
NORTH AMERICAN LASER ABLATION

WORKSHOP 2015

27TH AND 28TH MAY, JACKSON SCHOOL OF GEOSCIENCE, UNIVERSITY
OF TEXAS AT AUSTIN

PROGRAM AND ABSTRACTS

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DEAR NALAW PARTICIPANTS

On behalf of the Organizing Committee I would like to welcome you to the inaugural North American Laser Ablation Workshop (NALAW) at the University of Texas at Austin.

In the mid-1990's, a small collection of laser ablation users came together to informally exchange ideas surrounding the use of laser ablation. Over the course of ~ 20 years the European Workshop for Laser Ablation (EWLA) has evolved into a highly successful, international meeting attracting in excess of 200 participants from all over the world.

Several years ago, Japan created its own Laser Ablation Workshop attracting laser ablation users from all over Japan and keynote international speakers. There is no doubt that this Japanese Workshop will also evolve into a highly successful event.

Up until now, most laser ablation users in North America have had no forum to exchange ideas surrounding laser ablation and its implementation. The Organizing Committee felt that this needed to change, and thus "NALAW" was born with the goal of facilitating Laser Ablation knowledge transfer and promoting a sense of community amongst North American Laser Ablation users.

At the time of writing, almost 120 participants from Canada, United States, and Mexico and from further afield such as South Africa, Australia and Norway, are onboard.

It is, of course, the Organizers' goal that NALAW becomes a successful and regular event in its own right. We thank you for helping us take this first step, and we wish you an enjoyable and fruitful time in Austin.

On behalf of the NALAW Organizing Committee,

Ciaran O'Connor

(Bozeman MT, May 2015)

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PROGRAMME OVERVIEW

Wednesday 27th May (All sessions in JGB 2.216)

08:00 Registration open (Jackson School of Geoscience)

08:45 Welcome and Introduction

Session 1 LA-ICP-MS fundamentals and parameters

09:00 Overview of LA-ICP-MS and outstanding issues (Sylvester)

09:20 Workshop activity on optimization of LA-ICP-MS instrumentation (Miller)

09:40 Plenary: Laser Wavelength and pulse width: what should be used for which applications? (Gonzalez)

10:10 Moderated discussion

10:30 Tea/Coffee

Session 2 Standardization

10:50 Plenary: Quantitative analysis by LA-ICP-MS: when do we need matrix matched reference materials and when might we get away without them? (Koenig)

11:20 Plenary: Exploring the bounds of glass standardization for U-Pb geochronology by 193nm LA-ICP-MS (McFarlane)

11:40 Pb isotope ratios by LA-MC-ICP-MS using a new USGS synthetic glass spiked with NIST SRM981 (BPbISO-1) (Pribil)

12:00 GSx glasses as general purpose LA-ICP-MS standards for silicates (Loewen)

12:20 Moderated discussion

12:40 Lunch

Session 3 Instrumentation

14:00 Plenary: Ablation cells – what are the general features that are desirable for LA-ICP-MS and why? (McFarlane)

14:30 A comparison of LA Sector Field and Quadrupole ICP-MS for trace geochemical analysis (Luo)

14:50 Common Pb isotope LA analysis of volcanic glass with a magnetic sector ICP-MS. How good can we do? (Souders)

15:10 Moderated discussion

15:30 Tea/Coffee

Session 4 Data quality and analytical improvements

15:50 Plenary: Controls over data quality during analysis of complex natural materials using LA-ICP-MS (Kent)

16:20 Echidnas crossing! Ns-LA-ICP-MS of micro inclusions in Fe metal: can we really tell what is in the sample, and how best to characterize it? (Norris)

16:40 Plenary: Where can improvements be made in LA-ICP-MS analysis? (McDonough)

17:10 Moderated discussion

Session 5 Posters (with beer and refreshments, JGB 6.218)

17:30 – 1900

LA-ICP-MS optimization poster – Day 1: Hardware goals and controls (Hands on, real-time, fun had by all!!)

Cadmium measurement in olfactory rosette tissue of Coho Salmon using LA-ICP-MS (Paulsen)

Trace element distribution in giant clam shells: A potentially new microanalysis reference material for biogenic carbonates (Amini)

LA-ICP-MS of ice cores (Sneed)

Isotopic analysis and quantification of uranium in glass via LA-ICP-MS and a novel matrix matching method (Judge)

Comparative analysis of isotopic U-Th-Pb and trace element composition by LA-ICP-MS in zircons using different measurement modes (STDs, KEDs and CCTs). Preliminary results (Obregon)

Laser Ablation Molecular Isotopic Spectrometry of rare isotopes (Bolshakov)

Method development for the analysis of rare earth elements in phosphate matrices by LA-ICP-MS (Carelse)

Long term LA system stage return accuracy: sub micron performance in real applications (McLachlin)

Electro Scientific Industries Inc. (ESI) sponsored LA users evening

19:00 – late Scholz Beer Garten ALL WELCOME!

Thursday 28th of May - Parallel Morning Sessions

Session 1A Biomedical, biological and environmental applications (JGB 2.218)

- 09:00 Plenary: State of the art in LA-ICP-MS bio imaging (Doble)
- 09:30 Three dimensional bio imaging: towards a metal atlas of the mouse brain (Hare)
- 09:50 Emerging research in fish ecology facilitates by laser ablation of biogenic structures (Walther)
- 10:10 Application of LA-ICP-MS to examine changes in vertebral chemistry of three species of Charcharhinid sharks (Lewis)
- 10:30 Using LA-ICP-MS to refine ice core age-depth scales (Spaulding)

10:50 Tea/Coffee

- 11:10 Optimizing LA-ICP-MS analytical procedure for elemental depth profiling of foraminifera shells (Fehrenbacher)
- 11:30 Analysis of food samples by LA-ICP-MS (Todorov)
- 11:50 Development of geochemical proxies to evaluate larval pH-exposure history (Herrmann)
- 12:10 Moderated discussion

12:30 Lunch

Session 1B Earth Sciences Applications (JGB 2.216)

- 09:00 Plenary: State of the art in isotope ratio analysis and applications to solid Earth research (Cottle)
- 09:30 LA-ICP-MS U-Pb and trace element split stream analysis of accessory minerals by depth profiling of unpolished tape mounts (Stockli)
- 09:50 A continuous thermal history of Corsica derived from accessory mineral LA-ICP-MS depth profiling (Seymour)
- 10:10 U-Pb zircon geochronology by LA-ICP-MS combined with thermal annealing: achievements in precision and accuracy on dating standard and unknown samples (Solari)
- 10:30 Origins of enigmatic monzogranites, Ruby Mountain Core Complex, Nevada (Barnes)

10:50 Tea/Coffee

- 11:10 First row transition metals, Ga and Ge in Komatiitic Olivine (Locmelis)

11:30 Be and other "unusual" trace elements in TiO₂-bearing sapphire (Al₂O₃): Characterization by LA-ICP-MS, EPMA and nanoSIMS (Palke)

11:50 In-situ U-Th dating of accessory minerals using LA-ICP-MS (Bernal)

12:10 Moderated discussion

12:30 Lunch

Session 2 Posters (with beer and refreshments, JGB 6.218)

13:40 – 15:10

LA-ICP-MS optimization poster – Day 2: Feedbacks and best optimization practices (Hands on, real time, fun had by all!!)

Damp melting beneath West Antarctica from olivine-hosted melt Inclusions (Aviado)

U-Pb dating of Grossular-Andradite garnet using LA-ICP-MS (Seman)

Sediment input pathways from North American Highlands to the Gulf of Mexico based on detrital zircon U-Pb dating (Xu)

Trace element zoning in plagioclase as a record of eruption in ignimbrites from Dominica, Lesser Antilles (Manon)

Trace element zoning in metapelitic garnet: A LA-ICP-MS study (McCarron)

Depth profiling analysis of Li-ion batteries by LIBS and LA-ICP-MS (Quarles Jr.)

SelfSeal sample chamber: automation for industrial bulk analysis (McLachlin)

Mineralogy, chemical composition and provenance of volcanic black sands of Iceland (Norman)

Session 3 General Issues

15:10 LA-ICP-OES for production applications (Cook)

15:30 Plenary: LA-ICP-MS data reduction software: options and ideas (Petrus)

16:00 Moderated discussion

16:20 Results of workshop activity on optimization of LA-ICP-MS Instrumentation (Miller)

16:50 Moderated discussion

Session 4 Wrap up

17:00 Awards, feedback session, good bye (Sylvester and Miller)

ABSTRACTS: ORAL PRESENTATIONS

Overview of LA-ICPMS and Outstanding Issues

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This year marks the 30th anniversary of Alan Gray's landmark report [1] on the use of a ruby laser for solid sampling of rock powder pellets, and chemical analysis by mass spectrometry, or what is considered today to be the birth of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). By the early 1990s [2], geologists and chemists had embraced the method, revolutionizing *in situ* chemical analysis. Environmental, medical, biological, materials and forensic scientists found applications somewhat later, with each discipline adapting the technique for its own needs. LA-ICPMS is deceptively simple. Laser pulses remove small volumes from a sample, the ablated aerosols are transported in a carrier gas stream to the ICP and converted to ions, which are separated based on their mass to charge ratios by a mass spectrometer and measured with a detector. But optimizing the ablation and transport conditions, tuning the ICPMS, and proper calibration of measured signals against standards using data processing software can be challenging.

Further research on outstanding issues in LA-ICPMS is needed. In particular, new, well-calibrated reference materials of various matrices would improve tests of the accuracy and precision of LA-ICPMS analyses, particularly for high-precision trace element and isotopic ratio measurements. New femtosecond laser ablation systems need further evaluation of potential advantages over conventional nanosecond lasers. Measurement and data handling procedures could be better optimized for chemical mapping of solid objects. Analytical uncertainties should be quantified more rigorously for specialized techniques such as high-spatial resolution (small spot or single pulse) and split-stream (simultaneous analysis of ablation aerosols by 2 or more ICPMS instruments) analyses. Advances in data handling software could improve automated analysis and on-line quantification, needed for applications requiring high-throughput such as U-Pb detrital zircon geochronology.

[1] Gray, AL (1985). *Analyst* 110(5): 551-556.

[2] Jackson SE, Longerich HP, Dunning R, Fryer BJ (1992). *Can Mineral* 30:1049–1064.

Optimization Knowledge (“NALAW-ge”) - A Group Participation Activity

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NALAW Mission:

To facilitate Laser Ablation knowledge transfer and promote a sense of community amongst North American Laser Ablation users

Two common analytical objectives for laser ablation (LA) studies are determinations of elemental concentrations by LA-ICP-quadrupole-MS and isotope ratios by LA-ICP-sector field-MS. Obtaining high quality (precise and accurate) data from either platform requires system optimization of signal-to-noise and stability during the analytical session. Each analytical platform consists of integrated hardware components, each with a range of computer-adjustable controls. Several controls among hardware components have mutual performance feedbacks. Yet gauging the effect of various control adjustments is mainly based on integrative observations, namely: (1) visual changes to the sample during ablation (monitored using the video camera of the laser system), and (2) variations in intensities (or intensity ratios) detected while the laser is on or off (assessed from time-resolved data from the mass spectrometer). The logic of how to optimize platform controls, considering the range of possible control feedbacks, is a common learning challenge to new (and even seasoned) laser ablation users. Learning is largely empirical, ideally by working closely with experienced users, but because the laser ablation community is small, many users are substantially self-taught. In an effort to demystify the optimization learning curve and embrace the mission of the North American Laser Ablation Workshop (NALAW), a two-day poster exercise endeavors to generate a graphical summary of best practices for system optimization, through group participation and knowledge transfer among attendees with a wide range of laser ablation experience. Day one objectives are to define optimized functional goals and specific controls of hardware components. Day two objectives are to identify feedbacks among component controls and compile a list of effective strategies (what you do, why you do it and in what order) to optimize control settings. Following the workshop, a summary graphic and optimization logic table will be made available to NALAW attendees for use in their own laboratories.

Laser Wavelength and Pulse Width: What should be used for which Applications?

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Since the invention of the laser there have been a never-ending discussion concerning the ‘better’ wavelength in particular for laser ablation chemical analysis. Wavelength is believed to be an important parameter based on the sample’s optical penetration depth as well as photon energy for bond breaking. Although the choice of laser is still highly dependent on the application requirements, there are also distinct fundamental effects attributed to the laser pulse duration that drive the ablation sampling process. And while the most widely employed lasers for analytical applications are the nanosecond and UV based lasers such as excimer, based on an ArF mixture with a wavelength of 193 nm, and the solid state Nd:YAG, with wavelengths of 266 nm and 213 nm the development of ultrafast pulse lasers (femtosecond and picosecond) and their introduction to chemical analysis has reduced, and in some cases eliminated the so called fractionation effects in a most significant fashion that those mentioned ns-based lasers. Furthermore, the introduction of chemometrics tools has also help to reintroduce the use of IR-wavelength for a wide range of application such a classification and discrimination analysis.

Quantitative analyses by LA-ICP-MS: When do we need matrix matched reference materials and when might we get away without them?

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Along the way of testing the limits of quantitative analyses by LA-ICP-MS a number of myths and lab lore have developed. With 30 years of research involving increasingly shorter wavelength and pulse width LA systems there still are limited apple-to-apples comparisons of different systems under truly controlled conditions. Despite limited direct comparisons evidence suggests that shorter wavelengths often lead to less dependence on matrix matched calibration reference materials. With that knowledge in hand we can evaluate when non-matrix matched calibrations work and when they do not work. This talk will outline some examples of direct wavelength comparison using a range of matrix and non-matrix matched calibrations as well as pushing the limits of when matrix matching does not work. Using some examples of situations where matrix matched reference materials did not exist we can explore the effects of matrix mismatches and discuss possible solutions. We will also explore some situations where the results are in fact rather surprising where non-matrix matched calibrations actually work. Detailed examination of when improper calibration can lead to erroneous results will be presented. Some novel examples of quantitative results leading from proper methods development and validation will be presented. Now that we better understand some of the fundamentals of the LA and ICP-MS processes as well as recognize areas that we still do not fully understand we can examine some of the myths and lab lore and do some science.

On the quest for the magic black box that spits out correct answers for analyses of unknowns without the need for calibrations we have learned many things...

Exploring the bounds of glass standardization for U-Pb geochronology by 193nm LA-ICP-MS

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There are numerous U-bearing minerals, potentially suitable for U-Pb geochronology, for which no homogeneous natural mineral standards exist. In such cases non-matrix matching may provide an alternative means to obtain accurate U-Pb dates. Several widely-used glass reference materials (NIST610 and 612; USGS GSE-1G) were tested as potential candidates for non-matrix matching applied to a range of international reference standards and in-house U-bearing minerals from well-characterized locales. The first goal of this study was to establish working values for Pb/U and Pb/Pb in these glass standards assuming accurate reference values for NIST610 from [1]. Ablation time, repetition rate, and crater diameter were also optimized (i.e. <20sec ablation, 2.5Hz, ~40µm crater) to help minimize elemental fractionation. The effect of laser fluence on measured/true Pb/U values was also assessed. Establishing optimal laser fluence is shown to be a critical step since many minerals showed significant variation in Pb/U as a function of fluence. The results of these investigations show that allanite is in fact quite well matched to NIST610 once optimal ablation conditions are established. Using NIST610 as external standard, accurate and precise allanite U-Pb ages have been obtained for Daibosatsu (13 Ma), Siss3 (34 Ma) and six other in-house materials with independent age constraints. Hence, use of NIST610 as an external standard for allanite U-Pb geochronology appears to be viable. Use of other glass standards with other minerals such as titanite, zircon, phosphates, and Fe-Ti-REE oxides, is still being tested but show some promise. Advantages of this approach include the ubiquity of glass standards, good elemental and isotopic homogeneity, and well-characterized Pb/Pb ratios. Hence, the approach is particularly suited to common-Pb bearing minerals for which isotopically homogeneous natural reference materials are scarce.

References

[1] Horn & von Blanckenburg (2007) *Spectrochimica Acta Part B*, v. 62, 410–422

Pb isotope ratios by laser ablation MC-ICP-MS using a new USGS synthetic glass spiked with NIST SRM 981(BPbISO-1)

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Accuracy and precision for laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) determinations of Pb isotope ratios is limited due to the lack of solid in-situ isotopic standards. NIST SRM 997 Tl isotope standard is commonly used to correct for mass bias fractionation for solution Pb isotope measurements by MC-ICP-MS. This approach has resulted in numerous research studies investigating external normalization, internal correction and behavioural differences between Tl and Pb. Recent in-situ Pb isotopic studies have implemented various methods to correct for mass bias fractionation by LA-MC-ICP-MS including: 1) teeing in Tl from a desolvating nebulizer system; 2) standard sample bracketing (SSB) with NIST SRM 610, 612 or an internal Pb isotope reference material; 3) SSB with SRM 610 or 612 and externally reporting the differences to NIST SRM 981 solution results as deviation from SRM 981 in per mil notation. Methods 1 and 3 possibly introduce a separate source of mass bias fractionation by using an additional introduction system. Method 2 and 3 used SRM 610 and 612 as Pb isotope reference materials, which while thoroughly evaluated resulted in a range of isotopic composition without an agreed upon value. Here we present mass bias fractionation results related to laser ablation introduction, as well as the application of SSB using a new USGS synthetic glass material (BPbISO-1) spiked with SRM 981 Pb isotopic standard. Preliminary SSB analyses of SRM 610 using the USGS BPbISO-1 synthetic Pb isotope glass by LA-MC-ICP-MS resulted in $^{208}\text{Pb}/^{204}\text{Pb} = 36.9670 \pm 0.0045$ (2σ), $^{207}\text{Pb}/^{204}\text{Pb} = 15.5066 \pm 0.0032$ (2σ) and $^{206}\text{Pb}/^{204}\text{Pb} = 17.0403 \pm 0.0019$ (2σ), which are within error of previously reported values. The implementation of this new Pb isotopic spiked geologic glass (BPbISO-1) with external mass bias correction provides an improvement on previous LA-MC-ICP-MS measurements and useful inter-laboratory methodology.

GSx glasses as general purpose LA-ICP-MS standards for silicates

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Homogeneous and well-characterized standards are necessary for consistent and accurate determination of trace element concentrations by LA-ICP-MS. The overwhelming majority of LA-ICP-MS applications use NIST-610 or NIST-615 glasses for calibration despite the fact that these glasses have well-documented heterogeneities (1). The GSx glasses provide an alternative choice for calibration. Our work demonstrates that these glasses are reasonably homogeneous for a range of refractory to volatile trace elements. The primary limitation for accuracy, especially for volatile elements, is poor characterization of the GSx standards. Our results suggest that excellent precision can be achieved with GSx glasses but higher quality characterization of the standard is needed to achieve the best accuracy.

With 193 nm Ar-F Excimer lasers, the mafic composition of the GSx glasses appears to provide a good matrix match for silicate glass compositions from similar mafic basalts to high silica rhyolites. We here demonstrate this in diverse silicate reference standards as well as application to two natural systems: basaltic compositions from Kilauea Iki and high silica rhyolites from Yellowstone. Our results demonstrate that the GSx glasses provide an accurate and precise calibration for volatile and refractory elements in all silicate compositions and should be the preferred calibration standard for geologic investigations.

(1) Eggins and Shelley, *Geostandard. Newsl.*, 2002, v. 26, p. 269-286

(2) Guillong, Hametner, Reusser, Wilson, and Gunther, *Geostand. Geoanal. Res.*, 2005, v. 26, p. 315-331.

Ablation cells - what are the general features that are desirable for LA-ICPMS and why

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The ablation cell is arguably the most critical component of a LA-ICP-MS system. Cells must satisfy a wide range of performance specifications to ensure precise and accurate results. Key performance criteria include: 1) fast washout; 2) stability 3) reproducibility and minimal location-dependent elemental fractionation; 4) low carry-over; 5) high sensitivity; 6) stage reproducibility, and 7) cost-effectiveness in terms of gas consumption and throughput. These features are, in turn, related primarily to the engineering design, geometry, and hydrodynamic properties of the cell.

Fast-washout is required to resolve vertical or lateral chemical variations during drilling or mapping experiments and to ensure that signals return to background levels quickly at end of an ablation. A stable, resonance-free, carrier gas flow reaching the ICP-MS torch is also critical to minimize excess noise that contributes to high %RSD.

Additionally, all cells, regardless of their design, need to achieve a stable high-purity atmosphere because even small variations in carrier gas composition (e.g., small air leaks) can affect net sensitivity. Similarly, the reproducibility of ablation characteristics (i.e. similar elemental fractionation) throughout the cell is desirable to achieve accurate results over the largest possible working area. Cell geometry and gas inlets can also be designed to minimize interaction of ablation products with the walls and upper window and this helps to reduce carry-over effects on day-to-day background levels as well as washout-times. Although maximum sensitivity is obviously desirable, it must be balanced with stability and reproducibility to achieve accurate results. Stage reproducibility of a few microns is required to ensure that automated sequences can be acquired without missing targets. Finally, cost-effectiveness of cells can be measured in terms of the gas burden during sample exchange and throughput in terms washout times. In both cases, large-area two-volume cells hold advantages in terms of limiting the number of daily sample exchanges and, because of their fast washout characteristics, maximizing the number of ablations achievable per day.

A comparison of Laser Ablation Sector Field and Quadrupole ICP-MS for trace geochemical analysis

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A sector field ICP-MS instrument (Element XR) and a quadrupole ICP-MS (HP-7700) combined with laser ablation sampling (Resonetics, 193nm Excimer laser) were evaluated and compared for precise and accurate measurement of trace element determinations in geological glasses. Limit of detection, sensitivity, long term data accuracy, precision, and combined uncertainty were evaluated based on the same laser facility using the same ablation conditions. The detection system of the ELEMENT XR is composed of a dual mode, discrete dynode secondary electron multiplier detector and a faraday detector giving a combined linear dynamic range of over 12 orders of magnitude^[1]. The important differences between the detectors in the quadrupole ICP-MS and the sector field Element XR will be addressed. In contrast to the Faraday detectors usually installed in multi-collector ICP-MS and TIMS, the amplifier system of the Faraday in the Element XR is faster settling with a dynamic range which begins at a much higher signal level. Potential problems with multiple detectors and multiple modes will be investigated. A case study will be presented for the determination of trace gold in native Arsenic and PGE analysis in high purity metallic Fe using Faraday mode (after Faraday cup cross calibration) for internal standardization and triple mode for the trace analysis.

[1] M. Hamester, L. Rottmann & J. Wills.

Increased linear dynamic detection range sector field ICP-MS for geological applications. Goldschmidt Conference Abstracts 2005.

Common Pb isotope laser ablation analyses of volcanic glass with a magnetic sector ICPMS: How good can we do?

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Common Pb isotopes of volcanic glass present as melt inclusions in phenocrysts and quenched interstitial melt can provide valuable information about the sources and magmatic histories of igneous rocks. Because such glass is often present as tiny objects, in-situ analyses are the only practical way to measure its isotopic composition. The limitation of in-situ analyses however is that the precision of the isotope ratio measurements may be insufficient to distinguish differences between important sources.

For laser ablation ICPMS, the most precise in-situ measurements may be made with either a single or multi collector magnetic sector instrument. In order to provide a guide to when either technique might provide useful Pb-isotope data for petrogenetic studies of volcanic glass, we have determined the precision as a function of Pb sensitivity in a series of well-characterized volcanic glass reference materials (MPI-DING). Pb sensitivity is governed by the concentration of Pb in the glass and various laser and ICPMS instrument parameters, particularly ablation spot size.

Ablations for all analyses were carried out using a 193 nm ArF excimer laser (GeoLas). Using a single collector sector ICPMS (ELEMENT-XR) we find that precision (1SD) of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for glass T1-G (11.6 ppm Pb) increases from 0.9% and 0.8% respectively with a 49- μm spot to 0.3% and 0.31% with a 99- μm spot. The precision (1SD) of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for glass ATHO-G (5.7 ppm Pb) increases from 2.4% and 1.1% respectively with a 49- μm spot to 0.35% and 0.35% with a 99- μm spot.

The same laser analyses performed with a multicollector instrument (NEPTUNE) equipped with an ion counter (Channeltron) array allow for improved measurements of both $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. The precision of $^{207}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ for T1-G (49 μm) is 0.2%, 0.14% and 0.12%, respectively, and 0.4%, 0.1% and 0.1% for ATHO-G (69 μm), respectively.

Controls over Data Quality during Analysis of Complex Natural Materials using LA-ICP-MS

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Many naturally occurring materials, such as crystals, otoliths, speleothems, shells etc. contain compositional records critical for understanding and interpreting natural phenomena, including records related to past climate or oceanographic variations, animal life histories, and volcanic behaviour. In many cases the spatial complexity and need to translate spatial variations to temporal signals require high-resolution in-situ analytical approaches, and laser ablation ICP-MS is often preferred given the high spatial resolution, analytical flexibility, rapid data acquisition and low-pressure sampling mode of the technique. However compositionally complex natural materials also represent considerable challenges for LA-ICP-MS. Important issues include the interplay between spatial resolution and precision, effect of different ablation conditions, ablation chamber response and data processing methods. In this presentation I will talk about approaches to enhance analytical accuracy and precision, maximize spatial resolution and optimize analytical efficiency during analysis of complex materials by LA-ICP-MS. The methodology will be illustrated by examples of the analysis of crystals in volcanic rocks used to estimate magmatic conditions and time scales, but are applicable to many other materials.

Echidnas Crossing! ns-LA-ICPMS of micro inclusions in Fe metal: Can we really tell what is in the sample, and how best to characterise it?

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Analysis of volatile elements (Ag, Bi, Cd, Cu, In, Pb, Sb, Tl, and Zn) at trace levels in iron metal has lead us to fabricate a series of candidate calibration standards at high pressure and temperature in a piston cylinder apparatus.¹ At the microscale these materials contain high-density blebs 1-2µm in diameter spaced tens of microns apart. Using ns-LA-ICP-MS in scanning mode with a spot size of 12µm gives ICP-MS signals containing many spikes from the trace elements, as well as substantially abrupt variations to signal intensities lasting for several seconds. To better understand this process a comparison is made between the signal intensities obtained from ablating spots in a fixed position with a beam size of 50µm to the results from the 12µm raster analyses. Modelling of the responses from these materials in both analysis modes is performed in an effort to characterise the spatial distribution of these heterogeneities. Some workers² have excluded these abrupt spikes from the analysis, but we report that quantifying them can allow the bulk composition to be assessed as well as the mean size of the blebs in the metal to be estimated when used in tandem with appropriate data processing procedures.

¹Norris & Wood, "Fabricating matrix-matched iron standards for LA-ICP-MS analysis of Ag, Bi, Cd, Cr, Cu, Ga, Ge, In, Mo, Pb, Sn, Tl, V, W and Zn." European Laser Ablation Workshop, RHUL, London. 8-11 July 2014. Poster presentation.

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Where can improvements be made in LA-ICP-MS analysis?

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LA-ICP-MS analysis allows for submicron to submillimetre sampling of materials for its chemical and or isotopic composition over abundance levels ranging from weight percent to sub-nanograms per gram levels, with scaling being dependent on precision demands, number of atoms available, and other factors. Laser ablation sampling is complementary to ion beam methods, with the proviso that the former method typically excavated at a 1000 times greater penetration rates. Photon absorption via electronic transitions for insulators and semi-conductor require $>4\text{eV}$ and hence deep UV and shorter wavelengths are needed for nanosecond pulsed lasers to ablate effectively. Femtosecond pulsed lasers deposit their energies faster than phonon relaxation rates, can ablate over a broader range of wavelengths while also attenuating local heating aureoles in the non-ablated surrounding material. Laser induced chemical and isotopic fractionation varies as a function of matrix, laser system, and ablation parameters, with protocols available to reduce fractionation.

There are vast areas for improvements in LA-ICP-MS. Instrumental improvements include: the laser system, ablation cell, transport and torch environment, and MS. The ideal sampling system removes and transports material stoichiometrically to the MS leaving behind a sample that is undamaged beyond the ablation site. Depending on the application one might wish to have shortest transport time to assess spatial variability or longer transport time and aliquot mixing to obtain smoother signal responses. Improvements in technique practices can lead advances in (1) studies of elemental abundances and ratios at high precision ($\pm 3\%$, 2 sigma) levels, (2) determining chemical or isotopic gradients with high spatial resolution, (3) studies of elemental abundances at $<\text{ng/g}$ concentration levels, (4) large area sampling (mm^2) for sample characterization and (4) novel applications (e.g., nuclear forensics, material forensics, planetary missions). Vast improvements are needed in data and meta-data archive and publication practices. Finally, automation, including operator free practices, is an area that needs considerable attention.

State-of-the-art in LA-ICP-MS Bio-Imaging

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Bio-imaging by LA-ICP-MS finds numerous applications in diverse areas of investigations such as palaeontology, neurodegenerative disorders and basic mechanistic biology; and is now considered a key platform technology for Metallomics research. This presentation will highlight some recent applications of bio-imaging by LA-ICP-MS, as well as recent innovations in antibody metal tagging protocols that have facilitated the development of a universal imaging approach for the simultaneous measurement of elements and molecules.

Three-dimensional bio-imaging: Towards a metal atlas of the mouse brain

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Metals are critical for a healthy and functional brain. The central nervous system maintains a highly compartmentalized distribution of transition metals, ensuring their unique redox chemistry is harnessed for proper metabolism. Disruption of metal homeostasis in the brain has been associated with a number of neurodegenerative disorders, including Alzheimer's and Parkinson's disease. Although metals are recognized as playing an important role, neuroscientists have few resources to call upon with regard to typical biological conditions. The ubiquity of metals in the brain makes accurately determining both concentration and the ligands involved in metal binding more important than simple localisation. This talk will discuss our current efforts to produce a comprehensive roadmap of metal distribution in the standard laboratory mouse, using laser ablation-inductively coupled plasma-mass spectrometry imaging, metal immunolabelling and advanced data visualization software; and briefly discuss the implications this technology can have for the wider bioscience community.

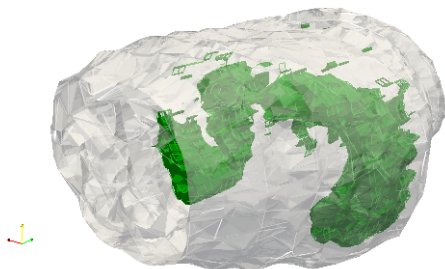


Figure 1: *Hippocampal zinc in the C57BL/6 mouse brain.*

Emerging research in fish ecology facilitated by laser ablation analysis of biogenic structures

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High-resolution laser ablation analysis of biogenic structures in mobile fishes has provided unprecedented insight into ecologically important dynamics including migration, habitat use and exposure to environmental stressors. This work relies on sequential analysis of incrementally-accreting calcified structures such as fish otoliths (ear stones) and scales that provide lifetime histories of movement between chemically distinct bodies of water. Such work has been driven by advances in laser ablation technology that has allowed increasingly precise, accurate and highly-resolved spatial analyses. We highlight three areas where laser ablation has provided new information about fish ecological dynamics. First, high resolution transects of Mn/Ca across otoliths in fish from low-oxygen hypoxic “Dead Zones” has revealed individually variable hypoxic exposure histories, allowing analysis of sublethal exposure effects of this important environmental stressor. Second, we have recently developed methods for cross-sectional analysis of calcified layers in fish scales as a non-lethal alternative to otoliths for assessments of estuarine habitat use using Sr/Ca. Finally, high resolution sampling of specified increments in otoliths, fin rays and scales of captive-reared fish fed diets containing Ba isotope spikes provides a novel way to mark hatchery fish to be released into the wild. Together these studies showcase the diversity of applications of laser ablation to the field of fish ecology. Future developments in analytical techniques will help resolve outstanding questions, including the rapidity of elemental uptake into structures and subseasonal analysis of increments in long-lived and slow-growing species

Application of LA-ICP-MS to Examine Changes in Vertebral Chemistry of Three Species of Carcharhinid Sharks

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The analysis of shark vertebral chemistry with laser ablation-ICP-MS provides a new method to investigate estuarine habitat use or residency questions difficult to address with conventional methods. The sequential accretion of hydroxyapatite within elasmobranch (sharks, rays, and sawfishes) vertebral centra produces a biogeochemical chronology of environmental conditions experienced by an individual. This is due to divalent ions directly substituting for Ca or otherwise being incorporated into the vertebral matrix, with these processes potentially affected by environmental and physiological factors. Ontogenetic shifts in habitat that accompany changes in salinity are of particular interest because low salinity inshore habitats are important areas for parturition and act as nurseries for young sharks, and salinity has been shown to be highly correlated with Sr:Ca and Ba:Ca in elasmobranch vertebrae. In the currently application, we constructed 2D maps of vertebral Sr:Ca and Ba:Ca, as well as Pb:Ca, of three shark species that exhibit different patterns of estuarine habitat use in early life. We observed interspecific differences in vertebral chemistry related to the degree to which species use estuarine and freshwater habitats. Our results also highlight the importance of understanding factors other than salinity that influence vertebral chemistry.

Using LA-ICP-MS to refine ice core age-depth scales

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Ice cores provide a robust reconstruction of past climate. However the closely spaced layers of ice cores collected in low accumulation sites or in regions of strong vertical shear add complexity to these reconstructions. (LA)-ICP-MS offers minimally destructive impurity analysis at unsurpassed sub-mm depth resolution. It is therefore uniquely suited for exploring sites such as the Alpine glacier saddle Colle Gnifetti (CG). CG is the only drilling site within the European Alps suitable for archiving multi-millennial records in spite of its limited ice thickness (< 100 meters), however its annual layers rapidly thin below the cm-resolution of conventional ice core analysis techniques, making the creation of an accurate age-depth scale challenging.

Here we present LA calcium (Ca) and sodium (Na) measurements from an ice core drilled at CG in 2013 along with co-registered Ca and Na measurements from traditional continuous flow analysis (CFA). Through comparison of these data sets we 1) validate LA based annual layer counting in the upper depths and 2) demonstrate that LA based annual layer counting can continue at depths where the CFA signal becomes plagued by strong, multi-year cycles. Considered more broadly, our findings from the CG ice demonstrate that this technique promises to be of great benefit to the refinement of age-depth scales for ice cores containing ultra-thin annual layers. This may be especially relevant for members of the ice core community pursuing million year old ice kilometers below the surface.

Analysis of food samples by laser ablation ICP-MS

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Rapid elemental screening of food samples and dietary supplements is a critical step in assessing the safety of these products and thus it is a central mission of the Food and Drug Administration. The method presented here provides direct solid sampling, producing rapid results for a number of toxic and essential elements. Solid samples are mixed with a mixture of internal standards (premixed in a cellulose matrix modifier), pressed using a pellet press and analysed by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS). Quantification was performed using an in-house prepared standard material based on infant formula and cocoa powder. The use of multiple internal standards for the analysis of the same elements ensures accurate quantification even if an internal standard element might be present in the food or supplement samples. Comparison between NIST SRM 612 and the in-house prepared matrix matched standard will be discussed. The LA-ICP-MS method is validated using food reference materials, as well as food samples and dietary supplements analysed by microwave digestion followed by ICP-MS analysis. Figures of merit and analytical performance of the method will also be presented. The limits of quantification for most elements are similar to these obtained by solution ICP-MS for the samples of interest. In this presentation we will discuss the advantages and drawbacks of LA-ICP-MS for direct solid analysis of powdered food samples and compare it to solution ICP-MS of digested samples.

Development of Geochemical Proxies to Evaluate Larval pH-Exposure History

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The goal of this project is to develop new proxies for ocean acidification that can be used to assess pH exposures in living organisms and potentially to interpret the geologic record. It is hypothesized that the isotopic composition of larval calcium carbonates reflects changes in seawater chemistry driven by ocean acidification and, in some instances, with associated decline in oxygen levels.

For this project, mytilid mussel and oyster species are targeted, each living naturally under a different pH regime. Larvae with known pH, oxygen and temperature exposure histories from laboratory larval rearing experiments and natural environments are used. So far, analyses have focused on obtaining B/Ca ratios from laser ablation ICP-MS analyses as a proxy for pH changes. Method development has focused on assessing mussel larvae cleaning protocols, optimizing background levels, mounting protocols, and standard development.

Different standards (MACS-3 and NIST 610/612 glasses) were evaluated for their utility for calibrating the LA-ICPMS analyses. This study confirms, as has recently been suggested, that the small scale heterogeneity of these standards and elemental concentrations makes them inappropriate for calibration of in situ B analyses of small larval material. However, nanoparticle pressed SRMs have the potential to serve as standards. Furthermore, cleaning the samples with B-free water (passed through amberlite resin) and mannitol is essential.

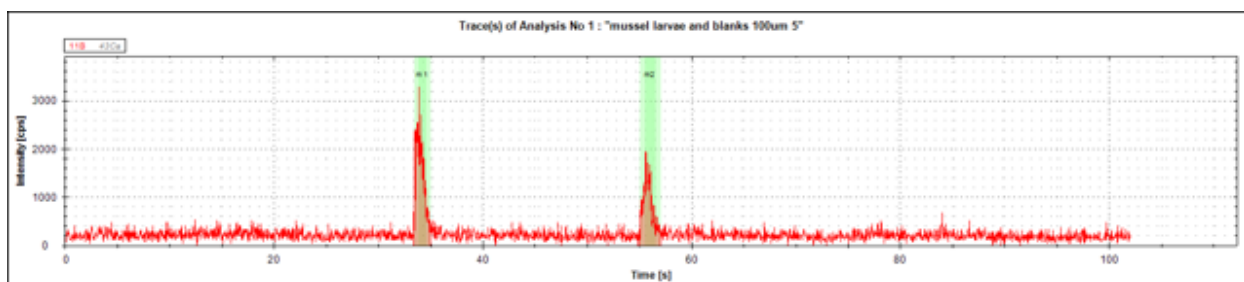


Fig. 1: ^{11}B trace of two mussel larvae ablations using LA-ICPMS (100 μm spot, 10HZ, 5% energy).

State of the Art in Isotope Ratio Analysis by LA-ICPMS and Applications to Solid Earth Research

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Isotope ratio analyses by LA-ICP-MS are now integral to a broad range of solid earth science studies - from determining sedimentary provenance to quantifying the timing, duration and nature of tectonic and petrologic processes. Drawing on examples from ongoing research projects at UCSB and elsewhere, this presentation will highlight recent advances and potential future directions in situ isotope ratio analysis by LA-ICP-MS. Specifically, I will focus on four key avenues of progress: 1) improvements in laser and mass spectrometry instrumentation that increase both the precision and accuracy with which measurements can be made and the spatial resolution at which isotope ratios can be measured; 2) development and application of novel data acquisition and reduction methods to interrogate data and produce the best quality results possible; 3) concomitant analysis of trace element abundances (e.g., Ti, Y, Zr, REE etc.) and isotope ratios in order to better integrate and interpret the latter with respect to specific structural, metamorphic and geochemical data and; 4) development of campaign-style isotope ratio data collection methods to elucidate the spatial and temporal extent of geologic processes at scales ranging from single crystals to entire orogens.

LA-ICP-MS U-Pb and Trace Element Split-Stream Analysis of Accessory Minerals by Depth Profiling of Unpolished Tape Mounts

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We can extract invaluable information from accessory minerals about the petrologic, geochemical, and thermal evolution of rocks. Time-resolved depth-profiling of accessory phases by LA-ICP-MS reveals different growth zones within a single grain, allowing for a more finely resolved quantification of geological processes. For this study, zircon grains were analyzed both mounted on tape (unpolished) and embedded and polished within epoxy to compare the results and test signal stability, precision, and equivalency of the two approaches. The advantage of analyzing unpolished grains is that the outer zones are accessible and growth zone mixing is minimized, with the disadvantage that the inner core of the grain might not be sampled. Depth profiling of unpolished tape mounts is only feasible using large volume ablation cells due to carrier gas turbulence caused by sample topography. The depth resolution during continuous ablation, rather than single-pulse analysis, is limited by wash out (<1 sec for our system corresponds to ~0.5 micron resolution at 10 Hz). In addition to depth profiling, we employ laser ablation split-stream analysis (LASS-ICP-MS) of the dry aerosol into two Element2 HR-ICP-MS instruments to obtain simultaneous measurement of a mineral's U-Pb age and corresponding trace element concentrations, thus yielding a more complete picture of crystallization and growth. Interferometric calibration of ablation rates and post-ablation SEM-CL imaging of grains perpendicular to ablation direction is used to verify interpretations. Detailed depth-profile REE/trace element analyses of accessory minerals, as described in this study, open unprecedented new avenues in the reconstruction of their crystallization history and petrological and geochemical environments, thus elucidating geological, tectonic, and petrological processes recorded by accessory minerals.

A Continuous Thermal History of Corsica Derived from Accessory Mineral LA-ICP-MS Depth-Profiling

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LA-ICP-MS depth profiling of U-bearing accessory phase geo/thermochronometers such as zircon, rutile, and apatite offer a new opportunity to examine thermal histories in regions that experienced amphibolite and granulite conditions, historically inaccessible due to thermal sensitivity limitations of conventional thermochronology [1]. Here we provide time-temperature (t-T) constraints on a Mesozoic fossil hyperextended rift margin in Corsica, where upper-crustal tonalites and lower-crustal gabbro-norites are juxtaposed along the ductile Belli Piani Shear Zone [2]. Low-temperature ($T_C < 300^\circ\text{C}$) thermochronometers were reset during Cenozoic greenschist-facies metamorphism, creating a need for higher-temperature methods.

Zircon ($T_C > 800^\circ\text{C}$), rutile ($T_C = 400\text{--}500^\circ\text{C}$), and apatite ($T_C = 400\text{--}450^\circ\text{C}$) were depth-profiled for simultaneous U-Pb and trace element concentrations [3]. Zircon U-Pb ages record primary igneous crystallization between 275–300 Ma, while 165–210 Ma overgrowths are present in lower crustal grains. The latter ages indicate that the margin reached temperature conditions sufficient for zircon saturation and growth. Ti-in-zircon thermometry yields temperatures of $\sim 700^\circ\text{C}$ ($\pm 20^\circ\text{C}$) in the hanging wall and $\sim 800^\circ\text{C}$ ($\pm 60^\circ\text{C}$) in the footwall. Apatite and rutile feature [Pb] profiles and U-Pb ages grading from ~ 200 Ma cores to ~ 150 Ma rims. This intragrain variation is attributed to thermally activated volume diffusion at temperatures above 400°C . Inverse modeling of concentration profiles yields a two-stage cooling path from $> 700^\circ\text{C}$ at 200 Ma to 500°C at 160 Ma, followed by slower cooling to 400°C between 135–120 Ma.

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U-Pb zircon geochronology by LA-ICPMS combined with thermal annealing: achievements in precision and accuracy on dating standard and unknown samples

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Although zircon U-Pb geochronology by LA-ICPMS is one of the most popular geochronological techniques, it still suffers from some accuracy and precision problems; mostly due to the requirement of natural zircons as external standards to bracket the analyses, and from which is possible to recalculate isotope ratios, errors and ages. Because of the inherent slight differences in behaviour between different zircons, among which, the crystal damage induced by alpha-radioactive decay (alpha dose), can lead to differences in the coupling of the laser with the zircon itself; resulting in difficult-to-predict and even irreproducible matrix effects, impinging on the precision and accuracy of the technique. Here, We explore the application of zircon thermal annealing as a new method to improve age results obtained by LA-ICPMS by restoring the crystal structure from the damage caused by the alpha-dose. We document the advantages of thermal annealing by means of two experiments on standard and several unknown zircons, spanning different degrees of crystallisation history complexity. In general, pretreatment of zircons by thermal annealing yields more accurate ages (e.g., 336.87 ± 0.49 Ma for the Plešovice standard zircon, vs 340.24 ± 0.49 Ma of not annealed zircons) with significantly less dispersion (e.g., MSWD which drops from 3 to 1.3 in the Panchita zircon, or from 11.6 to 2 in the OC6498 zircons). We also demonstrate that thermal annealing significantly reduces the scatter of the trace element data, but they preserve the primary characteristics (such as REE anomalies, igneous fluctuations and differences in overgrowths), as well as the capability of yield more accurate results for petrogenesis and geothermometry.

Origins of enigmatic Monzogranites, Ruby Mountain Core Complex, Nevada

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Late Cretaceous (LK)–Paleogene granitic magmatism characterizes the Ruby Mountain-East Humboldt metamorphic core complex, NE Nevada. Granitic magmas were emplaced as numerous tabular sheets connected by ‘riser dikes’, making regional correlation impossible except on geochemical bases. Moreover, U-Pb (zircon; SHRIMP) dating of high-level leucogranites yielded mixed ages [1], leading to confusion in terms of the timing and volumetric importance of granitic magmatism.

Detailed field study in upper Lamoille Canyon was followed by laser-ablation ICP-MS analysis of chemically abraded (CA) zircons. Three distinct post-Jurassic pulses of monzogranite were identified: (1) ~90 Ma equigranular gneiss with $\epsilon_{\text{Nd}} \sim -9$ and ϵ_{Hf} (zircon) from -10 to -20, (2) 80–66 Ma pegmatitic gneiss with ϵ_{Nd} from -15 to -17 and ϵ_{Hf} from -18 to -39 (mostly -21 to -36), (3) 39–34 Ma, weakly deformed biotite monzogranite with ϵ_{Nd} from -13 to -26 and ϵ_{Hf} from -36 to -48. One 60 Ma pegmatitic gneiss has ϵ_{Hf} similar to the Eocene granites. Partial melting of LK pegmatitic gneiss during Eocene time produced zircon in leucogranites with LK-age cores and Eocene rims. However, zircon domains that yield young ages retain their LK ϵ_{Hf} values of the protolith, providing a straightforward means of deciphering the distinct origins of the Eocene granites. The data indicate that in-situ melting was widespread but of small volume. Application of LA analysis to CA zircons improved isotopic resolution, thereby improving our ability to interpret thermal events in the core complex.

References [1] Howard et al., 2011, *Geosphere*, v. 7, p. 1220.

First Row Transition Metals, Ga and Ge in Komatiitic Olivine

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Olivine, the most abundant mineral in the upper mantle, constitutes up to 80 vol% of the mineralogy in layered komatiite flows, and close to 100 vol% in komatiitic dunite bodies. However, despite its abundance, detailed studies on the trace element chemistry of olivine are rare. We present the preliminary results of a comprehensive study on the contents of first-row transition metals (i.e. Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn), Ga and Ge in olivines from 2.7-3.5 Ga old Munro- and Barberton-type komatiites from the Kapvaal and Zimbabwe Cratons (Africa), the Yilgarn Craton (Australia) and the Superior Craton (Canada). The olivine major element chemistry was determined using a JEOL JXA-8900 Superprobe at the University of Maryland. Trace elements contents were then determined using a Photon Machines Analyte G2 193 nm Excimer laser ablation system coupled to a Nu Instruments AttoM high resolution ICP-MS at NASA GSFC. Spot sizes ranged from 85-150 μm , while the repetition rate (10 Hz) and fluence (3.4 J/cm²) were held constant. The ICP-MS analyses were conducted in medium resolution mode ($M/M\Delta = 2500$) using the variable slits offered by the Nu AttoM. Multiple external calibrating reference materials were used to account for isobaric interferences and non-spectral matrix effects. The results show that all olivines have high forsterite (~90-94 molar $[\text{Mg}/(\text{Mg}+\text{Fe})]*100$) and Ni contents (~2500-4000 ppm), typical of komatiitic olivine cumulates. All other elements show significant variability and allow to discriminate olivines based on localities, geochemical affinities and age, highlighting the potential of olivine trace element chemistry in deciphering the source composition/conditions and melting history of these ancient mantle-derived rocks.

Be and other “unusual” trace elements in TiO₂-bearing sapphire (Al₂O₃): Characterization by LA-ICP-MS, EPMA, and nanoSIMS

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In the early 2000's gemological labs had to grapple with a new treatment for sapphire (corundum – Al₂O₃) involving heat treatment in the presence of Be. This small, light element easily and evenly diffuses through a faceted stone and acts as a chromophore, dramatically altering color. In order to identify the treatment many gem labs turned to Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to quantitatively measure Be. It was soon discovered that many known-untreated stones also contained so-called “natural Be” which was detected in “cloudy” sections of the stones that were later determined to be composed of exsolved nanoparticles of α-PbO₂-structured TiO₂ (Shen and Wirth 2012). LA-ICP-MS analyses also showed the presence of significant Zr, Nb, Ta, W, and Th when natural Be was detected. These high field strength elements (HFSE) were assumed to be contained in TiO₂ particles but little is known about the host phase of natural Be. We present here the results of a Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) study of metamorphic blue sapphires containing natural Be. Analysis of micron-sized TiO₂ by Electron Probe MicroAnalysis (EPMA) shows that HFSE are always found in TiO₂ with up to 9 at.% Ta⁵⁺ replacing Ti⁴⁺. nanoSIMS (Secondary Ion Mass Spectrometry) is required to positively identify the host phase for Be as this element is too light to be detected by EPMA. When the concentration of HFSE is high the Be is concentrated in the TiO₂ particles. However, with fewer HFSE's, Be could not be detected in either the TiO₂ or Al₂O₃ phases. The results suggest that Be²⁺ will follow HFSE into the exsolved TiO₂ when HFSE concentrations are high in order to maintain charge balance for the substitution of, for example, Ta⁵⁺ for Ti⁴⁺. However, in the absence of significant HFSE, any Be contained within the corundum likely will not be incorporated into exsolved TiO₂.

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***In-situ* U-Th dating of accessory minerals using LA-MC-ICPMS**

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During the past 15 years *in-situ* U-Th dating of zircons has been carried out mainly using SIMS (1), even though the feasibility of using LA-MC-ICPMS was demonstrated several years ago (2). However, recent instrumental advances in ion transmission in MC-ICPMS have allowed to increase its sensitivity to levels that match or surpass the ion-yields usually seen in SIMS (3). This has led to the development of analytical methodologies that allow the fast and precise dating of quaternary zircons (3-5) on a routine basis.

Because zircons are mostly found within felsic rocks (rich in SiO₂), absolute dating of young (< 350,000 years) mafic rocks (SiO₂ poor, MgO and FeO rich) is usually limited to Ar/Ar and K/Ar dating.

Here we present preliminary data for the analysis of U and Th-isotopes in accessory minerals using LA-MC-ICPMS. In addition to the analysis of zircons, we focus our efforts to mineral phases such as apatite, titanite, and baddeleyite that are not exclusive of felsic rocks, and have been previously shown to be amenable for U-Th dating(6, 7). We assess the presence of complex molecular interferences (e.g. Zr₂N₂O⁺ and/or Zr₂O₃⁺ in zircon) upon ²³⁰Th⁺ and the instrumental factors modulating their abundance.

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Laser Ablation ICP-OES for Production Applications

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Precious metals are used extensively in a wide variety of industries. They range from medical and industrial device applications to jewelry, investment materials, and catalytic applications. As a result, there is a need to have physical, mechanical, and chemical properties of such alloys well defined and understood from contaminate to alloy levels. Johnson Matthey has evaluated the technique of Laser Ablation Inductively Coupled Argon Plasma – Optical Emission Spectroscopy to monitor and control a wide range of alloy and impurity levels compared to the traditional technique of Spark Ablation Inductively Coupled Argon Plasma - Optical Emission Spectroscopy. An examination of how the instrumentation also fits into the production flow of samples through the Analytical Laboratory was examined to evaluate the process controls and limitations of the equipment. General production considerations were investigated such as fit for purpose, cycle time constraints, and accuracy / precision metrics.

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ABSTRACTS: POSTER PRESENTATIONS

Cadmium Measurement in Olfactory Rosette Tissue of Coho Salmon using Laser Ablation-ICP/MS

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Loss of olfaction (i.e. sense of smell) occurs in humans exposed to olfactory toxicants such as metals and certain organic solvents. Most individuals will undergo at least a temporary loss of smell during their lifetime, typically as a result of upper respiratory infections, rhinitis, or workplace chemical exposures. Similarly, fish such as salmonids are extremely sensitive to loss of olfactory function on exposure to low concentrations of certain environmental pollutants, including certain metals and pesticides. We used coho salmon as aquatic models to study these processes. Salmon were exposed to low concentrations of cadmium relevant to environmental exposures for humans and aquatic organisms. Findings to date indicate that exposure to low levels of cadmium causes significant and prolonged olfactory deficits in salmon.

We used an ESI NWR-213 laser ablation system interfaced to an Agilent 7500 ICP-MS to measure cadmium in the olfactory rosettes and surrounding tissue of coho salmon. Raster and line patterns were ablated and then images were prepared using IGOR Pro and Lolite software. We could clearly visualize elevated cadmium in the rosettes relative to surrounding tissue and we also found a clear association between exposure concentration and accumulation of cadmium in the olfactory rosette tissue.

Trace element distribution in giant clam shells: A potentially new microanalytical reference material for biogenic carbonates

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The investigation of biogenic carbonates such as corals and mussel shells in-situ is an important application of LA-ICPMS. Time-resolved trace element analyses of these materials provide inherent information for paleo-reconstruction studies for which high spatial resolution in conjunction with low detection limits are required. However, LA-ICPMS analyses are severely limited by the lack of suitable reference materials with comparable low trace element levels and the particular matrix of these biomaterials. In this study, we explore the potential of shell material of the giant clam *Tridacna derasa* as a suitable reference material for LA-ICPMS for analyses of 12 trace elements. *Tridacna* spp. have a long life span and high growth rate. Their thick, purely aragonitic shells consist of an inner and an outer layer. A clear visible seasonal banding has been subject to investigation in previous studies for their elemental and isotopic compositions (e.g., Sano et al., 2012). We focus on the element distribution within the outer shell layer. Our analyses show evidence that the fast-precipitated outer layer provide sufficiently homogeneous element distributions of Mg, Sr and Ba for typical precisions obtained by LA-ICPMS and may hence be utilized as reference material for LA-ICPMS analyses of biogenic carbonates.

Sano et al., 2012, Nature Communications, v. 3, doi: 10.1038/NCOMMS1763.

LA-ICP-MS Analysis of Ice Cores

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Ice cores provide a robust reconstruction of past climate. However, development of time scales by annual layer counting, essential to detailed climate reconstruction and interpretation, on ice cores collected in low accumulation sites or in regions of compressed ice is problematic due to closely spaced layers. Ice core analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) provides sub-millimeter scale sampling resolution (on the order of 100 μm in this study) and the low detection limits (ng/L) necessary to measure the chemical constituents preserved in ice cores. To reduce sample preparation time and potential contamination we developed a cryocell that can hold a one meter long section of core. Also, we present an alternative calibration strategy incorporating both liquid standards and frozen standard reference material. Using ice core samples from central Greenland we: demonstrate the repeatability of multiple ablation passes; highlight the improved sampling resolution; verify the calibration technique; and identify annual layers in the chemical profile in a deep section of an ice core where annual layers have not previously been identified using chemistry. In addition, using sections of cores from the Swiss/Italian Alps we: illustrate the relationship between Ca, Na, and Fe to particle concentration and conductivity; and validate the LA-ICP-MS chemical profile through comparison with continuous flow analysis results.

Isotopic Analysis and Quantification of Uranium in Glass via Laser Ablation ICP-MS and a Novel Matrix Matching Method

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Laser ablation is gaining popularity due to the rapid analysis time, little to no sample preparation, high sensitivity, low detection limits, and a means to analyze samples that would typically take days to prepare (ashing, acid digestion, etc.). However, it suffers from poor quantification capabilities due to limited standards and matrix matching issues (matching standards of known elemental composition with unknown material in terms of composition, density, and bulk material properties). The combination of TIPS (thermal inkjet picofluidic system) elemental standard deposition and laser ablation could provide a rapid, accurate, and robust analytical tool that could greatly impact the quantification capabilities of laser ablation and many other surface analytical techniques. Preliminary results are presented on the novel method. In addition, isotopic analysis of uranium in glass using LA-ICP-MS is demonstrated for nuclear forensics and safeguards applications.

Comparative analysis of isotopic U-Th-Pb and trace element composition by LA-ICPMS in zircons using different measurement modes (STDs, KEDs and CCTs). Preliminary results.

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The new ICap Qc ICPMS allows three different measurement modes depending on the conditions of the Qcell ion-guide: No-gas pressurized cell – STD mode, Kinetic Energy Discrimination – KED, and Collision Cell –CCT. The latter two offer a lower background, reduction of molecular interferences and, importantly, enhanced sensitivity. Here we assess such measurement modes for the trace element and U-Th-Pb analysis in zircons by LA-ICPMS.

Using a 193 ArF excimer laser attached to a recently installed ICap Qc ICPMS, we compare the analysis of unknown (Xol and Panchita) and standard zircons (Plešovice and 91500) under STD, KED and CCT modes, with and without addition of N₂ to the plasma.

Under similar plasma conditions (ThO/Th < 1%, U/Th = 1 – 1.1 for NIST 612), we conclude that the results are comparable, with some notable differences: KED mode with N₂ addition yields data which is closer to the concordia and with lower dispersion (lower MSWD), closely followed by STDs mode. Addition of N₂ enhances signal by ~30% in both modes, but has little effect on the accuracy and dispersion of the obtained element and isotopic ratios. Data obtained in CCT mode, whilst more sensitive than the other two measuring modes, yields highly discordant isotopic data that, in some cases, yields reverse discordance. Consequently, the resulting ages obtained in this mode are far from robust, with MSWD values significantly larger than that obtained in KED and STDs modes.

There are many doubts with respect to the different ways of use of the collision cell in U-Pb dating by LA-ICPMS. While its use constitutes an overall improvement of the sensitivity, with the consequent internal error reduction, it is not evident that the gain in terms of sensitivity observed by the use of a pressurized cell, results in more accurate and precise U/Pb ages, particularly in CCTs mode.

Laser Ablation Molecular Isotopic Spectrometry of Rare Isotopes

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Laser Ablation Molecular Isotopic Spectrometry (LAMIS)¹ is a new technique that uses optical spectra of transient molecular species produced in ablation plumes in air or buffer gases for rapid isotopic analysis of solid samples. This technique is similar to LIBS but optical emission spectra in LAMIS are measured at longer delays after an ablation pulse than used in LIBS. Molecular spectra are advantageous for isotopic analysis because the isotopic shifts in molecular emission are considerably larger than in atomic spectra. Molecules are generated effectively when the ablation plume cools down, resulting in an increase of the molecular emission in the plasma afterglow. We demonstrated detection of rare isotopes of H, B, C, N, O, Cl, Fe, Sr and Zr using LAMIS.

LAMIS adds a supplementary function of isotopic measurements to the well-established benefits of LIBS (real-time elemental analysis at atmospheric pressure, minimal sample preparation, chemical mapping and depth profiling at high spatial definition, laboratory and field operation possible at a standoff distance to the sample). LIBS and LAMIS techniques can be accomplished on the same instrument.

A compact spectrometer can be sufficient to resolve molecular isotopic spectra, and therefore LAMIS measurements can be performed in the field. This is a significant merit of LAMIS, along with no sample preparation and data collection at ambient pressure. The ability of LIBS/LAMIS for simultaneous elemental and isotopic analysis makes it a useful tool for multiple applications anticipated in the nuclear power industry, medical diagnostics and therapies, forensics, carbon sequestration, agronomy and many other studies.

¹ R. E. Russo, A.A. Bol'shakov, X. Mao, C.P. McKay, D.L. Perry, O. Sorkhabi, *Spectrochimica Acta Part B*, **66**, p. 99–104 (2011).

Method Development for the Analysis of Rare Earth Elements in Phosphate Matrices by Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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A method was developed for the measurement of rare earth elements (REE) in apatite, to understand REE distribution in specific ores. This was determined for use with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). A 193 nm NEW WAVE laser system, coupled to an ELEMENT XR ICP-MS was used and analysis performed in a He atmosphere.

The aim of the investigation was not only to determine the most suitable laser energy and laser repetition rates but also to compare the use of standards that are matrix and non-matrix matched. The National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) NIST 610 glass was first tested as a suitable calibration material (CM) for the ablation of apatite by coupling it with a Durango apatite crystal as reference material (RM). A second set of experiments coupled the Durango apatite crystal as a CM with STD P5, a synthetic phosphate glass of Klemme *et al.* (2008) as RM.

Experiments designed to determine optimum laser operating conditions show that a laser energy of 4mJ and a laser pulse rate of 10Hz proves most suitable for the ablation of apatite. In addition, the NIST 610 was successfully applied as a CM for the analyses of REE in apatite. The Durango apatite also proved to be a suitable CM, using the STD P5 glass as RM.

Comparing non-matrix matched calibration vs. matrix matched calibration results of apatite ablation indicated that matrix matched standardisation, Durango apatite as CM and STD P5 as RM, provides a much smaller variance in the data set.

The degree of influence of the matrix on the analyses of REEs was further assessed and the difference in results varied between 35 and 125 % across the REE series. It was demonstrated that matrix matched standardisation using the Durango apatite as CM and STD P5 as RM was the preferable standardisation for the determination of REEs in apatite.

Long-term laser ablation system stage return accuracy: sub-micron performance in real applications

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Mineral grain analysis, in particular zircon analysis, is a common application for LA-ICP-MS and the theory and methodology are well established. The high throughput nature of the analysis requires the accuracy of manual ablation and the speed of hands-off automated analysis, however, to run in this manner for hours or even days significant confidence is needed that all ablations will run in the precise locations intended. An error of a few microns can result in ablation occurring in the grain rim, which is frequently a difference age to the core, ruining the analysis and wasting a valuable sample. ESI has met this challenge through evolution in sample chamber and stage design that have lead to improvements in short and long term stage accuracy. The most significant of these is ImageLock, a software-based feature which has been shown in controlled conditions to give long term stage return accuracy of <1 µm. Proving the performance in real laboratory conditions over a long analytical run on a real sample is important in benchmarking the performance of the NWR platform.

The Integration of LA with ICP-MS for the Most Effective use of Analysis and Data Handling

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The integration of Laser Ablation with ICP-MS, to be most effective, requires efficient integration of the two systems. This allows for ease of workflow and data handling between the two systems. Integration of the ESI NWR ActiveView plug-in with Agilent's ICP-MS MassHunter software is an example which allows the user to be more efficient when performing LA-ICPMS operations and analyses.

Damp melting beneath West Antarctica from olivine-hosted melt inclusions

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The West Antarctic Rift System (WARS) is one of the largest extensional alkali volcanic provinces on Earth, yet the mechanisms responsible for driving rift-related magmatism remain controversial. The failure of both passive and active models of decompression melting to explain unusually voluminous Cenozoic volcanism has prompted debate about the relative roles of thermal plume-related melting and ancient subduction-related flux melting. The latter is supported by ~500 Ma of subduction along the paleo-Pacific margin of Gondwana[1], a processes capable of infusing the mantle with easily fusible, hydrated lithologies and producing the broad seismic anomaly imaged beneath most of the Southern Ocean[2]. In-situ major oxide, trace element, and volatile (H₂O, CO₂, F, S, Cl) analyses of olivine-hosted melt inclusions (MIs) from mafic lavas provide a means to evaluate the chemical budget of the mantle responsible for active rifting. MIs are largely alkali-rich and silica-poor in composition, and exhibit water and CO₂ contents ranging up to 2.94 wt % and 4657 ppm, respectively. A subset of MIs analyzed for trace elements using LA-ICP-MS exhibit primitive mantle-normalized elemental distribution patterns similar to ocean island basalts produced by subduction processing of recycled ocean lithosphere (e.g. positive Ta-Nb anomalies and a negative Pb anomaly), although two samples exhibit pronounced positive Pb anomalies. Furthermore, Ba/Rb and Rb/Sr are consistent with melting of hydrated, amphibole-bearing lithosphere[3,4]. Major oxide modeling for MIs and primitive lavas support a volatilized peridotite source lithology, and also implicate pyroxenite as a potential source[5]. These data suggest that voluminous Cenozoic magmatism is the product of partial melting of subduction-modified lithosphere.

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U-Pb Dating of Grossular-Andradite Garnet using LA-ICP-MS

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The grossular-andradite garnet system is uniquely suited to U-Pb dating via laser-ablation ICP-MS. Found in the contact metamorphic aureoles of plutons, grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) and andradite ($\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$) form a solid solution, which typically incorporates single to hundreds of ppm's of U and Th into its structure. U-Pb geochronometry of skarn garnet allows for direct dating of mineral growth in these economically important deposits in a simple and cost effective manner. Furthermore, garnet U-Pb dating can determine relationships between skarns and plutons in complex, multi-stage cases. Most importantly, U-Pb dating from core to rim constrains the rate of garnet growth in skarn systems. This sheds light on both the lifespans of skarns as well as the kinetics of mineral growth in a transient metamorphic system. U-Pb dating using LA-ICP-MS has largely been applied to U-rich accessory phases which are tens to hundreds of microns in size. In contrast, skarn garnets are typically > 1mm in diameter, making it feasible to use a very large spot size (> 100 μm), improving count rates and overall precision, while maintaining high spatial resolution. However, like many other Ca phases, (e.g. apatite and titanite) grossular-andradite garnet also contains non-radiogenic common Pb. Fortunately, the concentration of common-Pb in grossular-andradite garnet is extremely heterogeneous on the micron-scale. This allows for the construction of robust regression lines in Tera-Wasserburg space with relatively few analyses over a small area. We standardized and downhole fractionation corrected data using a zircon standard, GJ1 Sri Lankan megacryst. As standard and sample are not matrix-matched, we collected data from large and shallow (110 x 5 μm) ablation holes to minimize the downhole fractionation effect. Age data obtained agree with the zircon U-Pb data from the genetically related pluton or from (U-Th)/He dating of the same garnet. Precision on data currently ranges between 2-8% (2σ), but this can be improved using matrix-matched standards. We propose two potential standards, Lake Jaco Grossular and Mali Grandite, both widely available gem-quality garnets of Oligocene (35.8 ± 3.3 Ma) and Triassic (208.6 ± 6.2 Ma) age respectively.

Sediment Input Pathways from North American Highlands to the Gulf of Mexico Based on Detrital Zircon U-Pb Dating

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The lower Miocene is a period of significant sediment input to the Gulf of Mexico (GOM) Basin that accompanied tectonic and climatic changes in North America. However, the resulting sediment pathways from continental upland sources to basinal sink remain poorly constrained. We employ detrital zircon (DZ) U-Pb dating to define both basement provenance and the exhumation histories of detrital source regions.

We have collected samples from outcrops across the northern Gulf margin in order to discriminate sediment pathways. Most of our data show a mixture of source terranes, including Oligocene volcanic centres, Cordilleran Arc, Laramide uplifts, Grenville, Mid-Continent, Yavapai-Mazatzal, and Appalachian-Ouachita orogeny terranes as major provinces and Wyoming and Superior regions as minor provinces. However, major DZ age peaks vary greatly between different samples, providing a means to differentiate drainage systems. Five major sediment input pathways are defined: the Paleo-Rio Grande, Paleo-Red, Paleo-Mississippi and Paleo-Tennessee rivers and a local river system in Florida draining from Appalachians. The Paleo-Rio Grande and Paleo-Red rivers show a significant sediment input from Oligocene volcanic centres, Laramide uplift regions and the Cordilleran Arc, whereas the Paleo-Tennessee River received most of its sediments from Appalachian-Ouachita and Grenville basement. The Paleo-Mississippi River lies within a transitional zone between western and eastern North American drainage systems.

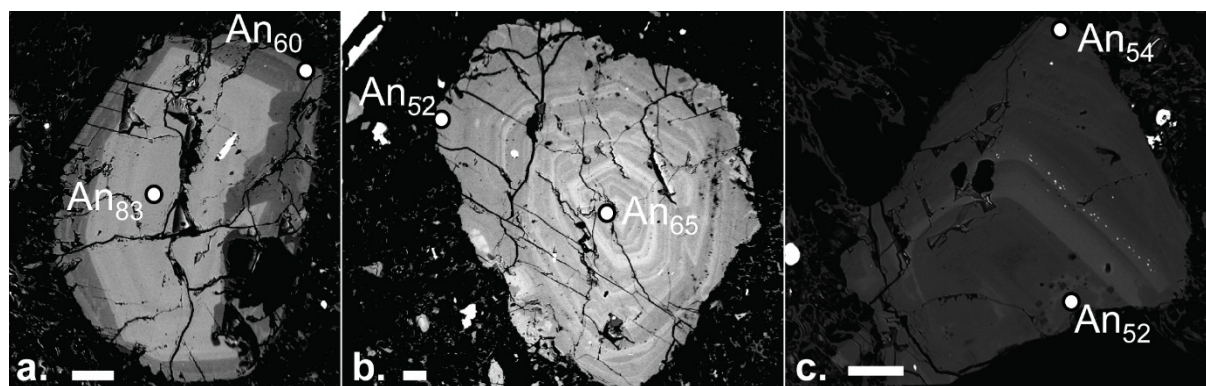
Trace element zoning in plagioclase as a record of eruption in Ignimbrites from Dominica, Lesser Antilles

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The island of Dominica in the Lesser Antilles was the site of the largest explosive eruption within the last 200 kyr in the Caribbean, erupting over 58 km³ of magma (Sigurdson, 1972). Using trace element chemistry of plagioclase phenocrysts determined using laser ablation, we test sources for several ignimbrite deposits, and assess the potential for eruption triggering by mafic injection. Trace element zoning in plagioclase was investigated using a CETAC 213 nm frequency quintupled Nd-YAG laser coupled with an ELAN 6100 DRC ICP-MS. The laser was fired at 10 Hz on a 25 µm spot, with 0.6 L/min flow of He as carrier gas, later combined with 0.8 L/min Ar used to generate the plasma. Standardization was performed using NIST glasses 610 and 612 using ⁴⁴Ca as the internal standard.



Plagioclase from all Dominican ignimbrites can be sorted into three textural groups, calcic cores (Fig. 1a, white bar is 100 µm), oscillatory zoning (Fig 1b) and oscillatory zoning with magnetite/ilmenite rich zones (Fig. 1c). Molar anorthite content ranges from 45 to 90, with a rim value of An 55 shared by all textural types, suggesting a common period of growth immediately prior to eruption. Sr and Ba compositions in plagioclase range from 400 to 700 ppm and 50 to 150 ppm respectively. Most of the plagioclase could have crystallized from a melt of similar to the whole rock, based on crystal/melt partition coefficients of Sr and Ba (Blundy & Wood 1991, Dohmen & Blundy 2014). Crystals with Ca-rich cores are clearly xenocrystic. Oxide rich zones have equilibrium cores and rims, however the zones themselves plot off of this trend, suggesting disequilibrium with the bulk rock at the time of their growth. The ignimbrites clearly experienced a small degree of mixing (Fig 1A), which disrupted portions magma chamber (Fig 1c) possibly leading to eruption, with equilibrium eventually re-established.

Trace Element Zoning in Metapelitic Garnet: A LA-ICP-MS Mapping Study

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Understanding the origin of trace element zoning in garnet as a function of mineral reaction history, and understanding how zoning of isotopes may influence Lu-Hf and Sm-Nd garnet geochronology, remain frontiers in metamorphic geology. To this end, trace element zoning in garnet-bearing metapelites, characteristic of the garnet-, staurolite- and kyanite-zones from a metamorphic sequence exposed on Cape Breton Island, Nova Scotia, have been investigated with high spatial resolution LA-ICP-MS. Trace element distribution maps for garnet porphyroblasts were prepared using a Resonetics S-155-LR 193 nm Excimer laser ablation system coupled to an Agilent 7700x quadrupole ICP-MS at the University of New Brunswick. Garnet porphyroblasts were ablated by a series of parallel rasters within a defined rectangular area using a 10 Hz repetition rate, 100 mJ output energy, craters ranging from 17 to 45 μm and a stage scan speed corresponding to half the crater size. Individual rasters were combined and integrated offline in Lolite (v 2.5) to produce quantitative maps.

Analysis of garnet porphyroblasts from the garnet-, staurolite- and kyanite zones has revealed systematic zoning for the REEs as well as Li, Sc, Ti, V and Co. HREEs decrease from core to rim with or without an annulus near the rim whereas LREEs typically increase from core to rim. Although the zoning patterns for the REEs are broadly similar amongst the analyzed garnets, the size, width, and intensity of the peaks for individual elements may vary considerably. Interestingly, samples with similar bulk rock chemistries, inferred to have similar temperature histories, may show considerably different REE zoning patterns. Lithium, Sc, Ti, and V decrease from core to rim whereas Co increases from core to rim in all garnets. Zoning patterns for these elements may be characterized by smooth core-to-rim variations with or without sharp discontinuities. Possible explanations for the observed zoning patterns include net-transfer reactions involving silicate minerals and/or accessory minerals, diffusion-limited uptake, influx of trace element-rich fluids and/or overgrowth of matrix heterogeneities. Varying degrees of mobility in the intragranular medium is inferred for different elements based on the presence of crosscutting zoning relationships. Chromium zoning in one syn-kinematic garnet records progressive rotation during growth indicating that trace element mapping may be useful for interpreting fabric development. Continued work aims to relate changes to the equilibrium mineral assemblage during garnet growth to observed trace element variations, as well as determining the main repositories for individual trace elements as a function of metamorphic grade.

Depth Profiling Analysis of Li-Ion Batteries by Laser Induced Breakdown Spectroscopy and Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Electronic devices such as smart phones and tablets are becoming a vital part of daily human activities. These electronics are constantly evolving to deliver a more compact form factor and lighter weight, yet, the power output and battery life requirements have become increasingly demanding. In order to meet these technical challenges, Li-ion battery technology has also advanced to generate higher energy output and provide enhanced cycling performance all while remaining compact and light.

The ability to use Laser Induced Breakdown Spectroscopy (LIBS) and LA-ICP-MS to perform depth-profiling measurements on Li-ion battery components will be presented. These types of analyses are critical for new design structures, quality control, and to assess potential contamination. Typical solution-based elemental analysis techniques, such as ICP-OES and ICP-MS, cannot reveal structural information of these components. XRF, another popular elemental analysis technique, cannot provide elemental coverage for important elements of Li-ion battery electrodes, such as Li, B, C, O, F, and N. Other surface and depth profiling analysis techniques, like SIMS, GD-MS, AES, and XPS, require complex vacuum instrumentation, suffer from low measurement throughput, or are expensive. However, combining LIBS and LA-ICP-MS offers depth profiling capability for Li-ion battery components with excellent throughput and elemental coverage from H – Pu with a large dynamic range (ppb to wt. %).

SelfSeal sample chamber: automation for industrial bulk analysis

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Elemental analysis to support mineral exploration requires accurate, precise and low detection limits, with an ability to meet high sample throughput demands. With respect to analytical figures of merit, LA-ICP-MS is an excellent fit. However, the current level of human intervention limits its ability to meet throughput requirements and thus the technique has not been widely adopted in the industry.

The most common approach for improving LA-ICP-MS throughput is to utilize large sample chambers that can hold a large number of samples at a time. This approach is non-ideal, however, as simply utilizing a large sample chamber fails to address the time and human involvement of placement of samples, purging, and focusing scans. Depending on the samples, this can take nearly as long as the analysis itself.

Additionally, recent studies have demonstrated that increasing the sample chamber dimensions without accounting for gas flow dynamics can either dramatically increase the purge time (actually decreasing throughput) or decreasing positional reproducibility (increasing error)¹. Even large sample chambers that are capable of rapid, efficient purges, such as the TwoVol2, require manual placement of samples and focus adjustments. Samples may also be cut, to increase the volume per batch, but this adds sample prep time and makes traceability more complex.

To reduce the time and human involvement between analyses, ESI has developed the SelfSeal sample chamber, specifically for industrial applications. The SelfSeal chamber requires no focusing time, no pattern adjustment, has a purge time of under 7 seconds, and maintains the positional stability and sensitivity expected of LA-ICP-MS. Here we demonstrate calibration curves on real XRF standards and repeatability figures on NIST glass, as well as providing a full analysis time from sample introduction to sample removal and realistic estimates of maximum samples per day.

¹ ESI Technical Note: NWR025 Comparison of Laser Ablation Cell Purging Techniques

Mineralogy, chemical composition and provenance of volcanic black sands of Iceland

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Iceland is a 100,000 km² volcanic island of Atlantic Ocean crust that has been thickened and exposed above sea level due to the interaction of the Iceland Mantle Plume and the Mid-Atlantic Ridge [1]. The geomorphology of Iceland is dynamic; frequent and laterally extensive volcanic eruptions [2] have led to the on-going construction of the island, but it is continuously modified by erosive forces, including aeolian, fluvial/glaciofluvial, and especially glacial activity [3]. This interplay has led to the formation of widespread volcanic sand sheets [4]. The purpose of this study is to determine whether the volcanic black sands of Iceland are derived from single or multiple sources, reflecting the extent of surficial mixing.

Grain chemistry is expected to vary depending on the nature of a particular source [4] and therefore, sands that sampled multiple sources should be readily identifiable using microbeam analyses of individual sand grains. Grains of basaltic and rhyolitic glass, plagioclase and pyroxene were identified in polished grain mounts using automated back-scattered electron (BSE) imaging and energy-dispersive x-ray (EDX) analysis on a scanning electron microscope (mineral liberation analyzer) [5]. Major element chemistry was determined for selected grains via electron microprobe analysis (EMPA), and trace element analyses were carried out via laser ablation inductively coupled mass spectrometry (LA-ICPMS).

The results indicate that most of the volcanic sands are samples of single volcanic systems. Despite the numerous sand transport mechanisms active in Iceland, the volcanic sands are surprisingly not well mixed. The detritus of most sand samples is apparently dominated overwhelmingly by local volcanic sources with little or no input from more distal sources.

[1] Jones, S. M. (2003) *Earth And Planetary Science Letters*, 208(3), 205-218

[2] Gudmundsson, M. T., Thordarson, T., Höskuldsson, A., Larsen, G., Björnsson, H., Prata, F. J., Jónsdóttir, I. (2012) *Scientific Reports*, 2: 572

[3] Geirsdóttir, Á., Miller, G. H., & Andrews, J. T. (2007) *Journal Of Geodynamics*, 43 (Hotspot Iceland), 170-186

[4] Baratoux, D., Mangold, N., Arnalds, O., Bardintzeff, J., Platevoët, B., Grégoire, M., & Pinet, P. (2011) *Earth Surface Processes & Landforms*, 36(13), 1789-1808

[5] Sylvester, P.J. (2012). *Mineralogical Association Canada, Short Course Series* 42, 1-16

STUDENT BURSARY AWARDS

Electro Scientific Industries Inc. (ESI), Applied Spectra Inc., Teledyne CETAC and Australian Scientific Instruments have all kindly sponsored a student bursary.

Congratulations to the successful winners below.

*Justin Lewis winner of the Electro Scientific Industries Inc. student bursary

*Yannick Bussweiler winner of the Australian Scientific Instruments student bursary

*Peter Ilhardt winner of the Teledyne CETAC student bursary

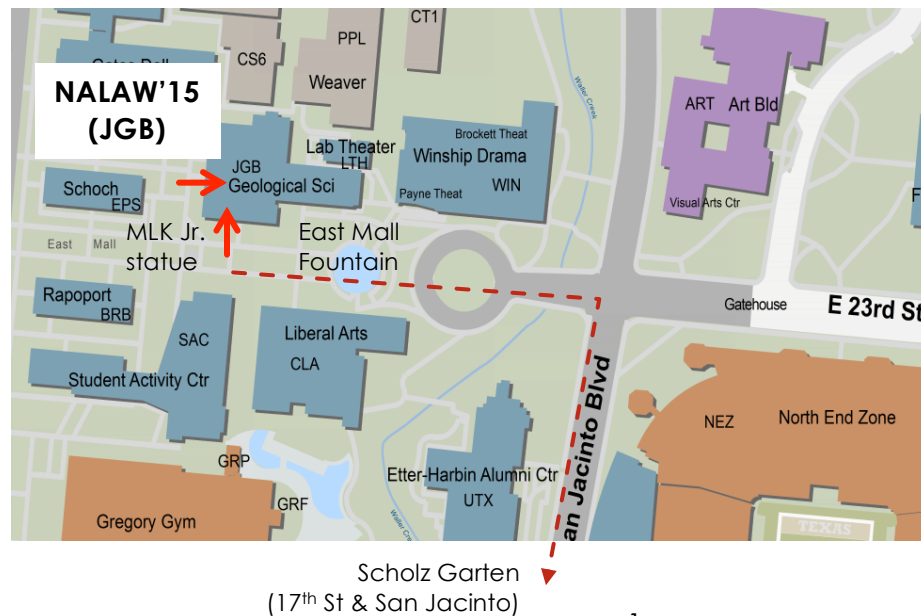
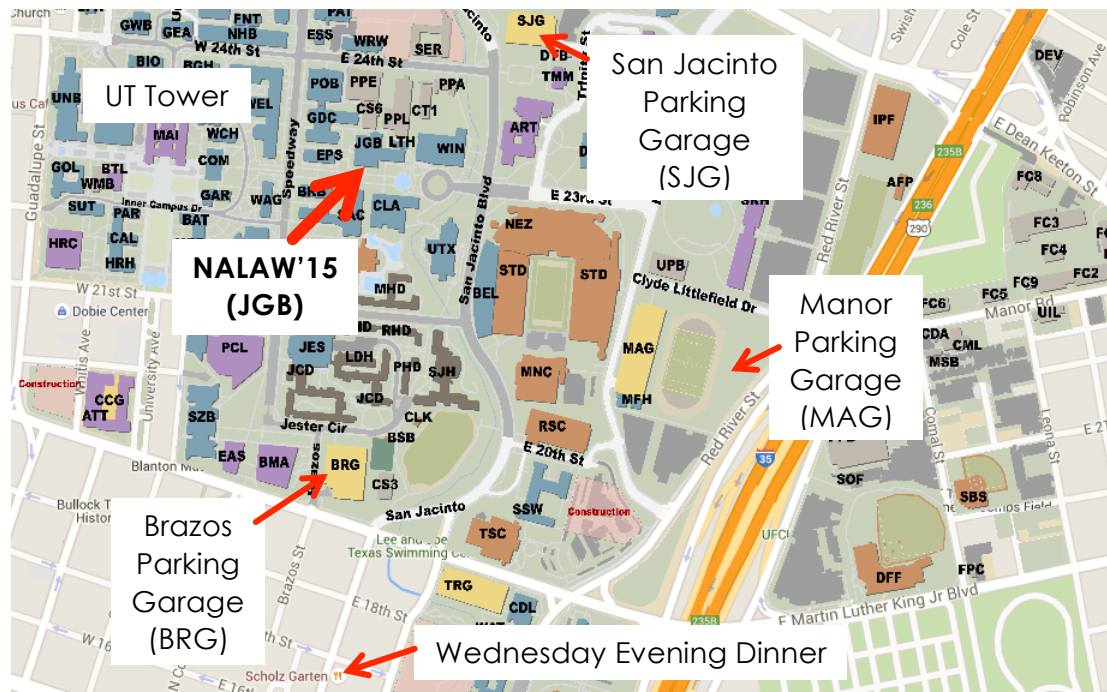
*Cheri Ackerman winner of the Applied Spectra Inc. student bursary

LOGISTICS

NALAW DIRECTIONS & MAPS

Jackson Geological Sciences Building (JGB) is located on the East Mall of the UT Austin main campus, between the UT Tower and the Football Stadium; immediately north of the East Mall Fountain and Martin Luther King, Jr. statue (lower map). The workshop will take place in the west (new) wing of JGB, with activities on the main (2nd) and 6th floors.

Scholz Garten is located on the corner of 17th St. and San Jacinto Blvd.





Parking Options (Main Campus)

Brazos Street Garage

- **Going North on Interstate 35**, take the Martin Luther King Blvd. Exit.
- Turn left, over IH-35 and head west on Martin Luther King Blvd. Go 4 blocks (1 block past San Jacinto).
- Take a right on Brazos and then an immediate right into the Brazos Garage.
- **Going South on Interstate 35**, take the Martin Luther King Blvd. Exit.
- Turn right and head west on Martin Luther King Blvd. Go 4 blocks (1 block past San Jacinto).
-

San Jacinto Garage

- **Going North on Interstate 35**, take the Dean W. Keaton St. Exit.
- Turn right into the traffic circle, which takes you around and under IH-35. Then head west on Dean W. Keaton Street. Go 3 blocks (1 block past Robert Dedman Drive).
- Take a left on San Jacinto and then an immediate left into the San Jacinto Garage.
- **Going South on Interstate 35**, take the Dean W. Keaton St. Exit.
- Turn right and head west on Dean W. Keaton Street. Go 3 blocks (1 block past Robert Dedman Drive).
- Take a left on San Jacinto and then an immediate left into the San Jacinto Garage.

