass spectrometry (LA-ICPMS) has arguably become the most commonly-applied and versatile technique for spatially-resolved elemental and isotopic analysis, at both ultra-trace concentration levels and high-precision, respectively, for a large variety of materials and thus applications. Notable developments for LA included the gradual decrease in laser wavelength from IR to deep-UV wavelengths and the move from ns to fs pulse lengths, besides important developments in LA cell design in order to reduce signal washout while maintaining flexibility in sample size [1]. Excimer lasers, utilizing ArF and thus operating at 193 nm, have by now become something akin to an LA community standard due to their superior per- formance for a vast range of materials combined with relative ease of use, but solid-state lasers at 213 nm still represent an alternative, despite drawbacks for common materials, such as carbonates. However, there is an even shorter excimer laser wavelength at 157 nm, using F2, that has received very little attention over the last ~25 years, with very few exceptions (e.g. [2]). There are very good reasons for this situation, namely the ~10-fold lower energy output of laser sources at 157 vs. 193 nm combined with strong attenuation of 157 nm radiation in air and at optics, making 157 nm LA technically challenging. However, there are equally good reasons *for* using LA at 157 nm, namely the ~20 % higher photon energy at 157 vs 193 nm (7.9 vs. 6.4 eV) that facilitates better bond- breaking during laser-matter interaction and, perhaps even more importantly, the improved absorption at 157 vs. 193 nm for some materials.

Here, we present our attempt of rekindling 157 nm LA. We have established a custom-designed Dual-Wavelength LA System featuring two separate laser sources that operate at 157 nm and 193 nm, respectively, based overall on a modified RESOlution SE LA system. Given that one of our main applications represents direct ablation of glacial ice to retrieve dust aerosol compositions, it also includes a 2nd generation cryo-holder compatible with the S-155 Laurin LA cell that will hold nearly 50 cm of ice core length. The rationale for ice ablation at 157 nm lies in the >8 orders of magnitude greater absorption at 157 nm than at 193 nm [3], which should result in significantly improved ablation of ice at this shorter wavelength. After an evaluation of the pros and cons we have opted for a dedicated laser for each wavelength rather than one excimer laser source operated at either of the two wavelengths, following a gas exchange. While technically possible, routine operation and durability arguments counter the use of just one laser source. Overall, our system design is modular, allows the 157-193 nm changeover with minimal hardware modifications and facilitates direct experimental comparison between the two wavelengths.

[1] Sylvester, P. J. and Jackson, S. E. *Elements*, 2016, **12,** 307-310.
[2] Telouk, P., Rose-Koga, E. F. and Albarede, F. *Geostandards Newsletter*, 2003, **27,** 5-11.
[3] Warren, S. G. and Brandt, R. E. *Journal of Geophysical Research,* 2008, **113,** D14220.

Initial Performance of a Dual-Wavelength (157 & 193 nm) Cryo–LA–ICP–MS/MS System (2)

Tobias Erhardt*[1,2], C. Ashley Norris[3], Linda Marko[1,2], Mike Shelley[4], Alexander Schmidt[1,2],
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Over the past decades, LA–ICP–MS has gradually moved towards short UV and DUV wavelengths to overcome poor absorption of longer-wavelength light by some minerals. 193 nm (ArF) excimer lasers are now commonly used to ablate a wide range of geological or environmental samples to achieve spatially resolved chemical or isotopic analysis. However, some materials such as quartz, carbonates, sulphates, fluorides or water ice can exhibit poor or uncontrolled ablation at DUV, posing the need for ablation at even shorter wavelengths [1]. Even though a few initial studies (i.e. [2, 3]) have been made using 157 nm (F2) VUV excimer lasers for LA–ICP–MS, no systematic comparisons with the more commonly used 193 nm wavelength have been made so far.

Here, we present initial results of a comparative study of the ablation characteristics of a range of materials that are typically challenging to ablate at 193 nm. These materials comprise quartz with different trace impurities, carbonate minerals such as calcite and aragonite or fluoride. Additionally, we will present results from the more transparent NIST612, 614 and 616 SRMs as well as fused silica alongside NIST610, MPI-DING glasses or apatite. Our custom-designed dual- wavelength (157 & 193 nm) LA–ICP–MS system is well-suited in facilitating such comparisons, because the key LA parts such as LA and optical design remain the same, and only a small number of components need to be exchanged in order to switch between the two wavelengths.

To assess the ablation characteristics of these materials at the two wavelengths we determine some key LA parameters such as the fluence threshold for ablation, the ablation rates at different laser fluence, crater morphologies as well as the extent of down-hole elemental fractionation for common volatile/refractory element pairs such as Pb/U, Bi/Th. Corresponding results will be presented.

[1] Müller, W., & Fietzke, J. (2016). Elements, 12(5), 329-334.
[2] Russo, R. E., Mao, X. L., Borisov, O. V., & Liu, H. (2000). Journal of Analytical Atomic Spectrometry, 15(9), 1115-1120.
[3] Tanner, D., Henley, R. W., Mavrogenes, J. A., & Holden, P. (2013). Contributions to Mineralogy and Petrology, 166, 1119-1142.

Ablating the transparent: testing femtosecond laser ablation ICP-MS in the UV absorption dead zone of ice

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LA-ICP-MS analysis of trace element concentrations in ice cores is attracting increasing interest due to high-profile international efforts to obtain the very oldest ice from the base of the Antarctic ice sheet where high spatial resolution analyses are essential. Different groups have achieved effective ablation on ice cores with 193 nm wavelength nanosecond lasers [1,2], although fluence must be increased by one order of magnitude at 213 nm wavelength [3]. The ablation characteristics of ice in the UV range are highly variable: measurements of the absorption characteristics of pure ice show a steep flank and wide minimum between 200 and 400 nm (Figure). In our pilot study we explored if a femtosecond laser can effectively ablate ice at a wavelength that falls within this absorption dead zone. We used a femtosecond laser ablation ICP-MS system (fsLA-ICP-MS), operating at 257 nm (Teledyne Photon Machines Excite Pharos). Ablation was highly effective and more consistent than with the high fluence ablation used at 213nm with nanosecond lasers. This illustrates the benefit of femtosecond ablation but also raises questions regarding potential differences in the absorption spectrum of actual glacier ice vs. pure ice. The ablation characteristics of fsLA does not appear to be affected by variable impurity content: we tested polar ice ranging from relatively dust- rich ice from Greenland to trace-level impurity Antarctic ice, as well as artificial ice, which all ablated cleanly at moderate energy output of the laser. Detailed imaging of impurity distribution within the ice matrix was possible, promising similar data quality as achieved with nanosecond lasers. This pilot work potentially opens another avenue of research in LA-ICP-MS ice core analysis and highlights the potential of fsLA for achieving ablation in transparent materials.

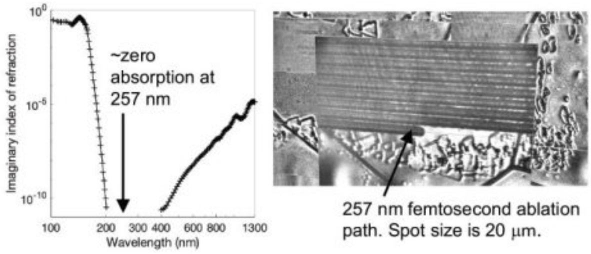

Figure: (Left) Imaginary part of the index of refraction of pure ice [4] implies that pure ice should be effectively transparent to 257 nm wavelength radiation; (Right) Screenshot showing clean, symmetrical ablation of polar ice with a 257 nm wavelength femtosecond laser.

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Laser-induced heating onto solid materials through annealing of fossil fission tracks

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Laser ablation (LA) coupled with ICP mass spectrometry is one of the principal techniques for *in situ* elemental and isotopic analysis. A short-pulsed high-power laser beam is focused onto a sample surface, and the laser beam converts the solid materials instantaneously into their vapor phases. Both the shorter wavelengths and shorter pulse-durations of the laser beam result in both the production of finer sample particles and smaller contribution of heat load onto the solid materials. For the quantitative analysis of volatile elements including He and Pb, the LA-induced evaporation of them from the surrounding area of the LA pit is a critical problem. This is especially serious in the elemental/isotopic analysis for high- to low-temperature thermochronometry with the combination of U– Pb, and (U – Th)/He or fission-track (FT) methods which require He extraction and U and Pb determinations from solid materials. Thus, great care must be given in small magnitude of the heat load onto the solid samples. This study demonstrates the effective approach to evaluate the contribution of the LA-induced heat load through annealing of FTs on apatite crystals. Fission-track method is widely used for dating of various U-bearing minerals such as zircon, titanite, apatite, or monazite. Among them, the apatite FT system is particularly important because of the low closure temperature (e.g., 100–150 ºC). This suggests that the FTs present in apatite can disappear through small magnitude of heat load. We take this feature as a sensitive sensor for evaluating the laser-induced heat load onto the solid materials. The apatite crystal used to monitor FTs was a FC1 (1.1 Gy old-Duluth Complex, US) having the highest fossil FT density [1]. Changes of the FT densities around the LA pits were monitored from laser pits produced through the different number of laser shots with constant laser system setup and energy fluence (i.e., wavelength of 260 nm, pulse duration of 200 fs, ablation pit size of 10 µm, repetition rate of 60 kHz, and fluence of 3.8 $\mathrm{Jcm^{-2}}$). The photomicrograph images of the FTs obtained after the laser ablation of 1,000, 2,000 and 3,000 shots are given in Fig. 1. Results showing the different magnitudes of annealing; the FTs around the laser pit produced after 3,000 shots were completely annealed in an area of about 20 µm. Based on the annealing kinetics, the total annealing of the FTs in apatite can occur when heating over 600 ºC for <1 s was achieved [2]. The present study demonstrates clearly that laser-induced heating can occur even with the femtosecond laser ablation. In this presentation, effect of fluence, laser wavelength, and pulse duration will be discussed.

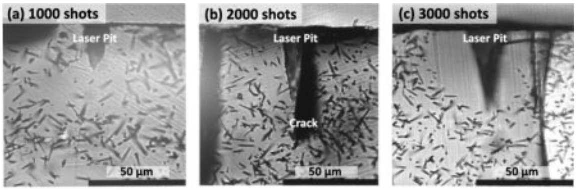

Figure 1 Effect of laser-induced annealing of fossil fission-track

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Ablation effects in nitrogen for LA-N_2-MICAP-MS

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Helium was established as ablation environment for LA-ICP-MS by the end of the 1990s, when it was shown that it enabled a signal increase up to a factor of 3 as compared to argon.[1] Further studies using other carrier gases were not possible due to the low tolerance of the argon plasma towards different gas compositions. Various gas mixtures have been tested in the past but only a minor fraction of ablation environment could be varied without altering the plasma stability. The addition of nitrogen into the ICP was previously shown to cause a signal enhancement but was mainly related to the plasma as a smaller effect was observed when nitrogen was mixed in the ablation cell.[2]

For the direct comparison of different ablation environments, the optimal gas flow needs to be introduced into the plasma without plasma extinction. The tolerance of the Nitrogen Microwave Inductively Coupled Atmospheric-Pressure Plasma (N_2-MICAP) now enables the evaluation of the ablation effects for different carrier gases. A previous study showed the quantification capabilities of this novel plasma source in helium,[3] but nitrogen as new ablation environment still needed to be characterized.

The results obtained using nitrogen as carrier gas were compared to helium and argon which could be used as known benchmarks from previous studies for the comparison of the figures of merit.[1] Complementary experiments such as microscopy was used to determine the aerosol deposition on the sample surface. Particle size distribution measurements will also be used to highlight key differences in the particle formation in the diatomic gas. Furthermore, the effect of various laser parameters such as the fluence and crater size were investigated for the different ablation environments. This detailed characterization of nitrogen as carrier gas allowed to better understand to what extent this gas could be used as an alternative to helium for LA-MICAP-MS.

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Analysis of Mechanism for Generation of Ions and Particles via Laser Ablation in Liquid (LAL) Technique using ICP mass spectrometry

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Laser ablation in liquid (LAL) is a method of generating nanoparticles through laser ablation of solid materials within a liquid media. The laser induced sample particles are directly collected in the solvent with minimal loss [1]. In recent years, the LAL method has attracted attention because of its capability for generating the metastable particles that are difficult to synthesize through conventional methods [2], suggesting that the LAL process is basically based on kinetic process. In fact, several organic compounds (molecules) can be successfully sampled by the LAL technique [3]. Moreover, our preliminary experiments revealed that ions of constituting elements were also present in liquid media through the LAL technique. Interesting point is that abundance ratios and oxidation status of the elements could be preserved through the LAL procedures. These findings indicate that the sampling mechanism of the LAL technique is still sketchy, and thus, detailed elemental analysis of both ionic components and individual particles produced through the LAL technique is highly desired. To do this, elemental analysis was conducted by ICP mass spectrometry combined with ion chromatography (IC-ICP-MS) and single particle ICP time-of flight mass spectrometry (sp-ICP-TOF-MS).

First experiment is conducted to test possible elemental fractionation through the LAL sampling by monitoring the elemental ratios of the individual solid particles using ICP-TOF-MS (Vitesse, Nu Instruments, Wrexham, UK). Several Fe-bearing minerals (e.g., olivine, pyrite, or magnetite) were subsidized to the analysis. For the pyrite (FeS_2) samples, Fe/(Fe+S) ratios for individual particles exhibits bimodal distribution, suggesting that the particles could be produced through at least two different processes with different contributions of crushing, evaporation, condensation, and crystallisation.

One may consider that the gaseous elements are highly reactive, and some of the evaporated components present in a cavitation bubble can be dissolved into solvents (hence deionised water). To test this, ionic components obtained through the LAL technique were also analysed using IC- ICP-MS (ICS-6000 DC, Thermo Fisher Scientific, Bremen, Germany; iCAP TQ, Thermo Fisher Scientific, Bremen, Germany). In naturally occurring minerals, Fe could present mainly as two valences (+2 and +3). In this study, not only abundances but also oxidation states of Fe in liquid media were investigated by IC-ICP-MS. As for pyrite (FeS_2), Fe ions present in liquid media were +2, suggesting that the oxidation status of Fe was preserved through the LAL sampling. In contrast, for olivine, Fe ions present in liquid media were +3. This indicate that Fe in olivine was nearly completely oxidised through the LAL technique. In this presentation, we will discuss production processes for both ions and sample particles through the LAL process.

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A novel sample preparation and calibration approach for nanoparticle analysis using laser ablation single particle- ICP MS

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Nanoparticles find diverse applications across a wide range of fields owing to the unique physicochemical properties exhibited by materials at the nanoscale [1] [2]. Accurate characterization of nanoparticles is crucial for both material manufacturing and assessing their environmental and human health impact. For this purpose, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has emerged as a crucial analytical tool for nanoparticle analysis [1]. However, traditional SP-ICP-MS, designed for nanoparticles in suspension, presents challenges related to sample stability, sample introduction efficiency, and potential spectral interferences from the suspension medium.

To overcome these limitations, it is possible to use solid sample analysis with laser ablation as the sampling technique [2] [3]. This method brings essential advantages to nanoparticle analysis, allowing for sizing and counting directly within a solid matrix. Moreover, it preserves embedded nanoparticles without altering their size and composition. Similar to conventional SP-ICP-MS, laser ablation SP-ICP-MS requires nanoparticle standards for signal calibration.

This study focused on creating nanoparticle dispersions within polymer matrices using a spin coating method. The primary goal was to achieve a uniform distribution of isolated nanoparticles within the resulting polymer thin film, preventing particle agglomeration. The spin coating approach offers the distinct advantage of producing even and consistently thin polymer films. These films can serve as standards for signal calibration when a specified quantity of solute analyte is added, and a precise film area with a defined thickness is ablated. The investigation explored the impact of different sample preparation procedures and the effects of laser energy during the ablation process and aimed to analyze the size distributions of nanoparticles.

Quadrupole ICP-MS was employed for analyzing nanoparticles consisting of a single element, while time-of-flight ICP-MS was utilized for multi-element nanoparticles. The findings from this study aim to contribute to the ongoing development of laser ablation SP-ICP-MS techniques.

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Quantitative protein bioimaging in individual cells by LA- ICP-MS; labelling with ruthenium red and metal nanoparticles

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The integration of laser ablation (LA) with ICP-MS enables the acquisition of compositional images not only of biological tissues but also of individual cells. While endogenous elements can be directly measured by LA-ICP-MS, the analysis of biomolecules requires proper labelling with detectable tags. However, two main challenges hinder the determination of target biomolecules within individual cells: (i) the high sensitivity required, and (ii) the lack of a universally accepted method for quantitative analysis, hindering the bioimaging of protein concentrations within cellular structures.

Regarding sensitivity, metal nanoclusters (MNCs) have emerged as highly promising tags for the determination of proteins due to their small size (below 3 nm) which prevents blocking of the recognition unit, and the high signal amplification provided. On the other hand, several approaches have been proposed for quantifying different analytes in cells (e.g., endogenous or exogenous metals, nanoparticles – NPs, biomolecules) by LA-ICP-MS. Authors have addressed this issue by using in-house calibration standards that aim to replicate the cellular matrix, such as gelatins, nitrocellulose membranes, or rhodamine microdroplets [1]. Isotope dilution has been also employed for determining AuNP in cells. Lores-Padin et al. achieved a fully matrix-matched calibration by using the same cell line as matrix and standards [2]. However, methods directly allowing for the determination of cell volume with the direct analysis of cells by LA-ICP-MS, and thus the bioimaging of analyte concentration in the cells beyond just mass, are still lacking.

This lecture will present an innovative method for determining the distribution and concentration of specific proteins within individual cells using LA-ICP-MS. A specific antibody tagged with AuNCs, each composed of several hundred Au atoms, was employed to label the target protein, while ruthenium red (RR) was used to label the cell membrane. As a proof of concept, the protein CYP1B1 was studied in ARPE-19 human cells derived from the retina pigment epithelium under pro-oxidative stress induced by AAPH treatment, alongside control conditions. By combining a metal–tagged immunoprobe (antibody:AuNCs) with RR labelling, it becomes possible to simultaneous analyze a specific protein and the cell volume in each cell. Consequently, quantitative images of specific proteins within individual cells can be acquired.

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Advancing Quantitative Mapping of Biogenic Carbonate Matrices with LA-ICP-TOF-MS

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Laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS) has evolved into a well-stablished micro-analytical technique for elemental mapping across a diverse variety of solid samples and applicable in multiple research fields, ranging from geology to biomedical investigations. Nonetheless, concerns are still focused on the inherent limitations associated with matrix effects and elemental fractionation that obstacles to achieving accurate results and reliable quantification. The necessity to investigate and address these challenges is a pivotal task to be carried out in order to upgrade LA-ICP-MS to the status of the benchmark technique for quantitative elemental mapping applications at low-µm spatial resolution [1].

To cope with these challenges, the broadly applied strategy of using external calibration based on matrix-matched certified reference materials (CRMs) is considered the most suitable approach. Nevertheless, the lack of CRMs for most sample types (especially those of environmental or biological origin) compromises its applicability. Thus, this leads to a situation where customized laboratory-prepared standards must be developed. Different methods and/or protocols that in the end cannot be fully reproducible to be well-established and comparable in laboratories worldwide.

In this study, comprehensive efforts were undertaken to characterize and assess a novel set of reference materials based on a $CaCO_3$ matrix, specifically nanoparticulate powder pressed pellets (NP-pellets) from MyStandards GmbH. In this context the use LA-ICP-TOF-MS allows to conduct a fast, quasi-simultaneous and multi-elemental study, first, carrying out homogeneity tests (i.e., different laser spot sizes or different ablated regions) as well as performing a cross-quantification using both NIST SRMS 61X series glass and others CaCO3 reference materials. Additionally, the investigation included an assessment of the necessity for internal standardization (^{43}Ca). In a last step and as a proof-of-concept, different biogenic carbonate matrices, e.g., otoliths and mussel shells, were analyzed using the same instrumental set-up alongside the novel set of NP-pellets employed as reference materials for quantitative mapping. This methodology enabled quantitative mapping of multi-elemental distributions within the samples under investigation.

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LA-MC-ICPMS analysis of Cu isotopes in biological material

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Stable metal isotopes receive increasing attention as medical biomarkers due to their potential to detect changes of the metal metabolism related to disease. Potential mechanisms causing isotope fractionation include biological processes that involve redox- or bond-forming reactions and interaction of metals during transmembrane import and export. In order to advance our understanding of the underlying processes responsible for isotope fractionation between normal and diseased cells, we need *in situ*, spatially resolved methods. Despite its frequent use, laser ablation - multi-collector - inductively coupled plasma mass spectrometry (LA-MC-ICPMS) analysis of biological material is severely limited by the scarcity of matrix-matched standards. Such matrix-matched standards are necessary to correct for instrumental sources of isotope fractionation such as particle size distribution, ablation physics and differential ionization.

Copper stable isotopes have proven to be a particularly powerful tool to identify differences in isotope composition between tumors and healthy tissue suggesting application in cancer diagnosis [1, 2]. To further our knowledge of Cu isotope fractionation processes induced by diseases we have developed gelatin-based bracketing standards allowing to correct instrumentally induced isotope fractionation during LA-MC-ICPMS analysis. Since gelatin properties resemble properties of protein-rich cellular material, they mimic biological matrices and their ablation behaviour. Hence, gelatin standards are spiked with known amounts of Cu stable isotopes of a known Cu isotope composition and used as matrix-matched bracketing standard. A Ni reference solution was aspirated to the plasma to allow for mass bias correction and laser energy densities were below the glass ablation threshold. The method achieved reproducibilities of better than 0.10‰ (2SD) for inorganic reference materials and reproducibilities of better than 0.17‰ (2SD) for biological reference materials. The developed routine is tested on biomedical samples and the *in situ* Cu isotope data will be presented.

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LA-ICP-TOF-MS – the essential tool for spatial single cell metallomics

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The concepts of single cell analysis and spatial omics are at the forefront of bioanalytical research. Spatial single cell metallomics is only emerging, targeting mechanistic studies on metal bioaccumulation. (e.g. as a result of metal exposure). In our lab, we combine quantitative metal imaging at single cell level with the successful concept of imaging mass cytometry. The aim is to unravel metal bioaccumulation in the tissue context of phenotypically characterized cell consortia. Our workflow (MeXpose) integrates several existing methodological components such as calibration approaches, technicalities regarding the LA-ICP-TOF-MS measurements and metal- based immunohistochemistry. MeXpose comes paired with a new end-to-end image analysis pipeline for statistical and quantitative analysis. The lecture will showcase the power of MeXpose in toxicity studies and studies on metal based drug development.

Unraveling cobalt skin permeation and cellular interactions: Novel insights from LA-ICP-TOFMS imaging

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Allergic contact dermatitis is a common form of allergy caused by metals, such as cobalt (Co), in which an immune response is triggered when ions penetrate the skin's barrier [1]. With society's increasing focus on sustainability, the demand for Co and subsequent occupational exposure is expected to rise [2]. Thus, it is crucial to fully assess the potential effects of dermal exposure to Co, which is considered a potential carcinogen [3]. LA-ICP-TOFMS imaging has the potential to provide new insights into this important research area. For this purpose, we studied FFPE sections of *ex vivo* human skin that have been treated with cobalt chloride ($CoCl_2$) and cobalt nanoparticles (Co-NP). Following staining with a panel of 15 metal-conjugated antibodies, the samples were analyzed using LA-ICP-TOFMS. For the first time, a study of Co permeation in human skin has included the quantification of metal uptake by single cells in the tissue, along with their spatial distribution and phenotypic characterization. Results show that Co significantly penetrates beyond the stratum corneum and accumulates in keratinocytes, particularly mitotic basal cells, causing increased DNA damage. Deposition of Co is also observed in vascular cells, raising concerns about the potential for systemic circulation and organ damage. In comparison to $CoCl_2$, Co-NP showed a lower penetration potential but higher affinity for keratin-rich regions such as the stratum corneum or hair follicles. LA-ICP-TOFMS proves valuable for characterizing exogenous metals in skin, offering insights into Co allergy mechanisms and toxicity.

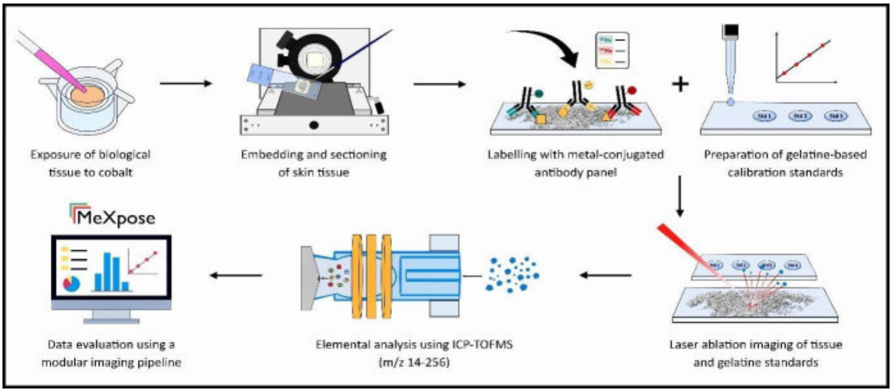

Figure 1: Schematic workflow for the analysis of *ex vivo* human skin by LA-ICP-TOFMS imaging

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Can metallomic imaging of TNBC tissues help predict the NACT response?

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Investigating the metallomic profile of biological tissues has received significant interest in diagnosis and understanding many diseases including metal metabolism and cancer[1]. This is understandable given 1/3 of all enzymes and proteins encompass a metal as an essential component[2]. 10-15% of all breast cancers are triple-negative (TNBC) and are both highly aggressive and challenging to treat[3].

Here we have a unique tissue collection from TNBC positive patients before they have received routine neoadjuvant chemotherapy (NACT) and clinical data relating to their response to treatment. Serial sections were obtained for several imaging modalities including metallomic imaging using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), protein and cell expression with imaging mass cytometry, spatial transcriptomics and molecular fingerprinting with vibrational spectroscopy and molecular mass spectrometry. All these modalities have been combined to understand tissue state and whether these data considered alone or in combination can help predict whether patients will respond to routine NACT. This has clear translational benefits given the damaging effects of chemotherapy and the cost implications to the health care provider. For this presentation we will focus on the metallomic data and how key metals (Mg, Mn, Fe, Cu, Zn) which are known to be essential in cancer are distributed. To our knowledge this is the largest cohort of cancer patients to be investigated with any elemental imaging technology with currently almost 100-patient tissues imaged. We will cover the technical details and challenges of longitudinal imaging projects (over 2 years) and the analyses implemented, including registration, deep learning, and neural networks for state predictions.

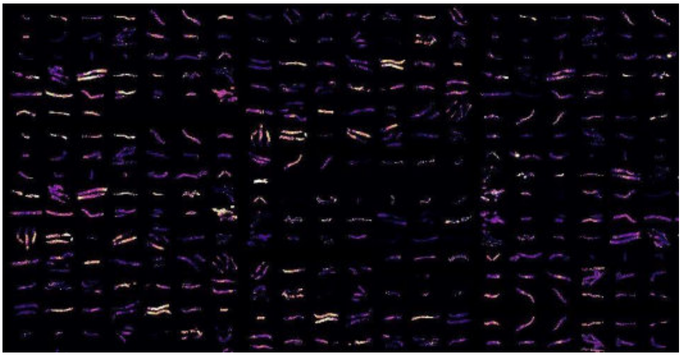

Figure 1. LA-ICP-MS images (multiple elements shown) of TNBC patient samples highlighting the enormous scale of elemental imaging performed.

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Laser ablation ICP-ToF-MS to investigate the interaction of MRI contrast agents the extracellular matrix components

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Non-specific Gd-based contrast agents (GBCAs) have long been routinely used in clinical magnetic resonance imaging (MRI). However, the interaction of such contrast agents with tissue components is not yet fully understood.

Alongside cells, the extracellular matrix (ECM) is an important component of mammalian tissue. It is a three-dimensional network of macromolecules that provides structural and biochemical support to the surrounding cells. Many diseases, including inflammation, fibrosis, and tumour invasion, are associated with characteristic ECM changes. The ECM consists of structural proteins (e.g., collagen, elastin) and proteoglycans, which are composed of glycosaminoglycans (GAGs) covalently linked to a protein core. GAGs are long, linear polysaccharides consisting of repeated disaccharide units widely varying in molecular mass, disaccharide structure, and sulfation degree. Characteristic of GAGs is their ability to form complexes with cations such as lanthanides. Thus, GAGs could be a potential binding partner for GBCA molecules as a whole or for dechelated Gd.

Currently, there are still many unanswered questions about the interaction of contrast agents with ECM components. This study therefore investigated the uptake and distribution of different GBCAs in spheroids that mimic biological tissue and have different ECM expressions.

Chinese hamster ovary (CHO) cells and GAG-depleted CRL-2242 cells were used to prepare spheroids. These were then incubated for several minutes with gadolinium chloride and various linear and macrocyclic GBCAs. Cryosections of the spheroids were used for imaging measurements with a low-dispersion laser ablation system coupled to an inductively coupled plasma time-of-flight mass spectrometer (LA/ICP-ToF-MS). Gelatine doped with multi-element solutions was used for matrix-matched quantification of Gd and other relevant elements such as Cu, Fe and Zn.

Although all spheroids were incubated with identical Gd concentrations, significant differences in the amount of Gd taken up were observed. Gadolinium chloride is absorbed more strongly than the contrast agents and accumulates mainly in the outer regions of the spheroids. In contrast, after incubation with the linear and macrocyclic contrast agents, Gd is detected in the interior of both types of spheroids.

LA/ICP-ToF-MS is a powerful technique to study the uptake and distribution of GBCAs and thus can make an important contribution to a better understanding of the relationship between the affinity of MRI imaging probes and ECM components such as GAGs. However, further studies are needed to elucidate such complex interactions, also using other (bio)analytical techniques.

Nano-savers for Ischemic stroke? Investigation using a combination of CT and LA-ICP-MS

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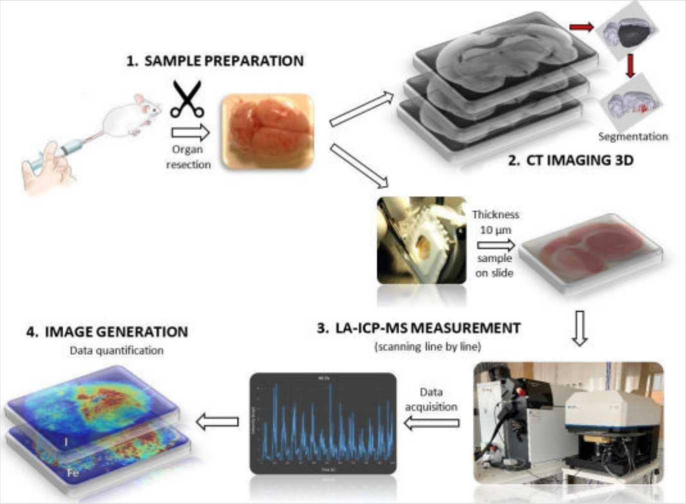
In the last decades, increased interest in imaging of elements/metals/proteins distribution of tissues, mainly in pharmaceutical, biomedicine research, or life science with direct application of research to specific problem/disease [1-3].



As WHO data indicates, cerebrovascular events are one of the main causes of mortality in developed nations. The key to success is time (as short as possible). Biodegradable iodinated nanoparticles (IoNPs) could be an invaluable addition to the existing contrast agents used in medicine.

A complete investigation into the pharmacokinetics and dynamics of IoNPs is essential to address this issue. With the combination of CT (computed tomography) and LA-ICP-MS imaging, this comprehensive evaluation verifies the treatment strategy's overall success, positioning LA-ICP-MS as a potential "gold standard" imaging method for researching and applying IoNPs in theranostics.

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Correcting Ablated Mass Differences in 2D LA-ICP-MS Mapping through Ablation Volume-Assisted Calibration

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2D LA-ICP-MS elemental mapping has undergone important developments in the last decade, leading to higher spatial resolution (and improved image quality) and faster mapping speed. However, obtaining quantitative data remains a challenge as the recorded signal often does not provide a complete representation of the sample composition. This is primarily due to problems related to elemental fractionation, such as non-stoichiometric effects during vaporization, transport, atomization, and ionization of the ablated particles in the plasma. In addition, matrix-dependent ablation rates contribute to variations in the ablated mass. Therefore, the quantification of elemental maps of laser ablation usually entails the use of matrix-matched standards in combination with internal standardization. However, suitable matrix-matched standards are scarce, and obtaining homogeneously distributed internal standards is rarely practical. Thus, we focused on compensating for differences in ablation rates within the sample as well as between the sample and the standards. This was achieved by normalizing the element maps based on the corresponding ablation volume per pixel measured with a 3D optical interferometer. We implemented the volume- corrected calibration approach for LA-ICP-MS quantification of elemental concentrations, focusing specifically on eight major, minor and trace elements in a decorative glass known as Murrina. SRMNIST610 and 612 were used as standards for calibration. The effectiveness of this approach was validated by complementary techniques, including scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDXS) and laser ablation with sum normalization calibration.

The results showed that calibration using the ablation volume leads to a more reliable quantification of elemental concentrations in 2D LA-ICP-MS maps. This innovative approach not only addresses the challenges associated with elemental fractionation and matrix-dependent ablation rates, but also provides a practical solution when conventional methods, such as matrix-matched standards and homogeneous internal standards, have their limitations. Validation of this method by multiple techniques underlines its robustness and its potential to improve the accuracy and precision of element quantification in 2D LA-ICP-MS analyzes.

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Laser ablation-atmospheric pressure chemical ionization- time of flight-mass spectrometry for molecular imaging

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Postionization methods enable the hyphenation of laser ablation (LA) and molecular mass spectrometry. These techniques offer the potential to expand the scope of LA applications compared to laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) by preserving molecular sample information.[1] Simultaneous analysis of analytes is made possible by time of flight-mass spectrometry (TOF-MS), a technique commonly employed for molecular analysis. These approaches also offer the advantage of enabling the imaging of native samples, addressing a primary limitation of matrix-assisted laser desorption/ionization (MALDI-MS).[1] Atmospheric pressure chemical ionization (APCI) is well suited for this purpose, as it is already a well-established ionization method that is used to ionize the dried aerosol of liquid samples. Due to the original design for liquid samples, the development of a suitable sample introduction system and the optimization of various parameters is necessary to allow for higher analysis speed and higher signal intensities in molecular imaging.

Different designs for the sample introduction system into the APCI source were developed and tested regarding their impact on the achievable signal intensities and the washout behavior of the system. For each of the designs, the influence of the nebulizer gas, the dry gas and the gas flows of the LA system was evaluated. These optimizations were based on gelatine thin sections spiked with a selection of analytes, which were ablated in a standardized manner. Experiments were performed using a 213 nm laser ablation system coupled to a TOF-MS. Tablets sold as nutritional supplements, containing amino acids and vitamins, were used as samples for imaging experiments to determine the impact of these optimizations.

The optional nebulizer gas flow used to augment the sample flow was determined to lead to an inferior washout behavior and was therefore disregarded. Optimal settings were found for a sample introduction system that is able to direct the sample into the space in front of the corona discharge needle without letting the aerosol expand into the APCI chamber. Using this setup at low gas flows from the LA leads to faster washout of the analytes and much improved intensities. Most amino acids and vitamins in the tablets were identified based on their exact mass, showing various distinct distributions that matched with features visible on the surface of the tablet. Clear signs of slow washout behavior could be mitigated due to the optimized parameters, which allows for higher ablation speed and therefore faster analysis times.

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Elemental and molecular Imaging of the boron drug BPA in the tissue sections of tumor bearing mice using LA-ICP-MS and DESI-MS

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Boron Neutron Capture Therapy (BNCT) is a binary radiotherapy modality that allows selective cancer treatment at the cellular level. In BNCT, boron drugs (usually enriched in boron-10) are delivered and accumulated in cancer cells; He-4 nuclei (alpha particles) and recoiling Li-7 nuclei, generated by neutron irradiation as a result of the nuclear reaction between neutrons and boron-10 isotopes, can precisely kill the cancer cells because these high-energy nuclei interact within a short range (~10 μm), specifically within a single cell.

The success of BNCT relies on the targeted delivery and high accumulation of boron drugs in cancer cells, achieving a high tumor-to-normal cell ratio (T/N ratio). However, available methods face many challenges, including the difficulty in accurate determination of the T/N ratio.

In this study, we use laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) and desorption electrospray ionization-mass spectrometry (DESI-MS) to study the distribution, metabolism, and quantification of an FDA-approved boron drug (p-Boronophenylalanine, BPA) in tumor-bearing mice. The LA-ICP-MS and DESI-MS images yielded identical T/N ratios of BPA. The developed method is capable of in-situ imaging of BPA and its metabolites and obtaining an accurate T/N ratio. The developed method is expected to be used to evaluate tumor targeting in the development of new generation drugs.

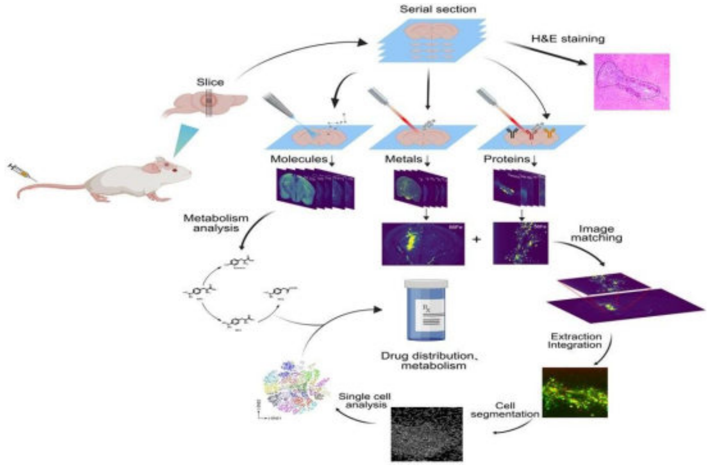

Figure. Schematic diagram of imaging of tumor-bearing mice with LA-ICP-MS and DESI-MS

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Prospects and challenges for in situ beta decay geochronology by MC-ICP-MS/MS

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The development of tandem mass spectrometers equipped with collision cells has enabled online interference removal for ICP-MS, with special attention paid to beta decay systems used for geochronology (e.g., Rb-Sr, Lu-Hf). The addition of pre-cell mass filters and collision cells for multicollector mass spectrometry has recently been utilized to constrain single laser spot Rb-Sr isochron dates in biotite with unprecedented precision [1]. This technique opens up avenues for campaign-style Rb-Sr geochronology, and adds a powerful new tool for constraining the chronologic history of rocks in many tectonic settings over a broad range of spatial and temporal scales.

Static multicollection from ^{85}Rb to mass-shifted ^{88}Sr^{19}F utilizing the Thermo Scientific™ Neoma™ MC-ICP-MS/MS coupled to an ESL™ imageGEO™193 excimer laser-ablation system enables the recovery of significant age information from individual integrations within single laser spot analyses. These data reveal single spot isochrons - some with multiple isochronous populations - from multiple orogenic belts. The high-precision simultaneous isotope measurement approach on the Neoma™ enables determination of distinct initial ^{87}Sr/^{86}Sr ratios based on the fit of individual isochrons within single laser spots, which is assisted by the use of 10^{11} and 10^{13} ohm amplifiers on Faraday cups. The large range of Rb/Sr ratios in micas opens up a new microsampling frontier for isochron-based geochronology that will transform our approach to unraveling continent-scale tectonic processes over Earth's history. Two extensive datasets from these efforts demonstrate punctuated geochronologic events not captured by other chronometers, suggesting the ability to uncover previously hidden thermal and fluid events using our approach.

Looking toward the future, the prospects for utilizing LA-MC-ICP-MS/MS for geochronology will expand the geochronologic toolbox beyond traditional accessory phase geochronology. For example, initial successes employing single collector MS/MS machines for *in situ* Lu-Hf analyses open the door for vastly improved precision by LA-MC-ICP-MS/MS, particularly on the Hf isotope ratio in low-Hf phases such as apatite and garnet. In addition, simultaneous LIBS analyses have the potential to provide major and trace element information in real time, further augmenting the *in situ* approach to petrochronology.

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Multiple Sulfur Isotope Ratios by LA MC-ICP-MS and LA MC-ICP-MS/MS: Unraveling Minerals at the Micron Scale

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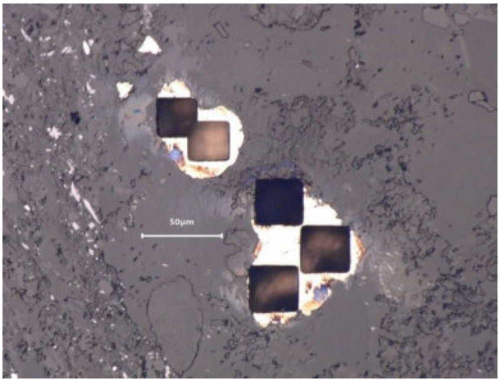
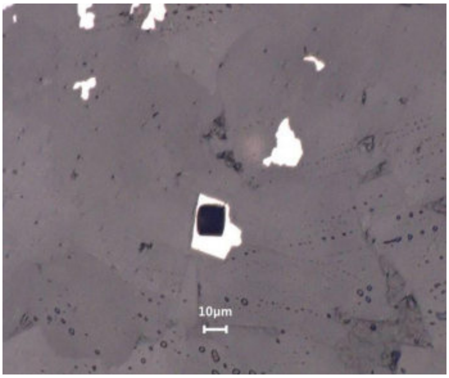
Recent improvements in aerosol transport efficiency and instrument sensitivity for multiple sulfur isotope measurements using a laser ablation (LA) system coupled to a Nu Instruments NP3 multicollector inductively coupled plasma mass spectrometer provide the ability to increase spatial resolution and precision for *in situ* measurements. High spatial resolution *in situ* measurements for multiple S isotopes (Δ^{33}S, evaluating mass independent fractionation (MIF)) down to 10 µm spot size and mass dependent fractionation (MDF) applying δ^{34}S at 3 to 5 µm spot size provide the opportunity to reveal complexities previously concealed at lower resolution or larger spot sizes on the order of 40 to 65 µm. *In situ* S isotope measurements using a NP3 MC-ICP-MS requires pseudo-high mass resolution instrument operation due to O2 isobaric interference which reduces the instrument sensitivity significantly with respect to low mass resolution operation. The recent addition of collision/reaction cell to MC-ICP-MS (Nu Instrument Sapphire MC-ICP-MS/MS) instruments offers the ability to measure S isotope ratios in low mass resolution allowing to increase the spatial resolution even more. We will present data collected from recent *in situ* measurements of S multiple isotope ratio using reference materials, previously analyzed samples measured by conventional DI-IRMS, as well as younger (non- Neoarchean) geological samples exhibiting Δ^{33}S MIF to better understand geological processes and S cycling.



Pyrite analyses at 30 µm spots



Pyrite analyses at 10 µm spot

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In-situ B and Ti isotopes in amphibole: a new potential geochemical tool

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Amphibole is a common mineral of the Earth's lithosphere capable of incorporating significant amounts of volatiles (H, F, Cl) and incompatible elements. It is considered a key component in rocks characterized by fluid circulation or in hydrous melts. Amphibole has a wide pressure- temperature stability field and often shows chemical zonation in response to multiple petrogenetic events. Among stable isotope systematics that can be analyzed in amphibole, those of B ($\delta^{11}B$) and Ti ($\delta^{49}Ti$) are the most promising. Boron is a fluid mobile element, and its isotopes are widely used to trace fluid-mediated Earth's processes from surface to deep interiors due to its large mass dependent isotope fractionation. It is present in low concentration in amphibole, from few to tens of µg/g. Titanium is a major element in Ca-amphibole from mantle environments (up to 6 wt.%), its presence is mainly related to the oxo-component $^{O(3)}O^{2-}$, and stable Ti isotope systematic is a reliable tracer of Earth's processes, with mainly applications related to magma differentiation and continental crust formation [1]. Therefore, we propose that the coupling of *in-situ* $\delta^{11}B$ and $\delta^{49}Ti$ can be used to disclose geological processes taking advantage of the fluid-mobile nature of B and the hydrous fluid-immobility of Ti. So far, precise B and Ti isotope signatures have been achieved on whole-rocks and mineral separates [1-2] and little is known about *in-situ* B and Ti isotope determination in amphibole [3].

Here, we provide a pilot project aimed to developing an analytical protocol to determine the *in-situ* $\delta^{11}B$ and $\delta^{49}Ti$ in amphiboles via LA-MC-ICP-MS and to provide suitable reference materials, which are mandatory in the sample-standard bracketing approach. Our *in-situ* results report an internal precision (2SE) of ± 1.5‰ for $\delta^{11}B$ at ca. 5 µg/g level (135-150 µm spot size), and better of ± 0.20‰ for $\delta^{49}Ti$ for amphibole with ca. 5.5 wt% of $TiO2$ (85 µm spot size). External reproducibility (2SD) is commonly better than ± 3.0‰ and 0.2‰ for $\delta^{11}B$ and $\delta^{49}Ti$, respectively. The proposed LA-MC-ICP-MS procedure allows to achieve adequately precise and accurate B and Ti isotope data for amphiboles, opening new avenues for micro-analytical research for a better understand fluid-mediated geological processes.

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In situ molybdenite and shale Re-Os geochronology: a comparison of reaction gasses

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Re-Os isotopic analysis is fundamental to establishing the geochronological architecture of sedimentary processes and ore mineralisation. Being a β-decay chronometer, the method cannot be applied on traditional LA-ICP-MS instrumentation. However, the introduction of reaction-cell mass-spectrometry has recently led to the development of *in situ* Re-Os geochronology by LA- ICP-MS/MS. The published *in situ* method has been demonstrated for molybdenite and is based on the reaction of ^{187}Os with CH_4 gas to form $^{187+14}OsCH_2^+$ at a significantly higher rate than the equivalent $^{187+14}ReCH_2^+$ reaction [1,2]. However, the isobaric interference of $^{187+14}ReCH_2^+$ on $^{187+14}OsCH_2^+$ can be very high (exceeding 50%), especially for young samples.

In this study we pilot *in situ* Re-Os geochronology to organic shales, which generally has much lower Re concentrations than molybdenite. In order to boost sensitivity, we use higher repetition rates and laser fluence, and add H_2 in the reaction cell. Additionally, He can be added to suppresses the Re interference. However, He also buffers $OsCH_2^+$ reaction and introduces mass-bias, requiring additional corrections.

We recently discovered that similar signal sensitivity can be achieved by reacting Os with N_2O to form $^{187+64}OsO_4^+$ reaction products. The advantage of this approach is that the isobaric interference of Re onto OsO_4^+ is ca. 3× smaller compared to the Re interference on $OsCH_2^+$. Moreover, when He is added in the reaction cell, the Re interference can be almost eliminated. However, shales often contain significant REEs that also react with N_2O, requiring a $REEO_4^+$ interference correction. Adding H_2 in the reaction cell induces Os-hydroxide production with more complex mass-shifts at lower sensitivity.

Hence, the optimal protocol is highly dependent on the sample of interest. While CH_4+H_2(±He) in the reaction cell allows the highest sensitivity, it also requires the largest interference correction, making it possibly unsuitable for dating younger (< early Palaeozoic) samples. N_2O+He appears to consistently produce the most accurate results for dating shales and is especially powerful for dating young samples.

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Implementation of laser ablation – ICPMS coupling for isotopic analysis of uranium micro-particles

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As part of its nuclear forensics and non-proliferation programs, the analytical chemistry unit of CEA's Military Applications Division (Bruyères-le-Châtel site, France) is developing analytical techniques and methods to characterize nuclear materials in order to determine their use, origin and industrial history. One of the key observables is the isotopic composition of uranium.

This isotopic characterization is usually performed by dissolving a significant mass of uranium (in the mg – g range) and then measuring a dilute fraction of the resulting solution using an ICPMS. However, this method generates radioactive chemical effluents and presents risks of contamination of instruments and exposure of personnel. What's more, carrying out dissolution operations in a controlled area increases the analysis time.

To provide a rapid response with reduced constraints, the laboratory has developed a direct isotope analysis method using a UV-nanosecond laser ablation device coupled with a multi-collector ICPMS (Thermo-Scientific "Neptune Plus") [1-3]. Only a few micrometric fragments, taken from the surface of the nuclear materials, are introduced into the ablation chamber and analyzed.

In this paper, we present the developed methodology and the results obtained from uranium micro- particles certified in isotopic composition and particles from unknown nuclear materials as part of an international nuclear forensics exercise. These performances will be compared with those of other methods used in the laboratory, such as isotopic measurement by liquid ICPMS after dissolution of mg of uranium, and particle-scale measurement by large-geometry secondary ion mass spectrometry (LG-SIMS). The results obtained by laser ablation-ICPMS coupling are in good agreement with these reference techniques. We also discuss the current limitations of the technique and possible solutions to overcome them.

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The application of LA-ICP-MC-MS for quantified, high spatial resolution imaging of Pb-Pb isotope ratios in ferromanganese crusts

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The low detection limits, near-full mass range coverage, and wide linear dynamic range of inductively coupled plasma-mass spectrometry (ICP-MS) combined with in-situ sampling by laser ablation (LA) provides a powerful tool for chemical mapping. Recently, there has been a proliferation of advances in both LA and ICP-MS instrumentation, as well as the introduction of accessories [1] which have helped improve the interfacing between the two. These developments were predominantly driven by demand for high spatial resolution, higher throughput imaging in the biosciences typically using time-of-flight or quadrupole ICP-MS platforms. Comparatively less attention has been paid to characterising these technologies for quantified imaging of geoscientific samples, particularly when using multi-collector ICP-(MC)-MS systems.

This study focuses on the application of modern LA-ICP-(MC)-MS technology for high precision imaging of discrete Pb-Pb domains in ferromanganese crusts, identified in the previous works of Josso et al [2]. Elemental and isotope ratio data were acquired using 193 nm LA systems, coupled to a ICP-(MC)-MS using low dispersion, high-efficiency transport accessories (*e.g.*, DCI, TwoVol2- and TwoVol3- ablation chambers). Several data collection parameters were investigated between experiments to optimise the balance between image quality, data quality, and sample throughput. These parameters included laser repetition rates, translation speed, spot size, fluence and integration times. Data reduction, processing, and generation of the final images was achieved using the post data collection processing package Iolite4 [3].

The results of this study focus on the detailed characterisation of a series of Pb isotope ratio imaging methods for complex samples previously unapproachable by earlier generation technology. Identification and quantification of the uncertainty components inherent to data of this nature has been performed, along with quantification of the true spatial resolution of the data acquired using differing approaches. The capability of modern map interrogation tools (*e.g.,* regions of interest and transects) for the extraction and representation of data directly from LA-ICP-(MC)-MS images has been documented.

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Advances on 3D-mapping by fs-LA-ICP-TOF-MS: quality assessment for the analysis of melt inclusions in Hawaiian olivine

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Compared to single-static spot analysis by LA-ICP-MS, and line-scan mode, the quantitative 2D mapping of multiple minerals at the micrometer-scale can reveal unequaled information, such as the element distribution in the mineralogy of the studied sample, zonation within single grains, and can also be helpful for micrometer-size mineral identification [1]. Mapping by LA-ICP-MS can be time consuming but recent development using time-of-flight ICP-MS (ICP-TOF-MS) and a laser ablation (LA) system, equipped with a fast-funnel (for rapid transfer of the aerosol), has demonstrated that fast-quantitative mapping of large areas (3 x 5 mm) can proceed on a daily basis [2]. This new method also involves efficient data reduction of multiple phases based on mineral recognition and normalization using the 3D-Traces-Elements data reduction scheme in iolite [3]. However, information provided from 2D-mapping is limited to the observed surface. In some cases, when small particles, such as trapped melt inclusions, are present in minerals, they may lie a few micrometers below the surface thus rending them inaccessible. The destructive nature of laser ablation has the advantage to remove material from the exposed surface, allowing access to material underneath. In this work, we present a new fully-quantitative 3D-elemental mapping protocol using a ~100µm glassy melt inclusion (MI) hosted in a Hawaiian olivine at a depth of ~120µm as an example. The 3D-map was constructed from 42 successive 2D-maps of 300x300µm, using a 5µm beam. Each map has a thickness of about 5µm, which results in a crater of ~200µm in depth. Fully quantitative analysis was achieved in both the host olivine and the melt inclusion and are in good agreement with data from the literature, thus demonstrating the ability to reach fully-quantitative analysis at depth. On the femtosecond-laser used on this experiment (J200, Applied Spectra), a fast-funnel is not yet installed, thus the accumulated acquisition time was 10h, but should be improved by a factor of 10x with the newly released Vertex-Tandem High Performance (Vertex-THP) ablation cell (Applied Spectra).

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Mineral liberation analysis using LA-ICPMS

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Mineral liberation analysis (MLA) of ore samples has important implications in mining development. It directly affects the overall efficiency and profitability of mining operations and SEM-EDS based instruments (e.g. QemSCAN) are widely used for MLA[1]. This instrument estimates particles and their approximate mineral species based on backscatter images and identifies mineral species by EDS spectral matching. The resulting mineral map is a two- dimensional (2D) distribution of mineral phases. In recent years, as ore grades have continued to decline, the recovery of trace amounts of valuable elements in ores needs to be improved to optimise resource recovery from low grade ores, but conventional SEM-EDS based instruments have difficulty in detecting trace elements. Therefore, there is a need for an ore evaluation method based on trace element distribution analysis, i.e. a 2D elemental imaging method using LA-ICPMS. We have developed MLA methods that also take into account trace element compositions.

First, 2D elemental imaging of resin-embedded crushed ore samples is performed by LA-ICPMS. A quantitative elemental composition is obtained for each pixel using the 100% normalisation method. To classify each pixel into mineral IDs, a compositional range is defined for each mineral ID and a mineral ID is assigned to each pixel whose elemental composition meets the condition. A particle-grain determination was performed using our own Phyton-based program. If adjacent pixels have the same mineral ID, both pixels are assigned particle IDs in order as the same particle, and if there are adjacent particles, both particles are assigned grain IDs in order as the same grain. The final output of the program is the mineral ID, number of pixels (area), free surface and average composition of each element for each particle comprising each grain. Based on these outputs, an evaluation of the mineral separation contributes to the index.

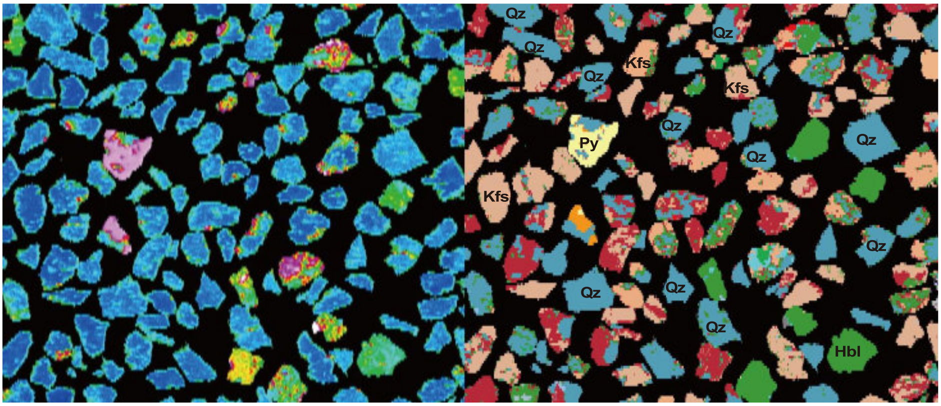

Fig. elemental image (Au) of silicate grains and mineral-ID map

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Towards 1,000 pixels/s acquisition rate for elemental mapping via LA-ICP-MS

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Recent developments in LA-ICP-MS technology such as, novel low-dispersion designs of ablation cells[1] and highly efficient aerosol transport systems[2], have enabled fast elemental mapping at high spatial resolution and its application in various research fields. These days, the fastest low- dispersion setups are capable of producing narrow peak profiles of less than 1 ms duration which enhances the signal-to-noise ratio, boosts the spatial resolution and pixel acquisition rate achievable for elemental mapping applications.

In this work, the analytical performance of a nanosecond 193 nm ArF* excimer-based kHz laser, housed in an Iridia LA-unit with Cobalt ablation chamber and low-dispersion tube-type ablation was evaluated, coupled to a quadrupole-based and TOF-based ICP-mass spectrometer for mono- and multi-elemental mapping with a variety of instrumental setups. Each set up was characterized by single pulse response (SPR) profiles in the range of 100 down to <1 ms duration (defined as full peak width at 10% of the peak maximum, FW0.1M, Figure 1). Parameters such as oxide formation, pulse- to-pulse energy stability, linearity of the signal response, elemental fractionation were evaluated. The duration of the SPR profiles determines the maximum achievable pixel acquisition rate for each instrumental setup. To showcase the capabilities, elemental mapping experiments of mouse liver tissue were performed at 1,000 pixels s^{-1} resulting in an estimated pixel cross-talk of only 10%.

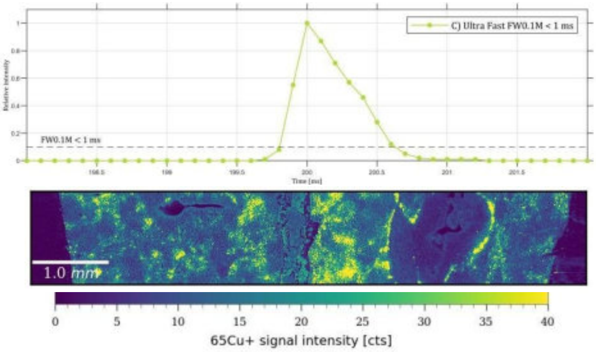

Figure 1. (Top) Average $^{65}Cu^{+}$ SPR profile upon ablation of a gelatin droplet standard and (bottom) $^{65}Cu^{+}$ signal distribution LA-ICP-MS generated at 1,000 pixels s^{-1}.

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Improving calibration standards for LA-ICP-MS bioimaging

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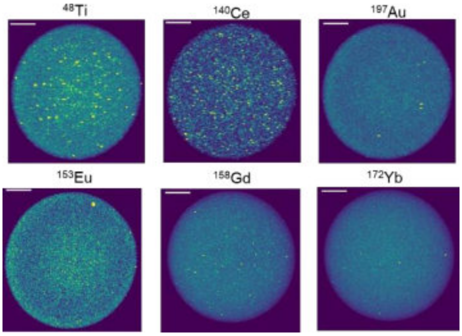
The field of LA-ICP-MS bioimaging has greatly progressed over the last few decades with advances in laser and ICP technology making fast high-resolution mapping of biological tissues and cells possible. Although qualitative imaging data is still relevant to some applications, acquiring absolute concentrations is essential for the purpose of data comparability. Despite increased efforts in the development of calibration standards for biological samples, the limited availability of well characterised calibration standards [1] available to the imaging community is a remaining challenge. As a result, there is a need for multi-element standards that are sufficiently homogenous, easy to use and characterised for batch-to-batch reproducibility and stability.

This work will describe an improved workflow for bioprinting and full metrological characterisation of multi-elemental calibration standards to underpin quantitative LA-ICP-MS bioimaging [2]. A key feature of these calibration standards is the micro-scale homogeneity of the elements within a gelatin matrix across a relatively large area (~1mm^2). This is possible due to adding the elemental spike in the form of nanoparticles. Elements such as titanium, cerium and gold are used to checked daily instrument performance, covering the low, mid and high mass range as well as monitoring oxide formation (cerium oxide). For all three elements average signal intensity varies < 5% across n=9 sub-sampled areas within a standard. The same calibration standards can also be spiked with a mixture of oxide and carbon dot-based nanoparticles for quantification of transition and lanthanide elements, that are of key interest in biological applications. Properties such as elemental composition, homogeneity, stability, thickness and their associated uncertainty will also be described.



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Fossilization of Leaves for Quantitative Bio-Imaging using LA-ICP-TOFMS

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With the emergence of fast washout laser ablation (LA) cells and recent developments of time of flight instruments (TOF), multi-element imaging and quantification have become popular tools in fields such as geology, medicine, biology and material sciences.[1] Since geological samples usually consist of different mineral phases with known stoichiometry, quantification using non- matrix matched standards and internal standardization or 100 wt% normalization has been widely demonstrated. Due to the complexity of biological samples, however, each laser pulse experiences a matrix with a different density and/or with a different absorption behaviour, which cause varying ablation rates and matrix effects. Unfortunately, the major matrix element carbon is not suited as internal standard due to gas phase formation during ablation. Therefore, quantitative imaging of biological material remains a challenge.[2] Recently proposed attempts to use gelatine standards to quantify biological material remains questionable due to gas phase formation of certain elements during ablation of gelatine and still cannot account for varying ablation rates.[3]

In this work, we propose a method for quantitative imaging of leaves of common crops. Through the use of in-vitro fossilization, the biological samples are embedded into a geological matrix, as water in the sample is replaced with silicate. In contrast to drying the samples, the three dimensional structure is preserved and the cells remain intact. This sample preparation procedure allows to use Si as internal standard and glass standards for quantification. In addition, a more controlled and regular ablation behaviour is given.

Based on the proposed sample preparation, various crop leaves were investigated using LA-ICP- TOFMS and some examples for quantitative high spatial resolution imaging will be discussed.

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Pros and Cons of LA-ICP-MS for fast, sensitive and high-spatially resolved elemental mapping of challenging samples.

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Laser Ablation Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) is becoming a well- established method for direct, highly sensitive, and high spatially resolved analysis across various fields such as geology, biology, and material science. Ongoing research and advancements are continuously pushing for the fastest, most precise, and efficient analysis. This includes efforts focused on enhancements like low dispersion setups and cell geometries to exert the finest control over aerosol trajectories and on the development and application of mass spectrometers with high mass-spectra acquisition rates. [1-3]

In this study, we evaluate the pros and cons of different LA-ICP-MS configurations, including the use of ns and fs laser ablation units, and the use of ICP-TOFMS and ICP-SFMS devises, for high spatially resolved analysis of challenging samples, encompassing:

- Determination of multi-elemental distributions in metallurgical samples, including laser-cladding coatings and superalloys.
- Determination of multi-elemental distribution in biological samples, including thin tissue sections from colo-rectal cancer patients.

LA-ICP-SFMS might be applied for fast and high-sensitive mapping of single isotopes; while LA- ICP-TOFMS technology emerges as one of the most compelling analytical approaches for fast multi-elemental mapping. Nevertheless, attention should be paid to limited linear dynamic range, to elimination of polyatomic interference and plasma gas ion signals; and to matrix elements, whose ion signals might saturate the detector. In this sense, different approaches are considered either for qualitative or quantitative mapping analysis.

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Towards the flight design and concept of operations of the CLPS-LIMS systems for NASAs Artemis program

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On February 23rd, 2024 NASA landed successfully its first Commercial Lunar Payload Service (CLPS) mission on the Moon, which represents a true milestone in NASA's Artemis program of lunar research. The University of Bern will deliver through such a CLPS mission no earlier than 2027 its miniature Laser Ablation Ionisation Mass Spectrometric (LIMS) system to the lunar surface. The system will analyse in-situ the chemical composition of the lunar regolith on a grain- by-grain basis. The regolith will be delivered by a sampling delivery system of the lander to the LIMS system's internal sampling handling system [1-2].

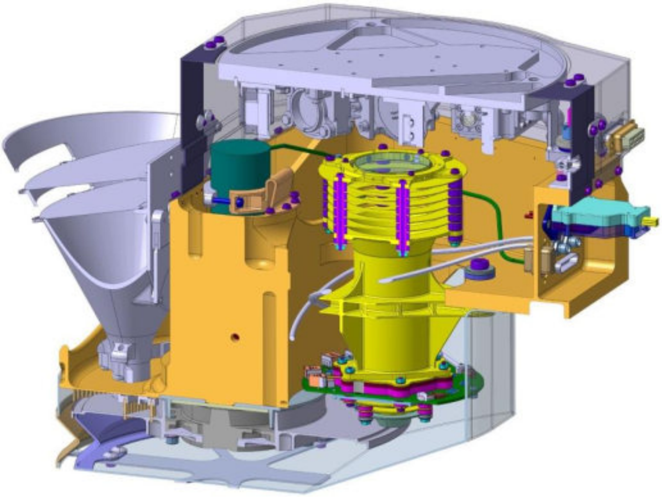

Fig. 1: Current mechanical design of the SpectroMetric Unit (SMU) of UBE's CLPS-LIMS system.

In this contribution, we will present in detail the current design of the LIMS system (see Fig. 1) and its concept of operations, ranging from the delivery of lunar material to the acquisition of mass spectra [1-3]. Moreover, we will focus on the technical challenges in designing and producing such an analytical system, which need to fulfil requirements as specified by NASA's General Environmental Verification Standard, e.g., the requirement that the payload needs of withstand 100 g quasi-static loads. We are on good track and are expecting to receive the first engineering models from the industry mid-2024, which will allow us first tests on representative flight hardware for functionality and performance.

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Effective data collection for large area mapping: insights from polar ice cores

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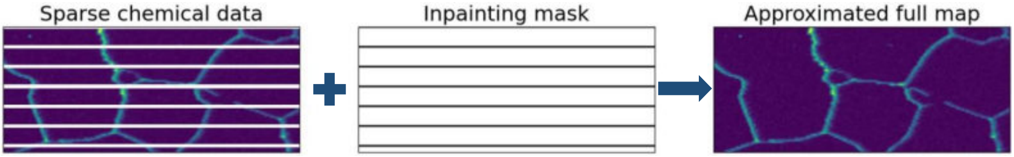
Invaluable and scarce ice extracted from the deepest regions of the Antarctic ice sheet requires high-resolution, ideally non-destructive, analytical techniques to extract information on past climates. These restrictions make high-resolution chemical analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) a valuable tool for the analysis of such ice. Traditionally, climatic information is extracted from ice samples by melting meters of square- centimetre cross-section cuboids of ice, giving a one-dimensional record of the bulk chemistry of the sample. To extract comparable information using LA-ICP-MS, spatial variations in chemical concentrations due to the interactions of the chemistry with the ice matrix must be captured[1]. Single profiles taken along the main axis of the ice core with laser spot sizes of tens or hundreds of micrometres are challenging to interpret as a climate signal due to the spatial heterogeneity of the localised impurities[2]. Additionally, the creation of two-dimensional impurity maps, delivering information on the microstructure-dependent impurity localisation, is limited to centimetre-sized snapshots due to the time taken to perform imaging.

To address these challenges, a procedure to collect and elaborate chemical data from ice cores has been developed to minimise measurement time and resources while collecting representative data. Utilising inpainting[3], guided by optical data representing the ice microstructure, as a post- processing step, this procedure allows sparse LA-ICP-MS profiles and maps to be upscaled to provide more comprehensive coverage of chemical data over the entire samples. This work can also be coupled with a three-dimensional structural model to give insight into bulk impurity concentrations. The experimental and computational procedures, their validation against an ice- sample analogue, and their application to ice samples will be presented. These insights will be crucial for the upcoming analyses of million-year-old Antarctic ice, and can also be transferred to other scientific disciplines and materials.



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Deconvolution of mixed LA ICPMS signals and quantification of trace element compositions of microinclusions in minerals

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Micro-inclusions in minerals are often too small to obtain confident analyses by LA ICPMS, however they may carry valuable information on the conditions of formation of the host minerals in alteration assemblages or on co-crystallising assemblages in magmatic rocks.

Micro-inclusions are often analysed accidentally when analysing host minerals for mineral chemistry or geochronology, however they are commonly excluded from the integration intervals at data reduction stage. The trace element compositions of micro-inclusions can potentially be extracted from mixed analyses, however care should be taken due to differences in matrix effects between the host mineral and micro-inclusions, differences in elements that can be used as internal standards for quantification, and other similar issues.

We present examples of the extracted compositions of micro-inclusions from two different environments. The first is the trace element compositions of apatite inclusions in zircons. The apatite compositions are important when assessing trace element signatures of zircons, as it was shown that co-crystallising apatite and titanite could influence the extents of Ce and Eu anomalies displayed by zircon, and therefore influence estimates of magma oxidation calculated based on zircon compositions [1]. The second is the compositions of rutile and titanite inclusions in chlorite and epidote. The latter two alteration minerals are often used for vectoring and fertility studies during exploration for porphyry Cu deposits with Ti being one of the elements used for vectoring [2]. Therefore, Ti bearing inclusions can affect the vectoring conclusions and are thus excluded from integrations intervals, but their compositions could carry vectoring information as well.

We explore an approach used to de-convolute mixed signals during analysis of framboidal pyrites [3] and an approach that involves utilising individual readings within the LA ICPMS signal to project towards the major element composition of micro-inclusion and to quantify their trace element compositions. We compare our results with the compositions measured independently using EPMA and LA ICPMS on inclusions that were large enough for confident analyses.

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Boron isotope ratio analysis of Cu-bearing tourmaline by LA-ICP-TOF-MS for origin determination

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Blue-to-green-colored Cu-bearing tourmalines have gained substantial popularity in the gem market in the recent years. Often referred to as “Paraiba tourmaline”, they were originally discovered in the late 1980s in Paraiba state, Brazil. Subsequent discoveries of this gemstone in Mozambique and Nigeria have expanded their availability. Due to the market price difference of Brazilian and African material, origin determination of the Cu-bearing tourmaline is often a request to gem testing laboratories. Although multi-element analysis has been found helpful to differentiate various origins [1], additional methods are demanded for improving confidence of the determination. Another potential approach was mentioned by Ludwig et al. [2], where they used SIMS to measure boron isotope ratios and reported a ratio difference of around δ^{11}B 15 ‰ between tourmalines from Brazil and Mozambique [2].

LA-ICP-TOF-MS is a valuable technique for high precision isotope ratios measurement, which is mostly limited by counting statistics [3]. In this study, we will assess the long-term comparability of boron isotope ratio measured by LA-ICP-TOF-MS system at SSEF, and analyze a bigger data set of Paraiba tourmalines as in [2] to evaluate the feasibility of this method for Cu-bearing tourmaline origin determination in a real industrial case.

To achieve long-term precision and data comparability, a suitable standard with high boron concentration and homogeneous boron isotope ratio distribution is required. The boron concentration in our routinely used standards, e.g. NIST 610 (c.a. 350µg/g), is much lower than that in tourmaline (c.a. 3.5wt%). This would introduce an uncertainty of >20 ‰ (1 se) in the boron ratio from standardization with NIST 610 alone compared to an uncertainty of <5 ‰ (1 se) for tourmaline measurements. Standard bracketing with a tourmaline standard while maintaining stable measurement conditions is providing comparable boron isotope ratio values.

Preliminary data indicate that the variation in boron isotope ratios within one country of origin has a bigger spread than the result reported in the literature, leaving this challenging method space for further development. However it provides complementary information to multi-element data in origin determination of Cu-bearing tourmaline.

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Online multiple-isotope analysis of individual nanoparticles generated through femtosecond laser ablation

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Elucidation of the mechanism for elemental fractionation during laser ablation (LA) is key issue for improving the quality of data obtained by laser ablation ICP mass spectrometry (LA-ICP- MS). The elemental fractionation is basically attributed to the process via release of materials as particles and gases by LA and transport of them into ICP. For reducing the magnitude of the elemental fractionation via LA, high efficiency for sampling of materials by LA and transport of the released materials into ICP is desired. This is partly achieved by utilising femtosecond LA (fsLA).[1] With the fsLA systems, the laser energy is effectively used for melting and evaporation of laser-irradiated areas, and most of the resulting fine particles are transported to ICP. These features are important for minimising the elemental fractionation.[2] Despite the advantages of fsLA, measured elemental ratio values can deviate from true values as reflecting different volatilities of analytes (e.g., Zn/Cu).[2] For further investigation on the mechanism of the elemental fractionation through the fsLA process, elemental-ratio analysis of individual nanoparticles generated by fsLA is desired. Faced with this problem, in this study, a new analytical protocol of online multiple-isotope analysis of individual nanoparticles generated by fsLA is developed. The ICP-MS system utilised for the single-particle analysis is high-time-resolution multiple-collector ICP-MS (HTR-MC-ICP-MS) with six pulse-counting ion detectors.[3] The time resolution of each detector is 20 μs, and this is enough shorter than the time duration of the signal events (i.e., 100–500 μs) emanating from the introduction of a single nanoparticle. Hence, simultaneous detection of multiple isotopes can be conducted. The major challenge with the separate analysis of nanoparticles is overlapping of the particle-derived isotope signals. The signal overlaps are avoided through the reduction of particle introduction rates into ICP, and this is achieved by the reduction of ablated volumes. In this study, the ablated volumes were minimised by developing an in-house fsLA system with the spot size of ca. 2 μm (Tandem; Fab Instruments, Tokyo, Japan).

Analysed samples in this study are monazite (rare-earth-element phosphate) references for U–Th–Pb geochronology having known ^{208}Pb/^{232}Th values. Since Pb and Th demonstrate the volatile and refractory signature, respectively, the behaviour of elements with the different volatility via the fsLA process can be elucidated through the determination of ^{208}Pb/^{232}Th for individual nanoparticles produced by fsLA on monazite. Based on the results obtained by the multiple-isotope analysis, the particles can be divided into two types: Pb-bearing particles and Pb- depleted particles. The bimodal compositions indicate that the Pb-bearing particles are condensed from a gaseous phase enriched in volatile elements while the Pb-depleted particles are derived from a molten layer depleted in evaporated elements. The compositional decoupling in terms of individual nanoparticles is the nature of the elemental fractionation via LA.

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Blasting dinosaurs in Brussels: new µXRF and LA-ICP-MS setup to unravel the origin of fossil bonebeds

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High-resolution geochemical techniques have been introduced in the field of vertebrate palaeontology more than 15 years ago, but their applicability remains largely underexplored. In contrast to most modern and archaeological bone remains, pre-Holocene vertebrate bones are often enriched in rare earth elements (REE) linked to diagenetic processes, making them ideal candidates for studying fossilization conditions using micro-X-ray fluorescence (µXRF) and LA-ICP-MS. Here, we present a novel workflow (Fig. 1) to investigate fossil bone material using a combined approach of high-resolution (25 µm) µXRF mapping and LA-ICP-MS profiling, combining the Bruker M4 Tornado µXRF and the newly installed Teledyne Iridia laser ablation system equipped with an Agilent 8900 ICP-QQQ-MS Advanced Applications at AMGC-VUB. We focused on well- preserved dinosaur bone thick sections from (1) a large bonebed of the iconic horned dinosaur *Triceratops* from the Upper Cretaceous of Wyoming (USA) and (2) the famous Bernissart bonebed from the Lower Cretaceous of Belgium, containing 30 skeletons of the duck-billed dinosaur *Iguanodon* currently housed at the Institute of Natural Sciences in Brussels. The LA-ICP-MS set-up applied a fluence of 4 J/cm^2, a repetition rate of 50 Hz, a spot size of 25 µm, and a scan speed of 50 µm/s in fixed dosage mode. The laser signal was optimized for low oxide production and Th/U ratio of ~1 using NIST612. Other certified reference materials include BHVO-1, GSE, BIR, and Durango Apatite, the latter for matrix-matched calibration to quantify Ca, Sc, Mn, Zn, Sr, Y, Ba, REEs, Hf, Pb, Th, and U. The LA-ICP-MS transects (from the outer cortical bone inwards) yielded rapidly declining concentration profiles for all REEs (Fig. 1) throughout the *Triceratops* bonebed, suggesting that the skeletal remains experienced rapid burial with minimal pore-fluid interactions in a river floodplain setting. Combined with well-preserved bone microtextures and local sedimentology, these REE profiles provide independent evidence for a mass mortality event of a group of animals. This hints towards complex social behavior in *Triceratops*, which has not been documented before. These data open many options to study in a rapid manner with limited damage a large number of fossil bone and teeth from museum collections to infer the paleobiology, habitat and fossilization processes of extinct vertebrates through time.

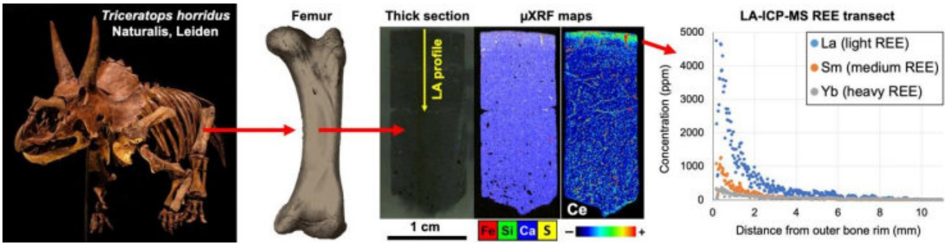

Fig. 1. Workflow based on µXRF and LA-ICP-MS set up at AMGC-VUB, exemplified with a study on *Triceratops*. Longbones were selected for histological thin sections, while the remaining thick sections were mapped by µXRF to screen for diagenesis and to select optimal locations for LA-ICP-MS transects.

Deducing Upper Paleolithic woolly mammoth mobility patterns with high spatial resolution trace element, O and Sr isotope analyses

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Bio-apatite, the main skeleton-forming compound, assimilates, via food and water, a wide range of trace elements whose abundance and isotopic composition reflect in vivo processes. Dental enamel, being the most resilient tissue, is particularly useful in reconstructing animals' paleoecology. Woolly mammoth molar teeth mineralize over a substantial amount of time (> 10 years) and are far more resistant to diagenesis than tusks, which makes them particularly suitable for studying life habits like mobility or seasonality. We determined mobility patterns of the Upper Paleolithic woolly mammoth from central and eastern Europe utilizing high spatial resolution analyses of trace elements, O and Sr isotopes. Due to sex-dependent mobility habits recognized among large mammals, we facilitated our study with DNA and proteome analyses.

Laser ablation MC ICP-MS Sr isotope composition measurements show negligible effects of all major isobar interferences and matrix effects. High accuracy and high precision data allowed us to establish robust mobility patterns at the sub-monthly resolution, which show migratory mammoths' lifestyles in nearly all the studied sites. Changes in $^{87}Sr/^{86}Sr$ correlate with changes in trace element composition. However, unlike most of the investigated trace elements, Sr isotopic composition is unaffected by maturation, suggesting a short time lag between the early secretion and subsequent maturation mineralization stages. Our histomorphometric measurements combined with LA ICP-MS line scans and 2D element mapping show that chemical changes follow the incremental enamel growth features, supporting the in vivo origin of the obtained records. We interpret variation in Sr isotopes and trace element distribution as a result of seasonal cycling associated with food availability during warm and cold periods. The observed seasonal migration pattern of woolly mammoth prevailed throughout the Upper Paleolithic until the last glacial maximum when the mammoths practically disappeared from this part of Europe.

Advancing Ultrafast Laser Ablation Sampling: From Femtosecond Filamentation to GHz Bursts of Ultrafast Laser Pulses

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Detection and quantification of solid-state material at remote distances remains a sustaining challenge in remote sensing applications. Challenges associated with such remote detection schemes include suppressing diffraction for remote laser plasma generation, as well as the development of optical technologies for isotopic analysis in solids[1,2]. In this talk, we will discuss emerging ultrafast laser sampling techniques that enable long-range beam propagation, as well as the development on new optical emission spectroscopy techniques for the detection and quantification of isotopes. Technologies include femtosecond laser filamentation for long-range propagation, filament-induced plasmas for optical emission spectroscopies, and the development of novel GHz bursts of femtosecond pulses[3] to improve sampling and solid-target coupling for isotopic analysis. These findings underline the importance of understanding and controlling ultrafast laser-mater interactions in the filamentation and GHz fs burst regimes to improve plasma formation and corresponding elemental and isotopic signatures remotely and in the lab.

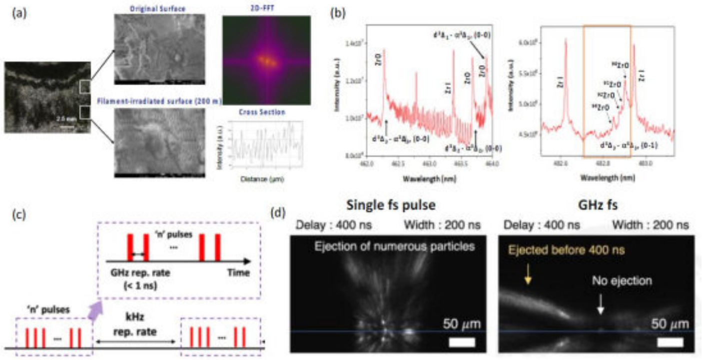

Figure 1. (a) Filament-matter interaction at 200 m and corresponding surface topographies. (b) Isotope detection from plasmas formed 110 m via filamentation. (c) GHz busts of fs pulses, and (d) laser scattering imaging from expanding laser plasmas using a single fs laser pulse and a GHz fs burst.

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Acquisition parameter optimization for single pulse resolved simultaneous LA-Q-ICP-MS multielement analysis

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In recent years, magnificent developments in laser ablation were achieved regarding ablation cells that enable fast aerosol washout in the millisecond range and thus provide the possibility for high pixel acquisition rates in spatially resolved ICP-MS analyses. However, so far only ToF-ICP-MS can exploit this benefit for fast and spatially resolved multielement analysis. With conventional quadrupole ICP-MS instruments, only one data point for each duty cycle is provided, thus the spatial representation is typically calculated from transient quasi-continuous signals using the scan speed of the laser and predetermined aerosol washout times. Using this conventional approach can lead to errors, such as pixel bleeding, image blur or distortions in case the washout times are not correctly determined or are changing during the analysis of a heterogeneous sample.

To circumvent imaging artifacts, single pulse resolved quadrupole ICP-MS acquisition is proposed. While ToF-ICP-MS provides complete m/z coverage for each datapoint of the transient signal of a single laser pulse, multielement analysis in the stated conditions is more complex with sequentially working quadrupole ICP-MS, requiring thoroughly optimized settling and dwell times to the signal duration that is depending on the aerosol washout from single laser pulses. This work explores the framework conditions needed to perform successful multielement analysis in single pulse resolved LA-Q-ICP-MS measurements – preconditions for fast multimodal imaging with absolute spatial correlation. The developed approach is applied for analysis of microplastics using a combined LIBS & LA-ICP-MS instrument, enabling a complete spatial correlation of the information acquired simultaneously with LIBS and ICP MS from single laser shots.

Utilization of Laser-Based Sampling for High-Throughput Particle Analysis

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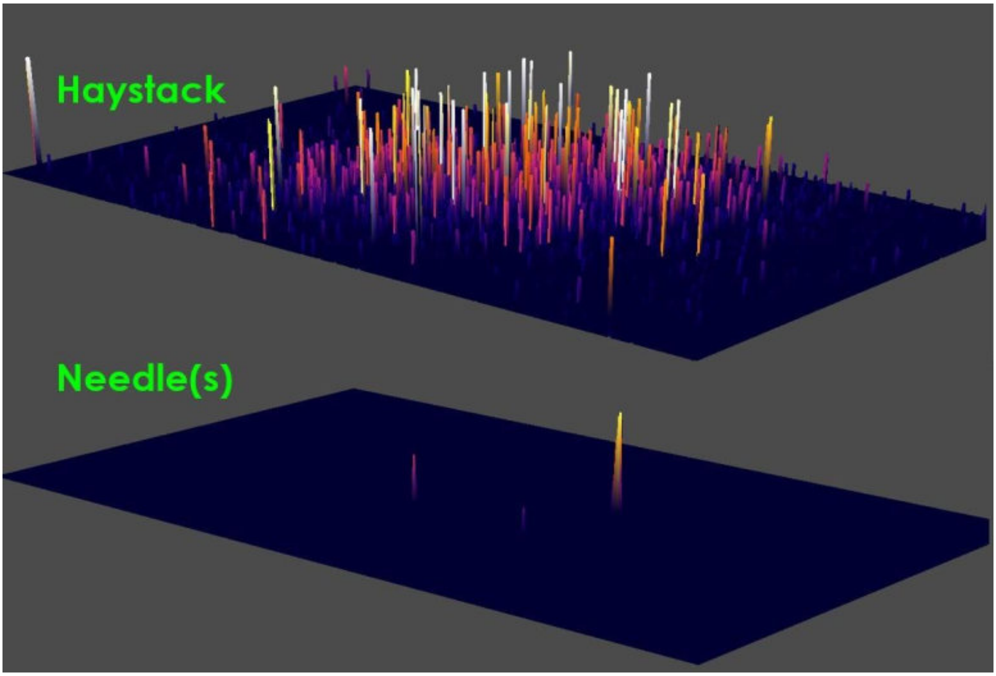
The detection of target analytes, in low abundance, within a complex matrix, is the typical "needle in a haystack" problem. Regarding elemental / isotopic analysis, a traditional bulk analysis approach will ultimately homogenize the results leading to possibly a misinterpretation of respective processes. Being able to directly (spatially) characterize the sample can provide a more comprehensive understating of such sample. The work presented here will demonstrate how laser ablation sampling coupled to spectroscopic (LIBS) and mass spectrometric (LA-ICP-MS) techniques can extract valuable information (needle) amongst complex matrices (haystack).



Exploring On-Board Data Reduction Techniques for Improved Space Mission Returns

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Science data collection in space exploration missions is often constrained by both storage on-board spacecraft (orbiters, landers, or rovers) as well as limited downlink capacities and opportunities. Depending on the instrumentation and the scientific objectives, not all collected data is inherently valuable. Transmitting data containing only signatures of low interest or data with low signal-to- noise ratios is inefficient. Therefore, pre-filtering the science data would allow for the collection and efficient downlink of additional valuable data without exceeding the previously mentioned limitations. This approach not only optimizes the usage of limited resources but also holds potential to enhance overall space mission returns.

In this contribution, we present a potential application of unsupervised machine learning to cluster mass spectrometric data on-board a spacecraft. Data were collected from a geological sample using our miniature laser ablation and ionization mass spectrometer (LIMS), which will be sent to the lunar surface in the near future to investigate the chemical composition of lunar regolith material in-situ [1-2]. The objective was to cluster the mass spectrometric data into groups of spectra with different chemical composition representing different mineral phases present within the studied sample. While the isolation of major phases is crucial, the detection of minor inclusions is equally important, particularly when seeking signatures with low abundance, such as potential biosignatures. Balancing the need for efficient data transmission with capturing nuanced details within the data requires careful selection and optimization of autonomous data reduction methods. Hence, different dimensionality reduction and clustering techniques are compared and their respective advantages and disadvantages regarding phase isolation and computational complexity discussed, considering the limited computational resources on board a spacecraft. Furthermore, it is important to evaluate the impact of data pre-processing and model parameter selection on the classification outcome [3].

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LA-ICP-TOF-MS Imaging in Reproductive Biology: Elemental Changes as a Marker for Fibrosis and Infertility in AIRE Deficient Male Mice

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Recent technological advances in laser ablation cell designs along with the advent of time-of-flight mass spectrometers (TOF-MS) have revolutionized high throughput elemental mapping, unlocking new frontiers in biology and medicine. Elemental mapping is opening doors to breakthroughs in biology and medicine in such diverse areas as Alzheimer's disease, stroke, and Wilson's disease among many others. These analyses are also leading to a deeper understanding of the interplay of inorganic regulatory networks in developmental biology, microbial homeostasis, metal dysregulation, and reproduction. In this presentation, we focus on reproductive biology and demonstrate how changes in elemental distribution can be used as markers for fibrosis and inflammation and may lead to a deeper understanding of immunodeficient infertility. The epididymis is an elongated tubule where testicular sperm mature and gain fertilization competence. Inflammation of the epididymis - epididymitis - is a contributing factor to male infertility, which can arise from an underlying autoimmune disorder such as Autoimmune Polyglandular Syndrome Type 1 (APS-1). APS-1 is caused by a monogenic mutation in Autoimmune regulator (*Aire*) which is a transcription factor that is expressed in the thymus. Among many symptoms, men with APS-1 can suffer from testicular insufficiency and infertility. The objective of this research is to determine the lesions in the male reproductive tract that cause male infertility in APS-1 and how the distribution and concentration of different elements, especially iron, play a role. Immunohistochemistry and Masson's trichrome were used to characterize the immune cells and fibrosis in the epididymis, respectively. Laser ablation Inductively coupled plasma time of flight mass spectrometry (LA-ICP-TOF-MS) was used to spatially map and quantify elemental concentrations in the epididymis. In addition, biodistribution analysis via ICP-QQQ-MS allowed for quantitative element analysis in the epididymis and surrounding tissues. Importantly, multiple tissue sections from multiple mice were used to improve upon the quantitative aspects of elemental mapping and allow for robust statistical analysis. We found that $Aire^{-/-}$ males had severely reduced fertility compared to WT and $Aire^{-/-};Rag1^{-/-}$ males. All $Aire^{-/-}$ males (n=10) had epididymitis, infiltration of CD8+ T and CD19+ B cells and fibrosis. LA-ICP-TOF-MS revealed increased iron deposition in the interstitial space of the epididymis, particularly in the corpus and cauda epididymis, but absent in the caput, and were observed in male mice as young as 9 weeks of age. No immune cell infiltration, fibrosis, or iron deposition were observed in $Aire^{-/-};Rag1^{-/-}$ mice, suggesting that T and B cells target the epididymis and contribute to fibrosis.

These results reveal the importance of *Aire*-mediated immune tolerance to the male reproductive tract and suggest that in the absence of *Aire*, T and B lymphocytes target the epididymis and contribute to fibrosis and iron deposition. Further studies will reveal the specific role of lymphocytes in causing these changes, and the significance of iron deposition.

Introducing a general cell membrane marker for bioimaging with LA-ICP-(TOF)MS

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Single cell analysis gives unprecedented insights in many biological processes and diseases (e.g. inflammation, hypoxia), drugs (e.g. anticancer drugs, immunosuppressives) or environmental factors (e.g. fine dust, metal exposition) affect different cell types in different ways. Up to now, for acquiring single cell data using LA-ICP-TOFMS, multiple expensive and very specific markers need to be purchased for tagging different cell types within one tissue samples (e.g. Macrophages, skin cells, glandular cells, hair follicle for skin samples). Statistical image analysis together with quantitative studies on metal bioaccumulation are preceded by applying cell segmentation procedures to the data, a procedure which requires the application of specific membrane or cytosolic markers. As a drawback, these markers need to be adapted to cell- and each tissue type, respectively. Recently, the first general segmentation marker kit was introduced.[1] However, the exact composition remains undisclosed. Besides being costly, it only comes with platinum-labels, ultimately hindering the single cell exploration in the context of the clinically established platinum-based drugs.

In this work, we developed a metal labeled antibody staining procedure to be used as visualization and segmentation marker costing a fraction of the current alternatives while staining all different type of cells. This strategy eliminates the need of multiple antibodies and enables as well as facilitates single cell data analysis.

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Improved Quantification of Solid Samples using LA-ICP-MS with Standard Addition and Isotope Dilution: A Promising New Technique

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Laser ablation (LA) coupled with mass spectrometry (MS) has been commonly used since the 1980s, but accurate quantitative measurements remain challenging.[1] However, a promising new technique has been developed that combines LA-ICP-MS with the concept of isotope dilution (ID) to allow for SI-traceable and quantitative measurement results without needing a solid, matrix- matched reference material.

The new LA-ID-ICP-MS method utilizes an element with a known mass fraction contained in the sample itself as the reference element. Solutions with different concentrations and isotope ratios are required for the analyte and the reference element. The solutions are introduced into the ICP- MS one after another. The ablated material reaches the ICP with the respective solution simultaneously so that a standard addition is performed. The isotope ratios in the solutions are adjusted by mixing standard and spike solutions. As a result, an isotope dilution is performed when mixing the ablated material with the respective solution. Linear regression models were used to analyze the measured isotope ratios for both elements. Afterwards, the regression parameters were used to calculate the mass fraction of the analyte element in the solid sample. With this new method, boron was quantified in the glass-based standard reference material SRM® 612 (NIST) to verify its applicability. The determined content of 33.3 µg/g ± 3.7 µg/g was reproducible and within the uncertainty not distinguishable from the value indicated on the certificate. To assess this result, boron was quantified not only by the new LA-ID-ICP-MS method but also by the established LA-ICP-MS method [2] which is also based on the standard addition of several solutions. It was found that using isotope dilution leads to greater accuracy and a reduction in the estimated measurement uncertainty by approximately a half, justifying the additional effort for critical applications.[3]

To demonstrate the potential of the new technique, magnesium in a complex $CaCO_3$-matrix was analyzed. The sample material was comprised of shells from single-celled marine organisms. The results show the potential of using the new method for highly pure as well as difficult matrices. It can be applied to samples containing a reference element with a known mass fraction, as well as those where the mass fraction of the reference element needs to be determined (using SI-traceable methods) before applying the technique. This opens a wide field of applications. Within the project "Agile Bio-inspired Architectures (ABA)", financed by the German State of Lower Saxony, it will be investigated if this method can also be transferred to clinical samples such as tissue.

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Application of in-situ Laser Ablation ICP-MS analysis in developing geochemical fingerprints to trace cobalt and nickel along the battery value chain

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Cobalt (Co) and nickel (Ni) are essential components in the cathode production of lithium-ion batteries. As the global electric vehicle market grows, the demand for Co and Ni in rechargeable batteries is rapidly rising. The Co-Ni supply chain is complex due to the uneven geographic distribution of primary sources, the wide variety of deposits and ore types with distinct refining processes and their manufacturing demand. The ability to identify the provenance of Ni and Co metals is critical to ensure a responsible value chain from ore to battery yet it is challenging due to complexity of the supply chain. In this study, we analyzed raw ores, mineral concentrates, as well as various metallurgical products sourced from a mine of major Ni-Cu-PGE deposit located in the Central Lapland greenstone belt in the northern Finland. Trace element compositions and sulfur isotope ratios in sulfide grains, e.g., chalcopyrite, pyrite, pyrrhotite and pentlandite of ore samples were measured in-situ with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Metallurgical processed samples such as solid residues and leachate solutions (evaporated to dry powders), iron-removed samples, and nickel sulphate powders, were prepared as pressed pellets and their trace elements and sulfur isotopic compositions were also directly analyzed in-situ by LA-ICP-MS. Finally, the trace element compositions and sulfur isotope ratios of these samples were compared by multivariate data analysis to extract robust fingerprints that possibly remained conservative along the value chain. The effect of extractive and refining metallurgy processes in altering geochemical signature of the original ore deposits are also evaluated. This study aims to provide a proof-of-concept of using geochemical/isotopic fingerprinting techniques for tracing Ni- Co metals along the value chain. The outcome of this research helps to improve transparency and sustainability of raw material supply along the battery value chain.

Two approaches for elucidating the origin of non-metallic inclusions in steels using LA-ICP-MS

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The presence of non-metallic inclusions (NMIs) is a critical parameter for the quality of high performance steels. NMIs can negatively affect the physical properties and corrosion resistance of steels. In addition, the aggregation of non-metallic particles during the continuous steel casting process (clogging) can further reduce steel quality or even interrupt the process [1]. In order to allow for a better control of NMIs, it is of central importance to understand their origin. In the present study, two approaches for tracing the formation of NMIs and clogging are presented, the so-called active and passive tracing methods, both of which are making use of rare earth elements (REEs) and their detection using ICP-MS and LA-ICP-MS [2]. In the active tracing approach, which is the more established method, individual REEs, such as La or Ce, are deliberately added to the steel melt in order to label the NMIs present at that point in the process [3]. These tracer elements can then be detected in samples of steel, slag, clogging layers, and individual NMIs by means of (LA-)ICP-MS. While the high REE contents thus generated also allow for detection of NMIs by means of manual or automated SEM/EDS analysis, another consequence is that the system under investigation is altered to a significant degree, e.g. the separation and wetting behavior of La or Ce containing NMIs is influenced. In addition, a tracer experiment on the industrial scale requires the use of tens of kilograms of La or Ce metal.

In contrast, the novel passive tracing approach uses pre-existing REE patterns for chemical fingerprinting. REE contents in NMIs or clogging samples are determined using (LA-)ICP-MS and normalized by dividing by a suitable reference data set in order to facilitate pattern recognition. The normalized REE patterns are then compared to patterns determined in potential source materials such as slag, aluminum, or auxiliary materials. Similarities in the resulting patterns indicate contribution of a source material to NMI or clogging formation. The main advantage of this approach is that it does not require any alteration of the process and can also be applied *ex post* if problems are encountered during or after the process. In an experiment on the industrial scale, the passive tracing approach allowed to link NMIs to mold slag and casting powder via corresponding REE patterns and indicated a contribution of sliding gate sand to clogging formation, while the results of active tracing showed that aluminum oxide particles formed during deoxidation contributed to both the formation of NMIs and clogging.

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Investigating Ablation Rates in Geological Materials: A Comparison of UV fs and ns Laser Ablation

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Understanding ablation behaviour and laser-induced elemental fractionation is crucial for accurate in-situ dating of geologic materials, particularly for uranium-lead (U-Pb) analysis by LA-ICP-MS. This study focuses on comparing the ablation rates of geological materials using femtosecond (fs) and nanosecond (ns) laser ablation systems. A comprehensive analysis was conducted on various matrices relevant to U-Pb dating, including Allanite, Apatite, Baddeleyite, Calcite, Cassiterite, Coltan, Glass (NIST610, GSD-1G), Rutile, Titanite, Vesuvianite, Wolframite, and Zircon.

Whereas the homogeneous beam of 193nm excimer lasers allows measuring crater depths with ease, the notoriously heterogeneous beam profile of the UV fs laser poses challenges in precisely determining ablation rates. To account for this known caveat, our approach involved scanning the fs laser beam over an area to average ablation rate. Compiled results show that nanosecond laser ablation produces relatively consistent ablation rates within a factor of 2 for the different geological materials mentioned above. On the contrary, femtosecond laser ablation exhibits significant discrepancies of up to a factor of 4-6 for the same geological materials.

Ultimately, this study investigates the sources and reasons behind the observed differences in ablation rates between UV fs and UV ns laser ablation. By addressing these variations, our aim is to enhance the accuracy and reliability of laser ablation techniques in geochronological dating applications.

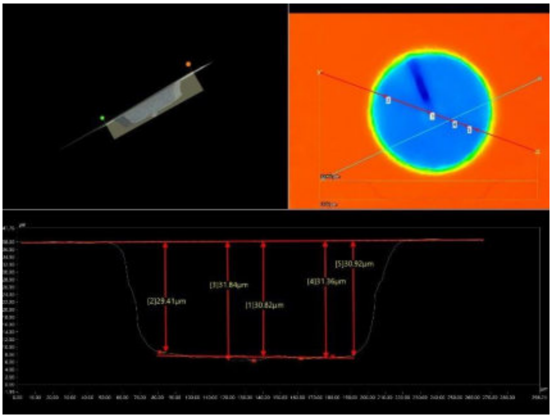

Figure 1: Example of a UV-fs LA crater generated by 8000 pulses in Apatite. Imaged by a Keyence VHX7000 digital microscope.

Empirical Insights into Crater Geometry: Modeling for Enhanced Laser Ablation Inductively Coupled Plasma Mass Spectrometry Analysis

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Analytical laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) instruments typically homogenize laser beam profiles to achieve a flat-top shape. In practical applications, however, they exhibit a super-Gaussian and even a Gaussian profile for smaller laser beam sizes. This suggests that the beam profile and ablation grid directly influence the amount of surface material sampled by the laser (ablation volume). Contraction of the ablation grid through sub-pixel mapping not only enhances the accuracy of surface sampling but also results in increased pixel density, improved spatial resolution, and a higher signal-to-noise (SNR) ratio. [1]

This research explores crater geometry, which can be described using the 2D super-Gaussian function, and its dependence on several factors such as laser beam shape, material ablation characteristics, wavelength, and energy density. Given the complexities of laser-sample interactions, an empirical model was devised to explore the relationship between super-Gaussian order (*n*), beam size, and laser fluence for circular beams. This model yields the factor *n*, facilitating the determination of the contraction factor (*k*).

Identifying the precise contraction factor for each beam size and *n* results in smoother post-ablation surfaces and improved image quality due to heightened pixel density. Such models deepen comprehension of crater geometry optimization, ultimately enhancing analytical outcomes in LA-ICP-MS analysis.

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Laser Ablation – Cavity Ringdown Spectrometry – A novel method for in situ measurement of light stable isotope ratios

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Elemental analyzers (EA) are the go-to sample introduction peripherals for light stable isotope analyses of solid materials. Sample preparation is labor intensive and time consuming, with high associated consumable and equipment cost. Sample recovery is impossible in case of malfunctioning, i.e., no repeat analysis when sample amount is restricted.

In the same way, Laser ablation (LA) is traditionally considered a sample introduction technique for Inductively Coupled Plasma Mass Spectrometry (ICP MS) where plasma-based instrumentation will ionize and measure with a high degree of accuracy and precision the aerosol generated during the ablation process.

In this contribution we present an innovative method of measuring C stable isotopic ratios of solid matrices, with an emphasis on carbonates, by hyphening two instruments that are not usually found in the same lab. We coupled a laser ablation system (Teledyne Photon Machines Fusions CO2) equipped with a specially designed ablation chamber (Terra Analitic isoScell Δ100) to a Cavity Ring Down Spectrometer (Picarro G2201-i) to perform spatially resolved, highly accurate and precise measurements of both inorganic (stalagmite) and bioaccumulated (freshwater bivalve) carbonate samples. This novel system requires minimal sample preparation, allows for in-situ sequential and repeat sampling, all while eliminating the need to individually prepare samples

Elemental fractionation in LA-ICP-MS quantified

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Elemental fractionation and matrix effects are persisting challenges in LA-ICP-MS. If not properly addressed, this may translate into data quantification inaccuracy. Excimer and femtosecond lasers have helped alleviate this issue, however fractionation may still occur for a variety of reasons, sometimes inherent to the ICP-MS, sample introduction system design or improper carrier gas flow rates. Day to day operations and/or consumable purchasing budgetary constraints may also challenge analysts, who might resort to operating their LA-ICP-MS systems under non-optimal conditions. Furthermore, tuning is most often carried on the NIST glass series, SRM 612 or 610 whereas ablated samples have different matrices. In this study, we document the response of a Thermo-Fisher Element 2 ICP-MS coupled to a Teledyne Photon-Machine Analyte G2 to surface scans of NIST SRM 610 vs USGS synthetic basalt glass standard GSE-1G. Both standards have similar trace element concentrations of ~ 400 ppm whereas their major element composition differs. Our LA-ICP-MS system at Northern Illinois University is typically tuned to maximize signal stability and intensity but this leads to U/Th intensity ratios ~1.8-2 on NIST SRM 612. We report the count rate discrepancy between both standards for the most commonly analyzed major and trace elements. Standard GSE-1G produces a response that is more internally consistent among elements, whereas standard NIST 610 provides higher counts which may however vary more substantially among elements, including potentially for element pairs with similar masses such as Th and U. Many pairs of elements that are far apart in mass, electronic shell structure and geochemical affinities however exhibit similar responses. We demonstrate that reliable trace element data can be collected if the right elements are selected as internal standard. We can produce excellent calibrations if using an internal standard with analogue behavior. We recommend that analysts select multiple elements in their method to use as potential internal standards, and empirically determine which one works best with each of their unknown elements.

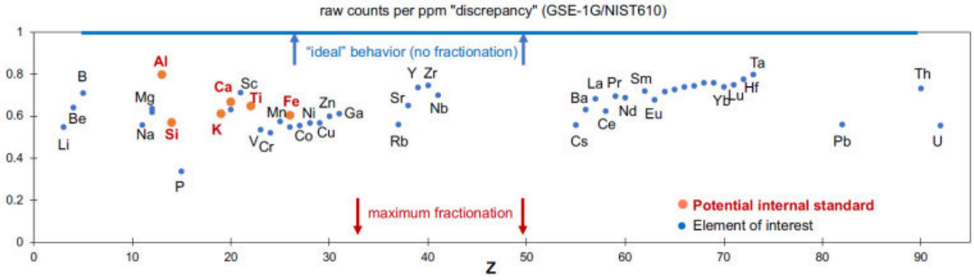

Fig.1: ratio of concentration and isotopic abundance normalized counts between GSE-1G and NIST SRM 610 collected on surface scans. Elements plotting closer to 1 exhibit the least fractionation, elements plotting farthest from 1 exhibit the most fractionation. We highlight major elements that can be used for internal standards. Together, these mimic the fractionation behavior of all tested trace elements.

Dual-phase formation during LA-ICP-MS analysis of biological tissue

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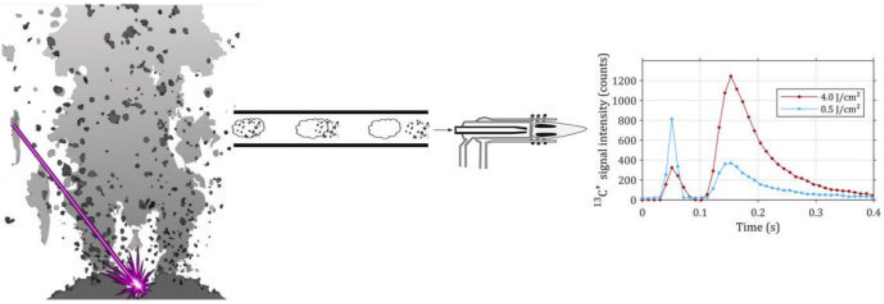
As the demand for high-throughput, sensitive and accurate LA-ICP-MS analyses has grown substantially over the last decades, so has the technology greatly improved with the development of low-dispersion ablation cells and efficient aerosol transfer systems. These improvements have, in their turn, driven the use of LA-ICP-MS for bulk analysis and 2D-mapping of soft biological tissues in the context of numerous biological and biomedical applications.

However, these technological improvements and shifts to new sample types have shed lights on fundamental issues. For instance, previously it was believed that upon interaction with a UV photon beam, the sample surface would be removed under the form of particles. However, past works have already described that this is not necessarily the case, as for instance C has been shown to form a significant amount of gas phase upon ablation of carbon-based materials. [1]

Recent work has exposed additional problems in relation to this dual-phase formation. The amount of formed gas phase has been shown to be dependent on laser wavelength, laser energy density, matrix type and is even element-specific. As these two phases are transported differently from the ablation cell to the ICP, this can lead to element-specific smearing. In addition, a negative impact on sensitivity was also observed since gases and particles are processed differently in the ICP, raising concerns in regard to accuracy of quantification when using non-matrix matched calibration standards. [2]



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Sculpting the ablation plume - using QuadLock to enhance sensitivity for isotopic analyses

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The development of the QuadLock (Norris Scientific), a laser firing control system, has been shown to remove aliasing artifacts in LA-ICP-MS imaging[1], especially when using a fast response interface. The technology operates between a quadrupole ICP-MS and the laser ablation instrument, to synchronize the firing of the laser with the cycling, or sweep time, of the quadrupole mass analyser. Signal smoothing devices that are commonly used to improve precision for isotopic analyses, both decrease spatial resolution and reduce the signal intensity by broadening the ablation plume. A fast response interface can increase the amplitude of each laser pulse but has been underutilized to date as it commonly increases signal noise from aliasing. However, given that isotopic analysis for geochronology (e.g. Lu-Hf method [2]), often relies on measuring very low count rates, increasing sensitivity might be more important than reducing noise to obtain useful precision.

In this study we use the additional capability of the Quadlock to control the timing of each individual laser pulse during a sweep of the quadrupole. A few laser pulses can be rapidly fired together to increase the amplitude of the ablation plume, while maintaining an average 5-10 Hz pulse rate. For example, firing 3 pulses with 10 ms spacing (100 Hz), over a 30 ms sweep time produces an average pulse rate of 10 Hz. This enables the arrival of the peak of the ablation plume to be synchronized with the dwell time of a specific isotope. In this study, we explore the QuadLock capabilities for improving precision for U-Pb and Lu-Hf isotopic analyses, by selectively pulsing the laser in alignment with the mass spectrometer to enhance the sensitivity for ^{176}Hf or ^{207}Pb isotopes.

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What's in a pixel?

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2D mapping of elemental and isotopic signals is of great interest in several fields of study where spatial information on the micron level feeds knowledge of biological, geological and metallurgical systems. The methods of generating elemental 2D maps from ICP-MS data co-ordinated with accurately placed laser ablation lines are well established for quadrupole systems but the limitations are well known concerning speeds of data acquisition, numbers of analytes possible in one mapping and aliasing between map pixels. Recent developments in laser ablation leading to single and sub- millisecond signal responses for individual laser shots and in time of flight ICP-MS where near full mass range data can be acquired for each shot of the laser has lead to the ability to map materials with more analytes in each pixel and more pixels per second.

These new techniques, whilst impressive and becoming accepted now as the state of the art for elemental mapping, do also need careful consideration for analytical parameter choices to obtain the best quality maps. This work will highlight some recent findings using the Nu Vitesse time of flight ICP-MS with the latest high speed mapping laser ablation systems from both ESL and Teledyne Photon Machines. The unique ability to fully characterise each laser shot in a line for multi-elemental content gives greater insight into ablation behaviour in different matrices and the impact of ablation conditions. Matters discussed will include:

- Characterising the transient signals from ultra-fast washout ablation cells.
    - How this is optimised and how this impacts image quality and acquisition speeds
    - How the signals change with spot size
    - How the signals change with changing matrices
    - Considerations for data acquisition parameters
- The benefits and drawbacks of improving signal to noise for each pixel by increasing the shot overlaps or dosage for a laser line [1]
    - Considerations for high speed data acquisition and processing data from spectra to pixels

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Technological prerequisites for high quality isotope ratio measurements using quadrupole ICP-MS

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Collecting isotope ratio measurements with well-defined and preferably high precision and accuracy is paramount to allow interpretations in various geological, medical, environmental, food or archeological applications. Quadrupole ICP-MS has long held a niche position in that field. This contribution reviews its role in the view of recent technological advances in quadrupole ICP-MS instrumentation. The technological prerequisites for high quality isotope ratio analysis are discussed and measurement examples presented going down to 0.02% internal precision, closely tracking achievable precision dictated by counting statistics.

The more, the better: new practices for U/Pb data reduction based on multiple reference material standardization

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It is a widespread practice for the LA-ICP-MS-based U/Pb protocol to rely on a so-called “standard- bracketing” approach that integrates a single reference material for standardisation (or calibration). In details, this reference material would be used to correct for (1) the instrumental drift; (2) elemental fractionation; (3) mass bias. Additional materials are used as validation only.

In this contribution, we present new practices of U/Pb data reduction that aims to provide a robust and careful standardization for LA-ICP-MS, by using conjointly several reference materials when possible. Our approach is focused on U/Pb dating, but part of the workflow presented here can be applied to other protocols (*e.g.,* trace element quantification). The main steps are summarized below:

(A) Elemental fractionation: similar to [1], the objective is to remove any laser-induced elemental fractionation (LIEF) pattern on spot analyses. The LIEF model is built with several matrix-matched materials, thus revealing potential discrepancies of LIEF between materials.

(B) Drift correction model: the drift is assessed with several homogeneous reference materials by inspecting the relative variation of the instrumental response through time. Using multiple materials is useful at this stage because it prevents assimilating heterogeneity-related discrepancy and drift-related discrepancy in the measurements.

(C) Mass bias model: multiple homogeneous reference materials are used to build a mass bias calibration curve. If present, non-linearity can therefore be accounted for. Integrating the uncertainties of the calibration curve itself provides a satisfying way to reach acceptable within- run MSWD statistic.

All together, these operations provide improved robustness for U/Pb data reduction. Distinct operations of drift and mass bias corrections provide a safe standardization. Finally, multiple material standardization simply better constrains the instrument behaviour in case the range of measurements is extreme (*e.g.,* detrital U/Pb dating, single-rock polyphase recording). We illustrate our approach with zircon, apatite and calcite U/Pb case studies.

[1] C. Paton, J. D. Woodhead, J. C. Hellstrom, J. M. Hergt, A. Greig, and R. Maas, “Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction,” *Geochemistry, Geophys. Geosystems*, vol. 11, no. 3, 2010

Characterisation of nano-pellets as potential reference materials for Pb-Pb isotope analysis in ferromanganese crusts

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One of the biggest challenges still faced by Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is the lack of robust matrix-matched calibration strategies which are essential for transforming qualitative observations into semi-/quantitative results. Specifically in the geosciences, there is paucity of adequately characterised matrix-matched reference materials (RMs) available which are homogenous on the micro-scale. In the absence of such materials, many geoanalysts have resorted to using non-matrix matched silicate glasses (*e.g.,* NIST series) for standardisation which are likely to lead to systematic biases in the results. Coarse and fine grained RM powders made from natural materials and cover most sample types are more readily available. These powders have the potential to be prepared as pressed pellets (PP) with and without binders and are used as a closer matrix-matched alternative. Due to this, much attention has been afforded to optimising the preparation workflows for PP, most notably, wet milling methods capable of producing undiluted nano-PP (NP) with improved homogeneity.[1].

This study focuses on the characterisation of several NP either purchased from the Christian-Albrecht University of Kiel or produced at the University of Southampton, from RM powders Nod- A-1, Nod-P-1, JMn-1, and an in-house powder, HRM, produced from a homogenised quantity of ferromanganese (Fe-Mn) crust material from Tropic Seamount [2]. These materials are typically used as a reference for Fe-Mn crust/nodule analyses and were investigated as part of a larger study focusing on the Pb-Pb isotope ratio signatures of Fe-Mn samples. The isotope ratio data were acquired using 193 nm LA systems, coupled to a ICP-MC-MS using low dispersion, high- efficiency transport accessories (e.g., DCI, TwoVol2- and TwoVol3- ablation chambers). For comparison, data were also acquired for pellets of the same materials produced directly from the stock rock powders without additional nano-milling. Data reduction and processing was performed using Iolite4 [3]. The results report the key analytical figures of merit for each of the materials, and associated uncertainties generated. The considerations required during processing of this type of data are also discussed.

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Real-time Measurement Of Mass Filter Position For Aligned LA–ICP–MS

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Mapping by LA–ICP–MS is a useful technique in a range of fields including geology[1], biology and medical sciences[2], thanks to its sensitivity, spatial resolution and wide dynamic range. Creating high-resolution images requires a significant time investment, in the order of dozens of hours of instrument time to gather data to generate an image of a thumbnail-sized sample. Total acquisition time is rate-limited by the washout time of the ablation cell, so a range of fast- response cells have been developed to reduce washout times, with washout times to 1% commonly achieved in under 50 ms, and for some systems in under 10 ms.

With fast washout, however, the potential arises for visible “beats” or aliasing in the resulting images[3]. Even with very careful selection of of initial laser and spectrometer timing parameters (which limit the experimental conditions under which the image can be collected) instrument timing can drift during a long analysis.

When using active alignment, the firing of the laser is aligned with the mass scan cycle of the mass spectrometer so the ablated aerosol reaches the detector at the exact same moment relative to every mass scan. This synchronisation is performed for each sweep of the mass filter, so the two instruments are kept in constant alignment, even during long acquisition sessions. Our “QuadLock” alignment device measures the voltage of the mass filter continuously during its normal operation. For instruments with multiple quadrupoles, only a single unit needs to be used, to monitor the second quadrupole.

QuadLock can be used not only with quadrupoles, but also with single collector magnetic sector field instruments. Recent developments have resulted in adaptation of the device for the Element single-collector mass spectrometer. While the sensitivity of these instruments is far superior to a quadrupole, their slow response times make them challenging to use for imaging. The QuadLock device optimises the throughput of the whole LA–ICP–MS system to reduce total imaging time compared to an unaligned system.

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Ultra-Trace-Element Imaging Using Aligned LA–ICP–MS With a Magnetic-Sector Single-Collector Mass Spectrometer

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The use of fast-washout ablation cells (“fast cells”, washout time to 1% < 50 ms) for LA–ICP– MS can improve spatial resolution of images, reduce acquisition time, and raise peak signal intensity – which in some cases may bring signals above detection. The obvious application of fast cells has been for imaging, which is a powerful and useful technique with a wide range of applications in the earth, material, and biological sciences[1].

The main issue caused by using fast cells with any sequential mass spectrometer is the prevalence of aliasing[2, and references within]. While strategies to mitigate this problem do exist, the resulting conditions will nearly always be sub-optimal and in some cases fail to work – high repetition rates or slow scan speeds will result in ablation that is too deep, using dwell times at laser period intervals is wasteful and results in sweep times that are much too long, and so on. One approach is to lengthen the response time of the ablation cell, which is then fundamentally at odds with the objective of collecting images that contain millions of pixels in a reasonable amount of time. As the problem of aliasing gets worse at longer sweep times, magnetic-sector single-collector instruments (e.g. Thermo “Element”, Nu “Attom”, etc…) stand out as a particularly poor choice for imaging applications.

Our new approach [2] is to align firing of the pulsed laser with the sweep time of the mass spectrometer. We call this aligned LA–ICP–MS and the technique can be implemented by way of an external circuit that monitors the mass filter position of the mass spectrometer in real time and fires the laser as required.

Use of this technique allows us to collect images free from aliasing, while levering the very high sensitivity of a magnetic-sector single-collector mass spectrometer (Thermo “Element XR”). We will demonstrate this application by characterizing potential garnet reference materials[3] for U–Pb geochronology along with synthetic glasses, and compare with results equivalent to those from a conventional quadrupole under similar conditions.

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What is dynamic range in LA-ICP-MS and how can it be extended?

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When choosing parameters user for the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), the correct parameters can make the difference between a stunning and an impaired image. While some of those parameters, such as the resolution can be very intuitive to understand, others like the dynamic range are more difficult to make sense of. State of the art quadrupole systems have a great dynamic range but lack the quasi-simultaneous detection which is crucial for the analysis of fast transient signals such as those from modern laser ablation systems. Therefore, taking a more suitable detector such as a TOF and extending the dynamic range is a favorable approach.

For many applications the dynamic range of the detector is of utmost importance. These applications include isotopic or elemental ratio analysis in tissues, geological materials, or particles, or the analysis of both major and minor constituents of a sample. Since the requirements in dynamic range for each sample type can vary greatly different approaches need to be applied to collect the optimal results.

In this talk we will be discussing what dynamic range looks like in LA-ICP-MS, how it is defined and how it can be improved. Data will be shown collected on the Vitesse TOF-ICP-MS coupled to an imageGEO or an Iridia laser ablation system.

Femtosecond Laser Ablation for High-Speed Elemental Mapping

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Femtosecond laser ablation (LA) systems offer many analytical advantages over nanosecond laser systems, namely smaller particle size distribution, reduced thermal effects and reduced elemental/isotopic fractionation, culminating in improved data precision. In addition to the analytical figures of merit, when compared to gas based 193 nm excimer LA systems, the solid- state 257 nm Yb:YAG also offers practical benefits for high-speed elemental mapping. This includes the ability to run at repetition rates of 1.1 kHz and beyond as well as a lower ongoing cost of ownership (no need to frequently exchange ArF gas and longer lasting optics due to the longer wavelength).

Due to the internal triggering of commercial femtosecond lasers, accurate placement of the first shot in sequential lines and subsequent shot spacing for LA mapping has been difficult. Controlling the first shot position and spacing, whilst also accounting for stage acceleration and deceleration, is critical to achieve undistorted maps at high-speed and high-resolution. Here we detail the implementation of encoder feedback controlled 3-phase linear motors of a high-performance sample chamber (TwoVol3) in combination with a femtosecond laser (ESLFemto) to eliminate these effects, enabling fast and distortion free elemental mapping.

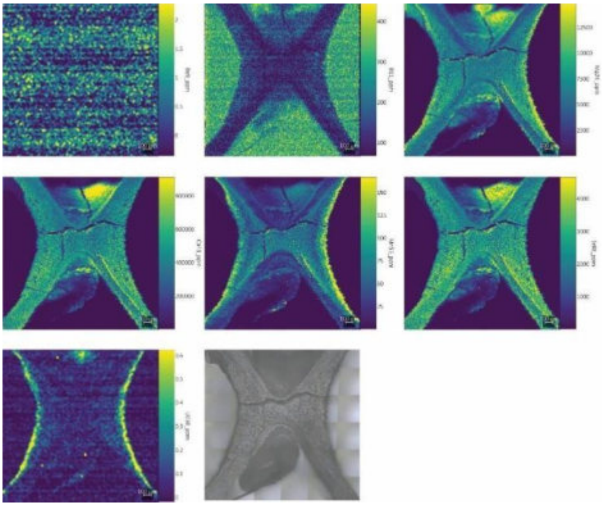

Figure 1: Elemental maps of a shark vertebrae obtained with the ESLfemto to demonstrate the resolution possible at varying elemental concentrations. The fs-LA system was run at a 10µm spot size and took 2 hours 40 minutes to obtain.

TACtool: A Targeting and Co-ordination tool for LA-ICP- MS and other spatially resolved methods

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LA-ICP-MS is one of many spatially resolved methods (e.g. SIMS, EPMA, LIBS) which target discrete sample areas for analysis. Data from these and other complimentary methods can be correlated when analysing the same or similar regions. In order for correlation to be possible, analyses to be performed in a time-efficient manner, and to enable traceability of data, a tool is required that links the spatial region analysed with the data acquired.

TACtool is a simple new 'Targeting And Co-ordination' software tool that enables prior imagery (e.g. from a SEM or optical microsope) to be imported and analysis locations placed in context, enabling co-ordinates and an image with overlaid spot locations, to then be exported. TACtool can be used to simply record the sites of analyses undertaken during an analytical session, or to prepare for a session away from the lab, by generating and exporting analysis positions for import into other analytical or sampling platforms (e.g. a laser system), populating them with predefined lists of analysis locations. This typically saves large amounts of laboratory time and allows for more considered targeting and preparation. Our development of this tool has focussed on linking LA-ICP-MS and SEM imagery and data, but as generic software it can be applied to other systems, for example using co-ordinates exported in a GIS-friendly format.

TACtool is a desktop GUI tool written in Python and is freely available on the BGS GitHub home page (https://github.com/BritishGeologicalSurvey/tactool/) for community use. Uptake by, and feedback from, users is actively encouraged through the GitHub site.

Automated Selection of Sites for Chemical Microanalysis Using Image Segmentation

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The acquisition of spatially resolved geochemical data often involves the complex integration of multiple techniques. A typical workflow to determine mineral chemistry often involves analysing samples using a scanning electron microscope (SEM), where specific zones are imaged and targeted for their major element chemistry, prior to more sensitive techniques to determine trace element compositions (e.g. LA-ICP-MS). Recent advances have enabled the full mineralogical classification using an automated SEM (aSEM) and the production of a false-colour image of the distribution of minerals in a thin-section or polished block. These images provide a powerful tool for the selection of sites for chemical microanalysis. However, manual selection is a repetitive and time-consuming task prone to error and bias, resulting in a non-representative distribution of analytical sites.

To improve efficiency and reduce bias associated with selecting sites for analysis, we have developed a Python application with graphical user interface to automatically select sites using segmentation of aSEM images (e.g. *.png) for minerals of interest. Segments smaller than a predefined size are discarded at this point. Analytical sites can either be distributed in the centre of segments, assigned to segments based on their relative area, then randomly distributed, or outlined for mapping. Selected sites can be translated into the coordinate system of an instrument by defining a transformation matrix using three corresponding reference points. To reduce errors when inputting, reference coordinates can be selected interactively on aSEM images and read directly from a given instrument.

This approach takes a few seconds per sample, saving up to 1 hour when selection is manual, and reduces human bias in analytical site selection. Our application is not limited to aSEM images but is compatible with any type of image file with sufficient contrast between areas of interest and background.

Hardware and software integration improvements in LA- ICP-TOF-MS for acquisition rates of 1000 resolved multichannel pixels per second.

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The evolution of low-dispersion aerosol transport systems (ATS) has brought significant advancements for LA-ICP-MS imaging, encompassing accelerated analysis speed, increased sensitivity and higher spatial resolution [1]. The most recent iterations of low-dispersion ATS now yield single pulse response (SPR) profiles with durations of <1 ms [2, 3], thereby substantially enhancing signal-to-noise (S/N) ratios and opening avenues for kHz acquisition rates. Time-of- flight-based (TOF) ICP-MS systems, with their rapid data acquisition and pseudo-simultaneous detection capabilities of elements spanning the entire periodic table, are ideally paired with low- dispersion LA systems. The integration of collision cells and advanced mass filtering tools in these systems has overcome most of the challenges facing the TOF mass analyzer related to spectral interferences and dynamic range. As the speed of ablation improves, the duty cycle decreases because of the fixed processing and translation overhead between each ablation event. The overhead hence becomes a significant limitation to sample throughput. Some of the overhead exists as a result of the communication across the software bridge between the laser and ICP-TOF-MS system.

This work will present improvements in the duty cycle > 90% through a reduction of the processing and translation overhead. This is achieved through efficient scanning workflows and improvements in the software bridge communication between an Iridia 193nm laser ablation system (Teledyne Photon Machines, Bozeman, MT, USA), equipped with the short pulse cell in the Cobalt ablation chamber, and the Vitesse ICP-TOF-MS instrument (Nu Instruments Ltd., Wrexham, UK).

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LA-ICP-MS/MS-based Rb-Sr isotope mapping for geochronology

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We highlight a new approach for in-situ Rb-Sr dating that utilizes rapid line scans instead of static spot ablation, enabling creation of two-dimensional ^{87}Rb/^{86}Sr and ^{87}Sr/^{86}Sr isotope ratio and Rb-Sr age maps[1]. Data acquisition is carried out using an ICP-MS/MS instrument with N_2O as the reaction gas, coupled to a 193 nm excimer laser via a low-aerosol-dispersion interface. This configuration allows for high repetition rates (> 100 Hz) and sensitivities, enabling data acquisition at a high scanning speed and small laser beam size (3-4 µm). Notably, this approach requires just about 1/30 of the sample volume typically utilized in conventional spot ablation mode, while achieving similar levels of precision and accuracy. One key requirement for accurate Rb-Sr ages based on line scan analyses is matrix correction using chemically matched crystalline mica. We will present Rb-Sr age maps of naturally deformed mica samples (Fig. 1), that highlight the potential of Rb-Sr mapping for extracting age data from rocks that exhibit complex metamorphic- metasomatic histories and microscale dynamic recrystallization. Additionally, we show that quantitative elemental information (e.g. Li, see Fig. 1) can be collected alongside Rb-Sr isotope data. This advancement offers a distinctly more insightful assessment of isotope mobility in natural systems, the timing of element enrichment processes and enables, in high-Rb/Sr mineral systems, precise and accurate isotopic dating of intricate geological processes at small scales.

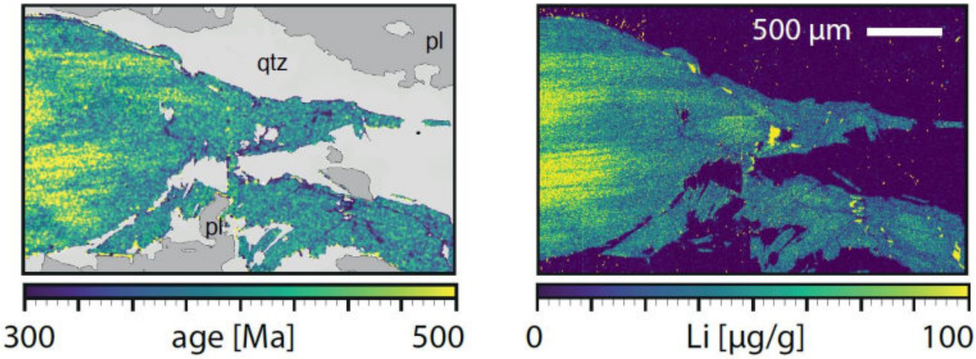

Fig. 1: Rb-Sr age map and co-acquired Li concentration map of a deformed muscovite from a meta-pegmatite within the Western Bohemian Massif in NE Bavaria (Germany). The sample consists of white mica (colored pixel in age map), plagioclase (pl) and quartz (qtz). Domains exhibiting ages of ~480 Ma in the mica core are remnants of the magmatic stage, while younger ages at mica grain boundaries and along cleavage planes are interpreted to result from age reset during a metamorphic event at ~370 Ma.

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High precision and spatial resolution chemical interrogation of planetary materials using fs-LA/LIBS in tandem with multi-collector ICP-MS

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Combining femtosecond laser ablation (fs-LA) with laser-induced breakdown spectroscopy (LIBS), together with multi-collector inductively coupled plasma mass spectrometry (MC-ICP- MS), can provide remarkable insights into the composition, structure, and therefore geologic history of planetary materials and their terrestrial analogs. Using the Applied Spectra iX-fs-Tandem LA-LIBS Instrument and the Nu SP1700 MC-ICP-MS housed within the Center for Isotope Cosmochemistry and Geochronology at the NASA Johnson Space Center, we present preliminary tandem fs-LA-(MC)-ICP-MS/LIBS measurements of planetary analog materials. The synergistic integration of fs-LA-LIBS offers high spatial resolution elemental mapping, enabling the identification of microscale variations within samples. Simultaneously, the MC-ICP-MS can deliver precise isotopic analyses, and integrating the two datasets yields a wealth of geochemical information for a given sample.

LA-based chemical mapping experiment designs are contingent on the information sought (i.e., quantitative, or semi-quantitative) and the preferred or available volume of material removed for the analysis. For example, occasionally, there are significant limitations in the depth of ablation due to the sample value, the amount of material available, or simply the need to coordinate with other *in-situ* techniques. In these limited sample scenarios, the "depth-controlled" chemical maps allow for precise post-mapping ion-polishing of the sample, while the isotopic and elemental maps can be used for targeting future analyses (e.g., conventional LA analyses, SIMS analyses, and micro milling for solution ICP-MS/TIMS). The emerging methodology will establish a powerful tool for investigation of astromaterials and materials returned by future planetary sample science missions.

Exploring the benefits of combining LIBS and LA-ICPMS for geological based applications

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For most geological applications elemental content and isotopic information can be quickly obtained by ICPMS or MC-ICPMS with relatively good precision. However, ICPMS is not routinely able to detect key stoichiometric components such as H, N, O, and F due to atmospheric or argon-based plasma conditions, respectively. In the case of F, the argon-based plasma does not have sufficient ionization potential to ionize fluorine. Due to these reasons, researchers will use various instruments to obtain all the information needed to characterize their samples. Popular techniques such as secondary ion mass spectrometry (SIMS) can be used for F, Cl, and S and electron probe microanalysis (EPMA) can obtain information about elements such as P, Si, Fe, Mg, Ca, Na, S, F, and Cl. EPMA is typically a slower technique in terms of data collection relative to ICPMS. In addition, it has poor sensitivity for rare earth elements (REEs), whereas, ICPMS is extremely sensitive for REEs. Laser-induced breakdown spectroscopy (LIBS) offers the ability to detect every element on the periodic table, including elements that are difficult to detect by ICPMS such as F, H, N, and O. LIBS can be combined with laser ablation (LA)-ICPMS, providing a single fast analytical technique to cover the entire periodic table with a wide dynamic range. Here, we explore the use of simultaneous LIBS and LA-ICPMS for the characterization and quantification of geological samples using known apatite samples. LIBS provides elemental information for elements such as F, O, H, Na, Ca, Mg, Si, P, Mn, and Al, whereas, LA-ICPMS provides elemental and isotopic information for dating by Pb, Th, and U.

Tracing thin water layers from the leaf surface into the plant: how the laser burns the doubt

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Conventional fertilizers are often inefficient and contribute to major environmental problems, ranging from biodiversity loss to climate change [1]. Applying fertilizers directly to the leaves instead of soils has the potential to significantly increase the uptake efficiency into crop plants. Foliar uptake of solutes and colloids varies greatly between different plant species, and the uptake pathways into plant tissues are largely unknown [2]. Current evidence points to stomata as the major entry points for aqueous solutions. For the uptake to take place, a thin layer of water needs to wet a hydrophobic stomatal cell surface, a process called hydraulic activation of stomata (HAS). Solutes and colloids are believed to travel along these thin water films into the cavity below stomata [3]. In this study, we combine a laser ablation ICP-MS (LA-ICP-MS) with confocal laser scanning microscopy (CLSM) and high resolution x-ray tomography (µCT) to investigate ion and particle uptake into leaves of barley and potato plants.

CLSM gives a good overview about the effect of different topographies on the distribution of solutions on varying leaf surfaces. However, the lipophilic properties of the available fluorescent dyes are suboptimal to follow thin water films on a waxy leaf surface, and the method is limited by the laser penetration depth and refractive properties of leaf tissues. We overcome this shortcoming by using µCT. Here, the use of water soluble contrast agents allows to trace thin water films from the leaf surface into the substomatal cavity of living plants at resolutions below the µm scale. While this gives more realistic information about the penetration of leaves by water, the contrast is created solely by variations in density within the sample, and artefacts are introduced easily. It gives no information about the chemical composition of the volume investigated, and data interpretation is difficult. Tracer ion mapping of thin leaf sections by LA- ICP-MS is the only method that allows us to verify that the contrast is generated by the solution that was applied to the leaf. A gel based calibration curve enables us to semi-quantitatively estimate the uptake efficiency into the leaf tissue. LA-ICP-MS also helps to investigate the varying distribution patterns of ions or colloids with different properties within the leaf. As such, LA-ICP-MS is the core method when it comes to verification of data from CLSM and µCT, and it plays a key role in the interpretation of the obtained images.

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Efficiency of foliar fertilization assessed by LA-ICP-MS

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Fertilizing plants via the leaves, a.k.a. foliar fertilization, has tremendous potential to improve the nutrient use efficiency in plant production, thus supporting the green transition of the agricultural sector. The success of foliar fertilization depends on how well the nutrient solutions adhere to leaf surfaces, as well as the mobility of the nutrients, once they enter the plant. Since leaf surfaces are hydrophobic and the nutrients are water-soluble, we are currently working with liposomes as potential nutrient vehicles. Liposomes are phospholipid spheres that we fill with a nutrient cargo, and we expect them to improve the mobility, especially of manganese (Mn) and boron (B), which are micronutrients with a poor mobility in all plant tissues. We are currently assessing whether liposomes remain intact in the tissues, and where their cargo is unloaded. This requires a combination of techniques, including confocal microscopy and LA-ICP- MS. As liposomes are too small (~100 nm) for identification via classical microscopy, we label their membranes with a fluorescent dye, to unravel their transport pattern from the leaf surface to the vascular system of the plant. By combining the precise localization of the liposomal membranes with LA-ICP-MS, to pinpoint increases in nutrient content, we are now starting to unravel the carrier properties of liposomes *in planta.* We have optimized the sample preparation to maintain all plant structures, as well as the ionomic composition of the dried leaf sections. With a spot size of 4 µm, we have now documented that Mn-liposomes enters the leaf and accumulates in and around the vascular tissues (xylem and phloem), within 3 hours after treatment. Our next challenge is to prove that Mn-liposomes can also travel to the rest of the plant, via the vascular tissues, in order to reverse Mn-deficiency of the whole plant.

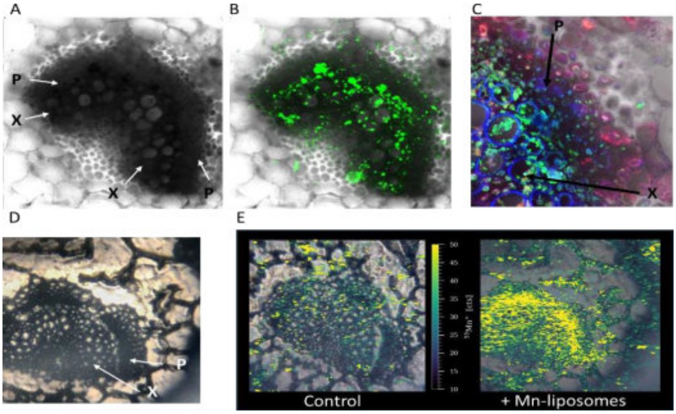

Figure 1. Localization of Mn-loaded liposomes in the vascular tissues of oil-seed rape (*Brassica napus*). The vascular bundle of liposome- treated leaf, imaged with confocal microscopy, on fresh plant tissue (**A-C**), or after sample preparation for laser ablation ICP-MS (**D-E**). **A-C.** Transmitted light and liposome fluorescence (green) of the whole vascular bundle, and a zoom-in (**C**) with highlighted chloroplasts (red)and lignin in xylem cell walls (blue) autofluorescence. **D-E.** Representative optical image (**D**) of the vascular bundles and its Mn content (**E**) of a control leaf and a leaf treated with Mn-liposomes. X: Xylem, P: Phloem.

Suberin restricts potassium leakage from plant roots

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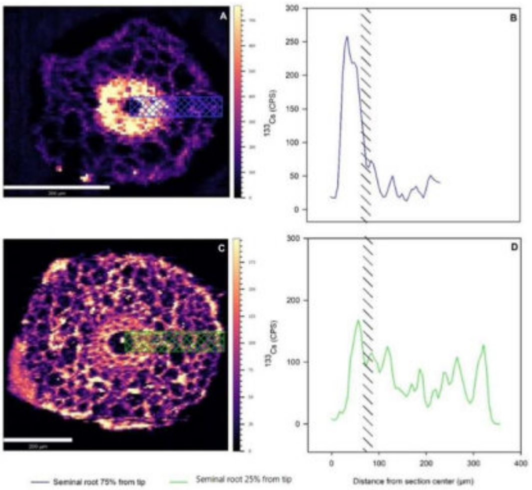
An urgent challenge within agricultural crop production is to maintain productivity in a world plagued by climate change. In this new reality, understanding root functionality is essential, as it not only affect plant-water relations, but also nutrient transport and food security.

The endodermis, or the “inner skin” surrounding the vascular tissues of plant roots, becomes suberized in response to various environmental cues, including drought and nutrient deficiency.[1] As such, it functions as a checkpoint for ions and water either entering or escaping the root. It has been hypothesized that suberin act as a physical barrier preventing radial potassium (K) leakage out of the vascular tissues during translocation to the shoots. Attempts to support this idea has, however, yielded contradictory results.

We developed an LA-ICP-MS method to study K leakage from roots with different suberin deposition. As K backgrounds are very high in any plant tissue, and K-isotopes overlap with strong interferences (^{41}ArH), we used cesium (Cs) as a tracer for K. We show that Cs is an excellent tracer for K, due to its very low background and high sensitivity, even at non-toxic trace concentrations in the investigated tissues. Element bioimaging of roots (fig below) and total shoot concentrations all showed a positive relationship between suberin deposition and K translocation efficiency.



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Quantitative bioimaging of boron-based contrast agents by means of LA-ICP-MS

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The presented study focuses on the development of a method for the spatially resolved quantification of boron in tissue thin sections to assess the distribution of administered boron dipyrromethene (BODIPY) nanoparticles within the body. BODIPY nanoparticles are tested as a contrast agent for multispectral optoacoustic tomography (MSOT) to investigate vascular permeability. A 213 nm laser ablation (LA) coupled to an inductively coupled plasma-mass spectrometry (ICP-MS) system is used for this purpose. The examined tissue sections originate from an animal study in which an aqueous solution of the BODIPY nanoparticles was injected into mice. The mice were then sacrificed at different time points after the injection and various organs were resected and cryosectioned.

The boron distribution was quantified in spleen and liver sections. In addition to the element boron, the endogenous elements phosphorus and iron were analyzed to obtain information about the microscopic structure of the organs and correlate it to the boron concentration. Matrix-matched gelatin standards were used for quantification. As it was observed that the boron content in the standards was not stable over a period of one week, the storage temperature was lowered and sorbitol was added for complexation, resulting in a stability over several weeks. The detection limit was minimized by optimizing various parameters, as the LA transport gas flow and the laser scan rate, and by comparing two combinations of LA and ICP-MS systems. In the tissue sections of the animals injected with the BODIPY nanoparticles, a higher boron concentration was found in both the liver and the spleen than in a negative control.

Titanium imaging in fish tissues exposed to titanium dioxide nanoparticles by quantitative laser ablation-inductively coupled plasma-mass spectrometry

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The second most cultivated species in the EU in 2020 was the sea bream, with a total contribution in 93,131 tonnes being, at the same time, the fourth most cultivated species in the world (259,443 tonnes) [1,2]. In addition, Spain was the leading producer country in tonnes in European territory. At the same time, we all witnessed the rise and rapid growth of nanotechnology, with nanomaterials (NMs), nanoparticles (NPs), and nano-based products present in virtually all industrial sectors, aquaculture included. Given the importance of the aquaculture sector (both nationally and internationally) and to meet the global growing demand for healthy and safer consumer aquatic products, new analytical methodologies for detection and quantification of NPs in fish species need to be developed. In this sense, laser ablation-inductively coupled plasma mass spectrometry (LA- ICP-MS) has great potential. It offers wide dynamic range, multi-element detection capabilities and high spatial resolution, among other advantages. The primary focus of LA-ICP-MS applications in biological tissues has been on bioimaging components in cells, tumor tissues, brain slices, and tissues from other organs. However, scarce literature is available for NP imaging using LA-ICP-MS, which poses a challenge to the scientific nano-community.

Considering the foregoing, the current work aims to develop a novel quantitative imaging method based on LA-ICP-MS for assessing the biodistribution of titanium in sea bream tissues (liver, kidney, and muscle) after exposure assays with 45-nm citrate-coated titanium dioxide nanoparticles. Results showed the presence of titanium in sea bream's tissues, as well as the presence of hot spots in kidney's tissues from exposed specimens. The use of high-rate scanning and low laser energy allowed us to obtain sensitive and quantitative bioimages with high spatial resolution.

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Determination of target metals and proteins, identified in drusen and senile plaques, in brain sections of APP/PS1 transgenic model supplemented with Zn using LA-ICP-MS

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Neurodegenerative diseases (NDs) are prevalent pathologies in the World's ageing population. Up to date the pathogenesis of these etiology is not fully understood, although ageing, oxidative stress, metal dishomeostasis and the formation of protein aggregates are known to play an important role. There are scarce preventive and protective therapies for treating NDs, consequence of the uncertainty surrounding their fundamental mechanisms and the absence of reliable biomarkers. Currently, existing treatments only provide relief from symptoms without halting the progression of neurodegenerative processes. Nutraceuticals and nutritional supplements contribute to reduce the risk of developing NDs although there is a lack of widely accepted dosage guidelines. Recent studies have demonstrated the protective role of Zn supplementation against neurodegeneration.

In this context, working with animal models allows for the study of alterations of metals and proteins involved in their homeostasis. Specifically, the APP/PS1 transgenic mouse model of neurodegeneration may be useful to study mechanisms related to NDs such as Alzheimer's disease (AD) and age-related macular degeneration (AMD). Endogenous metal distributions (Cu, Fe and Zn) have already been studied in brain tissue sections from this mouse model by LA-ICP-MS, comparing them with control individuals [1]. However, in this work we present a step forward, focusing not only on endogenous metals in brain tissue sections but also on target proteins directly associated with aberrant deposits found in NDs. Additionally, the effects of ZnSO4 supplementation (85 mg ZnSO4 H2O/L of drinking water) on metals and target proteins brain distribution have been evaluated on both control and APP/PS1 mice.

Brain tissue sections from 8 sample groups were studied by LA-ICP-MS: control and APP/PS1 mice, with and without Zn supplementation, at two different ages (4 and 16 months). Quantitative distribution of metals and proteins was studied in consecutive sections of the different mouse groups to determine changes in their concentration and localization during zinc supplementation and disease. Metal distribution was directly analyzed by LA-ICP-MS, whereas nanoclusters (NCs)- labelled immunoprobes were employed for protein analysis. Multiple NCs, made of different core metals, were employed for the simultaneous bioimaging of target proteins.

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Imaging of environmental toxic metals distribution in the brain by LA-ICP-MS

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Age, genetics, and environmental exposure are among the primary risk factors for developing Alzheimer's Disease (AD) and other dementias [1]. Among these, the role played by environmental exposures is the least studied. However, exposure to environmental toxicants is disproportionately high in disadvantaged groups, making research on this topic both a medical and a social justice concern.

LA-ICP-MS imaging is known as a potent new neuroscience research tool. This method provides ultra-trace elemental quantification and accurate anatomical localization. We used LA-ICP-MS to investigate toxic metal/metalloid accumulation and regional distribution in mouse brains after chronic exposure to Pb, Cd, and As in drinking water. We also studied gadolinium retention in rat and human brains after exposure to intravenous gadolinium-based contrast agents (GBCAs) [2].

We used the laser ablation system (Analyte Excite+, Teledyne CETAC Technologies) coupled to a quadrupole inductively coupled plasma mass spectrometer (iCAP-Q, Thermo Fisher Scientific). The samples were scanned line by line with the following scan parameters: spot size – 50 µm, line gap – 0 µm, scan speed – 100 µm/s. Calibrations were performed with thin sections of 10% gelatin and commercial gelatin-based micro-droplet standards [3].

We showed that neurotoxicants have non-homogeneous element-specific accumulation in different brain regions and sub-regions, including the hippocampus and cortex. We discovered prolonged gadolinium retention in human brains that lasted years after GBCA injection. These findings offer fresh insights into the most plausible processes behind the distribution, transportation, and retention of toxic metals in the brain.

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High-resolution LA-ICP-MS imaging of Pt-derivates in single cell and tumour tissue

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About 19 million of new cases of cancer were diagnosed worldwide in 2020. Mortality has been decreasing due to factors such as improved diagnostic processes, prevention, development of techniques, and experimental treatment in recent years; nevertheless, cancer still belongs among the main causes of death globally, with approximately one in six deaths. It is no wonder that the research assigned to cancer belongs to the dominant topic throughout various scientific disciplines. In general, cisplatin and other platinum-based compounds are used as a chemotherapy medication to treat number of cancers.

In this work, the single cells and soft tissues after cisplatin treatment were investigated by LA-ICP-MS. The implementation of Aerosol Rapid Introduction System into the LA-ICP-MS system provided high-resolved 2D multielemental images. Moreover, platinum distribution in single cells was monitored at various time intervals after drug uptake, simultaneously with Pt secretion by extracellular vesicles. Additionally, platinum transfer within tumour clinical specimens was investigated resulting in assessment that the platinum was excluded from the active tumour. Besides Pt, other elements such as Cu, Zn were monitored to assess elemental transfer and to indicate potential self-resistance mechanisms in real clinical specimens. The obtained results enable further research of tumour tissue resistance and testing of tumour responses to different drug doses.

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High-resolution LA-ICP-MS and tracing Ru-based metallocene in tumour cells

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The generic term, cancer, represents a manifold group of diseases with a common denominator such as uncontrollable and abnormal cell growth in any body tissue and organ. To avoid cancer development and its spread to other parts of the body, so-called metastasizing, prevention, and early diagnosis at the earliest stage play an important role.

Generally, medical treatment is based on the application of metal-based anticancer agents with platinum. However, the application of cisplatin and other Pt derivatives frequently shows side effects relating to Pt toxicity and a low efficiency given by the acquired resistance of tumour cells.

In this work we employed LA-ICP-MS for tracing a novel unique Ru-based drug in lung cancer cell lines. The implementation of Aerosol Rapid Introduction System and experimental parameters fit-for-purpose of high spatial resolution 2D single cell imaging at ultratrace level enabled to localize Ru in the cell nuclei. Furthermore, the laser ablation sampling was employed to clarify kinetics mechanism, when Ru-based drug cell influx was determined 6, 12 and 24 hours after drug application.

Our results provide essential information about drug uptake by cells, and at the same time, together with other advanced analytical methods, they can complement the set of information needed to obtain a comprehensive result in the sense of determining the mechanism of cell line resistance.

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Mass spectrometry imaging of renal alternations in mice with cisplatin-induced acute kidney injury treated with CeO_2 nanoparticle

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Acute kidney injury (AKI) is a sudden loss of kidney function that can be life-threatening, particularly for cancer patients. Recent studies have discovered that ceria nanoparticles have potential to prevent and treat clinical AKI.[1] In this study, we used mass spectrometry imaging techniques to visually demonstrate changes in elements, proteins, and metabolites in the kidney tissues of mice afflicted with cisplatin-induced AKI who were subsequently treated with CeO_2 nanoparticles. The kidney samples were sectioned serially, and the adjacent sections were imaged using different methods. Laser ablation-inductively coupled plasma-time of flight mass spectrometry (LA-ICP-TOFMS)[2] was used for fast multi-element imaging in kidney tissues. Metal- labelled antibodies were used to stain proteins, which were then imaged using LA-ICP-TOFMS. Metabolites were mapped using the desorption electrospray ionization mass spectrometry (DESI-MS). In combination with the in situ distribution of elements, proteins, and metabolites, our methods provide spatial information on renal alternations in these components. By revealing what happens in the renal tissues from metal to proteins and metabolites, the developed spatial multi- omics methods uncover pivotal interactions in the AKI kidney and offer insights into the role of CeO_2 nanoparticles in the therapeutic applications.

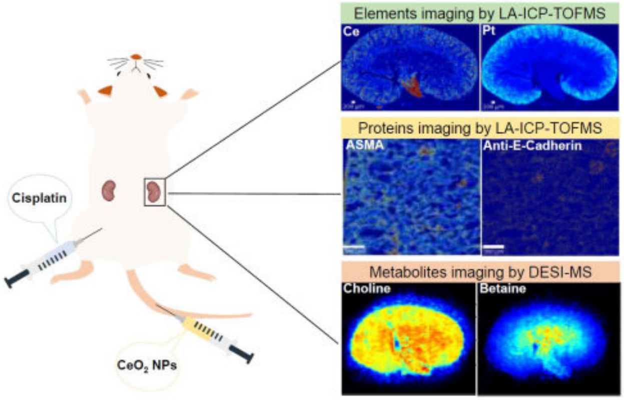

Figure 1. Schematic illustration of studying elements, structural proteins and metabolites distribution in kidneys of mice with AKI induced by cisplatin and treated with CeO_2 nanoparticles.

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Investigating the Use of Simultaneous Laser-Induced Breakdown Spectroscopy/Laser Ablation–Inductively Coupled Plasma–Time-of-Flight–Mass Spectrometry for the Analysis of Biological Materials

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Laser ablation (LA) is becoming increasingly popular for the analysis of biological material including brain, kidney, and lung tissues. Contaminants of interest in these matrices vary widely from silicates to heavy metals. Because of the breadth of these analytes, inductively coupled plasma (ICP)–time-of-flight (TOF)–mass spectrometry (MS) has become a prevalent detection technique owing to its inherent ability to simultaneously measure all nuclides ranging from ^{7}Li to ^{238}U in tens of microseconds. Not only does the wide analytical range interest users, but the fast acquisition times also permit rapid imaging with the use of ultrafast washout cells. Many of the benefits of ICP-TOF-MS are offered by laser-induced breakdown spectroscopy (LIBS), which measures the optical emissions of the laser ablation plasma. LIBS is sensitive to the entire periodic table, particularly the lighter elements, and can be performed in a single microsecond making the method also amenable to elemental mapping. The work presented here will investigate how simultaneous LIBS/LA-ICP-TOF-MS techniques can be applied using fast washout cells and how high-precision translation stages can extract valuable and complementary information for biological materials.

Platinum nanoparticles enhance LA-ICP-MS signal for trace element detection in serum spots

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Several metals are essential for human metabolism, but accurate dosing is critical because of the potential for adverse health effects from even small increases above normal levels. The emerging field of clinical toxicology has focused on the biomonitoring of these elements in organic matrices.[1] Central to this effort is the development of analytical methods capable of detecting trace and sub- trace levels of metals in organic fluids. Achieving ever lower limits of detection (LOD) and quantification (LOQ) has become paramount, along with the imperative to minimise sample volumes and speed up the diagnostic process. In this context, the integration of Dried Matrix Spot (DMS) as a sampling mode with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) offers a promising avenue for less invasive and accelerated analysis.[2] In this study, we propose a novel, simple and rapid approach to enhance the analytical signal of trace metals in human serum without changing the experimental set-up (i.e. laser parameters or gas carrier composition). The technique involves the application of platinum nanoparticles (PtNPs) to the sample surface. [3] This novel approach has been successfully tested for trace quantification in serum analysis using the DMS technique. The following elements were determined: Al, As, Co, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Sb, Se, Sn, V and Zn. A gelatine-based standard, consisting of porcine skin gels spiked with the calibration solutions, was developed and used, which allowed a better quantification of the metals compared to the standards usually used in the literature, due to its more similar structure to serum. This approach provides a well-defined and quantifiable signal, allowing the detection of elements that would otherwise remain undetectable due to their low concentrations and polyatomic interferences.

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Metallomic imaging of microbial nutritional immunity

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Metal ions play indispensable roles in diverse biological and cellular processes to sustain all living cells. In mammals, a variety of biometals serve as crucial factors that influence immune responses. However, microbial pathogens are also dependent on these biometals to fuel their growth and activate key virulence factors. Consequently, host immune cells have evolved at least two strategies to limit microbial pathogenesis: (i) metal sequestration, which limits access to essential biometals by pathogens, or (ii) metal intoxication to induce metal poisoning of pathogens, referred to as nutritional immunity. Whilst the role of biometals has been heavily investigated with respects to microbial pathogenesis in bulk samples (*in-vivo* and *in-vitro*) it is unknown if the spatial distribution of these metals within tissues impact susceptibility to the bacteria.

Using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) we present the elemental distribution of key biometals (Fe, Cu, Zn, Mg, Mn) alkali metals (K) and non-metals (S), which are known to modulate bacterial pathogenesis. A combination of triple-quad LA-ICP-MS (iCAPTQ, Thermofisher Scientific) and time-of-flight LA-ICP-MS (Vitesse, Nu instruments) enabled high selectivity and sensitivity (TQ) and full-mass coverage at high-speeds (ToF). An iridia (Teledyne) laser ablation system was used (0.5-1kHz) at resolutions of 10-30 ums.

We will present the findings relating to the distribution of metals across key biological features such as caseous, necrotic, and calcified granulomas which are routinely found in human tissues exposed to bacteria. Different lesions across different organs and patients presented a variety of metallomic profiles, unfortunately due to pending patent requests we cannot disclose specifics on the bacteria or metallomic signatures. We will also cover the analytical methods, experimental consideration and data analysis for interpretation. Including calibration with micro- gelatine droplets and drift corrections with respects to biological samples.

How to assess limits of detection for single-cell elemental bioimaging by LA-ICP-MS

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LA-ICP-MS has become an established bioimaging technique, providing high sensitivity, high- speed mapping and spatial resolution in the low µm range [1]. The growing interest in quantitative elemental bioimaging is reflected by a plethora of proposed standardization strategies [2].

In this context, gelatin has emerged as a fit-for-purpose calibrant, widely used in different versions such as micro-arrays, micro-droplets, molds and thin sections. Due to the similarity to biological material, it is considered to mimic the matrix of tissue sections and cells. In our laboratory, an external calibration approach based on multi-element gelatin standards produced by a robotic micro-dispensing device has been developed and validated [3]. Similar to ICP-MS bulk measurements of liquids, this quantification procedure employs a multiple-data point approach and enables comparable analysis times for a calibration sequence. Reliable standardization is the prerequisite for quantitative imaging, however, each quantification experiment has to be validated. Scrutinizing the analytical figures of merit for each LA-ICP-MS imaging application is key. We discuss how to use external calibrations to assess figures of merit such as sensitivity and limits of detection in the context of bioimaging applications at a single-cell level. We will compare different approaches to asses limits of detection and discuss their possible implementation in single-cell metallomics.

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LA-ICP-TOFMS imaging reveals Pt(IV)-drug bioaccumulation in tumor tissue at the single-cell level

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Laser ablation (LA) in combination with inductively coupled plasma-time of flight mass spectrometry (ICP-TOFMS) has been established as an essential tool in the development of metal- based anti-cancer drugs. The elemental imaging method can provide crucial understanding on drug distribution and specificity of drug accumulation in different tumor scenarios aiding (pre-)clinical research.

While quantitative bioimaging is well established in the field of metallodrug research, studies integrating metal-based immuno-histochemistry and single-cell resolution are still rare. In this study, we explore the promising Pt(IV) candidate drug BSO-OxMal, which showed higher tumor selectivity resulting in significantly enhanced overall survival compared to oxaliplatin.[1] The distribution of the albumin-binding compound was studied for the first time at the single-cell level in a murine colon cancer model.

Quantification was based on gelatin micro-droplet standards [2], which allowed to assess Pt uptake in fg per individual cell. The quantitative bioaccumulation was studied in the context of the tumor microenvironment, linking drug uptake to cell type and functionality. The investigation compared the candidate drug to the established clinical drug, oxaliplatin.

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Development of LA-ICP-MS analysis for quantitative elemental mapping in dendrochemistry

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Trees growth is made by the accumulation thin wood layers over the time. Seasonal variations lead to visible differences in wood density that create typical ring patterns commonly referred to as tree rings. Each ring corresponds to a new year and is characteristic of the tree's environment (soil, water and air) at its time of formation. Dendrochemistry (the study of chemical variations in tree rings) is therefore a promising method to trace pollution evolution in contaminated sites and soils. In order to develop this analytical tool for polluted soils and obtain quantitative elemental mapping of tree samples, existing analysis techniques need to be improved. Indeed, in most of dendrochemicals studies, the analysis techniques (XRF, PIXE, ICP-MS, etc.) are limited by the detections limits, the numbers of elements detected or analysis constraints. To obtain the most accurate and comprehensive results possible on the pollutants present in the soil at the sites studied, laser ablation coupled with mass spectrometry (LA-ICP-MS) was selected as the analytical method for the ARGOS project, in addition to microXRF.

Analyses were performed within the BRGM (French survey) laboratories (Orléans, France). The used LA-ICP-MS setup is a 8900 Agilent Triple-Quadrupole coupled to a Teledyne CETAC Excite Eximer (EXCIted diMER) 193nm laser. A first challenge has been to find suitable standards for quantifying our samples. These standards had to meet a number of requirements: 1) the concentrations of the chemical elements of interest for polluted sites and soils had to be known (certificate, prior liquid ICP-MS analysis, etc.). 2) the behavior during laser ablation of these standards had to be similar to that of the wood sample. We tested a wide variety of standards from certified powders (algae, cabbage, tomato, etc.), to 'homemade' standards based on crushed wood or leaves. Another challenge has been to adapt the conditions of ablation to wood samples. To this end, a literature review and a series of tests using different ablation conditions were carried out.

The results so far are very promising and are in agreement with those obtained by XRF. Many chemical elements have been detected in the various standards, as well as in the first tree samples available. Detection limits are reasonably low, from ppb to ppm range. This is especially important as there is a great disparity in the way different elements are absorbed in the tree rings. Some (such as Pb, As) can only be found in extremely low concentrations. The first maps on tree samples could be obtained and treated using the ARGOS software developed as part of the project. These maps satisfyingly show the evolution of the chemical elements within the annual rings and highlight the different behaviors or affinities of the elements in different parts of the tree. The yearly evolution of pollution indicator elements (Cl, Zn, Cu, Cd, As, Pb, etc.) is also clearly visible. These preliminary results point out the strong potential of LA-ICP-MS analysis for dendrochemical studies.

Comparing methods for quantifying elemental images obtained by quadrupole and time-of-flight LA-ICP-MS

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Elemental images or maps obtained by LA-ICP-MS contain a wealth of information about element and isotope distributions within zoned minerals and among co-existing phases. Qualitative applications of elemental maps included deducing cryptic magmatic, metamorphic, and hydrothermal processes, for which other evidence has been obliterated, and targeting suitable zones for *in situ* geochronological and isotopic analyses. More quantitative applications include mapping distributions of isotopic compositions or radiometric ages as well as using compositions extracted from single pixels or groups of pixels for trace element thermometry and diffusion time scale studies. A wide variety of data collection, calibration, and quantification methods have been employed (e.g., refs. 1-3). In this contribution, we directly compare elemental images of the same materials collected with quadrupole and time-of-flight (ToF) LA-ICP-MS systems and quantified using various calibration and data reduction approaches (Fig. 1). We investigate garnet, pyrite, and carbonate samples, covering minerals and rocks that are commonly imaged in geologic studies.

From these comparisons, we address several outstanding issues, including the following: (1) Are quantified results obtained via ToF and quadrupole systems equivalent? (2) What is required to consider an image fully quantitative? (3) What are the advantages and limitations of the different collection modes (i.e., line scans, single pulse, multi pulse)? (4) Do samples and standards need to be analysed in the same manner (e.g., spots vs. line scans)? (5) How do the various internal standardization and normalization approaches commonly used in multiphase maps affect results? (6) When, if ever, should post-acquisition smoothing be implemented? (7) How should pixels that overlap different phases (mixels) be handled? We expect this contribution to spark discussion on the robustness of (semi)quantitative LA-ICP-MS images generated in different ways.

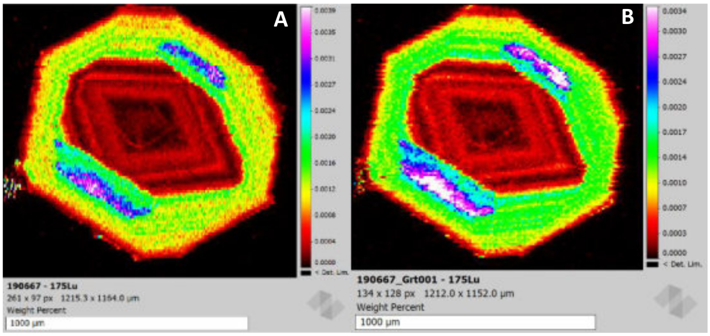

Figure 1. Lutetium maps of an igneous garnet crystal collected using (A) Agilent 7900 quadrupole and (B) Tofwerk icpTOF R LA-ICP-MS systems. In both examples, data were collected using line scans and LADR was used to generate and quantify the maps, using Al as internal standard and normalizing the oxide total to 100%.

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Pseudo-Isotope Ratios by LA-ICP-OES for Sea Surface Temperature Reconstruction

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The pseudo-isotope ratios of Sr/Ca are widely used as a paleothermometer to reconstruct sea surface temperatures (SST) using the carbonate skeleton of corals as a continuously growing archive. Dome-shaped corals (e.g. *Porites, Diploria, Siderastrea* sp.) grow all year long and build skeletons that can span more than 300 years into the past, and hence represent valuable archives to reconstruct the past climate conditions [1]. Subfossil corals provide records of seasonal to interannual variability in time windows spanning the Past Millennium, the Holocene and even the Past Interglacial. Such paleo-temperature data sets are urgently needed for validating models predicting the future of Earth climate.

The Sr/Ca ratio recorded in coral aragonite is inversely correlated with the seawater temperature during mineralization. Consequently, a small uncertainty in Sr/Ca ratio determinations accomplishes temperature estimates with high precision. Conventional Sr/Ca analysis is based on micro-drilled coral carbonate powder which offers spatial resolution of ~0.5 mm, allowing for biweekly SST estimations. However, this approach is extremely labor-intensive and time- consuming given the sample numbers needed to reconstruct a single temperature record (~1000 samples / 100 yrs), not including any replication.

Direct *in situ* laser ablation offers a huge potential for increasing the throughput and the spatial resolution. Published data from *in situ* Sr/Ca measured by sequential instruments however, are insufficient in the quality needed for high resolution temperature reconstructions and a truly simultaneous 'multi-collector' data acquisition is sought after. MC-ICP-MS instruments do not offer the mass dispersion needed for a simultaneous analysis of Ca and Sr.

We have thus coupled the only commercially available ICP-OES instrument providing simultaneous detection and adequate time-resolved acquisition of Sr/Ca (SPECTRO Arcos II MV) with a commercial LA system (ESL imageGEO193, fitted with a two-volume ablation cell, ESL TV2, and custom-made coral sample holder) to reconstruct weekly to biweekly SST in corals with a high throughput (75 years/day). A series of coral-carbonate nanoparticulate powder pellets ('nanopellets') [2, 3] with variable Sr/Ca ratios are used for intensity ratio calibration. We will report on the figures-of-merit of this setup for high-precision Sr/Ca analysis by LA-ICP-OES and compare it to conventional solution-based methods.

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In situ mapping of elemental dissolution at ultra-trace levels during aqueous corrosion of Al alloys

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Technological engineering heavily relies on aluminium (Al) alloys to design lightweight materials towards sustainable transportation. To enhance Al alloy longevity, the complex mechanisms that control Al corrosion in aqueous environments need to be better understood. Existing methods used in Al corrosion research are based on surface-sensitive *ex situ* analysis techniques. Despite their high spatial resolution, these techniques fail to detect the ultra-trace amounts of locally solubilized corrosion products and their interactions while corrosion takes place. Here, a novel approach based on recent work [1] using the diffusive gradients in thin-films (DGT) technique in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is presented, allowing for *in situ* mapping of elemental dissolution with high spatial resolution (50 µm), high sensitivity, high selectivity, and capability to measure two-dimensional (2D) diffusion patterns of multiple elements simultaneously. The approach was comprehensively evaluated and successfully used for quantitative mapping of Al along with zinc (Zn) and copper (Cu) solute release during short-term (t = 15 min) corrosion of a high-strength Al-Cu alloy (Al2219; w(Al) = 93.6 %, w(Cu) = 5.8 %, w(Zn) = 0.03 %) exposed to sodium chloride solution (w(NaCl) = 1.5 %). Results showed reproducible patterns of Al and Zn co-dissolution from the material surface with a spatial expansion of 50-1000 µm (Fig. 1), which were explained by localized corrosion processes also indicated by complementary solid-state data. Method detection limits (MDLs) for total solute masses of Al, Zn, and Cu were ≤0.72 pg, ≤8.38 pg, and ≤0.12 pg, respectively, for an area of 0.01 mm^2, demonstrating the method's unique capability to localize and quantify corrosion processes at ultra-trace levels and high resolution. Thereby, the developed approach overcomes the limitation of existing methods visualizing surface alterations without detecting localized elemental dissolution, effectively advancing the assessment of aqueous corrosion of Al alloys for enhanced material design.

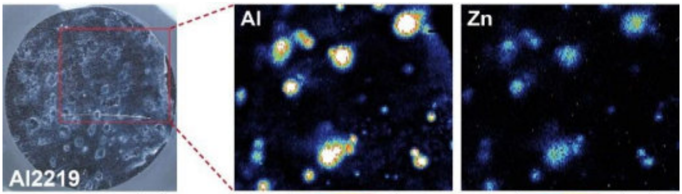

Fig. 1. Solute maps of Al and Zn showing their localized co-dissolution from the surface of Al2219.

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False signals: quantification issues of trace Si in non-silicate minerals by LA-ICP-MS

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Laser ablation ICP-MS is widely used for trace and ultra-trace (sub-ppb) elemental analysis in geological materials. While the level of detection for a given element is strongly controlled by the beam diameter used in the ablation, the gas blank can also significantly influence levels of detection. Lighter elements (m/z <85) typically have higher gas blank signals due to gaseous interferences (e.g., $^{40}Ar^{16}O$ at m/z 56). In theory the gas blank subtraction should allow for accurate quantification of an element, even with a relatively high gas blank, however; we observe some elements that appear to have elevated signal above gas blank during ablation when the element is not present in the target phase (e,g., S in quartz). Similar phenomenon has been documented in Schlöglova et al. 2017 [1] showing a false signal for Au, S and halogens in quartz, topaz and beryl; however, this previous work has utilized single volume ablation cells.

This study presents false signal during ablation for a number of elements (Si, S, P, halogens) in a large-format, two-volume ablation cell with an emphasis on the element Si. This overestimation of Si and other elements can affect quantification where normalization to a fixed total (e.g., 100%) is used and can lead to incorrect geological interpretations. We will present results using the mineral magnetite (Fe_3O_4) and a variety of other non-silicate mineral phases (barite, sphalerite, and carbonate) to show significant signals above gas blank for Si during laser ablation analyses. Comparing the LA-ICP-MS data to Si concentrations obtained by electron microprobe analysis, we observe significant (>10x) enrichments in Si in the LA-ICP-MS results. To better understand the cause of this false signal, a series of tests are performed using ICP-MS/MS technology to remove N, O and C based interferences on Si. Results show that the signal at mass- shifted Si isotopes in magnetite is due to elemental Si and not an increase in the N, O or C based interference during the ablation. The 'extra' Si seen in the LA-ICP-MS analyses is likely due to either laser beam interaction with previously ablated aerosol on the fused SiO_2 window or is due to remobilized Si particles in the interface tubing. Strategies to mitigate the false Si signal will be discussed.

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Concurrent determination of Sr-isotope signature and trace elements contents of depleted glasses via laser ablation split stream: Pros and Cons Of Different Approaches

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This study presents varied analytical approaches to quantify both the ^{86}Sr/^{87}Sr signature and trace element (TE) contents of geological material (mostly glasses) in laser-ablation split stream mode. Our aim in setting up this protocol is to obtain, with spot size below 40 microns, individual spot precision on the ^{86}Sr/^{87}Sr of ca. 0.0005 for material showing ca. 30 ppm of Sr and accurate measurement of highly depleted TE, such as U, which can be as low as 10 ppb in some of the reference material used. This method was developed in order to being able to obtain both Sr isotope composition and TE contents on < 40 microns wide melt inclusions hosted in high-magnesium olivine host from depleted rocks such as komatiites.

This analytical protocol has been developed at the ISTerre Micro-Analytical Platform (IMAP) hosted in Université Grenoble Alpes (UGA, France) using a Resolution-SE (Applied Spectra) 193 nm excimer laser ablation system, a Neptune XT (Thermo Fisher) multi-collector ICP-MS equipped with four 10^{13} Ω amplifiers for the measure of Sr isotopes and an 8900 (Agilent) triple quadrupole ICP-MS for the measure of TE contents. Reference material analyzed for Sr- isotope calibration are KL2-G and ML3-B (Sr = 350 ppm, Rb/Sr < 0.025), NIST-614 (Sr = 45 ppm, Rb/Sr = 0.019) and GOR128-G (Sr = 30 ppm, Rb/Sr = 0.013). In addition of those, NIST-612 and GSD1-G were also analyzed for TE calibration.

Several configurations of split stream were tested: (i) natural ≈ 50-50 split, (ii) non-symmetrical split with more aerosol towards the MC-ICP-MS with a longer tubing towards the 8900, (iii) non-symmetrical split with more aerosol towards the MC-ICP-MS through pressure constraint, right after the split, on the tubing going to the 8900 and (iv) non-symmetrical split via the use of a laser ablation mixing bulb in combination with a diaphragm pump.

This presentation will show results for all configurations and discuss the positive and negative sides of each protocols.

Analysis of ultra-fast transient signals by LA-MC-ICPMS – overcoming instrumental limitations

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Isotopic analysis of individual micrometer-sized particles containing U and/or Pu is a highly effective tool used by the International Atomic Energy Agency (IAEA) to detect the presence (or confirm the absence) of possible undeclared nuclear material and activities.

Laser ablation multi-collector inductively-coupled-plasma mass spectrometry (LA-MC-ICPMS) has been investigated as a complementary method to the traditional fission-track thermal ionization mass spectrometry (FT-TIMS).

It has been recognised that the ablation of micrometer-sized particles produces very short but intense transient signals with a length of hundreds of microseconds that are caused by individual particle fragments. These transient signals are under-sampled leading to biased isotope ratios.

In this work we present hardware and software developments for recording fast transient signals which substantially improve the accuracy of isotope ratios measured with a Neptune Plus^{TM} MC- ICPMS (Thermo Fisher Scientific, Bremen, Germany).

In particular, we suggest an approach for investigating transient signals under controlled conditions, discuss the effect of pulse pileup and detector shutdowns and propose approaches for reducing or correcting for biases that are introduced by transient signals in a commercially available MC-ICPMS. The results obtained with hardware developed in-house for transient signal monitoring demonstrate an improvement of the dynamic range of ion counters by up to one order of magnitude with simultaneous improvement of measurement accuracy.

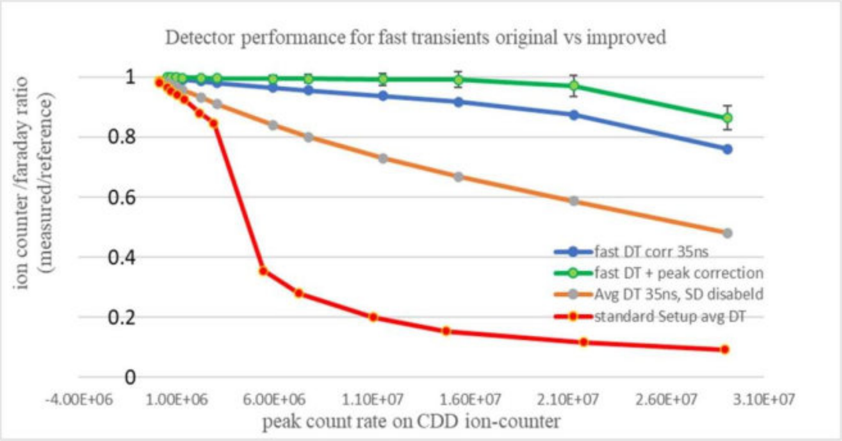

Figure: Evolution steps of detector performance for recording transient signals with ion count rates of up to 30Mcps from original setup (red) to improved performance (orange, blue, green).

In-situ, simultaneous measurement of oxygen and carbon isotope ratios via LA IRMS – study case on inorganic carbonates

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Oxygen and carbon stable isotope ratios ($\delta^{18}O$ and $\delta^{13}C$) measured on carbonates are frequently used to constrain paleoclimate models of past geological periods. Traditionally, these measurements are carried out using highly elaborate sample preparation techniques that often require manual sampling and precise weighing of samples, as well as acid digestion.

In this contribution we explore a streamlined method for measuring isotopic ratios simultaneously in carbonate samples, *in situ*, with minimal sample preparation. The hardware setup used for the measurements comprises a laser ablation system (Teledyne Photon Machines Fusions CO_2) equipped with a specially designed ablation chamber (Terra Analitic isoScell Δ100), coupled to a CryoPrep unit and an HS2022 IRMS (both Sercon). We investigate the effect that different experimental conditions (e.g., laser energy output, carrier gas flows, trapping time, etc.) have on the accuracy and precision of isotopic ratios as well as identify potential drawbacks of the technique.

Laser ablation IRMS analysis of δ^{13}C in creep affected Picea abies from Făgăraş Mountains, Romania

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The study area is situated on an anthropogenic slope in the Bâlea glacial valley (Southern Carpathians, Romania). Trees were selected for sampling based on visible signs of creep movements affecting their growth. Trees with d-shaped stems were chosen. Norway spruces (Picea abies) were sampled using a 30 or 40 cm Pressler increment borer with a 5.15 mm diameter bore. Two increment cores were extracted from each tree: one in the direction of the slope and the other upslope. Samples were extracted at the point of maximum curvature along the stems. Moreover, P. abies growing outside of the creep area but in the same microclimatic conditions were sampled to construct a reference chronology to distinguish climate signals from other land-forming events. The shape of the trees and sudden change in the width of tree ring growth (eccentric growth and reaction wood) were responses to the disturbance recorded in the trees following creep. Summer rains (June and July wettest months in the Bâlea Valley) are the most important factor in triggering creep.

Laser ablation isotope ratio mass spectrometry (LA IRMS) was used to measure δ^{13}C at high spatial resolution to detect metabolic changes in stable isotope signatures and see if there is a perceptible difference within the same growth ring between the creep affected, respectively unaffected sides. We used a CO_2 Fusions Laser (Photon Machines) fitted with an isoScellΔ100 sample chamber (Terra Analitic), a pyrolysis oven, CryoPrep unit and HS2022 IRMS (all three Sercon).

In creep affected cores the carbon signature is clearly distinguishable between the normal and abnormal growth areas within the same ring – in some cases the difference in δ^{13}C ratios is in excess of 1‰. The more negative δ13C values downslope, where the tree is depositing thicker rings to straighten its trunk.

Trace elements in quartz: a tool for sediment provenance

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Quartz is ubiquitous within continental crust and can virtually be found within all rock types (plutonic, metamorphic and sedimentary). During erosion, weathering and sedimentation processes, it has a very high preservation potential and is often used to trace sediments production and transport dynamics. The QUARTZ project (French ANR funding) aims to assess the potential of quartz as a quantitative tracer for sediment sourcing river dynamics by combining conventional characterization method such as Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), Laser-Induced Breakdown Spectroscopy (LIBS), and Cathodo-Luminescence (CL), with dosimetric methods, such as Electronic Spin Resonance (ESR) and Optically Stimulated Luminescence (OSL) which are more classically used for Quaternary sediment dating.

This study focuses on the Strengbach catchment (ca. 40 km²) draining a low-elevation mountain range located in easternmost France (the Vosges Mountains). Samples representative of the catchment main bedrocks units were collected and prepared mechanically and chemically to extract quartz grains. These grains were mounted on thin-sections for LA-ICP-MS, LIBS and CL analyses. Whole-rock thin sections were also prepared for comparison. Quartz trace elements were analyzed in all samples using LA-ICP-MS and LIBS. Specific thin-sections (100-µm thick) and a high energy LA-ICP-MS laser setup were used to prevent quartz tearing under laser ablation (193 nm Excimer laser). LIBS imaging analyses were carried out using an Ablatom microLIBS equipment allowing micrometric chemical analysis on a macroscopic scale (surface area of several square centimeters). LIBS is an excellent complement to LA-ICP-MS having a good sensitivity to light elements sometimes difficult or impossible to quantify using mass spectrometry (e.g. Li, B, Na, Mg, P, O).

Trace elements concentrations obtained by LA-ICP-MS and LIBS techniques were compared to CL, ESR and OSL signals. This allowed to identify specific quartz signatures, depending on rock type (gneiss, granite, or sandstone) and quartz origin (i.e. magmatic, metamorphic, recrystallized, hydrothermal or sedimentary). These chemical signatures are later to be compared to the measured quartz signatures of the Strengbach river sediments. Further comparison between whole-rock samples and separated grains permitted to assess the impact of the sample preparation on the quartz trace element signatures and to identify quartz populations likely to be more represented in the alluvial sediments produced by the different bedrock lithologies. Finally, ongoing analyses point out the complex contribution of trace elements to OSL, ESR and CL signals.

Late Neogene ENSO variability in the SE Pacific recorded in bivalve shells through Laser Ablation ICP-MS

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El Niño-Southern Oscillation (ENSO) determines periodic fluctuations of atmospheric and oceanic circulation patterns in the equatorial Pacific on multi-year time scales. As one result, El Niño phases cause the severe reduction of coastal upwelling off the western coast of South America, impairing primary production and adversely affecting the marine ecosystem. At the same time, warmer sea surface temperatures allow increased moisture influx to the hinterland, triggering torrential rainfall in otherwise arid to hyperarid areas.

Changes in the frequency and amplitude of ENSO behavior are often invoked to explain changes in paleoceanographic and paleoclimatic conditions in the SE Pacific and on the South American continent during the Neogene and Quaternary. The shells of mollusk species, widespread in coastal sediments, represent ideal archives of past ENSO variability. In this study, we evaluate the effectiveness of Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP- MS) for geochemical time-series analyses on bivalves to reconstruct ENSO variability off northern-central Chile during the late Neogene.

One pectinid (“*Chlamys*” cf. *simpsoni*) and two ostreid (*Crassostrea* sp.) shells recovered from upper Miocene and Pliocene sediments of the Bahía Inglesa Formation at Quebrada Tiburón in Chile (27°S) were examined. The shells show median $^{87}Sr/^{86}Sr$ ages of 6.49, 6.16 and 5.13 Ma. LA-ICP-MS was performed along transects following growth increments either on the shell surface (pectinid, surface cleaned with acetic acid), or on thick-sections of the hinge area (ostreids).

As a next step, we aim to integrate the results from LA-ICP-MS (in particular Mg/Ca, Sr/Ca, Ba/Ca) with stable isotope data (δ18O, δ13C) along parallel transects in order to evaluate fluctuations of sea surface temperatures, productivity, and continental run-off, ultimately reflecting ENSO variability in the late Neogene.

Probing the evolution of primitive achondrite parent bodies: insights from LA-ICP-MS analysis of silicate minerals

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Ureilites and acapulcoite-lodranite clan (ALC) meteorites are attractive targets to study the processes of early planetary differentiation, in which an unsorted mass of primitive meteoritic material evolves into a body with a silicate mantle and metallic core. These achondrites record the earliest stages of planetary differentiation: ALC meteorites are products of thermal metamorphism and low degree melt extraction from a primitive asteroid, and main group ureilites represent ultramafic mantle restites after extraction of metal and basaltic melts. As such, constraining the geochemistry of these ultramafic achondrite meteorites refines our understanding of the first critical stages of the planetary evolution.

Here, we present trace and major element contents in the major silicate minerals (olivine, augite, orthopyroxene and plagioclase) of 10 ureilites and 7 ALC meteorites measured *in situ* using LA- ICP-MS. The Fe/Mg/Mn relations within both meteorite groups confirm the absence of any igneous fractionation processes and Fe loss/gain, while high-Ca pyroxene in ALC suggests that these minerals are affected by low degree partial melting. The Cr distribution between olivine and pigenonite in ureilites, when interpreted as a geothermometer, [1] yields equilibration temperature ranges that are in good agreement with previous results for pyroxene. REE mass fractions of the ALC silicates reflect the complex nature of partial melting and migration of basaltic melts on the parent body scale. The mass fraction of moderately volatile elements, such as Cr, Mn, Zn, Pb, Cu are found to be depleted in silicate minerals compared to the chondritic reservoir, likely as a result of evaporation/condensation processes, either (i) due to incomplete condensation from the nebula, or (ii) due to evaporative losses from the parent body by e.g. catastrophic impacts. At the same time, the distribution of Zn between olivine, pyroxene and plagioclase minerals suggests that Zn can be fractionated during partial melting of the primitive ultramafic lithologies.

Combined, major and trace element systematics of silicate minerals in ALC and ureilites enable to reconstruct the meteorite petrogenesis complimentary to the partial melting histories of the parent body, described based on their petrology and mineralogy. Importantly, the element compositions do not correlate with the oxygen isotopic signatures, which are thought to record nebular processes. The ability to measure trace element compositions in separate minerals *in situ* adds an extra dimension in understanding complex processes during partial melting and cooling of asteroidal parent bodies.

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

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

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

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

Multi-element analyses of silicate glasses using a femtosecond laser ablation system coupled to an ICP-MS/MS

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In Earth Sciences, laser ablation coupled to ICP-MS is a common technique to analyze multi-element contents of silicate glasses, even though significant matrix effects occur. Recently, the development of femtosecond laser ablation systems has drastically reduced these effects. Pulse durations shorter than nanoseconds limit thermal heating during the ablation[1] and hence, fractionation of volatile elements is minimized. In addition, matrix effects related to particle size distribution can be mitigated because UV-wavelengths generate smaller particles than IR-wavelength[2]. However, determining with high accuracy and precision multi-element compositions in small samples such as melt inclusions trapped in minerals of volcanic rocks, and with concentrations ranging from few to tens of thousands ppm remains a major issue in geochemistry.

In this study, we investigate different laser parameters (dwell time of 30-60 s, spot sizes of 5-65 µm, fluence of 0.8-5 J.cm^{-2}, repetition rate of 5-20 Hz) and carrier gas flow (He of 0.8-1.0 L.min^{-1}) to determine the optimal settings limiting matrix effects during spot analyses. We measure multi-element contents in the reference materials NIST SRM 610, 612, 614 and MPI-DING glasses using a NWRFemto200 laser ablation system coupled to an Agilent 8900 ICP-MS/MS. We use ^{29}Si as internal standard and a sample-standard bracketing procedure to correct for mass bias with the bracketing standard being the same as the sample to match the matrix (e.g. NIST 612 vs NIST 612).

We observe that variable He flows provide no significant improvement in sensitivity nor precision. However, better accuracy and precision are achieved with a dwell time of 30 s, spot sizes higher than 40 µm, a fluence of 4 J.cm^{-2} and a repetition rate of 10 Hz, implying limited matrix effects for this setting. For instance, reproducibility for 4-5 spots in ML3B-G glass are within 1-3% RSD for ^{85}Rb (5.9 ppm), ^{88}Sr (313 ppm), ^{93}Nb (8.6 ppm), ^{137}Ba (80 ppm), ^{146}Nd (16.7 ppm), and LREE (2-20 ppm) and within 3-5% RSD for ^{133}Cs (0.15 ppm), ^{208}Pb (1.4 ppm), ^{232}Th (0.6 ppm) and ^{238}U (0.5 ppm). These first results look very promising for the study of small-size geological samples such as melt inclusions with trace element contents from ~0.1 to ~100 ppm.

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S isotopic analyses of S-bearing compounds using a femtosecond laser ablation system coupled to an ICP-MS/MS

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Femtosecond lasers offer significant analytical advantages due to shorter laser pulse durations, which minimize thermal heating, compared to nanosecond laser ablation systems. This characteristic may reduce matrix effects and mitigate laser-induced fractionation[1]. Additionally, ICP-MS/MS instruments allow the removal of matrix and spectral overlaps by targeting a restricted range of analyte ions in the first quadrupole. These selected analyte ions then interact with a specific gas within the collision/reaction cell, enabling the analysis of mass-shifted product ions in the second quadrupole while simultaneously drastically reducing interfering species before reaching the detector system.

Sulfur (S) is one of the most common volatile on Earth and plays key roles in biological and geological processes. S-isotopes thus represent important geochemical tracers but remain difficult to measure using ICP-MS due to high first ionization energy (> 10 eV), significant relative isotopic abundance differences between the four isotopes (^{32}S = 94.93 %, ^{33}S = 0.76 %, ^{34}S = 4.29 %, ^{36}S = 0.02 %) and polyatomic interferences (e.g., $^{16}O_2{}^+$ and $^{14}N^{18}O^+$ on $^{32}S^+$, $^{32}SH^+$ and $^{16}O_2H^+$on $^{33}S^+$, $^{33}SH^+$ and $^{16}O^{18}O^+$ on $^{34}S^+$, $^{36}Ar^+$ on $^{36}S^+$). Several studies[2] have demonstrated the utility of ICP-MS/MS in determining S content and isotopic compositions (^{32}S and ^{34}S) using O_2 as a reaction gas ($^{x}S^+ + O_2 = {}^{x}SO^+$) at m/z = 48 and 50 for $^{32}S^{16}O$ and $^{34}S^{16}O$, respectively, with reaction yields of ~ 30%[3]. Although precision may likely be lower compared to MC-ICP-MS instruments, the widespread availability and lower cost of ICP-MS/MS instruments make them more accessible.

In this study, we present our first results on *in situ* S content and isotopic compositions in S-bearing compounds using a NWRFemto200 laser ablation system coupled to an Agilent 8900 ICP-MS/MS. We aimed to characterize reference materials NIST 610, 612, 614 and MPI-DING glasses as well as sulfides through mass-shifted analysis with O_2 as a reaction gas, employing in- house basalt and sulfide, as external standards respectively. So far, these results represent the first S isotopic compositions ever measured in glasses using fs-LA-ICP-MS/MS.

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Imaging of Geological samples by fs LA-ICP-MS with ARIS

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We present high-speed washout imaging results using fs LA-ICP-MS(femto second laser ablation ICP- MS) equipped with ARIS(Aerosol Rapid Introduction System). ARIS, a device connecting the HelEX II laser ablation cell to ICP-MS, minimizes transmission losses and turbulence, providing fast washing without using internal valves or torch modifications, thus directly delivering the sample to the torch to offer combined wash-in and wash-out times of <20 ms and sampling speeds of up to 60 Hz for geological samples. This rapid washout enables mapping of samples with better spatial resolution. Therefore, in this study, imaging analysis via fs LA-ICP-MS was conducted on regions containing various minerals such as hornblende, quartz and plagioclase observed in geological sample sections, and mapping analysis was performed on standard materials including zircon standards 91500, Plesovice, TEMORA, SLZ and FC-1.

The fs LA-ICP-MS system used in this experiment is installed at the KBSI (Korea Basic Science Institute), with an Excite PHAROS fs laser ablation system (Teledyne CETAC Technologies, USA) coupled with a quadrupole-based Agilent 7900 ICP-MS (Agilent Technologies, USA) connected via ARIS. Parameters of the device were adjusted and optimized for low oxide formation, low laser-induced fractionation, and maximum sensitivity. Imaging analysis was conducted in line scan mode with a spot diameter if 3um and lateral scan speed of 30 μm s^{-1} for areas of interest. A laser repetition rate of 80 Hz, laser output energy of 1.0 mJ cm^{-2}, and carrier (He) and makeup gas (Ar) flow rates of 0.8 and 0.9 L min^{-1} were used. The analyzed fs LA-ICP-MS imaging data were processed using HDIP software.

The analysis results by fs LA-ICP-MS revealed clear images without blurring. Through the analyzed fs LA-ICP-MS imaging data, the chemical composition and spatial distribution of trace elements and rare earth elements in mineral grains within the sections could be determined, visualizing the distribution patterns according to the element's affinity to these minerals. Furthermore, through imaging analysis of zircon standard samples, we aimed to verify the homogeneity of trace elements within grains and identify available zircon standard samples for trace element analysis of zircons. Such fs LA-ICP-MS imaging data will be useful for integration with other in-situ analysis data to simultaneously understand the chemical composition and spatial distribution of materials.

Utility of LA-ICP-MS methods for reconstructing hydroclimate from stalagmite and cave monitoring archives

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Water resource planning is challenged in semi-arid central Texas (USA) due to rapid population growth and intensifying atmospheric warming that is forecast to increase severe drought and intense rainfall. The sensitive environmental proxy power of stalagmite records could provide useful analogs for understanding how regional rainfall changed over comparable periods of past climate change. Previous central Texas cave studies of diffuse flow drip sites and stalagmite records show that calcite accumulates seasonally during cool months when $p\mathrm{CO}_2$ is lowered by ventilation [1], faster drip sites accumulate more calcite [2], and stalagmite 2D-LA-ICP-MS chemical mapping (esp. Sr, Ba) can effectively resolve growth fabrics [3]. Toward a refined understanding of past central Texas hydroclimate, we present two LA-ICP-MS applications from the same cave system (Cave Without a Name): (1) continuous 2D chemical mapping of a highly age-resolved stalagmite record over portions of the last deglacial (19-11 ka) associated with abrupt cooling and warming events, and (2) direct *in situ* measurement of calcite deposited on glass monitoring plates deployed monthly over three years. Elemental maps resolve growth bands as thin as 20µm consisting of thicker lamina, interpreted as cool month deposition, and thinner lamina, interpreted as warm month deposition. Sr and Ba concentrations are consistently enriched in thicker lamina. Comparison of couplet thicknesses with average annual growth rate estimates from U-series dating confirms the seasonality of growth couplets. Although diffuse flow drip sites have unique flow paths, the amount of water stored in the epikarst is likely an important control of drip rate. Wetter climatic periods with more recharging precipitation should have faster drip rates in response to higher hydrostatic pressure, compared to drier intervals. The elemental maps demonstrate that deglacial cool excursions are repeatedly associated with thinning of growth layer couplets, consistent with increased aridity. In association with couplet thinning, is a reduction in trace element enrichment in both cold and warm months.

Although couplet thickness trends can be linked to variations in the amount of recharging moisture, we seek further understanding of controls on seasonal and longer-term trace element variations. Water-calcite distribution coefficients are currently being assessed from monitoring records of drip water and associated plate calcite. Chemical analysis of the latter is facilitated by LA-ICP-MS using a large format two volume laser cell, that enables simultaneous loading of standards and individual 10x10cm glass monitoring plates. Calcite accumulation on plates is found to be discontinuous as scattered polyhedral crystallites of differing sizes, thereby requiring targeted spot analysis. Results of this approach applied to a three-year monitoring period demonstrate that calcite compositions can be obtained to constrain K_d for comparison with associated drip waters.

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High-resolution in-situ Fe isotope measurements of fossil micrometeorites from Belgium using femtosecond laser ablation MC-ICP-MS

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In this study, we investigated the ancient extraterrestrial flux to the Earth contained in Belgian Phanerozoic limestone from Chanxhe (near Liège, Belgium). The limestone samples weighing ~4 kg were dissolved using multiple steps of HCl dissolution, and the micrometeorites were subsequently extracted using magnets and binocular microscopy. From these collected spherules, 13 particles were selected for in-situ iron isotope analysis: 11 particles determined to be iron-rich (I-type) micrometeorites and 2 characterized as terrestrial particles based on scanning electron microscopy (SEM) imaging and semiquantitative EDS analysis.

The high-precision and high-spatial resolution in situ Fe isotope analyses were performed at the Laboratoire Géosciences Environnement Toulouse (GET) in France using femtosecond (fs) laser ablation multiple-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). Long-term (~3 years) external reproducibility obtained on the USGS glass BIR-1G against Puratronic reference standard is 0.17‰ (2SD) for d^{56}Fe [1]. Uncertainties achieved on individual glass fragments, olivine crystals and bulk micrometeorites are in all cases better than 0.15‰ for d^{56}Fe. This precision obtained on the particles is associated with a high spatial resolution of 70 to 100 x 7 mm. The spatially resolved Fe isotope measurements display clear Fe isotope variations between the extraterrestrial and terrestrial particles. The micrometeorites display positive d^{56}Fe signatures ranging from 0.24 ± 0.03‰ to 1.31 ± 0.1‰, while the terrestrial particles display negative d^{56}Fe signatures from -1.44 ± 0.1‰ to -0.88 ± 0.14‰. The Fe isotope signature of the micrometeorites from Chanxhe are significantly heavier than the altered terrestrial particles, however the variations in Fe isotope ratios within the fossil micrometeorites are not as wide, and the signatures not as heavy as the d^{56}Fe values reported for the modern cosmic spherules from Mount Widerøfjellet in the Sør Rondane Mountains of Dronning Maud Land, East Antarctica [2]. This could imply that the Fe recorded isotope ratios do not fully reflect primary signatures, and the particles may have been affected by secondary (e.g., diagenetic) processes leading to mixed isotope signatures.

In this study, we show that iron isotope measurements can be used to distinguish terrestrial and extraterrestrial materials. Furthermore, iron isotope ratios display great potential to highlight the different processes these extraterrestrial spherules underwent. Further investigation needs to be performed on fossil micrometeorites from various localities and different stratigraphic intervals to confirm this hypothesis.

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Synthesising homogeneous calcium carbonate reference materials for in situ determination of U–Pb and Sr isotopes

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Recent years have seen a rise in applications of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to elemental and isotopic analysis of a wide range of geological materials. Standardising such analyses relies on a homogeneous matrix-matched primary reference material (RM) whose ablation, transport and ionisation characteristics will result in fractionating elements and isotopes in the same way as in the unknown of interest. LA-ICP-MS analyses of strontium isotopes, and one of the current frontiers of LA-ICP-MS geochronology, U–Pb dating of carbonates, suffer from a lack of such a material. For U-Pb geochronology, because the currently used primary RMs are heterogeneous in both age and U/Pb ratio, isotopic ratios are corrected on an isochron (whole-sample) basis rather than for each individual analytical spot, imposing excess uncertainty on all U–Pb ages. The Earth scientist's community is thus in need of homogeneous reference materials that would match the ablation behaviour of the unknown carbonate so that matrix effects, including the amount and depth progression of inter-element laser induced elemental fractionation (LIEF), can be corrected. Similarly, the availability of carbonate RMs for Sr isotopes analyses is limited, and analytical protocols rely on modern-day marine carbonates, which are believed to show the same $^{87}Sr/^{86}Sr$ ratio as modern-day seawater. We present a new method for preparing synthetic carbonate RMs that uses a natural calcite cement which is milled, homogenised, and recrystallised using high-pressure, high-temperature apparatuses. In this way, natural sample heterogeneity is removed through milling, while textural coarsening is aimed at generating ablation behaviour similar to that of routine unknown samples. Initial tests of synthetic calcite materials demonstrate the ability to achieve isotopic homogeneity at the spatial scale of a typical LA-ICP-MS laser spot size (70-110 µm), while the ablation rate and LIEF are comparable to those of a range of commonly used calcite RMs.

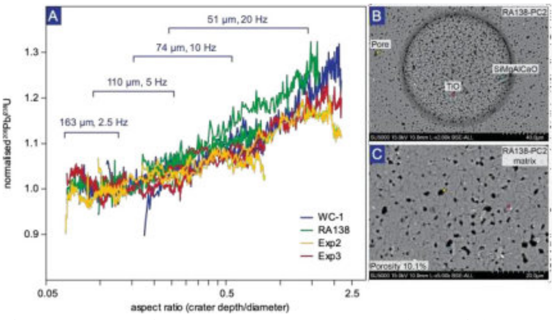

Figure: Preliminary results from a synthetic RM (Exp2, Exp3) using calcite cement powder (RA138) as a starting material. (A) Comparison of U/Pb fractionation effects with progressing ablation, illustrating near- identical behaviour of sintered materials Exp2, Exp3 and natural calcites WC-1 and RA138. (B-C) Backscatter electron images of Exp2 showing the spatial scale of heterogeneities in relation to a typical 110 µm diameter laser pit.

Historical trends of metal pollution in the metropolitan area of Milano, Italy: a combined dendro-chemical, dendro- magnetic and dendro-XRD approach

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A long-range view of temporal records of metal air contaminants in metropolitan areas is essential to better constrain potential sources of pollution for the assessment of containment strategies and protocols. The metropolitan area of Milano underwent a very rapid development after WWII rebuilding with rapid growth of population, vehicular traffic, and industrial activities with the side effect of introducing toxic metals into the environment. In the recent years traffic restrictions were imposed to buffer and reduce air pollution.

Here we reconstructed up to seventy years of metal pollution in the metropolitan area of Milano. Tree cores from *Ulmus* specimens were sampled in municipal parks from different areas of Milano and close to air monitoring stations. Single tree rings were analyzed with laser ablation (LA)-ICP- MS for the metal concentrations, with a Vibrating Sample Magnetometer (VSM) for the magnetic properties of the ferromagnetic microparticulate, and with X-ray diffraction and SEM for the mineralogical nature of the various solid particles.

Results show that metal concentrations trends are characterized by significant intra-sample variations that mimic (with a delay) those of the air monitoring stations. Sample to sample variations are also evident with values that in the Milano city center are historically up to 10 times lower than those in the more peripheral areas. The parallel dendro-magnetic study reveals the presence in the tree rings of ferromagnetic particles in variable amounts, which are periodically correlated with the metal distribution. Ongoing hysteresis analyses allowed to interpret these ferromagnetic particles as very fine (titano)magnetite grains likely at the nanometer scale-range, or in the micrometric range when arranged in aggregates, as observed also at the scanning electron microscope (SEM). Results from the X-ray diffraction reveal the occurrence of $(Fe,Ti)_3O_4$ (magnetite structure, in agreement with the VSM analyses), micro/nano crystalline *silica* and clay minerals (with the structure of chlorite and smectite).

This study represents a first attempt for an innovative approach to the investigation and monitoring of the environmental contamination of metals in metropolitan areas. We are confident that, although the physiology of the single tree and element mobility in soils may, in part, control the uptake of metals and thus alter or temporally shift the registry of the contamination peaks, the combined dendro-chemical, dendro-magnetic and dendro-XRD approach is the key for better identifying the source of contaminants.

Advancements in Isotope Analysis for Geochronology: Integrating MS/MS and Laser Ablation

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This poster discusses recent advancements in geochronology, focusing on the integration of tandem mass spectrometry (MS/MS) with laser ablation (LA) techniques for in situ isotope ratio analysis, particularly within the Rubidium-Strontium (Rb-Sr) dating system. By utilizing reactive collision/reaction cell gases, MS/MS circumvents mass resolution limitations, enabling precise discrimination between isotopes like ^{87}Rb and ^{87}Sr. LA-ICP-MS coupled with MS/MS offers rapid analysis, minimal sample preparation, and micron-scale resolution, revolutionizing traditional geochronological approaches. This innovative methodology enhances efficiency and expands the scope of mineral dating, facilitating a deeper understanding of Earth's geological evolution.

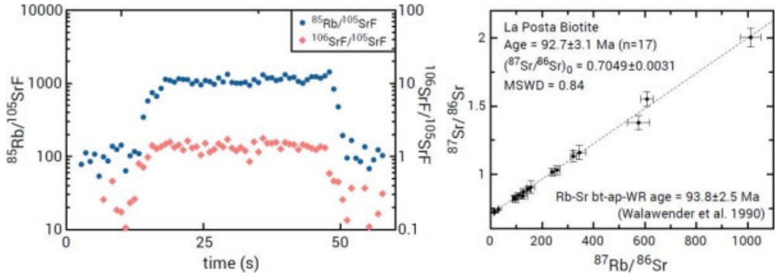

Figure Left: Time resolved signals for isotope ratios measured by LA-ICP-MS/MS. Right: LA-ICP-MS/MS Rb-Sr isochron for LaPosta Biotite. LA parameters were 50 µm spot size at 2.5 J/cm2 and 10 Hz

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Graphite LIBS analysis: Opportunities for elemental mapping and multivariate classification

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Graphite is an essential raw material in a range of applications due to its extraordinary chemical and physical properties. As graphite is also one of the fundamental raw materials in energy storage, its responsible sourcing is of prime importance. However, currently there is no routine methodology available to distinguish natural graphite deposits from each other as well as to map the spatial distribution of different elements in them.

Laser-induced breakdown spectroscopy (LIBS) is a fast and efficient technique for detecting trace amounts of impurities in various types of materials. In this study, we present results acquired by an ESLumen LIBS coupled to an ImageGEO193 system on a series of pressed natural graphite pellets. The described setup is capable of producing up to 1000 complete LIBS spectra per second, thereby providing an excellent basis for multivariate classification tools. We introduce two approaches on how to extract the most informative sections of the acquired data and evaluate the classification efficiency of the random forest algorithm on those filtered datasets. Our first tests indicate that individual shots on most graphite concentrates can be classified correctly in at least 85% of the cases. This makes LIBS a strong candidate for becoming a standard tool in graphite traceability tasks, in accordance with its successful forensic application on other materials (e.g. [1]). Moreover, by LIBS-mapping we can shed light also on the spatial distribution of impurities in graphite (Fig. 1). Most typical elements (e.g. Ca, Mg, O, Si) detected show high anomalies in spatially restricted regions implying mineral impurities as possible sources.

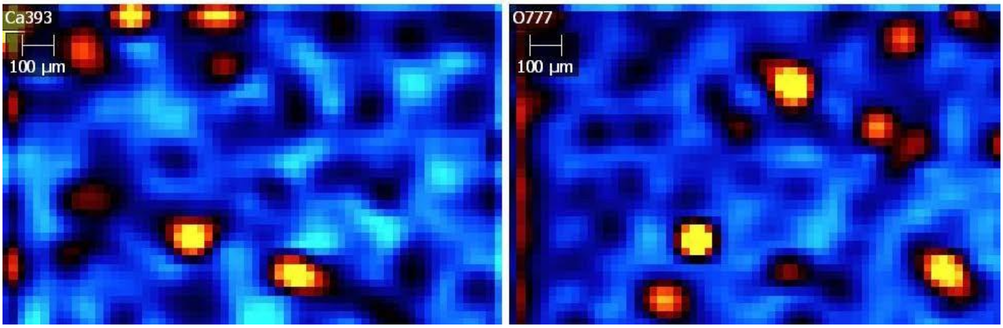

Fig. 1. LIBS element maps of calcium and oxygen in a graphite concentrate, based on intensities at characteristic optical emission lines (yellow=high intensity).

[1] M. G. Nespeca, A. L. Vieira, D. S. Júnior, J. A. Neto, E. C. Ferreira. Food Chemistry, 2020, 311,125886.

Ilmenite age determination using LA-ICP-MS technique

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Laser ablation ICP mass spectrometry (LA-ICP-MS) technique with both high sensitivity and high spatial resolution has opened trace-element geochemistry in mineral systems on sub μg g^{-1} (ppm) level [1]. Ilmenite ($FeTiO_3$) contains trace amounts of high field strength elements including Zr, Nb, and U and has a potential to shed light on the evolution of mafic igneous systems [2]. In this study, we perform the trace-element imaging analysis of ilmenite and discuss the mineralogical and petrological meaning of ilmenite U–Pb dates. Samples subsidized in this study were ilmenite from anorthosite (FC1, Duluth; ~1099 Ma) and magnetitite (BC269, Bushveld; ~2054 Ma). For analytical settings, the LA system was equipped with a Yb:KGW femtosecond laser (Jupiter Solid Nebulizer, ST Japan, Tokyo), and the mass spectrometers were a quadrupole-based ICP-MS (iCAP TQ, Thermo Fisher Scientific, Bremen) for trace element imaging and a multiple-collector ICP- MS (Nu plasma II, Nu instruments, Wrexham) for U–Pb isotope analyses.

The obtained trace-element maps show that i) ilmenite has a wide variation in U and Pb contents (U: 0–0.081 ppm, Pb: 0.002–0.027 ppm) and U/Pb values, ii) U and Pb in ilmenite are localized in hematite exsolution and vein-like areas, and iii) the Pb content in ilmenite is significantly lower than that of coexisting plagioclase and magnetite (3–5 ppm). These results suggest that the ilmenite U–Pb age corresponds to late magmatic activities, i.e., the exsolution formation and the enrichment of incompatible elements. For U–Pb isotope analyses, instrumental U/Pb fractionation was successfully calibrated using a matrix-matched reference of ulvöspinel (Fe2TiO4) whose U–Pb age was precisely determined using isotope dilution thermal ionization mass spectrometry (ID-TIMS) technique by the presenters. With the calibration of U/Pb, we obtained accurate and precise U–Pb ages from FC1 ilmenite: 1095 ± 24 Ma (2σ, n=10) and BC269 ilmenite: 2051 ± 29 Ma (2σ, n=23), which are in good agreement with the published ID-TIMS zircon U–Pb ages. One notable feature in this study is that both the ilmenites are spared from the influence of initial Pb. This is attributable to the extremely low partition of Pb compared to U for ilmenite under the paragenesis of Pb-enriched minerals (e.g., plagioclase) (Fig. 1). Therefore, this study indicates that the feasibility of ilmenite U–Pb dating with low U, Pb contents is highly dependent on the coexisting mineral phases.

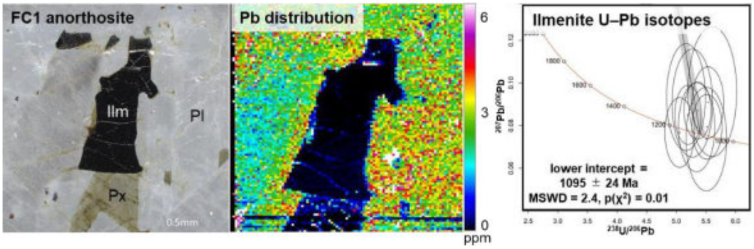

Figure 1 Occurrence and high U/Pb feature of ilmenite in FC1 anorthosite

[1] D. Chew, K. Drost, J. H. Marsh, and J. A. Petrus, *Chemical Geology*, 2021, **559**, 119917.
[2] J. M. Thompson, K. Goemann, I. Belousov, K. Jenkins, A. Kobussen, W. Powell, and L. Danyushevsky, *Journal of Analytical Atomic Spectrometry*, 2021, **36**, 1244-1260.

New cryogenic ablation cell technology for high sample throughput impurity mapping in ice-cores with LA-ICP-MS

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Its micron-scale sampling volume, trace-level detection limits and broad elemental coverage make laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) particularly suited for the analysis of chemical impurities in ice cores. When employed for state-of-the-art 2D mapping using fast aerosol transfer systems (ATS), LA-ICP-MS has the ability to visualize and describe the spatial distribution of impurities in ice. This will be particularly valuable to succeed in the "Oldest Ice Challenge" – the retrieval and analysis of a continuous 1.5-million-year climatic record from an Antarctic ice core. This challenge crucially depends on extracting paleoclimatic information from highly thinned deep ice, with misinterpretation by post-depositional signal alteration carefully avoided. For LA-ICP-MS analysis, such effort will require a 1D line profiles along the main core axis to be applied over several hundred meters of ice core samples, in addition to detailed 2D maps, necessitating an increased sample throughput beyond routine operations. At the same time, the deep ice cores are highly valuable and would benefit from being preserved in large sections. Through a collaboration between industry and research institutions, we have started i) the development of a cryogenic ablation cell capable of housing samples of up to 550 mm in length, in parallel with ii) developing a new cryogenic ablation cell for the latest generation of 1 kHz imaging lasers. In this study, we present results from the cryocell prototypes, including an assessment of imaging performance on ice. The extended volume cryocell demonstrates sufficient cooling performance and a high degree of bi-directionals accuracy over the stage travel. Based on this successful proof-of-concept, we aim towards a fusion of i) and ii), in order to combine fast mapping rates with large sample geometries. Going beyond ice core analysis, this technical development will ultimately enable a fast 2D analysis of either samples up to 550 mm in length, or a large number of smaller samples, thus achieving high throughput without sacrificing imaging performance.

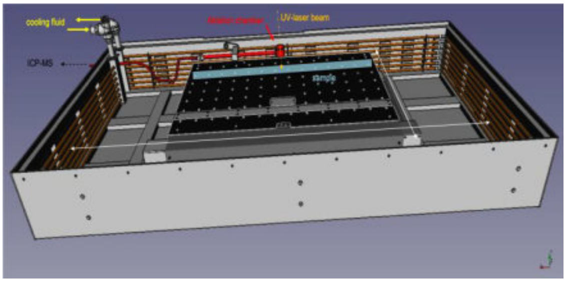

Figure 1: Schematic of the large cryocell prototype including a secondary volume "cup" for fast aerosol transfer. The prototype has been built and first tests performed at the University of Venice.

SelfSeal technology-based open-cell laser ablation system for trace elements analysis of full-size archaeological artefacts: application on historical Chinese enamelled copperware

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is considered as a mature technique for the quantification of trace elements on archaeological and heritage artefacts in a minimally destructive way. Because of the wide array of elements analysed, the low detection limits, and the limited sample preparation needed, this technique is nowadays widely used for several types of applications such as provenance studies, technological analysis, or conservation research. One of the main limitations of this technique is the size of the sample chambers. The typical dimensions of modern two volume chambers (10 cm X 10 cm) usually require a destructive operation of sub-sampling on larger objects. This is proving to be a limiting factor for the analysis of cultural heritage materials. Several institutions built their home-made devices to overcome this size limit and suggested different approaches such as the open-cell ablation, the ablation in ambient atmosphere or the portable laser ablation system.

We report here the results on two Chinese painted enamel copperwares from the late Qianlong - Jiaqing periods (1775-1820) acquired with the dual-chamber Artifact laser ablation system (Elemental Scientific Lasers). This platform includes a SelfSeal ablation cell (open chamber), coupled here with a 193 nm laser, enclosed in a large chamber allowing the analysis of large objects (up to 60 x 60 x 60 cm). Data were acquired on both the full-size objects using the SelfSeal and on smallfragments recovered from damaged areas using the Two Volume chamber (TwoVol2). The first objective of this study is to evaluate the results acquired with the open cell system by comparing the data from the SelfSeal chamber to the data acquired with the Two Volume chamber on the same painted layers and several glass standard reference materials. The second objective is to investigate the material recipes and the enamel technology through the analysis of the 5 different polychrome painted layers. The development of painted enamelling on copper in China during the Kangxi period (1662–1722) is seen as the result of a combination of Chinese innovation and European influence and is considered as a witness of technological exchanges between these two artistic traditions. These results provide a new insight on the complexity and the sophistication of this distinct art form.

Comparing interference removal tools for in situ analysis of ^{87}Sr/^{86}Sr in bioapatite

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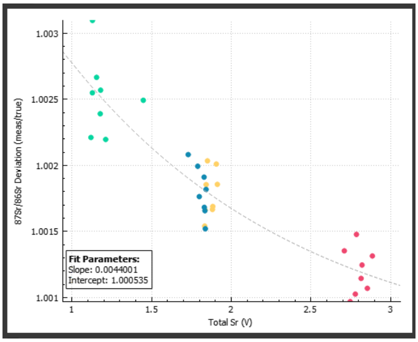
The analysis of Sr isotopic ratios in bioapatite is commonly used in the Archeological Science community as a means of tracing ancient human mobility and habitat use. As human teeth grow incrementally, and at different times throughout childhood, mobility can be recorded in changes in the ^{87}Sr/^{86}Sr isotope composition. The high spatial resolution obtained by laser ablation enables these changes to be resolved. However, it has long been known that during laser ablation analyses there is an isobaric interference on ^{87}Sr, either from ^{40}Ca^{31}P^{16}O or ^{40}Ar^{31}P^{16}O. This interference can cause offsets of up to 1500 ppm in low Sr/Ca samples; as such analyzing human teeth with low Sr concentrations becomes almost impossible. Here we will compare multiple methods for removing or correcting for the interference on mass 87.

Teeth with homogeneous ^{87}Sr/^{86}Sr isotope compositions and moderate Sr concentrations were selected and analyzed by traditional micro-milling and solution mode MC-ICPMS analysis. Following this the teeth will be analyzed by LA coupled with a Nu Instruments Sapphire MC-ICPMS using two different protocols. In the first method, the Sapphire will be used in high energy (or normal) mode. During the analytical session multiple standards with known Sr isotopic composition, and a range of [Sr] will be analyzed. These will be used to calculate a calibration curve of ^{87}Sr/^{86}Sr vs volts Sr (see Figure below) in Iolite using the "Sr_combined DRS", all unknowns will then be corrected using this calibration curve. The second method will utilize the Sapphire's low energy path, where the ions pass through the collision cell. Multiple gases will be tested to determine if the interference can be reduced or removed.



Understanding the Elemental Composition of SEI and CEI Layers in Li-Ion Batteries

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In a world that is becoming increasingly environmentally conscious, the demand for green energy has never been greater. A leading source of green energy is the lithium-ion battery. These batteries power everything from cell phones to power tools and electric vehicles (E.V.s). To ensure quality and performance of lithium-ion batteries, an extensive knowledge of the elemental composition in major components is needed, specifically the solid-electrolyte interphase (SEI) and the cathode-electrolyte interphase (CEI) that form on the negative and positive electrode, respectively, upon charge/discharge of the battery. Understanding how these major elements change in distribution as the battery undergoes aging is instrumental in battery development and QC.

Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) can provide spatially resolved data (elemental imaging) of elements that comprise the cathode and anode materials and show the accumulation of electrolyte aging products that make up the SEI and CEI. This information is not available using by traditional methods. For example, LIBS can measure elements that are not possible by ICP or ICPMS, such as F, O, and H when the ablation area is purged with helium gas. In addition, LA-ICPMS offers great sensitivity for trace elements that may be found as impurities in these cathode and anode materials. In this work, elemental imaging of lithium-ion battery electrodes will provide a thorough illustration of the SEI and CEI as well as depth analysis from lithium-ion batteries.

Fast analysis of trace elements and lithium isotopy by LA- (MC)-ICP-MS for the traceability of lithium in the battery supply chain

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The needs for sustainable and less greenhouse-gases emitting technologies in the transport domain has led to a growing demand for resources for the manufacturing of electric vehicles.

Environmental, social, political and economic impacts, as well as governance issues, are at the heart of the challenges facing the mining industry in meeting these new needs. The traceability of raw materials is important for regulating supply chains, making the industry more virtuous and countering potential fraud.

One of the focus of the EU-funded MaDiTraCe project - which aims to set up traceability methods for critical raw materials (lithium, cobalt, rare earth elements and graphite) used in the manufacture of electric vehicle batteries - is to use geochemical methods to identify intrinsic tracers for these materials throughout the production chain.

The type of deposit from which a lithium material comes from can be determined with Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) analysis in wet chemistry by its Li isotopic composition [1]. However, this method is expensive, requires long sample preparation and is not enough democratized to be widely deployed in the future for laboratory control of lithium provenance when fast and less expensive on-site methods fails to determine the origin of the product.

In this regard, one of the methods investigated by the project in order to develop faster and less expensive techniques is the analysis of trace elements in Li materials (i.e. ore concentrates, lithium salts, battery active material or cathode sheets), by Laser Ablation (LA)-ICP-MS analysis. The lithium isotopic analysis by LA-MC- ICP-MS is also investigated, with the possibility of a laser ablation split-stream approach, with both ICP-MS analysis for trace elements and MC-ICP-MS for lithium isotopes.

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Development of the LA-ICP-MS method for liquid analysis

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Inductively coupled plasma mass spectrometry (ICP-MS) is a common and widespread analytical method for elemental analysis. It is primarily intended for the analysis of aqueous solutions, and direct analysis of samples with high levels of organic solvents is not feasible, or may be accompanied by a number of issues such as plasma instability or non-spectral interferences. Laser ablation coupled to ICP-MS (LA-ICP-MS) is an analytical method currently used for the analysis of solid samples. In this method, only a small amount of sample in the gaseous state enters the plasma, so there is a lower effect of the sample on plasma conditions. Therefore, LA-ICP-MS should be a suitable method for elemental analysis of organic solvents, but the use of this method for the analysis of liquid samples is not typical. The aim of this work is the innovative utilization of this method for elemental analysis of liquid samples, primarily the analysis of oils. As the analysis of liquids by LA-ICP-MS is uncommon, it is necessary to develop a completely new methodology including the selection of suitable organic solvents considering their volatility, surface choice of the sample pad, and its design to achieve an appropriate contact angle of sample droplets and optimization of the ablation process.

Several materials for the sample pad were tested for the highest possible contact angle of tested liquids. A higher contact angle results in a lower evaporation rate, which is important in the case of liquids with a non-zero saturated vapor pressure. It has been shown that a higher contact angle is also better for laser-droplet interaction because there is less liquid dispersion. Among the tested materials were glass, polydimethylsiloxane (PDMS), and polytetrafluoroethylene (PTFE). PTFE was chosen as the final material because it results in the highest contact angle for most of the tested liquids and it also shows the best resistance to all types of organic solvents. After that, an optimal design of the sample pad, made from PTFE, was created to maximize the number of samples and eliminate interactions and contaminations between droplets of sample. To describe and predict the behavior of a liquid droplet in the ablation cell, a mathematical model was created. The model describes the evaporation time of a droplet in the ablation cell under certain conditions given by the ablation process (certain He flow, temperature, etc.). The model was created using and testing multiple liquids, such as ethanol, methanol, water, benzene, pyridine, and xylene. There are volatile liquids among the tested solvents, but that is only because of building and testing the mathematical model. Due to the absence of diffusion coefficients of vapors into He gas and to increase the number of tested liquids, the model was tested using air as the carrier gas.

The work brings preliminary results of experiments aimed at developing a method for direct analysis of less volatile organic solvents using LA-ICP-MS.

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LA-ICP-MS Calibration Strategy to Investigate the Ion Transport in Concrete

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Concrete is the most used construction material in the world. It consists of the aggregate, hardened cement paste (hcp) bulk, and the interfacial transition zone (ITZ) phase between them. According to the literature, the ITZ indicates higher capillary porosity than hcp. The capillary porosity is liable for material transport (e.g. ions) in concrete. This, in turn, can lead to ion transport acceleration in ITZ compared to hcp. Transport of deleterious ions, for instance, chlorides from seawater or de- icing salts, through the open capillary pores in concrete triggers rebar corrosion in reinforced concrete, which mitigates its durability. This study focused only on diffusion as an ion transport mechanism in concrete.

The aim of this study is to investigate the ingress of the lithium (Li^+) and iodide (I^-) ions into the ITZ and hcp in concrete due to diffusion. Thus, to examine it, we applied LA-ICP-MS. In our study, we used hcp prisms with various water/cement (w/c) ratios of 0.3, 0.4, and 0.5, two of each. Four calcite cubes were added to one prism of each mixture as a model aggregate during the sample preparation. It enabled to achieve an idealized ITZ, which facilitates obtaining interpretable data than a realistic ITZ with natural aggregate. The samples without calcite cubes were used as matrix- matched Reference Material (RM). To determine the position of each cube in the hcp prisms, micro-computer Tomography (μ-CT) measurements were conducted. After 28 days of air-tight curing, the samples were cut. The prisms with cubes were cut in the middle of every cube. The slices with cubes were immersed in a 3% LiI solution for 3 hours to enable diffusion. RM samples were submerged for 4 days to achieve complete saturation. The slices were cut in the middle of each calcite cube to measure the ion ingress into the concrete. Also, RM samples were cut, and one piece of the sample was used for chemical analysis using digestion/ICP-OES. Before the LA-ICP- MS measurements were performed, the samples were subjected to freeze-drying. In addition to the Li and I isotopes, the Ca, Si, Al, Na, and K, characteristic elements of hcp bulk microstructure, were detected. The proper RM was applied for the data evaluation, depending on sample w/c ratios. The results showed that the difference between the ingress of ions into the ITZ compared to the hcp was not noticeable. Only by the sample with a w/c ratio of 0.5, which indicates the highest capillary porosity, the concentration of Li^+, I^- and mobile ions like K^+ and Na^+ was higher in the ITZ than in the hcp. For the samples with w/c ratios 0.3 and 0.4, the leaching effect of K^+ and Na^+ in ITZ and hcp was observed upon penetration of Li^+ and I^- ions. However, in the sample with the w/c ratio of 0.5, the increased concentration of mobile ions with simultaneous ingress of Li^+ and I^- was noticeable. Independently of w/c ratios, the ingress of I^- ions was deeper than Li^+ ions. Additionally, the signal intensity of the first line, which was conducted in the ITZ next to the aggregate, was immensely lower than that of the further lines. It indicates that the ITZ has a higher porosity than the hcp and a thickness of about 30 μm. This result highlighted that the ITZ has different microstructures compared to the hcp. Thus, applying a proper RM for ITZ needs further investigation to obtain reliable results.