Invited Review Article: Recent developments in isotope-ratio mass spectrometry for geochemistry and cosmochemistry

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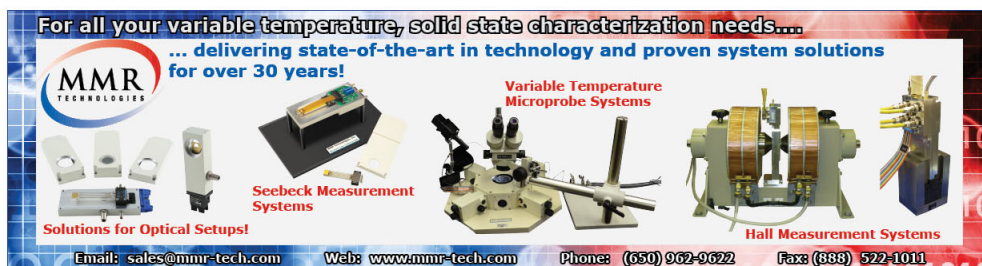
Invited Review Article: Recent developments in isotope-ratio mass spectrometry for geochemistry and cosmochemistry

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Mass spectrometry is fundamental to measurements of isotope ratios for applications in isotope geochemistry, geochronology, and cosmochemistry. Magnetic-sector mass spectrometers are most common because these provide the best precision in isotope ratio measurements. Where the highest precision is desired, chemical separation followed by mass spectrometric analysis is carried out with gas (noble gas and stable isotope mass spectrometry), liquid (inductively coupled plasma mass spectrometry), or solid (thermal ionization mass spectrometry) samples. Developments in *in situ* analysis, including ion microprobes and laser ablation inductively coupled plasma mass spectrometry, have opened up issues concerning homogeneity according to domain size, and allow ever smaller amounts of material to be analyzed. While mass spectrometry is built solidly on developments in the 20th century, there are new technologies that will push the limits in terms of precision, accuracy, and sample efficiency. Developments of new instruments based on time-of-flight mass spectrometers could open up the ultimate levels of sensitivity per sample atom. © *2013 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4765055]

I. INTRODUCTION

Isotope abundances can provide unique information regarding the nature of processes and their timing. In geosciences, the ability to measure isotope ratios has become an essential tool in constraining geological events. The small mass differences between isotopes cause them to respond at different rates in kinetic processes providing signatures of specific chemical reactions. Decay of radioactive nuclides results in a change in time of parent/daughter isotope ratios; measurement of these ratios therefore allows us to date geological events. In cosmochemistry, the primordial abundances of nuclides can be measured in grains that apparently condensed around stars that predated our sun, allowing information to be obtained from stellar nucleosynthesis through to incorporation of the elements in to our solar system.

A key aspect of isotope-ratio measurements in the geosciences is that the variability in isotope ratios varies greatly. The range in isotope abundances can be large, such as in the measurements of nucleosynthetic signatures in primordial grains, or the isotope signal can be very small, such as in a young rock where little ingrowth of a radioactive decay product has occurred. Samples can be small or large depending on the concentrations of the elements of interest, and the desired level of precision. Some measurements require chemical separation prior to analysis, while others can be carried out *in situ*. Ultimately as the level of precision improves, disentangling instrumental artifacts from natural variations can impose a limit on our ability to interpret the isotope record.

Isotope abundance ratios are measured with mass spectrometers. The development of mass spectrometers in the early 20th century was fundamental to the development of modern physics, but was also fundamental to the development of geosciences. Soon after Rutherford's experiments on the

nature of particles associated with radioactive decay, he had formulated the decay laws that would become the basis for U-Th-Pb geochronology.[1] As such, isotope abundances opened a whole new door into how we perceive the earth and the processes active on it.

This paper presents a review of some of the key aspects in mass spectrometry and its application in earth sciences. This is perhaps in some ways a mature field, but ongoing technological developments have allowed smaller samples, higher precision, and far better ability for interpretation. This paper is not intended to fully cover all mass spectrometry applications in geosciences. I have chosen to focus on isotope-ratio measurements because of my affinity to this field. However, there are also a number of new areas that could develop over time and so I have tried to highlight some of these in an attempt to look to future developments. I have tried to make this paper amenable to graduate students and others who are new to the field, but have also tried to place the field in a perspective of what might happen. Indeed, it is an exciting time.

A. Background

The basis for mass spectrometry is the differing response of ions of different mass to an external force. Very early in mass spectrometer development, two directions in instrument design appeared. On one side were the mass determinations that are fundamental to nuclear physics. These measurements required maximum resolution in the mass scale in order to accurately gauge the masses of various nuclides. On the other hand, isotope abundance determinations, which are fundamental to earth science applications, do not require accurate mass information, but rather require stable ion beams to allow precise and accurate measurements of the isotope abundances and isotope ratios.

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A mass spectrometer requires a system to ionize the element(s) under consideration, a vacuum system to maintain the ions, an analyser for dispersing the ions according to mass, and a detection system. In geosciences, specific types of sources are designed for gases, solids, and liquids, and for bulk and *in situ* work where the context of the sample is maintained. Mass spectrometers can use magnetic, electrostatic, or electrodynamic fields to separate the masses, although the preferred methodology for isotope ratio measurements is magnetic sector mass spectrometry. The resulting ion beams are quantified in two main types of collection devices (Faraday cups or electron multipliers), but 2D collectors are also used where spatial distributions of the ion beams are to be determined, such as in ion microscopes.

The fundamental consideration of a mass spectrometer is its ability to resolve ions of different mass. Where chemical separation of an element has occurred, unity mass differences are all that is required, but for *in situ* techniques in particular, molecular species of the same nominal mass to the atomic species (isobars) need to be resolved. The ability of a mass spectrometer to resolve ions according to mass is generally defined by the term "mass resolution." This will be more formally defined below, but mass resolution is a dimensionless number ($m/\Delta m$) that is used to describe the degree of peak separation of two masses in a mass spectrum. This can also be interpreted as the highest mass at which two masses that differ by one mass unit can be resolved. For example, a mass resolution of 400 indicates that masses 400 and 401 are only just resolved; heavier ions are not resolved from their next integer masses, whereas lighter ions show larger degrees of separation.

B. Historical aspects

Following his work on electrons (cathode rays), Thomson began investigations into the nature of positively charged rays. In 1913, he developed a mass spectrograph where ions were magnetically deflected on to a photographic plate where each individual mass defined a velocity parabola. He found that most of the gaseous elements he analyzed produced individual parabolas suggesting these elements were monoisotopic. An exception was the case of neon where he found two lines;[2] it was noted that the line from the heavier of the two species (mass 22) was much fainter that that of the lighter species (mass 21). Effectively this was the first isotope abundance ratio measurement.

In 1918, Dempster developed a mass spectrometer[3] that we would readily recognise today (Fig. 1). It had a 180° sector magnetic field that enabled directional refocusing, which vastly improved beam transmission. It had source and exit slits to spatially define the beam, and utilized a separate thermal ionization filament to produce and accelerate ions. Even though it only had a mass resolution of ~100, it produced extremely stable ion beams and was ideal for ion-abundance-ratio measurements.

Aston[4] joined Thomson at the Cavendish lab and in 1919 developed a mass spectrometer with separate electric and magnetic field sectors. This effectively removed the velocity
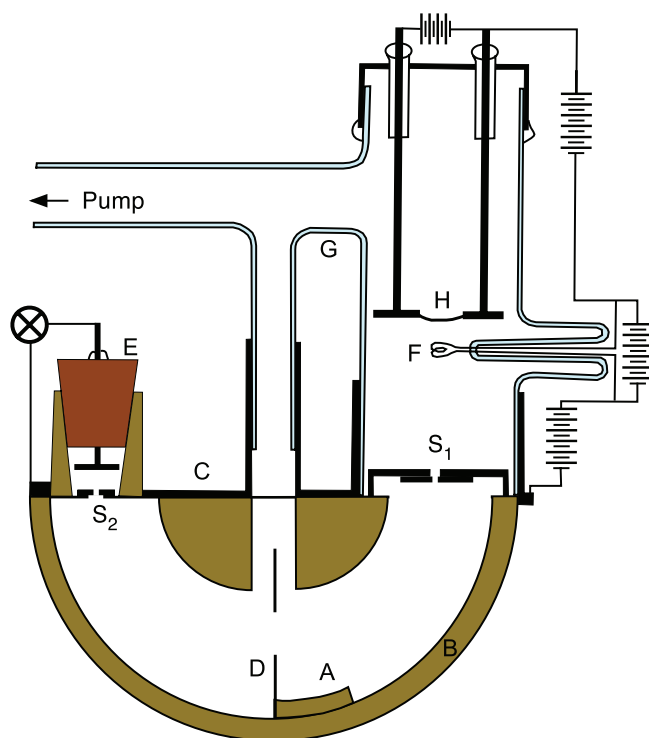

FIG. 1. Mass spectrometers consist of a source where the sample is ionized and accelerated, a mass analyser that produces mass separation, and a collector for measuring the abundances of the ion beams. The basic construct has changed little from Dempster's[3] first thermal-ionization mass spectrometer designed for isotope abundance measurements as illustrated here: (A) analyzing chamber, (B) brass tube fixed with iron plates, (C) brass plate seal with soldered tubes for three openings to the chamber, (D) defining aperture, (E) ebonite plug with electrometer, (F) electron-emitting filament, (G) glass tubing, (H) heating filament, (S_1) entrance slit, and (S_2) exit slit. The magnetic field covers the analyzer tube and is normal to this section. The source allows thermal ionization from salts placed on the heating filament (H), or through bombarding salts on the heating filament with electrons from the electron filament (F).

spread and yielded point images. He determined that masses of isotopes appeared to be multiple integer units. In assessing the stability of the nucleus it was clear to Aston that the nucleus would become unstable with increasing numbers of positively charged protons. This problem would not be resolved until Chadwick's discovery of the neutron over a decade later. Aston's mass spectrometer had a mass resolution of ~130, and was therefore suitable for separating ion beams with unity mass differences for light elements.

Aston's second mass spectrometer had a mass resolution of 600. It used curved electric plates and a magnetic field of 1.6 T. Voltage control was improved to 0.1% enabling major improvements in isotope abundance measurements. This capability enabled the resolution of mercury isotopes. It also enabled the specification of the hydrogen mass to 1.008, and that being the mass of the proton. From this definition Aston saw that this would be a suitable source of energy for the sun, and that nuclear energy could provide "powers beyond the dreams of science fiction," but he was also worried that a nuclear blast would be uncontrollable and could detonate all H on earth.

Nier developed many of the mass spectrometer designs that have become fundamental to mass spectrometry in the

earth sciences.[5] He produced analytic designs for 180° and 60° mass spectrometers, he designed sources (still used today and known as the Nier source), and mass spectrometers specifically for isotope abundance measurements.[6] Nier, together with Johnson, produced double focusing mass spectrometers with complete energy and angular refocusing. Nier measured isotopic compositions of many naturally occurring systems, defining the isotopic abundances of many elements including C, O, Ar, K, Rb, Zn, Cd, and Pb. His work on carbon was fundamental to the development of carbon isotopes as an environmental tracer.

Throughout the 20th century techniques were refined and instrumentation improved. However, it was the proposed Apollo mission to the moon that saw major advances in technology brought to bear on this branch of mass spectrometry. The prospect of only small amounts of material that would be available for analysis in the "best" laboratories in the world saw major advances in procedures. Ever smaller amounts of material were used to provide increasing levels of precision. This philosophy has proceeded at pace since that time. A few nanograms of material can provide precision levels down to several parts per million. A few nanograms of sample can provide enough material for isotopic characterization of trace elements *in situ*. There is an ever present expectation that we can do more with less but ultimately the physical limits of measurement will be met.

C. Mass spectrometers

Mass spectrometry is the separation of an ion according to its mass to charge ratio. Fundamental to mass spectrometry is that the ion must be moving. This is generally effected by an extraction voltage, which accelerates and focuses ions to an ion beam with appropriate characteristics to be accepted in to the mass spectrometer. The extraction voltage depends on the application but is generally in the order of 1–10 kV. The efficiency of the ion extraction is related strongly to the voltage. The higher the extraction voltage, the smaller the solid angle, and hence greater the concentration of ions at a particular point in the beam line.

The extraction voltage creates an electrostatic field, $E = V_E/d$, where V_E is the extraction voltage and d is the distance over which the acceleration takes place. The extraction potential is converted into kinetic energy of the ions (for singly charged ions: $qV_E/d = \frac{1}{2}mv^2$). Mass dispersion is then achieved by applying different electric and magnetic forces to the ion beams.

1. Magnetic sector

A magnetic-sector mass spectrometer[7] is based on the Lorentz law [$F = q(v \times B)$] (Fig. 2). A moving ion in a magnetic field experiences a force proportional to its charge, velocity, and intensity of magnetic field. The force acts at right angles to both velocity and magnetic field (right-hand rule). In a homogeneous field the ion will trace a circular pattern with radius r, where $mv^2/r = qvB$, or $r = mv/qB$. Hence different masses trace different trajectories (circular paths with
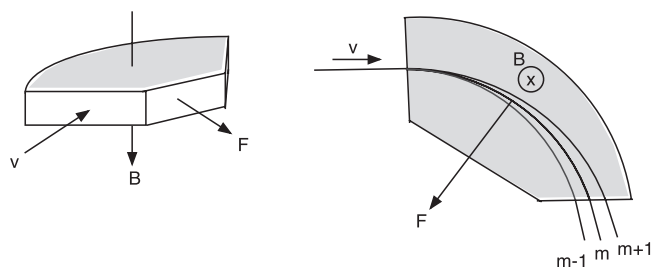

FIG. 2. Magnetic sector mass spectrometers are based on dispersion according to $F = q(v \times B)$. (a) The Lorentz force operates at right angles to both the velocity of the ion, and to the magnetic field, (b) ions move along circular paths with radius proportional to mass.

different radii) through the magnet. In a single-collector system, the magnetic field can be changed to switch the peak of interest into the collector, or in multiple collection detectors can be placed according to the mass dispersion in the collector to measure a number of ion beams simultaneously.

Magnetic sector mass spectrometers are very common in earth science applications particularly in applications requiring high-precision measurements of isotope ratios. While the mass analyzers and detection systems are common to a variety of instruments, fundamental differences lie in the source where gases (noble gas and stable isotope), solid samples (thermal ionization), and liquids (inductively coupled-plasma mass spectrometry) can be used. Another fundamental aspect of these types of analysis is that elements are chemically separated so that the elemental concentration can be high for greater ion yield and hence precision, and it also aids in the mass spectrometry in removing elements that might interfere with the peaks of interest (notably atomic isobars).

In noble-gas mass spectrometry (NGMS), the gas is introduced to the mass spectrometer and a filament-based source is used to ionize the gas. In NGMS, the gas mass spectrometer is isolated from a vacuum pumping system during analysis (static vacuum) and the gas is gradually "consumed" during the analysis. In stable isotope gas analysis (e.g., C and O as CO_2, or O as O_2) a duel inlet system is commonly used that allows switching between sample gas and a reference gas. These gases are continuously leaked into the mass spectrometer and the system must therefore be pumped dynamically. In thermal ionization mass spectrometry (TIMS), a sample is loaded onto the filament, often with an emission enhancer, and dried for insertion in the mass spectrometer. A current is passed through the filament to cause evaporation and ionization. For inductively coupled plasma mass spectrometry (ICP-MS), the sample stays in solution which can be fed directly into the Ar plasma that causes the ionization.

The above applications require a simple mass spectrometer based on only a sector magnet to produce mass separation. Mass resolution requirements are minimal because of the preparatory chemical separations, and the velocity spread of the extracted ions is not significant in terms of the measurements. One case where neither of these issues can be ignored is in secondary ion mass spectrometry (SIMS). A focused ion beam is used to sputter a sample causing ejection of atoms, molecules, and fragments from the target. This is an *in situ* method so there is no prior separation of elements that can
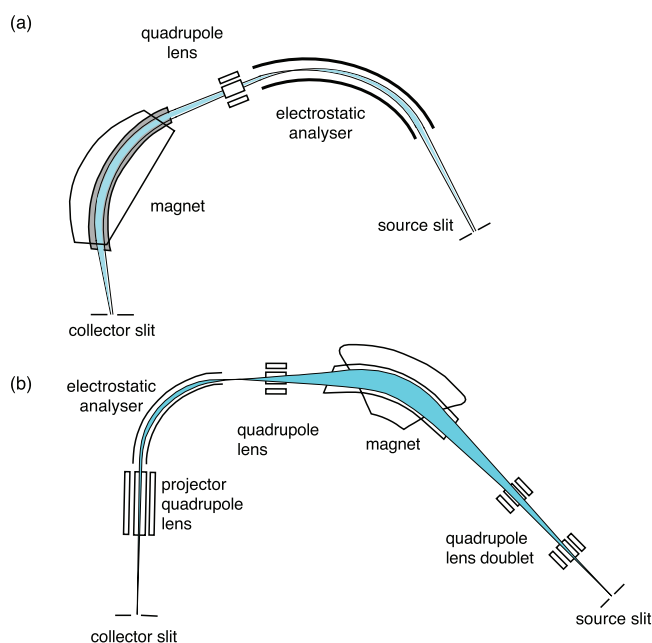
FIG. 3. A double-focusing sector mass spectrometer uses an electrostatic sector to compensate for the energy (velocity) dispersion that may exist in the ion beam. Shown are (a) a forward geometry mass analyser with electrostatic sector before the magnet, and (b) a reverse geometry mass analyser, where the magnet precedes the electrostatic sector. These designs[8,9] are used for the SHRIMP II and SHRIMP RG ion microprobes.
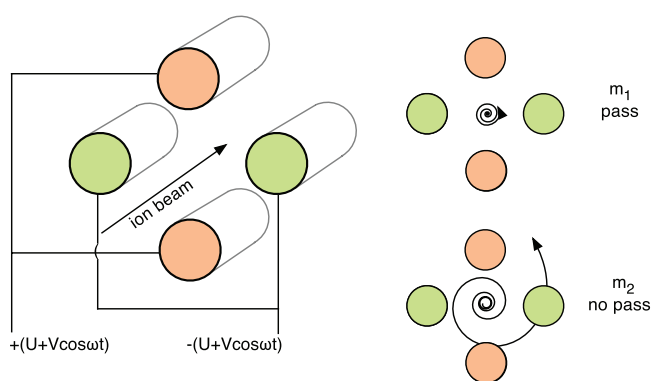

FIG. 4. In the quadrupole mass spectrometer, opposite elements of the quadrupole lens are provided a voltage that has a dc component (U), and a high frequency component (Vcosωt). Ions in the center of the quadrupole experience a resultant force such that only ions of a particular m/q are stable and can pass through the mass spectrometer.

cause interferences. Hence high mass resolution is required to separate molecular and in some cases atomic isobaric species. The secondary ions are caused by impacts from the primary ions and the secondary ions can receive additional energy (velocity). In going to high mass resolution, however, the velocity spread of the secondary ions causes beam spreading and must be negated. For these instruments, double-focusing mass spectrometers are always used where an electrostatic sector is used to compensate for the velocity spread of the magnetic sector (Fig. 3). In this case, ions of the same m/q are focused along a plane where the position is defined by the ion energy. These energy-compensated positions then act as the object positions for the ion paths through the magnetic sector. Reverse geometry instruments have the magnetic sector before the electrostatic analyser, but the same principles apply in this configuration.

2. Frequency (quadrupoles, ion traps)

While sector magnets are the most common means of dispersing ions according to m/q, ion acceleration, and hence mass dispersion, can also be produced through appropriate cycling of an electric field.[10] This is accomplished through applying time-variant fields to electrodes and can be used to trap ions in a 3D cell (hence ion trap), or pass specific masses through a linear quadrupole arrangement (e.g., Fig. 4).

Quadrupole mass spectrometers are used in the earth sciences where rapid switching between peaks is desirable. One of the issues with sector magnets is their slow switching speed; in comparison, electrostatic switching in a quadrupole mass spectrometer is extremely fast with dwell times on peaks

often being of the order of milliseconds. They are a common mass spectrometer coupled to a laser ablation ICP-MS where the rapid peak switching allows many masses to be sampled in a cycle. In terms of isotope ratio measurements, quadrupole mass spectrometers lack the stability of magnetic sector instruments and so are only used in a few specific cases, such as U-Pb measurements where there is a large natural range in isotope compositions, and therefore less requirement of precision for the measurement.

3. Velocity (time-of-flight, Wien)

During ion acceleration, the transformation of the extraction potential to kinetic energy means that heavier ions travel more slowly than lighter ions[11] (Fig. 5). In a time-of-flight (TOF) mass spectrometer (Fig. 5), a pulse of ions is introduced and these ions are allowed to travel for a specific distance and their arrival is recorded according to time. The lighter, faster ions are received earlier than the heavier, slower ions. A pulsed ion beam can be generated by pulsing an incident (primary) ion beam (hence TOF-SIMS) or with a laser system. A pulsed laser can be used to ablate the sample and a separate (pulsed) laser system can be used to ionize the ablated atoms. Resonance ionization schemes can be used to select specific elements for analysis, or a high-photon-energy laser can be used to ionize most elements at once. TOF systems are frequently used for surface analysis in the materials industry where the ion beam or laser can be rastered over the surface for a 2D distribution of elements and compounds, with 3D analysis produced as the beam penetrates into the sample. TOF is also used in organic analysis where signatures of particular organic compounds and fragments thereof can be recognized.

A different type of velocity selection is available in a Wien filter.[12] In this case, the ion beam is passed through orthogonal electric and magnetic fields. Like the quadrupole mass spectrometer, a Wien filter operates by allowing a specific mass (velocity) to pass through undeflected. It can be shown that the specific velocity ($v = E \times B$) will pass through the system undeflected.
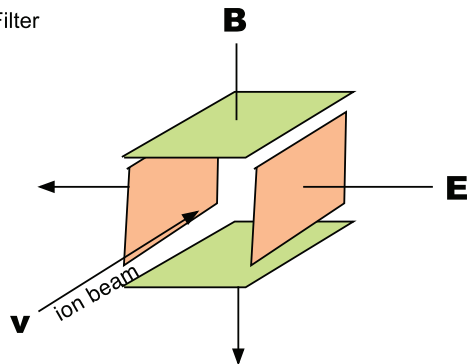
(a) time of flight
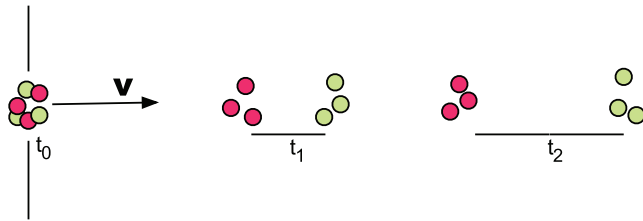
(b) Wien Filter

FIG. 5. Velocity-based mass spectrometers include time-of-flight mass spectrometers and the Wien filter. The ion is accelerated through an electric potential and the velocity of the ion is governed by $E = \frac{1}{2}mv^2$. (a) A time-of-flight mass spectrometer simply uses drift to separate ions of different velocity, with time of arrival at the detector being proportional to (the square root of) mass. (b) The Wien filter utilizes crossed electrostatic and magnetic sectors such that the electrostatic force can operate against the magnetic force. The Wien filter allows only one velocity ($v = E \times B$) to pass through undeflected.

D. Mass spectrometric figures of merit

A mass spectrometer of any type has figures of merit that describe the various performance aspects. The main parameters of interest describe mass separation in the instrument and the ability of a configuration to resolve specific interferences. These include mass resolution, mass resolving power, and abundance sensitivity for which all are defined as m/Δm where m is the mass where the definition is to be established, and Δm is the separation in mass under consideration.

1. Mass resolution

Mass resolution is generally inferred to represent the ability to separate two ion beams at the detector that differ by some specified mass difference.[13] For earth sciences, two different types of definition are commonly used. The valley definition indicates that at the specified resolution, the valley between two peaks is less than a specified fraction (e.g., 1%) of the peak of interest. However, the problem with this type of definition is that the mass resolution is not necessarily prescriptive; the definition is abundance dependent and is not commutative for differing peak heights. If the interfering peak has a higher abundance, then higher mass resolution is required to maintain the 1% valley. Conversely, if the valley is referenced to the other (different) peak height, then the 1%

valley will not hold because the reference height has changed, and the instrumental configuration must then be changed to achieve the specified valley.

The peak-width definition is probably the most common way of defining the mass resolution and is based on the width of the peak (Δm) at the 1%, 10%, or 50% peak height. The peak-width definition has an advantage in that a simple measurement of the peak width at a designated level can be recalculated as mass resolution. This definition can apply no matter the peak shape (trapezoidal, triangular, or Gaussian).

The trapezoidal peak shape in a magnetic sector mass spectrometer is produced by scanning the ion beam across a resolving slit (exit or collector slit). The trapezoidal shape indicates that the demagnified entrance or source slit image fits within the collector slit, with the degree of "flat top" being proportional to the ratio of the collector-slit size to the ion beam width; that is, the wider the collector slit with respect to the ion beam, the wider the flat top. For a trapezoidal peak, the peak-base width is approximately the sum of the widths of the demagnified source slit, and the collector slit (Fig. 6). As such, mass resolution can be improved by reducing the collector slit, but this is at the expense of flat top on the peak, which ultimately may affect the beam stability during analysis. Conversely, reducing the source slit can improve flat top, but at the expense of ion beam transmission.

Wile mass resolution is a useful figure of merit, it does have some limitations in practice. In particular, a value of mass resolution alone does not fully describe the peak shape; it provides no information regarding flat top, or specific circumstances where interferences will be a problem during analysis, except in the broadest sense.

For example, ^{48}Ca and ^{48}Ti require mass separation of around 10 500 based on the respective nuclidic masses ($R = 48/[m_{48Ca} - m_{48Ti}]$). These isobars must be separated if an isotopic analysis involving ^{48}Ti and ^{48}Ca is to be carried out. In equal atomic proportions (Ca/Ti = 1), the ratio of ^{48}Ca/^{48}Ti is small (~0.0025) and even with incomplete mass resolution (e.g., 7000 m/Δm) the contribution of ^{48}Ca under ^{48}Ti will be negligible. However, under the same conditions, addition of ^{48}Ti to ^{48}Ca might not be negligible because ^{48}Ti/^{48}Ca is large (~400) (Fig. 7).
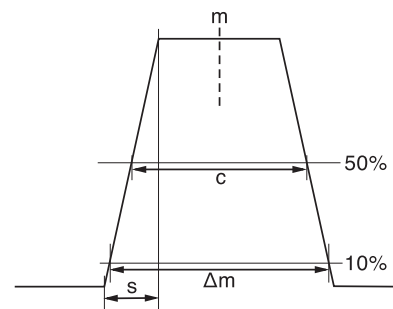

FIG. 6. For a trapezoidal peak shape, generally produced in a magnetic sector mass spectrometer, the side-of-peak slope is the demagnified source slit width (s), and the 50% height is the collector slit width (c). Hence, the base width is the sum of the collector slit and (de)magnified source slit widths. The mass resolution (m/Δm) is shown for the 10% level of the peak height.
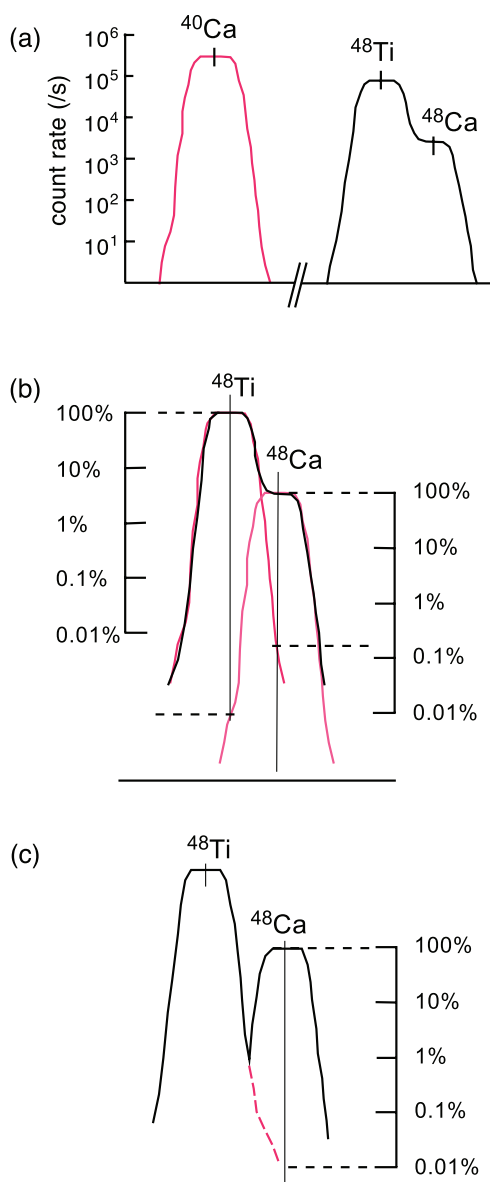
FIG. 7. Mass resolution is a function of the mass spectrometer geometry but is also a function of abundance. (a) An example is shown based for the mass spectrum of ^{48}Ca-^{48}Ti that are fully separated at 10 500, but which is often analyzed at a lower operating mass resolution of 7000 m/Δm to increase sensitivity. (b) It can be seen that ^{48}Ca does not contribute to the ^{48}Ti signal (<0.01%), based on the overlay of the ^{40}Ca mass spectrum, however, the converse is not true with the higher abundance ^{48}Ti contributing significantly to the ^{48}Ca signal (∼0.2%). (c) A Ca isotopic measurement requires higher mass resolution than a Ti isotopic measurement of the same sample if ^{48}Ti/^{48}Ca > 1.

2. Mass-resolving power

The term mass-resolving power is frequently used interchangeably with mass resolution as the ability to separate ion beams by mass. The International Union of Pure and Applied Chemists (IUPAC) definition of mass resolving power is based on the *observed mass divided by the mass difference between two masses that can (just) be separated*. This definition is very similar to that for mass resolution defined above, hence the frequent interchangeability in the terms.

One of the main issues is whether an exit slit is involved in the mass spectrometer. For sector-magnet mass spectrom-
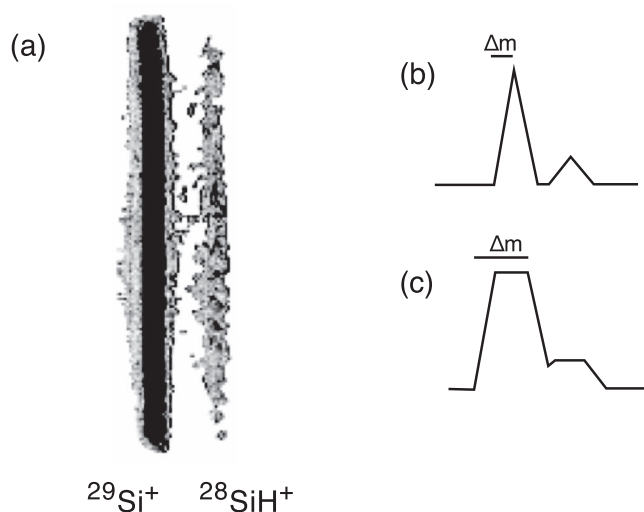

^{29}Si$^+$ ^{28}SiH$^+$

FIG. 8. Difference between mass resolving power and mass resolution as illustrated by an image of ^{29}Si and ^{28}SiH peaks shown in (a). These peaks are completely resolved in the image at the collector slit, which shows the mass resolving power is adequate to separate them. However, when a collector slit of the equivalent size of the peak width is convolved with this distribution, the mass spectrum shows triangular peaks (b), which are very difficult to analyze for abundance if there is any drift or noise in the mass analyser (equivalent Δm). (c) A wider collector slit must be used to maintain "flat top," but at the expense of peak overlap.

etry, the mass spectrum involves the concatenation of the ion beam with the exit slit. However, this is not the case for all forms of mass spectrometry. Even with a sector-magnet, resolution of peaks is possible without the exit slit, as shown in Fig. 8 for an image of the ion beams in an ion microscope. While the ion beams are clearly resolved, the mass spectrum shows varying mass resolution depending on the width of the exit slit.

In earth sciences, the definition of mass resolving power is often considered to be the effective mass resolution at the collector, without the influence of the exit slit. In terms of the trapezoidal peak in Fig. 6, the mass resolving power can be defined as the width of the side-of-peak (Fig. 9). This is effectively the demagnified width of the source slit, which defines the beam width at the collector. In order to avoid complications associated with aberrations at the shoulders, Δm can be defined as the width derived from the 10%–90% peak heights (Fig. 9).

Mass resolving power will always yield a larger number than mass resolution. As such there is a tendency to report mass resolving power for an instrument as if it represented the mass resolution. This is particularly the case when the collector slit is a fixed width and the analysis is carried out on a shoulder where it can be shown that the interference is minimal at the collection position. However, while it could be argued that mass resolution understates the ability to resolve masses, it can also be argued that mass resolving power overstates the separation and ability to do measurements at this level.

3. Abundance sensitivity

Abundance sensitivity is a parameter that expresses the tailing of a peak of one atomic mass onto another (Fig. 10).
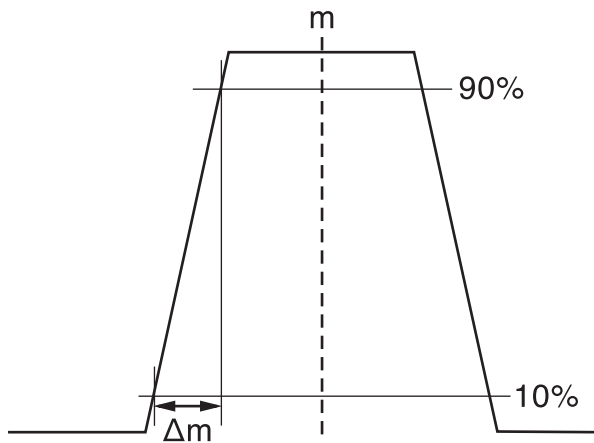
FIG. 9. Definition of mass resolving power. For geoscience applications, mass resolving power is generally defined as $m/\Delta m$, where Δm is defined as the equivalent mass width defined between the 10%–90% peak height levels. Δm is effectively the demagnified source slit width, and the collector slit width is ignored.

Tails are produced by ion-optic aberrations or gas scatter. At the measurement position a low intensity peak could be affected by tailing from a larger peak. In this case the Δm is fixed at 1, but the mass can vary and hence the relative offset is a function of mass. Hence the abundance sensitivity must be specified at a particular mass.

II. ISOTOPE MEASUREMENTS

The purpose of the mass spectrometric analysis is to resolve an isotope signal from a single sample or a series of samples. However, the mass spectrometer itself causes changes in the isotope abundances. A major component of the measurement relies on designing suitable procedures where
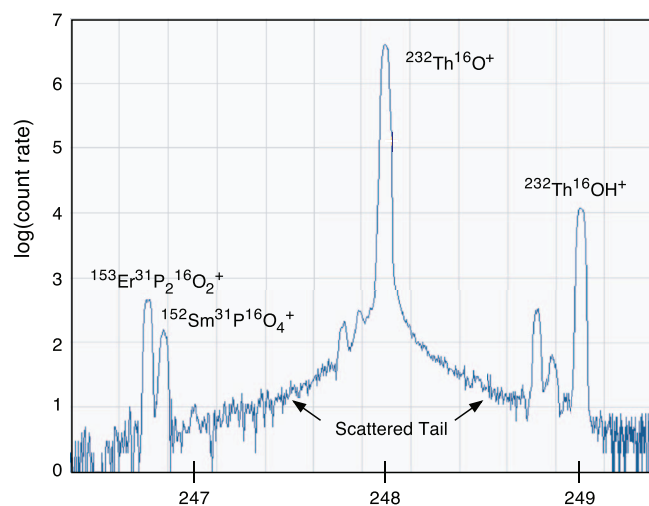

FIG. 10. Illustration of abundance sensitivity from mass 248 (ThO$^+$) from a monazite target. Gas scatter and lens aberrations cause tailing of intense peaks into adjacent peaks. In this example the abundance of the tail is around 10^{-6} at a mass offset of 1 amu. The abundance sensitivity is generally defined at a mass offset of 1 amu relative to the designated peak, but the fractional mass difference is not the same for all elements and hence the abundance sensitivity is mass dependent (and must be specified for a particular mass).

the instrumental component is essentially constant, or can be determined to a high level of accuracy.

A. Isotopic mass fractionation

Measurements of light elements are of fundamental importance in stable isotope geochemistry because these elements have the largest relative mass differences between the isotopes. As such, these elements have the largest natural isotopic fractionation signals and so are used to constrain kinetic effects, which have application in determining key aspects of a process, such as temperature.

The classical elements for stable isotope analysis include H, C, N, and O. The first three of these elements only have two isotopes, and while oxygen has three isotopes it is commonly treated as a two-isotope system for the determination of isotopic mass fractionation. For a two-isotope system, the instrumental mass-fractionation correction must be based on the concurrent measurement of a standard. The isotope ratio that is measured in the standard can be related to its accepted value, and the functional relationship between measured and accepted is assumed to be the same for the "unknown" sample that is being analyzed. So for C, which has stable isotopes ^{12}C and ^{13}C, the C isotope ratio of a sample can be expressed as δ^{13}C$_{sam}$, where

$$\delta^{13}C_{sam} = [((^{13}C^+/^{12}C^+)_{sam}/(^{13}C^+/^{12}C^+)_{std} - 1)$$
$$\times 1000] + \delta^{13}C_{std}$$

and where $(^{13}C^+/^{12}C^+)_{sam}$ and $(^{13}C^+/^{12}C^+)_{std}$ are the isotope ratios measured for sample and standard respectively, and $\delta^{13}C_{std}$ is the accepted value of the standard expressed in permil (‰). This formalism holds for all isotope systems where isotopic mass fractionation is to be determined.

A mass fractionation correction must also be determined for a radiogenic isotope measurement (e.g., ^{14}C) because the mass fractionation will affect the abundance of the radiogenic isotope as well (Fig. 11). Thus, if the carbon is fractionated, it is expected that the ^{14}C/^{12}C will respond in a similar way to ^{13}C/^{12}C except that the response for ^{14}C/^{12}C will be a factor of approximately two higher than ^{13}C/^{12}C because of the double mass difference. For an isotope system with three or more isotopes, one of the isotope ratios can be used to quantify the mass dependent fractionation, while the other isotope ratio(s) can be corrected for the mass fractionation, allowing the calculation of a "residual." However, this requires a formulation of the mass fractionation law that describes the response of the particular isotope system to a level of precision and accuracy commensurate with the measurement requirements. In general, the formulation can be expressed as

$$(^iA/^kA) = (^jA/^kA)^\gamma,$$

where ^iA, ^jA, and ^kA are isotopes of element A, and γ is a function of the masses of the particular isotopes.[14] For example for power law fractionation $\gamma = (m_i - m_k)/m_j - m_k)$, while for Rayleigh fractionation, $\gamma = (\sqrt{m_i} - \sqrt{m_k})/\sqrt{m_j} - \sqrt{m_k})$.

The residual expresses the deviation of the measured isotope ratio to a mass fractionated abundance determined from another isotope ratio (see Fig. 11). While mass
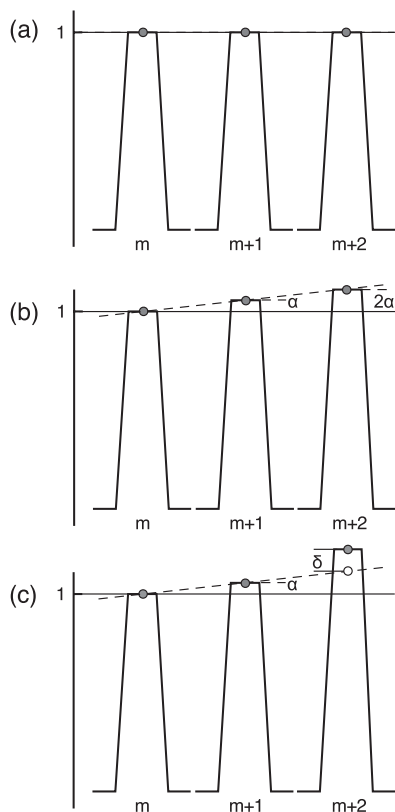
FIG. 11. Schematic isotope mass fractionation measurement and correction. (a) Spectrum with three isotopes at masses m, m+1, and m+2, whose abundances have been normalized to terrestrial and are not mass fractionated with respect to terrestrial. (b) Mass-fractionated abundance pattern where the abundance is linearly proportional to mass, i.e., $1+\alpha$ for mass m+1, and $1+2\alpha$ for mass m+2. Measurement of one isotope ratio can be used to quantify mass dependent fractionation. (c) In a three isotope system, one ratio can be used to quantify mass fractionation so that a correction can be applied, and the abundance of that isotope expressed as a residual, δ.

fractionation may be variable during an analysis, e.g., Rayleigh fractionation changes during evaporation from a filament and so the isotopic mass fractionation changes with time, the mass-fractionation-corrected residual will still increase in precision provided the process follows the particular law that is used.

For chemically separated materials, a known amount of a specific isotope can be added to the sample aliquot and this can be used to monitor for mass fractionation without using up one of the ratios of the naturally occurring isotopes. This is referred to as spiking. This can be a minor stable isotope, or a radiogenic isotope with a suitably long half life. A double spike,[15] where two isotopes are introduced, allows an absolute mass fractionation correction to be performed. In addition, samples are spiked with a known amount of material in order to calibrate concentrations for radiogenic isotope measurements and geochronology.

B. Counting statistics, signal to noise

The smaller the isotopic effect, the higher the precision in the isotope ratio that is required. The extreme limits in precision of an isotope ratio measurement are governed by Poisson counting statistics, where the ultimate precision is determined by $1/\sqrt{N}$, where N is the number of counts of the minor isotope. Hence 10^4 counts are required for 1% precision, 10^6 counts for 1‰ precision, 10^8 counts for 0.1‰ (ε unit), and so forth.

In a pulse counting system, Poisson counting statistics are generally the determining factor in precision. However, the accuracy of a pulse counting measurement can be affected by the dead time, that period of time following a count when it is not receptive to counting another incoming ion. The measured count rate can be expressed as

$$c_{meas} = c_{true} \exp(-\tau c_{true}),$$

where c_{meas} is the measured count rate, c_{true} is the actual count rate, and τ is the dead time. Typical dead times for pulse counting systems are of the order of 10–20 ns. Hence for count rates of 10^6 c/s the dead time correction to the abundance ratio is around 1%. However, it is not the dead time itself, but the uncertainty in the dead time that can be the limiting factor for isotope ratio analysis. This affects both the ultimate precision that is achievable, but also requires a limitation in the maximum count rate that can be used.[16]

To avoid problems with dead time at high count rates (over 5×10^5 c/s or so), the ion beam can be collected in a Faraday cup and measured as a current through a large resistor ($10^{10}-10^{12}$ Ω). The (lower) limiting factor for current measurement in a Faraday cup is the thermal noise of electrons passing through the resistor (Johnson noise). This current has the form

$$i = \sqrt{(4kT\Delta f/R)},$$

where k is Boltzmann's constant, T is the temperature (K), Δf is the frequency band of the noise under consideration, and R is the resistance. At 300 K, with a bandwidth of 1 Hz, and a 10^{11} Ω resistor, the noise current is 4×10^{-16} A, or 2,500 c/s.

Most mass spectrometers have counting systems that incorporate both ion counters for low signals (<1 to 100 000 c/s) and Faraday cups which can operate at count rates above 10^6 c/s (10^{-13} A). In the regime at the crossover of these devices, there can be a problem with obtaining sufficiently high precision by Faraday cup, and sufficient accuracy with an ion counter.

There are two possible methodologies to improve the performance of Faraday cups and thence to bridge the gap. The first is to increase the resistance in the electrometer feedback loop up to 10^{12} Ω or 10^{13} Ω. Increasing the resistance from 10^{11} to $10^{13}\Omega$ improves the Johnson noise by a factor of 10 (Fig. 12). However, the RC time constant of the circuit is also increased and so the response of the system to switching or short term signal fluctuations is degraded. The second possibility is to replace the feedback resistor with a capacitor.[17] This changes the characteristic of the electrometer from current mode to charge mode. A charge can be accumulated across the capacitor raising the potential of the amplifier input. The Johnson noise is eliminated from the circuit with the noise characteristic being expressed as
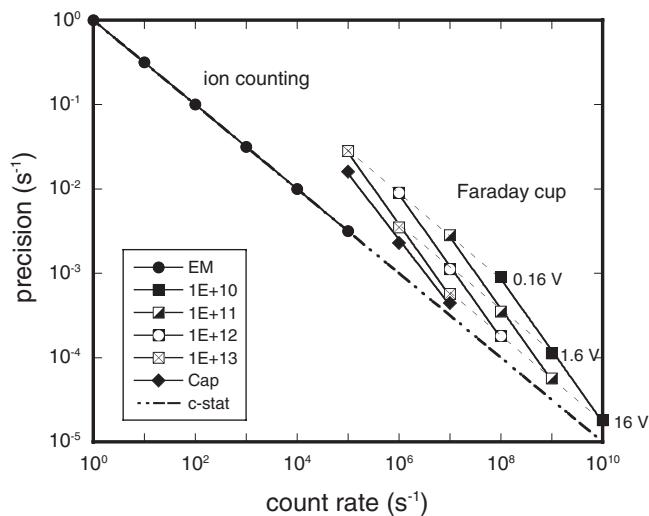
$$v = \sqrt{kT/C}.$$

FIG. 12. Measurement errors from background and counting statistics for electron multiplier (EM), and Faraday cup with resistive (10^{10} Ω, 10^{11} Ω, 10^{12} Ω) feed back and capacitative feedback (10 pF). Shown for the Faraday cup measurements are three signal levels of 0.16, 1.6, and 16 V.

For a 100 pF capacitor, this corresponds to a noise voltage of 0.006 mV, roughly a factor of 6 less than that for a 10^{11} Ω resistor, with an equivalent noise variability count rate of 400 c/s (Fig. 12). Charge mode can therefore offer lower noise and rapid response, however maintaining a low and constant capacitance in the circuit has proved difficult.

A mass spectrometer collector can rely on a single collector, or, particularly in the case of sector magnet instruments, an array of collectors distributed along the focal plane of the magnet. Such multiple collectors have advantages in that the external noise apparent on one isotope should be the same on the others and hence ion beam noise can be cancelled. Hence, multiple collection is a significant advantage for isotope ratio measurements. In general, multiple collectors with Faraday cups are very reliable. Multiple collectors with ion counters have proven problematic because of the gain drift that is manifest with multipliers. The intercalibration of the gains significantly reduces the benefit to be obtained in improved counting statistics.

III. DEVELOPMENTS

A brief overview of new developments in instrumentation as adapted to geoscience applications is given below. The listing is not intended to be complete but rather give some examples of interest and highlighting current developments.

A. Noble gas mass spectrometry

Although noble gases do not participate in chemical reactions on earth, their isotope abundances can be diagnostic to specific processes affecting earth.[18] The abundance of ^{3}He/^{4}He is an important tool for identifying mantle derived He because most crustal He is ^{4}He released as alpha particles in the radioactive decay of U. Cosmic ray spallation of target elements (such as Si) produces Ne isotopes in abundances that

differ from terrestrial, and this also allows dating. Radiogenic decay of ^{40}K to ^{40}Ar is the source of most of the Ar in the atmosphere, and Ar retention in minerals allows this decay to be used as a chronometer. The isotopic abundances of Xe have proved highly useful in tracing the origins of the solar system.

Noble-gas mass spectrometry generally involves a gas extraction system where minerals are heated to release the noble gases. A specific noble gas can be isolated cryogenically and can then be introduced to the mass spectrometer source region through a simple inlet. Ionization is effected by a filament causing ejection of an electron to produce positive ions. This methodology requires relatively large amounts of gas, which in turn requires relatively large amounts of sample. This might involve several tens of milligrams of a mineral, which is separated from the rock by crushing and mineral separation. As such, petrographic context is lost, and any indication of heterogeneity in the sample from, for example, multiple populations, will be lost also.

Geochronology either through ^{40}K-^{40}Ar or ^{40}Ar-^{39}Ar is the most important application of Ar isotope analysis. The original ^{40}K-^{40}Ar methodology has now been almost exclusively superseded by the ^{40}Ar-^{39}Ar method where ^{39}K is converted into ^{39}Ar in a reactor thus allowing the parent (K) and daughter (Ar) abundances to be measured in the isotope ratios of Ar alone. Ar geochronology is important because of the low inherent Ar concentration in rocks, and the simplicity of releasing Ar produced through decay. For highly retentive samples such as sanidine, the K-Ar system is closed and high precision and accuracy can be obtained. This has recently allowed a proposed refinement to the ^{40}K decay rate.[19]

Petrographic context is very important for Ar isotope geochronology. Multiple generations of K-bearing minerals can be present and any mixing of these generations will yield meaningless mixed ages. Step-heating of the mineral in a crucible allows separation of unwanted components, such as low temperature entrainment of non-radiogenic Ar. The exquisite temperature control available in a crucible allows multiple steps to be captured and analyzed. The presence of an age plateau is taken as an indication of a geological age component, whereas non-agreement of the ratios can be indicative of a geological disturbance. This is the basis for thermochronology where Ar release in feldspars can be shown to replicate the thermal history of the source rock.[20] While the step-heating method allows extreme refinement of the temperature steps, it does not necessarily separate Ar from multiple generations of minerals in complex systems that may involve finely intergrown minerals.

In situ techniques involving focused laser heating have proved to be difficult to manage. In part this is because an *in situ* analysis is effectively a bulk analysis and does not separate the components that are the basis for thermochronometric analysis. In an *in situ* laser heating system, there is the gain of petrographic selection, but temperature control is difficult to manage with a laser and so the analysis may be compromised by non-radiogenic component(s), or mixed components. In addition, early work used infrared lasers that produced a significant thermal halo around the spot and so admixture of Ar from surrounding phases could also be an issue.
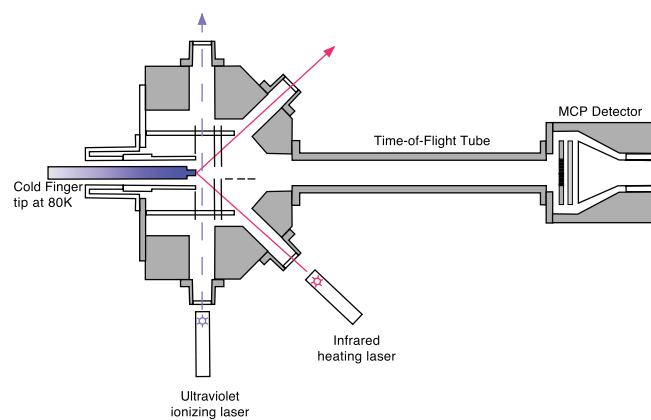
FIG. 13. The RELAX mass spectrometer system.[21] Xenon is collected on to the cold finger by releasing the Xe into the mass spectrometer. A pulsed infrared laser is used to locally heat and release the Xe, and a second pulsed laser of ultraviolet wavelength causes ionization of the Xe. Ions are accelerated from the source and detected with a time-of-flight mass spectrometer. A feature of this system is the extremely low Xe blank level and small samples that can be analyzed (several thousand atoms) Like all static mass spectrometers, the Xe gas that is not ionized may recondense on to the cold finger where it can be processed again.

Laser heating does have significant benefits though. In a crucible heating system, the crucible and environs can be brought up to high temperature thereby enhancing the possibility of memory effects and otherwise raising the blank in the mass spectrometer. With a laser heating system, heating can be restricted to a single mineral grain that has been placed in an appropriate tray. Heating can be controlled by an optical pyrometer feeding back to the control of the laser power. A tray consisting of multiple sample holes allows the system to be automated thereby improving throughput. A tray could consist of 100 or so sample places, whereas a crucible heating system would typically only allow for 10 samples.

An interesting variant of the conventional noble gas mass spectrometer is the refrigerator enhanced laser analyser for xenon (RELAX) designed and constructed at University of Manchester[21] (Fig. 13). This system operates with a standard isolation system for the noble gases, but this particular mass spectrometer isolates Xe on to a cold finger prior to evaporation and ionization by pulsed laser systems and extraction to a time-of-flight mass spectrometer. The feature of this mass spectrometer is the extreme sensitivity that is achievable—the blank is only of the order of 1000 atoms or less.[22] This allows measurements that are impossible by the usual techniques, such as measurement of plutogenic Xe in Hadean zircons[23] and measurement of Xe implanted in the solar wind during the Genesis mission.[22]

B. Stable isotope mass spectrometry

Stable isotopes tell us a great deal about processes in which light elements participate.[24] These reactions generally have a kinetic aspect in moving elements from one site to another and so reactions with the different isotope masses proceed at different rates.

Hydrogen is the lightest element and so the relative mass difference between H and D is the largest of all the elements.

Hydrogen isotopic analysis is commonly used for fingerprinting water compositions where substantial isotopic fractionations related to temperature, elevation, and latitude are found. Carbon isotope analyses ($^{13}C/^{12}C$) are widely used for processes occurring in the atmosphere, hydrosphere, biosphere, and the lithosphere. Nitrogen isotope analysis is important in organic geochemistry and particularly for biologic materials where ^{15}N is concentrated in successive digestions. In solid earth sciences, nitrogen isotope compositions in rocks are often interpreted in line with noble gas isotopes in terms of processes. Like carbon, oxygen isotope analyses based around $^{18}O/^{16}O$ are important in all fields of geological research. Sulfur isotope analyses ($^{34}S/^{32}S$) are commonly utilized in ore genesis for understanding the provenance of sulfur. Sulfur is highly fractionated by microbes and so biogenically processed S can be readily distinguished from primitive (i.e., mantle) S.

Isotopic analyses of hydrogen, carbon, nitrogen, oxygen, and sulfur can be carried out through gas source mass spectrometry. The sample gas and a reference gas are introduced through a dual inlet to allow rapid comparison, and hence normalization. The mass spectrometric techniques for many stable isotopes applications have not changed for many years.[25] There have been developments in sample handling to improve throughput but a simple magnetic sector is all that is required for mass spectrometry.

Precision and accuracy of C, O, and S isotope measurements are better than 0.1 ‰ when sufficient material is available for analysis. For D/H, the precision is much lower because of the low D abundance, and accuracy is often limited to several permil by instrumental artifacts.

1. Minor-isotope analysis

The two most abundant isotopes of the stable-isotope elements are generally used for determining the mass dependent fractionation. But, several of these elements have additional isotopes that are of practical benefit in geoscience.

Cosmogenic production of ^{14}C in the atmosphere is caused by high-energy neutron addition to ^{14}N ($^{14}C/^{12}C_{atmosphere} \approx 10^{-12}$). The ^{14}C is incorporated into life forms, along with the other C isotopes, and once the life form has died, ^{14}C progressively decays back to ^{14}N. The decaying abundance of ^{14}C is therefore a chronometer used for dating materials within up to 10 half lives of incorporation ($t_{\frac{1}{2}} = 5000$ yrs). ^{14}C measurement requires accelerator mass spectrometry for the measurement of the low abundance ^{14}C and to remove isobaric interferences (notably ^{14}N). Acceleration of the ion beam to MeV energies and passage through a stripper gas destroys molecules.

Oxygen has a third minor isotope, ^{17}O. Its abundance is important in reactions that are dependent on isotopic abundance rather than isotopic mass. For example, stratospheric ozone is highly (>100 ‰) enriched in ^{17}O and ^{18}O due to the stabilization of asymmetric molecules.[26] The abundance of ^{16}O is also found to be highly variable in meteorites and extraterrestrial objects with a total range of over 50% in solar system materials.[27] The issue with three-isotope oxygen measurements is that most $^{18}O/^{16}O$ measurements are carried out

TABLE I. Isotopologues of CO_2 and mass spectrometric requirements.

Nominal mass	Isotopologue	Abundance	Mass	Resolution
44	$^{12}C^{16}O^{16}O$	98.4%	43.9898	⋯
45	$^{13}C^{16}O^{16}O$	1.11%	44.9932	⋯
	$^{12}C^{17}O^{16}O$	748 ppm	44.9940	52 200
46	$^{12}C^{18}O^{16}O$	0.4%	45.9941	⋯
	$^{13}C^{17}O^{16}O$	8.4 ppm	45.9974	13 800
	$^{12}C^{17}O^{17}O$	0.14 ppm	45.9983	53 300
47	$^{12}C^{18}O^{16}O$	0.4%	45.9941	⋯
	$^{13}C^{17}O^{16}O$	8.4 ppm	45.9974	13 800
	$^{12}C^{17}O^{17}O$	0.14 ppm	45.9983	53 300
48	$^{12}C^{18}O^{18}O$	3.96 ppm	47.9983	⋯
	$^{13}C^{17}O^{18}O$	16.8 ppb	48.0016	14 400
49	$^{13}C^{18}O^{18}O$	44.5 ppb	49.0017	⋯

as CO_2^+ (where mass 44/mass 46 = $^{12}C^{16}O^{18}O/^{12}C^{16}O^{16}O$ = $^{18}O/^{16}O$). However, mass 45 ($^{12}C^{16}O^{17}O$) is compromised because of the presence of $^{13}C^{16}O^{16}O$ (Table I). Resolution of these two isobars requires 52 000 m/Δm, which is far beyond the mass resolution of most gas source mass spectrometers.

For silicate measurements, oxygen is released by reaction with chemically aggressive gases such as fluorine or bromine pentafluoride,[28] and then reacted with graphite to form CO_2. For ^{17}O measurement, oxygen is maintained as oxygen gas and the oxygen isotopes are measured as O_2^+ at masses 32, 33, and 34.[29]

In addition to ^{32}S and ^{34}S, sulfur has two minor isotopes ^{33}S and ^{36}S. The abundance of ^{33}S has been shown to be quite variable in sulfides occurring in rocks older than 2.4×10^9 years.[30] This has been ascribed to the atmosphere on earth at this time lacking oxygen. Measurement of ^{36}S is more difficult because of its very low abundance, but it also appears to show mass independent fractionation in the earliest terrestrial rocks.

2. Clumped-isotope analysis

A recent development in stable isotope analysis is the measurement of multiply substituted isotopologues, or "clumped" isotopes.[31] This is based on the analysis of the minor isotope abundances and their indications of physicochemical pathways, as opposed to analyses based on isotope ratios concerning the major isotopes. For instance, it would appear that the proportions of ^{13}C-^{18}O bonds in carbonate are sensitive to temperature, and are independent of the bulk composition.[31]

In terms of mass spectrometric analysis, a standard gas-source mass spectrometer can be used to measure the relative abundances of $^{12}C^{16}O_2$ and $^{13}C^{18}O_2$. These species have no isobars and so the measurements are straightforward, notwithstanding the low abundance of $^{13}C^{18}O_2$ which is only 45 ppb of the $^{12}C^{16}O_2$ species (Table I). In order to measure any of the other isotopologues, extremely high mass resolution is required, with the lowest requirement being for the discrimination of the mass 48 isotopologues $^{12}C^{18}O_2$ and $^{13}C^{17}O^{18}O$ at M/ΔM of 14 400. A new instrument being designed for construction at UCLA in an attempt to isolate these components.[32] Such mass resolutions have never been at-tempted previously for gas source machines with sector magnet mass spectrometers.

C. Thermal ionization mass spectrometry

For many years, solid source mass spectrometry has centered around TIMS and the various chemical procedures that are required to first separate the elements of interest from samples, and then characterize them through mass spectrometric analysis.[33, 34] The sample, be it rock, mineral, or skeletal remnants, is dissolved in a suitable reagent, and then the aliquot is processed to allow elemental separation in chemical procedures often involving ion exchange resins. Prior to, during, or after separation, the samples can be spiked with an isotopic label of known composition that allows determination of chemical concentration and instrumental isotopic fractionation.[35] For TIMS, the sample is dried down, picked up in a small amount of solution, loaded on to a filament, dried down, and then inserted into the mass spectrometer for analysis. A current is applied through the filament, and the temperature is raised until the sample evaporates. At higher temperatures, and through interaction between the sample, filament, and emission agents (material such as Re or silica gel used for loading), the evaporating species can become ionized.

Many of the advantages of TIMS are based on the chemical separation of the element of interest. This means that mass resolution requirements are generally at the level of appropriate separation of unit mass differences. Further differentiation between elements can be produced through the different temperatures that elements evaporate and ionize from the filament, or from different oxide speciation.[33] Thermal ionization means that the energy spread of ions is low and so no energy compensation (electrostatic sector) is required in the mass spectrometer. However, TIMS also has some drawbacks. Not all elements can be readily ionized by thermal ionization, such as Re and W, which are used for filaments for this reason. In addition, isotopic mass fractionation (or mass bias) continuously changes during analysis because of evaporation of a finite amount of material and hence Rayleigh fractionation is induced. The instrumental fractionation can therefore follow a different law than other natural systems, although overall instrumental mass fractionation can be controlled by instrument settings.[36]

TIMS is regarded as one of the cornerstones of isotope analysis in the geosciences for non-volatile elements. Many of the isotopic systems for which TIMS excels are focused on geochronology and radiogenic isotope measurements, including the systems ^{87}Rb-^{87}Sr, ^{147}Sm-^{143}Nd, and ^{146}Sm-^{142}Nd, and ^{238}U-^{206}Pb, ^{235}U-^{207}Pb, and ^{232}Th-^{208}Pb. In large part, this is based around the simplicity of the measurements in that isobaric interferences can be avoided through judicious chemistry, background signals can be extremely low, ionization yields can be reasonably high, and the mass spectrometry is reasonably controllable simply by the current applied to the filament.

For geochronology, minerals with high parent-daughter ratios are analyzed to obtain the best elevation in the daughter isotope ratio. These measurements hinge on obtaining reliable isotope ratios for the daughter and good calibration of

the parent-daughter ratio. For radioisotope chemistry measurements, the initial ratio of the daughter can be used as a probe of the prehistory of the rock. In this case, the issue is to get the best possible precision and accuracy of the daughter isotope ratio. In contrast to geochronology measurements, minerals with low parent-daughter ratios are used so that the correction for *in situ* radioactive decay is minimized.

The current generation of thermal ionization mass spectrometers can achieve precision and accuracy around the 5 ppm level or better. This level of operation has been achieved through painstaking efforts in stabilizing electric and magnetic systems to unprecedented levels. It also involves lengthy analytical times with multiple collection of large ion beams to achieve appropriate signal to noise, and counting statistics.

1. U-Pb geochronology

The pursuit of high precision and high accuracy in geochronology has been of prime importance in isotope geochemistry since the first discovery of radioactivity.[37] The U-Th-Pb system transmutes through the decay chains of ^{238}U-^{206}Pb, ^{235}U-^{207}Pb, and ^{232}Th-^{208}Pb. The U-Th-Pb system is probably the most widely applicable decay system for use throughout geological time. It has several major benefits in that the coupled decay chains from ^{238}U and ^{235}U allow an assessment of "closure", U is concentrated in a variety of minerals including zircon and monazite that also exclude Pb from their crystal lattices, and zircon in particular is a robust mineral that resists weathering and so is the basis for the discovery of the oldest mineral grains on earth.[38]

Developments in Pb isotope analysis have closely followed the developments of mass spectrometry in the earth sciences. Much effort has been put in to the chemical and physical treatment of zircon to remove domains that have lost Pb.[39] In terms of TIMS analysis, developments that led to increasing the level of precision from ever smaller quantities of zircon have been important.[40] U-Pb geochronology is the premier technique for calibration of the geological timescale. The earthtime initiative[41] is pursuing the reduction of systematic biases between laboratories and improvement in analytical protocols. Current levels of precision and accuracy are, of course, dependent on age and U concentration, and the specific mineral that is being analyzed, but the mass spectrometric limit appears to be around the 0.1 permil level, still allowing sub million year precision throughout the last 540×10^6 years of the Phanerozoic.

For the youngest rocks, U-Pb dating is not appropriate because the rocks have had insufficient time for equilibrium to be attained in the multi-isotope decay chains. However, this disequilibrium in itself can be a geochronometer allowing extremely high age resolution in samples younger than 500 000 years.[42]

2. High precision radiogenic isotopes with TIMS

In geochronology, the abundances of parent to daughter isotopes are measured so that the radioactive decay equation can be calculated for the closure time t. However, during various geological events, the decay products can be re-

distributed so that the time t is then based on a disturbed system. Such an age can be geologically meaningless being an average of two (or even more events). However, some of the complexity in such a system can also be drawn out from the radiogenic isotope compositions that remain proportional to the parent/daughter ratio. Such secondary isochrons can be used to ascertain geological events, such as metamorphic overprints.[43] In addition, the original daughter composition can be "frozen" into minerals that are free of the parent. This allows a model age to be calculated, often interpreted as a mantle extraction age, for the initial fractionation of parent from daughter. The measurement of the long-lived radioactive decay schemes ^{87}Sr/^{86}Sr (^{87}Rb-^{87}Sr; $t_{\frac{1}{2}} = 49$ Gyr), ^{143}Nd/^{144}Nd (^{147}Sm-^{143}Nd; $t_{\frac{1}{2}} = 106$ Gyr), and ^{176}Hf/^{180}Hf (^{176}Lu-^{176}Hf; $t_{\frac{1}{2}} = 39$ Gyr) are mainstays for determination of isotopic model ages. These measurements require high precision, of order 5 parts in 10^5 (50 ppm) or better to resolve geological events over the course of earth history.

The presence of a relatively short-lived isotope ^{146}Sm (revised half life of 68 ± 9 Myr[44]) has been inferred from anomalies in the daughter isotope ^{142}Nd.[45] With the age of the oldest crustal rocks being around 4000 Myr, the abundance of ^{146}Sm should be very low and the effects on the ^{142}Nd abundance small. The rate of change of the anomaly naturally decreases with time as well requiring an especially high precision to follow into Archean (<3.8 Gyr) rocks.[46,47] The resolution of these anomalies has been a driving force in development of techniques to push down the limits of precision and accuracy to unprecedented levels, of order 3 ppm.

D. Inductively coupled-plasma mass spectrometry

Some elements are difficult to ionize through TIMS because they are extremely refractory and cannot be evaporated and ionized on filaments without risk of failure. This includes elements such as Hf (^{176}Lu-^{176}Hf)[48] and W (^{182}Hf-^{182}Ta-^{182}W; $t_{\frac{1}{2}} = 9$ Myr).[49] The advent of inductively coupled plasma mass spectrometry[50] allowed these refractory metals to be analyzed in a simple and reproducible fashion.[51,52] In this case, the elements were separated and spiked, and then run as solutions into the mass spectrometer (Fig. 14). The solution effectively evaporates as it is drawn in and the gas is introduced to a plasma formed from an RF discharge through one of the noble gases (typically Ar[53]). The high first-ionization-potential of the noble gases works effectively to strip electrons off almost any other element.

The ICP source can be matched to the same type of multiple-collector sector mass spectrometer as typically used in TIMS. The main issue with an ICP source is that samples are introduced at atmospheric pressure, the torch operates at an intermediate pressure, and the mass spectrometer is at high vacuum. The stepping of the ambient pressure requires strict vacuum management, but the nature of the discharge also exerts extreme wear on the extraction cones. Another aspect of ICP-MS operation is that the source is best operated at ground potential because of the introduction of liquid or gas at ground potential, and the risk of an arc discharge in low vacuum regions. In comparison, the filament in a TIMS instrument can
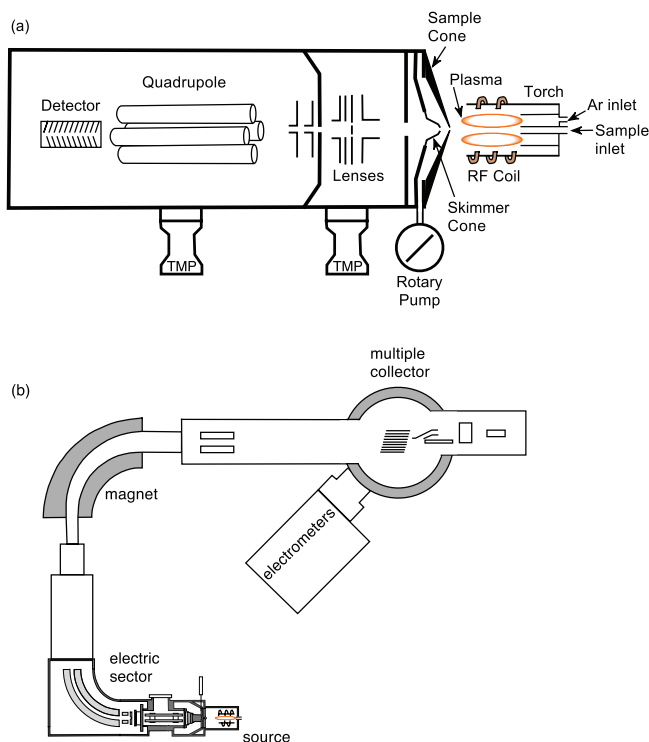
FIG. 14. Inductively coupled-plasma mass spectrometry. (a) Upper: ICP with quadrupole mass spectrometer. An argon plasma is generated through an RF discharge. The sample (gas, liquid) is introduced to the plasma with consequent ionization of all atoms. The mass spectrometer requires an efficient pumping system to allow the ions to be analyzed in the quadrupole mass spectrometer. In the example shown, two stages of differential pumping occur through the sample cone and skimmer cone. Operation of the source at atmospheric pressure requires that the source is kept at ground potential with the detector system at high potential. (b) Lower: ICP with sector mass spectrometer (Thermo Neptune). The setup is the same as the quadrupole mass spectrometer, but is complicated simply through the size of the mass analyzer that must be floated.

be operated at high voltage allowing the mass spectrometer to operate at a ground referenced potential. For the ICP-MS, with ground potential at the source, the whole mass spectrometer must be offset to the energy of the extracted ion beam, or the beam at least potentially isolated from the grounded surround. This also means that the computer system operating the instrument must be electrically isolated from the mass spectrometer.

ICP-MS has proved to be a highly versatile methodology. It allows analysis of elements that are rather difficult to ionize. Introduction of samples in solution is straightforward. It provides stable and consistent ion beams because of the use of an inlet. As such, and like a gas source mass spectrometer, instrumentally induced isotope mass fractionation is highly reproducible. However, the ICP-MS does have some drawbacks compared with TIMS. Isobaric interferences associated with the plasma gas can be large, such as argides from the argon gas and there is also a greater propensity for multiple charge states. ICP-MS also has a large intrinsic mass fractionation.[54]

1. Unconventional stable-isotope analysis by ICP-MS

One of the key developments in geoscience isotope analysis has been the use of the ICP-MS for analyzing the isotopic

compositions of elements that have hitherto been extremely difficult. This has allowed a range of elements that have not been considered simply because the elements were too heavy and isotope effects should be limited, or the chemistry and loading has not provided useful signals by TIMS. ICP-MS has provided a platform where the possible range of natural variations of any element can be quickly ascertained and procedures then developed for extremely high precision analysis. For instance, Fe isotope measurements have opened up opportunities not only in the rock record,[55] but also in characterizing biogeochemical processes[56] although the distinction between these can be difficult.[57]

Targeting the deficits in the radiogenic daughter has become a complementary technique to finding excesses of a nuclide correlated with the parent/daughter ratio. Another system where this has been attempted is for ^{60}Fe ($t_{\frac{1}{2}} = 2.6$ Myr) ^{60}Co ($t_{\frac{1}{2}} = 5.3$ yr) ^{60}Ni. The presence of ^{60}Fe in the early solar system is important because ^{60}Fe can only form in a supernova and so its presence is the "smoking gun" of a supernova explosion in close proximity to our solar system as it was forming. However, measuring the abundance of ^{60}Fe/^{56}Fe has been extremely difficult. In searching for excesses of ^{60}Ni related to ^{60}Fe decay, TIMS data from an igneous meteorite[59] suggested an upper limit to the abundance of ^{60}Fe/^{56}Fe of $\sim 2 \times 10^{-8}$. SIMS data from Fe sulfide in chondrules suggest a much higher value up to 4×10^{-7};[60] however, this appears to be an artifact of the data collection and reduction used.[61] Bizarro et al.[62] utilized ICP-MS to reveal ε unit deficits in ^{60}Ni in iron meteorites suggesting ^{60}Fe should be present. However, the anomalies were also found in differentiated meteorites with high Fe/Ni, where large positive anomalies should be found. Moreover, Regelous et al.[63] also found evidence for small Ni isotope anomalies but inferred these were mainly due to Ni nucleosynthetic anomalies. These authors indicated that the abundance of ^{60}Fe could be as high as 3×10^{-7} in ordinary chondrites, but less than 1×10^{-7} in carbonaceous chondrites. The search for proof of the existence of live ^{60}Fe in the early solar system continues.

2. Short-lived radionuclides in the early solar system

High analytical precision is of value for a number of short-lived isotopes in the early solar system. Of particular interest has been the ^{26}Al-^{26}Mg system ($t_{\frac{1}{2}} = 0.7$ Myr). The correlated presence of ^{26}Mg excesses with Al/Mg ratio in various minerals as well as whole rocks has been taken as evidence for the presence of ^{26}Al in the early solar system at an abundance level of ^{26}Al/^{27}Al of 5×10^{-5}. If this radiogenic isotope was homogeneously distributed through the solar system, then it follows that the ^{26}Mg abundance that we have now was augmented, and the earliest materials should have a deficit in ^{26}Mg. However, given the low Al/Mg of the solar system, and the low inferred ^{26}Al/^{27}Al, the deficit is very small, of order 30 ppm. This signal has been observed in ICP-MS analysis of early materials from the solar system providing confirmation of the widespread presence if not homogeneity of ^{26}Al in the solar system.[58]

3. Variable $^{238}U/^{235}U$

Uranium isotopes provide two geochronometers for dating rocks and minerals: ^{238}U-^{206}Pb and ^{235}U-^{207}Pb. One of the tenets in geochronology has been the adoption of a specific ratio of $^{238}U/^{235}U$ of 137.88 so that an age can be calculated directly from the $^{207}Pb/^{206}Pb$ ratio. A benefit in specifying the ratio is that there is a common reference frame for geochronology without a propagated error from the measurement of U isotopes. The low abundance of ^{235}U makes this a difficult measurement in the first place and resolution of any effects has only recently been realized.

With the precision available from multiple collector ICP-MS, variations in $^{238}U/^{235}U$ are now being observed.[64] In the oldest materials in the solar system, refractory inclusions, significant variability in $^{238}U/^{235}U$ was found (137.4–137.9) and ascribed to the presence of ^{247}Cm in the early solar system. Addition of ^{247}Cm-sourced ^{235}U could lead to anomalously high $^{207}Pb/^{206}Pb$ ages. Amelin *et al.*[65] determined that after correcting for minimal U isotopic fractionation in sample SJ101, the age of the earliest solids was 4567.2 ± 0.5 Myr. Variability in $^{238}U/^{235}U$ has only been found in refractory inclusions, however, the mean $^{238}U/^{235}U$ ratio for terrestrial and most meteoritic materials also appears to be offset from the ratio previously used.[66] An additional U isotopic measurement, with commensurate error propagation, would not necessarily lead to more accurate geochronology. On the other hand, the $^{238}U/^{235}U$ ratio in terrestrial and meteoritic materials was previously determined with much lower precision[67] than is available now, and a revision could produce better agreement between different geochronometers.

4. Laser ablation ICP-MS (LA-ICP-MS)

The ICP-MS has also been successfully mated to a laser ablation source for *in situ* analysis.[68] Rather than a liquid introduction system, the laser ablates the sample in a cell and the dissociated sample is picked up by a carrier gas and introduced to the plasma. The key to the operation of laser ablation is fragmenting the sample to a molecular or atomic level so that the plasma is predominantly causing ionization rather than having to break up "chunks" of material. The first lasers successfully used in LA-ICP-MS were Nd-YAG lasers operating at 1064 nm.[69] With these lasers, much of the ablation was thermal thereby large fragments of the target were produced as well as thermal effects such as molten spatter around the crater. Ultimately the shorter wavelength excimer lasers produced smaller and better-defined spots and ablated through bond-breaking in the target without thermal issues.[70]

One of the key features of LA-ICP-MS analysis is the ability to operate *in situ* and to ablate a relatively large volume of material quickly, thereby enabling good signal-to-noise. This is important for measurements of trace element abundances and isotopic analysis of trace elements. A quadrupole mass spectrometer is frequently used to allow rapid peak switching for multiple peaks. There are several details in the methodology that require attention. Down-hole fractionation can be a problem with different elements showing different degrees of signal change as the ablation proceeds. This has

been attributed to a condensation effect. Also, because the beam is ablating a relatively large volume, analysis of mineral and fluid inclusions can be an issue. Notwithstanding these issues, laser ablation ICP-MS is a key methodology in analysis of geological materials.

LA-ICP-MS is now widely used for U-Pb geochronology,[71] ^{176}Hf radiogenic isotope,[72] and trace element geochemistry.[73] The U-Pb scheme is amenable because the alpha decay schemes provide wide mass separation of parent-daughter. Hf isotopes can be carried out because of the chemical dissimilarity of the trivalent REE relative to quadravalent Hf resulting in (for example) high abundance of Hf in zircon. The opportunity for Hf isotopic analysis by ICP-MS had lead to the coupling of LA-ICP sources to multiple-collector sector-magnet mass spectrometers. This has a huge advantage over quadrupole systems in that any beam fluctuations caused by the pulsed laser are consistent across all detectors. However, the sectors are slow to peak switch and so are largely limited to isotopic analysis over a small mass range, or with only few peak jumps.

E. Secondary ion mass spectrometry

One of the key developments in geoscience mass spectrometry is the recognition that bulk analysis alone does not tell the whole story and that distinct domains in the sample can be recognized and analyzed. This is in effect the same issue concerning bulk (whole-rock) analysis for chemistry versus electron microprobe analysis of individual minerals. They each contain important aspects of information and their stories must be combined if the complete picture is to be revealed.

Ion microprobes (based on secondary ion mass spectrometry) were originally proposed as the logical extension of electron probes to access minor and trace elements that were difficult to analyze because of large x-ray backgrounds. However, the principles of operation are very different.[74] In an ion microprobe, a focused primary ion beam is used to ablate, or sputter, the sample and the resulting secondary ions are extracted and transferred to a mass spectrometer for analysis (Fig. 15). The primary ion beam is generally O^- or Cs^+; these elements are used because of their capacity to enhance electron transfer. The secondary ions can either be positive (metals) or negative (non-metals). The polarity of the instrument is generally set for opposite polarity of primary and secondary ion beams, so that the O^- primary beam is used to analyze metals, while the Cs^+ beam is used for non-metals. Typically energies for the primary beam are 10–20 keV, with secondary ion energies around 5–10 keV.

The key features of SIMS analysis are (1) the high secondary ion yields that can be achieved for many elements, and (2) the extremely low background signals facilitating high signal to noise. Drawbacks of the method are the low sputtering rates, which means that many analyses are limited by Poisson counting statistics of the ions detected, and the presence of isobaric interferences (molecules and fragments), which cause incorrect isotope ratios. In terms of counting statistics, there is a trade off in the spot size and the desired precision
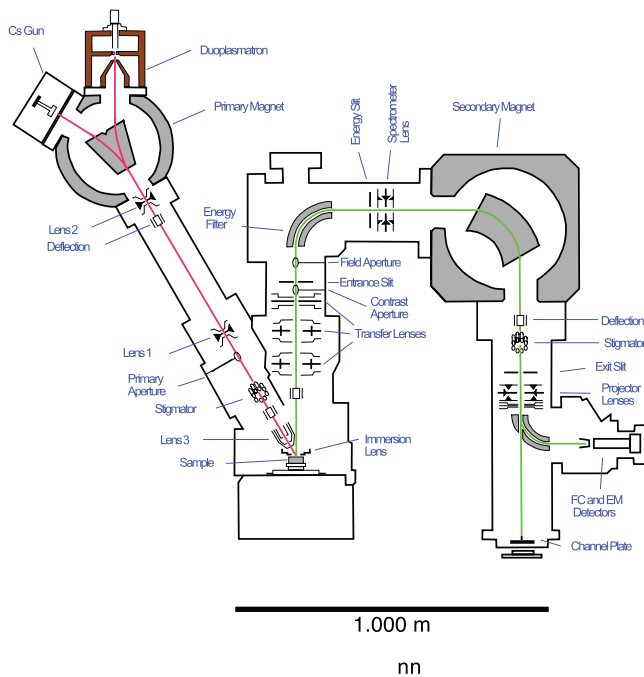
1.000 m

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FIG. 15. A SIMS instrument (Cameca ims 3f). Primary ions (typically O^- or Cs^+) are accelerated (10–20 keV) and focused on to a polished sample surface (spot order of 10 μm). Secondary ions are produced by the impact of the high energy ions and are normally accelerated back to ground potential. The secondary ions pass through transfer lenses, which shape the secondary ion beam. The mass analyzer is a double-focusing sector magnet. The detector system has two alternate paths. The channel plate allows the pot to be directly imaged in any desired species. A counting system for Faraday and ion counting allows isotope abundance measurements.

for the analysis. For the same ion density in the primary beam, the secondary signal is proportional to the area sputtered.

The first SIMS instruments had low mass resolution and low sensitivity; these could not resolve molecular isobars that are endemic in this technique. Second generation instruments (e.g., Cameca ion microscopes such as the ims-3f-7f (Fig. 15) had higher resolution but still only moderate transmission. The first mass spectrometer designed to deal with molecular isobars in geological materials was the sensitive high resolution ion microprobe (SHRIMP) with capabilities of combined high mass resolution and sensitivity (high transmission) (see Refs. 75 and 76). The key ingredient for the coupled high transmission and high sensitivity of this instrument is the size: the magnet turning radius is 1 m and beam length is 7 m (Fig. 16). One of the major success stories of SHRIMP was the ability to carry out U-Pb analyses on zircon allowing geochronology to be performed *in situ* on the microscale. It should be noted that SHRIMP analysis was not immediately accepted.[77] At the time of its development, a standard TIMS analysis required some tens of micrograms of zircon; a SHRIMP analysis only utilized 2 nanograms and hence counting statistics were a major limitation. Still, the ability to target and select specific domains and analyze magmatic and inherited zircon (for instance) or to exclude disturbed areas was groundbreaking.

The success of SHRIMP led to the advent of the Cameca 1270, which was designed around the Cameca 6f source, but with a larger mass analyzer enabling higher sensitivity at high
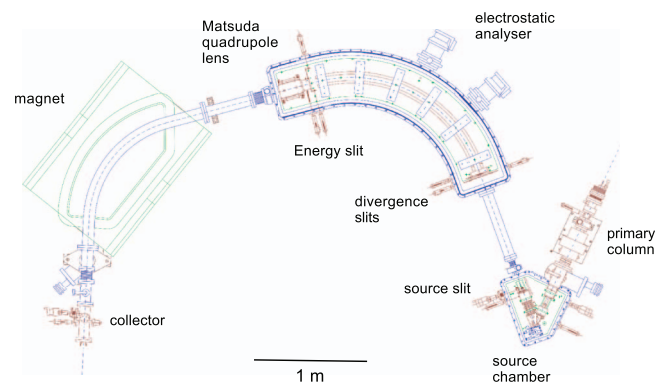

FIG. 16. SHRIMP uses a double-focusing sector mass spectrometer with only one additional lens element, a quadrupole lens between magnet and electrostatic analyser to correct second-order aberrations.[8] The key development of SHRIMP was making it large (magnet turning radius of 1.000 m) thus allowing high mass resolution and sensitivity. Illustrated is a single collector version of SHRIMP II.

mass resolution thereby circumventing some of the issues for the small geometry instruments for geological analysis.

Recently, it has been the Cameca nanoSIMS that has added a new dimension to *in situ* analysis (Fig. 17). This instrument features the ability to refocus a Cs^+ primary beam to around 50 nm. While nanoprobes have been available for some time in surface sciences, the nanoSIMS combines the fine scale spatial resolution with a sector mass spectrometer capable of isotopic analysis. However, as always there are tradeoffs to be made. With such a finely focused primary beam, only picoamperes (pA) are available to sputter the target, and secondary ion signals are therefore commensurately low. Hence only major elements can be analyzed in any realistic time frame. In the geosciences, this instrument is highly regarded for elemental and isotopic distributions and for dust analysis (particularly extraterrestrial[78]).

1. Stable isotope analysis with SIMS

The push toward higher and higher precision is highly evident in SIMS stable isotope analysis. The issue with stable
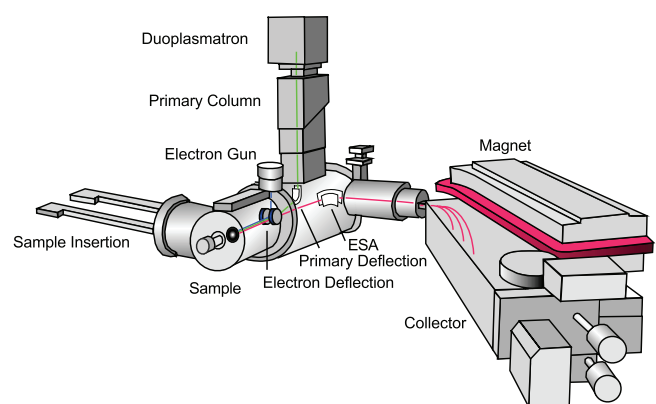

FIG. 17. The Cameca nanoSIMS uses a double-focusing mass analyzer that places the focal plane of the magnet very close to the magnet itself, and hence the collector is integrated with the magnet. The nanoSIMS uses normal incidence of the primary beam and a very shallow extraction field to produce extremely small primary ion spots on the target (down to 50 nm).

isotope analysis is that many elements require use of a positively charged primary beam (Cs^+) with the extraction of negative secondary ions (and electrons). In the analysis of insulators, the spot charges causing the secondary ion energy to change and hence degrades the stability of the beam that is required for precise and accurate analysis. For negative primary ions, the charge build up is simply drained off through the conductive coating on the sample. However, the conductive coat on the sample does not ameliorate positive charging and so electrons must be introduced to the sputter site. Initial attempts on the small Cameca ims 3f ion microscopes to bring a high energy electron beam across the extraction gap to the target were not particularly successful. The electrons failed to neutralize the charging at the surface because of the depth of penetration as well as the production of secondary electrons that were also removed from the surface.[79]

An elegant solution to this problem was designed by Cameca through a normal-incidence electron-flood gun. In this configuration, the electron beam is inserted into the secondary extraction system and focused with sufficient energy to just stall out above the surface. Charge compensation is then accommodated as the electrons are drawn to any charge build-up.

Analytical developments on the smaller Cameca ion microscopes allowed analysis of insulating materials but was limited by the secondary ion transmission and required long integration times with ion multipliers, effectively limiting precision to around 1 permil.[80] With the advent of large sector magnet mass spectrometers oxygen secondary ion beam intensity is high with several GHz count rates attainable on $^{16}O^-$ from 10–20 μm primary spots.[81,82] Initial work on the Cameca 1270 used combined Faraday cup and electron multiplier[83] followed by multiple collection with Faraday cups. At these count rates, measurement precision of the order of 0.1‰ for $^{18}O/^{16}O$ can be achieved in a matter of minutes. However, achieving external reproducibility at the same level has required extensive effort and attention to analytical detail.

It thus raises the question as to whether SIMS stable isotope analysis could reduce the requirement for conventional analysis using dangerous chemicals such as BrF_5. Such a scenario is not likely. One of the issues with SIMS is the requirement for matrix-matched standards because of the dependence of it on isotopic mass fractionation.[74] Effective matrix matching can only be achieved for sample domain sizes larger than the primary spot and not for mixtures of minerals in the spot. Moreover, many rocks have large mineral grains and if the bulk composition of the rock is required, a large sample must be taken in order to achieve a representative modal abundance of the minerals. However, the ability of SIMS to take individual samples of specific petrographically selected domains is, of course, one of its feature attributes.

2. MegaSIMS and the oxygen isotopic composition of the sun

Extraterrestrial materials show a wide range in oxygen isotope compositions. While oxygen on the earth predomi-

nantly shows mass dependent fractionation, materials from elsewhere in the solar system show variability predominantly in the ^{16}O abundance. The total range of this variation is of the order of 50% albeit with the most anomalous materials being small components from meteorites.[27] Of particular interest has been the 4% difference in composition between refractory inclusions, composed of Ca, Al, oxides, and representing the oldest known material in the solar system, and the compositions of planetary materials such as Earth-Moon, Mars, and various asteroidal parent bodies. The chemistry of the refractory inclusions suggests that they are, or are derived from, solar condensates. An outstanding issue has been the determination of the solar oxygen isotope composition because this could tell us a great deal about processes operating in the early solar system.

A sample of the sun is provided by solar wind that comes streaming out from the sun at an average speed of 400 km/s. The main goal of the NASA Genesis mission was to bring back a sample of solar wind in ultra-pure detectors where the oxygen could be analyzed. Measurement of the oxygen isotopic composition of solar wind is not straightforward. The velocity of the solar wind equates to around 1 keV per nucleon hence ^{16}O is implanted at around 16 keV. This results in oxygen being implanted into solid targets to depth around 100 nm. Moreover, solar wind oxygen is accompanied by the much higher abundance hydrogen. During sputtering, this oxygen combines with H to form an intense OH^- beam, which must be separated from the atomic O^- species, with a commensurate loss of signal.

A new instrument was designed specifically for the analysis of stable isotope compositions of solar wind. This instrument, called MegaSIMS,[84] marries a conventional SIMS source and extraction system to an accelerator mass spectrometer (Fig. 18). The SIMS components allow the selection of regions free of surface contamination to be analyzed. The emitted ion beam is mass separated into a narrow mass range and a recombinator system refocuses that mass range into a single ion beam for introduction into the accelerator. The accelerator takes the negative ions, accelerates them to MeV energies and passes them through a stripper gas where molecules are destroyed (particularly OH^-) and electrons are removed. The resulting positive ion beam can then pass through a high energy magnetic sector that allows dispersion of the three isotopes of oxygen and measurement in a multiple collector detector. Results from this unique and novel instrument indicate that the solar oxygen-isotope composition is similar to the refractory inclusions, enriched in ^{16}O by 6% with respect to terrestrial.[85]

F. Other mass spectrometers

In geoscience applications, TOF mass spectrometers have generally only been used in chemical characterization of surfaces,[86] or in highly specialized instrumentation. Surface analysis is a forte of TOF-SIMS and is widely used for characterizing species that reside on materials.[87] It is thus highly useful in the materials industry where the chemistry at interfaces can be extremely important.
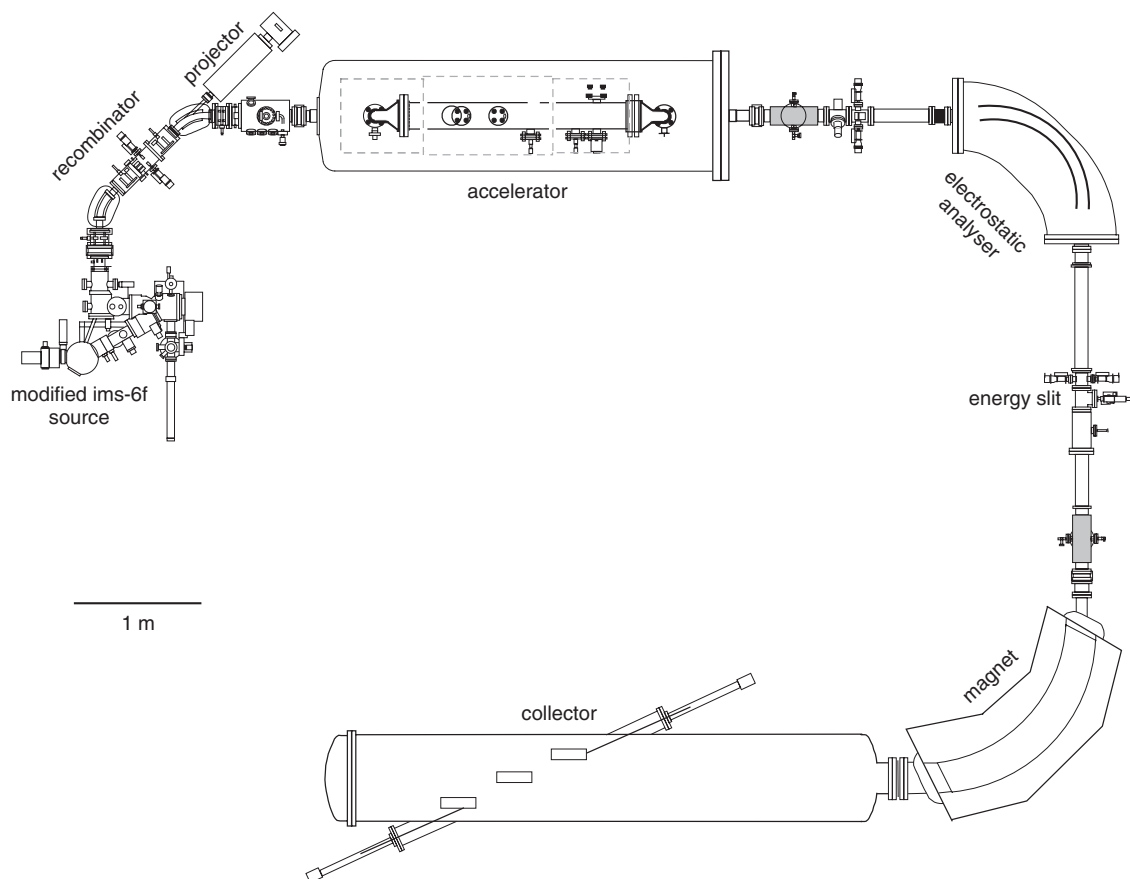
FIG. 18. MegaSIMS consists of a combined SIMS source, and an accelerator-based mass spectrometer. A modified Cameca ims-6f source allows selection of appropriate regions of the sample surface. Initial magnetic separation allows a specific mass range of ions to be selected (e.g., oxygen isotopes) and these are then recombined into a single ion beam before passing in to the accelerator. Ions are refocused in a high energy double-focusing mass spectrometer, with a multiple collector allowing simultaneous collection of the three stable oxygen isotopes.

TOF has also been used for isotope measurements, but these have proved somewhat difficult. The main issue is that with a pulsed system, the ions arrive in bunches. If a standard electron multiplier is used, then the first ion triggers the multiplier and so the number of ions in the bunch is not registered. This creates an effective dead time that is very difficult to quantify. Multipliers consisting of 2D arrays are a substantial improvement on single multipliers, but the signals from the individual channels must be summed and so there is still an issue with isotope ratios that can be related to the abundances of the isotopes. Where count rates are low, these issues are not so important and so isotope ratios can be determined within the limitations of Poisson counting statistics. Applications in cosmochemistry include fine scale resolution of isotopically anomalous material in interplanetary dust particles.[88]

The pulsed beam in a TOF-SIMS can be effected by pulsing the primary beam, or the secondary ion beam. Pulsing the primary beam has an advantage in not consuming the sample and so this method is beneficial where sample is limited. A pulsed secondary ionbeam can also be effected by scanning the secondary ion beam across the source slit. This has advantages in terms of the simplicity of incorporation into a mass spectrometer.

A SIMS source can also be used in a different way. The secondary ions can be discarded and a laser used to ionize the sputtered neutrals. The ionization can be selective—in this case a tunable laser or lasers can be used for the prescribed electron transitions (e.g., RIMS), or all of the neutrals can be ionized with a high energy laser pulse (e.g., femtosecond laser). Instead of an ion beam, a laser can be used to ablate the sample and then another laser system used to produce the photoionization. The is the basis of the CHARISMA instrument at Argonne National Laboratory.[89]

There are currently several intriguing instruments that have just been constructed, or are being constructed, based around SIMS, laser photoionization, and time-of-flight mass spectrometry.

MULTUM is a TOF instrument that features an innovative design including a "Figure 8" shaped mass analyser,[90] where ions can be left cycling, hence dispersing, for any appropriate time period (Fig. 19). In this case, greater dispersion between peaks means higher mass resolution. The MULTUM has achieved mass resolution of order of 250 000 (FWHM m/Δm). LIMAS[91] at Hokkaido University uses the MULTUM mass spectrometer with a focused ion beam for sputtering the target and a femtosecond laser to ionize the sputtered neutrals.

CHILI is the latest of the nanobeam instruments being developed between University of Chicago and Argonnel National Laboratory.[92] It is a new resonance ionization mass spectrometer with a focused primary ion beam down to a few nanometers with ionization efficiencies of the order of
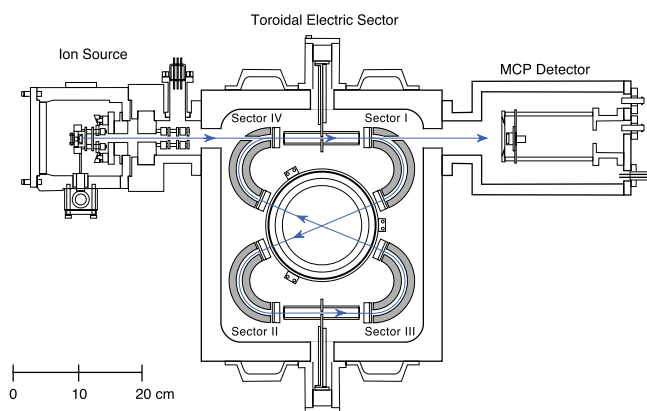
FIG. 19. The MULTUM II mass spectrometer is a time-of-flight mass spectrometer with four toroidal electric sectors. Ions can be cycled repetitively through the mass analyzer for a specified duration (number of cycles) before collection with the MCP detector. The toroidal sector allows the mass spectrometer to have a drift length that is simply proportional to the number of cycles, and hence can operate with extremely high mass resolution.

40%–50%. At this scale, even with extremely high ionization efficiency, the number of ions will limit the precision, but will still be capable of addressing a number of cosmochemical issues.

The Ionoptika J105 is a TOF SIMS instrument with a two stage time-of flight mass spectrometer.[93] This instrument operates with a constant (dc) primary beam with the secondary beam pulsed for the time reference. Secondary ions are bunched in the first stage, and then a pulse is accelerated and transmitted to the reflectron.

1. Future directions: How far can we go?

Mass spectrometry in the geosciences has made great strides over the past few decades with great increases in absolute precision as well as precision per mass unit of target element. This was the governing factor for many decades in realising high precision analyses where sample was essentially unlimited. With developments in TIMS and then ICP-MS, isotope ratios of nearly any multi-isotopic lithophile element can be determined to better than 10 ppm or so. This has largely been founded on better, more stable, electronics systems that allow this level of precision to be obtained, and to have that level of precision commensurate with external reproducibility and accuracy.

In situ isotopic analysis was effectively unknown 30 years ago. Now analyses by SIMS and LA-ICP-MS have evolved to being routine and can now be regarded as complementary to bulk analyses. The precision of *in situ* analyses can be limited by counting statistics of the finite number of atoms and ions ablated, but can also be limited by instrumental effects such as geometric aberrations in ion extraction.

Gas-source mass spectrometry is a mature field. For stable isotopes, there is only a limited push toward higher precision, and mainly for minor isotopes, or clumped isotopes, which can be limited by the amount of gas present. For isotope mass fractionation determinations by two-isotope measurements, there is little to be gained practically because of

the high precision already obtainable. However, recent developments to incorporate multiple collection in noble gases with multiple isotopes, could lead to gains in precision, especially where sample gas is limited.

So the question then becomes, how far can we go in pushing mass spectrometric analysis in the earth sciences. Where are the gains to be made in precision and accuracy, and in utilizing ever smaller numbers of atoms and ions?

2. Improvements in precision and accuracy

The precision for an analysis is generally controlled by the amount of material that is being analyzed. In bulk analysis this is not generally a limitation. Sufficient sample can be processed to yield the number of atoms that will yield the required counting statistics. These types of analysis are essentially limited by the mass spectrometry hardware: the mass spectrometer geometry that can affect the peak shape, magnetic field stability, stability of electronics, and so forth. Current limits of precision are at the level of 2–3 parts per million. Can this go further? Most likely it will. If the measurement is not limited by sample, then counting statistics are not an issue. Will electronics get better? Almost certainly. And with that, so will the precision that can be obtained from a measurement.

Of course, precision is desirable, but reproducibility and accuracy commensurate with precision are also required. Pushing a measurement to higher internal precision can be achieved by simply taking more ratio measurements. The external precision, or reproducibility, however, will not improve if there is an underlying cause of variability in the measurement. Increasing the internal precision will allow the effect to be better observed, and so there is an iterative procedure of improving measurement precision so that other sources of noise can be quantified or identified, or issues with the sample preparation can be improved (e.g., lowering blanks, more effective element extraction during chemistry).

Over the past several decades, improvements in precision have generally lead to better external reproducibility, and hence a desire to go to even higher precision and accuracy.

3. Improvements in sensitivity

Sensitivity is generally regarded as a relationship between the number of atoms in the sample (of a given target element) and the number of ions that can be collected from that element during the measurement. In a push to smaller sample aliquots, the effective ion yields can be a determining factor. The sensitivity can be governed by the ionization process, the efficiency of ion extraction in the source, and the transfer of ions through the mass spectrometer.

The efficiency of the ionization process is typically set by the physics of that process, whether it be thermal ionization, secondary ionization, ionization in a plasma, or in a form of electron impact source. It could be said that there would be only limited gains that can be achieved in changing the efficiency of the ionization process. However, it can be well noted that one of the major gains in TIMS was in using

electron-transfer agents on the filament (silica gel, powdered Re, etc.). Ion microprobe analysis also relies on the electron transfer properties of Cs and O. As such, there could remain a recipe for any of the mass spectrometric techniques that will produce a significant (factor of two or more) increase in ionization efficiency.

The efficiency of ion extraction is essentially determined by the ion optics of the mass spectrometer. In most cases, the initial ions have relatively low velocities and so the extraction can be readily modeled and high efficiency designs produced. In general, higher extraction potentials lead to higher extraction efficiencies through putting more ions in a given solid angle. Phase-space matching is also important in the extraction region so that the maximum transmission into and out of the mass spectrometer can be maintained. Of particular importance in terms of transmission in sector-magnet instruments is the vertical profile of the beam. While most attention is generally focused on the lateral (= mass resolution) profile, it is the vertical profile that can have some importance in beam transmission. However, it is now well-recognised that truncation of the beam on any defining slit can cause mass fractionation and so highly efficient beam extraction and transport is an attribute of the current generation of mass spectrometers.

4. Improvements in mass resolution

Mass resolution is a desirable commodity in a mass spectrometer. However, there is generally a tradeoff between higher mass resolution and sensitivity, that is, higher mass resolution can only be achieved by truncating the ion beam in the lateral (mass dispersive) direction. This is effected by changing the source slit width on a sector mass spectrometer, for example. Alternatively, the mass spectrometer can simply be scaled up in size. This was the guiding principle for the design of the SHRIMP, where maximum transmission while maintaining sensitivity was desired. However, size also creates greater expense in fabrication of the mass spectrometer.

So while mass resolution can be optimized to some degree, it is largely a parameter of the mass spectrometer design and can only be changed within a narrow range. It should also be remembered that high-mass-resolution mass spectrometers are available, and are being developed such as the MULTUM based mass spectrometers discussed above. However, the attribute preferred in the geosciences is the ability to measure isotope ratios to extremely high precision, and so mass resolution for its own sake is not desirable if it affects performance in other ways.

Nevertheless, larger higher mass resolution mass spectrometers are coming on to the commercial market including the Nu 1700 for ICP-MS analysis, and the Thermo Helix-MC is also getting a larger magnet for separating unwanted species in noble gas analysis (e.g., $^{40}Ar^{++}$ from $^{20}Ne^{+}$).

5. Improvements in sample usage

Achieving ever higher precision in isotope analysis for a given sample size has always been a major goal in mass spectrometry in the geosciences. Effectively, the larger the size of the sample, the greater the chance of multiple domains, possibly with different compositions, contributing to it. Conversely, the smaller the sample size being analyzed the lower the precision that can be obtained. Comparison of analyses at different size scales is always difficult and can be controversial, especially when two very different techniques are being used.

Cosmochemistry has always been a major driver toward ever smaller samples. In large part this is because smaller sample sizes have progressively yielded larger isotope anomalies thus requiring lower precision to resolve from terrestrial compositions. The construction of the nanoSIMS and now LIMAS and CHILI are extending analysis down to very small volumes where the numbers of atoms present are a fundamental limitation. But even here there are notable differences in methodologies that will provide exploitation. The nanoSIMS can only measure a limited number of species and so a highly anomalous stardust grain can be sputtered away simply during the initial characterization. CHILI will only focus on a few elements as well through specific laser photoionization schemes. However, TOF instruments such as LIMAS have the capability to effectively measure every atom in a sample so that correlations between elements can be investigated after the analysis.

6. Science drivers

Without doubt, scientific outcomes are the drivers of innovation and development. While a technical development may open a new area of research, it quickly becomes an issue of understanding the signals that are being measured and what they tell us regarding processes occurring in nature.

In the past 20 years, the advances in ICP-MS measurements have been startling. This has opened up a number of new systems for analysis that were difficult with existing techniques. It also stood on the developments of TIMS for ever increasing accuracy and precision. The combination with a laser ablation source has opened up *in situ* analysis to a wider community than had the opportunity to use the large sector-magnet ion microprobes when they first appeared.

One of the key issues is whether to pursue flexibility in allowing a variety of analyses versus designing for a specific goal. In technological development, the former can take precedence especially with instrument vendors requiring sufficient custom to make the instrument a commercial success. In the case of a specific science driver, this can be driven by a single institution or researcher where the goal is to achieve a particular outcome. The MegaSIMS development is a recent success in this regard.

In terms of general technology for geoscience application, it is difficult to see a new capability coming on to the market, largely because nearly all elements are covered to an appropriate analytical level. Effort in the coming decade will likely concentrate more on application and protocol development rather than establishing a specific new mass spectrometric technique. In TIMS and ICP-MS, the ever-demanding push to even higher precision and accuracy will continue. For *in situ* analysis in cosmochemistry, the drive will be to go to

ever smaller samples with higher utilization of the sample. For noble gas mass spectrometry, higher mass resolution mass spectrometers could provide new insights in to the origins of heavy noble gas components, and smaller sample sizes could drive on new fields in Ar geochonology.

One area where fundamental development could be made is in the ability to carry out remote analysis, particularly concerning extraterrestrial analysis on spacecraft. Sample return missions are important because they provide us with samples from known provenance. However, there is a huge price to pay (literally!) in bringing these samples back home. Some types of analysis will always require return to earth, such as dust analysis. However, if bulk characterization is all that is required, then remote analysis could be highly attractive. Arguably, there is no greater benefit than to be able to carry out oxygen three-isotope analysis remote from the earth on water ice. The main problem with this analysis is the interference of ^{16}OH on the ^{17}O peak (as an atom or molecule), which is ubiquitous in most mass spectrometers. Mass spectrometers that can resolve these species are typically extremely heavy and unsuitable for space flight. A new method is required. Perhaps, the MULTUM can be adopted for this purpose.[94] Such a capability would open up the origin of water on earth and in the solar system, and give us a new perspective on the origins of life.

G. Conclusions

Isotopic analysis in the geosciences has come a long way since the first developments in isotope abundance determinations in the early 20th century. Mass spectrometry in many cases is a mature science with ongoing development leading to higher and higher precision, and/or using ever smaller samples.

Gas source mass spectrometry still utilizes a number of the techniques developed over 50 years ago. The developments in this field are largely related to sample handling and throughput. However, the advent of cluster stable isotope analysis involving detailing the abundances of minor isotopologues is a new field requiring new instrumentation and development.

Thermal ionization mass spectrometry and ICP-MS of chemically separated materials are providing the highest precision levels in isotopic analysis. Still, there remain analytical or instrumental issues that can compromise analyses, such as interferences or ion scattering. Sector-magnet mass spectrometry dominates this type of instrumentation and is used for high precision analyses with levels approaching parts per million levels from chemically separated fractions of rocks and minerals.

Some of the major advances in the past 20 years involve *in situ* analysis. Ion microprobes and laser ablation ICP-MS analysis utilize ion and laser beams respectively to directly sample rocks and minerals. The main issues with *in situ* analysis revolve around separating molecular interferences and dealing with atomic isobars. These methods are using increasingly smaller volumes for characterization, but ultimately these methods are limited by the small number of target atoms present in the samples for analysis. While sector magnets are appropriate for isotopic analyses, the rapid switching capabilities of electrodynamic quadrupole mass spectrometers are ideal for laser ablation ICP-MS where chemical abundances and low precision isotope ratio measurements are required. Other types of mass spectrometric analysis, including resonance ionization and time-of-flight, particularly with *in situ* analysis are opening up an entirely new view of our solar system.

It can always be observed that a given field has approached maturity and there can only be limited advances in the future. Mass spectrometry in geosciences is indeed mature, but new applications in isotope analysis can be instigated by developments beyond the mass spectrometer. The key to mass spectrometry is ionization, and undoubtedly there remain new techniques that can be used in new and innovative ways as we push the limits even further.

[1]E. Rutherford, Philos. Trans. R. Soc. London, Ser. A **204**, 169–219 (1905).
[2]J. J. Thomson, Proc. R. Soc. London, Ser. A **89**, 1–20 (1913).
[3]A. J. Dempster, Phys. Rev. **11**, 316–325 (1918).
[4]K. M. Downard, Eur. J. Mass Spectrom. **13**, 177–190 (2007).
[5]J. De Laeter and M. D. Kurz, J. Mass Spectrom. **41**(7), 847–854 (2006).
[6]A. O. Nier, Rev. Sci. Instrum. **11**, 212–216 (1940).
[7]T. W. Burgoyne and G. M. Hieftje, Mass Spectrom. Rev. **15**(4), 241–259 (1996).
[8]H. Matsuda, Int. J. Mass Spectrom. Ion Phys. **14**, 219–233 (1974).
[9]H. Matsuda, Nucl. Instrum. Methods Phys. Res. A **298**, 199–204 (1990).
[10]W. Paul and H. Steinwedel, Zeitschrift für Naturforschung A **8**, 448–450 (1953).
[11]W. E. Stephens, Phys. Rev. **69**, 691 (1946).
[12]W. Wien, Ann. Phys. **301**, 440–452 (1898).
[13]A. D. McNaught and A. Wilkinson, *IUPAC: Compendium of Chemical Terminology*, 2nd ed. (Blackwell Scientific, Oxford, 1997); the "Gold Book": XML online corrected version: http://goldbook.iupac.org (2006) created by M. Nic, J. Jirat, and B. Kosata; updates compiled by A. Jenkins.
[14]T. M. Esat, Nucl. Instrum. Methods Phys. Res. B **5**, 545–553 (1984).
[15]R. D. Russell, J. Geophys. Res. **76**, 4949–4953, doi:10.1029/JB076i020p04949 (1971).
[16]J. M. Hayes and D. A. Schoeller, Anal. Chem. **49**(2), 306–311 (1977).
[17]T. M. Esat, Int. J. Mass Spectrom. Ion Process. **148**, 159–170 (1995).
[18]M. Ozima and F. A. Podosek, *Noble Gas Geochemistry*, 2nd ed. (Cambridge University Press, 2002).
[19]P. R. Renne, R. Mundil, G. Balco, K. Min, and K. R. Ludwig, Geochim. Cosmochim. Acta **74**(18), 5349–5367 (2010).
[20]I. McDougall and T. M. Harrison, *Geochronology and Thermochronology by the ^{40}Ar/^{39}Ar Method*, 2nd ed. (Oxford University Press, Oxford, 1999).
[21]J. D. Gilmour, I. C. Lyon, W. A. Johnston, and G. Turner, Rev. Sci. Instrum. **65**(3), 617–625 (1994).
[22]S. A. Crowther, M. J. Filtness, and J. D. Gilmour, Lunar Planet. Sci. **XXXIX**, 1762 (2008).
[23]G. Turner, T. M. Harrison, G. Holland, S. J. Mojzsis and J. Gilmour, Science **306**(5693), 89–91 (2004).
[24]Z. Sharp, *Principles of Stable Isotope Geochemistry* (Prentice-Hall, 2007).
[25]H. Craig, Science **133**, 1702–1703 (1961).
[26]M. H. Thiemens and J. E. Heidenreich III, Science **219**(4588), 1073–1075 (1983).
[27]T. R. Ireland, Austral. J. Earth. Sci. **59**, 225–236 (2012).
[28]R. N. Clayton and T. K. Mayeda, Geochim. Cosmochim. Acta **27**, 43–52 (1963).
[29]R. N. Clayton, N. Onuma and T. K. Mayeda, Earth Planet. Sci. Lett. **30**, 10–18 (1976).
[30]J. Farquhar, H. Bao and M. Thiemens, Science **289**(5480), 756–759 (2000).
[31]J. M. Eiler, Earth Planet. Sci. Lett. **262**, 309–327 (2007).
[32]N. Jones, Earth Magazine **57**, 40–45 (2012).
[33]J. Völkening, T. Walczyk, and K. G. Heumann, Int. J. Mass Spectrom. Ion Process. **105**(2), 147–159 (1991).
[34]R. L. Edwards, H. Cheng, M. T. Murrell, and S. J. Goldstein, Science **276**(5313), 782–786 (1997).
[35]P. J. Debievre and G. H. Debus, Nucl. Instrum. Methods **32**(2), 224–228 (1965).

[36] K. Habfast, Int. J. Mass Spectrom. Ion Process. **51**(2-3), 165–189 (1983).

[37] E. Rutherford, *Die Radioaktivität* (Springer, Berlin, 1907).

[38] D. O. Froude, T. R. Ireland, P. D. Kinny, I. S. Williams, W. Compston, I. R. Williams, and J. S. Myers, Nature (London) **304**, 616–618 (1983).

[39] T. E. Krogh, Geochim. Cosmochim. Acta **37**, 485–494 (1973).

[40] J. Roddick, W. Loveridge, and R. Parrish, Chem. Geol. **66**(1-2), 111–121 (1987).

[41] See www.earth-time.org.

[42] L. R. Edwards, J. H. Chen, and G. J. Wasserburg, Earth Planet. Sci. Lett. **81**(2-3), 175–192 (1987).

[43] A. P. Dickin, *Radiogenic Isotope Geology*, 2nd ed. (Cambridge University Press, 2005).

[44] N. Kinoshita, M. Paul, Y. Kashiv, P. Collon, C. M. Deibel, B. DiGiovine, J. P. Greene, D. J. Henderson, C. L. Jiang, S. T. Marley, T. Nakanishi, R. C. Pardo, K. E. Rehm, D. Robertson, R. Scott, C. Schmitt, X. D. Tang, R. Vondrasek, and A. Yokoyama, Science **335**, 1614 (2012).

[45] G. Caro, Earth Planet Sci. **39**, 31–58 (2011).

[46] G. Caro, B. Bourdon, J. L. Birck, and S. Moorbath, Nature (London) **423**(6938), 428–432 (2003).

[47] V. C. Bennett, A. D. Brandon, and A. P. Nutman, Science **318**(5858), 1907–1910 (2007).

[48] P. J. Patchett and M. Tatsumoto, Contrib. Mineral. Petrol. **75**, 263–237 (1980).

[49] C. L. Harper and S. B. Jacobsen, Geochim. Cosmochim. Acta **60**, 1131–1153 (1996).

[50] R. S. Houk, Anal. Chem. **58**(1), 97A–105A (1986).

[51] D. C. Lee and A. N. Halliday, Nature (London) **378**(6559), 771–774 (1995).

[52] J. Blichert-Toft, C. Chauvel, and F. Albarede, Contrib. Mineral. Petrol. **127**, 248–260 (1997).

[53] R. S. Houk, V. A. Fassel, G. D. Flesch, H. J. Svec, A. L. Gray, and C. E. Taylor, Anal. Chem. **52**(14), 2283–2289 (1980).

[54] D. Vance and M. Thirlwall, Chem. Geol. **185**(3-4), 227–240 (2002).

[55] H. M. Williams, C. A. McCammon, A. H. Peslier, A. N. Halliday, N. Teutsch, S. Levasseur, and J. P. Burg, Science **304**(5677), 1656–1659 (2004).

[56] C. M. Johnson and B. L. Beard, Science **309**(5737), 1025–1027 (2005).

[57] A. D. Anbar, J. E. Roe, J. Barling, and K. H. Nealson, Science **288**(5463), 126–128 (2000).

[58] M. Schiller, M. R. Handler, and J. A. Baker, Earth Planet. Sci. Lett. **297**(1-2), 165–173 (2010).

[59] A. Shukolyukov and G. W. Lugmair, Earth Planet. Sci. Lett. **119**(1-2), 159–166 (1993).

[60] S. Tachibana and G. R. Huss, Astrophys. J. Lett. **588**, L41–L44 (2003).

[61] R. C. Ogliore, G. R. Huss, and K. Nagashima, Nucl. Instrum. Methods Phys. Res. B **269**, 1910–1918 (2011).

[62] M. Bizzarro, D. Ulfbeck, A. Trinquier, K. Thrane, J. N. Connelly, and B. S. Meyer, Science **316**(5828), 1178–1181 (2007).

[63] M. Regelous, T. Elliott, and C. D. Coath, Earth Planet. Sci. Lett. **272**(1-2), 330–338 (2008).

[64] G. A. Brennecka, S. Weyer, M. Wadhwa, P. E. Janney, J. Zipfel, and A. D. Anbar, Science **327**(5964), 449–451 (2010).

[65] Y. Amelin, A. Kaltenbach, T. Iizuka, C. H. Stirling, T. R. Ireland, M. Petaev, and S. B. Jacobsen, Earth Planet. Sci. Lett. **300**(3-4), 343–350 (2010).

[66] J. Hiess, D. J. Condon, N. McLean, and S. R. Noble, Science **335**, 1610–1614 (2012).

[67] J. H. Chen and G. J. Wasserburg, Geophys. Res. Lett. **7**(4), 275–278, doi:10.1029/GL007i004p00275 (1980).

[68] P. Arrowsmith, Anal. Chem. **59**(10), 1437–1444 (1987).

[69] R. Feng, N. Macado, and J. Ludden, Geochim. Cosmochim. Acta **57**, 3479–3486 (1993).

[70] S. M. Eggins, L. K. Kinsley, and J. M. G. Shelley, Appl. Surf. Sci. **127-129**(1-2), 278–286 (1998).

[71] S. E. Jackson, N. J. Pearson, W. L. Griffin, and E. A. Belusova, Chem. Geol. **211**, 47–69 (2004).

[72] M. F. Thirlwall and A. J. Walder, Chem. Geol. **122**(1-4), 241–247 (1995).

[73] S. M. Eggins, R. L. Rudnick, and W. F. McDonough, Earth Planet. Sci. Lett. **154**(1-4), 53–71 (1998).

[74] N. Shimizu and S. R. Hart, Annu. Rev. Earth Planet Sci. **10**, 483 (1982).

[75] W. Compston, S. Clement, and G. Newstead, *Abstract presented at the International Secondary Ion Mass Spectrometry Conference*, Munster, 1977; see Ref. 76.

[76] T. R. Ireland, S. Clement, W. Compston, J. J. Foster, P. Holden, B. Jenkins, P. Lanc, N. Schram, and I. S. Williams, Austral. J. Earth. Sci. **55**(6-7), 937–954 (2008).

[77] U. Schärer and C. J. Allegre, Nature (London) **315**(6014), 52–55 (1985); W. Compston, D. O. Froude, T. R. Ireland, P. D. Kinny, I. S. Williams, I. R. Williams, and J. S. Myers, *ibid.* **317**(6037), 559–560 (1985).

[78] S. R. Messenger, L. P. Keller, F. J. Stadermann, R. M. Walker, and E. Zinner, Science **300**, 105–108 (2003).

[79] R. L. Hervig, P. Williams, R. M. Thomas, S. N. Schauer, and I. M. Steele, Int. J. Mass Spectrom. Ion Process. **120**(1-2), 45–63 (1992).

[80] J. M. Eiler, C. M. Graham, and J. W. Valley, Chem. Geol. **138**, 221–244 (1997).

[81] R. B. Ickert, J. Hiess, I. S. Williams, P. Holden, T. R. Ireland, P. Lanc, N. Schram, J. J. Foster, and S. W. Clement, Chem. Geol. **257**(1-2), 114–128 (2008).

[82] N. T. Kita, T. Ushikubo, B. Fu, and J. W. Valley, Chem. Geol. **264**, 43–57 (2009).

[83] K. I. Mahon, T. M. Harrison, and K. D. McKeegan, Chem. Geol. **152**(3-4), 257–271 (1998).

[84] K. D. McKeegan, D. S. Burnett, C. D. Coath, G. Jarzebinski, and P. H. Mao, in *Workshop on Cometary Dust in Astrophysics*, edited by D. E. Brownlee, L. P. Keller and S. R. Messenger (Lunar and Planetary Institute Contribution No. 1182, Houston, 2003), p. 47.

[85] K. D. McKeegan, A. P. A. Kallio, V. S. Heber, G. Jarzebinski, P. H. Mao, C. D. Coath, T. Kunihiro, R. C. Wiens, J. E. Nordholt, R. W. Moses, D. B. Reisenfeld, A. J. G. Jurewicz, and D. S. Burnett, Science **332**(6037), 1528–1532 (2011).

[86] E. A. Mathez and D. W. Mogk, Am. Mineral. **83**, 918–924 (1998).

[87] A. Benninghoven, Angew. Chem. **33**(10), 1023–1043 (1994).

[88] T. Stephan, E. K. Jessberger, W. Klock, H. Rulle, and J. Zehnpfenning, Earth Planet. Sci. Lett. **128**(3-4), 453–467 (1994).

[89] M. R. Savina, M. J. Pellin, C. E. Tripa, I. V. Veryovkin, W. F. Calaway, and A. M. Davis, Geochim. Cosmochim. Acta **67**, 3215–3225 (2003).

[90] D. Okumura, M. Toyoda, M. Ishihara, and I. Katakuse, Eur. J. Mass Spectrom. **11**, 261–266 (2005).

[91] K. Bajo, S. Ebata, H. Yurimoto, K. Uchino, M. Ishihara, S. Itose, M. Matsuya, and M. Kudo, in *6th Biennial Geochemical SIMS Workshop*, Hawaii (2011).

[92] T. Stephan, A. M. Davis, M. J. Pellin, M. R. Savina, I. V. Veryovkin, A. J. King, N. Liu, R. Trappitsch, and R. Yokochi, Meteorit. Planet. Sci. **46**, A222 (2011).

[93] R. Hill, P. Blenkinsopp, S. Thompson, J. Vickerman, and J. S. Fletcher, Surf. Interface Anal. **43**, 506–509 (2011).

[94] M. Toyoda, Eur. J. Mass Spectrom. **16**, 397–406 (2010).