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LASER ABLATION ICP-MS - FROM CRATERS TO CALCULATIONS

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ABSTRACT

Laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) is a technique for the analysis of chemical and isotopic compositions of solid materials. In this technique a laser is focussed on to the surface of a solid using a beam size typically ranging from ~ 10 µm to 100 µm. The laser will then fire at a constant repetition rate (usually 5 to 10 Hz) and will either drill a crater or a line raster into the target material. An aerosol is formed during this ablation process and is sent into an ICP-MS and signal intensities are recorded and quantified. We will discuss the various processes involved in each step of the laser ablation ICP-MS analysis and how quantitative results for major and trace elements from most of the periodic table in a range of geological materials can be obtained using this technique. Also discussed will be some limitations and challenges as well as new developments in instrument design that improve the performance of the technique.

1. INTRODUCTION

Laser ablation ICP-MS is an analytical technique that is the combination of two different instruments: the laser system which includes laser source, optical beam path to form a focussed beam, the laser ablation cell which is an enclosed vessel which holds the sample and ablation takes place, and a camera system for viewing samples within the ablation cell; and the ICP-MS which includes an argon based plasma (3,000 to 5,000 K) that ionises fine aerosols, interface cones that allow the transfer from an atmospheric pressure plasma to $\sim 1\times10^{-7}$ mbar, ion lenses for shaping and focussing ion beam, a mass filter (quadrupole, magnet or time-of-flight) for measuring specific isotopes, and a detector (electron multipliers, faraday cups or multichannel analysers). Fundamentally the technique is relatively simple, a laser is fired at a sample, the material is ablated and sent to the ICP-MS that records intensities for chosen isotopes in a time-resolved fashion. However, each step of the whole process has complications that affect the quality of the results and these need to be understood before resulting data can be fully utilised.

Laser ablation ICP-MS can be applied to many different geological materials to answer broader questions about earth history and processes. Common applications include major and trace element analysis of minerals, glasses and inclusions for understanding various petrological processes, U-Pb and Pb-Pb dating of accessory phases like zircon [1], monazite, titanite and apatite [2], and isotopic analysis of minerals, glasses and inclusions for geochronological and petrological applications.

2. LASER ABLATION

A laser pulse usually lasting 5 to 20 nanoseconds, depending on the laser system, will interact with the solid target and produce a laser induced plasma and plume [3], the properties of which are highly material specific. The ions formed from this initial plasma can coalesce and aggregate upon cooling and exiting the ablation cell [4] (Fig. 1). Early on it was found that the ablation gas medium was important in controlling the nature of the formation of these aggregates and how well they are transported away from the ablation site and that less dense gases such as helium offer better performance for many laser system [5.

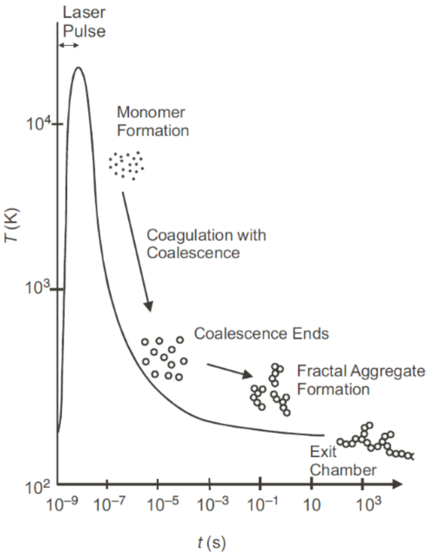

Figure 1. From Ullmann, Friedlander and Schmidt-Ott [4], showing particle / aerosol formation immediately after the laser pulse.

Early work in laser ablation showed that there was a non-representative sampling of different solid materials and that this issue was exacerbated by drilling deeper ablation craters where the ratio of the depth to the diameter was large [6]. This issue has been termed ‘element fractionation’ where one element is preferentially enriched or depleted by the ablation process. Element fractionation is believed to occur at two locations in LA-ICP-MS: 1) at the ablation site where the more refractory elements are preferentially left on the crater walls and condensate around the ablation site [7], and 2) in the ICP due to incomplete particle digestion [8]. It is likely both of these contribute to element fractionation.

Several methods have been utilised to minimise this element fractionation including use of helium [5] as an ablation gas, use of shorter laser wavelengths [9], use of lower laser fluence [10], use of shorter laser pulse widths [11], and ablation of line rasters instead of spots. However, the issue of element fractionation is still present and need to be corrected for in many cases where high accuracy is required.

The ablation cell and interface tubing that connect to the ICP-MS are also important aspects to obtaining accurate and precise results. Early ablation cells were simple designs like barrel cells and worked for a variety of applications, but were problematic for having heterogeneous gas flows that gave different results depending on location in the laser cell. With the introduction of two-volume ablation cells [12], much more precise and accurate results could be obtained by the LA-ICP-MS technique. Most applications such as mineral chemistry analysis and zircon U-Pb dating require some degree of signal smoothing from the pulsed laser so that there is a relatively constant stream of particles entering the ICP and this is often done using mixing devices (e.g., squid) or long amounts of tubing [12]. Other applications such as inclusion analysis and imaging require high spatial and temporal resolution so minimal mixing is desired so as to capture more detail. The laser tubing composition and connections are important for analysis as some types of materials can diffuse atmospheric air, CO_2 and H_2O more readily than others and can cause spectral interferences and affect analytical performance.

3. Inductively coupled plasma

Once the ablated particles / aerosol leave the laser ablation cell they are sent into an ICP where they are broken down and ionised. The ions are then extracted from the atmospheric plasma in a twostep process using a sample cone with an orifice of ~1 mm and a skimmer cone of ~0.5 mm behind the sample cone. There is a step down in pressure at each of these steps so that by the time the ions are detected they are already at 10^{-7} mbar. The skimming and extraction process of ions from the ICP is very inefficient [13] accounting for a substantial portion of the inefficiencies in ion detection of the instrument. For laser ablation the digestion of particles is particularly important and the instruments are typically tuned in such a way as to maximise the particle digestion [8], however this is complicated by the fact that different materials have different requirements for optimum particle digestion [14]. Normally the plasma residence time, a function of the distance between the plasma and the sample cone, or the gas flow rate through the plasma are tuned to get the optimum sensitivity and particle digestion and one is a trade-off for the other. The U/Th ratio has been used to assess the 'robustness' of the ICP to digest particles [8] with tuning optimised to have this ratio close to 1 for NIST 600 series glasses often used for tuning.

Diatomic gases such as H_2, N_2 and O_2 as well as H_2O vapour have been shown to strongly affect the sensitivity of the plasma during laser ablation [15, 16]. However the addition of these gases can cause various interferences so that the addition of these is very application specific. Because of the effect of diatomic gas addition, any residual atmospheric air in the laser ablation cell can affect the quality of analysis, particularly if it is heterogeneously distrusted [10]. Therefore, it is best to have a laser cell and interface tubing that is either very well degased with respect to atmospheric air, or to have constant levels of these diatomic gases.

4. *Inductively couple plasma – mass spectrometry*

The inductively coupled plasma has been utilised for more than 40 years as an ionisation source, initially for atomic emission spectroscopy, then later for mass spectrometry [17]. Development of the instrumentation has been around solution analyses, but early work proved sampling by laser ablation was possible [18]. Switching between the 'wet' plasma mode (solutions) and the 'dry' plasma mode (laser ablation) causes some fundamental changes in the nature of the ICP [19] as well as properties in the ion beam. Changes in the ICP and the ion beam can affect the nature of ion lens behaviour and the tuning of the instrumentation. For laser ablation the 'robustness' of the plasma is important to breakdown particles from the laser ablation process and as mentioned above, the plasma residence time needs to be optimized for laser ablation and will not be the same as for solution analyses.

As part of instrument optimisation, the amount of polyatomic interferences needs to be minimised for multi element analysis for accurate results. Often ratios such as ThO^+/Th^+ are used to assess the level oxide production and many LA-ICP-MS systems can be tuned to 0.2 % or less for this ratio. Other polyatomic interferences such as OH species have been monitored using the high Ca/Fe NIST612 glass [20] by keeping the 43/57 (m/z ratios) close to 100 where lower values indicate formation of $CaOH^+$.

There are several different mass analysers available and the quadrupole mass analyser is by far the most common due to its low cost, rapid (10s to 100s of millisecond) multi element capabilities and adequate sensitivity for most applications. Quadrupole mass filters are sequential in nature and so if a long element list is required, a sacrifice must be made with respect to time resolution. Magnetic sector mass analysers are also common with laser ablation due to their high sensitivity and high resolution capabilities. However, there are some limitations with the speed of magnet jumps for multi element analysis as well as the tau delay for faraday cup detectors that can compromise the transient signals from laser ablation. Magnetic sector instruments can be single collector, and subject to the same limitations as quadrupoles with respect to time resolution. Multi-collector magnetic sector instruments are available and have fixed arrays of detectors that are suited to high precision isotopic ratio analysis rather than multi element analysis. Time-of-flight (TOF) mass filters are theoretically an ideal fit for laser ablation due to their simultaneous detection of the full mass spectrum as well as the rapid (up to 33,000 Hz) duty cycles. However, sensitivity is lower than for the other mass filter types, but other more pressing issues include complex tailing of high abundance peaks on to low abundance peaks, the need for software to process the hyperspectral nature of the data and the limited dynamic range of the detector. Despite the these limitations of the TOF mass filter, its rapid acquisition rate and full mass spectrum capability make it a promising tool for laser ablation, particularly for inclusion analysis.

5. LASER ABLATION ANALYSIS

Laser ablation typically starts with a period of time (e.g., 30 seconds) where there is no ablation but any signal present in the helium and argon gas is recorded and this is referred to as the 'gas blank'. This is then followed by a period of time where the laser is fired at the sample either as a static spot or as a line raster. Typical ablation times are between 30 to 120 seconds. A disadvantage of spot analyses is the signal drop off and increased element fractionation as the laser drills down, while line rasters can avoid these issues. However, line rasters are not always possible for small analytical domains or for inclusion analysis. The total analysis time for each ablation is typically 1 to 2 minutes, giving time between analyses for the previous ablation to washout. A cleaning or pre-ablation is often done prior to the start of ablation and this is to clean any surface contamination from sample preparation.

Standard analyses are typically run before, after and in-between a certain number of unknowns – usually every hour. For trace element analysis glasses are used to calibrate and do secondary standard corrections and include the NIST600 series [21] as well as several basaltic standard from the USGS. There are very few mineral standards available, particularly for trace elements analysis, as homogenous mineral specimens are rare. A primary calibration is often done on a glass such as the NIST612 at a large spot size to obtain a calibration with good statistics, and a secondary standard correction is done matching spot size and other conditions with USGS glasses. For U-Pb dating it is generally required to have a mineral matched standard of known Pb/U composition as the element fractionation between minerals and glasses is generally greater than the precision of the measurements. In addition to the ICP-MS calibration, a down-hole correction is often applied to U-Pb dating applications as the amount of Pb/U fractionation is significant in most materials.

The analyst has several analytical conditions at their control including spot size, laser repetition rate and fluence. The spot size is often target dependant, while the laser repetition rate and fluence can to set to maximise sensitivity but at the cost of increased element fractionation.

6. LASER ABLATION DATA PROCESSING

Results from ICP-MS instruments are typically reported in signal intensities (either as detector counts or counts per second) for a given isotope relative to time. The frequency of detector readings is controlled by the element list for sequential mass filters and the integration time for the simultaneous ones. In an analytical session standards will be analysed with the unknowns and these are used to quantify the concentrations in the unknowns using equation 1. One issue with laser ablation is that different materials ablate at different rates making a direct comparison of signal intensities in one material to another not possible. A solution to this is to normalize all isotopes to an element of known concentration; either through stoichiometry or independently through electron microprobe analysis. Alternatively, the isotopes can be summed to an analytical total assuming that all major elements can be measured or confidently assumed.

$$\frac{\left(\frac{CPS}{PPM}\right)_{STD}^{IS}}{\left(\frac{CPS}{PPM}\right)_{STD}^{EL}} = \frac{\left(\frac{CPS}{PPM}\right)_{SAMP}^{IS}}{\left(\frac{CPS}{PPM}\right)_{SAMP}^{EL}} * X \qquad \boxed{X = C_{SAMP}/C_{ANAL}} \qquad (1)$$

X – correction factor,
a function of all analy-
tical parameters +
matrix dependent

Equation1: Longerich [22] equation for calculating concentrations using an internal standard and external calibration using a material of known concentration. IS = internal standard isotope, STD = standard, EL = isotope of interest, SAMP = sample, CPS = counts per second, PPM = parts per million.

While results can be calculated based on these first principles, more commonly some form of data reduction software is used to speed up the processing and apply corrections such as blank subtraction, drift correction for changes in ICP-MS sensitivity and error propagations. Current commonly available software packages available include, Glitter, Iolite, Lamtrace, LADR, and a range of other application specific (U-Pb dating) and in house Excel-based programmes. Each of these works of the similar to each other in how they fundamentally calculate concentrations, however each varies in detail on how it does other corrections such as the background subtraction, drift correction and error propagation. Typical precision and accuracy for trace element analysis can be between 2 and 10 % (1s) for most elements, while for U-Pb dating precision and accuracy is typically 1 % (2s).

7. CONCLUSIONS

The laser ablation ICP-MS technique uses a focused laser to ablate a sample and the resulting aerosol is sent to an ICP-MS for ion detection. Quantification of results is done via internal standardization and accurate results can be obtained, however element fractionation remains an issue for fully quantified results.

8. REFERENCES

[1] Jackson S E, Pearson N J, Griffin W L and Belousova E A 2004 The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U–Pb zircon geochronology. *Chem. Geol.* **211** 47-69
[2] Chew D M, Sylvester P J and Tubrett M N 2011 U–Pb and Th–Pb dating of apatite by LA-ICPMS. *Chemi. Geol.* **280** 200-216
[3] Gusarov A V and Smurov I 2005 Thermal model of nanosecond pulsed laser ablation: Analysis of anergy and mass transfer. *J. Appl. Phys.* **97** 014307

[4] Ullmann M, Friedlander S K and Schmidt-Ott A 2002 Nanoparticle formation by laser ablation. *J. Nanoparticle Res.* **4** 499-509

[5] Eggins S M, Kinsley L P J and Shelley J M G 1998 deposition and element fractionation processes during atmospheric pressure laser samp)ling for analysis by ICP-MS. *Appl. Surf. Sci.* **127-129** 278-286

[6] Mank A J G and Mason P R D 1999 A critical assessment of laser ablation ICP-MS as an analytical tool for depth analysis in silica-based glass samples. *J. Anal. Atom. Spectrom.* **14** 1143-1153

[7] Kosler J, *et al.* 2005 Chemical and phase composition of particles produced by laser ablation of silicate glass and zircon-implications for elemental fractionation during ICP-MS analysis. *J. Anal. Atom. Spectrom.* **20** 402-409

[8] Guillong M and Gunther D 2002 Effect of particle size distribution on ICP-induced elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry. *J. Anal. Atom. Spectrom.* **17** 831-837

[9] Russo R E, Mao X L, Borisov O V and Liu H 2000 Influence of wavelength on fractionation in laser ablation ICP-MS. *J. Anal. Atom. Spectrom.* **15** 1115-1120

[10] Thompson J M, Meffre S and Danyushevsky L 2018 Impact of air, laser pulse width and fluence on U-Pb dating of zircons by LA-ICPMS. *J. Anal. Atom. Spectrom.* **33** 221-230

[11] Poitrasson F, Mao X, Mao S S, Freydier R and Russo R E 2003 Comparison of ultraviolet femtosecond and nanosecond laser ablation inductively coupled plasma mass spectrometry analysis in glass, monazite, and zircon. *Anal. Chem.* **75** 6184-6190

[12] Muller W, Shelley M, Miller P and Broude S 2009 Initial performance metrics of a new custom-designed ArF excimer LA-ICPMS system coupled to a two-volume laser-ablation cell. *J. Anal. Atom. Spectrom.* **24** 209-214

[13] Hongsen N and Houk R S 1996 Fundamental aspects of ion extraction in inductively coupled plasma mass spectrometry. *Spectrochim. Acta B: Atom. Spectrosc.* **51** 779-815

[14] Gilbert S, Olin P, Thompson J, Lounejeva E and Danyushevsky L 2017 Matrix dependency for oxide production rates by LA-ICP-MS. *J. Anal. Atom. Spectrom.* **32** 638-646

[15] Durrant S 1994 Feasibility of improvement in analytical performance in laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) by addition of nitrogen to the argon plasma. *Fresenius J. Anal. Chem.* 349 768-771

[16] Hu Z, *et al.* 2008 Signal enhancement in laser ablation ICP-MS by addition of nitrogen in the central channel gas. *J. Anal. Atom. Spectrom.* **23** 1093-1101

[17] Houk R S, *et al.* 1980 Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Anal. Chem.* **52** 2283-2289

[18] Gray A 1985 Solid sample introduction by laser ablation for inductively coupled plasma source mass spectrometry. *Analyst* **110** 551-556

[19] Liu S, *et al.* 2014 Signal enhancement in laser ablation inductively coupled plasma-mass spectrometry using water and/or ethanol vapor in combination with a shielded torch. *J. Anal. Atom. Spectrom. 29* 536-544

[20] Guillong M, Danyushevsky L, Walle M and Raveggi M 20111 The effect of quadrupole ICPMS interface and ion lens design on argide formation. Implications for LA-ICPMS analysis of PGE's in geological samples. *J. Anal. Atom. Spectrom.* **26** 1401-1407

[21] Jochum K P, *et al.* 2011 Determination of Reference Values for NIST SRM 610–617 Glasses Following ISO Guidelines. *Geostand. Geoanal. Res.* **35** 397-429

[22] Longerich H P, Jackson S E and Gunther D 1996 Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation. *J. Anal. Atom. Spectrom.* **11** 899-904