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Secondary Ion Mass Spectrometry

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Welcome

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We sincerely hope you find our website: www.myscope.training an enjoyable environment. In there you can explore the microscopy space and leave ready to undertake your own exciting experiments.

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Introduction to SIMS – What is SIMS?

Secondary Ion Mass Spectrometry (SIMS) is a technique used to study solid surfaces by sputtering the surface of the specimen with a focused primary ion beam and analysing the ejected secondary ions (figure below). The secondary ions are identified by measuring their mass, thereby determining the elemental, isotopic, and/or molecular composition of the surface.

SIMS instruments are composed of the following fundamental elements:
1. an ion source, that produces the primary ions
2. a primary column, to accelerate and focus the primary ions on to a sample
3. a sample chamber and stage
4. a secondary column, to transport secondary ions to the mass analyser (in LG and nanoSIMS)
5. a mass analyser, which separates secondary ions by their mass to charge ratio
6. a detection system, to count ion species of interest
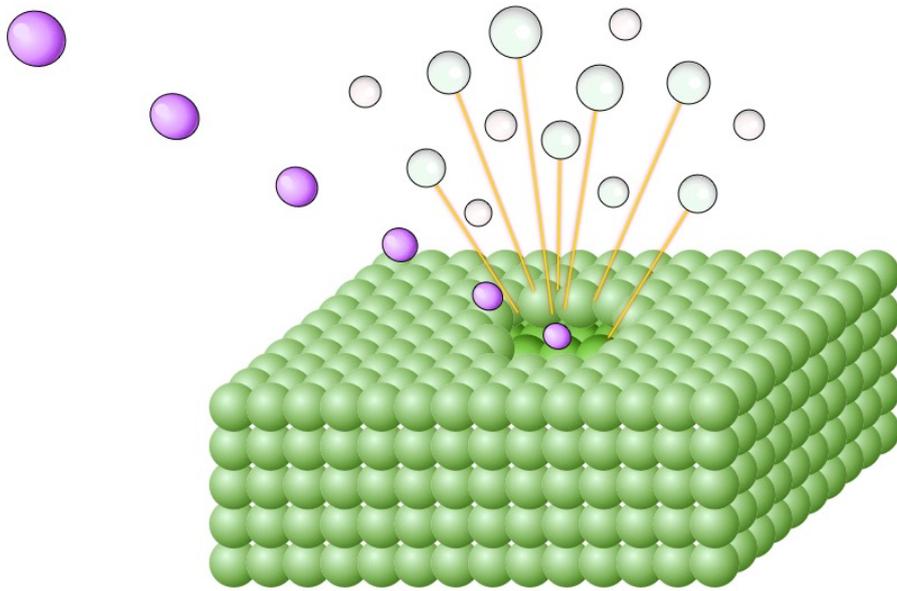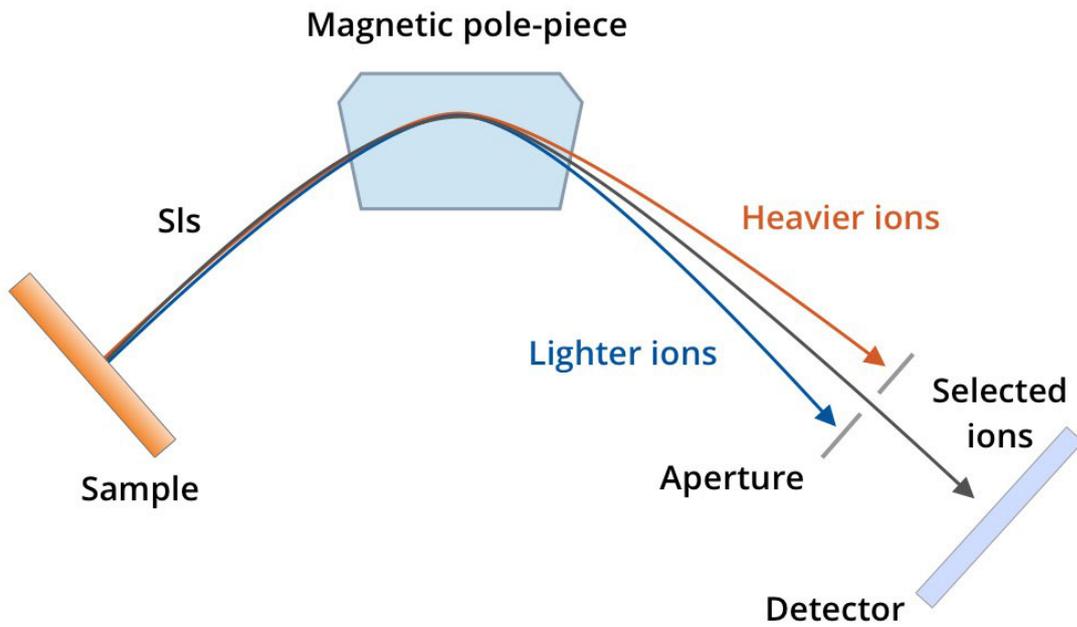
Mass analysers in SIMS

There are three main types of mass analysers used in SIMS instruments.

Quadrupole mass analyser: separates the masses by resonant electric fields, which allow only the selected masses to pass through. Although quadrupole mass analysers are able to scan full mass spectra, their ability to apply a stable field allows you to control which secondary ions pass through. Since fewer ions are scanned per cycle (only those ions within the selected mass-to-charge range), these analysers are able to greatly improve sensitivity towards specific mass peaks.
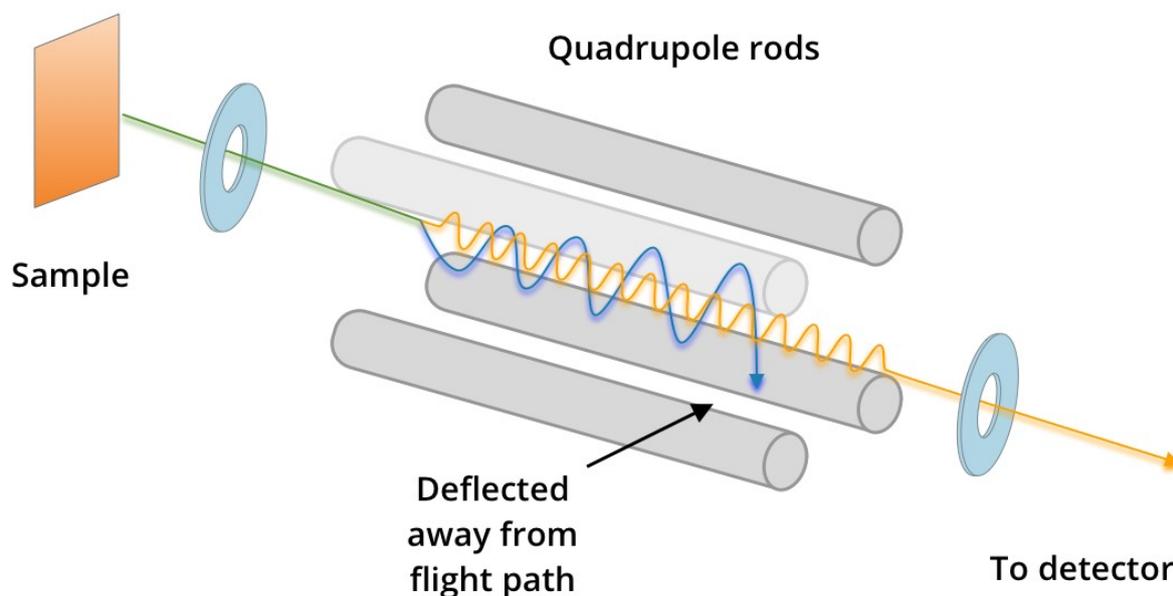

The rods apply a resonant electric field to the SIs passing through the analyser causing them to resonate at particular frequencies. If that resonance is stable (as indicated by the yellow wave), those ions will pass though to the detector. If the resonance is unstable (blue wave), they will be deflected and unable to pass through to the detector. The resonant electric field is set so that ions with the desired mass will achieve stable resonance and therefore be detected.

Magnetic and electrostatic sector mass analysers: a combination of an electrostatic analyser and a magnetic analyser can be used to separate the secondary ions by their mass-to-charge ratio. Magnetic fields deflect ions according to their mass, with lighter ions deflected more than heavier ions (of the same charge). This is helpful when you require refocusing or separation of specific ions. Electrostatic analysers work in a similar manner to magnetic analysers except that they use an electric field to focus ions based on their kinetic energies.

Secondary ions are deflected by a magnetic field, according to their mass, so that only those selected pass through the exit slit and on to the detector.

Time of flight mass analyser: separates the ions in a field-free drift path according to their velocity. Secondary ions with the same charge enter the analyser with the same kinetic energy (E_k). Their velocity (v), and therefore their flight time through the drift path, vary according to their mass (m), as determined by the equation $E_k = 1/2mv^2$.
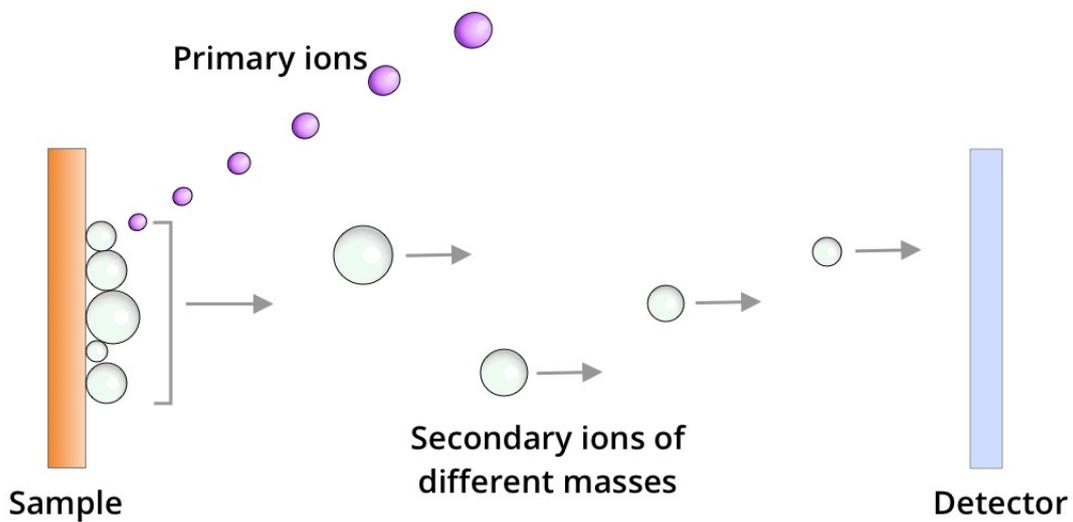
Separation of secondary ions on the basis of their differing masses inside a time-of-flight analyser.

Applications of SIMS

SIMS is used to analyse the distribution and relative concentrations of elements, molecules and isotopes in a solid sample under ultra-high vacuum conditions and is one of the most sensitive techniques for surface analysis. SIMS can be used for imaging, spectrometry and depth profiling/3D analysis.

Applications include:

Geoscience:

- trace element analysis
- stable isotope analysis
- geochemistry and geochronology

Materials science:

Elemental characterisation of surfaces, thin films, multilayered structures and interfaces e.g. dopant profiling in semiconductor devices.

Biology:

Stable isotope labelling for:
- tracking drug delivery
- observing metabolic pathways
- elemental/isotope/molecule mapping

Environmental:

- stable isotope labelling to follow nutrient cycling
- trace element/isotope/molecule identification and spatial analysis – e.g., contamination studies

Nuclear safeguards/forensics:

- uranium particle characterisation
- uranium isotopic characterisation of samples taken from nuclear facilities can provide strong evidence of the activities of that nuclear facility.

Basic principles of SIMS − Ion–Sample Interactions

Particles are liberated from a sample by bombardment with a beam of mono-energetic ions (meaning that all the impacting ions have the same energy). In general, these primary ions are produced either by:

- electron bombardment of gaseous atoms or clusters,
- plasma sources (e.g., duoplasmatron),
- thermal emission, or
- field ionisation (e.g., liquid-metal ion guns [LMIGs]).

They are then accelerated to energies in the kiloelectronvolt range to generate an ion beam.

On impact, the primary ions penetrate the surface of the sample, dissipating their energy through collisions with its constituent atoms. The recoil of these, in turn, displaces other atoms to produce a cascade of collisions, some of which are directed back towards the sample surface. If the momentum transfer to atoms at the surface is sufficient to overcome their binding energies, these are then ejected from the sample.
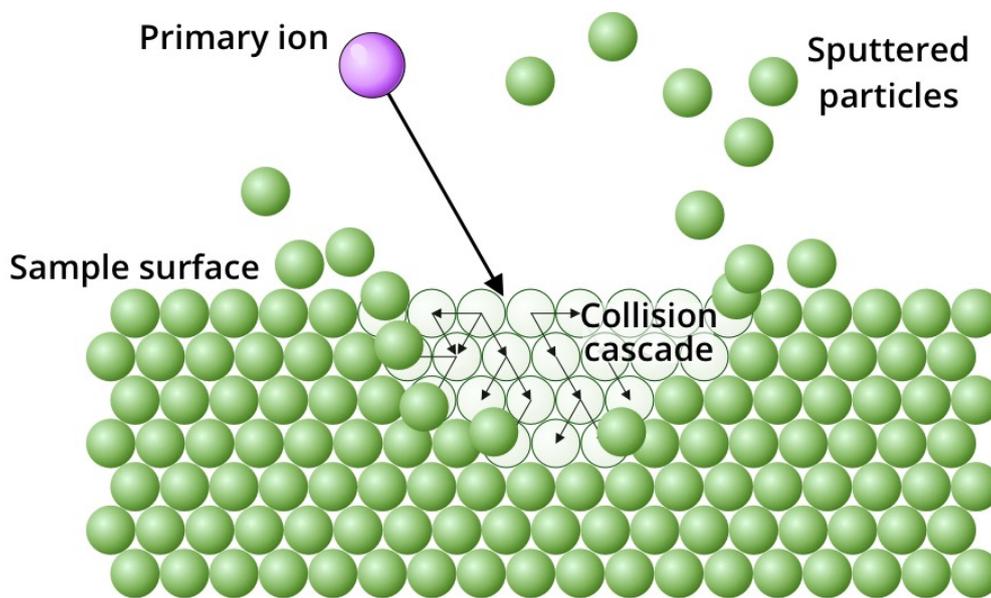
The ejected, or 'sputtered', particles comprise both atoms and molecules, most of which are uncharged. Those ions that are ejected by the bombardment—the 'secondary ions'—are directed to a mass analyser by an electrostatic field and it is only these that are analysed.

Because a particle must be both emitted from the sample and ionised to be detected, the signal intensity for the resultant secondary ion, X^+ or X^-, is dependent on:

- the fractional concentration of X,
- the number of X particles desorbed per primary-ion impact (the sputter yield), and
- the fraction of those that are charged (the ionisation probability).

These are strongly influenced by the chemical environment, often termed as the 'matrix'. For example, the yields of metallic secondary ions from oxidised metal surfaces are between one and three orders of magnitude greater than for the corresponding unoxidised surface. As a consequence, determining concentration from SIMS signal intensity is normally not possible without reference to calibration standards with varying concentrations of a given analyte. This is often not practicable.

Although the primary ions implant themselves to depths in the range of tens of nanometres, leaving a disrupted region in their wake, the majority (>95%) of sputtered particles originate from the two topmost atomic layers. Consequently, SIMS is potentially capable of providing a very surface-specific analysis of composition. However, as each primary-ion (PI) impact results in localised changes in surface composition, it is necessary to avoid 'revisiting' these damaged areas if you intend to

limit your analysis to the sample surface. This can be achieved by keeping the PI dose below 10^{13} ions cm^{-2}, or, more prudently, 10^{12} ions cm^{-2}. Conventionally, analyses carried out with PI doses below this threshold are termed 'static SIMS' as the surface is considered to be unchanged by the analysis.
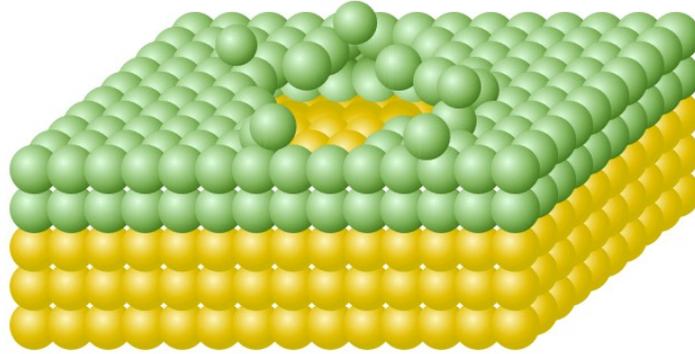
Schematic representation of the damaged region of a sample surface following the impact of a primary ion. Most particles ejected following the initial impact originate from the two outermost atomic layers (green). This exposes the underlying atoms (yellow) to subsequent impacts at the same location.

As the yield of secondary ions decreases with decreasing PI dose, a corollary of working under static conditions is a reduction in signal intensity. Consequently, for analyses intended to detect elements with low abundances (e.g., dopants), or when surface specificity is not critical, working within the static limit may not be practical. The competing requirements of working within, or outside of, the static limit have consequences for the type of PI source, analyser, and detector used. These will be discussed in subsequent sections of this module. Historically, this resulted in a divergence of secondary-ion mass spectrometers into so-called 'static' and 'dynamic' instruments.

Static vs dynamic SIMS

SIMS analyses are sometimes differentiated as 'static' or 'dynamic' according to the flux (number of ions hitting each cm^2 of sample) of ions in the primary beam. Dynamic SIMS uses a much higher flux of primary ions than static SIMS, resulting in greater penetration of the sample (nm to μm). This also provides greater sensitivity to the analysis of low-concentration ions, such as dopants and low-abundance isotopes.

The lower flux of primary ions in static SIMS reduces the analysis depth, making the technique more surface specific. It also reduces fragmentation, which is beneficial to the analysis of molecular species.

As different instruments can be capable of different modes of operation, the rest of the module will be structured around the types of instruments used.

| Static SIMS	Dynamic SIMS
Low flux (ion/cm²) primary	High flux (ion/cm²) primary ion beam
Typically uses gold, bismuth or gallium primary ions	Typically uses oxygen or caesium primary ions
Targeting atomic and molecular ions from the top monolayers	Erodes successive layers of sample (nm to microns)
Applicable to molecular, isotopic and elemental characterisation	Applicable to isotopic and elemental characterisation
Mass analysis is typically performed with a time-of-flight mass spectrometer	Mass analysis is typically performed with a magnetic sector or quadrupole mass spectrometer

ToF-SIMS − Primary-Ion Sources for ToF-SIMS − Liquid-Metal Ion Guns

Modern ToF-SIMS instruments, in general, use liquid-metal ion guns (LMIGs) as primary-ion (PI) sources. These provide higher 'brightness' (i.e., current density, ca. 10^{10} A m^{-2} sr^{-1}) and narrower beams than electron-impact, plasma, or surface-ionisation sources. Both beam brightness and diameter are key to achieving the focus quality required for imaging at sub-micron spatial resolution.

LMIG emitters comprise a fine tungsten needle within a reservoir of metal. When melted, the metal flows over the needle to form a thin layer. The application of a high-voltage extraction field at the tip of the needle (radius < 1 μm) results in ion emission.

Early LMIGs used Ga (M = 69 u); however, as secondary-ion (SI) yields generally increase with increasing mass of the primary ion, sources for ToF-SIMS instruments now usually use heavier elements, such as Au (197 u) or Bi (209 u). Most of the emitted ions are both monatomic and monovalent; however, cluster ions (Au_n^{m+} and Bi_n^{m+}) are also present within the primary-ion beam. As these have even greater mass, they are capable of further increasing the SI yields, although the concomitant improvement in signal intensity is offset by the diminishing proportion of cluster ions with increasing m and n.

An additional benefit of cluster ions is that they deliver greater relative yields of molecular SIs. This occurs because the clusters break up on impact, so that the total energy is divided evenly between the n atoms. This 'softens' the ion-target interaction, resulting in less fragmentation within the sample.
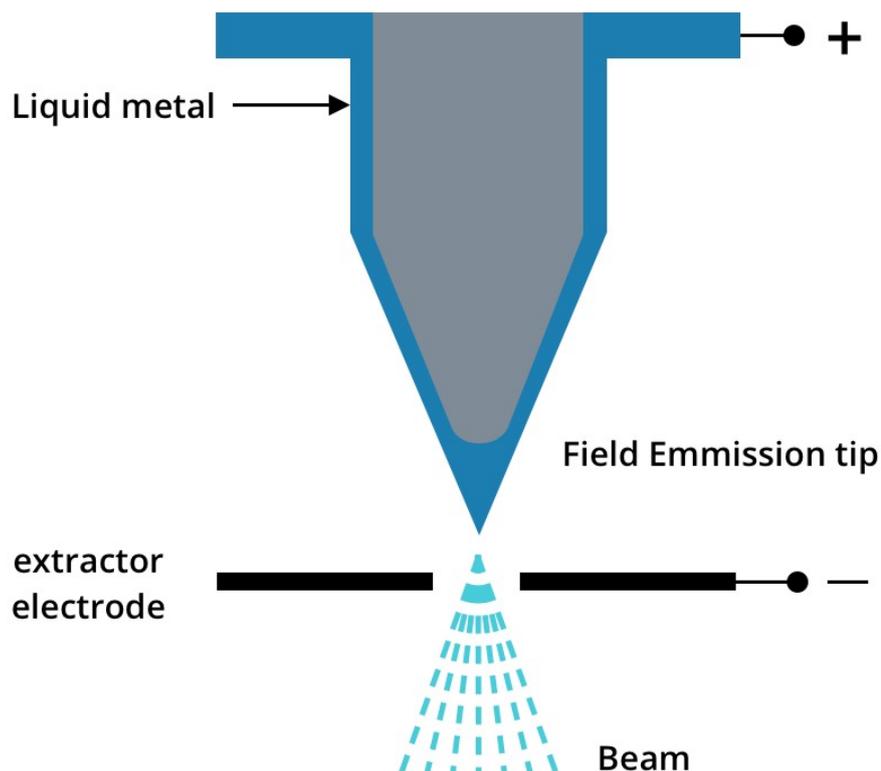
*Schematic illustration of an LMIG emitter generating an ion beam.*

Cluster Sources

The ability of clusters to provide increased yields of larger secondary ions is of particular benefit to the analysis of polymeric and biological samples, and has led to the development of even larger PI sources, such as C60+ and gas clusters (e.g., Ar_n^+, n = 102–103). In general, these cluster primary ions produce less chemical damage to the molecules within a sample; thus, the signals associated with these larger SIs don't drop off in intensity (decay) as rapidly. On the other hand, cluster sources are less bright than LMIGs, and have poorer spatial resolution.

Pulsing

As described earlier in this module, to avoid significant damage to your sample surface you will need to keep the dose of PIs low. Consequently, the ion current reaching the sample needs to be in the picoampere range. However, to achieve stable emission from the emitter, the beam current must be in the microampere range. To achieve the required picoampere range the continuous beam from the emitter is pulsed. The continuous beam from the emitter is deflected prior to it reaching a blanking aperture. The deflection voltage is periodically switched off, for around 20–50 ns, allowing packets of primary ions through the aperture.
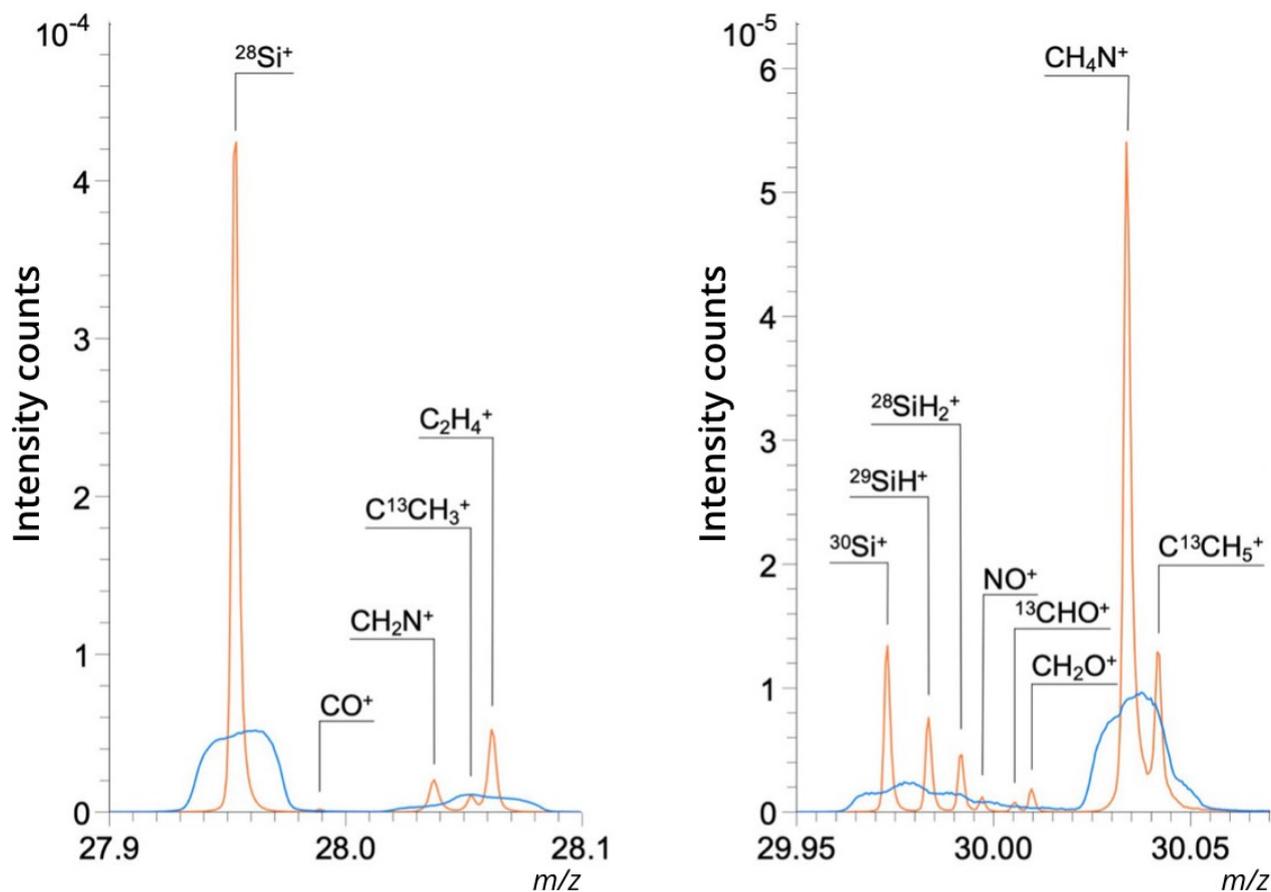
Bunching

For good mass resolution (m/Δm), it is necessary to reduce each pulse to a length of less than 1 ns. Simply shortening the time that ion packets are allowed to pass the blanking aperture would adversely affect both the SI signal intensity and spatial resolution. Instead, the pulses are normally compressed along their axis of travel, either by decelerating the front of the pulse with respect to the rear, accelerating the rear with respect to the front, or both (so that the pulse compresses around its centre). This compression is generally called bunching.
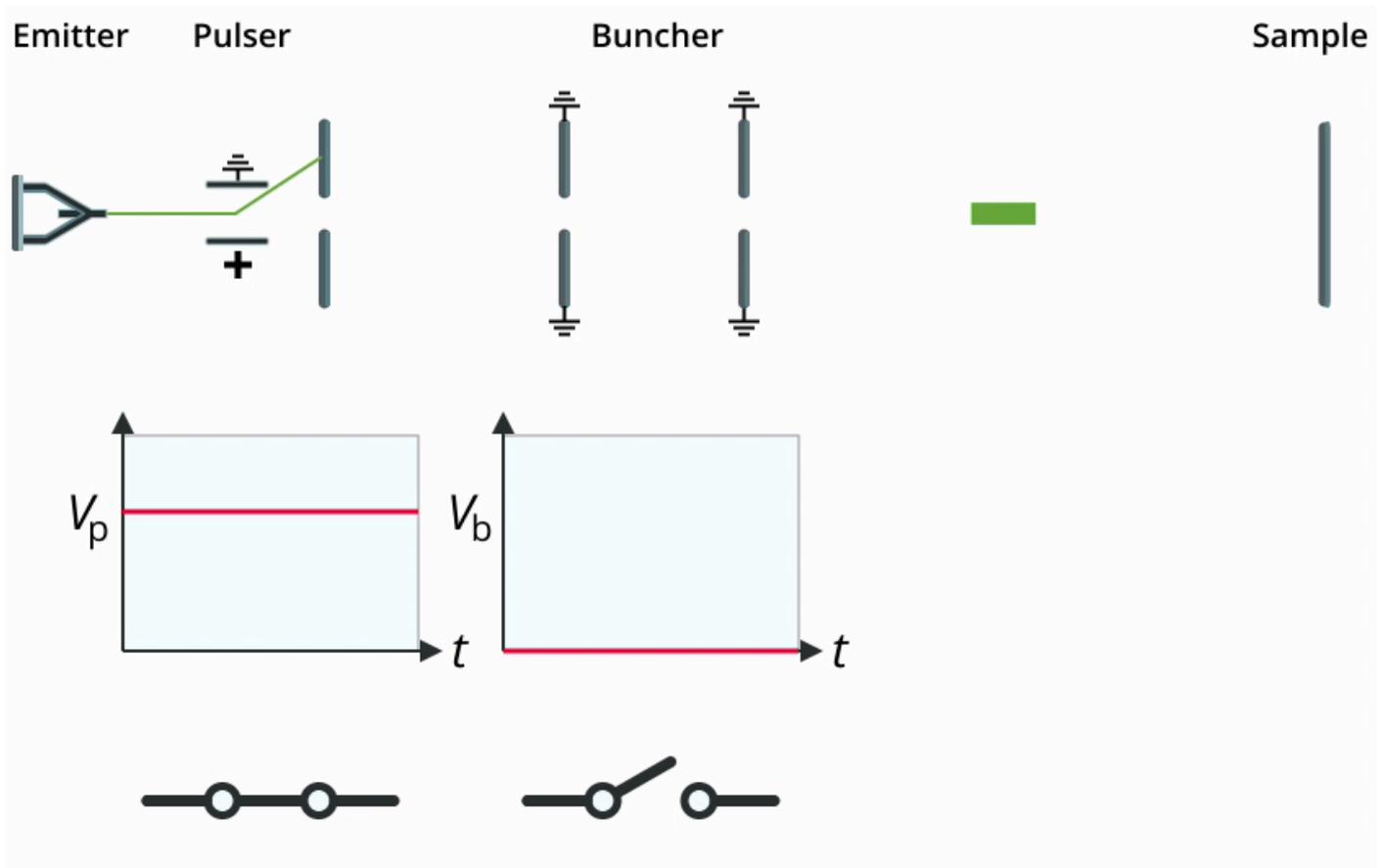
1. The continuous beam of primary ions from the emitter is diverted at the pulser by the application of a voltage (Vp) across deflection plates located in front of an aperture.
2. By intermittently switching Vp off, then on again, the beam is chopped into pulses, which pass through the aperture.
3. On entering the buncher, a voltage (Vb) is applied to the entrance aperture, which accelerates the ions within the pulse.
4. Ions at the rear of the pulse spend more time in the buncher than those at the front, and so are accelerated for longer. Consequently, they start to 'catch up' to the ions at the front, thereby compressing the pulse along its length, but with a concomitant loss of focus.
5. The buncher settings are tuned to attain a minimum pulse length when the ions arrive at the sample.

An adverse consequence of bunching is that it increases the spread of ion energies within the pulse, resulting in chromatic aberration and a subsequent loss in the extent to which the beam can be focussed. Unbunched beams can attain a spatial resolution of better than 100 nm, whereas that for bunched beams is typically > 1 μm. On the other hand, the mass resolution achievable with a bunched beam exceeds 10 000, compared to ca. 100 without bunching.

Positive-ion spectra acquired from a silicon wafer. Plotted in blue are the data acquired without bunching the primary-ion pulses, whereas those acquired with bunched pulses are plotted in orange. All other instrument and acquisition parameters are the same for each. Signals assigned to ions not containing silicon are the result of surface contamination from, for example, airborne organic compounds.

Several approaches have been developed in an attempt to resolve this dichotomy between mass and spatial resolution. Examples include dividing unbunched pulses into 'bursts', and bunching the secondary ions prior to their entering the mass analyser ('delayed extraction'). The availability of these techniques depends on the vendor and generation of ToF-SIMS instrument being used. These details are beyond the scope of this module and will not be discussed further.

# Collection optics − Time of Flight analysers − overview

Time of flight (ToF) analysers measure the time taken for the secondary ions (SI) to reach the detector as a function of their mass and their charge. SIs sputtered off the surface are gathered up by an extractor that pulses on and off to release them into a tube in which they travel through to the detector.

Ions of the same charge coming from the surface of the sample are accelerated to the same kinetic energy (E_k) by the extractor and therefore, because $E_k=1/2mv^2$, heavier SIs (larger m) have lower velocities (v) and therefore take longer to reach the detector. Lighter ions will have a greater velocity and will arrive at the detector before heavier ones.

The charge on an SI also affects the time it takes to reach the detector. Two ions of the same mass but different charges will have different kinetic energies. Those with a greater charge will arrive at the detector before those with a lesser charge.

These two concepts are shown schematically in the images below.
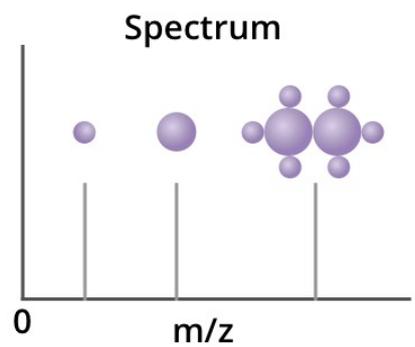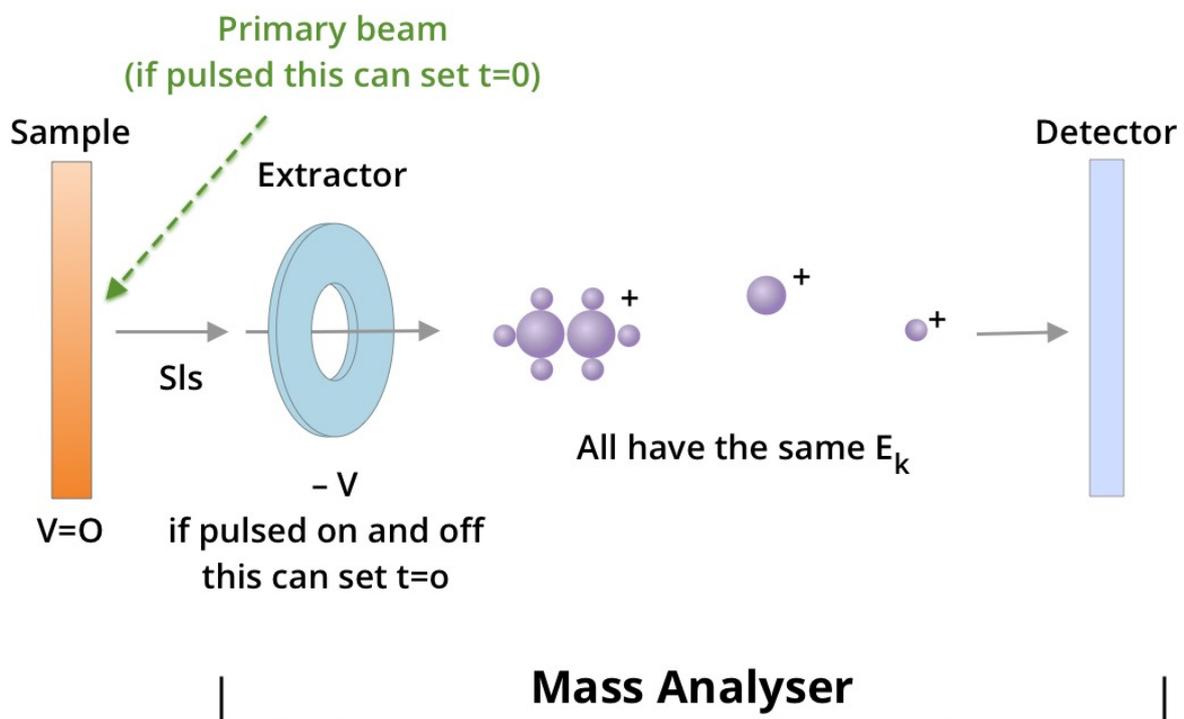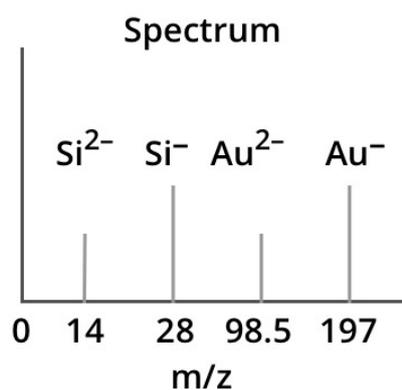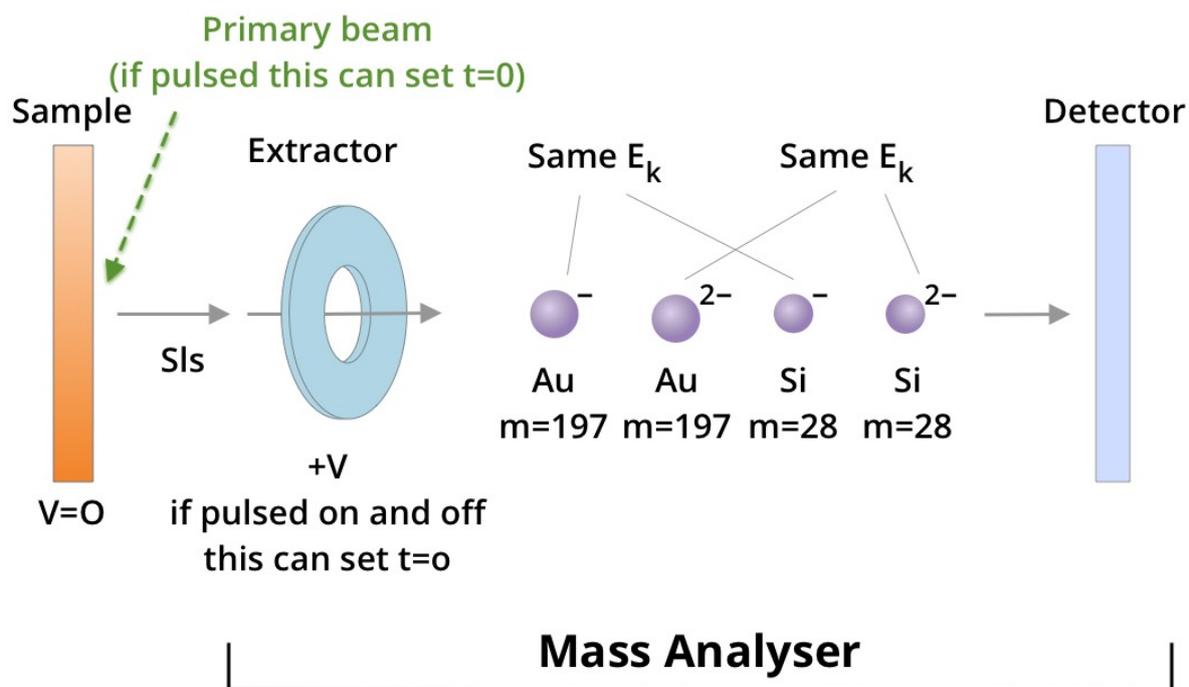
This illustrates the primary ion beam impacting the sample and releasing secondary ions (SIs). There is a voltage difference between the sample and the extractor, which determines the polarity of the ions to be collected. The SIs are gathered in by the extractor and, by switching its voltage on and off, a t_0 is set for each burst of SIs entering the analyser. Alternatively, t_0 is sometimes set by pulsing the primary beam so discreet packets of primary ions impact the sample at successive t_0s. It is necessary to set t_0 so the time of flight can be calculated.

A. shows the separation of several monovalent SIs according to mass and how this corresponds to the peaks on the resulting spectrum.

B. shows that ions of different mass and different charge separate on the basis of both. Bivalent ions passing through the extractor will have twice the kinetic energy of the equivalent monovalent ions and will therefore move faster through the analyser. Note the ions are separated by mass:charge ratio: it is this ratio that is shown on the x-axis of the resulting spectrum.

Inside the analysers − Inside the ToF analyser

Once the primary-ion (PI) pulse impacts the sample, there in an immediate emission of secondary ions (SIs) from the sample. These are accelerated towards a mass analyser by a potential gradient between the sample and the extractor. This extractor sits at the entrance to the analyser and the voltage it generates is known as the extraction voltage (U). The direction of this gradient determines the polarity of the SIs harvested during the analysis. Typical values of U are around 2 kV, and the distance over which it operates (i.e., the distance between the sample and analyser entrance) is a couple of millimetres.

Once inside the analyser, the SIs are allowed to drift in a field-free region, with an approximate length (l) of 2 m, before they reach the detector.

The kinetic energy (E_k) of these ions is determined by their charge (q) and the acceleration potential (i.e., U), such that:

$$E_k = qU = \frac{1}{2}mv^2$$

By far the majority of SIs have unit charge (q = ±1), and so the resultant spectrum is dominated by signals from these ions. Consequently, we will now limit our discussion to monovalent SIs.

Because these monovalent ions have the same kinetic energy, SIs within the drift region of the analyser disperse according to their mass. Heavier ions (larger m) will have lower velocities (v), and so take longer to reach the detector. The time taken (t) is given by:

$$t = \frac{l}{v} = l\sqrt{\frac{m}{2u}}$$

It is this relationship between the mass of an ion and its time of flight that gives rise to the name for this type of analyser.

$$m = at^2 + b$$

where a and b are constants, empirically derived from standards of known mass.

a and b are physically related. a is derived from t0 and b is related to the length of the flight path and the extraction voltage.

According to equation 2, two ions with the same mass should have exactly the same flight time to the detector.

In practice however, ions are sputtered off the surface with slight variations in their kinetic energies (influenced by factors in the instrument and the sample) (equation 1). This results in variations in their flight times (Δt) and, consequently, in their measured masses (Δm).

Practically, this becomes apparent as a broadening of the peaks in the mass spectrum (i.e., a lower mass resolution $m/\Delta m$), which then increases the uncertainty in assigning their identities. To improve resolution, ToF SIMS instruments commonly use one of two analyser designs to improve the 'energy focus': the reflectron, or the electrostatic sector analyser (ESA).

The resolution of the analyser will determine the extent to which you can distinguish SIs with similar masses (isobaric ions). For example, sulfur has a mass of 32.07, whereas an oxygen molecule has a mass of 2 x 15.99 = 32.00.

Reflectron-TOF

A reflectron ToF analyser ensures ions of the same mass arrive at the detector simultaneously regardless of their slight variations in energy. This is achieved using an ion mirror to reflect the ions. Higher energy ions will travel further towards the ion mirror before being reflected than those of a lower energy. This enables these ions of the same mass to charge to be focussed and arrive at the detector simultaneously regardless of their kinetic energy. Additionally, the use of a reflectron tube increases the flight path which can improve the resolution in the mass spectrum.
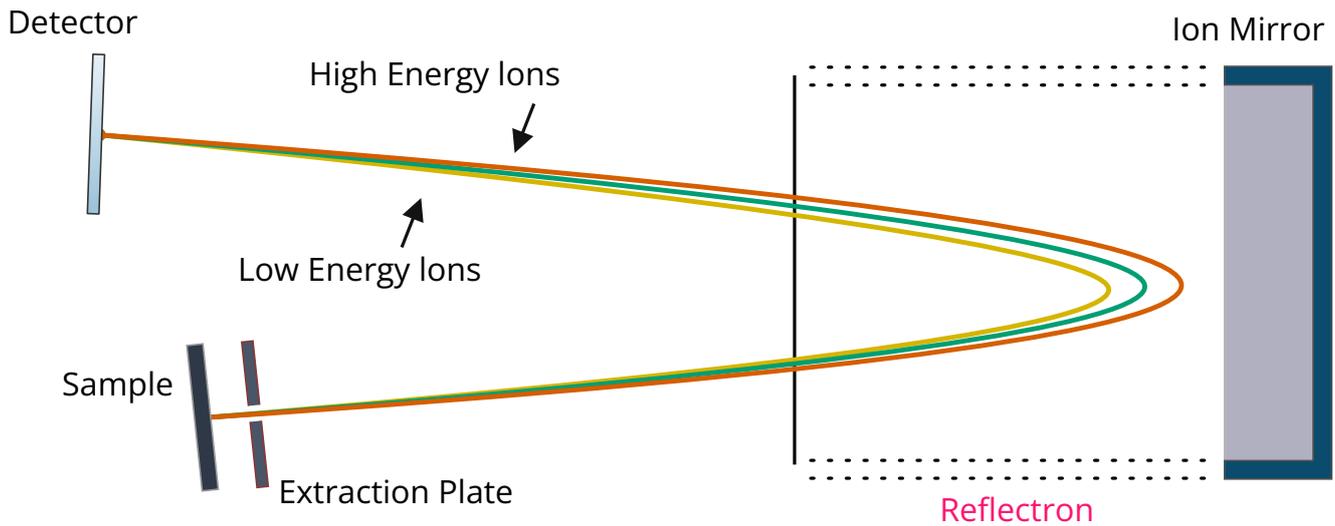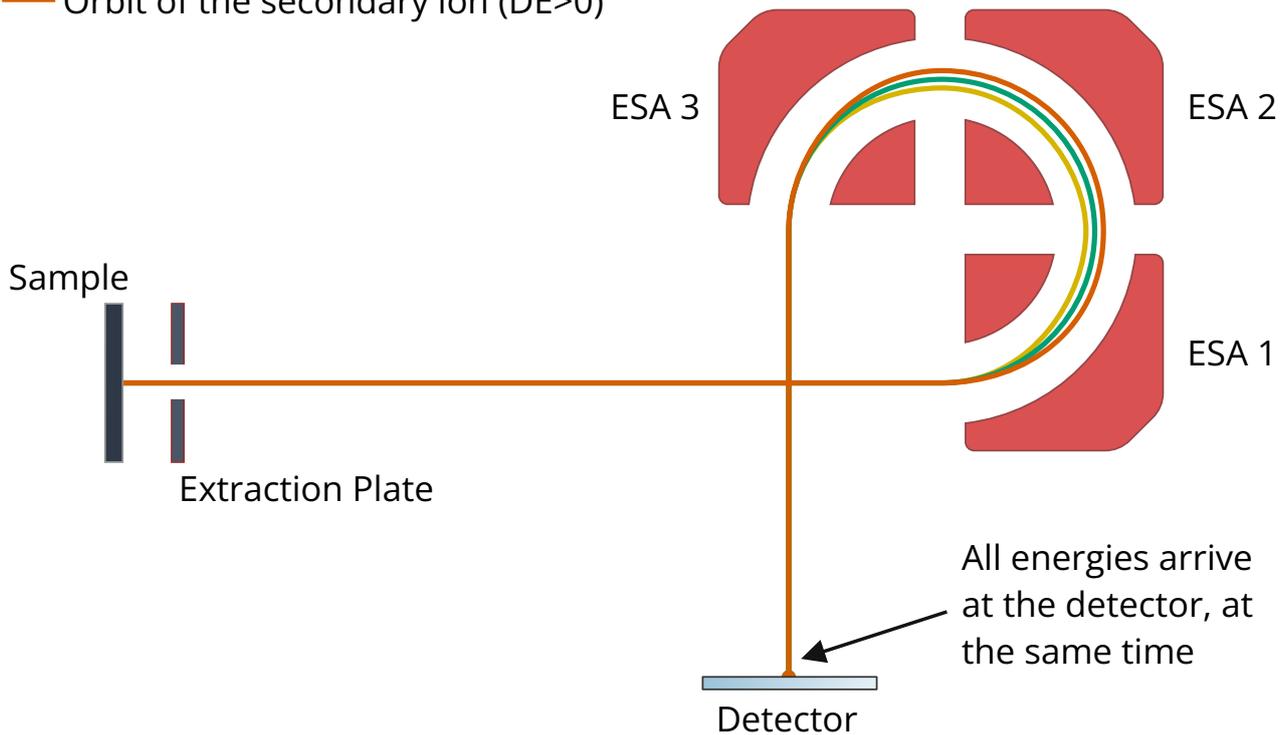

An animation showing how a reflectron Tof analyser uses an ion mirror to reflect ions of differing energies so they arrive at the detector at the same time.

ESA TOF

Similar to a reflectron, the ESA uses multiple electrostatic analysers to focus ions with a wide range of energies so they arrive at the detector simultaneously. As the ions travel through the electric field they are deflected through multiple electric fields, focusing the ions based on their kinetic energies. Due to the way they are deflected, ions that have kinetic energies that are too high or too low can be blocked from progressing fully around the analyser, thereby excluding them from the system. This only allows ions of specific kinetic energies to pass through, thereby eliminating any unwanted products of metastable ion decay. This technique provides high mass resolution with high transmission efficiency.

— Orbit of the secondary ion (DE<0)
— Orbit of the secondary ion (DE=0)
— Orbit of the secondary ion (DE>0)

ESA 3   ESA 2

Sample

ESA 1

Extraction Plate

All energies arrive at the detector, at the same time

Detector

An animation showing how an electrostatic sector analyser uses a series of curved channels to bring ions of differing energies together so they arrive at the detector at the same time.

Detectors

The detector in a ToF-SIMS instrument records the flight times of secondary ions as they exit the mass analyser. Because of the low flux of these, the detector must be able to detect single ions, and so modern instruments typically use microchannel plate (MCP) detectors.

An MCP comprises a glass plate containing an array of parallel channels, with diameters of ca. 5–50 μm, extending from the top face to the bottom. These are inclined at around 10° to the perpendicular, so that an SI entering the channel will collide with its walls. A coating on the channel walls emits electrons in response to the impact. The electrons are propelled down the microchannel by a potential applied between the two faces of the plate. Further collisions of the electrons with the channel walls generates more electrons to produce a cascade, thereby amplifying the signal from the original SI impact (e.g. by a factor of 10^3).

The electron cluster exiting the plate can either be collected by an anode, or converted to photons, by impact with a scintillator, which are then detected by a photomultiplier. The latter provides further signal amplification. A time-to-digital converter (TDC) assigns the signal to a time scale.

Heavy, and therefore slow-moving, SIs may exit the analyser with insufficient momentum to induce electron emission on arrival at the detector. To improve the registration of these, a 'post-acceleration' voltage may be positioned in front of the detector.

The time taken to register the impact of an SI is typically tens of nanoseconds, during which the detector is not able to record any subsequent impacts. This is known as the 'dead time' and, if the frequency of SI impacts exceeds this, the detector is said to be 'saturated'. Practically, this means that two (or more) ions arriving at the detector within the dead time will be recorded as one count, so that the relationship between the number of SIs generated, per PI pulse, and the number detected is no longer linear.

If the number of SIs arriving within the dead time is below, for example, four, this linear response can be recovered by the application of a Poisson statistical correction to the data. This is often automatically implemented by the instrument software.

Some instrument analysers may have an extended dynamic range (EDR) capability, in which SIs producing detector saturation are redirected through filters that attenuate their signal intensity. For example, if a PI pulse yields 25 X^+ SIs, the signal associated with this ion will be saturated; however, if these ions are passed through a filter with a 10% attenuation, only 2 or 3 will reach the detector, which is within the Poisson-correction range.

If an ion of analytical interest is producing a saturated signal, and an EDR analyser is not available, it may be possible to mitigate the saturation by reducing the number of PIs per pulse (e.g., by reducing the pulse length). A disadvantage of this is that there will be a commensurate reduction in the intensities of all the other SI signals. An EDR, on the other hand, filters only nominated SIs.

Data

Unlike other techniques that detect electrons, light or energy, SIMS detects ions (charged particles) and is able to detect elements from hydrogen to uranium and a wide range of molecular ions up to a mass in the range of 10^5 atomic mass units (amu). These are separated in the analyser based on their mass/charge (m/z), which directly correlates with the atomic mass units.

For example, Cu has two natural isotopes, one with a mass of 63 amu and the other with a mass of 65 amu. So we see two peaks for Cu^+ at m/z 63 and m/z 65. The ratio of the intensities of the two signals is the same as their isotopic abundance.

Ionisation of a sample will be different for each atom and molecule depending on their ionisation potential (K_i). Some elements and molecules ionise better than others. For example, if we consider a sample with an equal concentration of Cu and Zn, the ionisation potential for Cu = 750 kJ/mol whereas Zn = 900 kJ/mol. Consequently, Cu is more likely to be ionised than Zn and will result in more Cu^+ ions being detected than Zn^+ ions despite these elements being present at the same concentration.

Ionisation efficiency is impacted by a number of factors, particularly the chemical environment of the atoms of interest. Consequently, quantification with SIMS is complicated and requires matrix-matched standards for all ions.

In some newer instruments large complex molecular ions can be selected from the first mass analyser and sent to a second mass analyser to be fragmented so they can be identified more precisely.

# Sample preparation – Sample requirements for ToF-SIMS

As this is an ultra-high vacuum (UHV) system, liquid, volatile samples or any substance that contaminate the chamber of the instrument under the vacuum, should not be put into the instrument. Due to the highly surface-sensitive nature of ToF-SIMS it is important to ensure that the samples are handled in an appropriate manner and are not contaminated.

When you prepare ToF-SIMS samples, it is recommended that you should handle the samples and the sample holders with clean tweezers and gloves. It is important to note that due to the high surface sensitivity of the instrument, even some types of gloves, such as powdered gloves and some latex gloves, may contaminate the samples. Silicone is one of the most common contaminants of surface, and it is easily introduced by various materials such as oils, greases, heater transfer fluid, sealants, adhesives, surfactant, and medical devices. You should pay particular attention to not let these near your sample.

In general, solid substrates and samples can be mounted directly onto the flat sample platens with carbon tape. However, some samples, like powders, must be treated carefully to prevent loose particles from entering in the vacuum chamber as they will contaminate the vacuum system. There are multiple ways recommended ways to prepare powdered samples for ToF-SIMS.

Powders

To prepare powder, it can be embedded into carbon tape, low background paper or indium. Simply stick some carbon tape to a substrate (e.g. clean silicon wafer) and gently press or sprinkle the sample into the carbon tape. Remove all excess powder by tapping the substrate on its side. Although this is the easiest way prepare a sample, the spectrum can present some peaks from the carbon tape. This can sometimes be avoided by using a low background adhesive paper or using indium foil as an interlayer between the sample and the carbon tape.
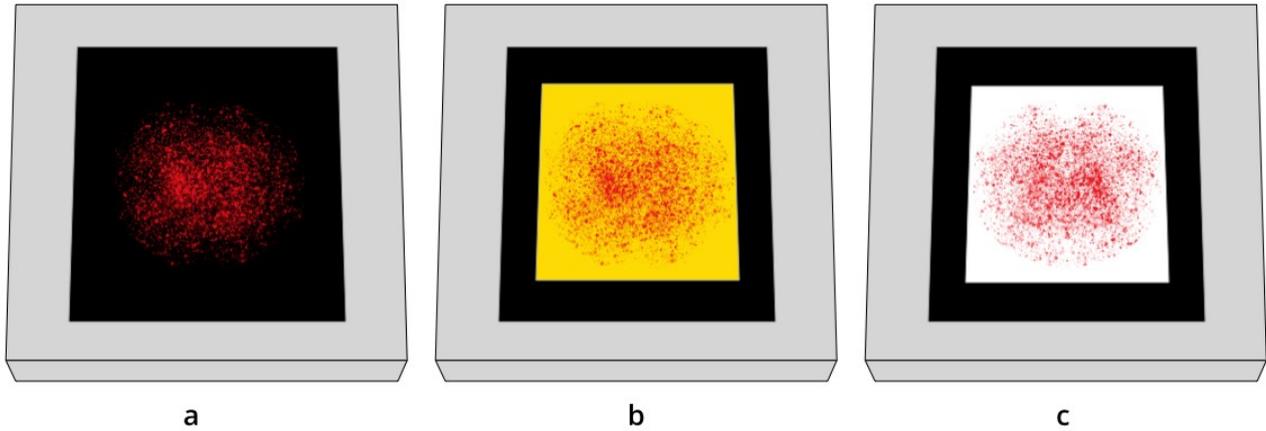

Solid conductive substrate with a) carbon tape, b) carbon tape with low background paper, c) carbon tape with indium foil loaded with powered sample

Solid conductive sample directly loaded onto carbon tape (a), carbon tape covered with a low background paper (b), carbo tape covered with indium foil. Carbon tape = black, low background paper = yellow, indium foil = white.

Suspensions and solutions

For extra-fine powders in suspension or substances in solution, you can simply pipette a micro-drop of the liquid onto a substrate (usually a clean silicon wafer) and let it dry. This method has been used for examination of nano-particles and drug solutions.
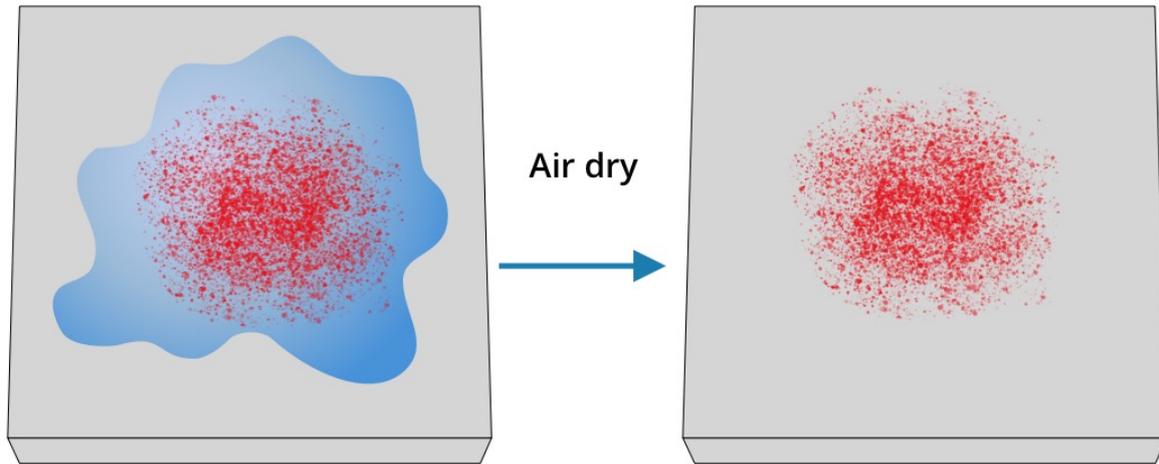
Suspensions and solutions can be pipetted directly onto a conductive substrate, such as a silicon wafer, and left to air dry.

Applications of ToF-SIMS − Typical applications

Initial applications of ToF-SIMS tended to be dominated by analyses of inorganic materials and minerals, including the chemical analysis and mapping of semiconductors, industrial materials and coatings, and organic contamination. More recently, as there have been large technological advancements with associated with the technique, there has been increased ToF-SIMS analysis of polymeric samples, pharmaceuticals, biomolecules, tissue samples and cells, and application-driven use such as those for forensic analysis or diagnostics.

Pharmaceutical science

It has been shown that the coating of cohesive particles with lubricants can improve the aerosolisation of inhalable pharmaceuticals at a low excipient concentration (Zhou et al., 2013). As this is purely related to the outermost surface chemistry, ToF-SIMS can be used to analyse changes in the surface and to identify composition and distribution of excipients on the surface. (Bhujbal et al, 2021; Adhikari, et al. 2022).

The influence of surface-active l-leucine and 1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine (DPPC) in the improvement of aerosolisation of pyrazinamide and moxifloxacin co-spray dried powders has been studied using Tof-SIMS.
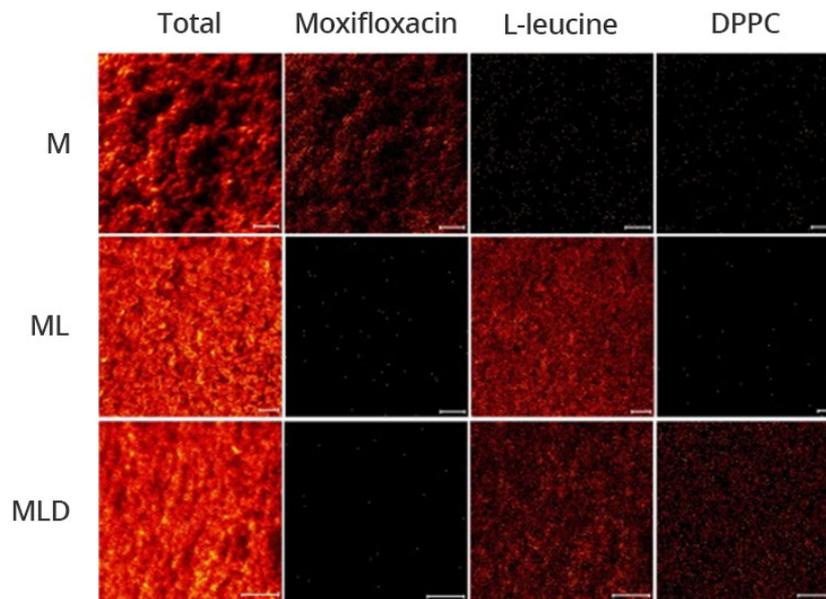
ToF-SIMS chemical mapping of L-leucine and DPPC moxifloxacin co-spray powders adapted from Eedara et al., 2018

Geology and mineralogy

High precision analysis of trace elements and surface chemistry plays an important role in geology and minerology. ToF-SIMS can provide elemental and molecular information about the uppermost atomic layers of the surface on a particle-by-particle basis.
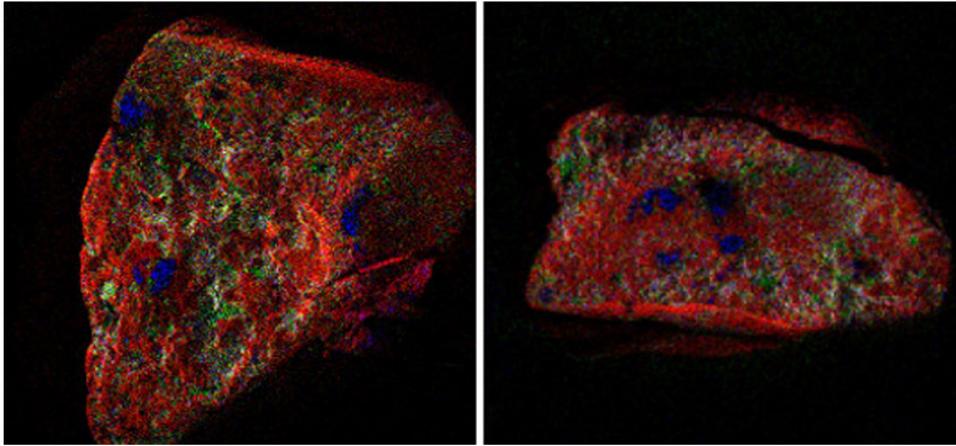
*Single Silica sand particles showing silicon in red, aluminium in green and iron in blue.*

ToF-SIMS is commonly used in the mineral processing field to observe the interaction of chemical activators or depressants in flotation. More recently, ToF-SIMS data has been used to predict mineral wettability, or hydrophobicity, based on outermost surface chemistry of individual particles.
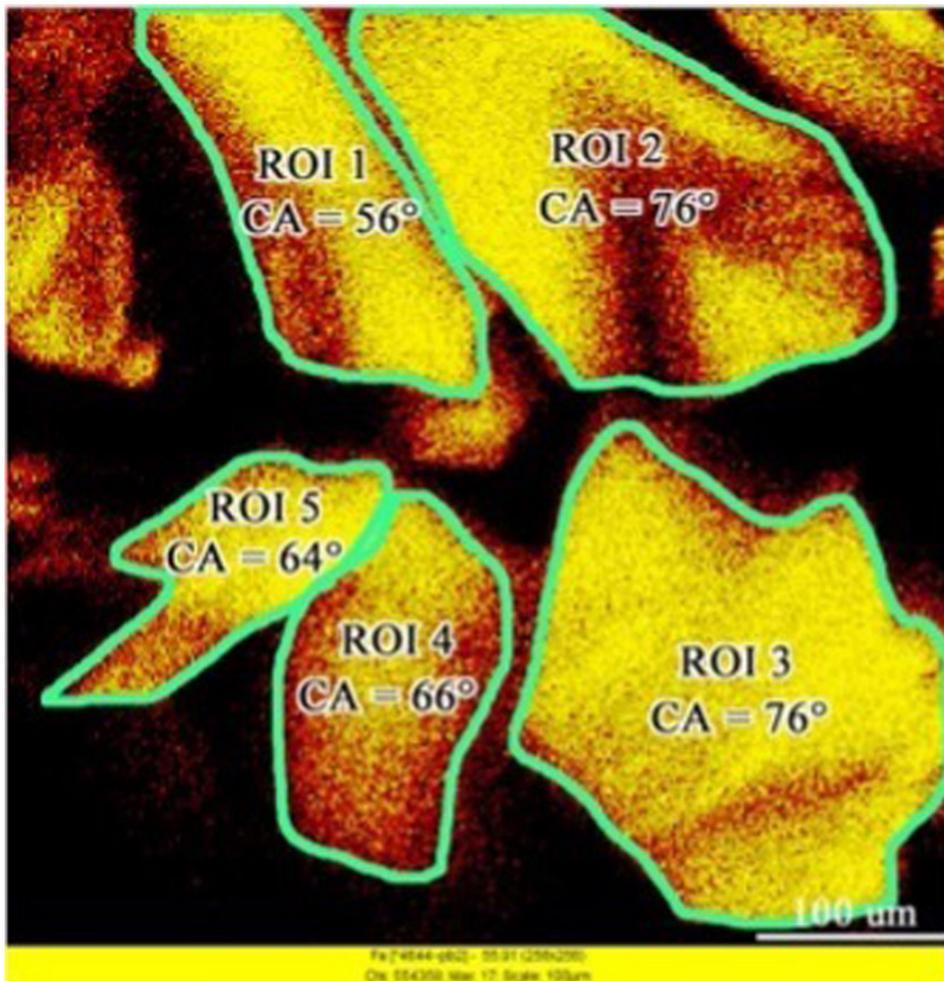

Predicted contact angles of different pyrite particles from a ToF-SIMS image (Xu et al. 2020)

Forensics

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provides small area analysis to characterise the elemental and organic composition of surfaces. ToF-SIMS is suitable to identify and interrogate suspect markings by pencils, ballpoint pens and some dyes (Denman et al. 2010). This may be useful in determining the origin of fraudulent or altered documents.
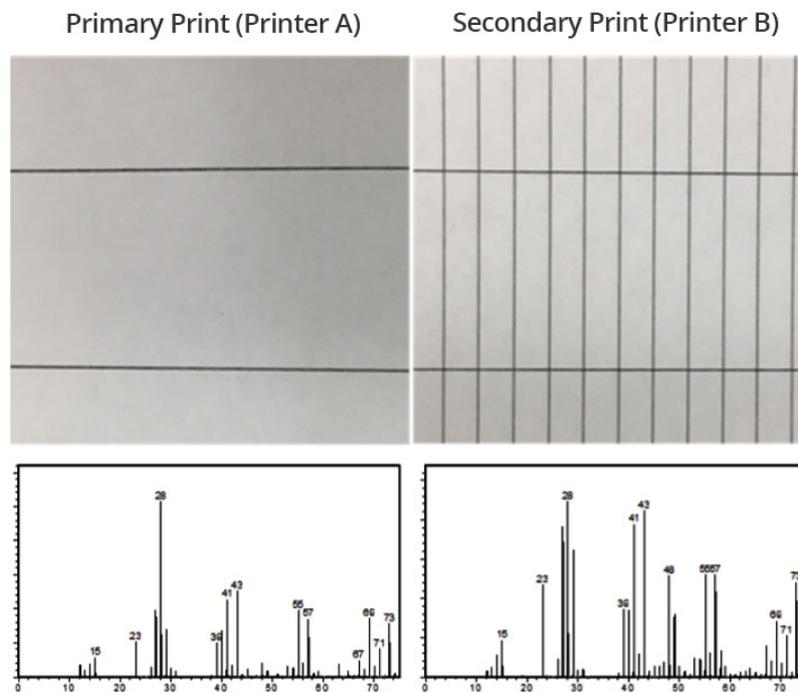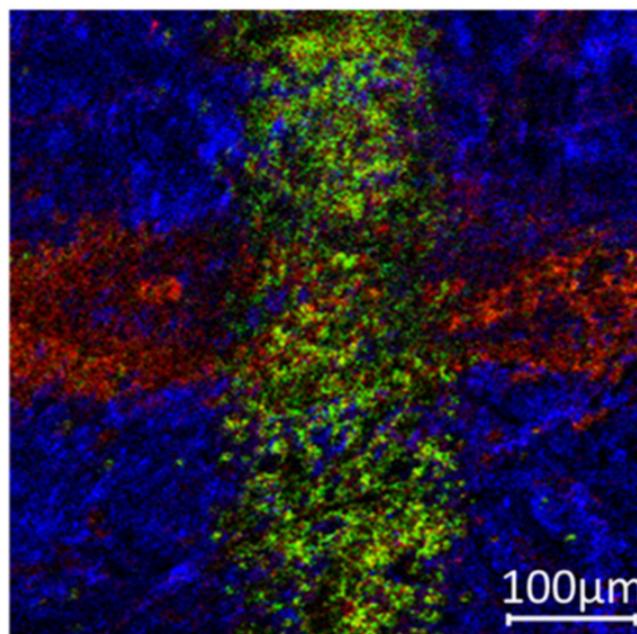

ToF-SIMS spectra and image of different printer inks

The majority of ammunition tends to use glass powders in their primer which become fused with other components within gunshot residues. Due to the extremely low detection limits of ToF-SIMS, specific signatures of both organic and inorganic substances within residues from different sources can be identified.
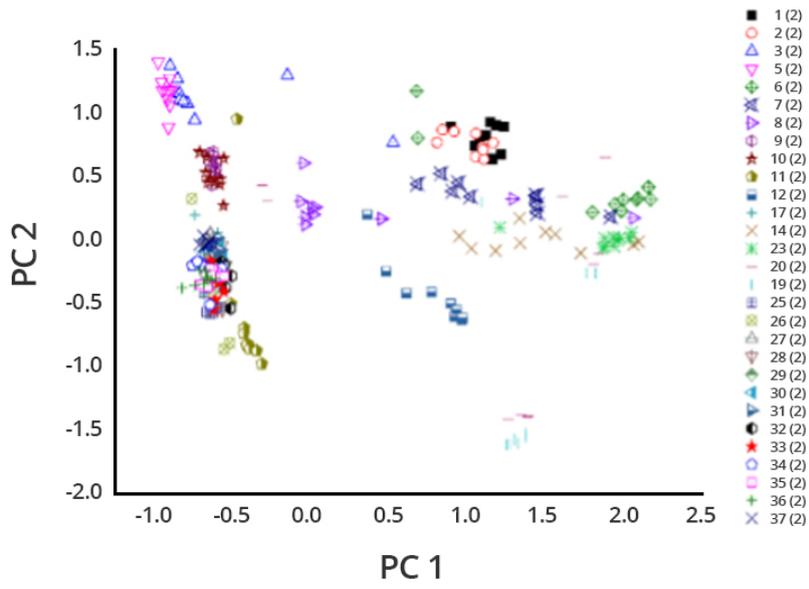
Multi-variate analysis of ToF-SIMS spectra for 29 gunshot residues from 17 different manufacturers (K.E. Seyfang et al 2018)

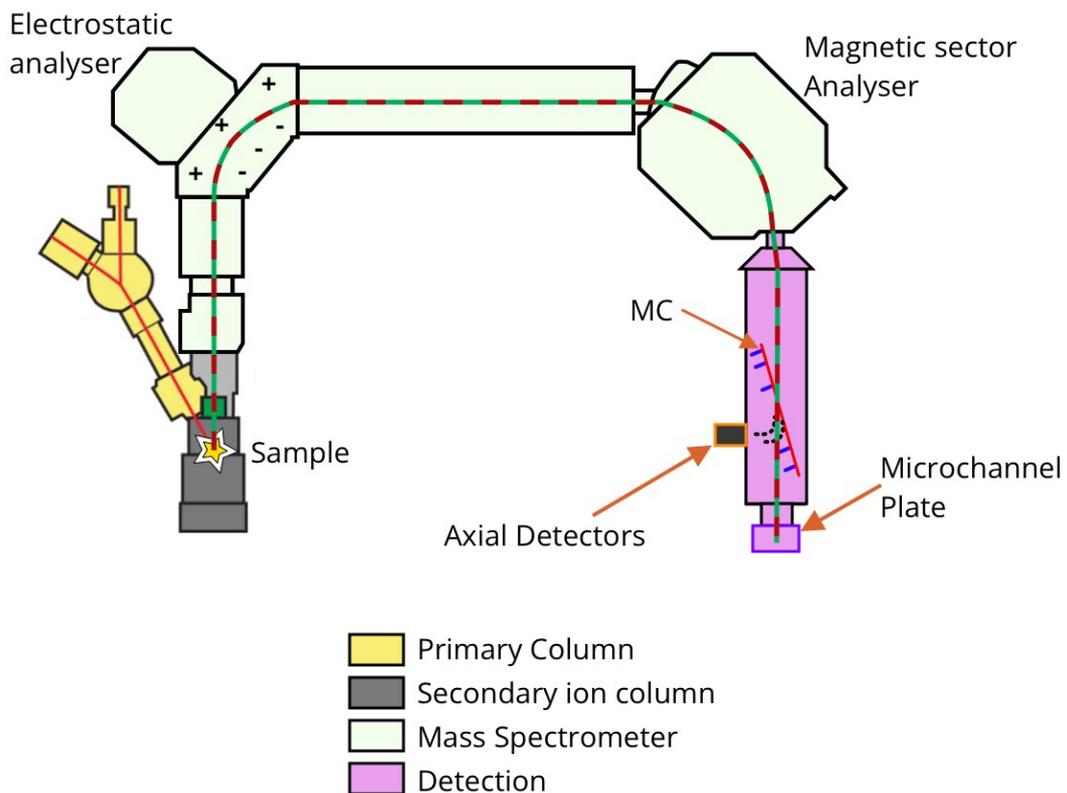# Large Geometry SIMS and NanoSIMS − Common features − Common features of the Large Geometry and NanoSIMS

Both types of instruments operate in dynamic mode and are equipped with a magnetic sector mass spectrometer, which separates the secondary ions on the basis of their mass:charge ratio. However, different designs in the primary columns, secondary ion extraction systems, and mass spectrometers impart these two instrument types with different capabilities.

Photo of the Cameca IMS1280 at UWA
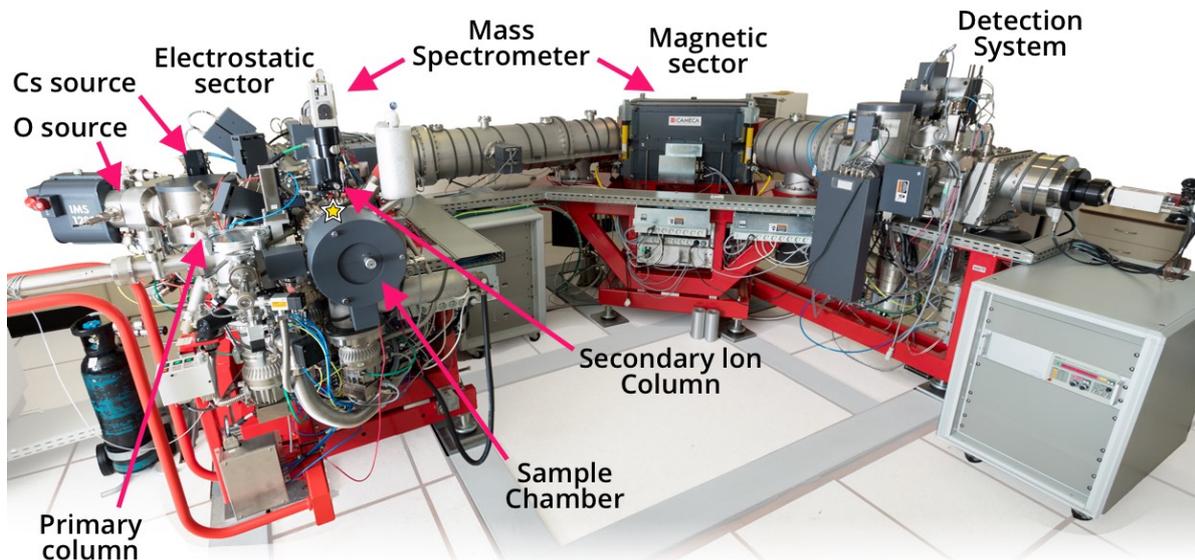
Schematic, view from above

An example of LG-SIMS, the Cameca IIMS1280. (a) photo showing the different part of the instrument, schematised in b (view from above).

Primary Ions and Primary column

Large geometry SIMS (LG-SIMS) and NanoSIMS instruments use reactive primary ions to sputter secondary ions from the sample. Oxygen species (O^-, O_2^-, O_2^+) and Cs^+ are the primary ions used on LG-SIMS and nanoSIMS because of their strong reactivity with the sample substrate during sputtering, which favours the formation of secondary ions.

- Cs^+ favours the formation of negative ions
- O species, both negatively or positively charged, favour the formation of positive ions.

Periodic table showing the elements preferentially ionised with O- and Cs+ primary ions. Modified from Evans Analytical Group: https://www.eag.com/app-note/sims-tutorial

O species and Cs primary ions are generated in the primary column by two distinct sources. Oxygen ions are generated by a radio frequency (RF) plasma source, which produces a high-brightness beam. In contrast, Cs^+ ions are generated through the interaction between a caesium carbonate pellet and a hot tungsten plate.

The highest beam density and spatial resolution is achieved using O^-. In contrast, O_2^- is best used when a compromise between ion yield and resolution is needed. O_2^+ has a shallower penetration depth and is used when you need higher depth resolution. However this comes at the expense of secondary signal intensity. Also, it may have more problems with

charging effects when a sample is not conductive. O_2^+ is particularly applicable in depth profiling semiconductors as they require as high a depth resolution as possible and samples are sufficiently conductive.

Primary ions generated by the primary source are then filtered, focused, and transported through the primary column to the sample being analysed. Filtering is necessary to remove unwanted ion species generated within the ion source. A common filter used for this is the Wien filter, where crossed magnetic and electric fields are used to separate ions of different mass to charge (m/q) ratios. The ions experience a change in their trajectories proportional to the applied field and their m/q ratio. The remainder of the primary column comprises a series of electrostatic lenses, deflectors and apertures that are used to shape and focus the beam onto the sample surface.

Sample chamber and stage

This is where the primary beam hits the solid sample under analysis, generating secondary ions by the impact.

The sample is typically placed into a holder and loaded into the sample chamber. This allows for sample navigation and movement in three dimensions. Samples must be flat with a mirror-like polish, vacuum compatible and conductive. They are typically coated with metal (usually Au or Pt, 10 to 30nm-thick) or carbon to provide conductivity. Some examples of sample holders for the NanoSIMS 50L and LG-SIMS are shown below.

NanoSIMS sample holders can accommodate flat polished discs with diameters of 7 mm, 10 mm, 13 mm (1/2 inch) and 25 mm (1 inch). Two types of holders are shown here. The individual stubs slot into the holes and are secured by clamps on the back of the holder. Left: this holder can accommodate 8 x 10 mm diameter discs and is typically used for biological sections mounted on silicon wafers. Right: this larger holder can accommodate 1 x 1 inch, 2 x ½ inch and 2 x 10 mm diameter discs and is typically used for larger geological samples mounted in resin discs.


LG-SIMS sample holder for 1 inch in diameter mount

Dynamic mode

Dynamic SIMS analyses the elements and small molecules from multiple atomic layers within the sample surface. It uses a primary ion dose in the range of 10^{17} ions/cm^2, which results in the continuous erosion of the surface (dynamic surface) and recording of sputtered ions. Dynamic SIMS produces a higher flux of secondary ions than static SIMS, which results in a better sensitivity or capacity to detect small differences in concentrations of elements or isotopes. As a result of the higher beam current, secondary particles are more fragmented during the sputtering process resulting in mainly mono-atomic ions and some small molecular ions. Large molecules are usually not preserved.

Due to the complex interactions between the highly energetic primary ions and the atoms in multiple layers of the sample, secondary ions emerge with a wide range of kinetic energies.
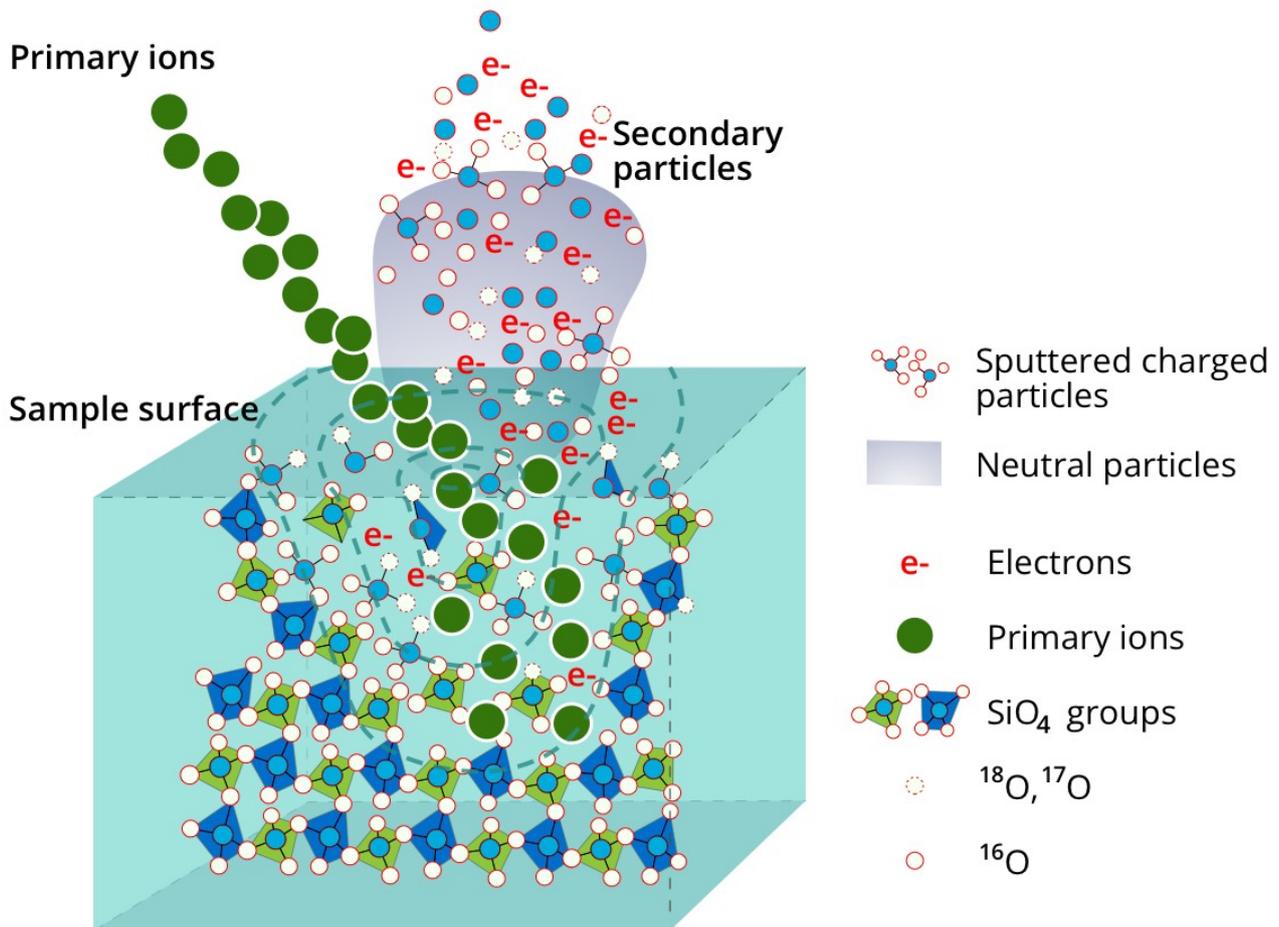

figure_24: Sputtering process in dynamic mode

Secondary column

The secondary ion column is the part of the instrument in which secondary ions emitted from the sample are accelerated, extracted, and shaped/focused by electric fields, to be transported to the mass analyser. Only secondary ions of a given polarity are extracted at any one time.

Double focussing mass spectrometer - overview

The trajectories taken by secondary ions in the mass spectrometer are controlled by their velocity v, (kinetic energy E_K), and the angle at which they emerge from the sample. Secondary ions have a range of kinetic energies, resulting from the impact energy of the primary ions and on the energy acquired by the secondary ions during the sputtering process.

In LG-SIMS and nanoSIMS, the mass analyser consists of an electrostatic sector analyser and a magnetic sector analyser. The electrostatic sector analyser first filters out the ions of interest based on their velocity (energy) and focuses those with different trajectories. The ions then enter the magnetic sector analyser where they are dispersed on the basis of their mass: charge ratio.
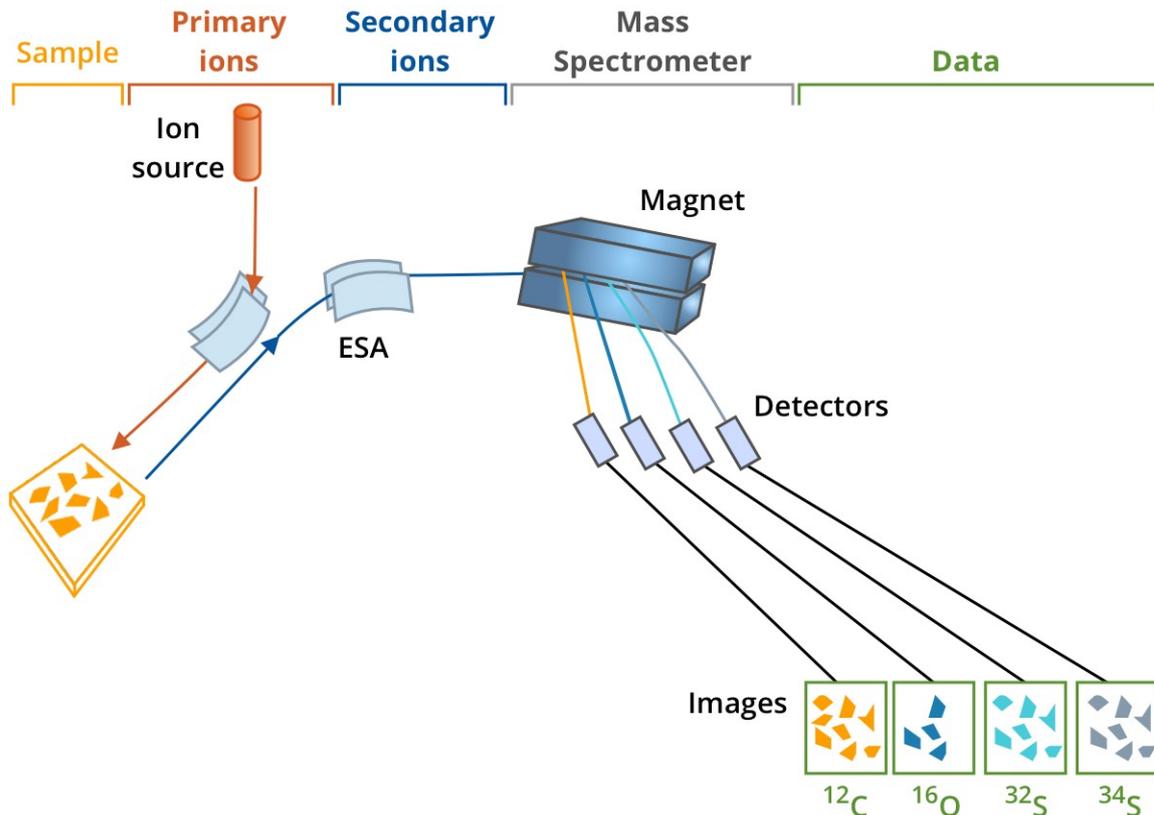
Double focusing system composed of an electrostatic sector thet first disperses and filters ions based on the kinetic energy (velocity) and a magnetic sector that then disperses and filters ions based on their mass/charge.

Practically, let's consider the example where we want to analyse ^{16}O in a zircon crystal. When we start bombarding the zircon with Cs^+ ions, O in the sample will be ionised as a negative ion. We adjust the magnetic field to collect mass 16 in our detector and check for other potential ions at mass 16 (known as interferences). In zircon there are no interferences and there is plenty of oxygen. We therefore finely adjust the magnetic field to collect the highest signal at mass 16, which should correspond to ^{16}O. Then, the position of the energy slit is adjusted in the X direction (up and down in the figure_above) to maximise the count rates on ^{16}O. Reducing the width (size of the opening) of the energy window can help to focus the secondary ions even more to get a better peak shape.

Let's now consider when the isotope of interest has an interference with a molecular ion and cannot be easily separated using the magnetic sector analyser. This is the case of ^{87}Sr, which interferes with $^{40}Ca^{31}P^{16}O$ in apatite crystals. In this case, ^{87}Sr and $^{40}Ca^{31}P^{16}O$ have very different energies (velocities) and the X position of the energy slit to optimise their signal in the detector will be different. We can thus adjust the slit position to optimise one or the other species. This technique,

called energy filtering, is used to improve the separation between two neighbouring signals, hence improving the mass resolving power of the instrument.

Identifying the energy range of your ions of interest is, in practice, an iterative process. Often a standard is used initially, and the slits adjusted to capture the full range of known isotopes for elements in that standard. Further fine tuning is conducted on the sample to maximise detection of the ions of interest.

Inside the mass spectrometer − Electrostatic analyser

An electrostatic sector analyser is made of two concentric and curved metal plates with a voltage applied across them, producing an electric field **E** (bold denotes a vector) with magnitude E. The electric force $\mathbf{F_E}$ applied to an ion with charge q passing through the electric field is defined as:

$$\mathbf{F}_E = q \times \mathbf{E}$$

The role of the electrostatic sector is to disperse secondary ions based on their kinetic energies independently from their mass/charge ratio. Ions with same kinetic energy, but different angles are focused when they enter the magnetic sector analyser whereas ions with different kinetic energies but the same trajectory are dispersed when they enter the magnetic sector analyser.

Energy selection can be done in two ways.

1. A slit, or energy window is located at the exit of the electrostatic sector analyser. Its position can be moved, and the width of its opening can be adjusted to limit and select a certain range of energies corresponding to the species of interest.
2. Alternatively, the slit can be kept in a set position and the energy of the secondary ions can be adjusted by changing the sample voltage.

Magnetic sector analyser

The magnetic sector analyser is composed of excitation coils and magnetic pole pieces that produce a magnetic field **B** (bold denotes a vector) perpendicular to the incoming ion trajectory. The magnetic force $\mathbf{F_M}$ applied to an ion with velocity **v** and charge q is defined as:

$$\mathbf{F_M} = q \times \mathbf{v} \times \mathbf{B}$$

The magnetic sector analyser disperses ions following an arc of radius r, dependant on their mass:charge ratio and kinetic energy.

$$r = \frac{\sqrt{2\,Ek\,m}}{qB}$$

A slit is used at the exit of the magnet to limit and select the secondary ions of interest, based on their mass/charge ratios. By far the majority of the ions carry only a single charge meaning that the ions are effectively separated on the basis of their mass.

As secondary ions have a wide energy distribution, a magnetic sector alone would not be able to make precise isotope measurements, hence the need for an electrostatic sector and a magnetic sector analyser to be used in sequence.
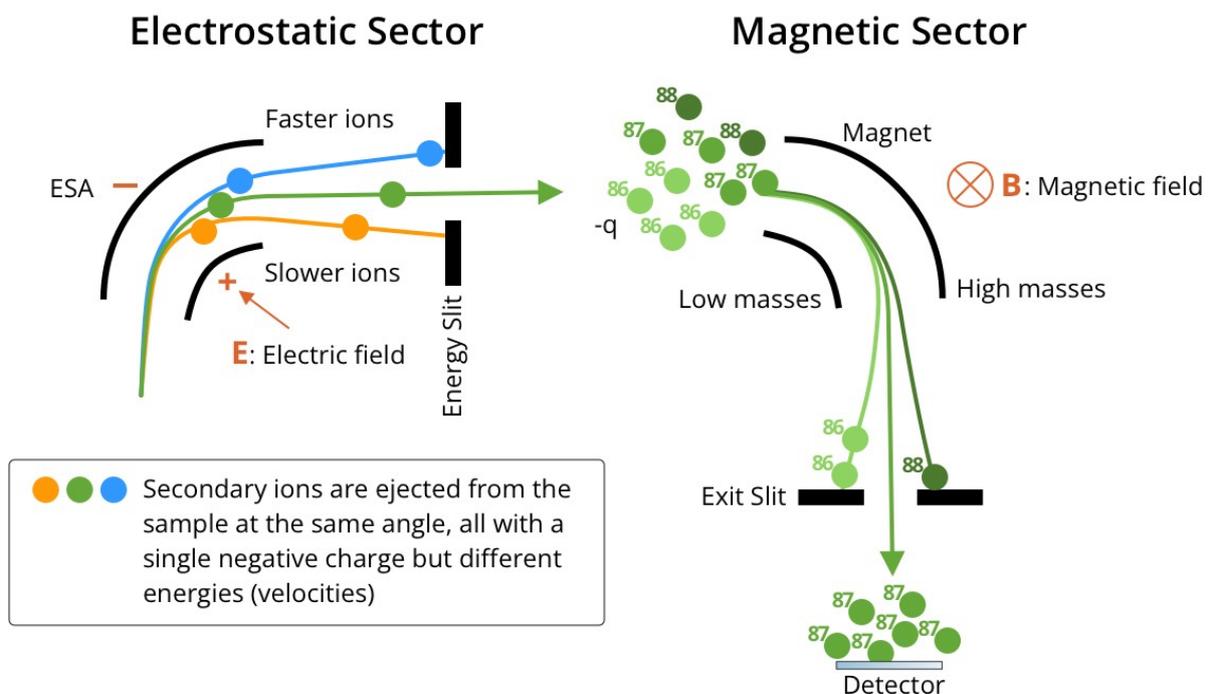

Illustration showing how the secondary ions that emerge from the electrostatic sector are further separated in the magnetic sector based on their mass:charge ratio. As the overwhelming majority have a single charge, the magnetic sector essentially separates them according to their mass. In this case, the exit slit is adjusted to detect only the ^{87}Sr ions.

Collection system − Magnetic sector analyser operation

The magnetic sector analysers in LG and NanoSIMS instruments have two modes for collecting data and can operate in either.

1. In mono-collection mode, ion species of different mass:charge are detected one after the other by sequentially adjusting the magnetic field. The ion species are counted one after the other in a single fixed detector. This mode is used when masses are too far apart to be analysed together on the multicollection axis. This is especially important for the LG-SIMS, where masses that are different by less than ~15% can be simultaneously analysed in multicollection mode. This mono-collection mode, where all isotopes are collected in the same detector, avoids the need for detector intercalibration.
2. In multi-collection mode, the magnetic field is fixed, and a series of movable detectors are positioned along an axis to record ion species of specific masses simultaneously. The main advantage of this mode is that it is faster.
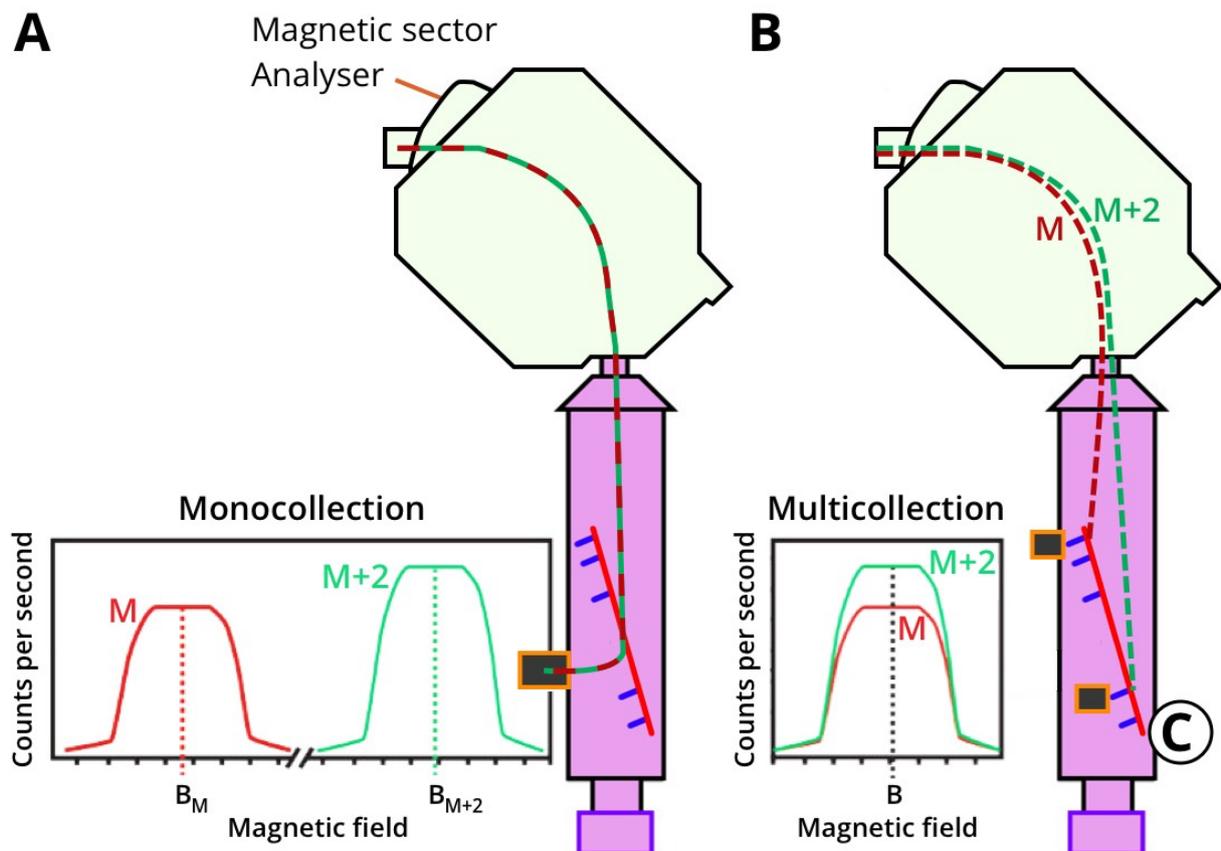
C
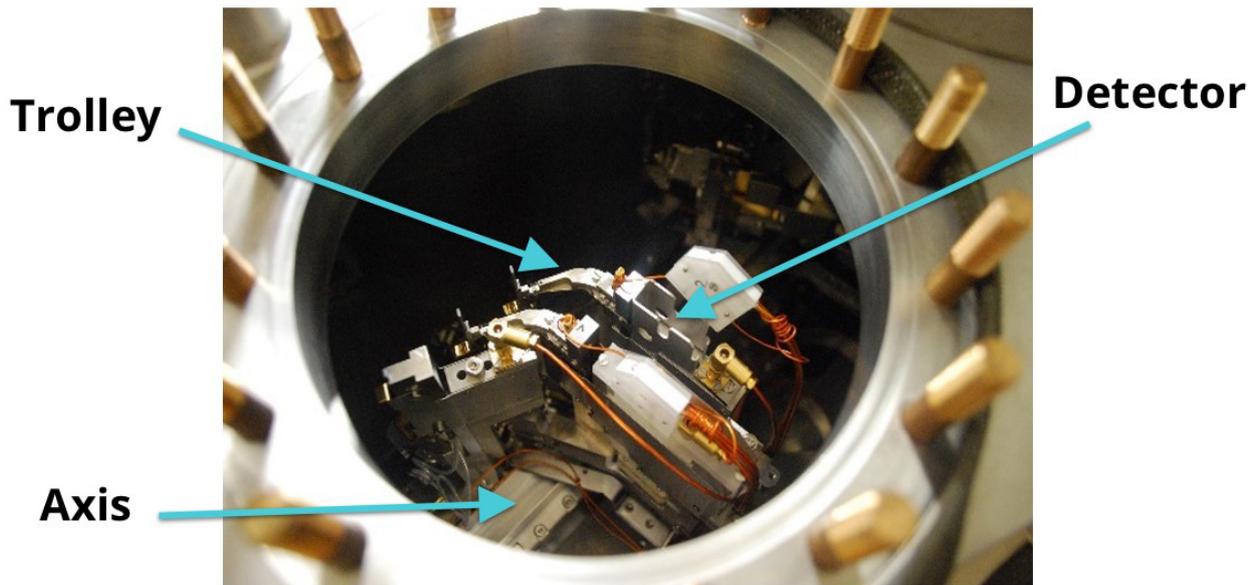
Two detection modes in the LG-SIMS. (A) mono-collection (B) multi-collection. (C) photo (below) taken at position C showing the inside of the multicollection cell showing the multicollection axis (the solid red line in A and B) with moveable trolleys (blue marks in A and B) with inserted detectors. In mono-collection mode (A), ions of the two different masses to be separated are shown as a dashed red and green line. One (M) is detected first and then the magnetic field is adjusted so that ions of the different mass (M+2) travel along the same trajectory to arrive at the same detector (black rectangle) after the first dataset has been collected. In multi-collection mode (B), ions with two different masses are shown taking two different trajectories through the magnetic sector analyser, being separated by a uniform magnetic field within the magnetic sector analyser and arriving at different detectors simultaneously.
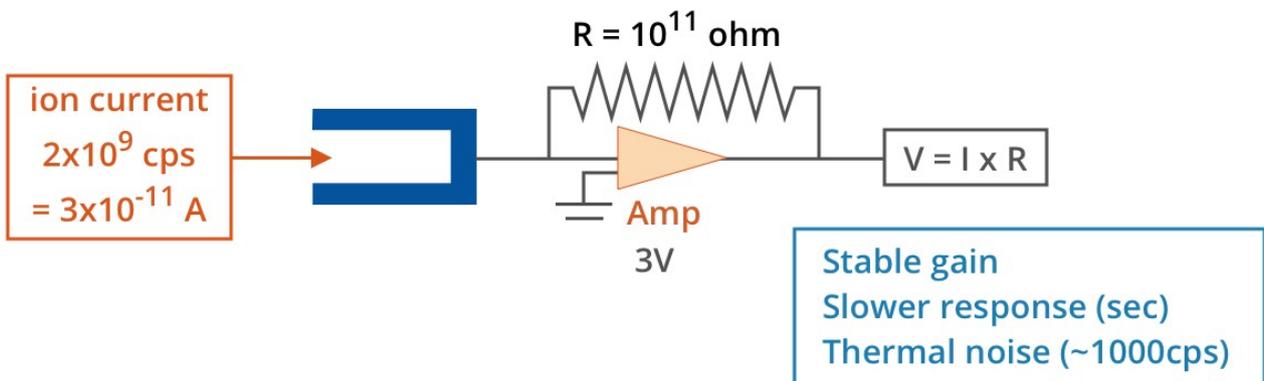
Detectors

The detector counts the number of ions passing through some point in space per unit of time. Electron multipliers and faraday cups are the two different types of detectors typically used in LG-SIMS and nanoSIMS.

Electron multipliers (EMs) come in several types, the most common being discrete dynode EMs. EMs are typically used for lower signals (well below 10^6 counts per second). They operate on the principle of electron multiplication – an ion striking the first dynode generates secondary electrons, which then strike subsequent dynodes, generating an electron cascade and producing a short pulse of millions of electrons at the output of the detector. Electron multipliers can register a single ion striking the detector.

Faraday cups are used for higher signal intensities (greater than 10^6 counts per second). A Faraday cup collects secondary ions and measures the ion current flow at its output. Faraday cups are often used in high-precision isotope ratio measurements, however, compared to EMs, their response time is slow.
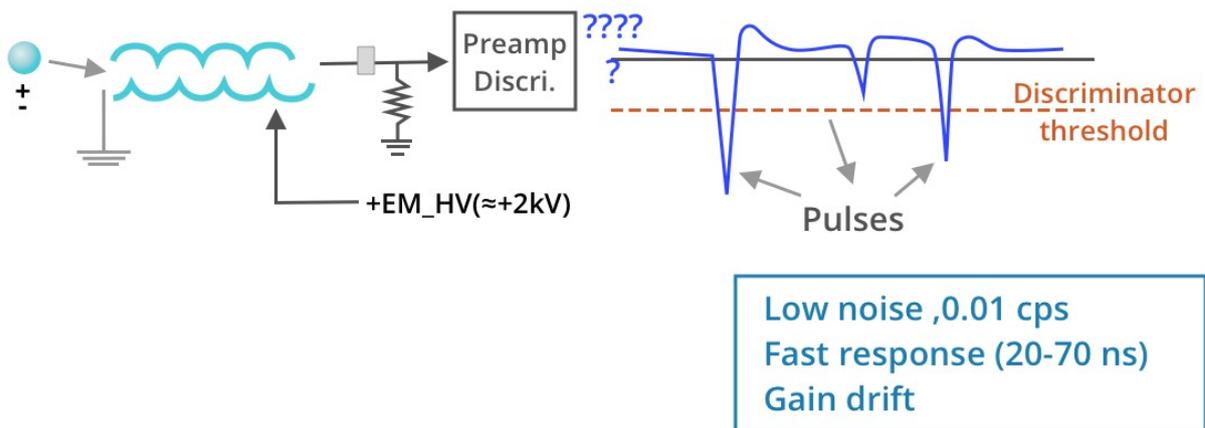
FC (Faraday Cup)

Direct ion current measurements > 10^6 cps

ion current
2×10^9 cps
= 3×10^{-11} A

$R = 10^{11}$ ohm

$V = I \times R$

Amp
3V

Stable gain
Slower response (sec)
Thermal noise (~1000cps)

EM (electron multiplier)

Pulse counting < 10^6 cps

+
-

+EM_HV(≈+2kV)

Preamp
Discri.

????
?

Discriminator
threshold

Pulses

Low noise ,0.01 cps
Fast response (20-70 ns)
Gain drift

Series of dynodes (N~20): each ejects 2-3 electrons

10^8 electrons produced per single ion - detected as an electronic pulse

Sample preparation for LG and Nano-SIMS

The position-specific nature of LG- and nano-SIMs means that it is important to first characterise your sample with other techniques to identify the most suitable locations for your SIMS analysis. This could include the use of SEM, EDS, EPMA, EBSD or light microscopy. This initial data can then be correlated to your SIMS data to provide a rich dataset of positionally specific information.

Once you are ready to undertake SIMS analysis, sample prepation for LG and NanoSIMS must be conducted according to strict guidelines to optimise the accuracy and precision in the dataset.

Sample Constraints and design

Samples must be vacuum-compatible, so if they need to be embedded, a low degassing resin substrate must be used.

The sample to be analysed is typically placed into a holder and loaded into the sample stage. Sample dimensions thus need to adapt to the available holders, which can vary between nanoSIMS and LG-SIMS. Some examples of sample holders for the NanoSIMS 50L are shown below


The electrical conductivity on the surface of the sample must be optimised by polishing the sample flat to remove relief (different in height between the resin and the grains of interest). Relief can cause some instability during data acquisition and must be minimised.

To ensure the conductivity of the samples, they are usually coated with a metal, generally gold, but platinum or carbon can also be used.

As LG and NanoSIMS analyse down to the first couple of micrometres of a surface, that surface needs to be perfectly clean. This is done using a solvent (usually ethanol) and distilled water. The contamination is more important for some elements such as Cl, K and Na or Pb, which are commonly found on all surfaces.

Standards, or reference materials (RM in the figure below), are included in the resin block close to the sample for maximum accuracy.

For LG-SIMS instruments, all grains of interest must be located close to the centre of the mount and to the standard grains to avoid holder edge effects. When analyses are done far away from centre and standards, they can be biased and inaccurate.
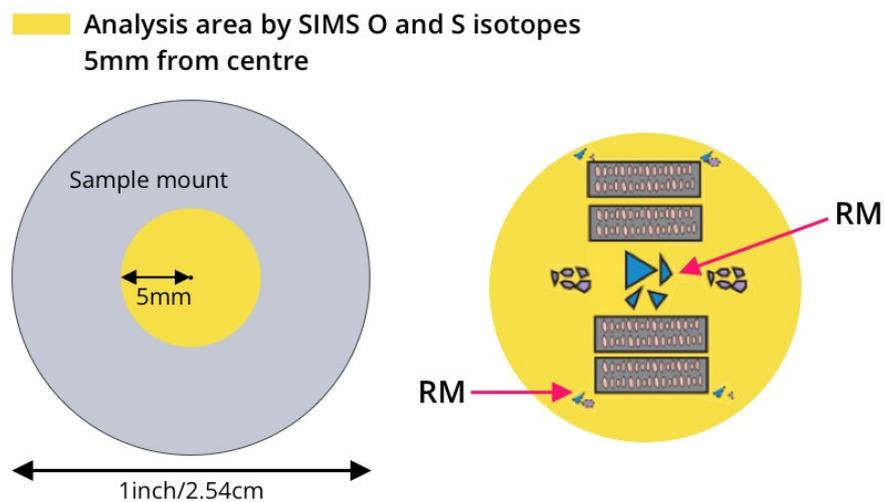
For LG-SIMS instruments, all grains of interest must be located close to the centre of the mount and to the standard grains to avoid holder edge effects. When analyses are done far away from centre and standards, they can be biased and inaccurate. RM = reference material.

LG-SIMS - specific capabilities − Benefits of LG-SIMS

LG-SIMS are designed for the in-situ measurement of isotopes or element concentrations in solid materials with high precision. Spot size is routinely 10–15µm, but can go down to a couple of µm but only at the expense of precision (reproducibility). Precision obtained on oxygen isotope measurements in zircon using a 10–15µm spot size is typically 0.15 parts per thousand (also known as 0.15 per mil). The large geometry of an LG-SIMS and the double focussing system optimise the transmission of the secondary ions, even when high mass resolution is required.

Data Output from LG-SIMS

Data output from an LG-SIMS can have different formats, corresponding to different functionalities:

1. Spot analyses return the isotope ratios measured over an area of 10–15 x 10–15 µm and a couple of µm in depth.
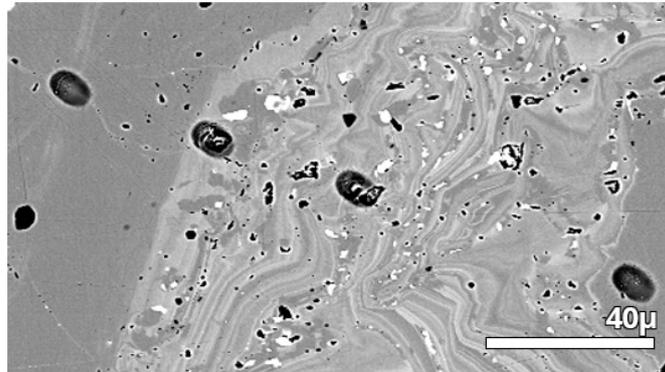
Typical analytical spot for LG-SIMS IMS1280, here in a pyrite crystal (BSE image, courtesy of Dennis Sugiono).

2. Depth profiling: distribution of isotope concentration in sample's depth.
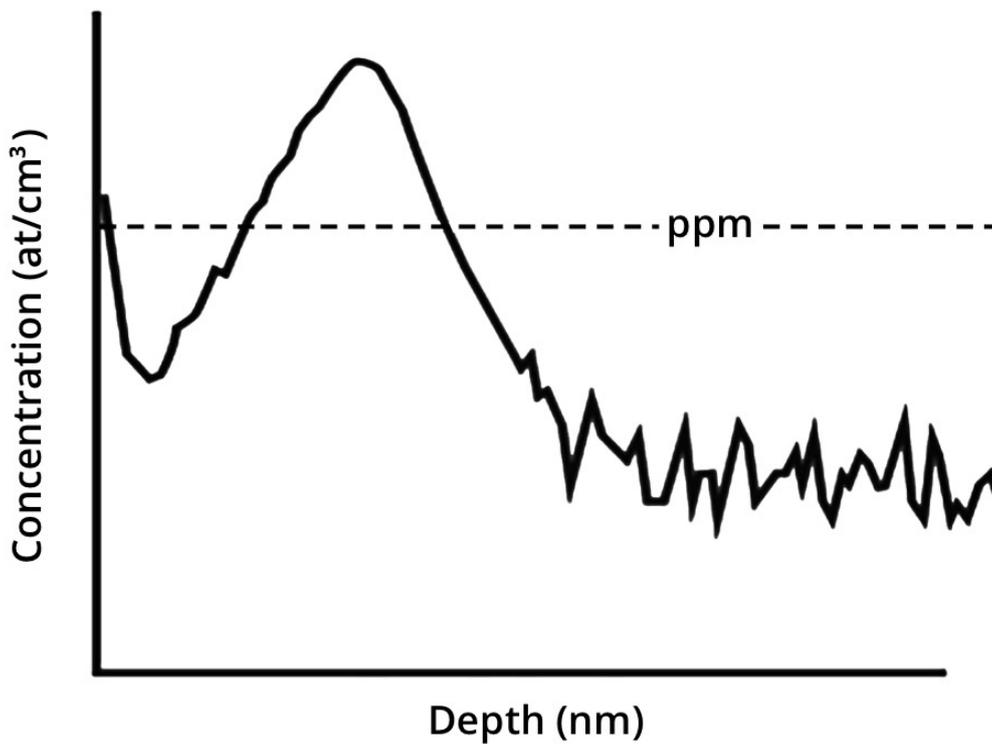
Example of depth profile of ^{11}B in Si chip. Courtesy of Jan Lorincik.

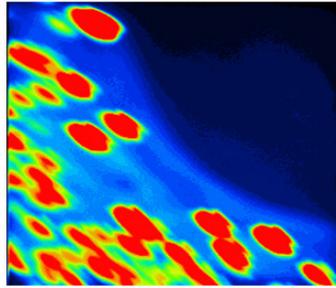3. Scanning Ion imaging (SII): distribution of isotope over a given area, usually > 20 x 20µm in size.

Image of ^{32}S in apatite by secondary ion imaging. Field of view is 60 x 60 μm

4. Combining secondary ion imaging and depth profile provides a 3D view of a scanned area (figure below). In microprobe mode, the beam is scanned over the surface to produce 2D elemental or isotopic images. By recording successive 2D images, depth dependent information can be obtained, making it possible to generate 3D images of a sample.

A

B
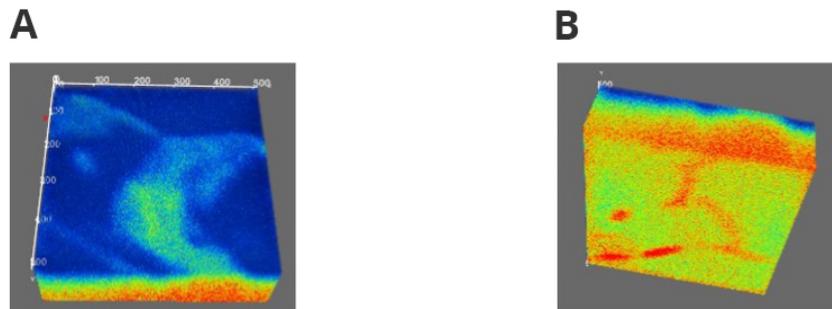
Instrument performance

Three criteria contribute to the performance of a SIMS instrument with mass resolving power and transmission being the two main parameters defining the performance of a mass spectrometer.

1. Transmission:
   Mass resolving power (MRP) describes the ability of a mass spectrometer to distinguish between two spectral peaks that correspond to two adjacent masses (we consider that charge= +/-1). As described above, these are also known as interferences. Transmission is a measurement of how efficiently a mass spectrometer extracts and guides secondary ions from the entrance of the mass spectrometer to the detectors. It is a comparison between the number of secondary ions extracted from the sample and the number collected by the detector. Transmission can usually be optimised, but to the detriment of mass resolving power. In LG-SIMS, the double focusing system combined with the large geometry of the mass spectrometer, which favours mass dispersion by the magnet, optimises the transmission of secondary ions, even when working at high mass resolving power. LG-SIMS can generate highly precise isotope ratios, even when a high mass resolving power is needed for the resolution of interference. Typical precision on stable isotope ratios of element-forming minerals (such as O in silicates or S in sulfides) is ~0.5 per mil or below. Typical precision on U–Pb dates in zircon measured by SIMS are ~1-2% and sub% for Pb-Pb ages for zircon older than ~1000 Ma.

2. Sensitivity:
   Sensitivity is the capability of an instrument to detect small differences in concentrations. LG-SIMS is the most sensitive technique amongst the SIMS instruments. Measurement sensitivity depends on the element and its secondary ion yield but can be as low as 1 part per billion (ppb).

3. Spatial resolution:
   Although one of the most destructive SIMS techniques, the volume of material consumed during LG-SIMS analyses is still very low. When using a 3nA Cs+ primary beam, the spot size is commonly 10 to 15μm in size, laterally, and 1-2μm deep. This spatial resolution well suits geological and biogenic solid materials (minerals, glasses) as they can exhibit heterogeneities as this scale and even below. The spatial resolution of the SIMS is also particularly suitable for rare or precious materials.

Calibration

LG-SIMS can generate highly precise isotope ratios. However, the raw ratios measured by SIMS must be calibrated against a reference material (RM) to ensure accuracy of the results. It is strongly advised to use secondary standards, processed as unknowns, to check the accuracy of the results. All RM, primary and secondary, should have the same chemistry and mineralogy as the unknown samples. For isotope measurements, the difference between the known and measured values of the RM is called Instrumental Mass fractionation (IMF).

Instrumental mass fractionation on LG-SIMS

Matrix effect

Minerals are often solid solutions (typically the garnet group) so their chemistry can vary between several end-members. For example, many garnet group minerals have the general structural formula $X_3Y_2(SiO_4)_3$, where X can be Ca, Fe, Mn or Mg. So these garnet minerals can have intermediate composition between end-members grossular (X=Ca), almandine (X=Fe), pyrope (X=Mg) and spessartine (X=Mn). Garnet minerals consequently often show internal chemical variations (Fig. A), or unknown composition may vary from that of the RM. This difference in chemistry can make the calibration inappropriate, resulting in an isotope bias, often referred to as 'matrix effect'.

A

Example of chemical variation in a garnet
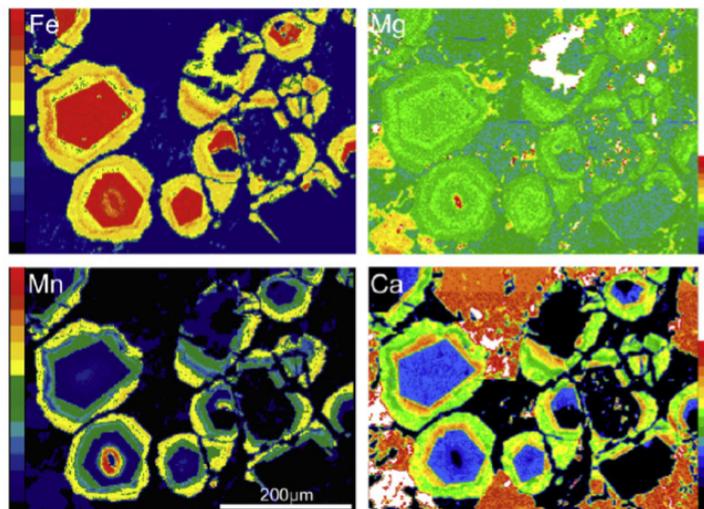
Martin et al. (2011)

B
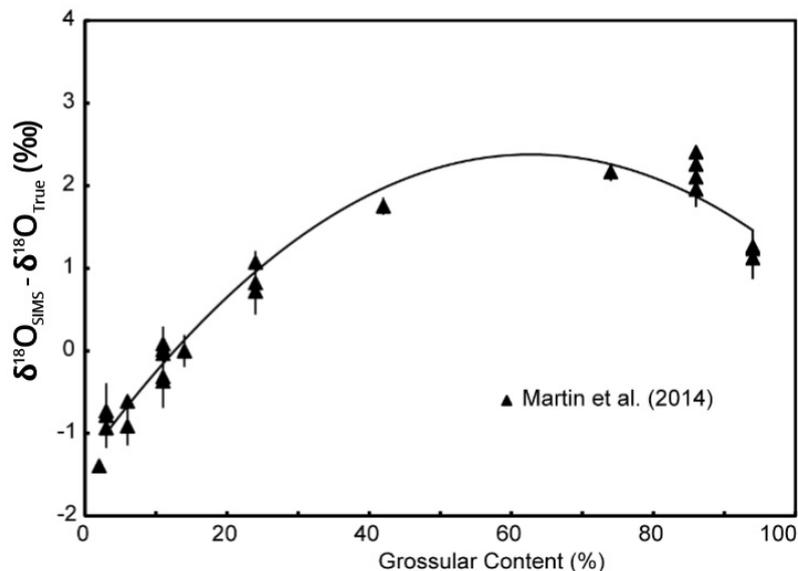
Matrix effect on isotope measurements by LG-SIMS. (a) example of internal chemical variations within garnet minerals (here shown X-ray maps for different element, obtained by EPMA). (b) Matrix effect of grossular content in garnet on oxygen isotope ratios (here expressed as delta notations, reported in per mil) by LG-SIMS.

To overcome this, several standards with different compositions are typically used to bracket the chemical range and model the resulting matrix effect or bias on isotope ratios. This is done by inferring a bias versus composition relationship that can then be applied to the unknown (Fig. B). The existing studies on matrix effect in minerals show that the magnitude of the bias can be significant (up to 10 per mil for O isotopes in garnet and dolomite) and the relationships is often not linear (polynomial for O isotopes in garnet, Fig. B).

LG-SIMS for isotope geochemistry

LG-SIMS are designed for the measurements of precise isotope ratios, with many applications using isotope chemistry (radiogenic or stable isotopes) to date processes or reconstruct the environmental conditions of the sample formation. Atoms are composed of a nucleus surrounded by one or more electrons. The nucleus is composed of neutrons and protons.

$$\text{N neutrons} \; + \; \text{Z protons (atomic number)} \; = \text{ATOMIC MASS (A)}$$

$$146 \text{ neutrons} \; + \; 92 \text{ protons} = {}^{238}\text{Uranium}$$

The number of protons and electrons determines the element and its chemical properties. Two isotopes of a same element differ only in the number of neutrons: they have the same number of electrons and protons and thus have the same chemical properties.

Two types of isotopes can be distinguished:

1. Radiogenic isotopes are formed by radioactive decay of unstable atoms. As an example, Lead (Pb) has three radiogenic isotopes: ^{206}Pb, ^{207}Pb, ^{208}Pb formed by radioactive decay of ^{238}U, ^{235}U and ^{232}Th, respectively. Isotope ratios depend on the age of the system and can therefore be used for dating applications.
2. Stable isotopes. As an example, oxygen (O) has three stable isotopes: ^{16}O, ^{17}O and ^{18}O. In contrast to radiogenic isotopes, the nuclei of stable isotopes do not undergo radioactive decay. Their relative abundances do not vary in response to radioactive processes. However, small variations in the relative abundance of stable isotopes of one element occur in response to chemical or physical processes. For example, during sea water evaporation, ^{16}O is preferentially concentrated in vapour and ^{18}O in the remaining water. The partitioning of one isotope over another between two substances is called isotopic fractionation. Isotopic fractionation is the basis of stable isotope geochemistry. Stable isotope geochemistry helps to characterise the environment in which minerals were formed.

Applications of LG-SIMS in geoscience

The in-situ capability of LG-SIMS makes it perfectly adapted to analysing the complex geochemical information recorded in minerals. Minerals can hold information from different episodes of growth or re-equilibration, sometimes within just 200µm, or even well under.
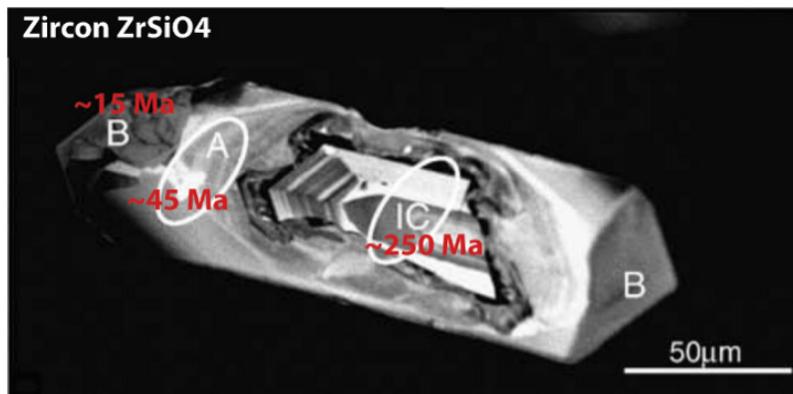
Example of cathodoluminescence image of zircon, showing 3 growth episodes at ~250, 45 and 15 Ma.

In situ capability can also be used to target rare or precious samples

U–Pb Geochronology

One of the most important applications of LG-SIMS is mineral dating using the U–Pb method. The most common mineral used for dating is zircon, a zirconium silicate ($ZrSiO_4$) that contains trace amount of U. During a U–Pb analysis by LG-SIMS, U and Pb isotopes are analysed in zircon using oxygen primary ions. Knowing the decay constant of U isotopes (235 and 238) in Pb (207 and 206), the age of the mineral can be calculated.

## Structure and Geodynamic of Mars retrieved from a 4.2Ga zircon record.

Many analyses had been done before on Northwest Africa meteorite samples by thermal ionisation mass spectrometry (TIMS) on whole, single grains and had returned ages at 4.4-4.5Ga. However, a single zircon from this study was analysed in-situ by LG-SIMS and returned a much younger set of dates (~1548 Ma). This work has extended the zircon record down to 1.5 Ga. These younger records have been associated with long lasting magmatic activity related to a mantle plume. Costa et al. 2020. The internal structure and geodynamics of Mars inferred from a 4.2-Gyr zircon record. PNAS 117, 30973-30979

Early Earth processes revealed from stable oxygen isotope.

Western Australia is composed of some of the oldest rock on Earth and has long been used as a natural laboratory to elucidate the early evolution of our planet. The oxygen isotope signature in zircon extracted from very old rock samples was used to identify the primordial source of the water involved in the formation of the first continental crust and helped refine the model explaining the appearance of the first earth crust. Smithies et al., 2021, Oxygen isotopes trace the origins of Earth's earliest continental crust. Nature 592, 70-75.

LG-SIMS for Nuclear Safeguards and Forensics

LG-SIMS instruments are used to provide the analysis of environmental samples for the detection of undeclared nuclear activities at facilities around the world. IAEA inspectors collect environmental samples on swipes that are sent to the IAEA's Network of Analytical Laboratories (NWAL). Particles on those swipes are analysed to identify U-rich ones and analyse their U isotope ratios. U isotope ratios are used to identify the type of nuclear activity occurring in the source facility.
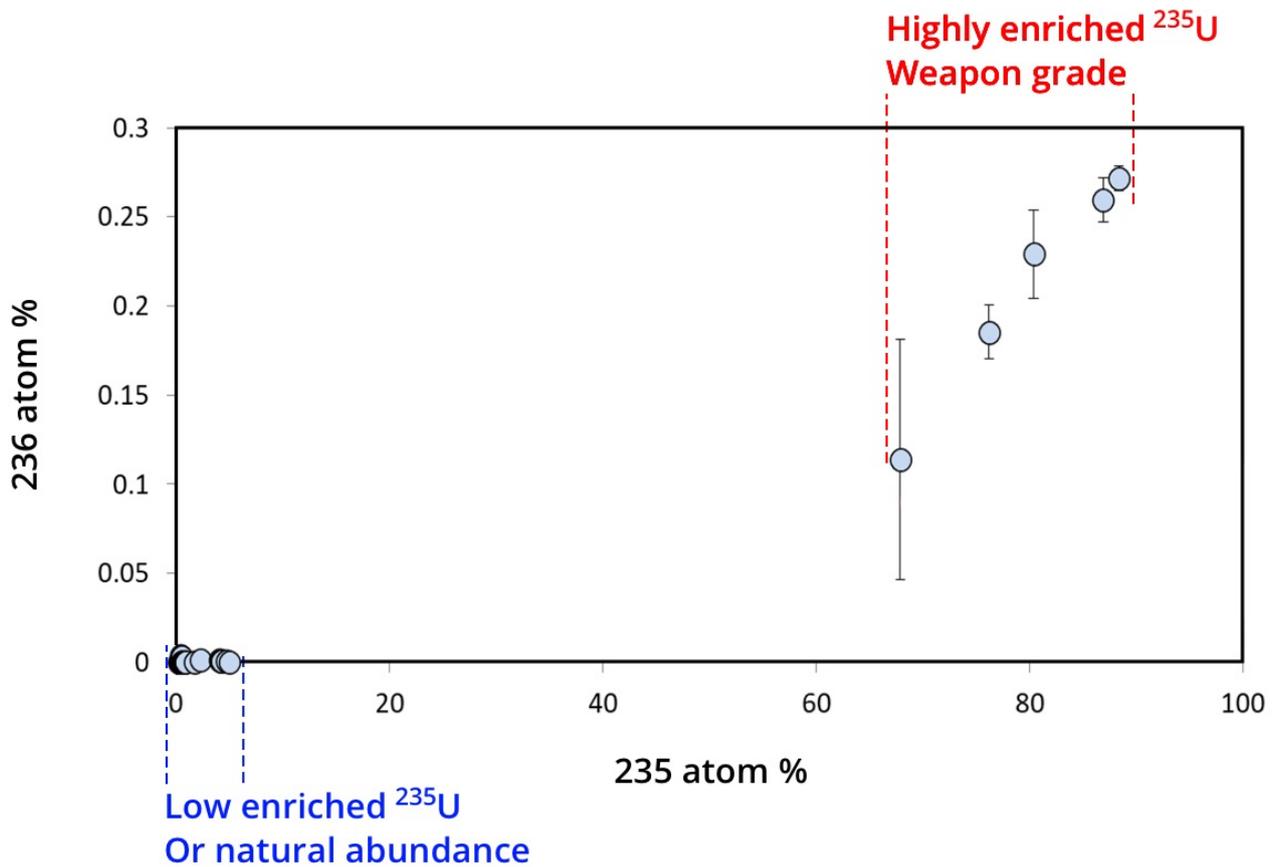
NanoSIMS - high resolution imaging mass-spectrometry – Benefits of Nano-SIMS

As with other SIMS instruments, in NanoSIMS, a primary beam bombards a sample generating secondary ions that are counted by a mass spectrometer. One key difference is that the NanoSIMS has been optimised for SIMS measurements with high spatial resolution – the primary beam is focused down to a small spot, in the range of 50 nm. As a result, the NanoSIMS is primarily used as a tool for imaging and mapping. Elemental and isotopic images can be generated by scanning or rastering the beam over particular areas of a sample. The instrument has seven detectors, so the spatial distribution of seven different elements or isotopes can be visualised simultaneously.

Mass range	^{1}H to ^{238}U
Spatial resolution	Down to 50 nm
Sensitivity	ppb levels for some elements
Mass resolution	High mass resolution e.g. can separate ^{13}C from ^{12}C ^{1}H at mass 13
Deformation	7 detectors – simultaneous analysis of 7 isotopes or elements
No. of detectors	Highly versatile – applications in geology, biology, medicine and materials science

The strength of NanoSIMS is that it combines excellent sensitivity and spatial resolution with high mass resolution. The image below shows the high-resolution mass spectra at masses 13, 27 and 17, where the isotopic signal of interest is easily separated from other ions of similar mass (isobaric interferences).
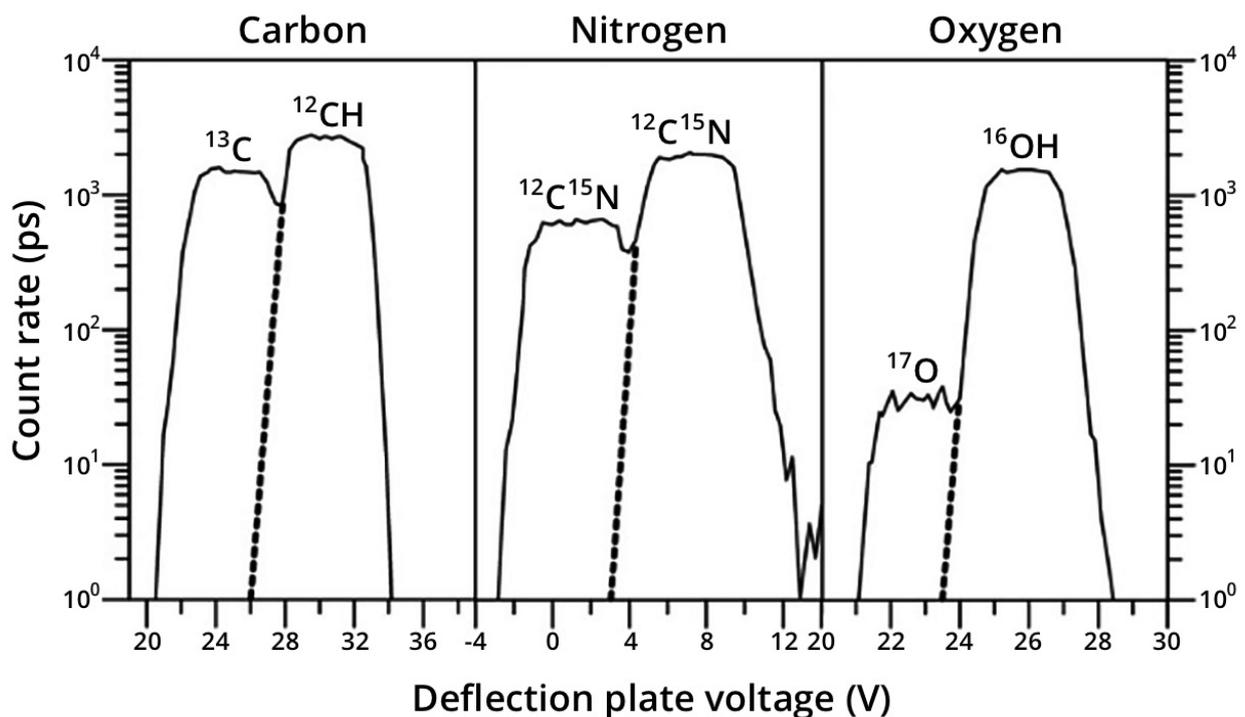
High-resolution mass spectra scans at masses 13, 27 and 17
Taken from: 'NanoSIMS: Technical Aspects and Applications in Cosmochemistry and Biological Geochemistry'. Hoppe, Cohen. June 2013. Meibom, Geostandards & Geoanalytical Research, Volume37

Photo of the NanoSIMS 50L at the University of Western Australia The grey cover houses the multicollection system – 7 detectors, 6 of which are on movable trolleys.

Secondary Ion Mass Spectrometry

NanoSIMS applications

Combining stable isotope labelling with NanoSIMS lets you directly visualise the distribution of labelled components within an experimental system, without changing the system's chemical nature. For example, ^{15}N and ^{13}C labels can be attached to specific molecules used in biological systems (which has applications for tracking nutrients and drugs), and deuterated ^{18}O labelled water may be used to investigate mineral–fluid interactions. Furthermore, isotopic labels can be conjugated to specific antibodies to identify proteins of interest, or to oligonucleotides to detect the presence of different species of bacteria. Some further examples of NanoSIMS applications, involving both isotopic and elemental imaging, are given in the following sections.

NanoSIMS – Cancer therapeutics

Isotopes can be used to label cancer therapeutics so they can be tracked within cells

| BBR3464 | X = Cl | n = 4 |
| TriplatinNC | X = $NH_2(CH_2)_6H_2N_2$ | n = 8 |
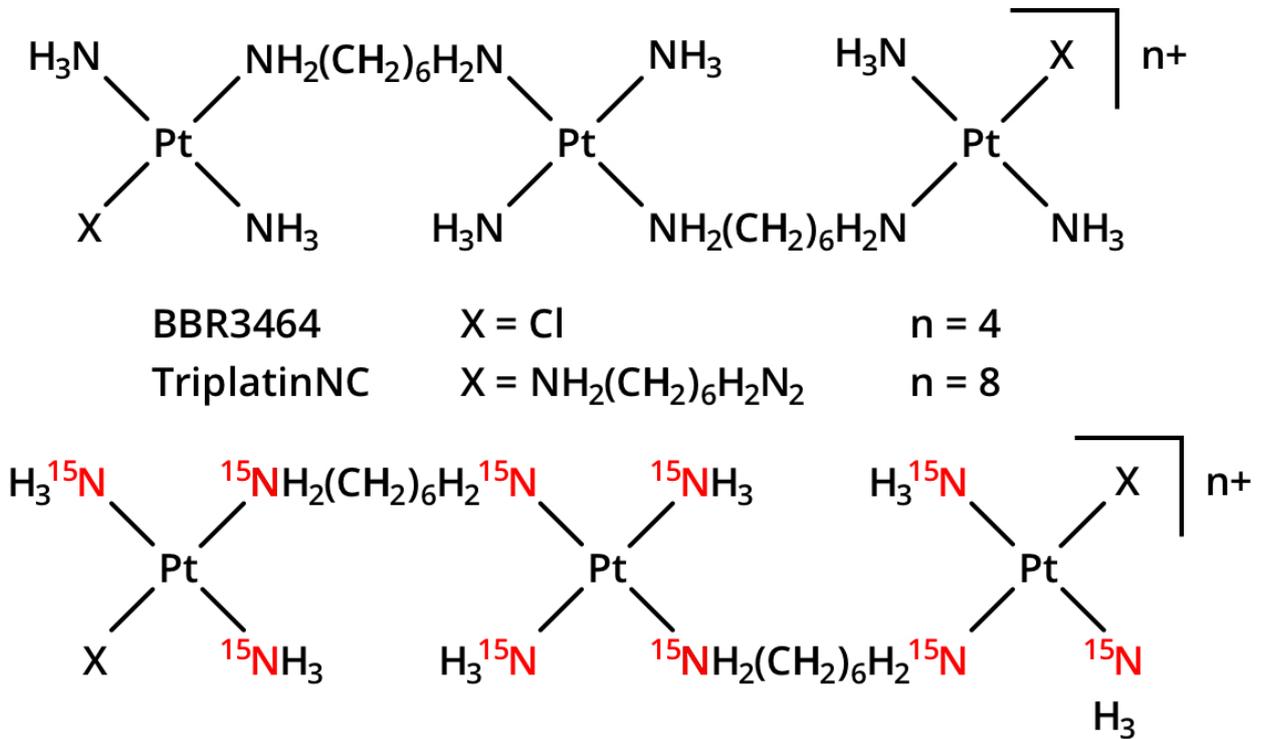
Pt-based cancer therapeutics synthesised with an isotopic tracer – the major isotope ^{14}N has been replaced with ^{15}N. As Pt is not normally found in cells, it does not need to be replaced with tracer.
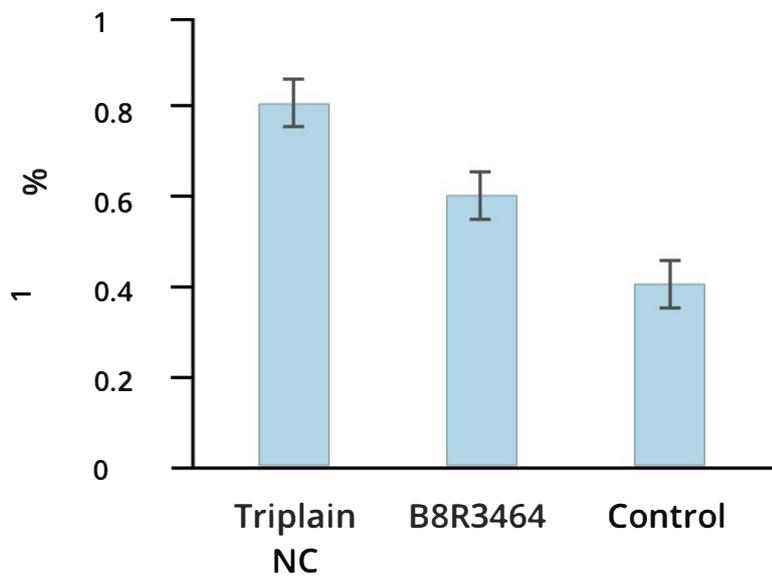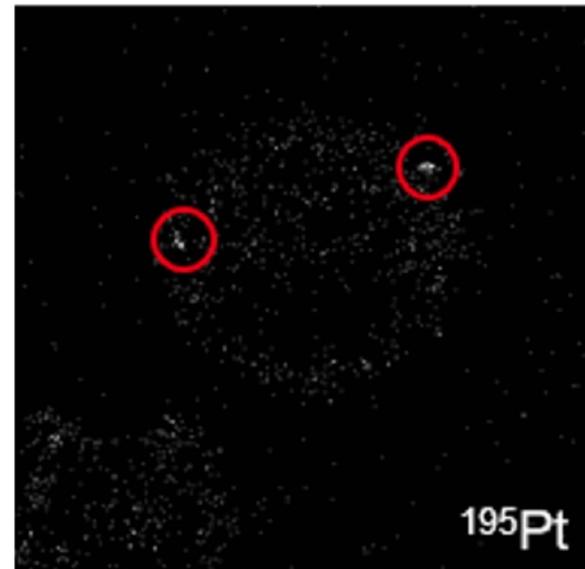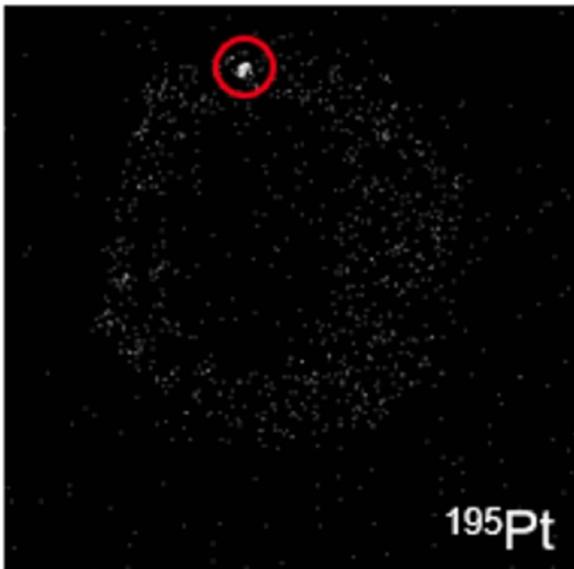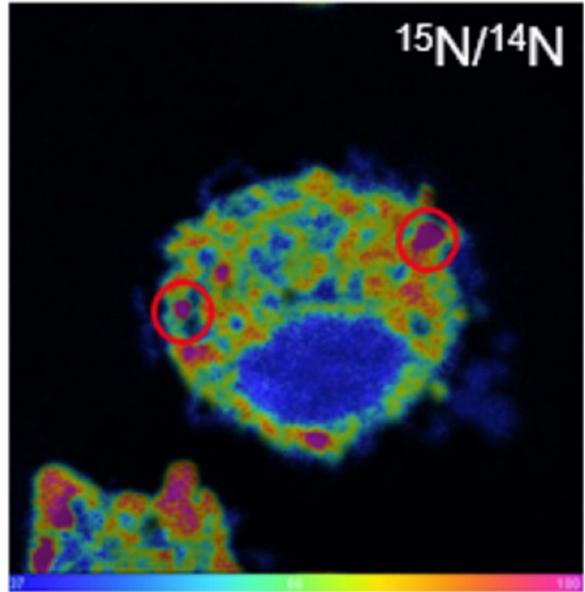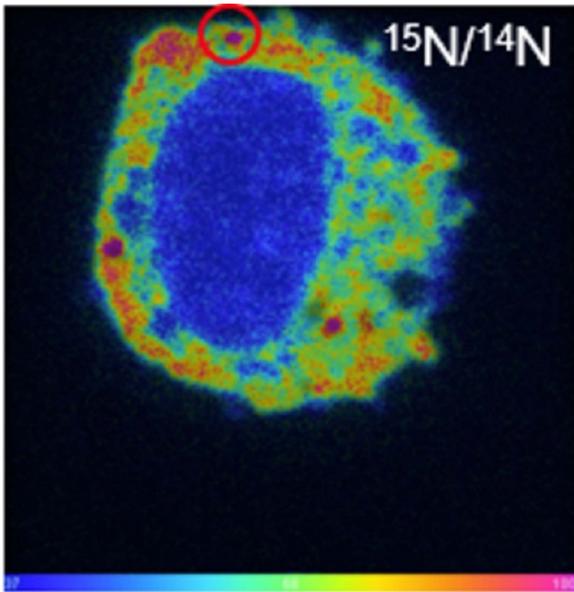
The distriubtion of isotpically labelled cancer theraupetics can be visualed at the subcellular level with NanoSIMS (need to add numbers to ratio image scale)

NanoSIMS – Environmental processes

NanoSIMS analysis has proven to be very useful for studying environmental processes, both biotic (concerning living organisms in an ecosystem, such as plants and bacteria) and abiotic (non-living ecosystem components, such as the mineral components of soil). The ability to observe the presence of natural elements and isotopes, as well as introduced isotopic tracers, has been used in studies in a diverse range of fields, from marine biology to cosmochemistry.

Below are NanoSIMS images comparing nitrate uptake (24 hours incubation with $^{15}NO_3$) by coral (Stylophora pistillata) and its algal symbiont growing at normal temperature (top) and growing in heat stressed conditions (bottom; after 10 days). The left images are $^{12}C^{14}N$ ion images, useful for ultrastructural detail; the right images are $^{15}N/^{14}N$ ratio images showing points of ^{15}N enrichment (0.37 atom % is natural abundance).
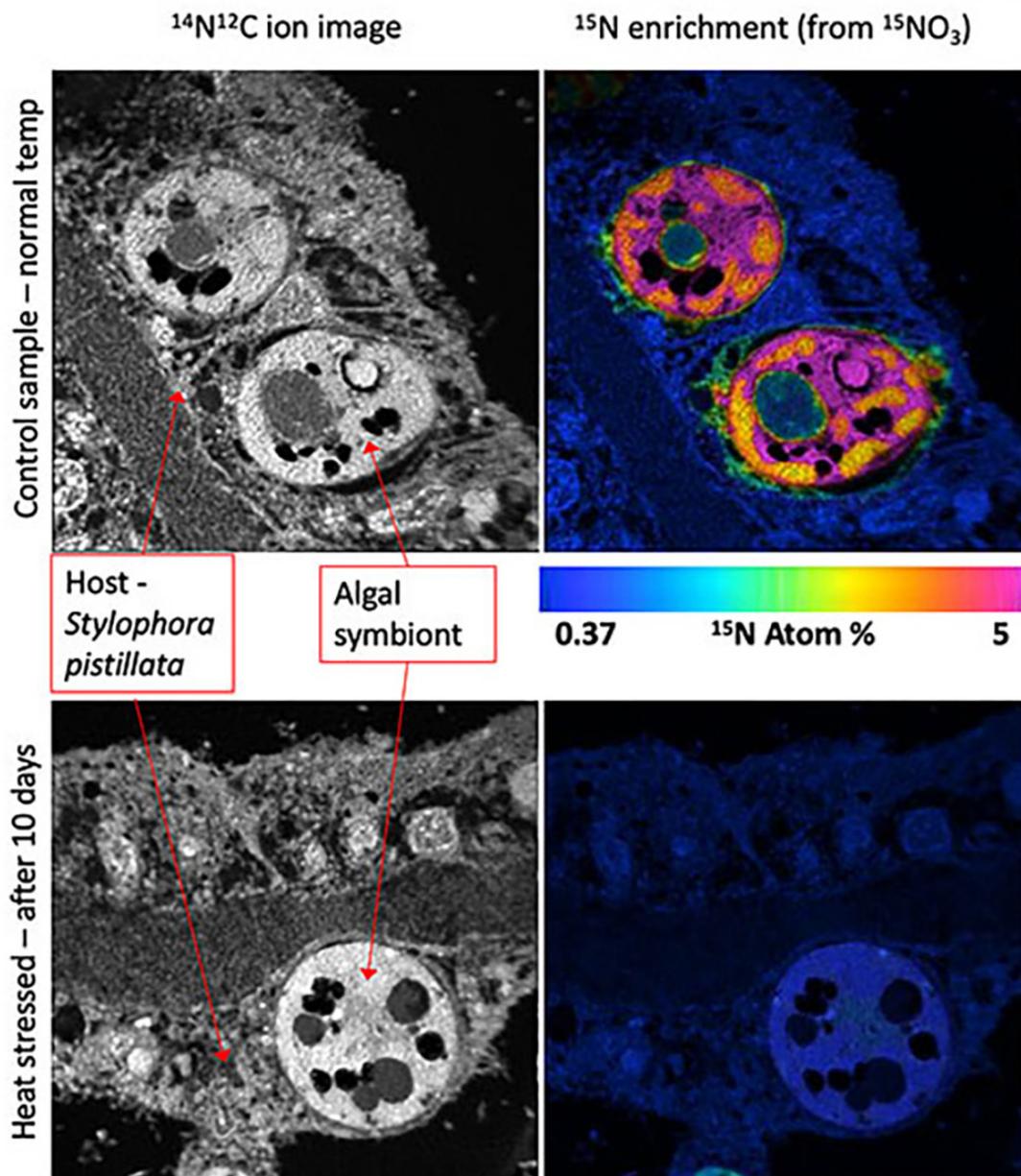
NanoSIMS – Medical

NanoSIMS analysis has great potential in medical research. In the example below a bromine labelled nucleic-acid-based therapeutic (modified antisense oligonucleotide, or ASO) is ingested by a mouse, and the distribution of ASO in various tissue types is observed by NanoSIMS at the subcellular level. The results show that NanoSIMS imaging reveals the distribution of ASOs in both cultured cells and in the tissues of mice with both high sensitivity and high spatial resolution. https://academic.oup.com/nar/article/49/1/1/6020208?login=true
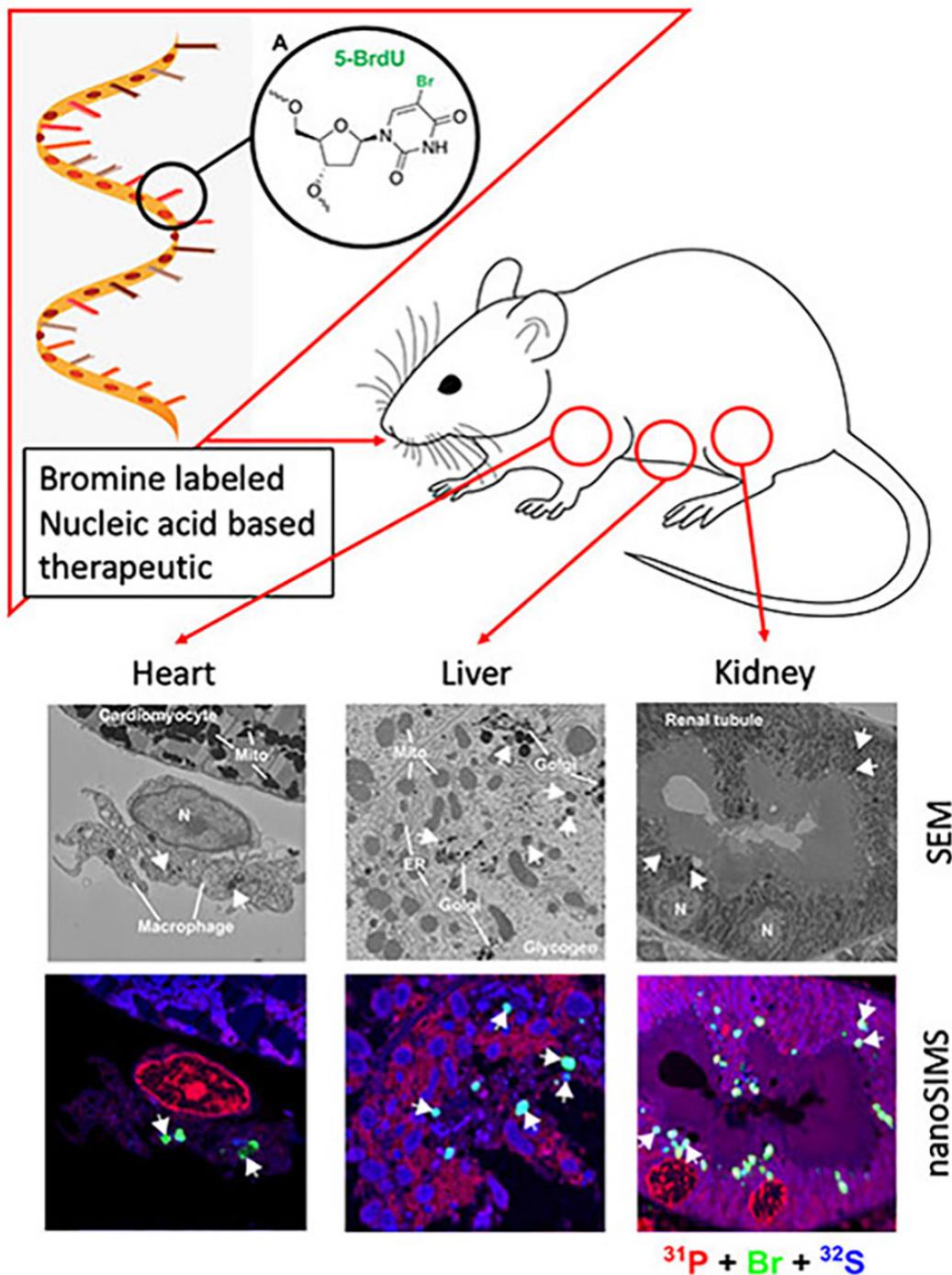
NanoSIMS – Geology

NanoSIMS analysis has proved to be a versatile technique for microscale elemental and isotopic profiling of a wide range of sample types. The ancient pyrite grains in the figure demonstrates how elemental (top) and isotopic (bottom) information can be extracted from very small samples at very high resolution. Studying this beautifully zoned pyrite provides us with insight into the conditions in which it formed, as well as information about the system that supported microbial life on the early Earth. NanoSIMS reveals the complexities present within the pyrite grain, by providing images of the distribution of elements within the sample at nanoscale-resolution.
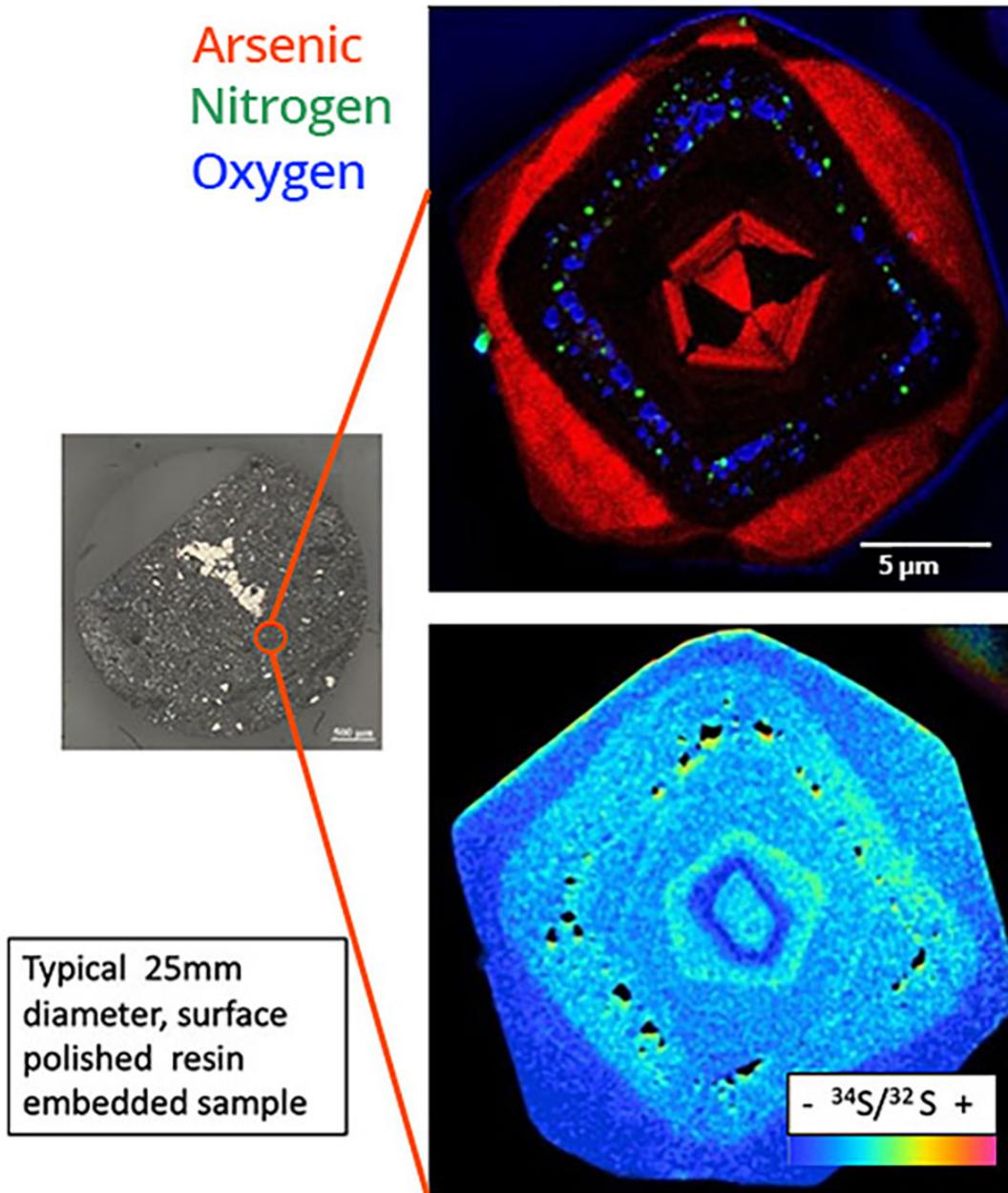
NanoSIMS – Materials Science

NanoSIMS has been used to study a range of problems in materials sciences, such as dopant and contamination effects in semiconductors, hydrogen damage in steels, oxidation and corrosion, crack and defect evolution, as well as diffusion and segregation processes.

Depth profiles can also be generated, providing information about chemical variations as a function of depth from the surface. This information is very useful for the analysis of thin films and layered structures, such as those found in semiconductor devices. The below figure shows a NanoSIMS map of a steel alloy produced by strip-casting, revealing information about the segregation of the substitutional solute elements, silicon, aluminium and carbon during the solidification process.

Silicon Aluminium Carbon   5 µm
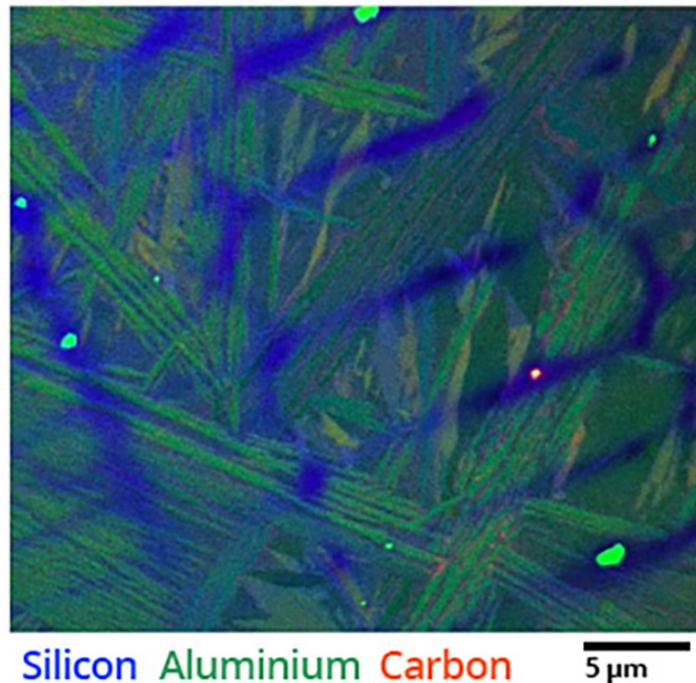
Credits

Microscopy Australia acknowledges the huge input of time and expertise by the many staff members and associates who have contributed to the development of MyScope over the years.

For the SIMS module we particularly thank: Rob Jones, Laure Martin, Matvei Aleshin, Alex Cavallaro, Georgia Guild, Will Rickard, Paul Guagliardo, Mitchell Nancarrow, Brett Hamilton and Jenny Whiting.