

# LA-ICP-MS

This item contains selected online content. It is for use alongside, not as a replacement for the LA-ICP-MS experiment, which is the primary study format and contains activities and resources that cannot be replicated in the printed versions.

Copyright © 2022 The Open University

## Contents

1	Welcome	3
2	Learn about LA-ICP-MS	4
	What is LA-ICP-MS analysis?	4
	Making a plasma	4
	Introducing samples to the ICP	5
	Choosing elements for analysis	6
	ICP-MS/MS analyses	8
	Solution versus laser ablation	9
	What is solution ICP-MS analysis?	10
	What is laser ablation (LA) ICP-MS analysis?	15
	Preparing samples for LA-ICP-MS analysis	19
	Transport of aerosol from the LA to the ICP-MS	25
	Data handling	28
	Application of LA-ICP-MS analysis	29
3	Getting started	37
	Introduction	37
	Safety first	38
	Overview of the Virtual LA-ICP-MS functions	39
	Handy hints from the virtual technician	40
	Getting to know the sample change tab	41
	Why are the NIST glasses different colours?	43
	Loading your samples in the sample cell	44
	Viewing your samples in the sample cell	46
	Turning on the laser	47
	Spot sizes and repetition rates	48
	Using the ICP-MS tab to light the plasma	50

Picking elements that you want to analyse	51
Tuning the ICP-MS	52
Setting up a batch of analyses	56
Downloading your new data	59
What does the ICP-MS show when I fire the laser?	60
Running a batch of standards	61
Setting up a long batch of analyses	63
Virtual LA-ICP-MS lab	68

# 1 Welcome

Our mass spectrometry team at the School of Environment, Earth and Ecosystem Sciences (Open University) work together each week to help our Open University students and scientists, as well as visiting students and scientists from other universities, to get high-quality data using our mass spectrometry labs.

We have quite a few instruments in our labs, including two Agilent ICP-MS (inductively coupled plasma mass spectrometer) instruments and a laser ablation system. We also have lots of machines that are used to crush and polish samples (e.g., rocks) and a clean laboratory where rocks and other samples can be digested using acids.

We enjoy undertaking all types of mass spectrometry analyses, but we particularly love doing laser ablation (LA) ICP-MS analyses. Hence, we wanted to try to share the experience with as many people as possible! The aim of our virtual LA-ICP-MS lab is to give an overview of the steps that a scientist would usually take when running the LA-ICP-MS for a day.

Video content is not available in this format.

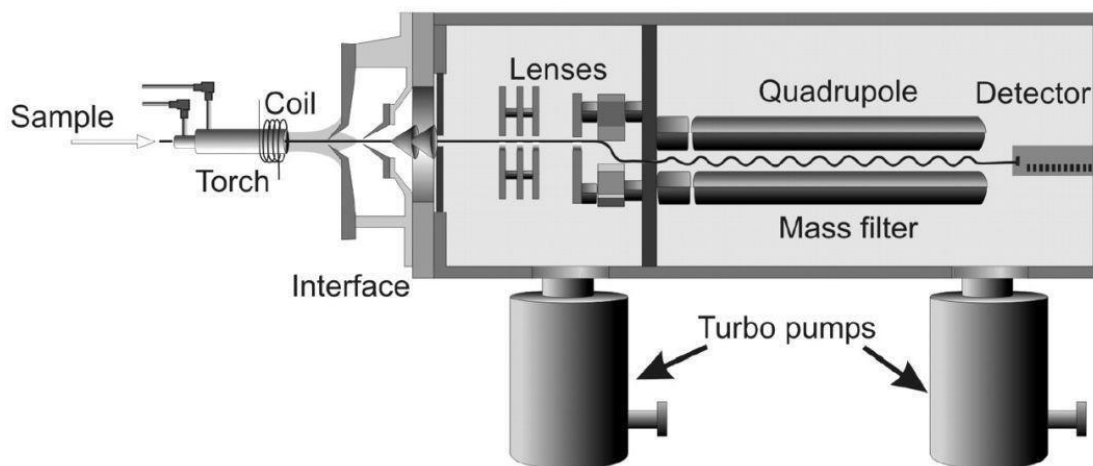
One week in the ICP-MS lab. (This video has no sound.)



## 2 Learn about LA-ICP-MS

### What is LA-ICP-MS analysis?

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a highly sensitive analytical technique used to measure the abundances of elements in different materials.



Schematic cross section of a quadrupole ICP-MS [Košler et al., 2005]

Above is a simplified schematic of the main parts of an ICP-MS. In summary, when a sample is introduced into the **torch**, it becomes ionized by the plasma. Once the sample has become ionized, the ions pass through the **interface** (e.g., the cones) and then through a series of **lenses**. The **quadrupole** separates the ions according to their mass to charge ratio and then the **detector** measures the intensity of the ions. The intensity of the signal, together with a bit of maths, is used to provide the analyst with the contents of different elements in their sample.

References: Košler, J., M. Wiedenbeck, R. Wirth, J. Hovorka, P. Sylvester, and J. Míková (2005), Chemical and phase composition of particles produced by laser ablation of silicate glass and zircon-implications for elemental fractionation during ICP-MS analysis, *Journal of Analytical Atomic Spectrometry*, 20(5), 402-409, doi: 10.1039/B416269B.

### Making a plasma

The ICP consists of a glass (quartz) torch and the end of the torch is surrounded by an induction coil. The coil is connected to a radio-frequency (RF) generator, which generates a strong magnetic field inside of the torch. Argon is fed through the torch and an electric spark is used to introduce free electrons into the argon stream. These electrons interact with the rapidly changing magnetic field and collide with argon atoms. Some of the collisions cause an electron to be stripped from an argon atom (ionization). The electron that is released either collides and causes another argon atom to release an electron, or collides and combines with an argon atom that has previously lost an electron. The continual process produces a plasma that is ~10 000 K, which is significantly hotter than the surface of our sun at 'only' 5778 K or 5505 °C!

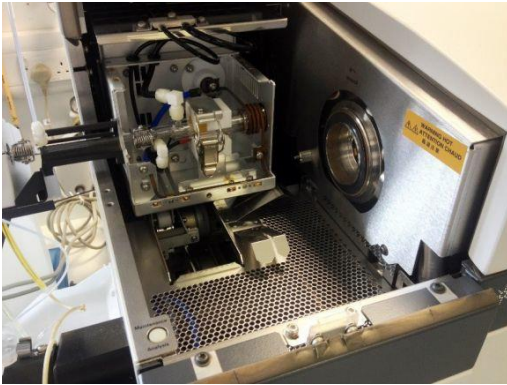


Photo of the Inductively Coupled Plasma (ICP) section of the ICP-MS at the School of Environment, Earth and Ecosystem Sciences (Open University). Inside the central metal cage is the glass torch (centre of the photo), which is held in place within the white casing. Argon flows into the torch from left to right. The right-hand side of the torch has a coil wrapped around it. The circle to the right of the torch is the interface which holds the cones.

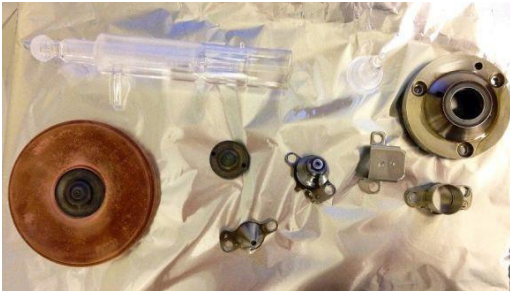


Photo of the plasma on the ICP-MS housed at the School of Environment, Earth and Ecosystem Sciences (Open University). The plasma is focused onto the cone, which is to the right of the plasma. The cone has a small hole in the centre and allows ions to pass into the mass spectrometer.

## Introducing samples to the ICP

When samples are introduced into the plasma, the extreme temperature of the inductively coupled plasma causes molecules to break down (atomization) and the individual atoms become ionized. The amount of energy required to remove an electron is called the ionization energy or ionization potential. The ionization energy of elements shows a broad increase from top to bottom (down the groups) and from left to right (across the periods) across the [periodic table](#). Elements that have a high first ionization energy are difficult (e.g., selenium) or impossible (e.g., fluorine, helium and neon) to measure using ICP-MS.

Once the sample has been introduced into the plasma, the ions pass through a series of cones and lenses (see photos below) and into the mass spectrometer. The cones have a small hole in the middle and are designed to sample only the centre of the ion beam that is produced by the plasma. The lenses collimate the positively charged ion beam (i.e., make the transport parallel and focused) and focus it on the entrance to the mass spectrometer.



The ICP-MS typically has two cones: a sampler (large circle) and a skimmer (small circle) cone. Above the two cones is the glass torch and to the left of the cones are the lenses. This is what the cones look like when they have just been cleaned.



The cones can get quite dirty and end up covered in residue following analysis (i.e., the stuff that does not make it through the hole in the centre of the cone and into the mass spectrometer). Because the residue causes the hole in the centre of the cone to become smaller and limits the ability of ions to pass into the mass spectrometer, they have to be cleaned regularly to prevent a reduction in sensitivity of the ICP-MS.

## Choosing elements for analysis

Some elements have multiple isotopes (i.e., the same number of protons, but a different number of neutrons). For example, lithium (Li) has two naturally occurring isotopes: 6 and 7. In chemistry we use the notations  ${}^6\text{Li}$  and  ${}^7\text{Li}$  to distinguish between different isotopes of a given element.

Below is a picture of part of the mass chart that we use each day when we are deciding which isotopes of a given element we want to measure in our samples.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
H	99.99	0.01															H
He				100													He
Li						7.59	92.41										Li
Be								100									Be
B									19.9	80.1							B
C										98.93	1.07						C
N													99.64	0.36			N
O															99.76		O
	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	
O	0.04	0.2															O
F			100														F
Ne				90.48	0.27	9.25											Ne
Na						100											Na
Mg							78.99	10.00	11.01								Mg
Al										100							Al
Si											92.22	4.69	3.09				Si
P														100			P
S															94.99		S
	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	
S	0.75	4.25		0.01													S
Cl			75.76		24.24												Cl
Ar				0.34		0.06		99.60									Ar
K						93.26	0.01	6.73									K
Ca							96.941		0.647	0.135	2.086		0.004		0.187		Ca
Sc												100					Sc
Ti													8.25	7.44	73.72		Ti

The top part of the mass chart, for elements H to Ti.

If you locate Li in the pink list of elements in the chart above and scan across the Li row, you will see the number 7.59 in column 6 (atomic mass of 6) and the number 92.41 in column 7 (atomic mass of 7). These numbers are the percentage (%) natural abundances of the two lithium isotopes as found naturally on a planet.

Some elements only have one isotope and are referred to as 'monoisotopic'. For example, if you look down the list of elements in the chart above you will see phosphorus (P) has a natural abundance of 100. This is because P exists as a single isotope, with a natural abundance of 100%.

The quadrupole is a type of mass spectrometer that separates ions according to their atomic mass-to-charge ratio and a detector is used to measure the signal. The ion signal that is received by the detector is proportional to the concentration of a given element. When an analyst is choosing which elements they want to measure, they have a few difficult decisions that they need to make. For example:

$^{78}\text{Se}^+$  (i.e., a Se atom that lost one electron when it became ionised) has a mass of 78 and a charge of 1. Hence, the mass/charge ratio is 78.

However:

$^{78}\text{Kr}^+$  (i.e., a Kr atom that lost one electron when it became ionised) has a mass of 78 and a charge of 1. Hence, the mass/charge ratio is 78. Yes, that is right, two elements with the same atomic weight. This is referred to as a 'direct mass interference'.

TO MAKE THINGS WORSE...

$^{156}\text{Gd}^{2+}$  and  $^{156}\text{Dy}^{2+}$  (e.g., a Gd atom that lost two electrons when it became ionized) has a mass of 156 and a charge of 2. Hence, the mass/charge ratio is also 78.

Because  $^{156}\text{Gd}^{2+}$  and  $^{156}\text{Dy}^{2+}$  has the same mass/charge ratio as  $^{78}\text{Se}$ , the mass spectrometer is unable to tell the difference between the three! We refer to this as a 'doubly charge interference' or alternatively, 'a really annoying problem'.

We know, we are upset about this too! We have some other problems... You might have been wondering earlier 'why are there only 16 masses along the top of the relative isotopic abundance table above'. It is not for aesthetic reasons. The answer to this question is that oxygen has a mass of 16 and unfortunately, oxide interferences are extremely common during ICP-MS analysis. Let's use our selenium example again

Se<sup>+</sup> (i.e., Se atom that lost one electron when it became ionised) has a mass of 78 and a charge of 1. Hence, the mass/charge ratio is 78.

However:

<sup>62</sup>Ni<sup>16</sup>O<sup>+</sup> also has a mass of 78 (i.e., 78+16) and a charge of 1. Hence, the mass/charge ratio is 78.

Thus, the reason that the table above only has 16 columns is because it gives us analysts one less thing to worry about! For example, find <sup>78</sup>Se on the table above and look at the block above and you will see that <sup>62</sup>Ni is directly above <sup>78</sup>Se!!!! Yes, that is right. You can get so tired during an analytical session that someone must have decided that doing simple subtraction was too taxing and came up with this table! In our lab we get quite grumpy if people hide this table and we have posters of this table in our offices, our lab books and a scanned copy on our computers just in case we are travelling and need to check something!

So, you might be thinking, what is the solution to this TERRIBLE problem? Well, sometimes the choices are quite easy. For example, during ICP-MS analysis of volcanic glasses for <sup>88</sup>Sr, there are no direct mass interferences (i.e., no other elements have a mass of 88), negligible oxide interferences (the <sup>72</sup>Ge<sup>16</sup>O production rate is inconsequential), negligible argide interferences (the <sup>48</sup>Ti<sup>40</sup>Ar and <sup>48</sup>Ca<sup>40</sup>Ar production rate is inconsequential) and negligible doubly charged interferences (the <sup>176</sup>Yb<sup>2+</sup> production rate is inconsequential). Hence, when analysing mass 88 in volcanic glasses, the analyst can be confident that the signal that the detector is measuring is Sr.

Unfortunately, the problem is not so simple for our beloved Se. Consequently, our group has spent a considerable amount of time finding a way to accurately measure Se in volcanic glasses, which we discuss in the next section.

## ICP-MS/MS analyses

Our ICP-MS is special, as it has two quadrupoles separated by a reaction cell (see schematic below). Because there are two quadrupoles, the machine is referred to as an 'ICP-MS/MS'.

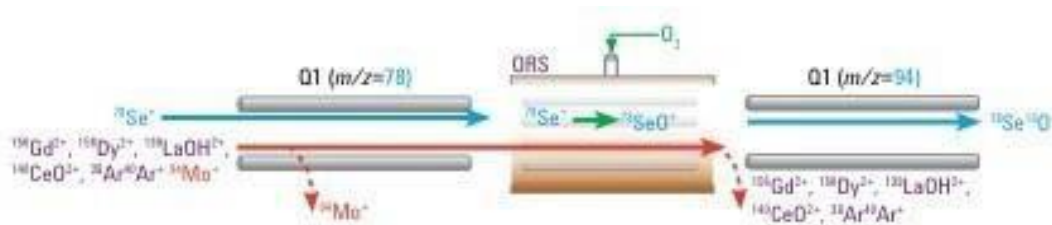


Cutaway diagram of the Agilent 8800 ICP-MS/MS. Q1 and Q2 refer to quadrupole 1 and 2. 'ORS' is the octopole reaction system.



The octopole reaction system that is located between the two quadrupoles can be pressurised with a collision (e.g., helium) or reaction (e.g., oxygen) gas. Quadrupole 1 lets a selected mass enter the octopole, the selected ions react or collide with the gas in the octopole, the resulting ions are then filtered by the second quadrupole (Q2) before finally travelling onwards towards the detector.

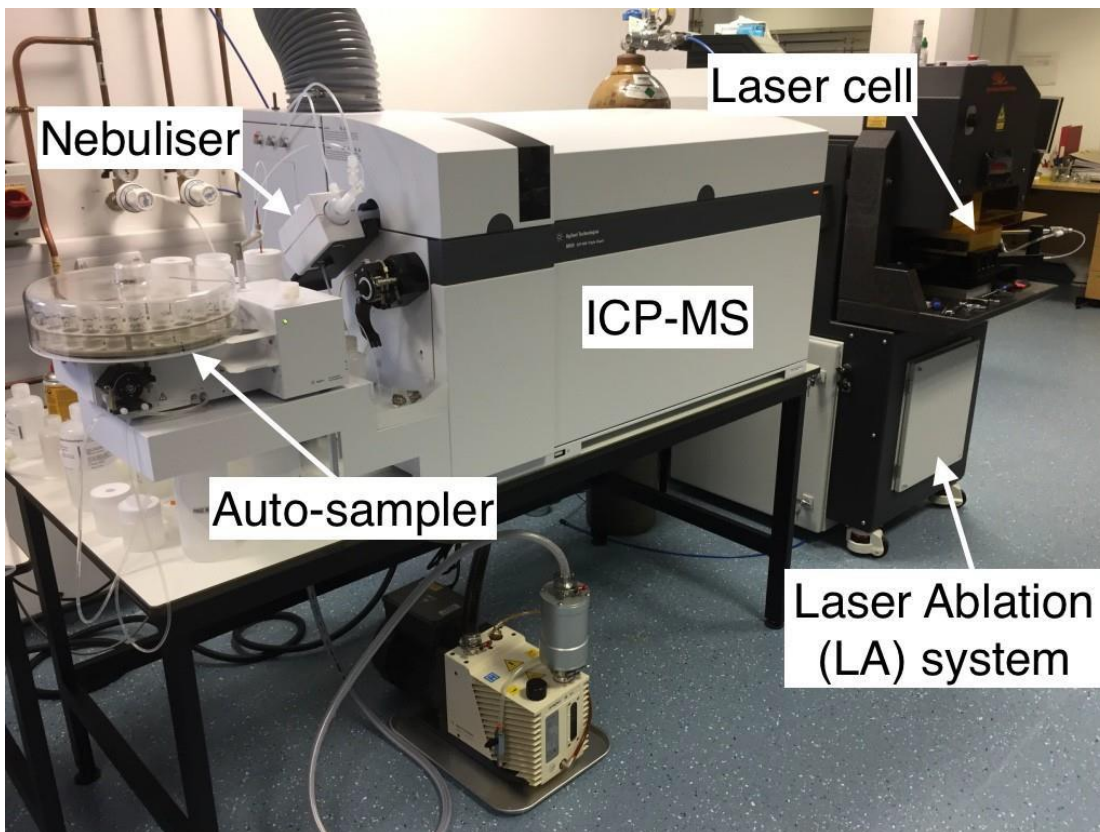
Below shows the way that we analyse Se using our ICP-MS/MS. Quadrupole 1 is set to let only mass 78 enter the octopole reaction system, which includes not only  $^{78}\text{Se}$ , but also a range of interferences such as  $^{156}\text{Gd}^{2+}$  and  $^{38}\text{Ar}^{40}\text{Ar}^+$ . Oxygen gas in the octopole reaction system reacts with  $^{78}\text{Se}$  to form  $^{78}\text{Se}^{16}\text{O}$ , but the interfering elements do not react with oxygen. Hence, we set quadrupole 2 to only let mass 94 (i.e.,  $^{78}\text{Se} + ^{16}\text{O}$ ) pass through to the detector and all of the interferences, which have a mass of 78, do not make it to the detector. This technology lets us separate Se from the interfering elements!



## Solution versus laser ablation

Using the ICP-MS at the [School of Environment, Earth and Ecosystem Sciences \(Open University\)](#), we focus mainly on the analysis of volcanic and metamorphic rocks and the analysis of tiny microfossils called foraminifera.

Samples are introduced into the ICP-MS as solutions using an auto-sampler and a nebuliser, or as an aerosol using a laser ablation system. The picture below shows our ICP-MS and the different sample introduction systems at the School of Environment, Earth and Ecosystem Sciences (Open University) ICP-MS laboratory.



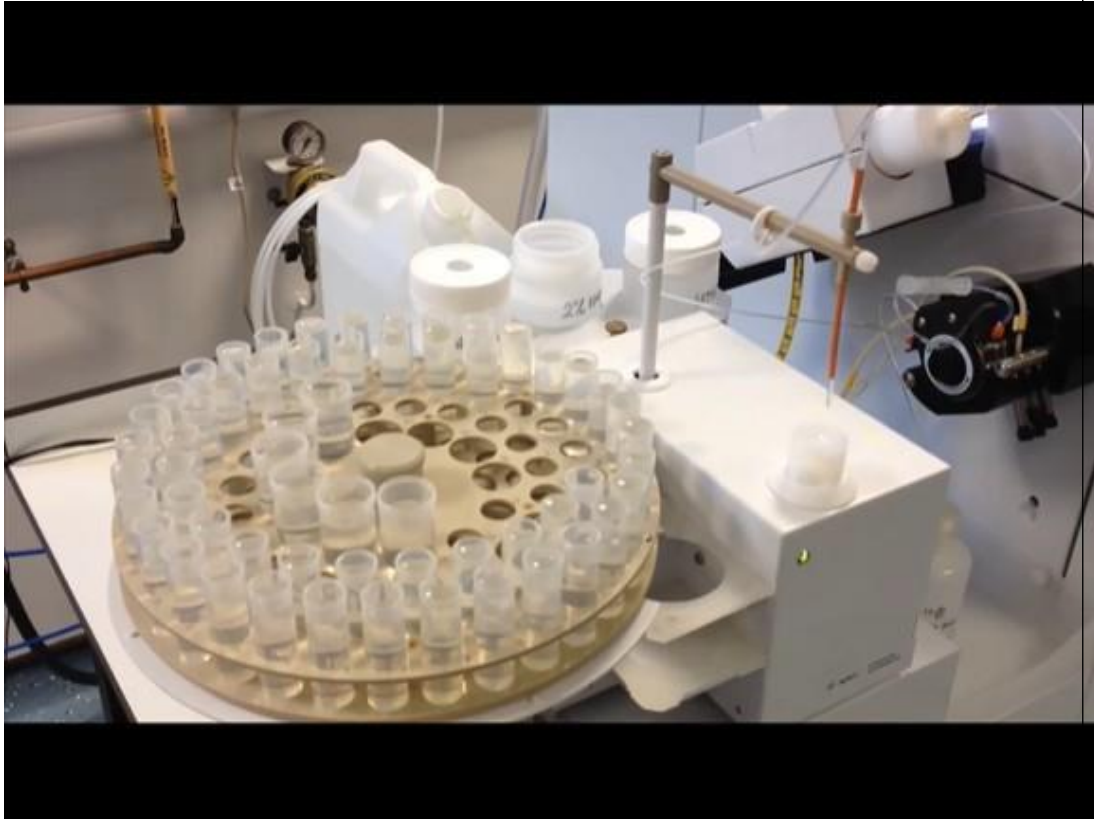
An annotated photo of the ICP-MS facility at the School of Environment, Earth and Ecosystem Sciences at the Open University. Solid samples can be introduced into the [Agilent](#) ICP-MS by ablating the sample in the laser cell using the [Teledyne](#) laser ablation (LA) system. Whole rock samples can be analysed by digesting samples in acid, placing them in the auto-sampler, using the nebuliser to convert the solution to an aerosol and then running the sample through the ICP-MS.

## What is solution ICP-MS analysis?

For solution ICP-MS analysis, a nebuliser converts liquid samples (e.g., sea water or digested whole rocks) into an aerosol and the aerosol is carried via tubes into the plasma. An auto-sampler can be loaded with dozens of different samples and the ICP-MS software can be programmed to automatically introduce samples into the nebuliser and ICP-MS. This automation makes ICP-MS analysis highly efficient and means that our scientists at the Open University can get on with other tasks (e.g., teaching) while the ICP-MS is collecting their data!

Here is a video of the auto-sampler 'feeding' our ICP-MS.

Video content is not available in this format.



Some rocks are quite difficult to digest or dissolve so that they can be analysed as solutions by the ICP-MS. Hence, the School of Environment, Earth and Ecosystem Sciences at the Open University has a clean lab that is used to prepare the samples.

A small amount of powdered rock (~0.1 g) is digested using strong inorganic acids (hydrofluoric, and nitric acid, depending on the sample type) in Teflon beakers. We use Teflon as it is inert to the acids used during digestion. The acids break apart bonds in the sample, allowing us to form a solution of the original rock! Below is a picture of our lab manager Sam Hammond in her clean lab kit preparing samples.



To avoid contamination of samples and as a protection against chemicals, one must wear clean lab shoes, a lab suite, a hairnet, gloves and safety goggles.

Once the acid has been added to the samples, the beakers are placed on a hotplate that has a temperature of around 120 °C. This helps with the digestion process, and means we can go from a powdered rock to a solution in a few days. After the samples are digested, we dry off the strong acids and dilute our samples in a 2% nitric acid solution to be run on the ICP-MS. We usually dilute the original sample 1000 times, as the ICP-MS nebuliser cannot cope well with more concentrated samples.

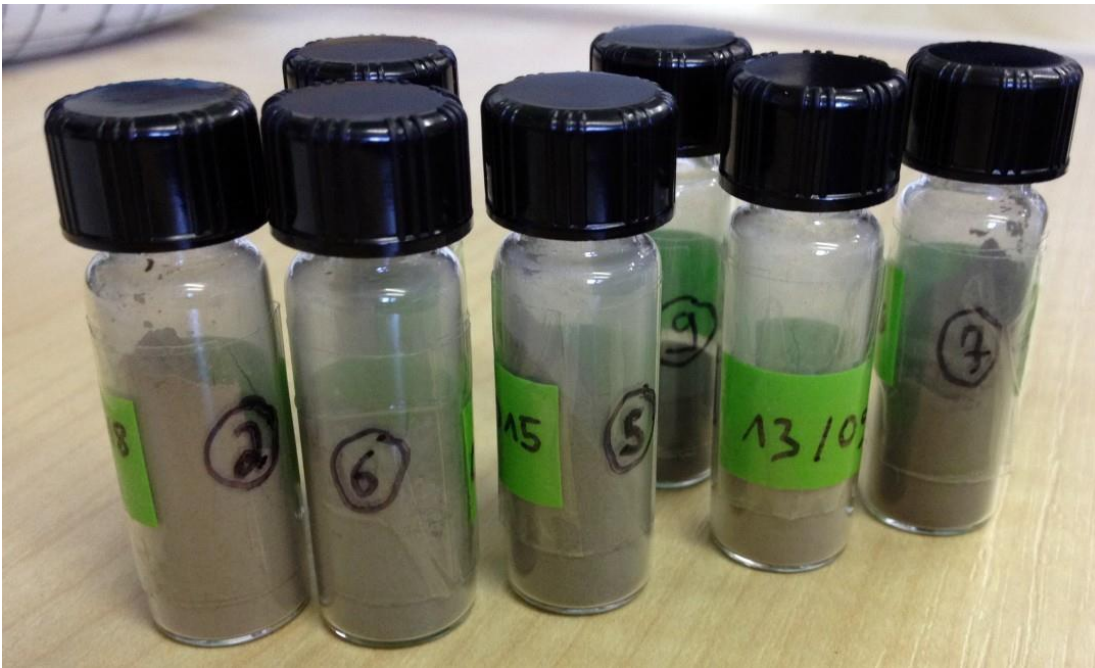
In addition to digesting our own unknown samples, we also always prepare a chemistry blank (to check that the very low signatures we measure on the ICP-MS are not an artefact of our chemistry) and also some reference materials. There are a whole host of rock reference materials out there – so you need to pick the one that most closely matches your unknowns in terms of composition, and hope when you do the analysis you come up with similar values to everybody else who has analysed that reference material (a measure of your accuracy).

The following 6 images show the stages of sample preparation.



1. Rock sample before powder preparation



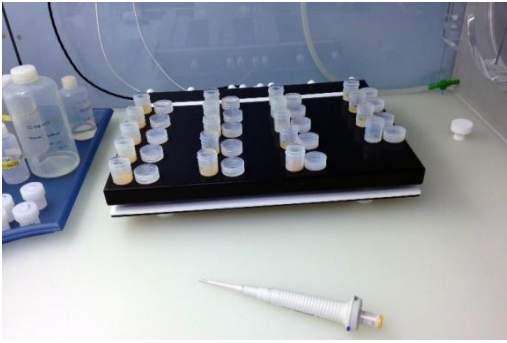


2. The samples get milled to fine-grained powders



3. Reference material for quality check of unknown samples





4. Sample beakers with acid digest on the hotplate to evaporate the acid



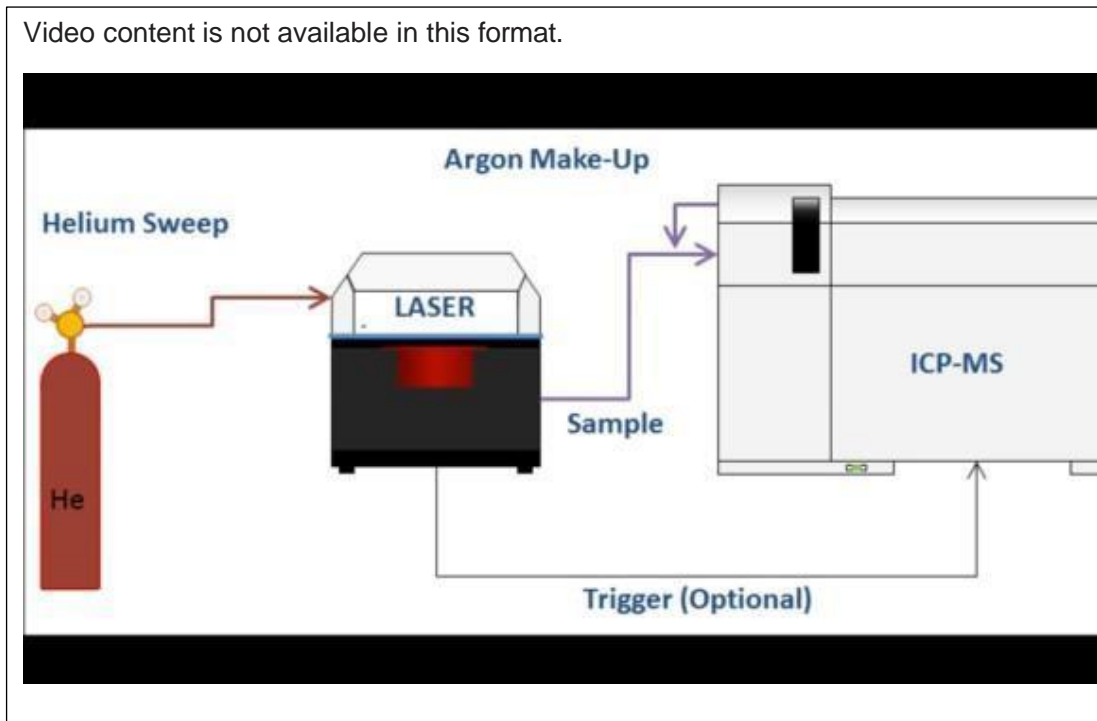
5. After all digestion stages the samples get diluted before measurements



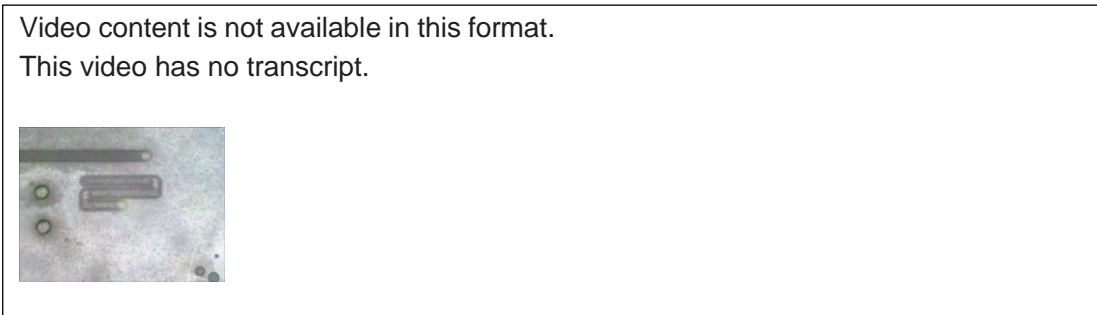
6. Bottles with diluted samples ready for analysis

## What is laser ablation (LA) ICP-MS analysis?

Laser ablation (LA) ICP-MS is a micro-sampling technique that can be used to undertake in situ analyses of geological samples such as volcanic glasses and minerals. In the video below, our friend Nick Westaway from Teledyne Photon Machines discusses the main parts of a typical LA-ICP-MS system.

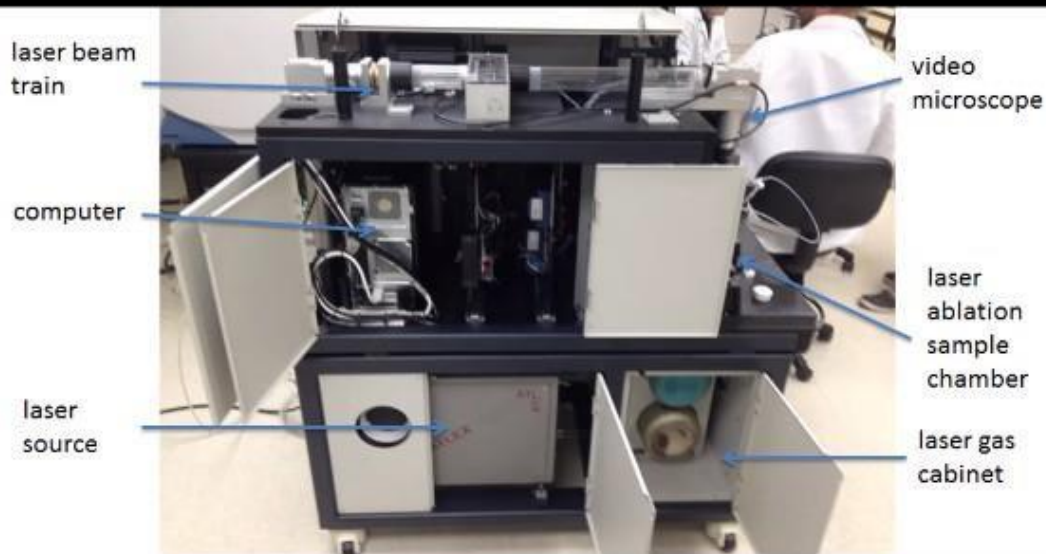


Excimer (short for 'excited dimer') laser ablation systems, such as our [Teledyne Cetac laser](#) produce a type of deep ultraviolet 193 nm wavelength light. This laser light is focused using a series of lenses and is used to ablate holes in solid samples. The video below shows a laser ablating solid material (warning: contains flashing lights!)



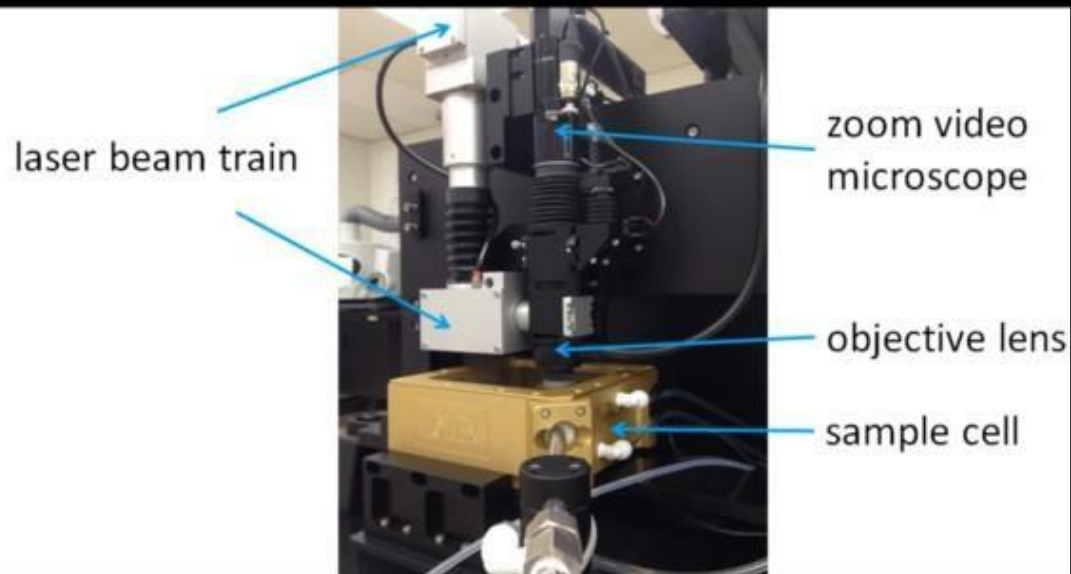
Below, Nick Westaway describes the different parts of the laser ablation instrument.

Video content is not available in this format.



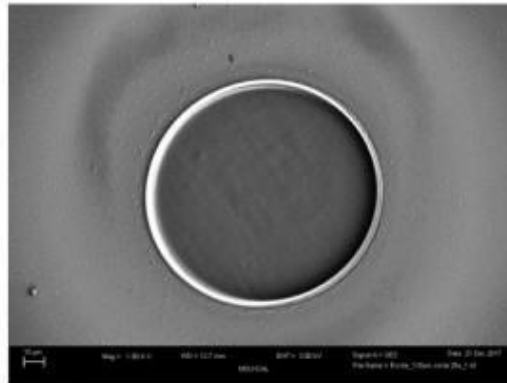
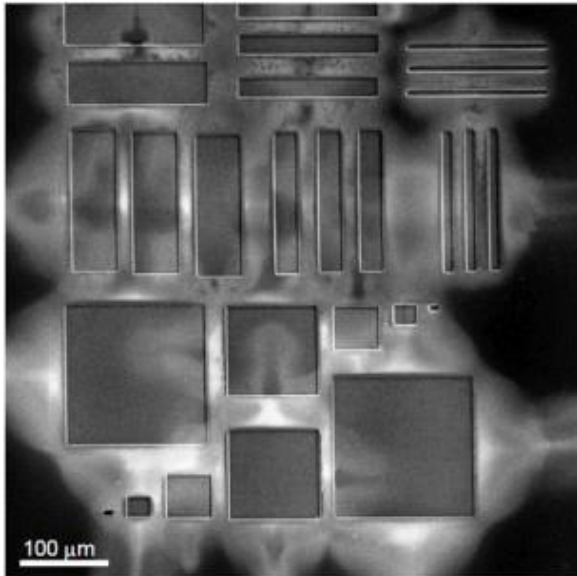
And here, Nick describes the part of the laser beam train (silver column on the left) that is positioned next to the video microscope (black column on the right). The gold coloured box is the laser ablation cell which holds the samples.

Video content is not available in this format.



In the following audio, Nick Westaway from Teledyne Photon Machines discusses how the laser ablates different shapes, such as the ones in the photo below.

Audio content is not available in this format.



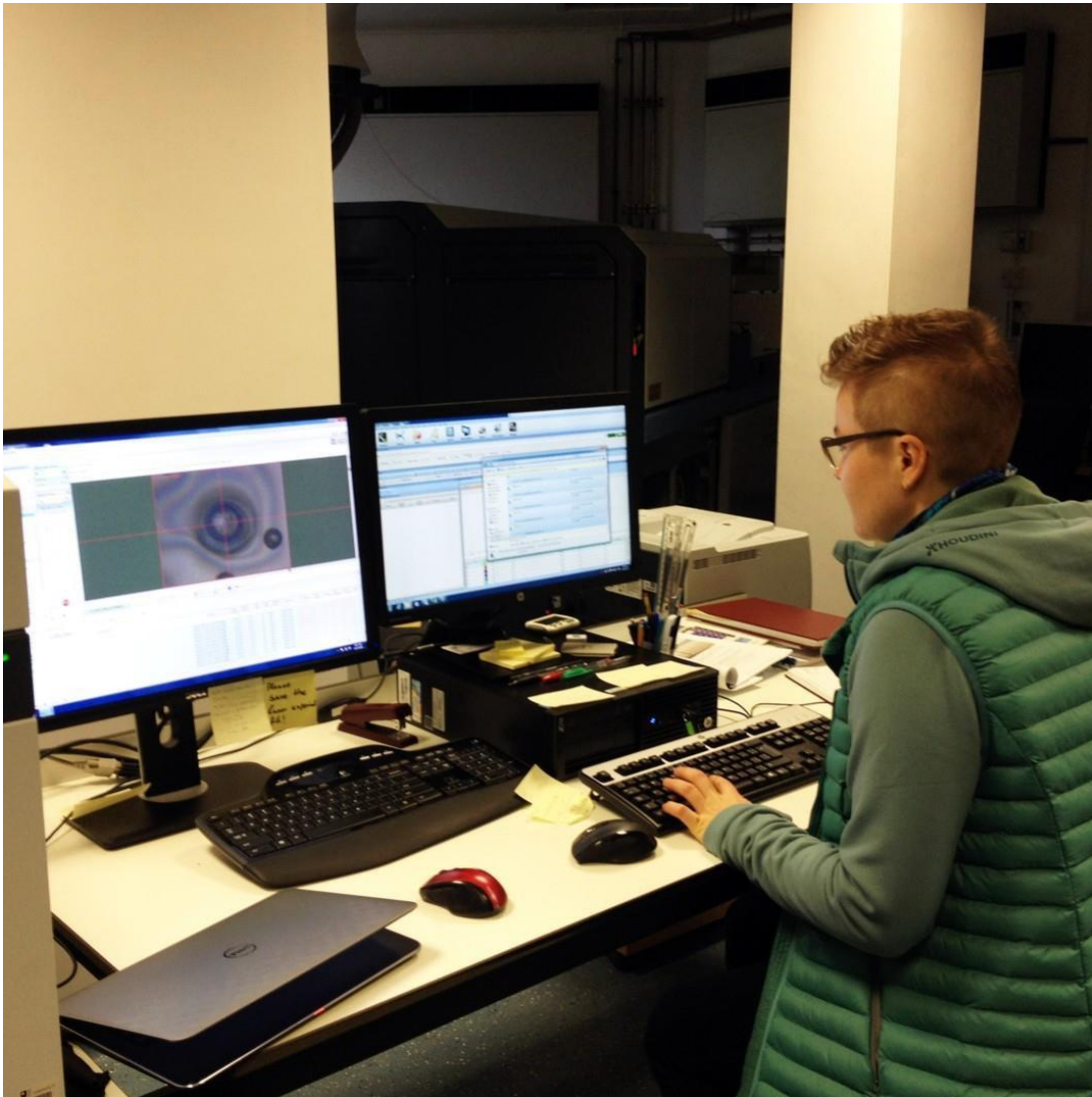
### Ablation shapes

Below is a photo of the laser ablation system at the School of Environment, Earth and Ecosystem Sciences at the Open University and another of Barbara Kunz using LA-ICP-MS analysis to collect data for a NERC funded grant.



Our laser ablation system at School of Environment, Earth and Ecosystem Sciences (Open University) is an excimer laser ablation system made by Teledyne





The computer on the left is used to control the laser ablation system (in the centre of the screen you can see a round laser ablation pit) and the computer on the right is used to control the ICP-MS.

## Preparing samples for LA-ICP-MS analysis

Before the samples can be analysed, the samples are first mounted in epoxy and they are then polished to produce a scratch-free surface. For example, in the photo below (left) is a picture of a volcanic rock that has been retrieved by dredging from the seafloor (~3000 m below the sea surface!). The glassy exterior of the sample, which is called 'volcanic glass', can be chipped away from the surface, mounted in epoxy and polished. The process starts off in the same way that you might polish wood (i.e., using progressively finer grit sandpaper), but the last stages of the polish require something called diamond paste, which produces the high-quality polish that we need for analysis. Below (right) is a picture of some 'ready-to-analyse' sample mounts. One of the mounts contains nine volcanic glasses from various parts of Iceland. The other mount hosts lots of big olivine grains.



(photo 1) a pillow lava with quenched glass exterior and mineral-rich interior. During eruption of pillow lavas on the seafloor, the rapid cooling of the exterior of the sample (from  $>1000\text{ }^{\circ}\text{C}$  to  $<5\text{ }^{\circ}\text{C}$  in a few seconds) causes the formation of volcanic glass. (photo 2) The volcanic glass can be chipped away from the rock, mounted in epoxy and polished. Because the glass is very homogenous, these samples are ideal for in situ LA-ICP-MS analysis.

Once the samples are polished, they are loaded into our sample holders. In the following audio you will hear a description of the different types of sample holders, shown in the photo below.

Audio content is not available in this format.





**Thin section sample holder:**

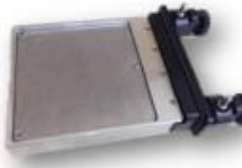
- 3 x 25 mm pucks
- 2 x 12.5 mm standards
- 4 x petrographic slides / thin sections

**Traditional sample holder:**

- 9 x 25 mm pucks
- 4 x 12.5 mm standards

**"Open" sample holder:**

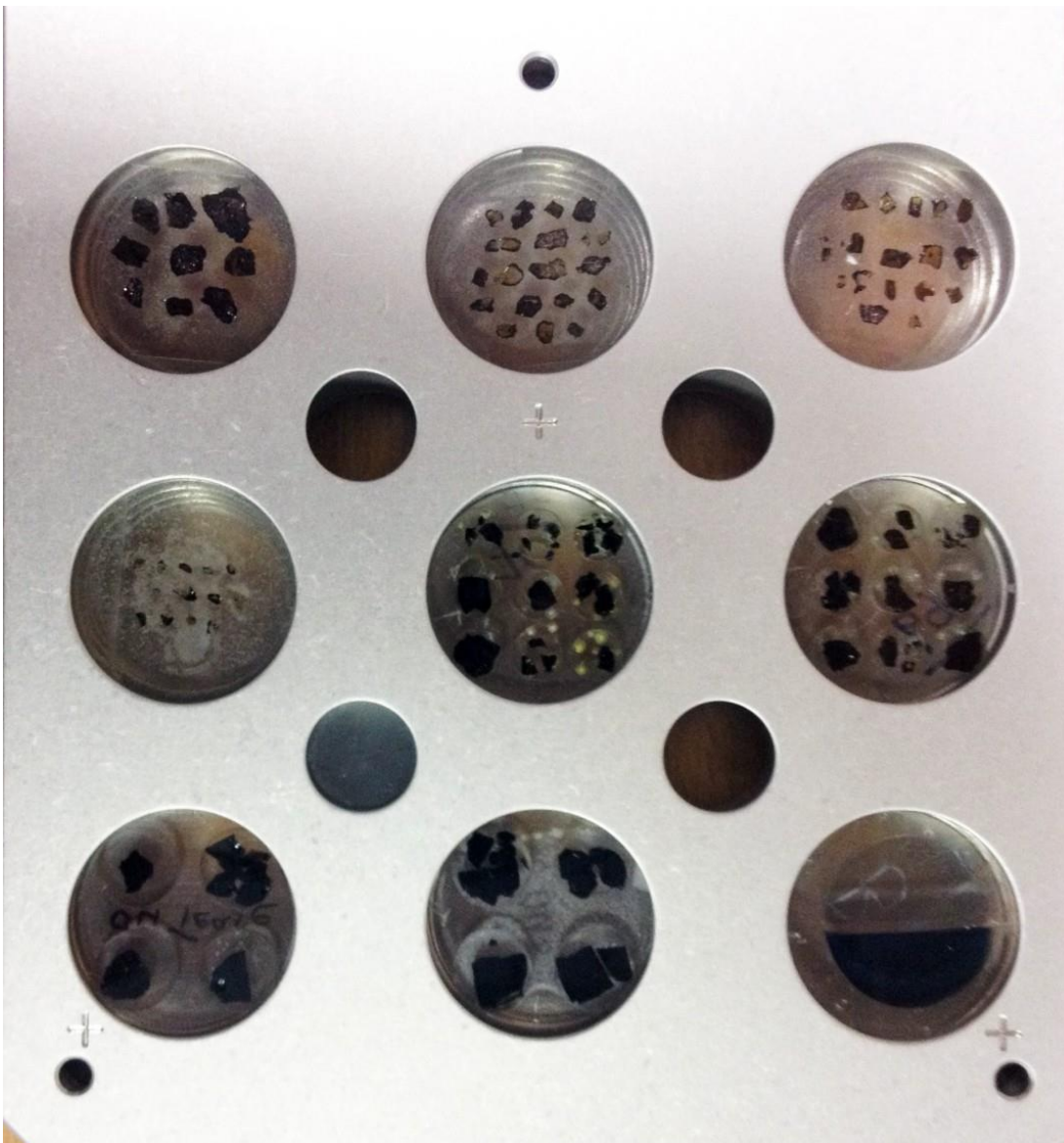
- Empty drawer of 100 x 100 x 18 mm
- Removable, height-adjustable shelf

**Cryo sample holder:**

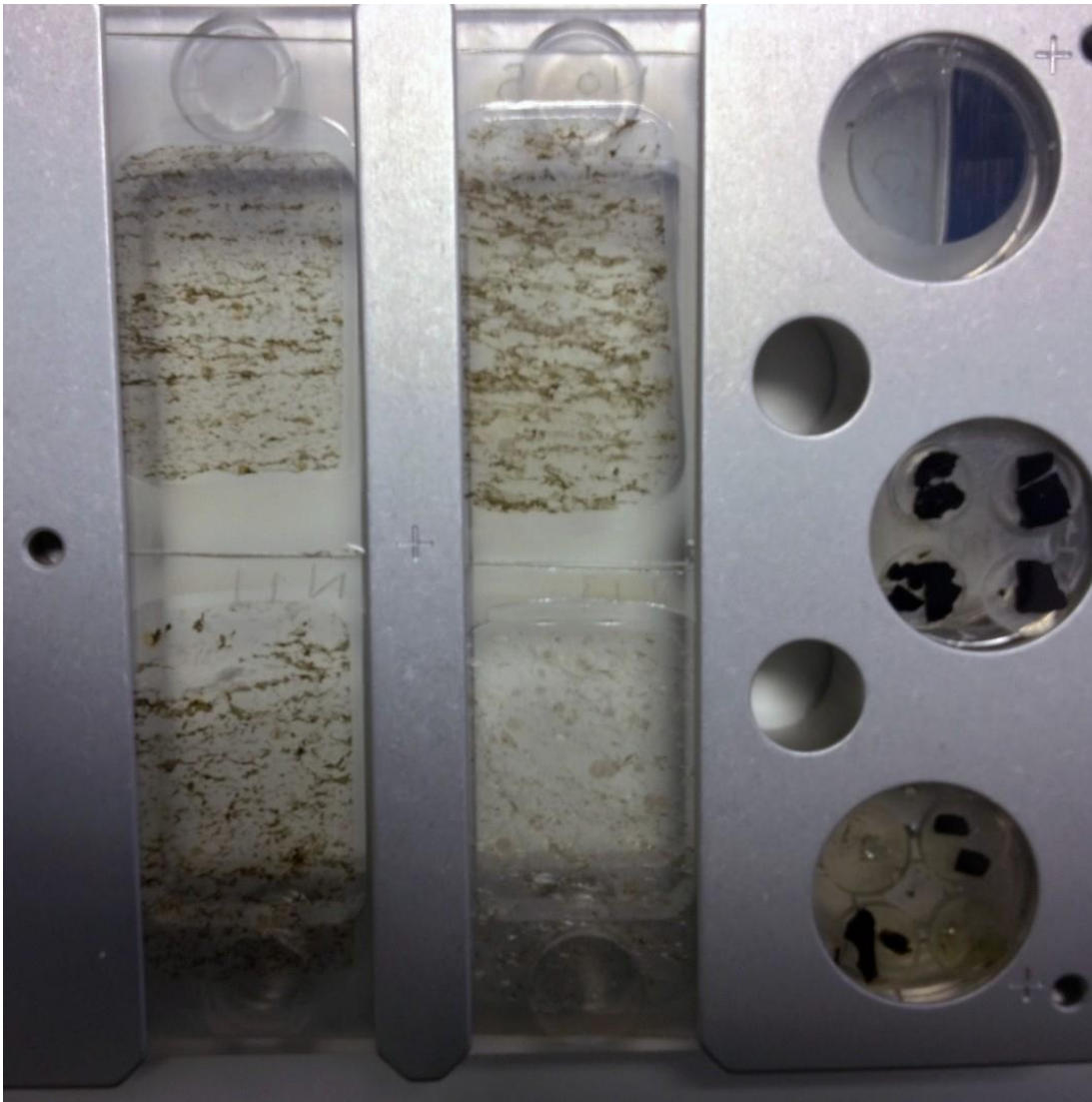
- -25 to +100 °C
- Includes cryostat

## Sample holders

We have two sample holders that we use regularly. In the pictures below you will see that one of the sample holders is only able to hold our round epoxy mounts. The other holds both epoxy mounts and thin sections.

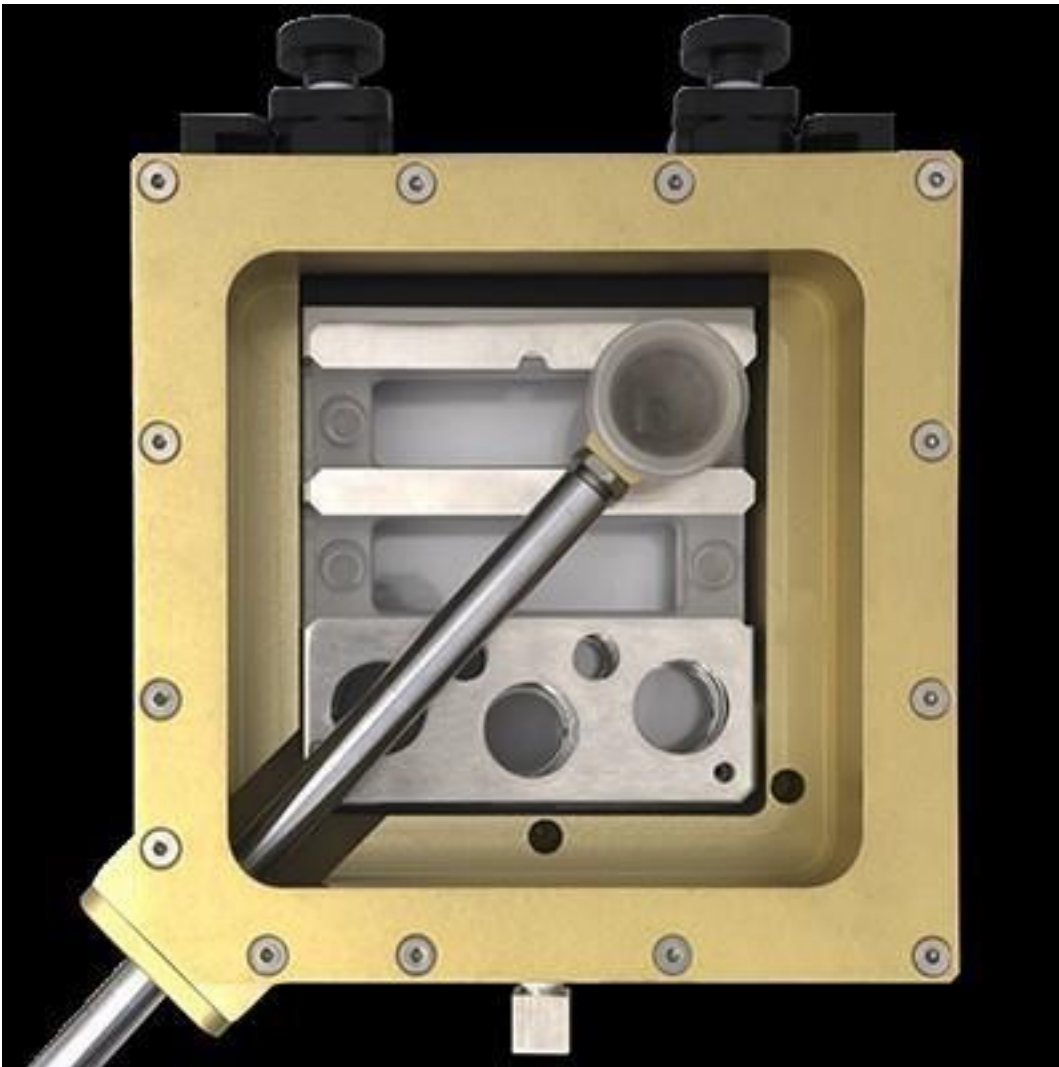


This sample holder is used when the analyst has only epoxy mounts to analyse.



This sample holder is used when the analyst has a mixture of thin sections and epoxy mounts that they want to analyse.

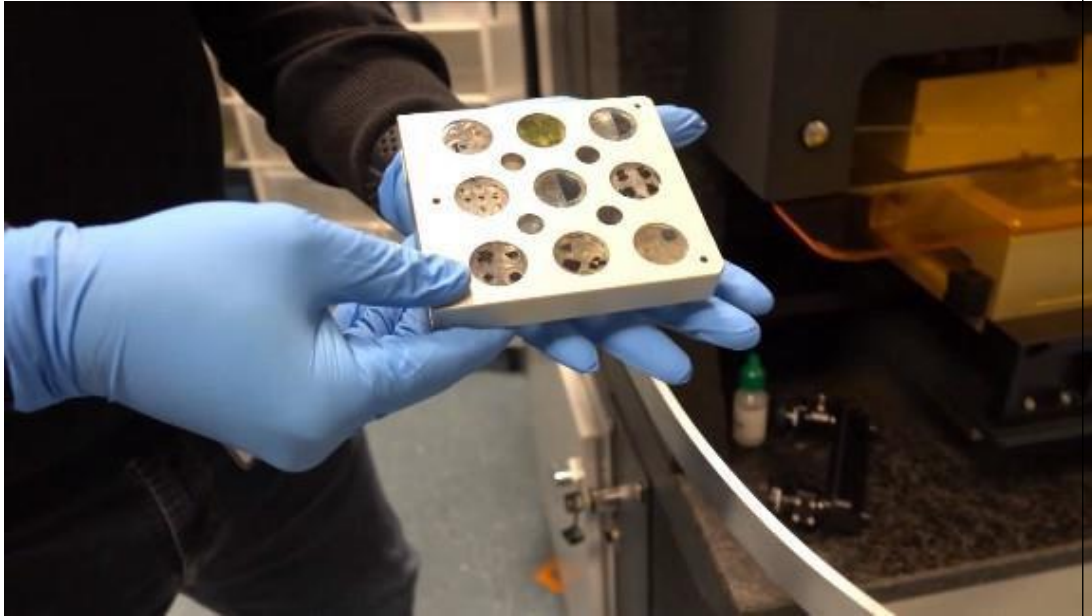
Once the samples have been loaded in the holder, the holder is then placed in the cell of the laser ablation system (see photo above) and the door to the cell is closed.



A close up picture of our sample cell. The ablated signal is carried down the 'arm' towards the ICP-MS.

Play the video below to see the samples being placed in the holder and then the holder being placed in the laser ablation cell.

Video content is not available in this format.



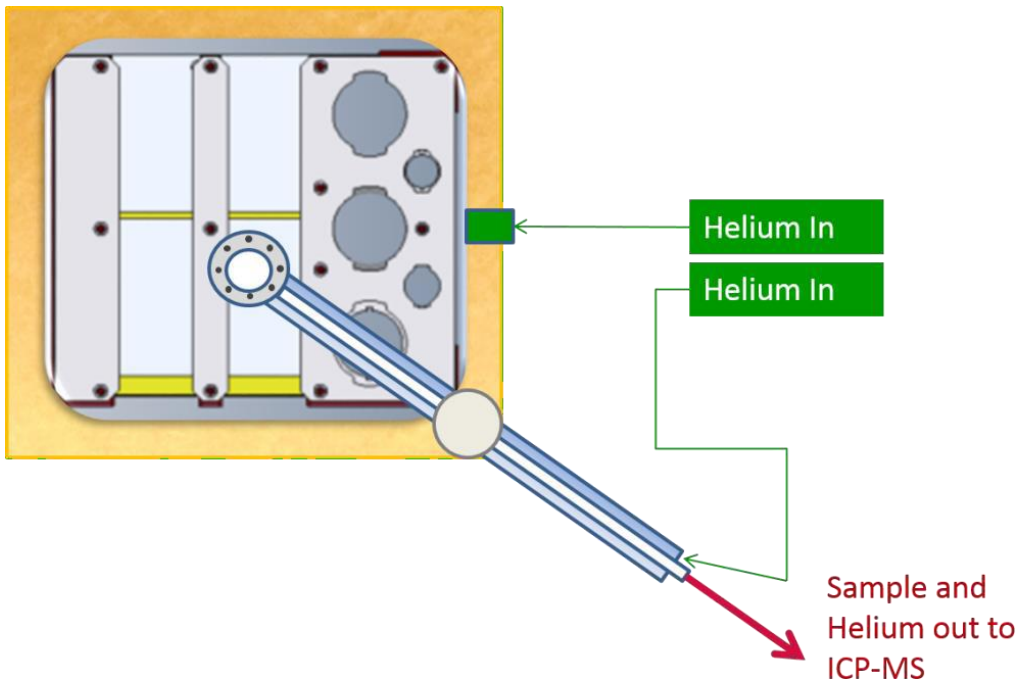
## Transport of aerosol from the LA to the ICP-MS

Once the sample holder has been placed in the sample cell, the sample cell is then filled with helium ready for LA-ICP-MS analysis. When the sample is ablated, the laser-induced aerosol becomes mixed with helium and is transported towards the ICP-MS. The helium + sample mix is then mixed with argon and sometimes a little nitrogen and finally, the mixed signal is carried into the torch of the ICP-MS. Below are a series of animated images and audio files discussing the process of ablating material and carrying the aerosol towards the ICP-MS for analysis.

In this first audio, Nick Westaway from Teledyne Photon Machines describes the gas flows in and out of the laser ablation sample cell, which are shown in the schematic diagram below.



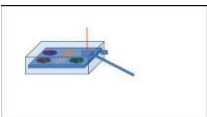
Audio content is not available in this format.



Gas flow in and out of the laser ablation sample cell

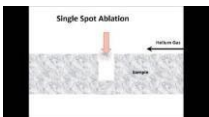
In the following animation, Nick Westaway describes the movement of the sample cell.

Video content is not available in this format.



In this animation, Nick Westaway describes the process of sample ablation.

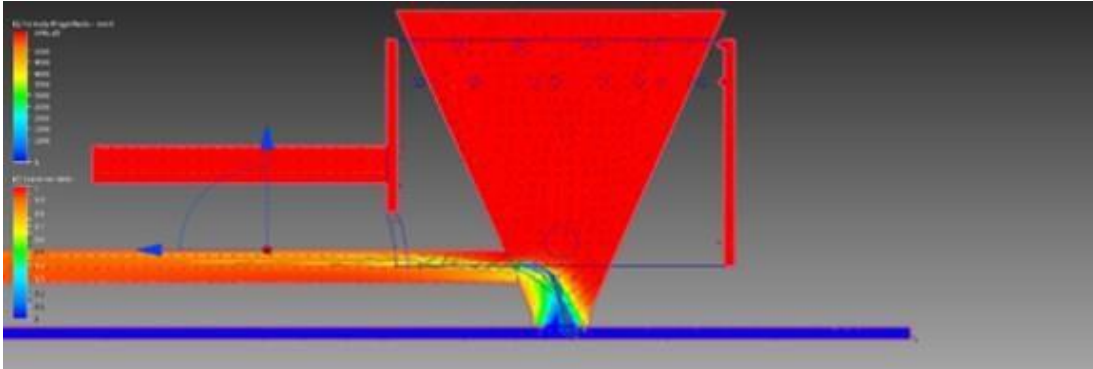
Video content is not available in this format.



Play the audio below to hear Nick Westaway discussing the fluid dynamics within the inner cup of the sample cell (shown in the image below).



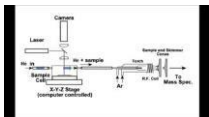
Audio content is not available in this format.



Inner cup of the sample cell

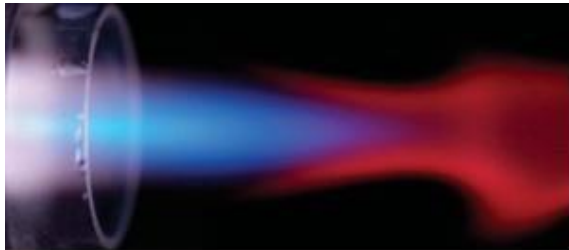
In this animation, Nick Westaway describes the journey the signal takes between the laser and the ICP-MS.

Video content is not available in this format.



In this final audio, Nick Westaway talks about the difference in the appearance of the plasma between ablation and solution modes.

Audio content is not available in this format.



← Liquid Nebulization

Laser Ablation →



Ablation and solution modes

## Data handling

Unlike during solution ICP-MS analysis, to convert the ion signal intensities measured using LA-ICP-MS into contents of element in a given sample requires prior knowledge of the content of one element in the material that is being analysed. The Electron Probe Micro Analyser (EPMA) is an analytical tool commonly used to measure the abundances of major and minor elements in geological materials, such as volcanic glasses and minerals (see photo below) prior to LA-ICP-MS analysis. The polished samples are carbon coated and then placed in the EPMA. During analysis, a finely focused electron beam bombards the surface of the sample. This interaction causes the sample to emit X-rays at wavelengths characteristic of the elements that are being measured.



The EPMA that is housed at the Open University ( <https://www.open.ac.uk/stem/environment-earth-ecosystem-sciences/research/analytical-facilities/earth-science-laboratories>) and is used to measure the contents of major and minor elements in geological samples.

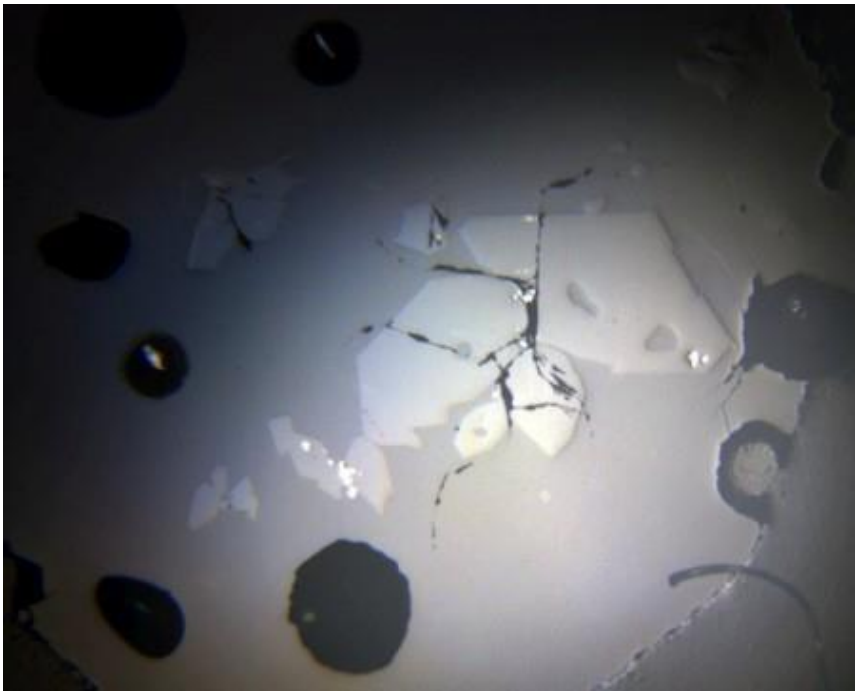
As shown in the photo below, EPMA can also be used to have a really close up look at your samples and for example, a laser ablation pit!



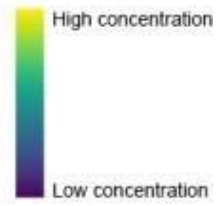
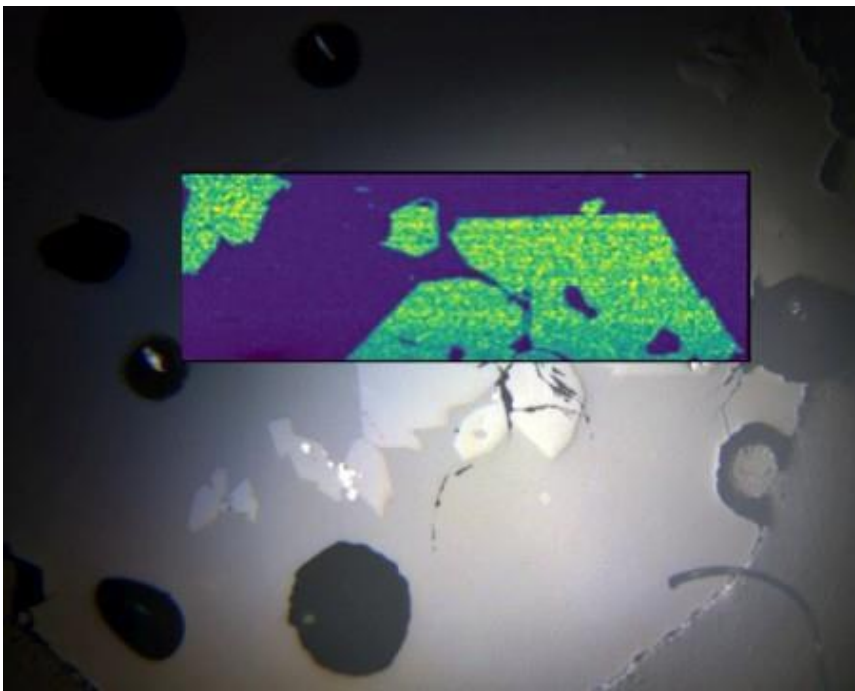
EPMA pit

## Application of LA-ICP-MS analysis

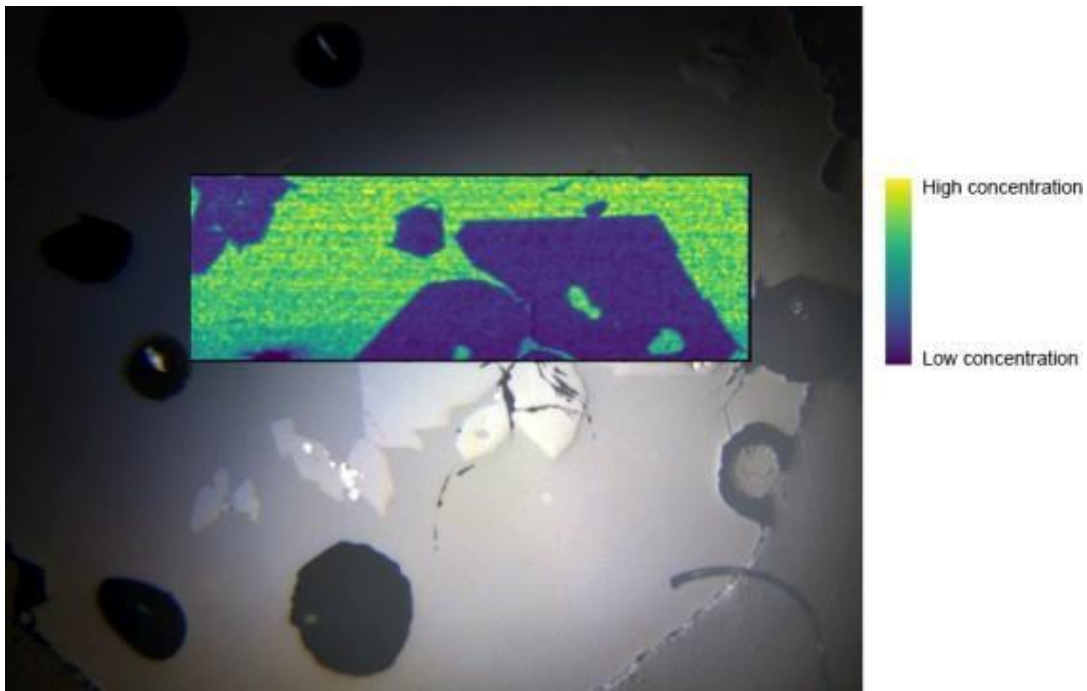
LA-ICP-MS analysis is a highly versatile technique that can be applied to most aspects of science. At the School of Environment, Earth and Ecosystem Sciences at the Open University we use the laser system to measure the contents of >60 elements in volcanic glasses and minerals from all types of rocks (e.g., sedimentary, igneous and metamorphic). For example, below is LA-ICP-MS image of Sc and Mg distributions between minerals and volcanic glass.



Volcanic glass



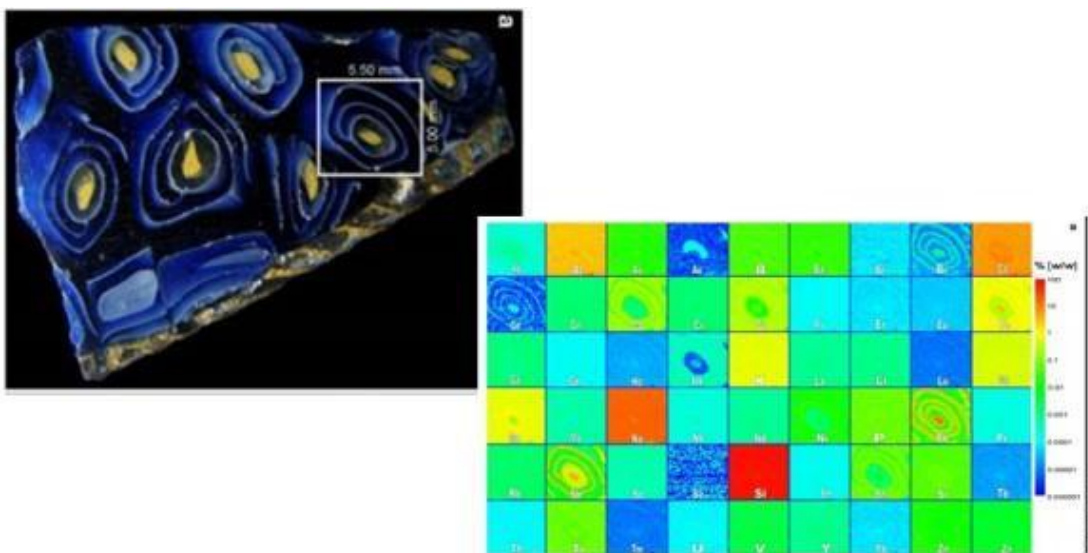
MgO map



### Sc map

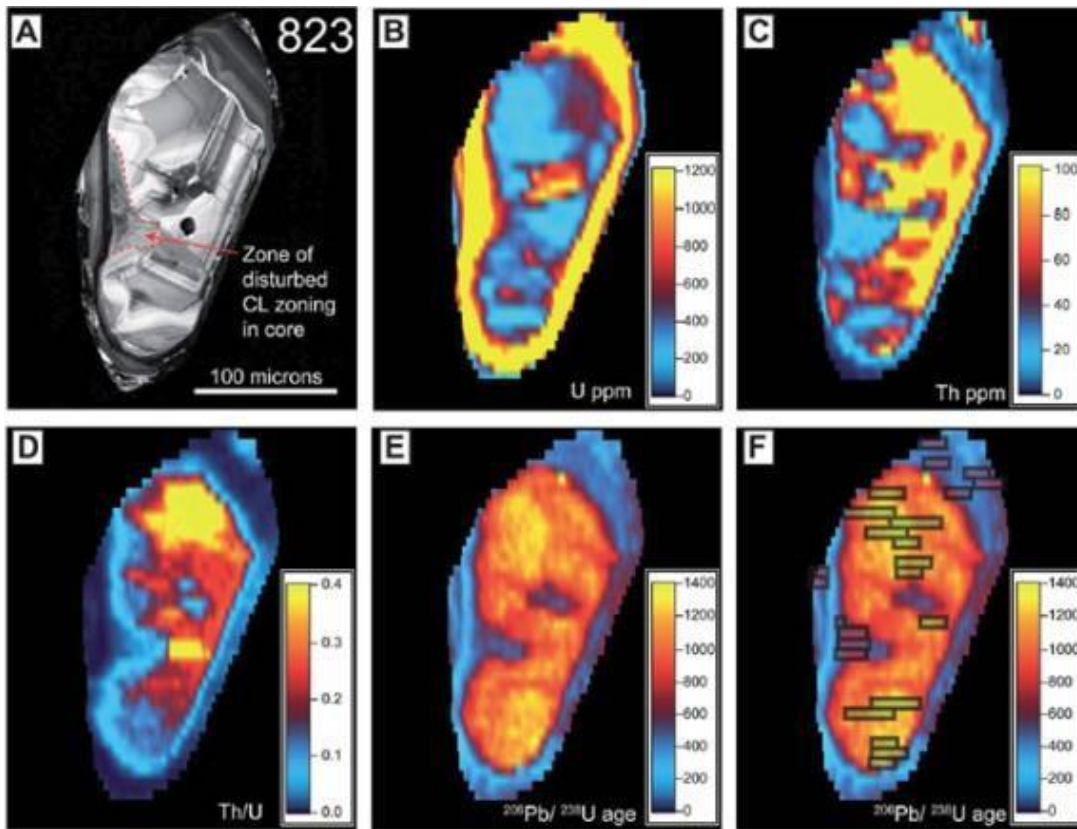
Use the next and back arrows to look at five examples of various other application areas of LA-ICP-MS analysis, taking place at other universities. Each example has an audio description.

Audio content is not available in this format.



Laser imaging Roman era glass (Dr Šelih, National institute of Chemistry, Slovenia).

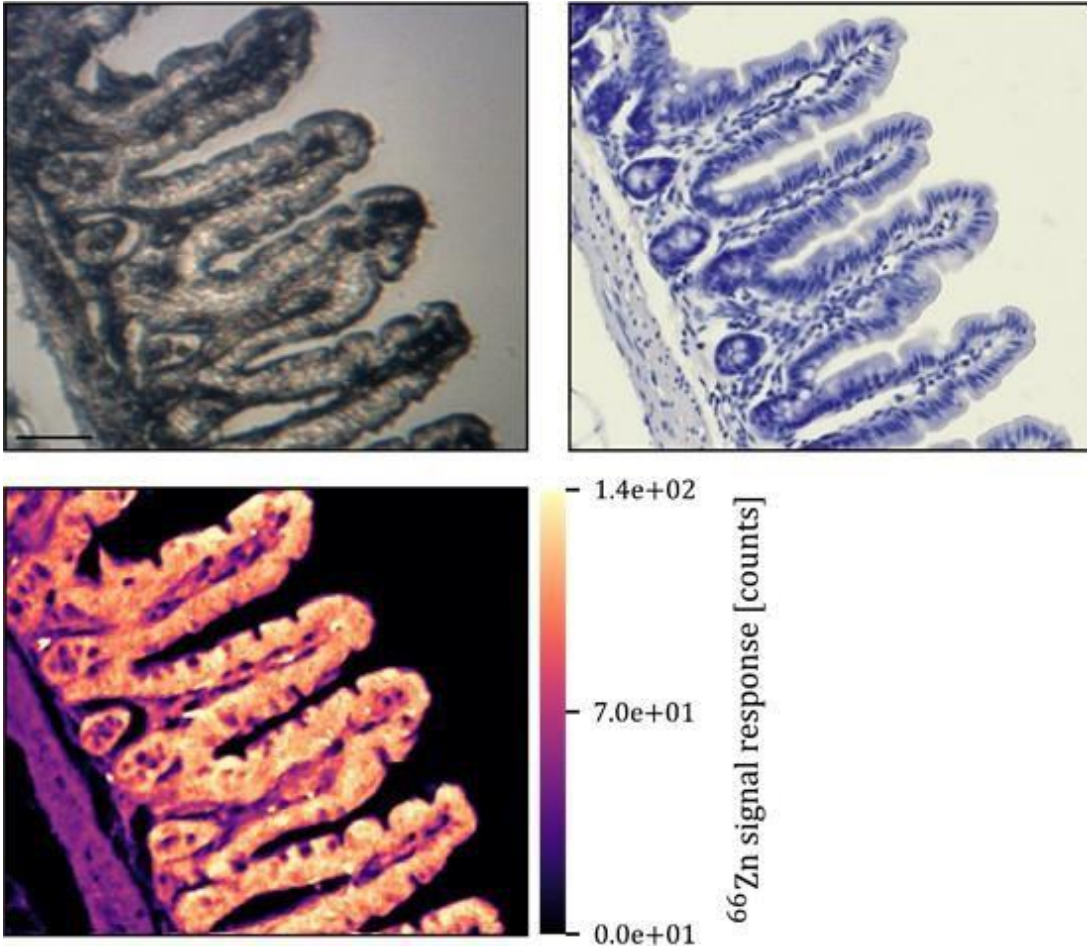
Audio content is not available in this format.



Age mapping zircon (Chew et al., Trinity College, Dublin)

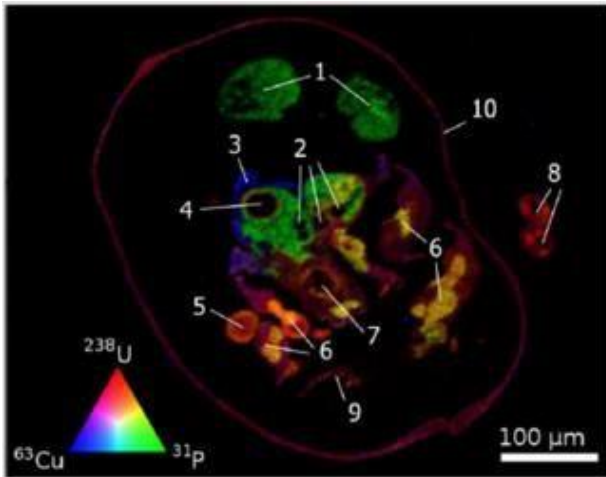


Audio content is not available in this format.



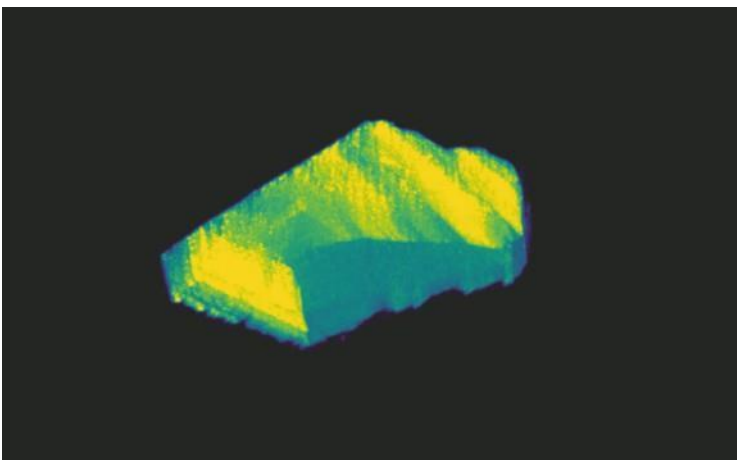
Laser imaging mouse small intestine (Thibaut Van Acker, Ghent University, Belgium).

Audio content is not available in this format.



Laser imaging a water flea (Stijn Van Malderen, Ghent University, Belgium).

Audio content is not available in this format.



3-D imaging of zircon

## Application Areas



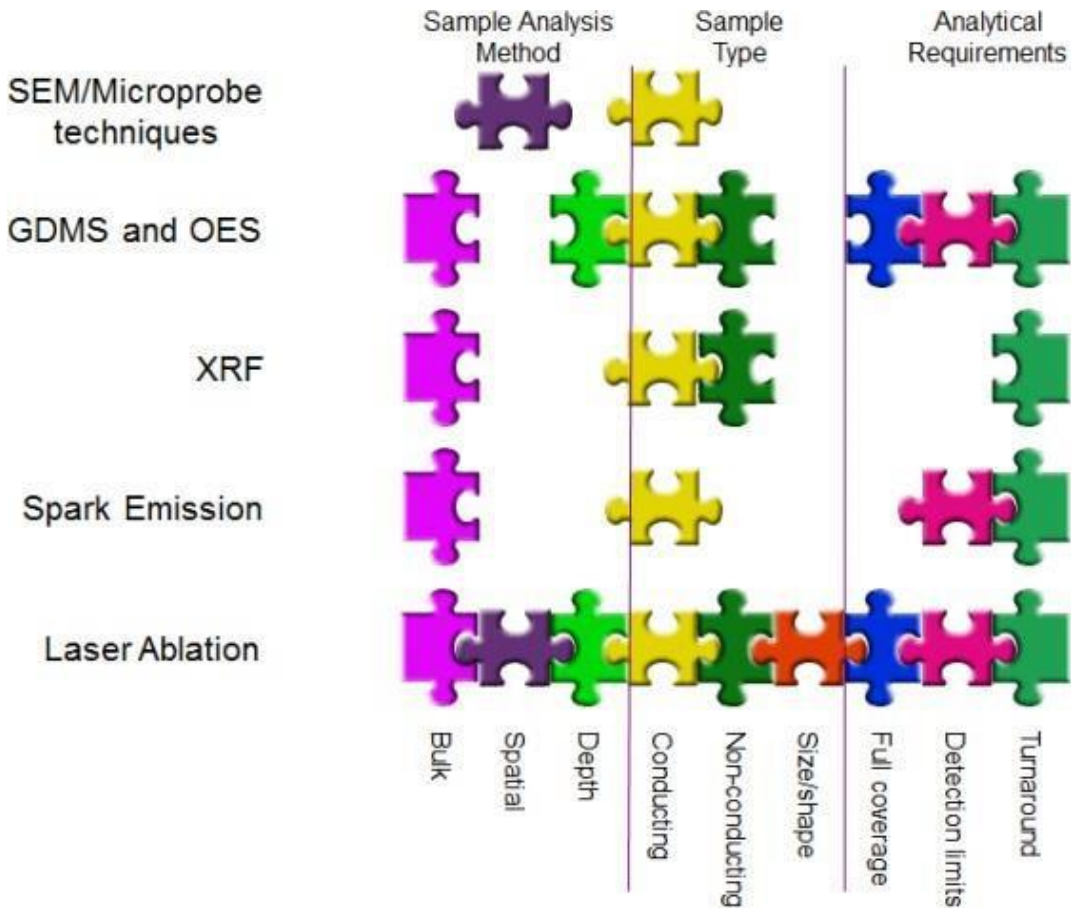
- **Earth Sciences**  
Minerals, toxic elements, zoning, U-Pb dating, coral, environmental record, etc.
  - **Forensics**  
Glass, paint, plastic, metals, inks, etc.
  - **Archeology**  
Ceramics, shards, bone, teeth
  - **Pharmaceutical**  
Tablet powders and coatings
  - **Metals**  
- Alloys, precious metals, QC and defects, etc.
  - **General Industrial Materials**  
Glass, quartz, silicon, etc
  - **Biological/Medical**  
Tissue (frozen or dried), bone, teeth, etc.
- .....



Some of the application areas for LA-ICP-MS

Finally, in the following audio, Nick Westaway compares the LA-ICP-MS technique to other in situ techniques.

Audio content is not available in this format.



**In situ techniques**

For further examples of the way that we use LA-ICP-MS and solution ICP-MS data to place new constraints on processes such as the evolution of the Earth’s mantle and crust throughout the history of the Earth, the behaviour of elements during volcanic eruptions and the formation of economically important ore deposits, see this [list of recent publications](#).

## 3 Getting started

### Introduction

While working through the 'Getting started' material, we suggest that you open a new browser window so that you can easily switch between this teaching material and our Virtual LA-ICP-MS software. This will make it easier for us to talk you through the use of our virtual LA-ICP-MS lab. Additionally, for people who do not spend most days using excel, we give some simple worked examples showing the steps needed to assess the quality of your data and to make various geochemical plots.



## Safety first

Audio content is not available in this format.



### Laser warning

We have tried to make our virtual laser as realistic as possible. When you fire the laser, you will hear the laser firing (note: this will get annoying!) and you will see a flashing light on your screen. If you suffer from epilepsy or you are prone to light-triggered migraines, please click the 'don't show flashing effects on laser' checkbox below (also available

within the virtual lab) to disable the flashing laser effect. Everything else will work the same. Below there is a video of the laser flashing, which will help you make your decision.

Video content is not available in this format.

When you are running the laser, you will see a light that flashes at 5 Hz (5 hertz means 5 times per second) or 10 Hz (10 times per second). The video above may help you decide if you want to disable this aspect of our virtual LA-ICP-MS. Note: The only sound is the hum of the machine, so there is no transcript.



Most laboratories are clean areas and our lab manager is quite strict about the need to change from your outdoor shoes into your lab shoes before you enter our lab.

## Overview of the Virtual LA-ICP-MS functions

When you enter the Virtual LA-ICP-MS lab, you will see two windows.

The screenshot shows the Virtual LA-ICP-MS lab interface. The top navigation bar includes 'Welcome', 'Learn about LA-ICP-MS', 'Getting started', and 'Virtual LA-ICP-MS lab'. The left panel has tabs for 'Sample change', 'ICP-MS', and 'Laser'. It includes a search bar, a table for sample settings, and a visual representation of a sample disc with four spots. The right panel has tabs for 'Scan list/ messages', 'Signal monitor', and 'Data output'. It includes a search bar, a table for scan data, and a messages section.

Setting	Sample disc
*Reference material*	NIST SRM 612
*Reference material*	BCR-2G
Backarc	MANUS-1

Spot number	Sample name	Spot size (µm)	Rep rate (Hz)
No data available in table			

Showing 0 to 0 of 0 entries Previous Next

**Messages:**  
No samples in the sample cell.  
Helium is not on.  
ICP-MS is not tuned.

### LA-ICP-MS lab initial windows

The window on the left of the screen-shot above has three tabs. These tabs let you flick between the different windows that are used to control the LA-ICP-MS hardware:

**Sample change:** use this window to load your samples into the laser ablation cell

**ICP-MS:** Use this window to control the ICP-MS

**Laser:** Use this window to control the laser ablation (LA) system

The window on the right also has three tabs that can be used to switch between the following windows:

**Scan list/Messages:** This window records the order in which you want to analyse your volcanic glasses. It also gives a summary list of messages of the tasks that need to be completed for you to collect ICP-MS data.

**Signal monitor:** This window lets you watch the change in signal intensity of elements that are being measured by the ICP-MS when you 'fire the laser'!

**Data output:** this window lets you see your LA-ICP-MS data and export the data as an Excel spreadsheet.

If you get stuck at any point, we have included 'more info' buttons on each of the windows of our Virtual LA-ICP-MS lab.

A rectangular button with rounded corners and a light blue border. The text "More info" is centered in a blue font.

More info button

When you press the 'More info' boxes you will see a list of the pages in this 'getting started guide' that might be able to help you if you get stuck.

Next, we will take you through each of the different tabs in a bit more detail and we will give you a few tasks to do :-)

## Handy hints from the virtual technician

Before we do anything, take a look at the 'Scan list/Messages' tab. At the bottom of this window there will be a list of 'messages' from our virtual technician that you need to solve before you can undertake any analyses:

*No external reference material (NIST SRM 612) loaded in the sample holder (required for data calibration)*

*No reference material (BCR-2G) loaded in the sample holder (required for data quality check)*

*No samples in the sample cell.*

*Helium is not on.*

*Laser is not on (you can't ablate samples).*

*Plasma is not on (you can't measure the contents of elements).*

*ICP-MS is not tuned.*

*No elements selected for analysis.*

The screenshot shows the 'Virtual LA-ICP-MS lab' interface. The 'Sample change' tab is active, displaying settings for reference materials and a sample disc image. The 'Messages' window, circled in red, displays the following error messages:

```

Messages:
No external reference material (NIST SRM 612) loaded in the sample holder
(required for data calibration)
No samples in the sample cell.
Helium is not on.
Laser is not on (you can't ablate samples).
ICP-MS is not tuned.
No elements selected for analysis.

```

## Messages

Don't worry, we will take you through each of the tasks. This one-to-one level of teaching is something that we give each of our new users that enter our LA-ICP-MS lab. These 'messages' are instructing you to complete tasks that every scientist needs to do each day when they come in to use our LA-ICP-MS. The tasks are listed in the order that you would usually complete sequentially each morning when you start a LA-ICP-MS session.

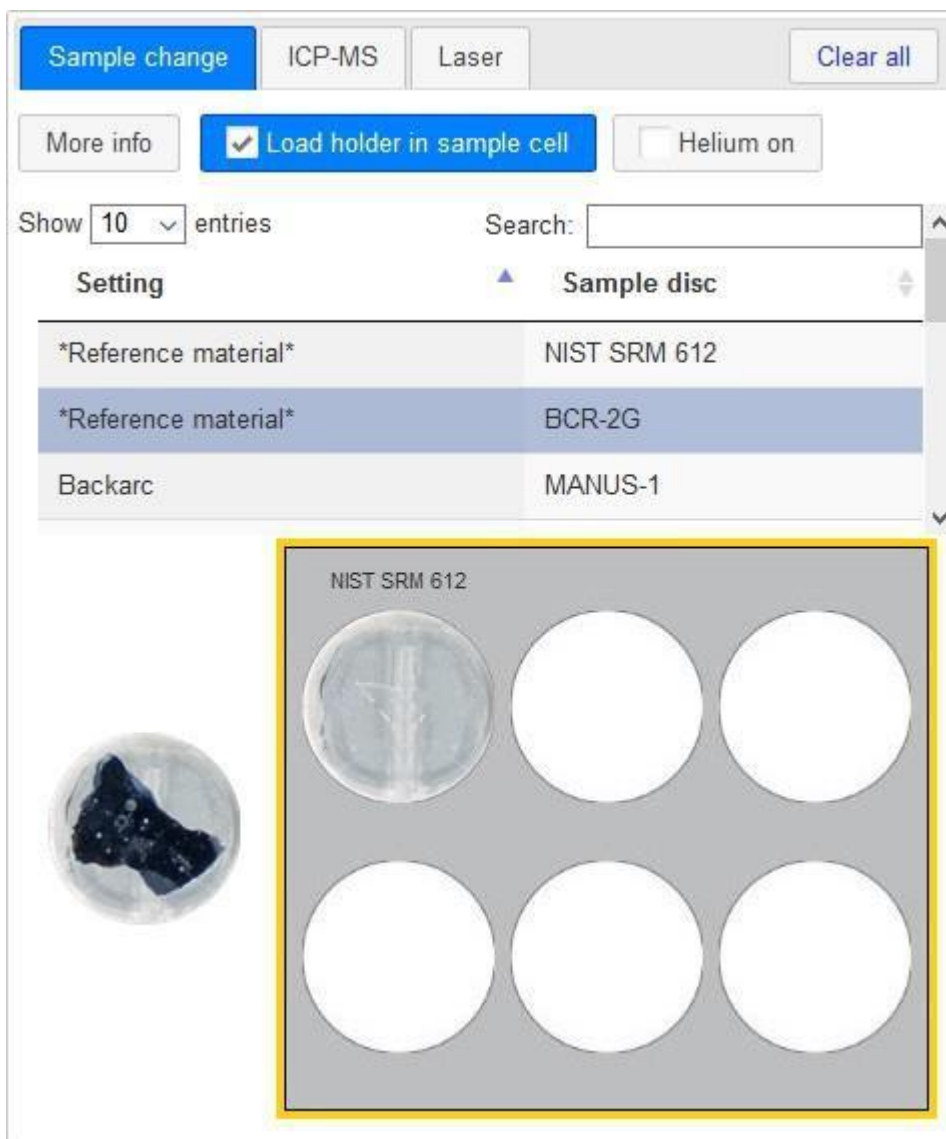
If at any point you want to go back to the start of a Virtual LA-ICP-MS session, click the 'Clear all' button at the top right of the 'Sample change' tab. You will notice that this option sends you back to our 'welcome message' window. Please note, clicking this option will reset **all** of the Virtual LA-ICP-MS settings that you have chosen (i.e., in all of the different tabs) and will clear the data from the data output table. Hence, **only** click this button if you are confident that you want to finish your virtual LA-ICP-MS session.

## Getting to know the sample change tab

First things first. You need to decide which samples and reference materials you want to analyse to solve the first three tasks in the 'messages' from the virtual technician.

- No external reference material (NIST SRM 612) loaded in the sample holder (required for data calibration)
- No reference material (BCR-2G) loaded in the sample holder (required for data quality check)
- No samples in the sample cell.

The 'Sample change' window shown below allows you to choose different samples to place in the sample holder for analysis by LA-ICP-MS. As shown below, the sample holder can hold six epoxy disks.



### The 'Sample change' window

LA-ICP-MS analysis requires that the user analyses their 'unknown' samples in batches and each batch must be bracketed by analyses of a 'known' sample. The 'known' sample is referred to as an 'external reference material' and the analysis of the external reference material is required to calculate the contents of elements in your unknown sample. Because the analysis is essential to data reduction, we always analyse the external reference material twice (i.e., two ablations on the same piece of glass), in case something unexpected happens during the analysis. Unexpected things commonly happen when you are doing ICP-MS work!

If you have two unknown samples, the order that you would set up ablation sites for analysis would be:

1. **known (external reference material)**
2. **known (external reference material)**
3. unknown (e.g., volcanic glass)
4. unknown (e.g., volcanic glass)
5. **known (external reference material)**



## 6. known (external reference material)

External reference materials are samples that are used by the global community of geochemists, because the contents of most of the elements in the standard reference material are known to very high levels of precision and accuracy. The most commonly used external reference materials are the **National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 612** (NIST SRM 612 for short), NIST SRM 610 and occasionally, NIST SRM 614.

Because we use the NIST SRM 612 glass for tuning the ICP-MS and to quantify the compositions of our unknown samples, you must load the NIST SRM 612 glass in the sample holder during each analytical session. You also need to load an additional reference material, BCR-2G, in the sample holder, which you will need to check that the Virtual LA-ICP-MS is running properly and is collecting accurate and precise data.

## Why are the NIST glasses different colours?



### Different NIST glasses

In the picture above you will see three round circles and one epoxy mount. From left to right these glasses are NIST SRM 614, NIST SRM 612 and NIST SRM 610. We have cut the NIST SRM 610 and NIST SRM 612 glasses in half and we have mounted them in epoxy for analysis. You will notice that the NIST SRM glasses are different colours...

GeoRem is a website that many geochemists use on a regular basis to find information regarding the contents of elements in different standard reference materials. Click [here](#) to be directed to the GeoRem website. If you are interested, we have written down some instructions below that will let you find the information for the NIST SRM glasses. If not, go straight to the next page of our tutorial.

Once you have clicked on the link to the GeoRem website (<http://georem.mpch-mainz.gwdg.de>), if you click on the 'Samples and Materials (published values)' button (this is located beneath the 'Query GeoRem Database by' button), you can type '612' in the 'Enter a Part of the Sample Name' search.

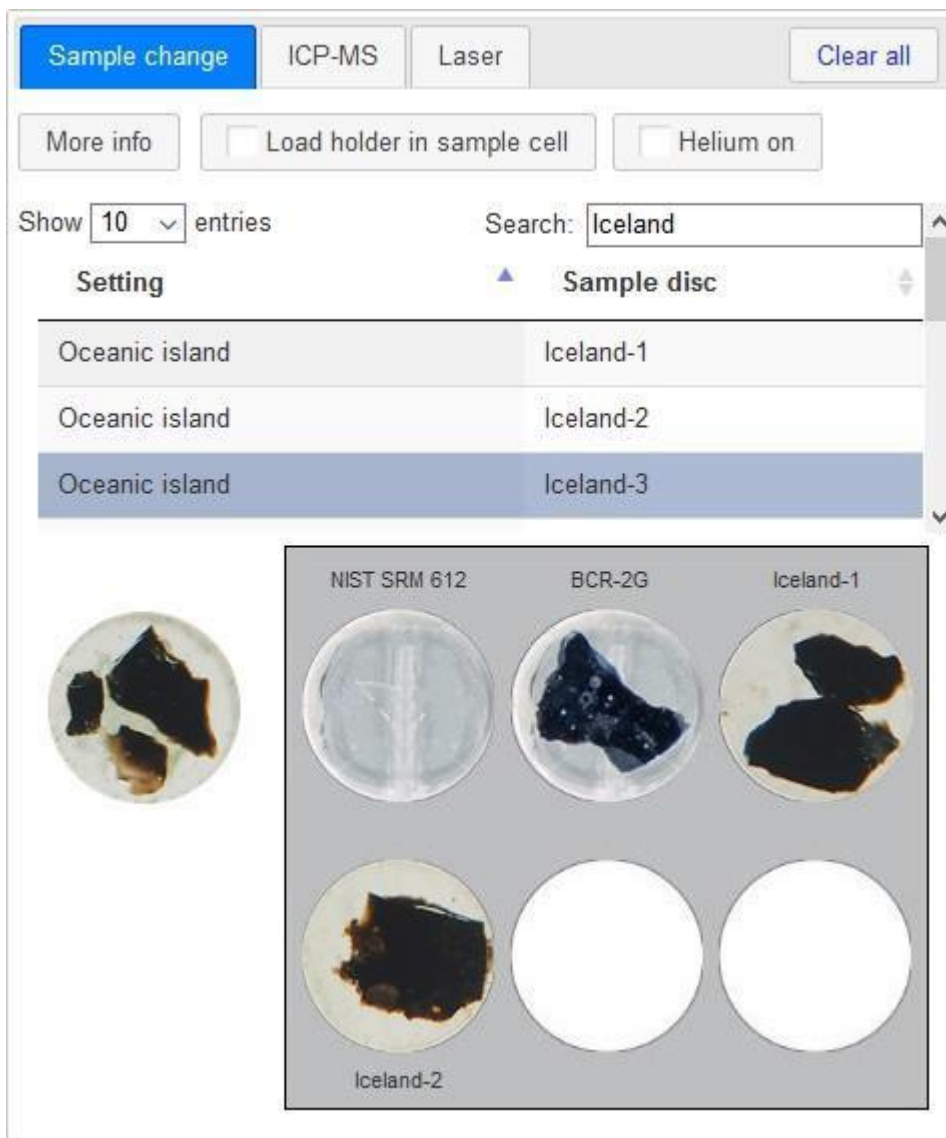
Click on 'NISTSRM612' and then press the 'Add =>' button and then press the 'search' button. If you scroll down you will see the range in published values for the contents of lots of elements in NIST SRM 612. If you then click on the 'Preferred Values' option, you will get a table of the GeoRem preferred values for NIST SRM 612. You will notice that many of the elements have concentrations that are ~30-40 ppm (parts per million). The reason that many elements in the NIST SRM glasses have a similar concentrations is because the NIST SRM glasses and synthetic (man-made) reference materials. Now conduct a similar search for NIST SRM 610.

You will notice that the contents of many of the elements in NIST SRM 610 are ~400-500 ppm. This is because the concentrations of elements in the NIST 610 glass are less diluted with SiO<sub>2</sub> compared to the NIST SRM 612 glass (i.e., NIST SRM 610 has 69.7 wt.% SiO<sub>2</sub> and NIST SRM 612 has 72.1 wt.% SiO<sub>2</sub>). These compositional differences are why the NIST SRM 612 (light blue) and NIST SRM 610 (dark blue) glasses have different colours!

Unlike the NIST SRM glasses, BCR-2G is a fused (heated to extremely high temperature in a platinum crucible and then rapidly cooled) glass of a powdered volcanic rock. If you use GeoRem to conduct a search for BCR-2G, you will see that the compositions of volcanic samples are quite different from the synthetic NIST glasses.

## Loading your samples in the sample cell

As shown in the screen-grab below, a selection of different volcanic glasses from various tectonic settings are listed in the table above the sample holder.



### Sample change tab

If you click on one of the samples in the table, you will see that the image on the left of the sample holder changes. The search bar allows you to limit the list of samples that you have to choose from (you can scroll up and down through the list). For example, if you type 'Backarc' into the search, you will see a list of samples from a backarc tectonic setting.

Once you have decided which sample you would like to put in the holder, simply click on the image of the sample that is pictured next to the holder and drag the sample into any of the empty spaces within the sample holder. To *remove* the sample from the holder, you simply need to 'click' on the sample that you want to remove.

Once you have loaded your samples in the sample cell, you need to put the sample holder in the laser cell. To do this, click on the 'Load holder in sample cell' button to ensure it is selected (blue).

Load holder in sample cell

'Load holder in sample cell' button

Once you have pressed this button you will notice that the 'no samples in the sample cell' task has now been removed from the list (see Scan list/Messages window).

As discussed in the 'Learn about LA-ICP-MS' tab, the laser sample cell is filled with helium for analysis. Hence, once you have loaded the sample holder into the laser ablation cell, you need to press the 'Helium on' button to ensure it is turned on.

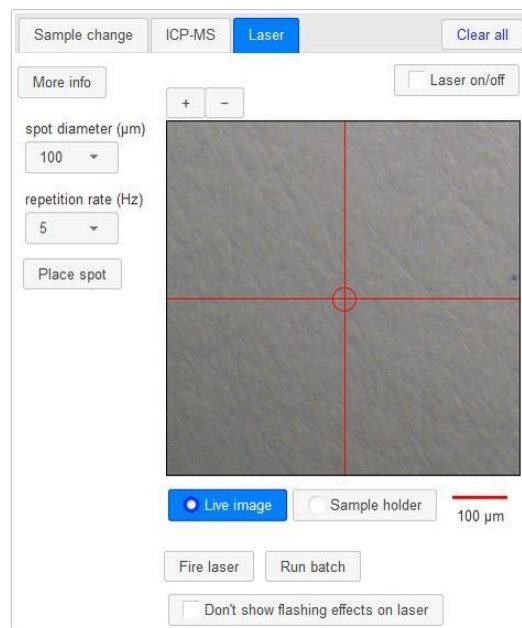
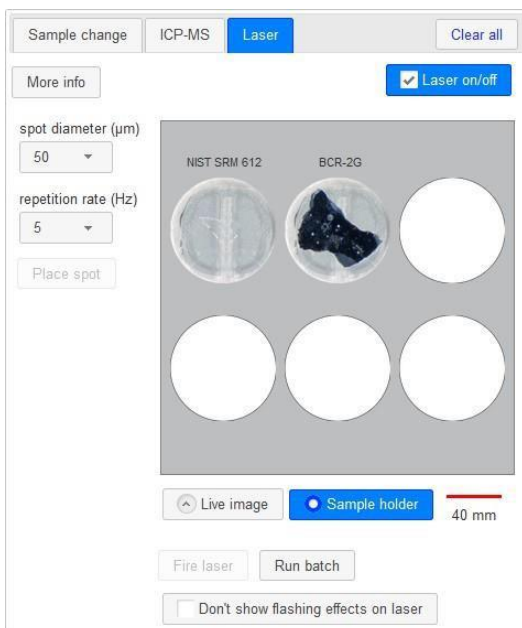
 Helium on

'Helium on' button

Now the 'no samples in the sample cell' task has now been removed from the list (see Scan list/Messages tab) and we are ready to learn about the use of the laser :-)

## Viewing your samples in the sample cell

Now that our samples are in the sample holder, let's have a look at them a little closer at higher resolution and using reflected light. First, click on the 'Laser' tab and you will see images like the ones below. Take a look at the screen-grab image on the left. You will notice that the 'Sample holder' button is blue. On the image to the right, the 'Live image' button is blue.



### Laser windows

When the 'Sample holder' button is pressed, in the centre of the laser window you will see an image of the sample holder. The 'Sample holder' view allows you to see a scanned image of your selected samples in the sample holder.

If you tap on one of the samples, a close-up image of the sample will suddenly appear! If you look at the bottom of the image, you will see that the 'Live image' button is now active

(highlighted blue). If you click on the 'Sample holder' button, you will go back to a view of the entire holder.

Click the 'Live image' button again. The 'live' image option allows you to view the sample that you have selected through the camera on the laser ablation system. The centre of the red cross marks the location that the laser will ablate when it is turned on! You will notice that the image is lot higher quality than the scanned 'Sample holder' image.

To move the same around, you simply need to 'click' and drag the sample around using your cursor. You can use the zoom buttons above the image to zoom in (+) and out (-) of the image.



Zoom buttons

If you want to take a look at one of your other samples, simply click the 'Sample holder' button and select a different sample. Easy!

## Turning on the laser

The next message from the virtual technician that is on your list of tasks that you need to complete (Scan list/Messages window) is the 'laser is not on' error. This problem is easy for you to solve.

Find a bit of glass that you would like to ablate using the laser. Now cast your eyes down to the bottom left-hand corner of the laser window and you will see a button labelled 'Laser on/off'.



Laser on/off

When you click on this button you will see a tick icon and the button will turn blue. You will also see that the 'laser is not on' message from the technician has now gone (see Scan list/Messages tab). Now that the laser is on WE ARE READY TO FIRE THE LASER!!!!!! Sorry, we get a bit excited about 'lasering' things, so we accidentally shouted there.

Below is a video showing you what to expect when you are firing the laser on our virtual LA-ICP-MS. WARNING: only click 'play' here if you are OK with flashing images.

Video content is not available in this format.

N.B. This video contains flashing lights. The only sound is the hum of the machine, so there is no transcript.





Time to have a go at firing the laser on our Virtual LA-ICP-MS yourself! First, make sure that you click the 'live image' button. Now, if you look at the bottom of the 'laser' tab and you will see a button labelled 'fire laser'.



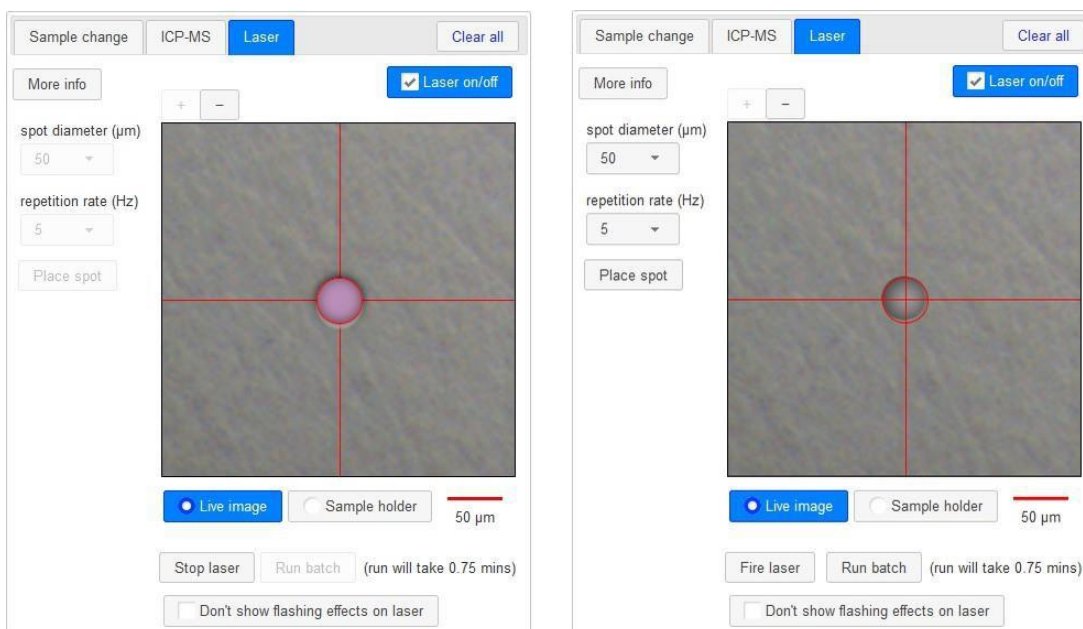
### Fire laser button

Click this button and you will notice that the laser is firing and is flashing at a rate of 5 pulses per second (5 Hz). The laser will automatically stop firing after 30 seconds. While the laser is firing, the fire laser button instead reads 'stop laser'. This button allows you to manually stop the laser from firing at any point. If you now look at your sample, you will see that you have ablated a hole in it!

If the laser has stopped firing, press the 'fire laser' button again. Now click on the 'sample holder' button and you will notice that you cannot see the laser firing. This is because the sample holder image is a scanned image and only the 'live image' button allows you to watch what the laser is actually doing.

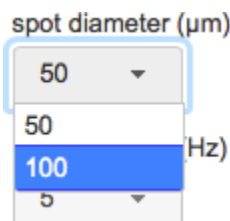
## Spot sizes and repetition rates

The laser is programmed to only fire for 30 seconds before stopping. Click the 'fire laser' button again. While the laser is firing you will notice that you are not able to move the sample stage. You will also notice that the boxes on the left of the sample holder are a light grey colour and you cannot select them. Once the laser has stopped firing, you will notice that the boxes on the left of the sample stage image are now a darker grey colour and you can now use the drop-down options. Below are two screen-grabs which also show you the differences in selection options when the laser is either firing (image on the left) or not firing (image on the right).



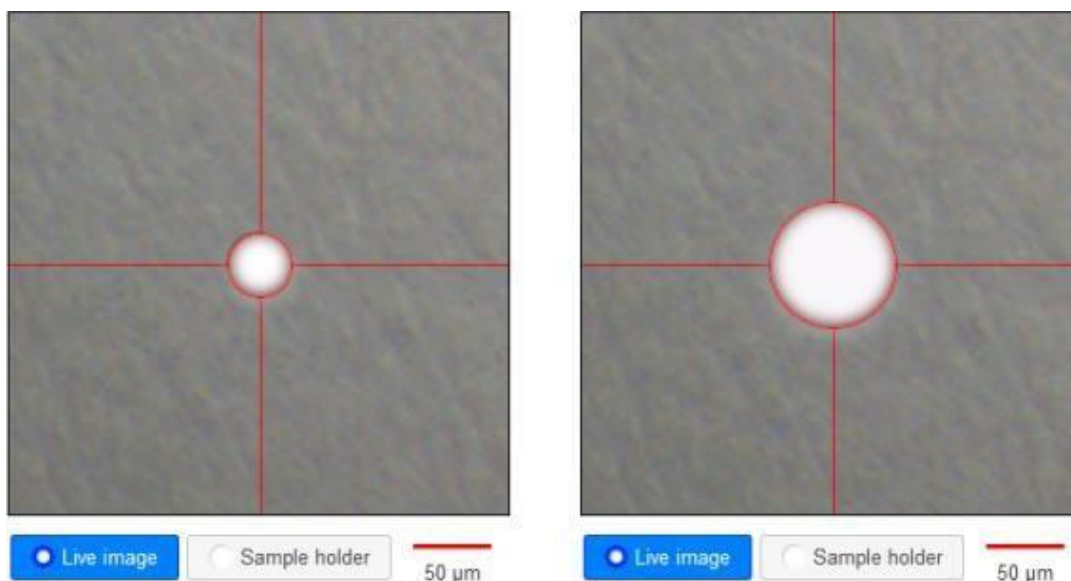
Options available when Laser is firing and not firing

The spot diameter drop-down box (see image below) gives you two choices. You can either ablate a 50  $\mu\text{m}$  diameter laser ablation pit (note, this is the default spot size that you just used) or you can ablate a 100  $\mu\text{m}$  laser ablation pit.



The spot diameter drop-down box

On the live image, you will be able to see that the size of the two spot diameter options are different. We also demonstrate this point in the screenshots below. The scale bars on both images are identical. The image on the left shows the 50  $\mu\text{m}$  ablation pit that we just made. When you select the 100  $\mu\text{m}$  spot size (image on the right), you will see that the spot size is bigger than the pit that you just ablated using the 50  $\mu\text{m}$  spot size.



Different spot sizes

There are also two repetition rate options, 5 Hz and 10 Hz. The 10 Hz selection means that the laser is firing 10 times per second. Have a go at firing the laser using the two different settings to see if you can notice the difference.

We have given you only two repetition rates and two spot sizes to choose from when using our Virtual LA-ICP-MS. However, in our LA-ICP-MS lab the laser can be used to ablate a large range of different spot sizes and shapes. It gets very noisy on the days that we are running the laser at >100 Hz!

An analyst decides which laser settings to use depending on the material that they are analysing. If they are analysing really small samples, they would choose the smaller ablation size. However, if the contents of the elements that they are analysing are really low (e.g., selenium in volcanic glasses), they would want to increase the amount of material that they are sending to the ICP-MS to measure. Hence, they would likely choose to use the biggest laser ablation spot possible.

The repetition rate shows a similar effect to differences in the spot diameter. The faster you fire the laser, the more material enters the ICP-MS per second. However, this means that you drill through your sample very quickly!

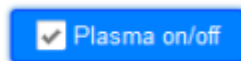
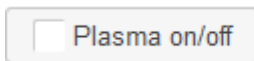
## Using the ICP-MS tab to light the plasma

Now that you have had a play around with the different functions in the laser window, it is time to deal with the next error message that is listed in the 'Scan list/Messages window: the 'plasma is not on' error. Click on the ICP-MS tab which lets you see the window that allows you to control the ICP-MS. Yes, it is time to produce something that is hotter than the surface of the sun!

The screenshot shows the ICP-MS control interface. At the top, there are tabs for 'Sample change', 'ICP-MS' (selected), and 'Laser', along with a 'Clear all' button. Below the tabs, there is a 'More info' button and a 'Plasma on/off' button with a checked checkbox. Underneath, there are three sliders labeled 'torch (x)', 'torch (y)', and 'carrier gas'. A 'Tune ICPMS' button is also present. The main area displays a periodic table with Gallium (Ga) highlighted in a blue box. The box contains the atomic number '31', the element name 'Gallium', the symbol 'Ga', and the atomic weight '69,71'. The periodic table itself has several elements highlighted in orange, including Li, Be, Na, Mg, Al, Si, P, S, Cl, Ar, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Kr, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Xe, Cs, Ba, La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, At, Rn, Fr, Ra, Ac, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, Ts, Og, and the Lanthanides (Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and Actinides (Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr).

### ICP-MS tab

To analyse elements using LA-ICP-MS, we obviously need an inductively coupled plasma! To light the plasma, click the 'plasma on/off' button on the top right of the ICP-MS tab.



Plasma on/off

Once the 'plasma on/off button turns blue, you will notice that the 'plasma is not on' message from the technician has disappeared from the list. Another task completed!

## Picking elements that you want to analyse

Now that the plasma is on you need to select the elements that you want to analyse. If you click the ICP-MS tab and view the ICP-MS window, you will find the periodic table. The elements in the periodic table that you are able to analyse in volcanic glasses are shaded orange. Some of the other elements (the ones in grey) are also possible to analyse using LA-ICP-MS (e.g. Te). However, the contents of many of these elements are extremely low in volcanic glasses (e.g., often less than one part per billion). Hence, you can't select those elements because we don't have enough LA-ICP-MS for the simulation.

1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lanthanides		58	59	60	61	62	63	64	65	66	67	68	69	70	71		
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides		90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Periodic table

If you move your cursor over the different elements on the periodic table, a blue box will appear above the periodic table (see screen-grab below).

<div style="border: 1px solid black; padding: 5px; width: fit-content; margin: 0 auto;"> <p><b>34</b>                      <b>Selenium</b></p> <p style="text-align: center;">74,76,77,78,80,82</p> <p style="text-align: center;"><b>Se</b></p> </div>																	
1																	2
H																	He
3	4											5	6	7	8	9	10
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	Selenium	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lanthanides		58	59	60	61	62	63	64	65	66	67	68	69	70	71		
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
Actinides		90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

### Periodic table - Selenium

This box shows the name of the element, its symbol, the atomic weight and mass and the first ionization potential of the element. To select the elements that you want to measure, simply click on the element on the periodic table. The elements that you select to analyse will turn red. *Everyone, Most* Ok fine, ONE of our lab team really loves selenium. Hence, we have selected 'selenium' in our example above.

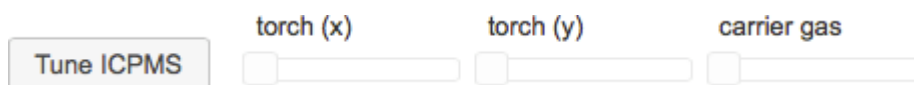
If you want to remove an element from your analysis list, click the element and if it is not included on your analytical list, it will turn to an orange colour.

You can only select 10 elements at a time using the Virtual LA-ICP-MS lab. This is not the case for actual ICP-MS systems (we often analyse 50 elements in one routine). We have limited the selection to a maximum of 10 elements for teaching reasons. This is to ensure that our students have to make decisions regarding which elements they want to analyse to answer different scientific questions. Hence, you can't simple analyse everything every time using our Virtual LA-ICP-MS!

## Tuning the ICP-MS

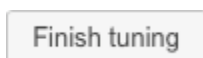
At the start of every analytical session, the ICP-MS is tuned to ensure maximum sensitivity for the elements that you want to measure. The two main settings that are tuned each day are the argon carrier gas rate and the torch position. There are a lot of other settings that we tune daily, such as the various lenses. For simplicity, we have not included the tuning of the lenses in our Virtual LA-ICP-MS lab. You are able to tune the Virtual LA-ICP-MS using functions in the ICP-MS window. There are a series of toggles next to the Tune ICP-MS button (see image below). These toggles control the horizontal (x) and vertical (y) position of the torch and the amount of argon carrier gas that is going through the torch.





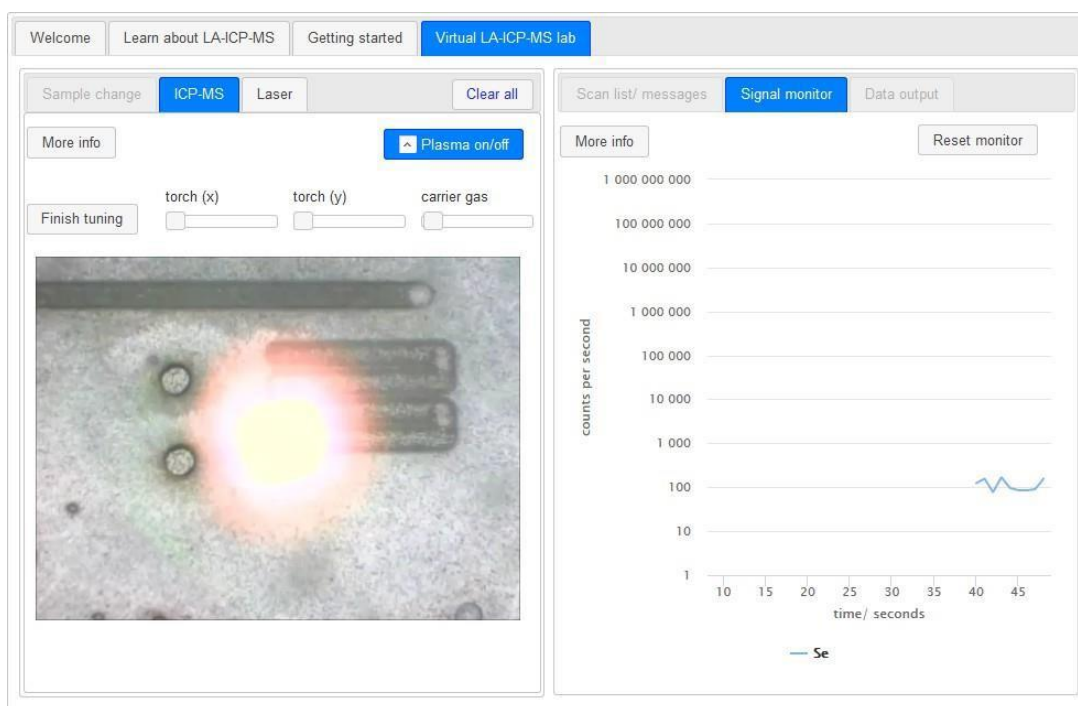
### Tune controls

Now that you have selected your elements that you want to measure (you will receive an error warning if you have not selected some elements), you can click the 'Tune ICP-MS' button that is located in the ICP-MS window. Once you click this button, it will now instead say 'Finish tuning'.



### Finish tuning button

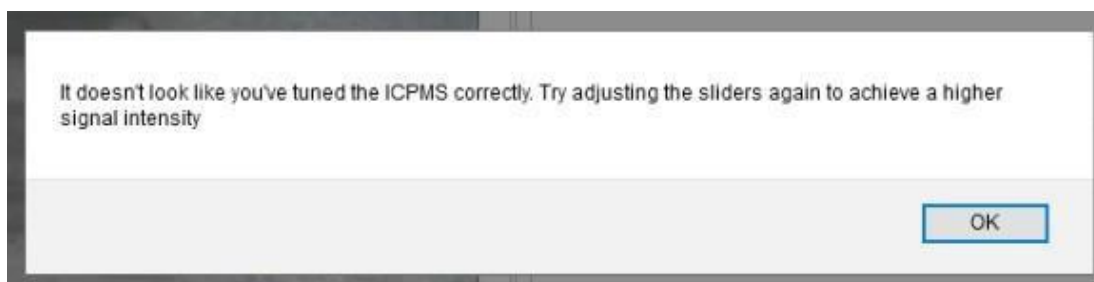
When you clicked the 'Tune ICP-MS' button, a video will appear in the place where the periodic table used to be and the window on the right will automatically change to the signal monitor window (see screen-grab below).



### 'Tune ICP-MS' windows

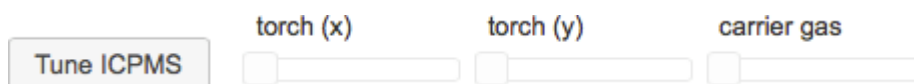
The video on the left shows the laser ablating a line on the NIST SRM 610 glass. Ablating in a line is used to send a constant signal to the ICP-MS so that it is easier for you to see if your tuning of the torch position and the carrier gas are increasing or decreasing the sensitivity of the ICP-MS. Note, if you click on the 'laser' tab and view the laser window, you will see that the laser is ablating the NIST SRM 610 glass.

The signal monitor shows the counts per second of each of your selected elements and how they change with time during ablation. Because we have not tried to tune anything yet, the counts per second of selenium are really low. The Virtual LA-ICP-MS will not let you continue unless you improve the tuning!!! For example, try clicking the 'finish tuning' button. You will see the following message:



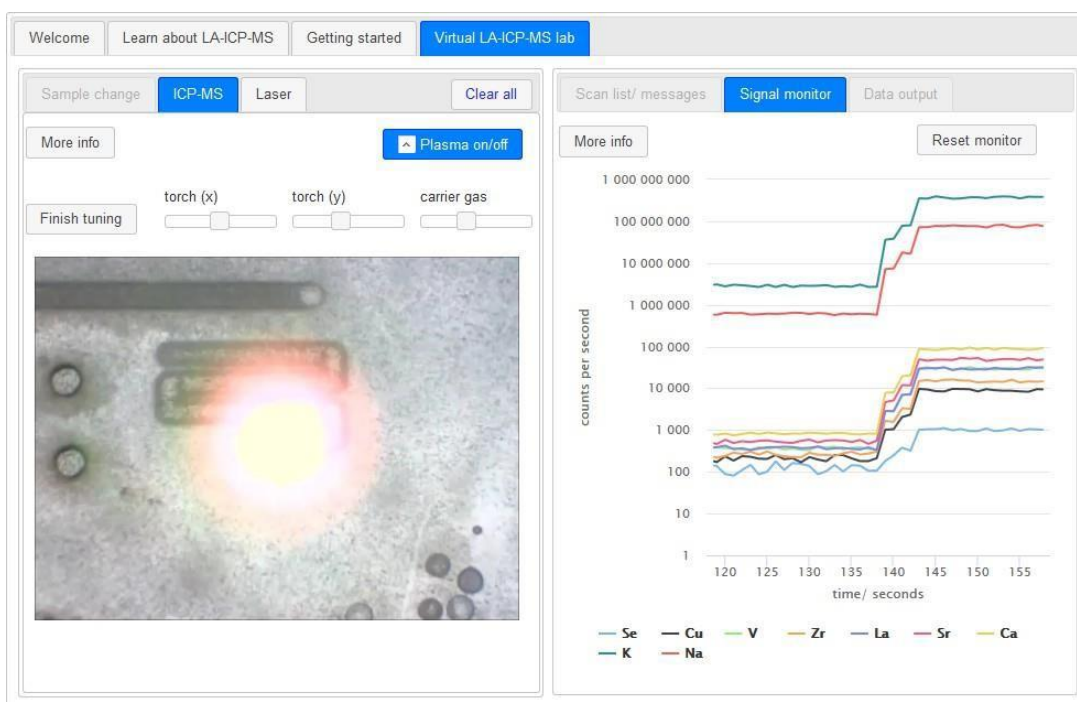
### Not tuned alert message

We do not let any users run the LA-ICP-MS on samples until they have demonstrated that the ICP-MS is tuned properly. Hence, you need to close this window and try to improve the tuning! Located within the ICP-MS window are three sliders that can be used to adjust the torch position and the carrier gas.



### Tune controls

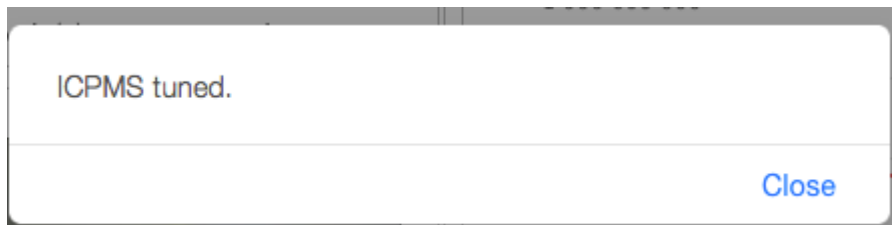
To improve the tuning you need to adjust the torch position and argon carrier gas rate to maximise the counts for your selected element. Try moving the torch (x), torch (y) and carrier gas sliders. In the example below, you can see that the counts per second of various elements in the signal monitor window are variable rather than constant. This is because we moved the sliders around and changed the tuning.



### Results of adjustments

You should be able to find a combination of settings for the three sliders that gives you a maximum amount of counts per second compared to other combinations. When you are

happy you can click the 'Finish tuning' button. Hopefully, when you press the 'finish tuning' button we will be happy with the job that you have done with the tuning and you will see the message below.



Tuned alert message

Now that you have completed the tuning, click on the Scan list/Messages tab.

The screenshot shows a software interface with several tabs: 'Scan list/ messages' (highlighted in blue), 'Signal monitor', and 'Data output'. Below the tabs are three buttons: 'More info', 'Go to selected spot', and 'Delete selected row'. There is a 'Show 10 entries' dropdown and a 'Search:' input field. A table with four columns is shown: 'Spot number' (with an upward arrow), 'Sample name', 'Spot size (µm)', and 'Rep rate (Hz)' (with a double-headed arrow). The table body is empty, with a message 'No data available in table' centered. Below the table, it says 'Showing 0 to 0 of 0 entries' and has 'Previous' and 'Next' buttons. At the bottom left, there is a section labeled 'Messages:'.

Scan list/ messages tab

You should be excited to see that we not have no more messages from the virtual technician!!!! We are now ready to start doing analyses!!!!

## Setting up a batch of analyses

The next thing that we need to learn how to do is to set up spots that you want to analyse. To do this, you need to go back to the laser window by clicking on the laser tab. Please also click on the Scan list/Messages tab and your Virtual laser windows should look the same as in the screen-grab below.

The screenshot shows the 'Virtual LA-ICP-MS lab' interface. The 'Laser' tab is active, displaying a live image of a sample with a red crosshair. The 'Scan list/ messages' tab is also visible, showing a table with columns for Spot number, Sample name, Spot size (µm), and Rep rate (Hz). The table currently displays 'No data available in table'.

**Virtual LA-ICP-MS lab**

Sample change | ICP-MS | **Laser** | Clear all

More info |  Laser on/off

spot diameter (µm): 50

repetition rate (Hz): 5

Place spot

Live image | Sample holder | 100 µm

Fire laser | Run batch

Don't show flashing effects on laser

**Scan list/ messages** | Signal monitor | Data output

More info | Go to selected spot | Delete selected row

Show 10 entries | Search:

Spot number	Sample name	Spot size (µm)	Rep rate (Hz)
No data available in table			

Showing 0 to 0 of 0 entries | Previous | Next

Messages:

### Scan list/Messages and Virtual laser windows

If you look at the Scan list/technician window, you will see that the table currently says 'no data available in table'. In the laser window, now press the 'place spot' button. If you press the zoom (+) button a few times, you will see that a yellow cross now appears on the glass. Additionally, if you compare the screen shot below to the screen shot above, you will see that the text in the Scan list table now has an entry! You have just set up your first laser ablation spot!

The screenshot shows the Virtual LA-ICP-MS lab interface. The top navigation bar includes 'Welcome', 'Learn about LA-ICP-MS', 'Getting started', and 'Virtual LA-ICP-MS lab'. The main interface is divided into several sections:

- Sample change / ICP-MS / Laser:** Includes a 'Clear all' button and a 'Laser on/off' checkbox (checked).
- More info:** A 'Place spot' button.
- spot diameter (µm):** A dropdown menu set to 50.
- repetition rate (Hz):** A dropdown menu set to 5.
- Live image:** A central window showing a green sample with a yellow crosshair. Below it are 'Live image' (selected) and 'Sample holder' radio buttons, and a 100 µm scale bar.
- Buttons:** 'Fire laser', 'Run batch (run will take 0.75 mins)', and 'Don't show flashing effects on laser' (checkbox).
- Scan list/ messages:** Includes 'More info', 'Go to selected spot', and 'Delete selected row' buttons.
- Table:** A table with columns for Spot number, Sample name, Spot size (µm), and Rep rate (Hz). It shows one entry: Spot number 1, Sample name NIST SRM 612, Spot size 50, and Rep rate 5.
- Navigation:** 'Showing 1 to 1 of 1 entries', 'Previous', '1', and 'Next' buttons.
- Messages:** A section labeled 'Messages:'.

### Scan list table with an entry

Because this is the first spot that you have placed, the spot number in the left-hand column of the table in the Scan list/ Messages window reads '1'. The next to the right gives the sample name. The next two columns have recorded the spot diameter (50 µm) and the repetition rate (5 Hz) that the laser will use for the analysis. For example, if you look at the laser window, you will notice that the 'spot diameter' and the 'repetition rate' settings also read as 50 µm and 5 Hz.

Now use the drop-down boxes in the laser window to change the spot diameter size to 100 µm and the laser repetition rate to 10 Hz. Now move the stage slightly (press anywhere on the live image to move the sample around), so that the spot that you have already placed is now in the bottom left quadrant of the live image. Press the 'Place spot button' again (located in the laser window). You should now have two yellow crosses (see screen grab below). Additionally, the spot position cross that you have just placed should be bigger than the first spot position cross that you placed. If you look at the screen-grab below, you will see that we now have two lines in our table in the Scan list/ Messages window. You will also notice that the ablation settings for Spot number 1 and Spot number 2 are different (e.g., the spot sizes are different).



The screenshot shows the 'Virtual LA-ICP-MS lab' interface. On the left, the 'Laser' control panel includes a 'Live image' window showing a green sample surface with a red crosshair and a yellow spot. Below the image are controls for 'spot diameter (µm)' (set to 100), 'repetition rate (Hz)' (set to 10), and buttons for 'Fire laser', 'Run batch', and 'Don't show flashing effects on laser'. On the right, the 'Scan list/ messages' panel displays a table with two entries:

Spot number	Sample name	Spot size (µm)	Rep rate (Hz)
1	NIST SRM 612	50	5
2	NIST SRM 612	100	10

The table also shows 'Showing 1 to 2 of 2 entries' and navigation buttons for 'Previous', '1', and 'Next'.

### Scan list table with two entries

If you click on the first row in the scan list table, it will become highlighted a blue colour as show in the screen grab below.

This close-up screenshot shows the 'Scan list/ messages' panel. The first row of the table is highlighted in blue. The table data is as follows:

Spot number	Sample name	Spot size (µm)	Rep rate (Hz)
1	NIST SRM 612	100	5
2	NIST SRM 612	50	10

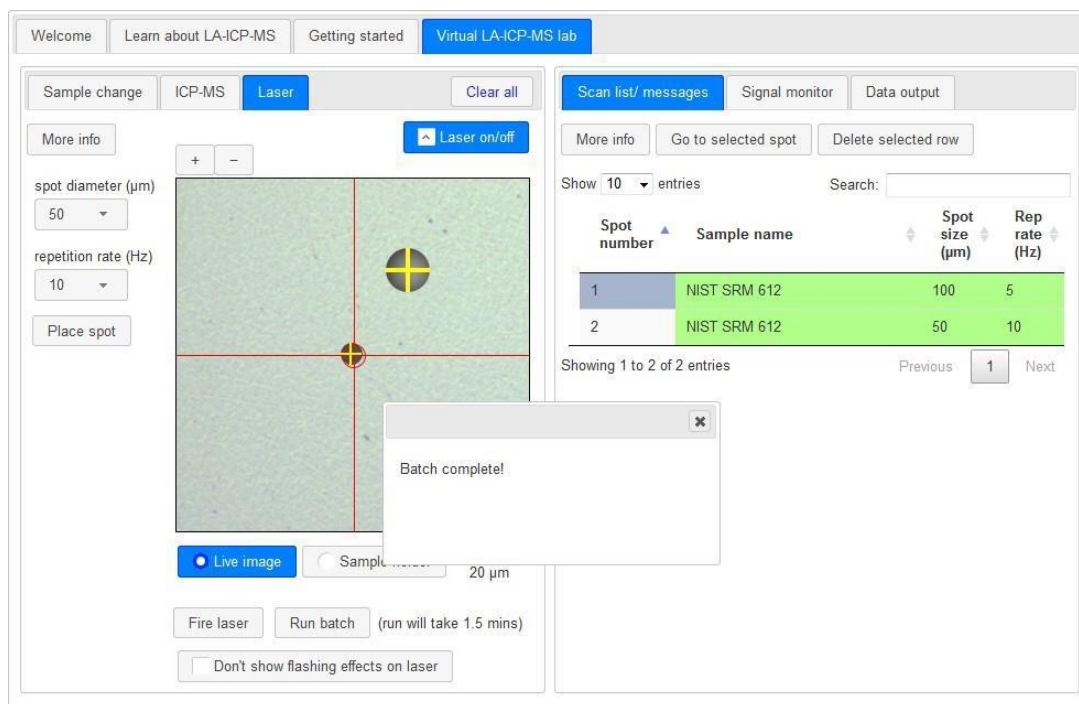
The interface also shows 'Showing 1 to 2 of 2 entries' and navigation buttons for 'Previous', '1', and 'Next'.

### First row in the scan list table highlighted

If you now press the 'Go to selected spot' button above the scan list table, you will see that the live image video on the laser window moves to place the centre of the red cross over the first spot that you chose!

Now press the 'Delete selected row' button that is also located in the Scan list/errors window and you will see that the first spot that you placed has now been removed.

Now that we have an entry in the scan list, we are ready to run this analysis! Press the 'run batch' button that is at the bottom of the laser window. When you press this button, the LA-ICP-MS will automatically start analysing the volcanic glass! When the analysis has finished, you should see a message saying 'Batch complete'!



Batch complete message

Close the 'Batch complete' message and next we will show you how to retrieve your data.

## Downloading your new data

Now that you have run your first analysis you 'probably' will want to look at your data! Now click on the 'Data output' tab and view the 'Data output' window.

As shown in the screen-grab below, the table within the 'Data output' window now has an entry that includes the data that you just produced! If your data table is too large to fit within the window, simply scroll back and forwards and you will see that you are able to view different parts of the table. To retrieve the data, you can either choose to press the copy button and to paste the data into an Excel or a Word document, or you can download the data as an Excel table by pressing the 'Excel' button.

Sample name	Se (ppm)	Cu (ppm)	V (ppm)	Zr (ppm)	La (ppm)	CaO (wt%)
BCR-2G	0.285	21.283	421.665	183.476	25.006	7.084
BCR-2G	0.274	21.096	421.506	185.349	24.553	7.051

### Data output tab

The data in the table is presented in units that are either weight percent oxide (wt.%) or parts per million (ppm).

You might have noticed that something 'magical' has occurred. The data that you collected has been converted from counts per second (CPS) to contents without you having to do anything (i.e., you have not had to 'reduce the data'). This is because the data-reduction software that is required to reduce the data and to convert it to concentration data is quite expensive to purchase and is quite difficult to use.

### Compiling your final dataset

LA-ICP-MS is typically used to measure the contents of elements that are in low abundances. Additionally, as discussed on Slide 11 of the 'Learn about LA-ICP-MS' Tab, to convert the ion signal intensities measured using LA-ICP-MS into contents of element in a given sample, requires prior knowledge of the content of one element in the material that is being analysed. Although the virtual laser outputs all the data that you collected without you needing to undertake 'data reduction', if you click on the 'Download major element data for volcanic glasses' link provided on the Data output window, you will be able to access major element (analysed using the Electron Probe Micro analyser, or EPMA for short) and volatile element data (analysed using Secondary Ion Mass Spectrometry, or SIMS for short) for all the volcanic samples listed in the Sample Change tab. You might even want to look at the range in compositions before you choose which glasses that you want to load in the sample holder before starting your analytical session!

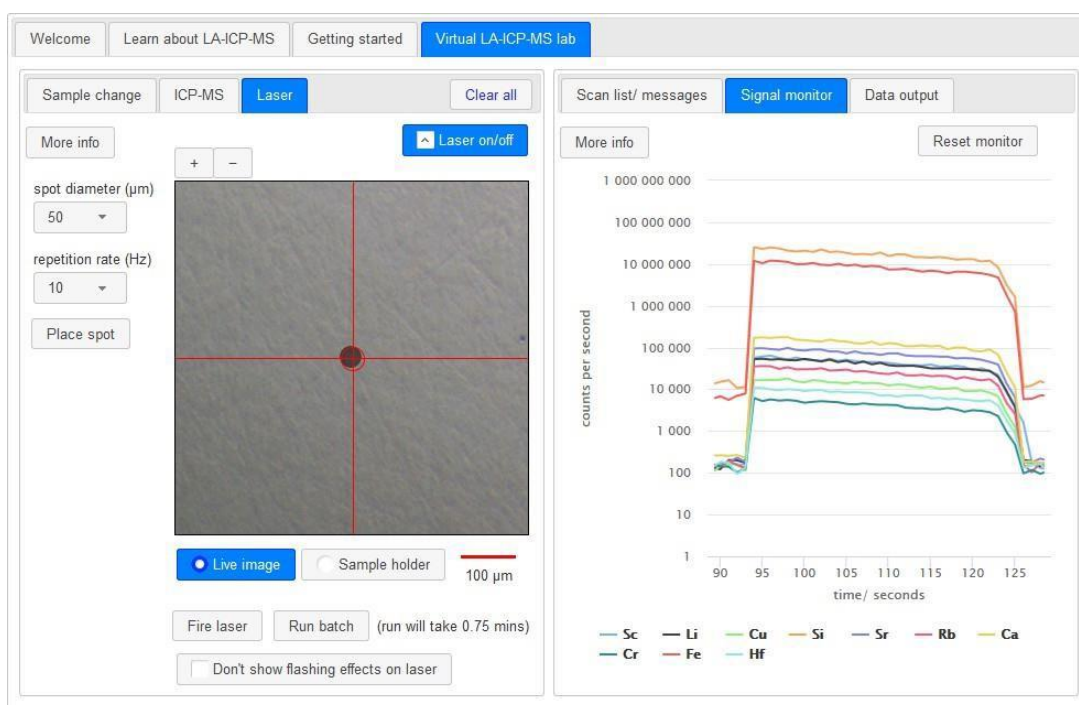
## What does the ICP-MS show when I fire the laser?

We have just learned how to run an analysis. However, things were happening quite fast during the analysis, so we did not get a chance to show you what the ICP-MS records when we turn on the laser and start ablating a signal!

When we undertake LA-ICP-MS analyses, the information that we are interested in is the increase in counts per second (CPS for short) during ablation, compared to the machine background CPS. To allow us to demonstrate this point, please select the laser tab and the signal monitor tab.

The CPS that are currently being recorded by the signal monitor represents the machine background. The machine background is different for each element. If the laser is positioned over a sample and you press the 'fire laser' button in the laser window, you will notice that the CPS for each element rapidly increases. The laser will fire for 30 seconds. When the laser stops firing, the CPS for each of the elements quickly decrease back to the background levels.

We have captured the start and the end of an ablation in the screengrab below so that we can talk you through a few interesting points about the laser ablation signal that is recorded by the ICP-MS.



### Ablation signal

As we mentioned above, the signal rapidly increases as soon as you start the laser and rapidly decreases when the laser stops firing. This is because our laser ablation system has something called a 'rapid washout'. This means that within less than a second after then laser has stopped firing, the signal (CPS) for the majority of elements are back to 'background levels' and you are ready to undertake another analysis. To be able to achieve this rapid washout has taken a number of decades of developments by the manufacturers. Part of the push to decrease the washout time is because this is essential for laser imaging.

Take another look at the laser scan above and you will notice that the signal slowly declines during the analysis while the laser is firing. This is because the diameter of the laser decreases during ablation. Consequently, with time during ablation 1) less material is being ablated and the signal declines and 2) elements find it more difficult to get swept up by the helium flow in the sample cup and the signal decreases.

## Running a batch of standards

Before we analyse any precious samples, we always start our analytical session by analysing the composition of a reference material. We measure the contents of our

selected elements in the reference material and then we compare our new data with published 'preferred values' for that reference material. If the data is in good agreement with the published data, we are then ready to analyse our volcanic glasses. Every morning we undertake 3 repeat analyses of the reference material BCR-2G for a large range of elements, which is loaded in the sample holder beneath the NIST SRM glasses. BCR-2G is a man-made glass, but unlike the NIST SRM synthetic glasses which were intended to have the majority of elements at the same contents, the BCR-2G glass was manufactured by heating natural basaltic composition rock powders to produce a magma and this magma was then quenched rapidly to form a glass.

Next, we would like you to set up a batch of 3 analyses of BCR-2G for the elements Si, Ca, Ti, V, Cu, Zr, Nb, Ce, Gd and Lu. Remember, each batch of analyses needs to be bracketed by 4 analyses of NIST SRM 612. Hence, your scan list table should end up with this order:

1. NIST SRM 612
2. NIST SRM 612
3. BCR-2G
4. BCR-2G
5. BCR-2G
6. NIST SRM 612
7. NIST SRM 612

Now go to the Data output tab and download your data using the excel button. Also in the Data output tab, you will see a button labelled 'reference material values'. If you press this button, you will automatically download a table with the contents of lots of elements in BCR-2G and NIST SRM 612. These are what we call 'preferred values' and they are used to assess the accuracy of the data that you have produced.

Open up the Excel file with your new analyses and you will see that you now have data for Si, Ca, Ti, V, Cu, Zr, Nb, Ce, Gd and Lu for your three analyses of BCR-2G. The first thing that we need to calculate is the precision of the data. To do this, first click on cell B7 beneath your data. Type '=average(B3:B5)' in the cell and press 'enter'. You have now calculated the average BCR-2G value for your three analyses. In the cell below (B8), now type '=stdev(B3:B5)' and press 'enter'. You have now calculated the standard deviation, which is a measure of how widely the three analyses vary from the average value. In the cell below now type '=100\*B8/B7' and press enter. You have now calculated the relative standard deviation (RSD) as a percentage (%).

You will notice that the %RSD is different for different elements. This is because the precision of analyses varies as a function of the content of an element (i.e., the lower the content the harder it is to measure elements) and other factors such as natural variability in samples.

The next thing that we need to do is to look at the accuracy of the data. To do this, we need to compare your new analyses of BCR-2G with the preferred values. If you now open up the preferred values table, you will see data for each of the elements that you analysed. We need these values in your data table. First, find the value for SiO<sub>2</sub> and click on the content (i.e., the SiO<sub>2</sub> of BCR-2G is 54.4 wt.%). Now paste this value into cell B11 of your data table. You need to do this for all 10 elements that you analysed. Now go to cell B12 and type '=B7/B11' and press 'enter'. You have now calculated the average/preferred value. If the analysis is perfect, the value should be 1. Anything within 10% of the preferred value (i.e., a value between 0.9 and 1.1) is pretty good, although you will notice that many elements are quite a lot more accurate (closer to 1) than that.



## Setting up a long batch of analyses

Now that you have successfully run a batch of analyses and you are confident about the data quality, it is time to set up a long list of analyses of volcanic glasses. We need you to set up a batch of 30 analyses of your 'unknown' samples to demonstrate some extra features of our Virtual LA-ICP-MS lab software.

First thing that you need to consider is how many NIST SRM 612 analyses you are going to need. 30 analyses take quite a bit of time to measure and the LA-ICP-MS tuning might change during the analysis of a long batch of samples (e.g., sometimes it can get a little bit less sensitive during the day). This effect is called 'instrument drift'. Hence, you will need to analyse the samples in a few batches to ensure that you have enough NIST SRM 612 analyses for your calibrations (see also page 5 of the 'Getting Started' section).

We don't like to analyse any more than a **maximum of 20 samples** without doing two analyses of our known standard reference material (NIST SRM 612). Hence, we might as well separate the 30 'unknown' analyses into two batches of 15 unknowns. We also want to make sure that we analyse our 'known composition unknown' (BCR-2G) in each batch to ensure that the data is accurate (we usually analyse BCR-2G three times within each batch). Hence, the running order of your sequence of analyses will probably end up looking like this:

1. **NIST SRM 612 (calibration material)**
2. **NIST SRM 612 (calibration material)**
3. unknown 1
4. unknown 2
5. unknown 3
6. unknown 4
7. unknown 5
8. unknown 6
9. unknown 7
10. unknown 8
11. unknown 9
12. unknown 10
13. unknown 11
14. unknown 12
15. unknown 13
16. unknown 14
17. unknown 15
18. BCR-2G (data quality monitor)
19. BCR-2G (data quality monitor)
20. BCR-2G (data quality monitor)
21. **NIST SRM 612 (calibration material)**
22. **NIST SRM 612 (calibration material)**
23. unknown 16
24. unknown 17
25. unknown 18
26. unknown 19
27. unknown 20

28. unknown 21
29. unknown 22
30. unknown 23
31. unknown 24
32. unknown 25
33. unknown 26
34. unknown 27
35. unknown 28
36. unknown 29
37. unknown 30
38. BCR-2G (data quality monitor)
39. BCR-2G (data quality monitor)
40. BCR-2G (data quality monitor)
41. **NIST SRM 612 (calibration material)**
42. **NIST SRM 612 (calibration material)**

Once you have set up your sequence, we can show you a few extra features of the software. In the screen-grab below you will notice that there are lots of spot locations marked on the 'live image' view of the 'laser' window. In the example below we have quickly placed 20 spots on the same glass sample and it is ok for you to also do that in this worked example. Once you have set up all of your analysis points you will notice that only 5 of the entries are shown in the table within the 'Scan list/Messages' window below.

The screenshot shows the 'Virtual LA-ICP-MS lab' software interface. The main window is titled 'Laser' and contains a 'Live image' of a sample with 20 yellow crosshair spots. The 'spot diameter (µm)' is set to 50 and the 'repetition rate (Hz)' is set to 10. Below the image are buttons for 'Fire laser' and 'Run batch (run will take 21.75 mins)'. On the right, the 'Scan list/ messages' window displays a table with 7 entries for 'BCR-2G' with a spot size of 50 µm and a repetition rate of 10 Hz. Below the table is a 'Messages' section.

Spot number	Sample name	Spot size (µm)	Rep rate (Hz)
3	BCR-2G	50	10
4	BCR-2G	50	10
5	BCR-2G	50	10
6	BCR-2G	50	10
7	BCR-2G	50	10

### Multiple spots

If you move your cursor up and down over the table, you will see that you will be able to scroll up and down and view only 10 of the different sample positions.

At the bottom of the table you will see a series of buttons numbered 1, 2 and 3. Button '1' is currently selected (the button has a square around it) and there is text saying 'Showing

1 to 10 of 30 entries'. If you press button '2', the text now says, 'Showing 11 to 20 of 30 entries'. In case you are having any problems, we show these features in the screen grab below.

Scan list/ messages	Signal monitor	Data output
More info	Go to selected spot	Delete selected row
6	BCR-2G	50 10
7	BCR-2G	50 10
8	BCR-2G	50 10
9	BCR-2G	50 10
10	BCR-2G	50 10
11	BCR-2G	50 10
12	BCR-2G	50 10

Showing 1 to 10 of 30 entries Previous 1 2 3 Next

Messages:

Scan list/ messages	Signal monitor	Data output
More info	Go to selected spot	Delete selected row
16	BCR-2G	50 10
17	BCR-2G	50 10
18	BCR-2G	50 10
19	BCR-2G	50 10
20	BCR-2G	50 10
21	BCR-2G	50 10
22	BCR-2G	50 10

Showing 11 to 20 of 30 entries Previous 1 2 3 Next

Messages:

### Scan list/ messages pages

If you scroll back up to the top of the Scan list table, you will see that there is a drag down-box within the Scan list/errors window, that indicates that you are showing '10 entries'.

Show 10 entries

### Show 10 entries

If you click on the up down arrows next to the number 10 (see above), you will see that you are able to change the number of entries that are displayed by the table.

Show 10 entries

25  
50  
100

Sample name

### Change number of entries shown

Click on the 'Show 25 entries' option and scroll back down to the bottom of the Scan list table. Your table should look like the screen-grab below: you can now view 25 entries in the Scan list window and there are now only buttons '1' and '2'.

21	BCR-2G	50	10
22	BCR-2G	50	10
23	BCR-2G	50	10
24	BCR-2G	50	10
25	BCR-2G	50	10
26	BCR-2G	50	10
27	BCR-2G	50	10

Showing 1 to 25 of 30 entries      Previous    1    2    Next

Scan list/ messages with 25 entries per page

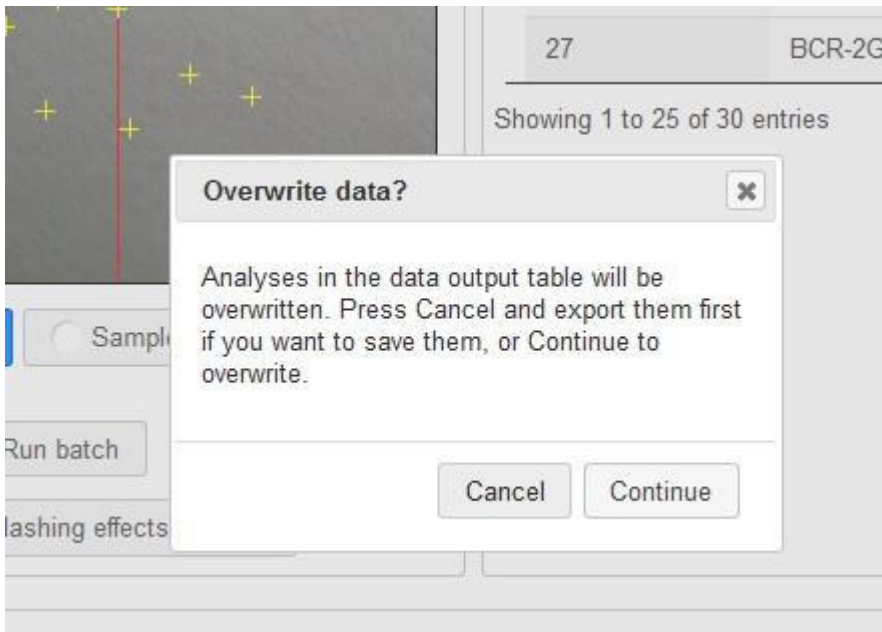
Remember, if you want to go back to one of the locations or delete one of the entries, simply click on the row in the table and press the 'go to selected spot' or 'delete selected row' buttons.

If you scroll back to the top of the window, we have also included a 'Search' option.

Search:

Search box

Now it is time to set your scan running. All you need to do is press the 'run batch' button at the bottom of the laser window. You might see the warning in the screen-grab below. If you have already downloaded your previous analyses or do not want to download your previous analyses, select 'continue' to overwrite the previous analyses. If not, click 'Cancel' and make sure that you download your previous dataset using the 'excel' button in the Data output window. Now press 'run batch' again to continue.



### Overwrite data message

While this long batch is running, it is a good opportunity to have a flick through the different windows to watch what is happening during your analyses. If you click on our video here, you will see that the Virtual LA-ICP-MS experience is close to what we see during our actual LA-ICP-MS sessions. When your batch is done, you can now download your data and you can use excel to make lots of data plots! To give you a few suggestions, click here to view an excel workbook with a selection of different types of plots that geochemists often use when looking at their data.



## Virtual LA-ICP-MS lab

All rights including copyright in these materials are owned or controlled by The Open University and are protected by copyright in the United Kingdom and by international treaties worldwide.

In accessing these materials, you agree that you may only use the materials for your own personal non-commercial use.

You are not permitted to copy, broadcast, download, store (in any medium), transmit, show or play in public, adapt or change in any way these materials, in whole or in part, for any purpose whatsoever without the prior written permission of The Open University.