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Poster Abstracts



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Influence of Excitation Energy of Spectral Lines on Signal Enhancement in Collinear Double Pulse Laser-Induced Breakdown Spectroscopy

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Double pulse Laser-Induced Breakdown Spectroscopy (DP-LIBS) is a potential tool to improve the precision of conventional LIBS, enhance the signal intensity and decrease the limits of detection. However, the mechanisms of atomic and ionic emission enhancements are still unclear, which reduces the usability of DP-LIBS in various applications. In this work, the influence of excitation energy of spectral lines on signal enhancement in collinear DP-LIBS configuration is studied. The temporal evolution of emission intensities and plasma temperature is estimated. It is observed that there is a linear increase in the enhancement with increasing excitation energy and we have tried to explain the observed trend theoretically.

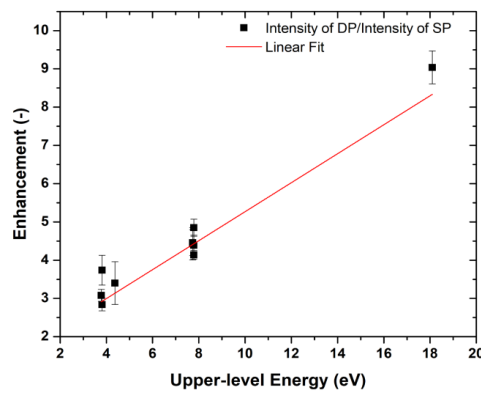


Figure 1: Signal enhancement as a function of upper-level energy of spectral lines. The temporal parameters of the experiment were interpulse delay = 2 μ s, gate delay = 1 μ s and Gate width = 0.1 μ s.

[1] Gautier, Céline, et al. "Quantification of the intensity enhancements for the double-pulse laser-induced breakdown spectroscopy in the orthogonal beam geometry." *Spectrochimica Acta Part B: Atomic Spectroscopy* 60.2 (2005): 265-276.

[2] Prochazka, David, et al. "Triple-pulse LIBS: laser-induced breakdown spectroscopy signal enhancement by combination of pre-ablation and re-heating laser pulses." *Journal of Analytical Atomic Spectrometry* 35.2 (2020): 293-300.s

Laser fluence and beam size influence on precision in single pulse LA-ICP-MS analysis

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis has evolved significantly over the last few years. While improvements have caused a number of advantages, accurate analysis and quantification still continue to present a challenge. Elemental quantification in LA-ICP-MS entails that the stoichiometries of the ablated material and the generated particles are the same. However, the processes involved from ablation to detection, *i.e.*, the interaction of the laser beam with solid material, the transport of ablated aerosols from LA cell to ICP-MS and the vaporization, atomization and ionization in the plasma, are complex and often result in non-stoichiometric conversion of elements and consequently lead to elemental fractionation [1]. Additionally, uncertainties associated with the selection of appropriate ablation conditions may also affect the precision of the LA-ICP-MS work, making quantification even more demanding. This contribution focuses on investigating the influence of fluence and beam size on signal pulse behavior, signal intensity, LA crater volumes and noise. A series of experiments was conducted using both glass (NIST 610, NIST 612) and custom gelatine standards. Example of fluence impact on signal intensity and noise in gelatin standards is shown in Fig. 1. The findings show that a careful selection of the operational conditions, can improve the quantification in LA-ICP-MS analysis, by minimising Flicker and/or Poisson noise, averting the formation of double peaks of washout profiles and attaining maximum sensitivity.

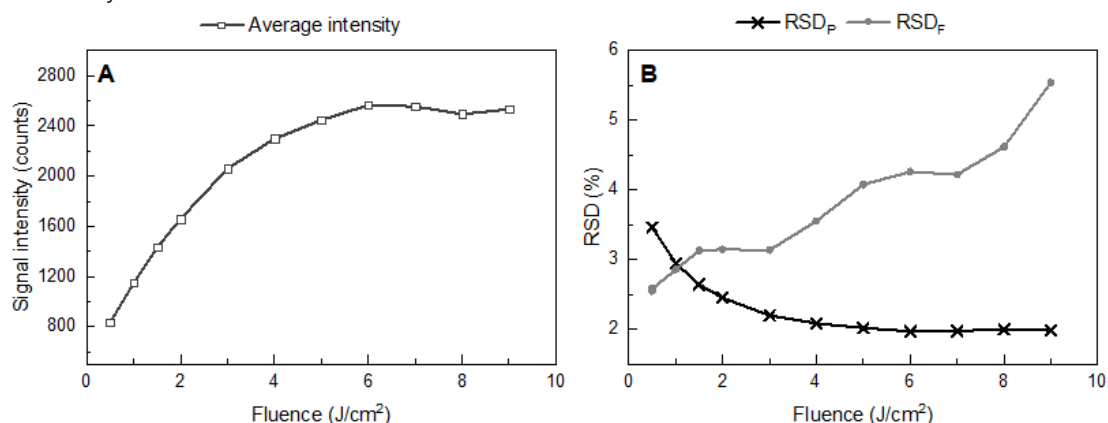


Figure 1 Average line intensity (A), Poisson (RSD_P) and Flicker (RSD_F) noise as a function of fluence for single pulse experiments for Gd in gelatine standards.

[1] S. Zhang, M. He, Z. Yin, E. Zhu, W. Hang, B. Huang, Elemental fractionation and matrix effects in laser sampling based spectrometry, *Journal of Analytical Atomic Spectrometry* 31(2) (2016) 358-382.

High-speed imaging of geologic samples by LA-ICP-MS

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Here we present the results of high-speed imaging by laser ablation ICP-MS with the ESI TwoVol3 (TV3) cell equipped with an ultra-fast washout imaging cup and dual concentric injector (DCI) ICP-MS torch. The TV3 cell enables trace element and isotope mapping at spatial scales down to 1 μm . Peak widths of 2 ms per laser pulse result in exceptional sensitivity, opening up avenues for high sample throughput at unprecedented speeds and spatial scales. For example, sensitivity on ^{238}U for a single laser pulse ablated using a 10x10 μm square spot is ~ 3000 cps/ppm at 10 ms peak width, and 25000 cps/ppm at 2 ms peak width, using a ThermoFisher iCAP TQ run in single quad mode. Fully quantified maps are processed using the iolite 4 software, which allows datasets from multiple instruments to be synchronized and processed simultaneously, thus enabling quantified 2D maps from multiple sources; for example, split stream data.

The speed of analyses and ease of image processing opens up avenues for evaluating large sample sets. For instance, analyses of fish otoliths generally require hundreds of samples to be analyzed in order to robustly evaluate population life histories that inform fisheries management decisions. High-speed imaging of trace elements in fish otoliths reveals differences in trace element incorporation of Mg and Mn compared to Sr and Ba in different structural areas of the otolith (Fig. 1). This has important implications for the interpretation of traditional core-rim line transects of otoliths that are used to interpret the life histories of fish, such as migration between rivers and the ocean, and may potentially reveal a link between trace element uptake and carbonate structure (i.e., aragonite vs. vaterite), which is often overlooked in line scan analyses.

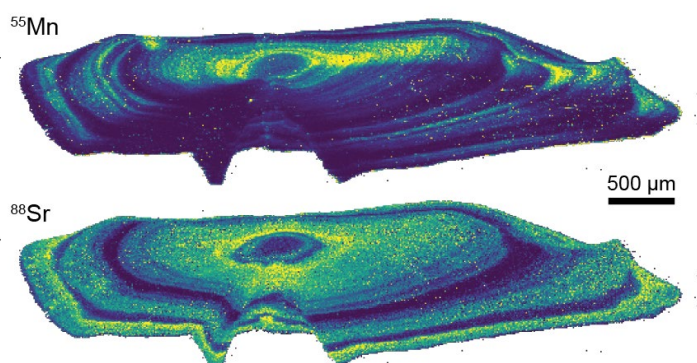


Fig. 1. Elemental distribution of ^{55}Mn and ^{88}Sr in a striped bass otolith. Note area of low Mn that is not present in the corresponding Sr map.

Spatial resolution of element distribution maps obtained by LA-ICP-TOFMS and μ XRF – the ferromanganese nodule example

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Ferromanganese nodules (Fe-Mn nodules) typically occur on the seafloor at water depths of 4000-6500 m. They have been studied since the 1960s because of their resource potential for a variety of elements, their layered structure as a record for oceanic and climatic conditions, and their involvement in geochemical processes that control concentrations of some elements in the ocean [1]. With a size in the cm range and a very slow growth rate of about 1-250 mm per 10^6 years Fe-Mn nodules develop layered structures in the μ m range of varying geochemical composition [1]. Microanalytical techniques with multielement capabilities and high spatial resolution have to be used to unravel these structures. A polished section prepared from a Fe-Mn nodule was mapped by LA-ICP-TOFMS (IRIDIA Teledyne CETAC, icpTOF 2R TOFWERK), μ XRF (AttoMap Sigray, M4 TORNADO PLUS Bruker) and SEM-BSE (FEI Quanta 650F ThermoFisher).

The results show that significant differences in the spatial resolutions occur for the microanalytical techniques despite having comparable applied beam diameters (5 μ m laser spot in LA-ICP-TOFMS, 9 μ m X-ray beam AttoMap, estimated excitation volume of 3 μ m width and 5 μ m depth by electron beam at 25 kV in SEM-BSE) (Fig. 1). SEM-BSE gives the highest spatial resolution and detects differences in the composition of a sample. LA-ICP-TOFMS shows a spatial resolution, which is not much lower than that obtained by SEM-BSE and provides quantitative element-specific distribution maps. However, μ XRF gives a lower spatial resolution while providing element-specific distribution maps as well. In μ XRF the X-ray beam penetrates deeper into the solid sample and excites fluorescence of elements from deeper layers. Sharp boundaries at the sample surface become blurred, because signals originating from deeper layers are detected as well.

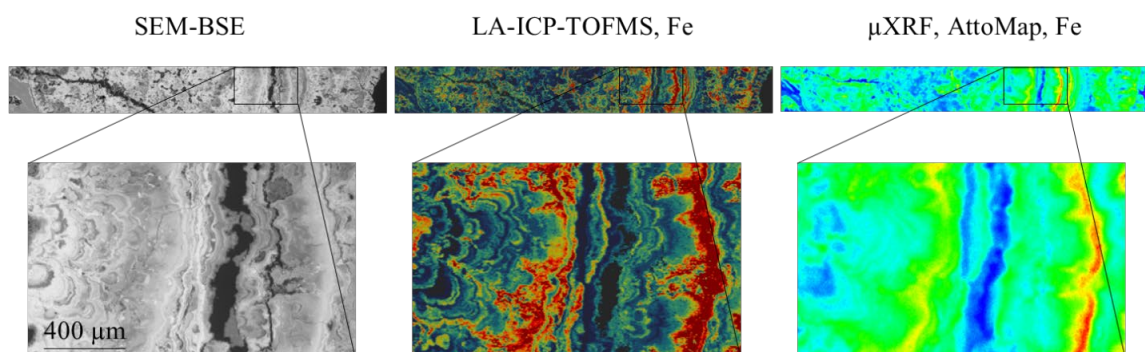


Figure 1: Part of a Fe-Mn nodule mapped by different microanalytical techniques.

[1] Hein JR, Koschinsky A (2014) Deep ocean ferromanganese crusts and nodules. In: Holland HD, Turekian KK (eds) Treatise on Geochemistry, 2nd Edition, volume 13, Elsevier, pp 273-291.

Proving the capabilities of Laser Ablation ICP-TOF-MS data at speeds up to 1kHz

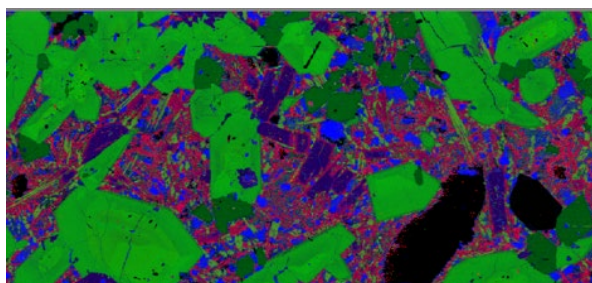
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In recent years, commercially available Excimer laser ablation systems (193nm) have evolved into robust high repetition rate systems able to fully transport sample aerosol from point of ablation in the sample chamber to analytical detection in the ICP in times as short as a single millisecond [1]. A recent sample chamber design has now been proven to operate at high duty cycles with laser repetition rates of between 1 Hz and 1000 Hz without compromising data quality in any way [2]. Unfortunately, such high speeds are outside of the typical operating regime demanded by the traditional quadrupole based ICP-MS systems, where the Single Pulse Response (SPR) may dictate the acquisition of a sole isotope unless a multiple-dosage approach is used [3]. To fully evaluate the analytical capabilities of systems operating up to 1kHz a pseudo-simultaneous ICP-TOF-MS setup is required. This work presents preliminary data generated using a 1kHz Teledyne Photon Machines Iridia laser ablation system coupled to a Nu Instruments Vitesse ICP-TOF-MS and demonstrates the performance advantages such technology can provide.



Basalt sample analyzed at 1kHz repetition rates, 250 pixels/second.

[1] Van Malderen, S.J.M *et al* 2016. Recent developments in the design of rapid response cells for laser ablation-inductively coupled plasma-mass spectrometry and their impact on bioimaging applications., *J. Anal. At. Spectrom.*, DOI: 10.1039/c5ja00430f

[2] Van Acker, T. *et al* 2021. Analytical figures of merit of a low-dispersion aerosol transport system for high-throughput LA-ICP-MS analysis. *J. Anal. At. Spectrom.*, DOI: 10.1039/D1JA00110H.

[3] Šala, M. *et al.* 2021. Implications of laser shot dosage on image quality in LA-ICP-QMS imaging. *J. Anal. At. Spectrom.* <https://doi.org/10.1039/d0ja00381f>

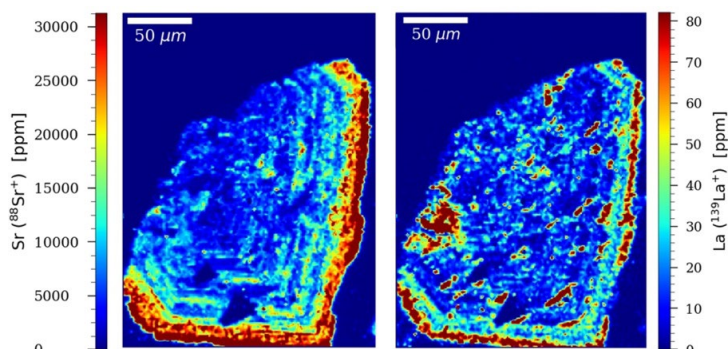
High resolution LA-ICP-MS mapping for the determination of partition coefficients using the example of natural barite

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In deep geological repository systems, containers for highly radioactive waste may encounter groundwater, which ultimately leads to the release of radionuclides like Ra, U and Pu. For the exploration of new atomic waste repositories, the retention of these radionuclides in hydrothermally grown barite and calcite has drawn much attention recently [1]. Here, partition coefficients are important parameters as they are helpful to evaluate the immobilization potential even on long timescales. However, to derive meaningful partition coefficients, only those parts of the crystals in equilibrium with their host fluid should be taken into account, which is often challenging due to the complex chemical zonation patterns. Differences in partition coefficients between synthetic and natural calcite have been observed [2] and might at least partially stem from such analytical complications.

In this study, we developed a method which combines both, the advantages of visualizing growth structures at the μm scale and element sensitivity down to the ppm level via LA-ICP-MS. Objects of investigation are natural barites from a borehole in the Äspö Hard Rock Laboratory, Sweden, that have been sampled together with their host fluid. These high-resolution mappings with a spot size of $2\ \mu\text{m}$ (fig. 1) allow us to define discrete growth zones and calculate equilibrium partition coefficients based on pixel clusters that represent the latest crystallization events. This method outshines the classical LA-ICP-MS spot analysis by ensuring to avoid a mixture of two growth zonation signals. The measurement uncertainty reaches a



mean of $\pm 1.9\%$ for Sr and $\pm 1.4\%$ for La. Adjustments on the Agilent 8900 MS/MS aerosol inlet combined with an ARIS system enables tuning of washouts to either the number of elements recorded simultaneously or the mapping speed.

Fig. 1: Sr and La distribution in barite. Sr and La are assumed to behave like radionuclides, due to similar chemical properties. Calculated partition coefficients from the youngest zone are $P_{\text{La}} = 5.78 \times 10^{-2} \pm 8.56 \times 10^{-4}$ and $P_{\text{Sr}} = 2.7 \times 10^{-4} \pm 5.32 \times 10^{-6}$ [with $P_{\text{Me}} = (\text{Me}/\text{Ba})_{\text{barite}}/(\text{Me}/\text{Ba})_{\text{solution}}$ expressed as ratios by weight]. La values are in line with continental barite data, Sr values are one order of magnitude below published seafloor barite data, whereat the latter were calculated with interpolated fluid values [3]. The mapping includes the elements Na, Sr, Y, Ba, La, Nd, Yb, U, and took approx. 10 min.

[1] Brandt F. et al. (2015). *Geochim. et Cosmochim. Acta.* doi: 10.1016/j.gca.2015.01.016

[2] Drake H. et al. (2017). *Procedia Earth Planet.* doi: 10.1016/j.proeps.2017.01.056

[3] Jamieson J.W. et al. (2016). *Geochim. Cosmochim. Acta.* doi: 10.1016/j.gca.2015.10.021

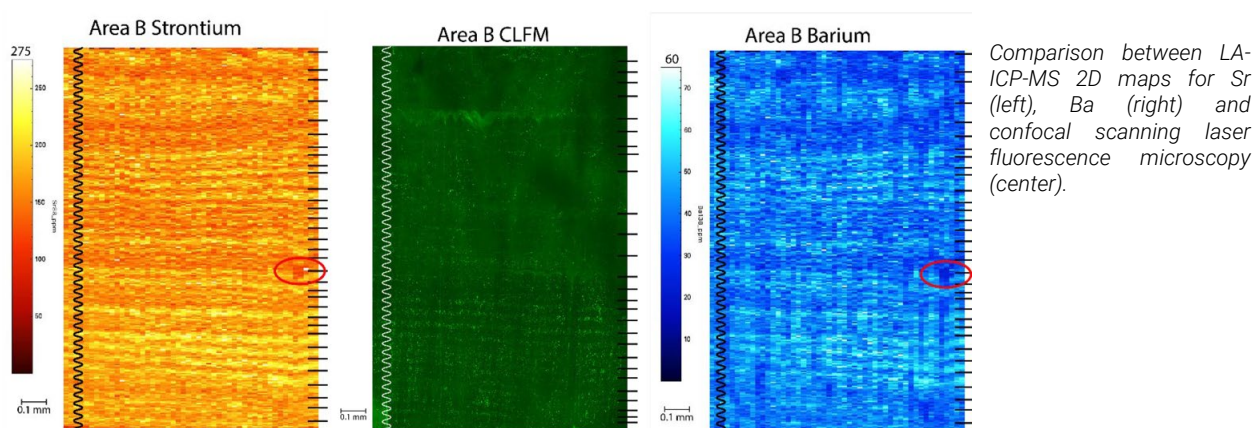
Seasonal chemical banding in stalagmites as revealed by 2D-mapping

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Stalagmite records that preserve how local rainfall varied in the geologic past could offer useful analogues for assessing how hydroclimate may change with continuing 21st century warming. Many Texas caves undergo strong seasonal changes in cave air $p\text{CO}_2$ that regulate carbonate equilibrium. During warm months, CO_2 levels rise to levels that suppress CaCO_3 precipitation, whereas in cool months CO_2 levels drop to levels favoring CaCO_3 precipitation as a consequence of ventilation with denser external air. Stalagmites therefore grow during cool months and stall during warm months, with growth fabrics that encode a seasonal chronometer. Monitoring also demonstrates that drip sites feeding stalagmites are continuous throughout the year, that drip waters have interannual residence times within the overlying epikarst, and that calcite accumulation at a given drip site follows drip rate. Because the volume of recharge water in the epikarst is thought to be a major control on drip rate, stratigraphic variations in the amount of stalagmite growth may proxy recharge amount. The ability to efficiently document long-term variations in seasonal stalagmite growth would constitute a powerful tool for assessing paleohydroclimate variations (e.g., how did rainfall change, and at what rates, following deglacial warming events?). This objective is impractical by conventional petrography due to difficulty resolving seasonal growth bands in thin section. Confocal scanning laser fluorescence microscopy offers improved resolution of growth bands but requires time-intensive comparisons of variably stacked and flattened imagery. Growth variations could also be expressed chemically, depending on factors such as seasonal contrasts in calcite precipitation rate or prior calcite precipitation in the epikarst, but this possibility has not been studied in Texas. Here we apply 2D elemental mapping by LA-ICP-MS and μXRF to a well-dated Texas deglacial (19-11 ka) stalagmite record to assess whether seasonal growth bands can be chemically resolved. U-series age constraints predict annual growth rates over six orders of magnitude (15-90 $\mu\text{m}/\text{yr}$), with a major increase in growth rate after the 14.7 ka Bølling warming transition. We find that growth bands imaged by both techniques are indeed expressed chemically, particularly by winter growth enrichments in Sr and Ba, and that the number of resolved bands is consistent with seasonal growth. Current imagery by LA-ICP-MS has used $100\mu\text{m}^2$ pixel sizes ($10\times 10\mu\text{m}$, $5\times 20\mu\text{m}$), which effectively delineate growth bands with growth rates in excess of $30\mu\text{m}/\text{yr}$. Ongoing work will assess the efficacy of mapping thinner growth bands.



Novel dual fs-LIBS & fs-LA-ICPTOFMS system (not simultaneous) for high dynamic range multi-elemental micro-analysis: a preliminary evaluation

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Multi-elemental analysis of solid samples using rapid and direct methods is a key point in the development of analytical sciences. Over the years, techniques based on Laser Ablation such as Laser Ablation Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Laser Induced Breakdown Spectroscopy (LIBS) have been widely used, rapidly evolving into well-established, mature powerful tools for direct, highly sensitive and high lateral resolution analysis in numerous fields such as geology, biology, metallurgy, or environmental sciences [1]. Significant research and advances continue to thrive for achieving the fastest, most accurate and efficient analysis, such as those focused on improvements such as low dispersion setups and cell geometries for the finest control of aerosol trajectories [2].

Femtosecond laser ablation reduces melting effects around the ablated area as well as fractionation effects. The combination of a fast-response femtosecond laser ablation unit and novel ICP-TOFMS technology provides one of the top-most interesting analytical methods for high spatial resolution determination -imaging- in samples of different matrices and nature. Moreover, the possibility of extracting the fs-laser beam out of the ablation unit, for LIBS analysis, provides a complimentary tool for the determination of major elements or those non-accessible to ICP-TOFMS.

In the present work, the analytical capabilities of a NWRfemto laser both for LIBS studies and coupled to a Nu Vitesse ICP-TOFMS, are evaluated. In particular, the potential of this novel ICP-TOFMS is investigated for fast elemental imaging applications and for single shot multielemental analysis. Additionally, the option of configuring the attenuation of the ion signals at different levels in multi-segmented methods allows for the analysis of highly abundant isotopes next to other low abundant/trace ones, hence boosting the dynamic range of LA-ICP-MS at the low micrometric scale.

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

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

High-speed mapping of the distribution of Hg and Se in biological tissues via LA-ICP-MS

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Over the last decade, elemental mapping performed by laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) has evolved towards higher spatial resolution, sensitivity and analysis speed. This evolution has been two-fold: technical improvements have been realized based on reducing the aerosol dispersion by development of improved tube-type ablation cells, mixing bulbs and transfer lines, leading to a reduction in single pulse response (SPR) duration.[1-2] On the other hand, a better understanding of various image artefacts has led to improved matching of the selected instrumental parameters with the SPR duration, further enhancing image quality.[3] However, for some elements this improvement is less pronounced than for others. For example, Hg and Se exhibit long SPR durations, and while these elements are of considerable importance in a biological context, their mapping (especially multi-elemental) has remained difficult due to the long SPR durations on the one hand and incorrect matching of ICP-MS data acquisition conditions with the SPR duration on the other. Recent work performed at the A&MS research group of Ghent University (A&MS-UGent) was focused on the optimization of mono- and multi-elemental mapping of the distribution of Hg and/or Se in biological tissue sections. By systematically investigating the effect of different components of the instrumental setup, SPR durations for $^{202}\text{Hg}^+$ and $^{77}\text{Se}^+$ could be respectively reduced to 50 ± 2 ms and 64 ± 4 ms under optimized conditions, compared to at least 204 ± 10 ms and 185 ± 6 ms on a traditional setup. By correctly matching the acquisition rate to the SPR duration, multi-element mapping experiments were performed with a spot size as low as $5 \mu\text{m}$ and a pixel acquisition rate of up to 20 pixels s^{-1} , demonstrating a significant improvement in speed of analysis, sensitivity and spatial resolution.

[1] T. Van Acker, S.J.M. Van Malderen, T. Van Helden, C. Stremtan, M. Šala, J.T. van Elteren, F. Vanhaecke, *J. Anal. At. Spectrom.*, 2021, 36, 1201-1209.

[2] S.J.M. Van Malderen, T. Van Acker, F. Vanhaecke, *Anal. Chem.*, 2020, 92, 5756-5764.

[3] S.J.M. Van Malderen, J. T. van Elteren, V. S. Šelih, F. Vanhaecke, *Spectrochim. Acta B: At. Spectrosc.*, 2018, 140, 29-34

How to Measure Mass Spectrometer Mass Filter Position For The Purpose of Aligned LA-ICP-MS

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Imaging by LA-ICP-MS has shown great utility in a range of fields^[1] due to its sensitivity, reasonably high spatial resolution, and wide dynamic range, though imaging at high spatial resolution comes with a significant time penalty^[2]. Fast-response ablation cells (e.g. “S155 Fast Funnel”, “ARIS”, “TwoVol”, “Cobalt”, etc...) have been developed to reduce washout times down to < 50 ms to 1% and in some cases down to 1–2 ms to 1%. Because optimal imaging couples scan speed to washout time, doing so can significantly reduce total acquisition times.

However, with the rise in popularity of these fast-response cells, the issue of aliasing, or “beats”, in images collected by LA-ICP-MS becomes problematic^[3]. Increasing the washout time will resolve this issue, but negates all of the benefits of using a fast-response cell.

When using aligned LA-ICP-MS^[4] the firing of the laser is aligned with the scan/sweep cycle of the mass spectrometer so that the arrival of the ablated aerosol reaches the detector at the same moment of every sweep. This synchronisation is performed for each sweep of the mass filter, so the two instruments remain aligned continuously, even during very long analyses.

Our alignment circuit (called “QuadLock”) uses a very high impedance voltage divider to measure the DC component of the AC+DC mass filter voltage, without interfering with the normal operation of the quadrupole. Because QuadLock directly measures the DC voltage on the quadrupole it is compatible with a wide range of different instruments. For instruments with multiple quadrupoles (e.g. “triple quad” or “MS-MS” instruments) we have found it sufficient to measure the mass filter position of the second quadrupole.

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

We will describe how the mass filter position is sampled in real-time without affecting the performance of the instrument, and how QuadLock is physically interfaced with commonly available mass spectrometer hardware.

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

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

[3] Van Malderen, Stijn JM, et al. *Spectrochimica Acta Part B: Atomic Spectroscopy* 140 (2018): 29-34.

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

Exploring the matrix effect for boron isotope measurements via laser- and solution-MC-ICPMS

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The boron isotopic composition of carbonates has proven to be a reliable proxy for past pH/pCO₂ reconstructions beyond the range covered by ice-cores, i.e. >800ka. Although typically measured using N-TIMS or solution MC-ICPMS, after careful cleaning and chemical boron separation procedures, recent developments have shown that the boron isotopic composition of CaCO₃ can also be measured with sufficient data quality using laser ablation MC-ICPMS (e.g. Sadekov et al., 2019).

While *in-situ* analysis avoids the complex sample preparation necessary for solution-based boron isotopic analysis, several recent studies have shown that (at least) the ThermoFisher Neptune Plus MC-ICPMS is characterised by substantial inaccuracies when laser ablation is utilised as sample introduction methodology and when synthetic NIST61x glass is used for standardisation (Standish et al., 2019; Evans et al., 2021). Specifically, it was found that the ablation of carbonates creates a background elevation around *m/z* of 10-11. This interference biases isotopic measurements as the background elevation is proportionally larger around the ¹⁰B ion beam compared to that of ¹¹B and scales with the Ca concentration of the sample. As the boron concentration in the analyte decreases, the ratio between interference and signal increases and creates greater inaccuracies at lower boron concentrations.

We explored the mechanistic reason for this matrix-related interference through the lens of variable analyte loading in two ways. First, we conducted analyses of well-characterised carbonate standards with different spot sizes. We found that the interference remained constant in spite of different plasma loading conditions. Second, we conducted mass scans in dry-plasma solution mode using an Aridus desolvating nebulisation system to mimic the dry plasma conditions of LA (Yu et al., 2020). We measured solutions characterised by different concentrations of matrix elements and different plasma tuning conditions. Tentatively, we can demonstrate that plasma robustness is a key controlling factor of the fractionation of boron and the magnitude of the interference around ¹⁰B.

As plasma robustness increases, mainly controlled by RF power and sample gas flow and monitored via NAI and ThO/Th (Fietzke and Frische, 2016), the isotopic bias decreases. Although more robust plasmas may be associated with a lower sensitivity, our data highlight that striking a balance between the two is important for reproducible boron isotopes measurements.

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Characterization of $\delta^{34}\text{S}$ variability in pyrite and pyrrhotite using LA-(QQQ)-ICP-MS.

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Sulfide minerals, particularly pyrite (FeS_2) are ubiquitous in various geological environments and provide an accessible proxy for investigating geological processes. Pyrite genesis occurs under specific conditions which leave distinct trace element (TE) and sulfur isotope ($\delta^{34}\text{S}$) signatures in its chemical composition. Thus, pyrite TE and $\delta^{34}\text{S}$ are powerful tools in investigating (bio)geochemical processes ranging from sulfide-ore formation to finding evidence of early life on Earth and potentially beyond. Laser Ablation multi-collector (LA-MC) ICP-MS is an established in-situ analytical technique capable of measuring sulfur isotope ratios as well as their spatial distributions in solid samples. On the other hand, the usage quadrupole-based systems to analyze sulfur isotope ratios is hindered by the presence of polyatomic interferences on ^{32}S and ^{34}S (i.e., O_2^+ and NO^+ at $m/z=32$ and $m/z=34$), which can be reduced or eliminated by the use of reaction gases.

This study discusses an approach for characterizing $\delta^{34}\text{S}$ variability in single generation pyrite and pyrrhotite samples using a mixture of N_2O and He in the reaction cell. Normalization of $\delta^{34}\text{S}$ data was performed applying an in-house pyrite standard obtained from Ward's Science (previously characterized at Washington University in St Louis) and an in-house pyrrhotite standard. Signal stability was improved by implementing a signal smoothing device consisting of a "squid", coiled tubing, and a cyclonic spray chamber. While operating in pulse detector mode, this setup resulted in single ablation $\delta^{34}\text{S}$ (2SD) of 1.5‰. Measured $\delta^{34}\text{S}$ 10 spot averages of natural pyrite ($n=3$) and pyrrhotite ($n=6$) samples were typically within 1‰ range of control values obtained by micro-drilling and subsequent analysis by Isotope-Ratio Mass Spectrometry (IRMS). Ten spot average $\delta^{34}\text{S}$ (2SD) ranged from 2.4-4‰. This approach can serve as a relatively fast and initial in-situ screening tool for measuring sulfide's $\delta^{34}\text{S}$.

Depth-Resolved LA-ICP-MS investigations for the Determination of Diffusion Coefficients of SO₂ in thin Polymer films

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Polymers play a significant part in the coating industry, where they are applied as a counter-measure to corrosion. This is achieved by isolating the material, which is to be protected, from contact with potentially corrosive species in the surrounding environment, such as acidic or alkaline aqueous media, mobile ions, or gaseous species. To effectively prevent corrosion, the physical and chemical properties of the coating need to be thoroughly tuned and optimized to the protected material and the intended exposure conditions. This makes the development and testing of new coating materials an ongoing research topic.

This work focuses specifically on assessing the protection capability of polymer films against atmospheric corrosion induced by sulfur dioxide. The uptake of sulfur as a consequence of exposure during weathering experiments was determined using Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS). This technique provides the required high sensitivity, as well as the possibility to carry out depth-resolved measurements with sub-micrometer resolution. Using the dynamic reaction cell with oxygen as reaction gas, sulfur was measured at an m/z of 48 (³²S¹⁶O), thereby circumventing the O₂⁺ interference at $m/z = 32$ of the most abundant sulfur isotope. Quantitative analysis was achieved by using matrix-matched calibration standards. Depending on the polymer type, the developed method reached LODs from 0.7 – 3.0 µg/g sulfur and a depth resolution of 120 – 300 nm.

The acquired quantitative depth profiles of sulfur were evaluated using model fitting to determine the diffusion coefficients of SO₂ in the corresponding polymer material, which is an excellent indicator to assess and compare the suitability of the materials regarding their protection capability against SO₂. In performing repeated weathering experiments with different temperature and relative humidity settings following the given analysis routine, the influence of those parameters on the diffusion of SO₂ were investigated and the examined polymer materials were rated regarding their behavior.

Depth-resolved analysis of composite materials using Laser Ablation combined with Electron Ionization-MS and ICP-OES

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Polymeric composite materials have a multitude of applications due to their versatile adaptability and find use as paints, varnishes, coatings and packaging materials and many more. For processing and recycling of these materials, as well as for forensic analytics, reliable analysis methods are required. Information such as type of polymer, prevailing additives and potential contaminants is necessary to characterize the materials' organic and inorganic composition. Samples consisting of more than one polymer, either in mixtures or in structured or layered systems, are especially challenging to analyze. [1]

Conventional analytical techniques used for polymer analysis, such as pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) or Fourier transform infrared spectroscopy (FTIR), provide only molecular information. Moreover, they cannot efficiently deliver spatially and/or depth-resolved information, hampering their applicability for the investigation of structured materials. [2] Solely Laser induced breakdown spectroscopy (LIBS) enables elemental analysis as well as depth profiling but shows limited selectivity for organic materials. [3]

In this work, we present a novel method for advanced composite material analysis, including depth profiling. The proposed approach is based on firing a focused laser beam onto a solid sample placed in an ablation cell. The generated gaseous and particulate ablation products are measured online by electron ionization mass spectrometry (EI-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) at the same time. EI-MS determines the molecular structure of the fragments, while ICP-OES detects the corresponding elemental composition. Thus, with this multi-modal approach, direct characterization of the main organic and inorganic sample components could be accomplished. It thereby provides ideal preconditions for discrimination and classification, provenance determination, or authentication studies. The applicability of the developed procedure is demonstrated by the depth-resolved analysis of layered nail polish samples

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Assessing sulphur evolution in ore-related magmatic systems using laser ablation mapping of apatite

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Sulphur is a key volatile element in magmatic systems and is a major constituent of ore-deposits. Fluxes of S in the crustal magmatism results in the formation of major ore deposits that are the source of society's metals. The evolution of S in magmatic systems can be tracked either directly from volcanic gases, where S strongly partitions into the volatile phase during fluid saturation, or through the analysis of minerals and melt inclusions. Apatite is a common accessory phase in magmatic systems that incorporates S and has been used to monitor the S evolution in ore systems [1]. However, apatites in porphyry systems may not preserve their primary igneous chemistry as they tend to re-equilibrate with hydrothermal fluids.

Electron microprobe (EMPA) is traditionally used to analyse S in apatite as it can achieve reasonably low detection levels (c. 0.1 %) at high spatial resolution (c. 5 – 10 μm). However, if a range of elements are analysed this technique can be relatively slow (several minutes per analysis), and it cannot achieve sufficiently low detection levels required for many trace elements in apatite (e.g. Th, U). Sulphur concentrations in apatite are not analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) due to high background interferences from $^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{17}\text{O}$ and $^{16}\text{O}^{18}\text{O}$ on the S isotopes species. However, the ability to reduce these interferences using reaction gases (O_2) has made it possible to measure the major S isotope (^{32}S) as a reaction product ($^{32}\text{S}^{16}\text{O}$) therefore opening new avenues for S analysis by ICP-MS [2]. Furthermore, the new generation of laser ablation systems have ultra-fast signal washouts, permitting rapid elemental mapping at high repetition rates at small spot sizes. Here, we present LA-ICP-MS mapping of apatite crystals using the 193 nm Teledyne Iridia laser ablation system combined with an Agilent 8900 ICP-QQQ-MS. The full width of a single pulse at 10% of the maximum peak intensity was optimised at <5 ms in order to increase sensitivity and decrease imaging time. Individual maps (<100 x 100 μm to 300 x 100 μm) take between 1 and 5 minutes. Image processing and quantification was carried out using HDIP (v. 1.6). Routine analysis of Durango apatite reveals accuracy within the published range of S concentrations.

We evaluate the potential of high-resolution mapping of apatite grains to investigate the controls of S contents in the formation of magmatic hosted ore deposits on two case study areas (Bajo de la Alumbraera, Argentina and Meghri-Ordubad pluton, Armenia). We compare S concentrations obtained from LA-ICP-MS maps with previously determined EMPA concentrations to demonstrate the validity of our approach. Concentration maps reveal the presence of primary igneous zoning of S in the least altered rocks, however more altered samples from the mineralised part of the system show evidence of hydrothermal re-equilibration along grain cracks. We carry out statistical analysis of the inter- and intra-grain variations to establish systematic relationships to track the evolution of S in apatite through time before ore formation and evaluate the impact of hydrothermal alteration. This approach provides opportunities for the rapid assessment of S concentration in apatites and may provide insightful tools for mineral exploration.

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U-Th disequilibrium dating by LA-ICP-MS beyond zircon.

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In situ U-Th disequilibrium dating is applicable to Uranium bearing minerals crystallizing the past 300 ka and has long been the domain of ion microprobes [1]. [2] introduced analytical protocols employing laser ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) to date igneous zircons. Using a high sensitivity sector field ICP-MS and applying corrections for interferences yields zircon U-Th isotope data comparable in precision to SIMS data.

When zircon is not available in the sample of interest, other minerals may be used for U-Th geochronology. Thanks to the unbeatable versatility of LA-ICP-MS to employ large crater sizes in the 100s micron range, we showed that this technique is suitable for dating minerals with as little as ~1 ppm U [3]. U-Th disequilibrium dating of ilmenites (containing inclusions of apatite and melt) represents a promising new approach. In this contribution we present details and challenges, including an unexpected interference from contamination, on the method by reporting ilmenite ages obtained on samples from the Aso-4 caldera-forming eruption at 83.6 ± 8 ka and Nisyros.

U-Th disequilibrium dating of magmatic garnets from eruptions at Somma-Vesuvius has been recently proven to give important insights into the lifetime and dynamics of phonolitic magma chambers[4]. Additionally, U-Th disequilibrium dating of vesuvianite in the skarn lithic clasts from the same deposits provides important information about the timing of interaction of the alkaline magmas from Vesuvius with the carbonate country rocks. The versatility of this technique opens up a variety of new avenues for quantifying the timing of magmatic and hydrothermal processes beneath Pleistocene to active volcanoes.

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Laser ablation ionization mass spectrometry on the Moon

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With NASA's increased focus on exploration of our Moon within the Artemis program, new scientific goals have been formulated to better understand the history of our Solar System, including the evolution of the Earth-Moon system. Additionally, the possibility for *in-situ* resource utilization (ISRU) of lunar material, which is a cornerstone of permanent human presence on the Moon, should be investigated. These tasks require sensitive instrumentation capable of determining the elemental and isotope composition of geological features found on the lunar surface [1]. Moreover, NASA's Artemis program represents a precursor program for future Mars exploration, meaning that instrumentation applied successfully on the Moon might find its application in the future on Mars.

In this contribution, we present the challenges involved in designing, building, and testing a miniature laser ablation ionization mass spectrometer (LIMS) prototype instrument for *in-situ* measurements on the lunar surface. Such an instrument is foreseen to be deployed on a Commercial Lunar Payload Service (CLPS) mission to be flown late 2025. Defining and determining the necessary technical requirements of such an instrument and building it accordingly is key for maximizing the scientific value of the mission's results. For this task, appropriate laboratory test setups are necessary. To this end, a Nd:YAG microchip laser system (SB1 series, Bright Microlaser Srl, Italy) operating at 532 nm (max. pulse energy of 40 μ J, pulse repetition rate of 100 Hz), was integrated into our laboratory LIMS setup consisting of a miniature reflectron-type time-of-flight mass analyzer (160 mm x \varnothing 60 mm) designed for in situ space applications [2, 3, 4]. The laser source and the optics are modelled after the envisioned flight design, and therefore are used to determine the required optical and electronical performance characteristics of the future flight instrument.

The results of laser ablation experiments on NIST SRM 610 aimed at demonstrating the technical feasibility of the setup will be discussed. Additionally, the design of the planned sample introduction system based on an electrostatically charged conveyor belt to attract lunar dust particles and their transport into the instrument, will be presented in more detail.

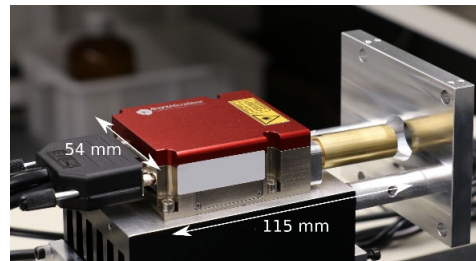


Figure 1: 532 nm microchip laser used in the test setup

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Laser Desorption Mass Spectrometry for Future In Situ Measurements to detect traces of Life on Icy Moons

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Is there extra-terrestrial life? The answer to this question is rapidly becoming one of the main scientific objectives in space exploration, leading to an increasing number of missions commissioned that aim to detect traces of extinct or extant life on other planetary surfaces.

Among the multitude of moons in the Solar System, Jupiter's moon Europa and Saturn's moon Enceladus have caught the interest of researchers due to observed plumes that may release material directly from subsurface oceans to the surface [1]. Consequently, Europa and Enceladus have become prime candidates in the search for extra-terrestrial life, which could thrive in the subsurface ocean, from which material is transported to the surface via jets and water vapour plumes. Therefore, *in situ* analysis of this material is of utmost importance in finally giving a definitive answer to the question of extra-terrestrial life. However, the conditions on the surface of the icy moons are difficult to simulate in the laboratory, with temperatures as low as 33 K (Enceladus) or 50 K (Europa) and a harsh radiation environment. Furthermore, the presence of chloride salts on the surface of these moons could significantly compromise the performance of GC-MS systems typically applied in current space exploration missions devoted to life detection [2].

In this contribution, the development of a novel setup to investigate planetary and interstellar ice analogues is shown, as well as an outlook to integrate a space prototype Laser Desorption Ionization-Mass Spectrometer (LDI-MS) instrument into the system, developed for in situ space exploration missions. The LDI-MS system consists of a miniature reflectron Time-of-Flight mass spectrometer, built in-house, to desorb and identify molecules.

During measurements with the setup, a sample holder is placed in a high vacuum chamber ($P < 10^{-8}$ mbar) and cooled down to temperatures as low as 4 K using a cryostat. Gas can be injected into the chamber via a leak valve, where it condenses onto the sample holder due to the low temperatures, forming a layer of ice. The setup is currently equipped with an Electron Gun to irradiate ice analogues with high energy electrons.

By combining cryogenics and LDI-MS, as well as a high vacuum environment and irradiation by electrons, the setup allows for simulation of the conditions on icy moons, offering the possibility of evaluating the performance of a space exploration prototype R-TOF in an environment relevant for the icy moons.

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LA-ICP-MS analysis of major and trace elements in ash and oil shale samples using lithium borate flux glasses

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The concentration of various major and trace elements in combustion ashes are often the limiting factors for its reuse suitability. Distribution of heavy metals and major oxides in different ash fractions produced in the combustion plants and also in the raw materials therefore need to be well characterized. The analysis of these materials is usually performed with the combination of XRF and liquid digestion ICP-MS. However, analysis of lithium borate flux glasses prepared for XRF analysis by LA-ICP-MS offers a fast and robust alternative, circumventing problems of incomplete dissolution during acid digestion.

Samples of ground oil shale and oil shale combustion ash alongside ACIRS-A1 fly ash reference material and USGS SGR1b Green River shale were fused with LiT/LiM/Li 49,75/49,75/0,5 flux. The same materials were also subjected to microwave acid digestion using HNO₃ and 4-acid digestion on a hotplate and analysed using liquid introduction ICP-MS. LA-ICP-MS analysis was performed using spot analysis with 50 to 100µm beam on a ESI NWR213 laser coupled to a Thermo iCAP Q ICP-MS. Calibration was performed in two ways: 1) by using NIST 610, 612 or 614 glasses with Ca as internal standard element, previously determined by XRF or 2) by using SGR1b flux glass as reference material and Li or B as internal standard element.

Calibration with NIST glasses yielded accurate (within SD of reported values) results for a majority of elements for both reference materials. However accurate determination of Fe and Ti was not achieved. Concentrations of the majority of elements in all samples calibration with SGR1b flux glass yielded results within 10% SD of NIST glass based results and Fe, Ca, Ti in the same range, compared to XRF analysis. Comparison with acid digestion results showed good agreement between elements for which full dissolution could be achieved.

Accurate measurement of K/Ca in geological materials using LA-SF-ICPMS for reconstructing past seawater chemistry

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Potassium and its isotopes are important tracers for studying the geochemical cycling in the Ocean. The present-day seawater K concentration is ~ 10.3 mmol/kg, and it has remained relatively constant throughout the Phanerozoic Eon (9-11 mmol/kg)¹. Therefore, K/Ca measurements of marine carbonates have the potential to provide information about past changes in seawater $[Ca^{+2}]$ beyond its residence time. However, the low concentration of K in marine carbonates means that it has traditionally been difficult to measure by conventional Q-ICPMS. The key challenges of K measurements by ICPMS include the interference of ArH^+ on K^+ and the lack of well-characterized carbonate reference standards. We analysed K/Ca in different geological standards, including NIST glasses (NIST 610 and NIST 612), MPI-DING glasses (GOR 128-G, GOR 132-G, ATHO-G, KL2-G, and StHs 6/80-G) and carbonate standards (JCp-1, Jct-1, and MACS-3) using LA-SF-ICPMS and investigated the utility of both NIST 610 and NIST 612 as calibration standards for K measurements. We observed elemental fractionation of K during ablation, depending on sample composition and concentration². The fractionation of K/Ca with respect to NIST 610 in GOR 128-G, GOR 132-G, ATHO-G, KL2-G, and StHs6/80 are 6.4%, 7.5%, 2.5%, 6.1%, and 3.6%, respectively. Whereas the K/Ca fractionation of low K carbonate standards, MACS-3, JCp-1, and Jct-1 are 13%, 8.9%, and 8.8%, respectively. This suggests that an accuracy correction may be warranted in the case of non matrix-matched standardization, which we show can be linked to matrix-dependent down-hole fractionation. To estimate the influence of ArH^+ on K/Ca data, we compared our results from medium and high resolution measurements. This analysis demonstrates that medium mass resolution is sufficiently capable of minimizing the effect of ArH interference despite the fact that the peaks are fully separated only in high resolution mode. This yields long-term relative standard deviations (RSD) of less than 10% for all standards, and an accuracy of 9% for the carbonate standard JCp-1. This inaccuracy can be explained by the different down-hole fractionations between carbonates, NIST glasses and felsic glasses and therefore we show how accurate results can be obtained after accounting for this.

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Cryogenic cave carbonates by high resolution LA TOF MS imaging – from understanding genesis to documenting ancient anthropogenic air pollution

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The mechanisms responsible for the formation of cave carbonates (commonly found in speleic environments where the ambient temperature is or was below freezing at the time of formation) are well documented and linked to the water becoming increasingly saturated in ions as it reaches the freezing temperature to the point where it achieves supersaturation and precipitates carbonates [1]. Cryogenic carbonates are good indicators of ambient temperatures as well as temperature-related processes at the time of their formation and because they can be dated, they represent reliable proxies for paleoclimate studies. Due to their rather extreme formation mechanisms, they can be used as proxies in the study of carbonates formed in similar conditions in the solar system [2].

In this contribution we present LA ICP TOFMS elemental distribution of cryogenic cave carbonates from the Scărișoara Ice Cave, Romania. The samples were analyzed using state of the art laser ablation time of flight mass spectrometry instrumentation and the main goal was to identify potential chemical signatures that could be used for rapid and reliable identification of cryogenic carbonates. Additionally, since the cave is in the proximity of a gold/silver mining region which was active since before 100 AD we have investigated the ability of cryogenic carbonates to document air pollution linked to mining activities.

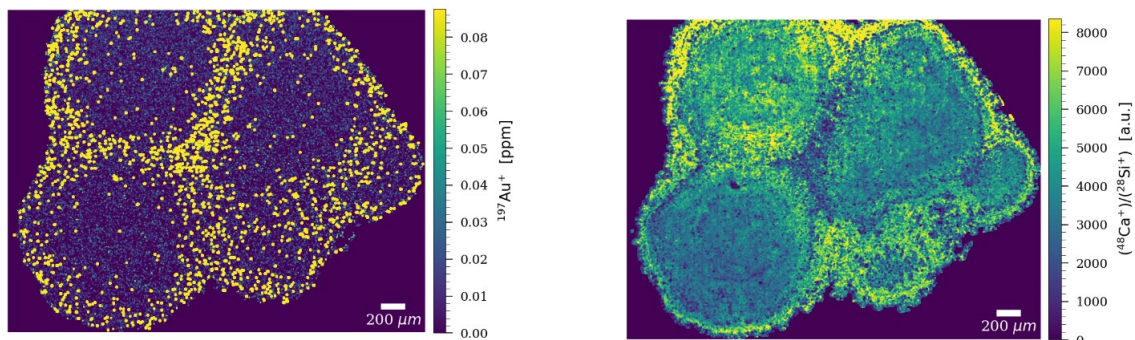


Figure 2. Elemental imaging of a cryogenic carbonate showing the presence of detrital material (right), including Au particles (left).

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Comparison of In-house matrix-matched standards for elemental imaging in tree rings

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Laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) is one of the most suitable methods for the analysis of tree rings due to its high spatial resolution (laser spot size from 10 – 200 μm), minimal requirements for sample preparation, and wide range of elements and isotopes that can be measured. All this makes LA-ICP-MS the main method of choice for use in dendrochemistry for study of environmental pollution, environmental changes, tree physiology, etc. However, one of the drawbacks of this method is the quantification of obtained data.

Classically, calibration of LA-ICP-MS is performed by using silicate standard reference materials provided by NIST or USGS. The matrix of these reference materials is glass which makes it unsuitable for the use as an external calibration material for quantification of elements in tree rings due to large differences in the matrix and lack of carbon, which can be used as internal standard element for analysis of wood samples.

The lack of commercially available matrix-matched standard reference materials leads to the need of "In-house" matrix-matched standards. These reference materials are usually made by homogenizing and pelletizing material with the same or similar matrix and doping it with a predefined amount of elements of interest.

The main aim of this study was to prepare and compare different In-house matrix-matched standards for quantification of element concentrations in tree rings.

Cellulose as a main constituent of wood was used as the base material for the preparation of reference materials. Three different microcrystalline cellulose powders (50 μm , 20 μm , and nanosized, Sigma-Aldrich) were doped with various elements (Al, As, Ba, Be, Bi, B, Cd, Ca, Ce, Cs, Cr, Co, Cu, Ga, Fe, La, Pb, Li, Mg, Mn, Ni, P, K, Rb, Na, Sr, and Zn) and pressed into 10 mm size pellets. The content of elements in prepared cellulose pellets was verified by the means of liquid digestion ICP-MS analysis. For comparison, pressed pellets were also made from available certified reference material powders – IAEA 336 (lichen), IAEA 413 (algae), IAEA 392 (algae), and BRC 692 (white cabbage).

The obtained results showed that the homogeneity of the prepared standards (the lowest scatter of LA-ICP-MS line scan measurements) depend directly on the particle size of the material used for the preparation of pellets. It was also found that reference material IAEA 392 (algae) powder can be directly pressed into a pellet without additional milling to produce a sufficiently homogenous material and used as a matrix-matched standard.

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High resolution LA-ICP-ToF-MS imaging of cells: A strategy for quantitative analysis of multiple elements in transient signals

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Single cell analysis is increasingly important to a wide variety of applications such as drug development and understanding of disease pathology. A population of cells is sufficiently heterogeneous, driving the need to obtain data from individual cells rather than average bulk analysis to better understand the characteristics of the cell population and potential links to disease diagnosis and treatment [1].

Multi-element imaging analysis of transient signals like those produced by single cells have been shown to benefit from the combination of fast ablation cells and fast quasi-simultaneous multi-element detectors. One of the drawbacks of fast transient signals for measuring highly heterogeneous samples is the potential inconsistency across peak intensities arising from the individual laser pulses. This can be potentially corrected for by normalizing the analyte signal against a suitable internal standard.

In this work, we describe a strategy for multi-element quantitative imaging of single cells using the coupling of ImageBIO (266nm, ESL) laser ablation system with TwoVolume3 chamber design to ICP-Time of Flight-MS (2R, TOFWERK). Cell samples have been tagged with europium (Eu) and holmium (Ho) containing nanoparticles to mimic multi-element antibody tags. A novel internal standard normalization method is presented for the quantification of these nanoparticle tags using gelatin-based calibration standards and monitoring the ratio of two elements used as internal standards (IS) deposited onto the microscope glass substrate. The ratio of these IS elements was used to normalize those of Eu and Ho in both calibration standards and tagged cell samples. The use of this approach helped improve the calibration correlation coefficients from 0.9885 to 0.9971 and 0.9805 to 0.9980 for Eu and Ho, respectively. Such improvement impacted the recovery data for the quantification of an *in-house* quality control sample from $123\% \pm 5.30\%$ for Eu and $125\% \pm 2.90\%$ for Ho (SD, n=6, before normalization) to $93.7\% \pm 4.90\%$ for Eu and $95.0\% \pm 4.02\%$ for Ho (SD, n=6, with normalization).

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Correlative analysis approaches between LA-ICP-MS and histology

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The cellular composition of soft tissues is routinely used to understand the biological response to adverse changes within a system. Alongside histological analysis, elemental images of soft tissues could help to elucidate the aetiology of an observed cellular response, whether that be changes in endogenous element concentrations within cells or the association of exogenous elements with specific types of cells. The typical methods used to co-locate histological structures with elemental compositions require serial sections for independent analysis of either cell groups or element distributions. However, cellular co-locative analysis using serial sections is limited due to the inherent variation of small features between adjacent tissue sections, a problem that can only be effectively reconciled when the two components are taken from the same image field. In this study, tissue sections previously exposed to titanium debris through in-situ implant degradation were stained with elemental labels (metallic intercalators and conjugated antibodies) and imaged at a cellular resolution using laser ablation inductively coupled mass spectrometry. This approach enabled co-locative analyses of the same tissue section to understand the relationship between cell populations and an exogenous metal exposure. These data guided two-dimensional nearest neighbour approaches in areas of tissue inflammation. This was used to statistically assess the associated immune cell response with key factors of the exogenous including titanium concentration and the number, size and shape of implant debris particles. This technique is a feasible and robust analytical method that permits the identification of immune cell populations and the inflammatory response to exogenous materials in the body.

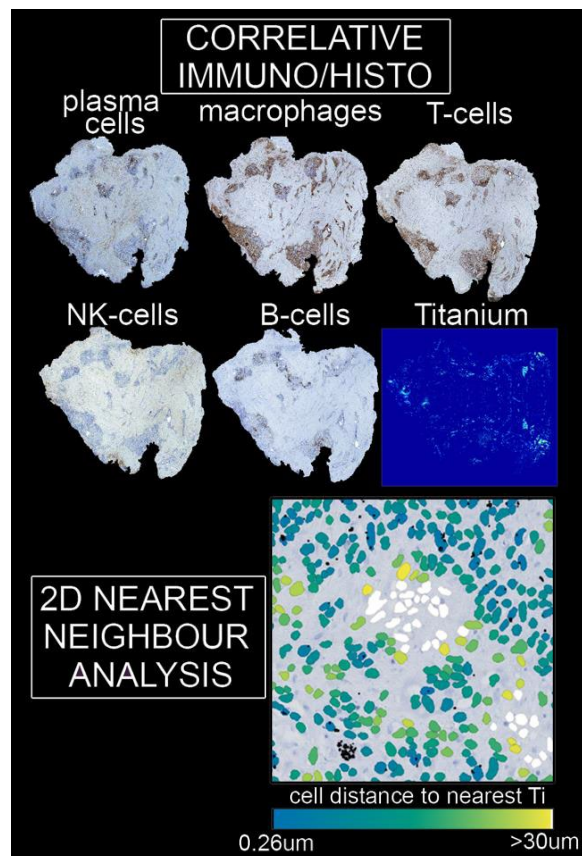


Figure 1. Serial sections showing the different cell types and the distribution of titanium from implant debris; two-dimensional image analysis displaying the distance between cells and titanium particles.

Development of LA-ICP-MS Methods for the Analysis of Multivitamins and Lipsticks

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Monitoring nutritional and toxic elements present in food and cosmetics is part of the United States Food and Drug Administration's mission to protect and promote public health. The analysis of toxic elements in multivitamins and cosmetics typically involves nitric acid digestion followed by Inductively Coupled Plasma – Mass Spectrometry analysis. Because of the chemical composition of lipsticks, hydrofluoric acid (HF) is also often required for the complete decomposition of samples. Acid digestion is not only time consuming, but also leads to known health and safety concerns, especially when using HF.

We present the development and optimization of analytical methods based on Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS) for the analysis of multivitamins and lipsticks. This technique offers quick and automated sample analysis without the need for corrosive acids and extensive sample preparation. The methods we have developed are especially useful for products that are resistant to nitric acid digestion but also require the use of hydrofluoric and/or perchloric acids.

Different calibration approaches were studied for the analysis of multivitamins and lipsticks. For multivitamins, calibrations using cellulose and matrix-matched calibrations using a multivitamin reference material (VITA-1) were evaluated. Due to the lack of lipstick reference materials, custom standards were created to imitate the lipstick's matrix and were used in an external calibration approach. Two types of custom calibrants were created using elements added in oil form or as pigments, mixed in a wax base. Calibration standards, multivitamin tablets and lipstick samples were digested using nitric acid and hydrofluoric acid, respectively, analyzed by solution ICP-MS, and compared to the laser ablation results.

All samples were ablated using a UV laser followed by ICP-MS analysis. Instrumental parameters were optimized to obtain the best signal while reducing fractionation and the variability between replicate measurements. Sample preparation procedures were evaluated to produce the calibration standards that were most consistent with the sample matrix. Limits of detection, recoveries, and precision will be presented for the analyses of 10 lipsticks and 20 multivitamins.

Bioimaging of specific proteins by single cell laser ablation ICP-MS employing iridium nanoclusters as elemental labels

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Cell populations in all biological systems are well-known for their heterogeneous nature. In fact, individual cells of the same line, under same physiological conditions and external stimuli, may show different biomolecule expression. Therefore, differences among cell populations can be difficult to elucidate unless biological systems are studied on a cell-by-cell basis. At present, there is a need for innovative analytical techniques that allow for the determination of elements and biomolecules in individual cells.

In this work, LA-ICP-MS and single cell (sc) ICP-MS are presented as complementary strategies for the determination of specific proteins in cell cultures. On the one hand, LA-ICP-MS has demonstrated a huge potential for determining the spatial distribution of metals in individual cells. Although the bioimaging of endogenous cellular proteins still remains a challenge, an immunoassay in fixated cells using immunoprobes conjugated with an elemental label can be employed for proteins detection. On the other hand, sc-ICP-MS has been proposed for high-throughput cell-by-cell quantitative determination of target proteins within cell cultures [1]. Therefore, combining these two techniques it is possible to determine the concentration of sought proteins in single cells as well as to obtain their spatial distribution along the cell structures.

In the proposed methodology, well characterized small iridium nanoclusters (IrNCs) providing a high signal amplification were employed as labels for the bioimaging of membrane and cytosolic proteins in individual retinal pigment epithelia cells (ARPE-19 cell line) by LA-ICP-MS (NWR193 laser equipped with a TwoVol2 ablation cell and DCI interface coupled to a 7900 ICP-MS). Protein quantification in individual cells was studied by sc-ICP-MS (microFAST Single Cell system coupled to a 7900 ICP-MS) and the proteins distribution was evaluated by LA-ICP-MS. The novel approach was based on immunoassays (cells fixed on chamber slides for LA-ICP-MS and cell suspensions for sc-ICP-MS) using IrNCs conjugated to specific antibodies for determination of the sought proteins under control and stress conditions (glucose treatment, 100 mM).

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LA IRMS – the cost-efficient, sample prep-hassle free, minimally destructive answer to single/sequential analyses of most solid, organic matrices

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Elemental analyzers (EA) have long been the standard sample introduction instrument for IRMS analyses of solid, organic materials. It involves carefully portioning and weighing minute amounts of sample individually into tin/silver capsules. If sample amount is restricted, malfunctioning of any part of the system can be disastrous, as sample recovery is impossible. But what if there is a better alternative? One that offers minimal to no sample preparation, allowing for minimally destructive measurements and repeat or even in situ sequential sampling. We present LA IRMS as an effective alternative. We tested LA IRMS on a variety of organic materials: pollen, wood [1], fingernail, hair, collagen [2], and chitin. For some of these we also present EA data, to show method equivalency.

The instrument setup is an LSX 213 G2+ laser (Teledyne Photon Machines) interfaced to an HS2022 IRMS via a CryoFlex sample preparation module (both Sercon). The sample chamber we use was specifically designed for LA IRMS and is an isoScell Δ100 (Terra Analytic). The EA IRMS used for inter-instrument comparison is also Sercon.

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

Samples where spatial resolution is crucial (e.g., wood, hair, fingernail) can be ablated sequentially at intervals of down to 20 μm (matrix dependent). As each ablation removes a minute amount of sample, replicate analysis will not be an issue for homogenous matrices.

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[2] <https://sercon-instruments.com/wp-content/uploads/App-Note-040-Bone-Collagen-LAIRMS.pdf>

Comparing the skin permeation of cobalt salts and nanoparticles in ex vivo human skin using LA-ICP-TOFMS imaging

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Allergic contact dermatitis is one of the most widespread forms of allergies, with metals playing a major role in addition to preservatives and fragrance compounds [1,2]. Cobalt, nickel, and chromium are common sources of contact allergy, where exposure to everyday objects is able to trigger immune responses through metal ions penetrating the skin barrier. [1,3] Therefore, there is great interest in investigating the permeation of these metals into different layers of the skin. The question also arises as to whether shape and size of the metal (e.g., nanoparticles) have a decisive effect on the permeation mechanism.

The aim of this study was to compare the permeation of cobalt salts (CoCl₂) and nanoparticles into the skin using LA-ICP-TOFMS imaging. For this purpose, an ex vivo human skin model was subjected to different concentrations of the Co solutions. Skin tissue sections were labelled with multiple metal-conjugated antibodies and consecutive cuts were stained with Hematoxylin/Eosin. Using state-of-the-art LA-ICP-TOFMS instrumentation the cobalt distribution, tissue structure, immune cells, as well as physiological elements (e.g., P, Ca, Fe, Zn) could be visualized in a single measurement with resolutions at the cellular level (1 μm pixel size). Micro-droplet-based calibration enabled quantification of the Co accumulation inside the skin. This in turn provided comprehensive insight into the mechanisms of Co skin permeation, showing high accumulation of Co in the epidermal layers (especially in stratum corneum, granular and basal layer) with low concentrations in the dermis and subcutaneous tissue.

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[3] J. P. Thyssen, T. Menne, *Chem. Res. Toxicol.*, 2010, 23, 2, 309–318

Laser ablation/ionisation mass spectrometry for in situ geochemical analysis of planetary rocks and soil

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Although several important improvements of laboratory instruments are witnessed in last decades, the instruments for in situ sensitive geochemical analysis of planetary surfaces are less advanced. Until now more spectroscopic than mass spectrometric measurements were conducted. The development of miniature mass analysers and laser ablation ion sources allowed to prepare space or space prototype instruments such as a laser ablation TOF mass analyser and laser ablation Orbitrap mass analyser with significant improvement of sensitivity allowing for accurate elemental abundance analysis and determination of isotope ratios [1]. A miniature laser ablation/ionisation TOF mass spectrometer (LMS) developed in our laboratory in the last two decades is currently transformed into space instrument to be flown to the Moon within NASA's Artemis program) [2-5]. We will discuss some examples of its capabilities to investigate mineralogical context and some of the geological process.

A miniature TOFMS offers sufficiently high mass resolution ($m/\Delta m > 500$) to resolve individual isotopes and a dynamic range ($> 10^5$) to perform sensitive measurements. The measurements allow for simultaneous comparison of nearly all elements either by conducting depth profiling or surface chemical imaging. These capabilities are of importance while analysing geological samples and offer new opportunities for planetary space research. Knowledge of chemical composition of planetary surfaces is important to understand the origin and evolution of planetary objects. With the accurate determination of elemental and isotopic composition of geological materials (rocks, minerals, soils, sediments) one gains insight into basic geochemical transformation and can perform geochronological studies. Particularly helpful in such studies are the measurements of trace element/isotopic concentrations of lithophile (Rb, Sr, Cs, Ba), rare earth (REE), platinum group and field strength elements (Zr, Nb, Zr, U). We will discuss the results of the mass spectrometric studies on rock material, crystalline solids and minerals such as calcite carbonate, silicate minerals, apatite, biotite and zircon. The studies include chemical imaging and depth profiling analysis allowing characterisation of elemental heterogeneities or identification of microsized inclusions. Due to the high spatial resolution, measurements of trace element distributions in minerals can be used to obtain an insight into key geological processes apparent during mineral (crystal) formation. We demonstrate also that isotope ratio measurements can be conducted with sufficiently high accuracy to obtain meaningful insight into rock characterisation and geological dating.

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[3] Riedo, A. Neuland, M. Meyer, S., Wurz, P., *J. Anal. At. Spectrom.*, 28, 1256-1269 (2013).

[4] Ligterink, N.F.W., Grimaudo, V., Moreno-García, P. et al., *Sci Rep* 10, 9641 (2020).

[5] <https://www.nasa.gov/specials/artemis/>

Quantification of gadolinium distribution in sheep bone tissue by means of LA-ICP-MS

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Gadolinium-based contrast agents (GBCA) are used worldwide for contrast enhancement in magnetic resonance imaging (MRI). The paramagnetic Gd³⁺ ion shortens the relaxation time of the surrounding water protons. Due to its similarity with the Ca²⁺ ion, it is toxic in its free form. To secure a safe use and the complete excretion, the Gd³⁺ ion is chelated with either a macrocyclic or a linear ligand. Still, some gadolinium deposits are found in the body of healthy patients especially after the administration of the less stable linear GBCAs. One site where gadolinium is not only stored in high amounts but also for a long time are the bones. While there are some studies that quantified the total amount of gadolinium in the bone, not much is known about the gadolinium localization.

This study takes a closer look at the gadolinium distribution in the bone tissue via elemental bioimaging. The laser ablation - inductively coupled plasma - triple quadrupole - mass spectrometry (LA-ICP-TQ-MS) with oxygen as a reaction gas was used for this purpose. LA-ICPMS enables the localization of analytes with a high resolution and low detection limits. In addition, quantification is carried out using matrix-matched standards.

The investigated samples originate from a sheep study. The healthy animals received a single clinical dose of a macrocyclic or linear GBCA or saline. Ten weeks later, they were sacrificed and the femur was harvested. Thin sections of three different parts of the bone, epiphysis, diaphysis and bone marrow were prepared and mounted on quartz slides prior to analysis.

For the analyses conducted in this work, an external calibration with gelatin standards was used to quantify gadolinium in the tissue thin sections. The endogenous elements iron, zinc, sulfur and calcium were detected to depict the structure of the bone. A correlation of the distribution of gadolinium with that of zinc, iron or calcium is also an indication of a possible transmetallation of gadolinium. As an overview of a larger sample area, an image with a spot size of 25 µm was acquired. Based on these images, areas of interest were selected and analysed at a higher resolution.

Determination of Ion Diffusion in Polyimides using LA-ICP-MS

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Polyimides (PIs) are high-temperature engineering polymers that exhibit an extraordinary combination of thermal stability, chemical resistance and mechanical properties. Due to their low dielectric constant and very good electrical insulation properties, they are particularly interesting for electronics and electrical engineering applications and are extensively used as isolation and protective medium. To prevent corrosion and improve the reliability of microelectronic devices, the uptake and diffusion behavior of corrosive species within polymers is of great interest [1][2][3]. In general, LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) is a powerful analytical technique for the investigation of the uptake of corrosive species within a polymer [4].

In this work, commercial polyimide films were investigated using LA-ICP-MS after exposure to various aqueous solutions (potassium chloride, copper(II)chloride). Depending on the corrosive test parameters, different diffusion profiles for K, Cu and Cl with a high depth resolution (< 150 nm) were obtained.

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Applications of an improved ArF excimer laser system: The implementation of selective imaging

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Dopants and trace elements can significantly impact material properties and can also be the cause of material failures. Thereby the accurate determination of distributions or diffusion paths of trace elements is a crucial task to optimize materials. One method that is ideally suited for this purpose is laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Considering the improvements of new laser systems in the last decade regarding the lasers per se and the ablation chamber designs and introduction system that result in washout times of a few milliseconds, the application range could be increased drastically. Thereby the analysis of trace elements with a lateral resolution of a few μm and a depth resolution in the 50 nm range is now within the realms of possibility.

In this work, the applicability of an ArF excimer laser system coupled with an inductively coupled plasma mass spectrometer (ICP-MS) in the field of material science will be presented. For this purpose, we utilized the increased scan speed and frequency to improve elemental mappings in terms of resolution and sensitivity. However, in composite materials, a clear differentiation between the individual constituents is still challenging. To overcome this limitation, the ablation threshold of different materials can be utilized. This adjustment of laser energy allowed selective ablation of only one phase. Thereby, the distribution of trace elements between different phases can be clarified.

Where are you from, originally? An inter-instrument (LA vs. EA IRMS) comparison of $\delta^{13}\text{C}$ in various sugars and sweeteners

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The modern consumer no longer focuses solely on food safety and affordability, instead becoming more aware of food origin and source traceability, so much so that spending habits are often shifted based on this latter point. For most food products a reliable solution for tracing is offered by either elemental or stable isotope geochemistry. The methods are well defined and applied by industry and regulators alike. For elemental tracing of food source, laser ablation (LA) is often the standard front end of the instrumental setup. It offers speed, high sample throughput with minimal sample preparation and is also economical when considering consumables. For stable isotope analyses, the elemental analyzer (EA) has been the standard sample introduction method for solid samples. But why not "borrow" the easier to use, faster, and hassle-free laser as a common front end to both ICPMS and IRMS?

We present here as example a series of sugars/sweeteners made from a variety of plants (sugar cane, sugar beet, corn, birch, coco palm, etc.), analyzed via LA IRMS, with a Teledyne Photon Machines LSX 213 G2+ laser connected to a Sercon HS2022 IRMS via a CryoPrep sample preparation module. A specially designed LA IRMS sample chamber was used (isoScell Δ 100, from Terra Analytic). Split samples were also analyzed via traditional EA IRMS (Sercon), for inter-instrument comparison.

Our data shows that LA IRMS can reliably replace EA IRMS for accurate and precise determination of $\delta^{13}\text{C}$ in various solid matrices, while offering the significant advantage of drastically reduced sample preparation and reduced overall analytical costs. Replicate analysis when sample is limited is not often possible by EA but given the minuscule amount of sample removed through ablation, this is a viable option with LA, if the sample is homogenous.

One other clear advantage of LA vs. EA IRMS? A single sugar crystal (beet) was enough for at least five ablations and the $\delta^{13}\text{C}$ standard deviation was 0.03‰.

Investigation of the Interfacial Transition Zone of Concrete in a Model System by LA-ICP-MS

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Laser Ablation-Inductive Coupled Plasma- Mass Spectrometry (LA-ICP-MS) puts forward much merits in material characterization like spatially resolved measurements of elemental distribution on macroscopic samples, or multi-element analyses with low detection limit in a short time. Although the many advantages, LA-ICP-MS is not immensely employed in the field of building materials. In this study, we applied LA-ICP-MS as a method for examining the composition of the Interfacial Transition Zone (ITZ) in concrete. The ITZ describes the contact zone between aggregate and hardened cement paste. This zone typically shows significantly higher porosity and contains more calcium hydroxide than bulk hardened cement paste. Consequently, the ITZ affects the mechanical properties and the durability of concrete considerably [1].

The aim of this study is to develop an optimal strategy to evaluate the LA-ICP-MS results of a heterogeneous material like concrete for a quantitative interpretation, in an attempt to have a deeper look at the ITZ composition in concrete structures. For our research, we prepared special prisms (4 x 4 x 16 cm) consisting of cement paste with various water/cement ratios ($w/c = 0.3; 0.4; 0.5$) and randomly distributed cubic aggregates (0.5 x 0.5 x 0.5 mm; calcite, dolomite or granite). To determine these positions, we conducted CT measurements. This made it possible to cut the prisms in the middle of every dice with a precision saw, achieving adequate surface quality to carry out LA line scans from the aggregate through the ITZ into the bulk cement paste.

With the obtained results, we will investigate the variation in composition between disturbed (ITZ) and non-disturbed (bulk) hardened cement paste. A crucial step in LA-ICP-MS measurements is the calibration strategy, especially in our case of materials with different ablation behavior [2]. The currently most adequate calibration strategy for our results is an external calibration with internal standardization over the sum of all oxides and water to 100%. However, we plan to improve the calibration strategy, especially when the laser ablates different materials in one shot.

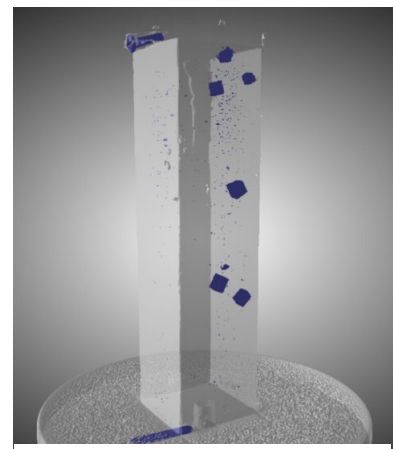


Fig. 1: CT scan of prism with dices

[1] The Interfacial Transition Zone (ITZ) Between Cement Paste and Aggregate in Concrete, K.L. Scrivener, A. K. Crumbie, P. Laugesen, *Interface Science* 12 (2004), 411-421

[2] LA-ICP-MS on hardened cement paste: laser-material interaction, signal formation and optimization of laser fluence, M. Decker, J. Siegel, H. Hilbig, D. Heinz, *Materials and Structures* (2021) 54:144; <https://doi.org/10.1617/s11527-021-01736-4>