CHAPTER 30

SIMS Measurement of Stable Isotopes

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Abstract

Secondary Ion Mass Spectrometry uses a primary ion beam to sputter a solid sample and produce secondary ions. SIMS offers an in situ analytical capability with spatial resolution of down to 50 nm for imaging and around 10-30 µm for high precision isotopic analysis. Isotopic compositions can be measured from the secondary ions of a variety of elements including those of the common stable isotopes (H, C, N, O, S) and rock-forming elements (Li, B, Mg, Si). Electropositive elements (metals) are best analyzed as positive ions from negative oxygen primary beams, whereas electronegative elements (non-metals) are sputtered with positively charged cesium and have higher negative ion yields. For negative ion analysis, sample charging of insulating targets must be controlled by introduction of electrons to the sputter site. Recent advances in ion microprobe design have allowed in situ negative ion measurements at the same level of precision as for positive ions. Measurement errors down to 0.1 ‰ are achievable for major elements, but at this stage, the external reproducibility for ion probe analysis is of the order of 0.5 ‰ because of variability in instrumentally induced fractionation. The goal of current work is to see this external reproducibility improve to a level commensurate with the internal measurement errors. SIMS is best used when in situ analysis of small domains in a heterogeneous target is required.

30.1 Introduction

Secondary ion mass spectrometry (SIMS) is a versatile technique for analyzing solid materials. A primary ion beam sputters or erodes a sample causing the emission of ionic species from the target. These secondary ions are transported through a mass spectrometer where the mass separated beams are measured. In the geosciences, SIMS is accomplished with ion microprobes or ion microscopes which use focused primary ion beams either in static or scanning mode to analyze samples. A typical analysis consumes only a few nanograms of material leading to the labeling of this technique as virtually non-destructive.

Stable isotope analysis requires some special conditions owing to the nature of information that geochemists are trying to obtain. In particular, geological materials require primary beam (spot) resolution of the order of 10 µm and in situ analysis is
preferred. This is the basis for ion microprobe mass spectrometry, a static spot allowing measurement of isotopic abundances in a given volume. With such a small volume of material, obtaining high precision is not always possible. However, the strength of ion microprobe analysis is not in the ultimate precision that can be obtained on any given spot, but rather the ability to assess heterogeneity of samples on a microscale. If large variations are present in a sample, then ion microprobe analysis offers petrographic control of measurements that is unsurpassed by any other technique. Furthermore, ion imaging with spot resolutions down to 50 nm of such a sample may give a visual display of isotopic distributions.

Stable isotope analysis is often thought of as the analysis of O, C, H, and N because it is these elements that have proven to be highly versatile in characterizing biological and geological processes. These elements are also important in stable isotope research by ion microprobe, but isotopic analysis of any element can provide important information regarding formation conditions such as temperatures, chemical species of reactants, reaction pathways, and so forth. The limitations for stable isotope analysis on the ion microprobe are governed typically by the amount of material available for analysis, the concentration of the target element, and the ion yield of that element under the chosen analytical conditions. Intrinsic to ion microprobe analysis is measurement of isotope abundances and a very wide range of elements can be analyzed. In general, electropositive elements (metals of the periodic table) can be analyzed as positive ions from a negative O ion beam, whereas electronegative elements (non-metals) ionize best as negative secondary ions from positive Cs-ion bombardment. The relative ionization efficiencies for different elements are shown in Figure 30.1.

A great deal of stable-isotope technique development has been associated with analysis of extraterrestrial materials. Such samples can have natural advantages over terrestrial materials; the effects that are being sought are often large and analytical precision is therefore not so much an issue. Also, non-mass-dependent effects are common, such as the 4% 16O anomaly in refractory inclusions (e.g. McKeegan et al. 1998) and so limitations imposed from the determination of instrumental mass-dependent fractionation are not so stringent. The drive for higher precision and accuracy comes from the requirements of terrestrial geochemists who are used to the high precision of bulk methods. Unfortunately, measurement of stable isotope compositions in terrestrial samples is more than obtaining intense secondary ion beams. Mass fractionation produced during sputtering and within the ion microprobe must be well characterized and stabilized if routine determinations of intrinsic fractionation of stable isotopes are to be made. SIMS isotope measurements are always referenced to standards and the reproducibility of the standard is paramount in accurate stable isotope measurements.

Ion microprobes are complicated instruments with a multitude of lenses, slits, defining apertures and other components that are used to define the trajectories of the ion beams. As such it is difficult to give specific recipes for conditions of use. The following discussion is offered if only to bring to mind some preferred options and potential pitfalls, but SIMS is a highly versatile technique and different targets may...
require completely different conditions to those offered below. Over the past 10 years there have been substantial developments in stable isotope analysis by ion microprobe. In particular, measurement of negative ions from insulators is now possible through charge neutralization by way of electron injection schemes.

This chapter covers general features of stable isotope analysis by SIMS. A more detailed review of historical developments in terms of geological analysis can be found in Shimizu & Hart (1982a), Zinner (1989), Ireland (1995), Hinton (1995) while instrumental aspects are covered in more detail by Benninghoven et al. (1987). Besides the primary references cited, additional useful source material and discussion should be consulted from the compilations of Harmon & Hinton (1992) and McKibben & Shanks (1998).
30.2 Secondary Ion Mass Spectrometry - SIMS

A primary ion beam is focused to erode, or sputter, the target. The energy of the primary ions (typically 10-20 keV) causes a fraction of the atoms and molecules to become ionized. These secondary ions are electrostatically transferred into a mass spectrometer where they are separated according to mass and energy before being passed into a detector.

The principles governing secondary ionization are not well understood, and it has not been possible to derive a quantitative model that predicts the abundances of the secondary ion species relative to the actual concentrations in the matrix. For stable isotope analysis, this is not a fundamental limitation. Of primary concern is that a stable secondary ion beam can be generated and that the composition of the secondary ion beam reflects the composition of the target. Of the sputtered material, most of it is neutral atoms and molecular fragments, and a fraction that depends on the element and the matrix (as in Figure 30.1), is ionized.

A characteristic feature of SIMS is that the observed isotope ratios of the secondary ion beam is enriched in the light isotopes relative to that of the target. Both experimental and theoretical considerations suggest that this observed enrichment is a result of more efficient momentum transfer through lighter atoms (and molecules) so that they are more likely to become ionized. Alternatively, mass fractionation could be produced by neutralization processes where the heavier, slower ions have a greater probability of neutralization (for further discussion see Williams, 1979, 1982). The exact site of ionization is not clear. However, observations such as the matrix dependence of isotope fractionation as well as inter-element ionization variability, suggest that it must occur while the target can have an influence over the ionization probability. The accurate assessment of this instrumentally induced fractionation is essential to quantitative stable isotope measurements with an ion microprobe.

30.2.1 Ion microprobes

An ion microprobe consists of a primary column, to generate, accelerate and focus the primary beam to a spot on the target, a source chamber, where the primary beam interacts with the target and the secondary ion beam is formed, and the mass analyzer where mass and energy separation of the secondary beam is produced and the mass-separated ion beams are measured (Figure 30.2). Ion microprobes require ultrahigh vacuum (≤10⁻⁸ mbar) to reduce the effects of gas scattering on the ion beams and limit neutralization through charge exchange. In some cases deposition on the sample from the residual gas is also of concern, especially if the sputter rate is very low.

30.2.2 Primary beam considerations

The primary ion beam is typically composed of O or Cs because these elements produce a significant enhancement in the ionization yields of electropositive and electronegative species, respectively. Thus, most lithophile metal elements are best analyzed with an oxygen primary beam, while the halogens and other electronegative species are better analyzed with Cs. Cesium can only be utilized as Cs⁺, while oxygen can either be O⁻ or O⁺. Of further consideration is the choice of polarity for the pri-
Figure 30.2 - Schematic Cameca ims 3f ion microscope (adapted from Ireland, 1995).
mary and secondary extraction fields. In general, the secondary extraction voltage is given the opposite polarity to the primary. Selection of like voltages requires the banking of power supplies such that +10 kV primary and +10 kV secondary would require a potential difference of 20 kV to real ground at some position in the ion probe. As such, the most common electrical configurations used are O\(^-\) primary with positive secondary ion extraction and Cs\(^+\) primary with negative secondary extraction. Accelerating voltages for primary and secondary ion beams are typically 10-20 kV and 5-10 kV respectively.

The oxygen primary beam is typically generated in a duoplasmatron discharge. The most common type of duoplasmatron consists of a cold hollow cathode (cold indicating it is heated by the plasma, rather than a hot filament as occasionally used), an intermediate electrode for geometrical confinement, a surrounding magnetic field for magnetic confinement, and the anode extraction aperture where the ion beam is formed. The axial beam formed in the discharge is dominated by electrons with an annulus of O\(^-\) ions. Thus the extraction aperture is offset from the axial position for extraction of the O\(^-\) beam. This is not the case for an O\(^+\) beam because the electrons are repelled from the extraction aperture and so the extraction aperture is axial for O\(^+\) beams. The negative plasma consists predominantly of O\(^-\) and O\(_2\)^\(^-\) with a higher proportion of the atomic species than the molecular (O\(^-\)/O\(_2\)^\(^-\) ≈ 3 - 10). The atomic species is commonly used but the advantage of the molecule is that double the mass is delivered to the sample per unit charge, thus increasing the ionization yield per nanoamp of primary. Hinton (1995) has demonstrated that O\(_2\)^\(^-\) generates almost exactly a factor of two higher yield than O\(^-\). There is also less potential for charge build up on the target when using the O\(_2\)^\(^-\) ion to generate the secondary ions. In addition, it is possible that matrix effects on the secondary ion beam are ameliorated by using the heavier species. However, sufficient O\(_2\)^\(^-\) must be generated to produce the required secondary ion beam and if high yields are required the molecular beam may not be an option. It should be noted that the optimal tuning for the atomic species is not necessarily the best for the molecular ion beam and some degree of retuning can improve O\(_2\)^\(^-\) delivery relative to O\(^-\).

The Cs beam is generated in a thermal ion source. A reservoir of Cs (either as metal or Cs-bearing compound) is heated to cause vaporization of Cs metal. The Cs vapor is then passed through a super heated frit causing ionization of Cs. While the use of Cs metal produces a lot of Cs vapor for the ion source, and hence brighter ion beams, the handling of Cs metal is rather onerous. Once the Cs metal is exposed to the vacuum, it must be maintained in vacuum until exhaustion. Cs compounds such as chromate, carbonate, or silicate have the benefit of being inert in air and so once the source is cooled it can be safely vented to air.

The primary ion beam is accelerated away from the ion source and shaped with various ion optical elements. A standard feature on most ion probes is a mass filter, either a sector magnet or a Wien filter, that allows a specific species such as O\(^-\) or O\(_2\)^\(^-\) to be selected, or for contaminants to be eliminated from the beam. The main contam-
inants to the beams are hydrides, the $^{16}$OH$^-$ peak is prevalent after servicing the duoplasmatron, so a mass resolution of ca. 32 is advisable to be able to separate O$_2^-$ from O$_2$H$^-$ if O$_2^-$ is to be used. Introduction of H to the sputter site is undesirable because of the additional complication to the secondary ion speciation. Other minor contaminants (e.g. hydrocarbons, metal ions from the cathode discharge) will also be removed at this mass separation.

Cameca ion microscopes generally have both duoplasmatron and Cs source permanently mounted on the primary column and so the primary magnet allows the selection of ion beams from the two alternate sources. Along with computer controlled primary and secondary voltage systems, it allows rapid switching between the different polarities and settings. A Wien filter is used on the SHRIMP primary column because the duoplasmatron and Cs gun are interchangeable and no ion-source switching capability is required. The Wien filter is therefore a more effective option when no primary deflection is required. Both systems perform equally well in terms of the requirements of the respective instruments.

The Wien filter uses crossed electrostatic ($\mathbf{E}$) and magnetic ($\mathbf{B}$) fields such that only an ion with a specific velocity $\mathbf{v}$ will be transmitted undeflected when $\mathbf{v} = \mathbf{E} \times \mathbf{B}$. The Wien filter operates as a mass filter because the velocity of an ion passed through an electric potential $V$ is mass dependent, i.e. $qV = \frac{1}{2}mv^2$, where $q$ is the fundamental charge (for singly charged species), $V$ is the extraction potential, $m$ is the mass of the ion and $v$ is its velocity.

The primary column is generally at an angle of 20-45° away from normal where it has been shown that there is optimal secondary ion emission for normal (i.e. to the sample surface) secondary-ion extraction. As such ion probe spots are typically ellipsoid although these can be shaped back to circular images if required. An exception is the Cameca nanoSIMS where the primary ion delivery and secondary ion extraction axes are coaxial and normal to the surface. This is one of the parameters that enables the extremely small spots (order 50 nm) on the nanoSIMS to be obtained coupled with high sensitivity.

Spot size plays a fundamental role in experimental design on an ion microprobe. Spot size can be as small as the 50 nm spots on the on the Cameca nanoSIMS, or as large as possible to extract the most secondary ions. Spot size is generally selected on the basis of the smallest domains to be analysed with the tradeoff of the reduction of primary beam current with spot size. The smallest spot on the Cameca nanoSIMS has an intensity of only 10 pA and so the total secondary ion yield will be far less than when using a 30 µm spot with 10 nA. Fewer ions means lower precision and so there is a tradeoff in the intensity of the primary beam to be used and the required precision.

On the other end of the scale, the largest spot that can be used will be governed by the refocusing ability of the primary column, but also the useful transmission of the secondary extraction system. If the secondary extraction system cannot accept the
ions from the larger diameter, there is no point in operating with a larger spot. In effect, a useful upper limit to spot size is around 30 µm for isotope analysis. This holds for negative as well as positive primary ion species. Even for negative ions, the spot will charge, affecting the secondary ion characteristics and in turn, instrumental fractionation stability.

Theoretical counting statistics can be calculated from the number of atoms in the target, and this can then be translated into a volume, and a depth for a given spot diameter. As an example, to achieve 0.1‰ counting precision for oxygen isotopes in quartz (SiO$_2$) assuming a 10 % O$^-$ ion yield, a volume of 10 µm$^3$ of SiO$_2$ is required. For a 10 µm diameter spot, this requires a spot depth of approximately 0.1 µm, but for a 1 µm spot the depth would need to be 10 µm. The most stable and best analytical conditions are obtained when the spot depth is substantially smaller than the spot diameter. Consequently there is a fundamental limitation on the use of the smallest spots depending on the precision required. For a 1 ‰ oxygen isotope analysis, a 1 µm spot with depth of 0.15 µm is sufficient. These are optimal calculations for a major element and the required sample could be substantially larger depending on the elemental concentration and other conditions.

The nature of the focusing of the primary ion beam on to the surface can have an effect on the composition of the secondary ion beam. A common method of beam transport is to produce a spot on the target that is the demagnified image of the anode extraction aperture (for the case of an oxygen beam from a duoplasmatron). However, such an image is often less than perfect with the summing of aberrations produced through the various lens elements. If the final spot on the target is Gaussian (in the extreme), then there is differential sputtering across the spot from the center to the rim. Such behavior is of obvious detriment if depth resolution is required, but could also affect the stability of instrumentally induced isotope mass fractionation.

In order to ameliorate differential sputtering across a static spot, a method analogous to the optical microscopy method of Kohler illumination (Liebl, 1983) can be used. The specific analog is that the defining aperture is placed at the focal length of the final lens of the primary column. This configuration theoretically also removes the effects of any upstream aberrations and the final spot on the target is simply the demagnified image of the defining aperture (Figure 30.3). In a modified approach, the aperture can be placed at a position intermediate between single and double focal length depending on the desired (de)magnification, but the illumination at this aperture must be uniform. In practice even the true Kohler method is improved by having a uniform intensity distribution at the aperture.

The drawback to Kohler illumination is that it is best used with quite large spots (of order 15-30 µm). If high spatial resolution is required there may be no option but to use highly demagnified spots. In this case, Fitzsimons et al. (2000) show that measurement uncertainties approaching counting statistics can be obtained provided standards and unknowns are measured under identical conditions. Even illumination can also achieved by rastering of a finely focused beam over a given area. This method
also offers the possibility of electronic gating where only a selected part of the area is accepted. This method is widely used in depth profiling methodologies.

The impact of the primary-ion beam causes energy and charge transfer to the sample. If the net flow of charge is not dealt with, the spot can charge up, the sample potential can change, and the secondary ion beam may no longer be focused through the mass analyzer. For analysis with O− primary ion beams (and positive extraction), the resultant charge build up can be quite satisfactorily handled with the use of a thin conductive layer (C, Au, Au-Pd, etc) which allows the dissipation of electrons. This enables the potential of the sample to remain uniform and hence a stable extraction field is maintained. The extraction field geometry is also improved by the use of well-polished samples. Under such conditions stable secondary ion signals can be produced that last several hours. Furthermore, stability of isotopic mass fractionation can be achieved over reasonable analytical times as well. In the circumstance of a long

Figure 30.3 - The primary ion spot allows the selection of sites for analysis that are free of contamination through inclusions, cracks, or other possible sources of isotopic heterogeneity. Importantly, a well-defined primary spot with even illumination is essential for maintaining stable isotopic mass fractionation during analysis. Plotted are δ34S/32S isotopic compositions in a heterogeneous sulfide.
analysis, some charge build up may be produced because of progressive removal of
the conductive coating in proximity to the spot. The charge build up can be monitored
by measuring the energy distribution, and a suitable offset on the sample accelerating
voltage or steering can be applied such that the energy distribution passes through
the same trajectory through the mass analyzer. In this case, compensation for move-
ment of the energy distribution over a few tens of volts can be accomplished satisfac-
torily.

With non-normal primary beam incidence, the ion probe crater floor will not only
move progressively into the sample, it will move across it. Thus, in the extreme, the
floor of the crater could be optically masked from the extraction system, and the max-
imum ion transmission will likely fall out of optimization. Furthermore, the crater
walls will likely charge up, also changing secondary ion tuning conditions. For these
reasons, the optimal configuration for an ion microprobe spot is for it to be relatively
large and the analysis time (i.e. penetration depth) limited such that crater geometry
is not an influence on the effective composition of the measured secondary ions. In
general, with 15-30 µm spots and analysis times of less than ca. 20 minutes, this will
not be an issue (c. 2 µm depth for 5 nA). However for very small spot sizes (order 1
µm or less) the penetration depth in 20 minutes could indeed exceed the hole diame-
ter. For the Cameca nanoSIMS, the primary beam incidence is normal to the sample
surface and so tuning conditions will not change geometrically to the same degree. At
this stage there is no published information on high precision isotopic analyses with
the nanoSIMS.

The use of the Cs⁺ primary beam with negative secondary ions presents the great-
est analytical difficulties. The impact of Cs⁺ at the sputter site requires neutralization.
At low Cs currents, there may be a significant degree of self-neutralization, but in
most cases for stable isotope analysis on non-conductors, insufficient electrons can get
to the sputter site from the conductive coating. Furthermore, the extraction system
responsible for acceleration of negative secondary ions also removes secondary elec-
trons from the sputter site, further exacerbating the charge build-up. The resulting
charge effectively changes the potential of the crater and so the tuning through the
mass analyzer degrades quickly, especially if energy dispersion is limited through
defining slits or apertures. This problem is particularly important here, because stable
isotope measurements of O, C, and S are best performed with negative secondary ion
beams.

McKeegan (1987) ameliorated charging by taking fragments of interplanetary dust
particles and pressing them into gold foil. For fragments smaller than ca. 15 µm, there
was only a minimal charging effect and stable negative secondary ion beams could be
obtained for oxygen isotopic analysis. However, such a method is not desirable where
petrographic constraints need to be placed on the material analyzed, which is of
course the strength of in situ analysis.

The alternative approach developed has been to deliver electrons to the sputtering
region so that the positive charge is balanced by the incoming electrons. The most
straightforward approach instrumentally is to inject electrons in a similar fashion to the primary beam, that is, an electron gun is aimed at the sample directly (Figure 30.4). The electrons must have sufficient kinetic energy to traverse the secondary accelerating potential, between the sample and the extraction lens, and arrive at the sputter site. If the electrons have insufficient energy, they cannot reach the sample, and the beam is simply deflected away from the sample. The impact of these electrons produces secondary electrons, the number of secondary electrons produced being dependent on the material and the energy of the impacting electrons. At low energies,
there is insufficient energy to knock a secondary electron out, and at high energies, the
electrons penetrate the target also resulting in fewer secondary electrons escaping
than primary electrons arriving. But at intermediate energies, more secondary elec-
trons are produced than there are primary electrons being delivered to the target and
as such the electron beam cannot neutralize the charge build up on the target. This sit-
uation is also affected by the composition of the conductive coating material. Gold is a
very strong secondary electron emitter, but C coatings have very low secondary elec-
tron emission characteristics and so should be used for this methodology. This
method does not necessarily compensate for the charge build-up on the spot. More
likely it swamps the sample with electrons, with excess electrons being dissipated
through the conductive coating. As such, the sample potential is not self regulating
and the use of a fixed energy window, for example, could effect mass fractionation.
The use of high-energy electrons can also cause deterioration of the sample through
heating. Hervig (1992) developed this technique on a Cameca ims-3f. For a 2-3 nA Cs
primary beam, a high-voltage, high-current electron gun was used to neutralize the
charge. The filament was held at –7.5 keV with 10 µA of electrons striking the target
with a net energy of approximately 3.4 keV. Under these conditions, stable secondary
ion beams could be obtained but Hervig (1992) resorted to energy filtering in an
attempt to better stabilize instrumental mass fractionation (see below).

The problems with a high-energy electron gun can be ameliorated through instru-
mental designs that include a low secondary-ion extraction field (Isolab 54, SHRIMP)
such that the impact energy of the electrons can be reduced. Lyon et al. (1995) describe
the use of the Isolab 54 for stable isotope measurements with high-energy charge com-
ensation; Cs+ beams of 0.1 to 5 nA could be used producing up to 5 x 10⁻¹¹ A of ¹⁶O⁻.
Saxton et al. (1996) document the difficulties of focusing the electron beam through
the extraction potential, with resultant electron beams 100 microns wide by several
hundred microns long. On SHRIMP instruments, the electron gun floats on the sam-
ple potential and so the electrons only see a 700 V or so potential difference allowing
well focused electron beams to strike the target.

An alternative approach developed by Slodzian et al. (1986) for Cameca ion micro-
scopes is to transport the electrons down the secondary extraction axis such that the
electron beam is normally incident on the sample (Figure 30.5). The energy of the elec-
trons can then be matched to the surface potential of the sample and because they
have no horizontal momentum, the electrons essentially stall out in a cloud above the
spot. Thus there is no impact with the target and no secondary electrons are pro-
duced. The build up of charge through Cs sputtering causes electrons to move to the
spot and so a self-regulating charge-neutralization system can be achieved.

30.2.3 Secondary beam considerations
The secondary ion beam is electrostatically accelerated and focused to the source
(or entrance) slit of the mass analyzer. In ion microscopes, masking apertures can be
used to select ions only coming from a particular location on the sample (for example
to exclude the spot walls) or from a particular part of an ion optical crossover if aber-
rations are present. For the ion microprobe mode proper this is not possible because of
Figure 30.5 - Schematic of extraction region for low-energy charge compensation used on Cameca ion microscopes. The electron beam is inserted along the secondary ion axis with the use of an insertion magnet (A). The extraction energy of the electron source is adjusted such that the electrons stall out in a cloud just above the sample producing a self-regulating charge compensation. Any charge build-up will attract electrons from the cloud. Because the secondary ion beam is also deflected by the insertion magnet (A), its trajectory must be compensated by two correction electromagnets (B,C). Figure adapted from Cameca promotional materials (http://www.cameca.fr/).

astigmatic focusing to increase transmission. The secondary ion beam is then passed into the mass spectrometer.

30.2.4 Mass analyzer

Geological materials are not chemically simple compounds, and SIMS produces a plethora of non-stoichiometric species. These two factors combine to produce complicated secondary ion mass spectra. The function of the mass analyzer is to produce sufficient mass dispersion to eliminate, to the highest order, all possible isobaric interferences from the isotopes of interest, and to produce ion beams suitable for high-precision measurement. There are a variety of mass spectrometer types (e.g. quadropole, time-of-flight) that will achieve sufficient mass resolution, but magnetic sector instruments are preferred for isotope ratio measurements of high precision.

The magnetic sector deflects ions through a specific radius depending on the ion’s mass, charge, and energy. Because sputtering produces secondary ions with a variety
of energies, double-focusing mass spectrometers are required such that secondary ion beams of disparate energy can be refocused. The essential elements of a double-focusing mass analyzer are the electrostatic analyzer and the magnet. The ESA disperses the ions according to energy and the magnet refocuses them on the basis of the energy and mass. The net result is the cancellation of the energy term to yield a mass focus. The parameter most often cited in terms of mass analysis on ion microprobes is mass resolution. The American Society for Testing and Materials Standard Terminology (ASTMST) for Surface Analysis – SIMS defines mass resolution as \( \frac{M}{\Delta M} \) where \( \Delta M \) is the full width at half maximum of the peak at mass \( M \), but in practice ion probe analysts use a mass resolution definition where \( \Delta M \) is defined as the full peak width at the 10 % or 1 % height of a peak (Figure 30.6a). This is essentially the width of the transferred source slit of the mass spectrometer (typically demagnified but with aberrations) convoluted with the collector slit width. Mass resolving power is frequently used interchangeably with mass resolution. The specific ASTMST definition of mass resolving power is the peak to valley ratio between adjacent equal sized peaks separated by one mass unit. It can also be formulated like the mass resolution calculation except \( \Delta M \) is defined as only the magnified source slit image (plus aberrations) and is represented by the 10-90 % rise on one side of the peak. Thus some care should be exercised in evaluating figures of merit concerning mass resolution and mass resolving power because of the different definitions. Note that the ASTMST definition of mass resolving power would be more readily equated with abundance sensitivity, the peak to tail signal strength at a distance of one mass unit.

In practice, peak separation at full mass resolution may not be required if it can be shown that the interfering signal does not contribute to the measurement point of the mass of interest. If the interfering species is small, it may not contribute to the analysis even though a valley between the peaks is not defined (Figure 30.6b,c). If the interfering species is large with respect to the peak of interest, it may be fully resolved at the 10 % level, but could still contribute to the measurement. In this case higher mass resolution is required (Figure 30.6d).

Isobaric interferences can be either atomic or molecular, but isotopes with atomic isobars are often avoided for isotope ratio work because they require extremely high mass resolving power. For most elements, atomic isobars can be avoided by selection of an alternative isotope. There are no atomic isobaric interferences of consequence for the common stable isotope systems. The molecular interference of most consequence for stable isotope analysis is the hydride. A proton has a mass excess relative to \( ^{12}\text{C} \) of 0.0078 AMU. The isotopic mass deficits of elements with atomic mass less than 100 systematically increase a few mAMU per AMU and so the hydride appears as a heavier species than the atomic. For instance, \( ^{16}\text{OH}^{-} \) \((15.9949 + 1.0078 = 17.0027) \) is heavier than \( ^{17}\text{O} \) \((16.9991) \) by 3.6 mAMU and therefore requires a minimum of \( 17/0.0036 = 4,400 \) \( \text{M}/\Delta \text{M} \) for resolution. However, the abundance of \( ^{16}\text{OH}^{-} \) relative to \( ^{17}\text{O}^{-} \) often necessitates the use of higher mass resolution. Separation of \( ^{18}\text{O} \) from \( ^{17}\text{OH}^{-} \) only requires 2300 \( R \), and the abundance of \( ^{17}\text{OH}^{-} \) is low compared to \( ^{18}\text{O}^{-} \). Such resolutions are well within the capabilities of most ion microprobes involved in the geosciences. Increased resolution is obtained by closing down slits which decreases trans-
Figure 30.6 - Peak schematics showing mass resolution, mass resolving power, and estimation of the contribution to a peak from an interference. (a) The linear representation of peak shape allows an assessment of the degree of flat-top which is essential for determination of best-focus for the mass spectrometer. Under these conditions the peak shape is trapezoidal. The collector slit width can be determined at the FWHM through the mass dispersion formula for the mass analyzer. Mass resolution, in this case defined at the 10% level ($\Delta M_1$) is given by $M/\Delta M_1$. This is essentially the source-slit image-width at the collector added to the collector-slit width (c). Mass-resolving power is often cited for mass spectrometers. This is commonly formulated as the ratio of $M/\Delta M_2$ where $\Delta M_2$ is the demagnified source slit image defined at the 90% - 10% level of the slope of the peak. (b) The logarithmic representation of the peak shape allows the degree of contribution from interferences to be ascertained. In this case Peak M2 is not clearly resolved from Peak M3. (c) The overlay of a clean peak (M1) shows that M3 does not contribute to M2 above the 0.1 permil level even though a valley of resolution is not achieved between the peaks. The converse does not hold with M2 contributing to M3 at the permil level. This difference is due to the differing intensities of these peaks. (d) In order to effect complete resolution of M2 from M3 requires higher mass separation with resolution in excess of that calculated simply from the relative masses of the interferences.
mission and also increases the prospect for instrumental mass fractionation. As such, the measurement of $^{17}$O is likely to be at the expense of signal as well as reproducibility of fractionation measurements.

Molecular interferences can also be excluded by the energy filtering method (Shimizu & Hart, 1982a; Zinner & Crozaz, 1986). This is based on the observation that polyatomic ions have a narrower energy distribution than atomic ions. Energy filtering is achieved by a suitable energy window at the energy focus of a double-focusing mass analyzer that selects high-energy ions. This is the preferred method for trace element analysis in the region of the rare earth elements because of unresolvable (in terms of mass) isobaric interferences. But, it is at the expense of a large fraction of the beam (generally greater than 90%) and this can hinder high precision isotopic measurements. However, there are benefits to energy filtering that offset the potential loss in sensitivity that will be discussed below.

### 30.2.5 Detection systems

Ion beam measurement is fundamental to mass spectrometry, but ion microprobe measurements present conditions that are quite often at the edge of operation of the different systems used. While a stable isotope measurement in a gas source mass spectrometer can be tailored to give satisfactory signal strength, SIMS analysis has limitations associated with analytical conditions including concentration of the target element in the sample, primary beam strength, and mass resolution requirements. As such a variety of detection methods is required that cover many orders of magnitude of signal strengths.

Until recently, ion microprobe measurements have been carried out on single electron multipliers operating in a pulse-counting mode. An incoming ion hits the first dynode and generates 1 or more electrons. The potential drop across the multiplier accelerates the electron(s) into succeeding dynodes typically with an amplification of two or more per stage. Hence the charge delivered by a single ion striking the first dynode can be amplified by factors of $10^7$ or more. This charge burst is passed into the detection circuitry mainly consisting of an amplifier-discriminator and a counter. The discriminator is used to block zero-point noise produced by ambient electrons in the circuitry such that only pulses of a specific minimum height are counted as real events. A single event takes a finite amount of time to be processed through the counting system and during this time an incoming ion may not trigger the multiplier resulting in a lost count. This loss of counts is referred to as dead time and must be corrected in order for accurate analyses to be made. It can be shown that for a retriggerable counting system:

$$c_{\text{meas}} = c_{\text{true}} e^{\tau c_{\text{true}}}$$  \[30.1\]

where $c_{\text{meas}}$ is the measured count rate, $c_{\text{true}}$ is the actual number of events per second, and $\tau$ is the system dead time. The true count rate can then be expressed as:
\[ c_{\text{true}} = c_{\text{meas}} \exp \left( c_{\text{meas}} \exp \left( c_{\text{meas}} \exp (\ldots) \right) \right) \]  
\[ \text{[30.2]} \]

and approximated by
\[ c_{\text{true}} = c_{\text{meas}} \exp \left( c_{\text{meas}} \exp \left( c_{\text{meas}} \right) \right) \]  
\[ \text{[30.3]} \]

The typical dead time for the pulse-forming process in the multiplier is of the order of 5 ns in terms of full-width half maximum, although pulse pair resolution at the discrimination level is longer and the total system dead-time is longer still because of amplification and discrimination. Typical dead times for counting systems may range from 10 to 30 ns depending on the specific setup. For instance, a higher discriminator level can produce a shorter dead time, but at the expense of pulses under the discriminator level. If this is suspected, the efficiency of the multiplier can be obtained by comparing a suitable signal from the Faraday Cup with the multiplier response.

The main limitation on precision of a pulse counting system is the total counts (N) on the minor isotope for which Poisson counting statistics dictates a variance of N, and hence the limitation on precision to be \(1/\sqrt{N}\). Thus \(10^6\) counts of the minor isotope will yield 1 \(\%\) precision \((1\sigma)\), whereas \(10^8\) counts are required for 0.1 \(\%\) precision. Clearly higher precision is preferable and hence the highest number of counts is required. But the nature of electron multipliers dictates that count rates be kept under ca. 2 MHz so that the electron multiplier life and stability is not compromised.

Hayes & Schoeller (1977) have shown that there are limits imposed on an analysis due to the uncertainty in the dead-time. When ratios differ significantly from unity the uncertainty in the dead time can be the limiting factor. However, when only two peaks are being analyzed it can be argued that the dead time effects from the pulse counting system are the same for all analyses provided the count rates can be kept close, and thus are removed in the normalization process.

The situation is slightly different when mass fractionation is monitored from one isotopic ratio and used to determine the residual in another isotope ratio(s). In this case, the uncertainty in the residual can be quite small and not limited by the standardization process and so the dead time must be accurately determined. This can be accomplished through analysis of standards at a variety of count rates. Where dead time variability is found, it is often associated with the multiplier gain being off the plateau. The gain of a multiplier slowly degrades with time and if the gain falls off the plateau rapid changes in gain are apparent, resulting in changes in efficiency and dead time. One methodology to remove uncertainty from the dead time is to gate the pulse counting system electronically such that it will not retrigger within a set period. This is generally accomplished by taking a gate period longer than the system dead time \((i.e. 30-50 \text{ ns})\). The correction for dead time will be larger, but theoretically there is no uncertainty on the correction.

Slodzian et al. (2001) note another phenomenon that is similar to the dead time effect in that it affects the high-abundance isotope preferentially. The Quasi Simulta-
The simultaneous Arrival (QSA) effect is related to the efficiency of secondary ion collection and conversion of primary ions to secondary ions. A high efficiency of production and collection will therefore mean a higher chance of a simultaneous arrival of two ions from a single incident primary ion. For instance with Si isotopes, there is a much higher probability of collecting two $^{28}$Si ions than there is of two $^{29}$Si atoms or two $^{30}$Si ions. Therefore QSA produces an undercount of the most abundant species and is independent of count rate and dead time. However, in most experimental setups where dead time is a variable, the effect of QSA will be masked by the dead time measurement, that is, the underproduction of $^{28}$Si will be compensated by a longer deadtime. This effect will however be very apparent when a gated dead time is used. For two isotope systems, the effect will be normalized through comparison of standards at given count rates.

Pulse counting is the preferred method for low count rates up to approximately 1 MHz. In most instances, a 1 permil precision can be obtained in a straightforward manner, better than 0.7 permil is possible with care, but obtaining precisions at the 0.1 permil level, although theoretically possible (Slodzian et al. 2001), is simply not practical with an ion counter. Essentially only a few analyses could be achieved in a day thus inhibiting the determination of analytical reproducibility.

The main limitation of pulse counting is the maximum allowable count rate. This is circumvented by the use of Faraday cup measurement. The secondary ion beam is captured in the cup and the current can be measured in an electrometer across a high-resistance feedback resistor (typically $10^{10}$ – $10^{12}$ $\Omega$). The impact of an ion directly transfers one charge unit ($1.6 \times 10^{-19}$ C) and so there is no problem associated with dead time. The limitation to Faraday cup measurement is the minimum current that can be collected. This is a result of Johnson noise from thermal electrons moving across a high impedance resistor. The current can be expressed as:

$$I_{N\text{RMS}} = \sqrt{4kTBW/R}$$  \[30.4\]

where $k$ is the Boltzmann constant, $T$ is temperature (K), $BW$ is the frequency bandwidth of the noise to be examined, and $R$ is the resistance of the circuit. At $T = 300$ K a frequency bandwidth of 0-10 Hz, and a resistance of $10^{11}$ $\Omega$, the Johnson noise (RMS) is $1.2 \times 10^{-15}$ A or roughly 8,000 c/s. This is comparable to the analytical noise of commercial electrometers (Keithley™ Model 6517A is listed at 0.75fA). Thus a Faraday cup is not the optimal device for measuring low intensity secondary ion beam currents. There is no explicit upper limit to the current that can be collected on a Faraday cup, but potential problems can occur with the linearity of the system where intense ion beams are to be compared to weak ones.

The dynamic range of the counting system can also limit the inherent precision possible as well. Typically the current arriving at the Faraday cup is translated into a pulse train where the frequency of the pulses is proportional to the frequency of arrival of secondary ions at the detector. A typical upper limit to the frequency of this
signal is 1 MHz for a full-scale deflection of the electrometer. If both large and small signals are collected on the same range, then the resolution of the smaller signal can be compromised, particularly for small beams such as $^{18}$O vs $^{16}$O which is a ratio of $\frac{1}{500}$. If the $^{16}$O signal generates a full scale deflection = 1 MHz, the $^{18}$O signal will be 2000 c/s. If a precision of 1 ‰ is required, there is only a 2 c/s window left to ascertain precision. Clearly this situation can be ameliorated by changing the range of the electrometer, but the two ranges must be calibrated against one another, and another background measured, thus introducing other uncertainties.

The minimum count rate that can be measured can be substantially improved if the feedback resistor is replaced with a capacitor. In this case, charge is collected on the capacitor and the Johnson noise across the resistor is not measured during the analysis. Rather, an analysis of signal strength consists of allowing the capacitor to charge up for a specified period of time and then determining the amount of charge that has accumulated on the capacitor. Measurements of this type have not been successfully carried out until recently on thermal ionization mass spectrometers (Esat, 1995) and background currents of $10^{-17}$ A may be possible. Such a technique may benefit data collection where signal strengths are intermediate between multiplier and Faraday cup.

Often in stable isotope analysis, the situation arises where there is insufficient beam for the Faraday Cup on (one of) the minor isotope(s). For example, in oxygen isotope analysis, $^{16}$O might be readily measured on the Faraday cup, but not the $^{18}$O. In this situation, the $^{18}$O can be measured on the ion counter in the same cycle with the $^{16}$O measurement on the Faraday cup. The relative sensitivity factor between the electron multiplier and Faraday cup can be ascertained through the measurement of the standards provided the count rates are kept uniform throughout the measurement period.

Recently, multiple collectors have been added to large ion microprobes. A multiple collector has two or more multipliers or Faraday cups or a combination of the two that simultaneously detect the isotopes of interest. Multiple collection offers great advantages in ion microprobe analysis. The collection efficiency is improved because all peaks are being collected simultaneously. Temporal variations in the secondary ion signal strength due to primary beam instability or through heterogeneity of the target element in the sample do not affect the determination of an isotope ratio. However, multiple collection devices for most mass spectrometers have used Faraday Cups exclusively. Secondary ion signal strengths on ion microprobes are not always conducive to Faraday cup measurement and multiple collection with electron multipliers has presented a number of problems. The main issues have been the size of the multipliers and cross talk between multipliers causing erroneous signal detection. To address these issues, the Cameca 1270 utilizes very small discrete dynode electron multipliers (Hamamatsu Photonics K. K.) that are contained within the Faraday cups. The SHRIMP II multiple collector utilizes Sjuts™ channeltrons (continuous dynode electron multipliers) the design of which also limits electron cross talk. These detectors can be stacked at the very small spacing between adjacent Pb isotope peaks.
Channel plate detectors, such as used for direct ion imaging, can be used for isotope ratio measurement although they have low dynamic range, and unstable gain characteristics (see for example, Saxton et al., 1996).

30.3 Measurement of stable isotope ratios

30.3.1 Mass fractionation

The goal of SIMS analysis is to obtain an isotopic measurement that can be related to the absolute composition of the target. The main process affecting this determination is mass fractionation, the dependence of the measured isotopic composition on the mass of the isotope.

Isotopic mass fractionation is intrinsic to SIMS (see discussions by Shimizu & Hart, 1982a; Ireland, 1995). Thus a measurement requires the separation of the instrumental factors that might be variables during an analytical session, from the fractionation produced in the sputtering process, which must at some level be assumed to be constant for the course of the analytical session. The constancy of instrumental and sputtering fractionation (i.e. total measured fractionation) is generally taken as constancy for both components.

For any given element with multi-isotopic composition, sputtering will give a lighter isotopic abundance than expected. In practice, the measured composition may be more variable owing to other instrumental parameters. The difference between the actual composition and the measured fractionation can be large, commonly percent level for low masses and tending to smaller fractionations for heavy isotopes. However, the measurement of a relative fractionation difference is not affected by the absolute fractionation i.e. it doesn’t matter if there is 20% fractionation relative to actual composition provided it doesn’t change. The constancy of measured fractionations to a level concomitant with measurement errors indicates that relative fractionation measurements between standards and unknowns are viable and can give accurate results at the level of cited precision.

30.3.2 Isotope Analysis

SIMS isotope measurements can be divided into two types. Where only two isotopes are measured, mass fractionation is calibrated to an external standard of the same mineralogical composition and known isotopic composition. In this case, mass fractionation cannot be known to a level better than that determined for the standards. This is the methodology commonly used for stable isotope measurements of C, O, and S where the mass dependent fractionation effects are sought as indicators of physical processes.

Where three or more isotopes are measured, one of the ratios can be used for an internal calibration such that the deviations of the third isotope ratio from a mass fractionation law can be used to derive a residual. The feature of this method is that an analysis can continue provided the internal reference ratio stays within limits prescribed by experimental determination. Analytical uncertainty in the normalized ratios can often be limited by counting statistics. This method can be used to deter-
mine mass independent effects such as the abundance of a radiogenic decay product, or mass independent fractionation such as that observed in $^{33}\text{S}$.

The fractionation law is generally derived empirically, but based on the measured isotopic composition of an element over a range of mass dependent fractionation. The simplest of these laws, the linear law, simply expresses the mass fractionation law as a linear dependence of the mass differences. For example, the $^{33}\text{S}/^{32}\text{S}$ deviation will be half that of $^{34}\text{S}/^{32}\text{S}$. Other normalization laws are used that are based on more elaborate formulations e.g. Rayleigh, power, exponential laws. Esat (1984) has shown that these laws all have the same basic form. If we define the ratios $R_{ik}$ and $R_{jk}$, where $R_{ik} = iA/kA$ and $R_{jk} = jA/kA$, then

\[
\text{power law: } R_{ik} = (R_{jk}) \frac{(m_i-m_k)}{(m_j-m_k)} \quad [30.5a]
\]

\[
\text{Rayleigh law: } R_{ik} = (R_{jk}) \left(\sqrt{m_i-\sqrt{m_k}}/\sqrt{m_j-\sqrt{m_k}}\right) \quad [30.5b]
\]

\[
\text{exponential law: } R_{ik} = (R_{jk}) \frac{\log(m_i/m_k)}{\log(m_j/m_k)} \quad [30.5c]
\]

from which the generalized form of the fractionation laws can be seen to be

\[
R_{ik} = [R_{jk}]^\gamma \quad [30.6]
\]

For example, the $\gamma$ values for the Mg isotopes ($^{24}\text{Mg}$, $^{25}\text{Mg}$, $^{26}\text{Mg}$) are $\gamma_{\text{power}} = 1.996$, $\gamma_{\text{Rayleigh}} = 1.976$, and $\gamma_{\text{exponential}} = 1.957$. Therefore the different laws can be seen to be simply imparting different degrees of curvature to the mass fractionation function for any given element. In practice, the real functional relationship must be determined for each element on each mass spectrometer.

If an element in a sample experienced complete ionization, rather than having only a fraction of the sputtered atoms ionized, there would be no fractionation associated with the ionization process (although fractionation in the mass spectrometer is also present). Elements that experience high degrees of ionization to positive species (e.g. Ca, Mg) have relatively low degrees of isotopic mass fractionation. A relationship is apparent between an element’s first ionization potential (for positive ions) and the degree of isotopic fractionation as measured on an ion microprobe. But measured mass fractionation is quite variable owing to a number of parameters and generalizations concerning ion yields and fractionation have many exceptions. Indeed, the observation between ionization and mass fractionation is not so apparent for negative ion production on the basis of electron affinity.

The real problems associated with SIMS stable isotope analysis are in achieving stable analytical conditions for sustained periods of time such that the uncertainty of a single analysis is consistent with the reproducibility of a population of analyses of that same material (assuming a constant composition of the target) (Fitzsimons et al., 2000). Or at least, the reproducibility of the standards has to be at a level commensurate with the required precision.

The goal is to achieve a constant measured isotopic mass fractionation in the standard [that doesn’t seem to be enough, one also has to be sure that it is the same on
standard and unknown. This is the analytical requirement; note also mineralogical differences in standard and unknown, standard heterogeneity, will also affect the measurements, and hence from the knowledge of the isotopic composition of the standard, calculate the instrumental mass fractionation component that can then be subtracted from the unknown. A typical analytical session would consist of a series of measurements of the standards (std) and unknowns (unk) comprising std – unk – std or std – unk – unk – std such that there is at least one standard in close proximity to the unknown. The std measurements can be assessed for internal consistency (e.g. temporal changes of composition) as well as consistency over the whole analytical session (drift, reproducibility). If the std analyses are consistent, the mean fractionation can be used to calculate the instrumental fractionation and can be removed from the individual unk analyses. The errors of the means from both standard and unknown must be combined suitably because the absolute fractionation for the unk cannot be known any better than the standard. Such a treatment still only involves random errors from measurements and does not address the possibility of systematic errors, such as from matrix effects, or from intrinsic variability of the standard itself.

A potential systematic effect may be induced by having standards and unknowns in different plugs, or even different mounts or otherwise mounted in dissimilar fashion. Geometric effects may play a role in the instrumental mass fractionation, such as mounting of grains too close to a discontinuity (holding ring, gap between plug and holder), and these might affect the extraction field geometry, as could different conductivities of coatings on std and unk.

Uncertainties for stable isotope measurements are usually limited by external effects, not internal measurement errors. It could be argued then that there is no point in reducing measurement errors significantly below reproducibility if the parameters affecting reproducibility are not going to be addressed. Thus time spent on obtaining internal measurement errors of 0.1 permil is wasted if the reproducibility is limited to 1 permil. But, for advancement of the analytical technique to higher levels of overall precision, the ability to obtain measurement errors significantly below reproducibility is required if the factors governing the limitations are to be addressed.

### 30.3.3 Matrix effects

The matrix is possibly the most important determinant in the relative isotopic mass fractionation of secondary ions from a given element given stable analytical conditions. The chemistry of a specific mineral is known to produce changes in ionization yields as indicated by correction schemes that are related to chemistry (Deloule et al., 1991). Structure can also be important, for example, different polymorphs of Ti oxides give different Ti isotopic mass fractionation factors that are correlated with the Ti-O bond strength (Ireland, 1986). In most cases, the matrix effect is probably a combination of chemistry and structure (mineralogy) and so suitable standards must be used for calibrating mass fractionation. It appears however, that such relative mass fractionation effects can be calibrated over a variety of minerals and only one phase need be analyzed during the analytical period, although some error propagation would be necessary.
These effects indicate that the target can play an important role in the measured isotopic mass fractionation and so beam overlap onto surrounding mineral species must be treated with caution. However, Riciputi & Greenwood (1998) have documented S and C isotope ratios in synthetic mixed matrices and have found that the presence of another mineral phase does not influence the mass fractionation from a given mineral species provided that element is not present in the other phase. Poorly defined matrices where an inappropriate instrumental mass fractionation factor is applied can also result in residual artifacts.

Eiler et al. (1997) have conducted an extensive study of matrix effects during O isotope analysis covering 40 silicate and phosphate minerals and glasses. Trends and correlations of fractionation were found for mean atomic mass of the target, chemistry of specific cations (e.g. Mg/Mg+Fe in olivine, Na/Na+K in feldspathic glasses, structural differences between minerals and glasses of the same composition, and sputter rate in silicate glasses. Correlations are sufficient to allow correction for different suites of particular type, but Eiler et al. (op. cit.) conclude that mineral standards close to the composition of the unknowns must still be characterized and measured.

An important parameter in spot locations must be the complete characterization of samples prior to analysis and also after analysis. Electron-beam imagery (back-scattered electron, secondary electron, and cathodoluminescence) provides important information for assessing spot placement. Cracks, mineralogical imperfections (such as exsolutions, alteration), small inclusions, can all affect the measured isotopic mass fractionation and should be avoided.

### 30.3.4 Factors affecting instrumental fractionation

In general application to stable isotopes, the object is to maintain the measured fractionation of the standards (hence instrumental fractionation) as constant as possible such that any deviations for unknowns can be reliably construed to be intrinsic fractionation in the unknown. In order to achieve this constancy, it is worth noting some of the instrumental parameters that can affect the measured fractionation. Then, it is worth avoiding changing those parameters that cause great change in fractionation for a small change in the given parameter. Ion microprobes are complicated instruments with many operational variables all of which may have the potential for changing the instrumental fractionation. For each isotope of a single element the method of analysis and instrument setup can change the absolute number of ions that are formed, the proportion that are transmitted through the mass spectrometer, and the relative proportion that are counted in the detector. Implicit in this, is an appreciation that different isotopes have different mass, and possibly different energy distributions, and that unintentional physical separation on the basis of mass and/or energy occurs within all instruments.

The primary beam affects the absolute fractionation because it is responsible for the sputtering event. Thus it is clearly worthwhile having a well-controlled primary beam. The stability of the primary beam is important because any noise on the primary beam will be immediately transferred to the secondary beam as well in terms of
intensity fluctuations. While it might be argued that a multiple collector would remove all these instabilities, there is a tendency for a poorly performing primary beam to also affect mass fractionation. That is, a fluctuating beam does not give fractionation measurements that are consistent with the expected measurement errors. The primary beam spot itself is also important. The spot is essentially the manifestation of the ion beam density within the primary column as projected on to the sample surface. The primary spot should be well focused with no internal aberrations that might form transient sputtering loci. In this regard, the Kohler-illumination method (Liebl, 1983) affords the best stability in terms of continuous sputtering. For routine ion microprobe analysis, best (i.e. most reproducible) results are obtained from a ca. 15-25 µm spot. However, stable isotope analysis is not limited to such spot sizes and analysis can be carried out to much smaller spots provided due care is exercised.

Once the primary ion beam is setup for an analytical session, it is generally not changed and so the sputtering fractionation might be regarded as constant. During the course of the analytical session, a variety of secondary ion extraction and shaping lenses, as well as steering plates may be changed, apertures inserted and removed, etc. Thus, it is the control of the secondary ion system that provides for the most factors affecting measured fractionation. If the secondary ion beam is truncated anywhere, it can cause fractionation in the isotope ratios. This is particularly the case if there is isotopic heterogeneity in the distribution of the ion beam paths in the secondary ion beam, which is almost certainly the case. Generally this means the instrument must be reasonably tuned for analysis, and be reproducibly tuned in the same way for all analyses.

Shimizu & Hart (1982b) reported a number of ion probe parameters that affect isotopic mass fractionation. These observations still hold for the operation of the small Cameca ion microscopes. For example, they demonstrated the necessity of proper and stable alignment of the primary beam spot with the secondary ion extraction axis to achieve reproducible isotopic mass fractionation measurements. The measured fractionation is a function of the energy of the secondary ions and is thus affected by the width and position of the energy slit.

Essentially, accurate mass fractionation measurements require that the analytical conditions remain as fixed as possible during the analytical session. The maxim for stable isotope measurements is beam truncation produces fractionation. The corollary is therefore that if transmission is maximized and beam truncation minimized, possible instrumental fractionation is minimized. Thus apertures and closed slits should be avoided if at all possible. For the large ion microprobes, this condition is automatically ameliorated because narrowly closed slits are not required to obtain the mass resolution required for stable isotope analysis.

A further source of analytical variability lies in the methods for charge compensation/neutralization from Cs⁺ sputtering of insulators. These methods can change the sample potential and in doing so can affect the tuning and by extension instrumental mass fractionation. The general philosophy is to achieve equilibrium conditions for a
sample such that instrumental effects are stabilized but under certain conditions the charge compensation can be unstable due to instabilities in the electron beam, ripple on the electron gun potential, or poor focusing of the electron gun.

30.3.5 Specific operating conditions

There are a number of laboratory factors that can have a significant impact on data collected. For example, oft cited concern is the need for stable temperature in the laboratory and while not quite as disturbing, stable humidity as well. These parameters can upset Hall effect probes for magnet calibration, and cause drifts in electronics and high voltage power supplies. Obviously, if the lab is not in order, the data will not be either.

In the first instance, the mass spectrometer is operated to exclude all unwanted species. This is generally accomplished by sufficient closure of source and collector slits to produce the requisite mass resolution. The objective then is to produce a stable analytical configuration.

High mass-resolution is generally preferred to energy filtering in isotopic analysis because of the higher transmission and hence better precision that is ultimately available. However, isotopic mass fractionation is found to be quite dependent on the energy of the secondary ions selected. The form of the relationship is that for low secondary ion energies there is a steep slope to the function whereas at higher energies the relationship flattens out (Figure 30.7). For example, in the case of low-energy secondary ions illustrated in Figure 30.7, a 10 eV change in the sample potential could cause a 7 ‰ shift in instrumental fractionation, while measurements taken at very high energy offsets should show a lower degree of dependence on variability in secondary ion energy. However, the instrumental mass fractionation is substantially higher for the high-energy offsets.

Riciputi (1996) has evaluated the two techniques (energy filtering vs. high mass resolution) for S-isotopic analysis in conductive phases on a Cameca ims-4f and determined that energy-filtering is favored in terms of precision and accuracy for a given analysis on this instrument. In particular, energy filtering produced more consistency for instrumental mass fractionation between mounts and this is important if the standard cannot be loaded onto a particular mount. It is worth noting that in order to obtain high mass resolution conditions in the ims-4f, substantial masking of the secondary ion beam is required at the entrance slit as has already been indicated. As such, the low-resolution conditions and the selection of high-energy ions is a better configuration in terms of instrumental mass fractionation reproducibility on the small Cameca instruments. However, for large sector instruments (Cameca 1270, SHRIMP), the source slit can be operated wider open for a given mass resolution and therefore the proportion of the secondary beam stopped by the slit is low and hence the possibility of instrument induced fractionation lower.

The energy slit performs several functions in the setup of a double focusing mass spectrometer. For high mass resolution operation on the Cameca ion microscopes, an
The measured instrumental mass fractionation (IMF) for O isotopes is a strong function of secondary ion energy. For secondary ions measured close to the extraction potential (i.e. zero initial kinetic energy), fractionation changes rapidly with sample charging requiring well-constrained analytical conditions. At higher energies, there is less dependence so analytical uncertainties from variation in sample potential are less critical. As illustrated, the mean of thirteen analyses with initial kinetic energy ≥ 350 eV gives a statistically coherent mean. However, the use of the high-energy ions is at the expense of a large proportion of signal. Data from Hervig et al. (1992).

If an electron multiplier is used as the detector, its condition can have a substantial effect on the data (Slodzian et al., 2001). Eiler et al. (1997) report that drift in isotopic mass fractionation was associated with changes in multiplier detection efficiency and when the gain of the multiplier was recalibrated after a session showing drift, the
mass fractionation data were stable. The detection efficiency is a function of both gain of the multiplier and discrimination of the counting system. The fact that the multiplier itself can induce shifts in isotope ratios indicates that it is a source of variability and so a stable configuration must be established. Often, the count rate of a particular isotope is initially specified (e.g. 500,000 c/s) to avoid problems with dead time. However, this alone may not be sufficient to guarantee data is free of counting artifacts. The multiplier should be clearly on the gain plateau of the multiplier (count rate vs. voltage), and a valley established in the discrimination of counts from the background noise (grass) in the counting system. In addition, in setting the count rate for the start of an analysis, it should be established that the parameter being changed does not itself induce a change in instrumental mass fractionation. For example, changing the entrance slit setting is commonly used to control the secondary ion count rate in dead time measurements. Under certain conditions this could have an effect on isotopic mass fractionation because of the trimming of the beam.

30.3.6 Instrumentation

The general features of ion microprobes have been covered above. Following are specific instrumental features that can aid in stable isotope measurements on individual types of instrument. Analytical protocols are usually established for a specific instrument, but the caveats that hold for any given laboratory are still relevant for the design of new techniques in any laboratory. That said, specific conditions that exist on one type of instrument may not be apparent on another. URL locations for manufacturers and some SIMS laboratories carrying out stable isotope measurements are given in Table 30.1.

Cameca ion microprobes are by far the most common instrument used for stable-isotope analysis. The small Cameca ims-nf (where n=3,4,5,6) have proved to be reliable and capable instruments despite the narrow entrance and exit slits required for isotopic analysis and concomitant loss of transmission. The Cameca ims-nf operate as stigmatic ion microscopes and allowance is made for masking apertures to be positioned to exclude undesirable parts of the ion beam. In this way, for example, residual surface water sputtered from the edge of the spot can be excluded such that only secondary ions from the center of the crater are passed, thus minimizing the OH⁻ interference in O isotope measurements. The ion microscope mode can also aid in spot selection in terms of avoiding areas of non-optimal behavior (cracks, inclusions, etc). Possibly the most important feature related to stable isotope research is the ability, introduced in the Cameca ims 4f, to produce stable negative secondary ion beams through the normal-incidence electron gun/charge compensation system. This allows stable secondary ion beams of electronegative elements to be produced from insulating samples.

The Cameca ims 1270 uses the same extraction system (i.e. primary column and source chamber) as the ims-nf models, but it has a large mass analyzer allowing high transmission (high sensitivity) analysis at high mass resolution, and has wide dispersion allowing multiple collection. The Cameca 1270 can operate either in a microscope mode (i.e. stigmatic with direct ion imaging) or a microprobe mode where the second-
ary optics are retuned to maximize transmission (astigmatic – high transmission mode). The benefit of the high transmission is that there is little truncation of the secondary ion beam and sufficient beam is available for Faraday cup measurement (McKeegan et al., 1998; Mojzsis et al., 2001). Multiple collection with Faraday cups allows high precision analysis of O and S in a matter of minutes (examples below).

Cameca has recently commissioned their nanoSIMS instrument. This differs from previous Cameca instruments in having a Mattauch-Herzog geometry that offers refocusing over a wide mass range. The feature of this instrument is the ability to produce extremely small primary beam spots of order 50 nm. This is accomplished by having the primary beam normally incident on the sample surface, that is, bringing the primary beam down through the secondary extraction optics. This allows the immersion lens to be placed very close to the sample surface allowing high degrees of demagnification and also improves secondary ion extraction efficiency.

SHRIMP ion microprobes have been somewhat neglectful of stable isotope analysis although some of the first reliable S isotope results were produced on SHRIMP I (Eldridge et al. 1987). Despite the lack of application, there are a number of features that make SHRIMP well suited to stable isotope analysis. One of the main features is a shallow-depth-of-field optical microscope that essentially places the sample into the same position with respect to primary and secondary ion-optical axes each time the sample is brought into focus. Such a simple operation therefore affords great reproducibility in terms of analytical conditions. The potential between the sample and first

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**Table 30.1 - URL for SIMS Laboratories**

<table>
<thead>
<tr>
<th>Manufacturers</th>
<th>URL for Cameca instruments</th>
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<tr>
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<th>URL for Cameca ion microprobes</th>
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The extraction plate is only a few hundred volts and so perturbation of potential field lines has less of an effect on the total extraction system than with the Cameca extraction geometry. SHRIMP typically operates with no energy filtering while still maintaining a high mass resolution capability. Thus, there is less opportunity for truncation at the energy slit and hence influence on isotopic mass fractionation. For charge compensation, a high-energy electron gun is used with impact energies of 1-1.5 keV.

The Isolab 54 is another ion microprobe, similar in concept to SHRIMP, with a much lower extraction field than the Cameca source geometry (England et al., 1992; Saxton et al., 1996). For stable isotope measurements (e.g. Lyon et al., 1995), a high energy electron gun is used for charge compensation, and a multiple collector is used for ion detection incorporating Faraday cup for the light isotope (e.g. $^{16}$O) and conversion dynode/channel plates for the heavier isotopes (e.g. $^{17}$O and $^{18}$O). This system requires extended deadtime for the conversion dynode and channel plate to avoid double pulsing.

### 30.4 Recent examples of stable isotope measurements

Ireland (1995) included some details of specific ion microprobe analytical arrangements for stable isotope configurations. Much has changed in the past few years such that capabilities that were cutting edge at the time of that review are now commonplace.

#### 30.4.1 Oxygen

Oxygen is perhaps the quintessential element for stable isotope analysis in geochemistry. Oxygen is a difficult element to analyze because of the large difference between the abundance of $^{16}$O and the minor isotopes $^{17}$O and $^{18}$O and because of the large $^{16}$OH interference on $^{17}$O. In extraterrestrial O-isotope analysis it is essential to measure all three O isotopes whereas in terrestrial applications measurement of the $^{18}$O/$^{16}$O will suffice because the main parameter of interest is mass-dependent fractionation. At mass 18, the interferences of $^{17}$OH and $^{16}$OH$_2$ are smaller than $^{18}$O and readily resolved at around 2,300 R. However, the hydroxide species are sputtered not only from the primary spot but also the area surrounding the spot, causing degradation of the OH$^-$ peak shape. Tailing of the OH$^-$ species is therefore a potential problem and should be monitored during the course of analysis. The OH$^-$ is apparently due to surface water migrating on the sample; water is a residual to the vacuum and the $^{16}$OH$^-$/17O$^-$ falls with time after sample insertion and hence pumping time. Hence methods for excluding water from the analysis are required. For example, water can be minimized through a variety of sample preparation methods such as extended pumping in a sample lock prior to insertion, or heating, sample under vacuum conditions. During analysis, the edge of the spot can be masked on Cameca ion microscopes to accept only the center of the spot where water contamination is minimal.

O is best analyzed as a negative ion through Cs$^+$ bombardment. Other schemes involving F$^-$ primary ion beams have been tried but have rather grave consequences for the duoplasmatron (Hervig, 1992). As discussed above, the main problem with
Cs+ bombardment is the charge build up on the surface of the sample. Electrons can be delivered with either low or high energies, and similarly secondary ions can be selected for either low or high energies. As an example, Graham et al. (1996) used Cameca ims 4f with a Cs+ primary beam (1-4 nA) defocused to 20-30 µm on gold-coated samples with a net impact energy of 14 kV. The normal-incidence electron gun was used for charge compensation with compensation indicated by adjusting the electron flux to yield zero net sample current. Secondary ions of 325-375 eV were extracted with count rates kept close to $5 \times 10^5$ for $^{16}\text{O}^-$.

McKeegan and coworkers (e.g. McKeegan et al., 1998; Leshin et al., 1997; etc.) have developed techniques on the Cameca 1270 to use lower-energy secondary ions for stable isotope analysis. This methodology requires that the instrument be kept in a very stable configuration in order to avoid instrumental fractionation variability caused by the secondary ion energy dependence. The Cameca 1270 can operate at high mass resolution without a severe loss of sensitivity. Leshin et al. (1997) used a 1 nA Cs+ beam defocused to 25-30 µm. Secondary ions within a 95-120 eV window were selected and the mass resolution was set at $\approx 6100 \, \text{M}/\Delta \text{M}$, sufficient to completely resolve any hydride contribution of $^{16}\text{OH}^-$ from $^{17}\text{O}^-$. Secondary ions were measured on an electron multiplier. Ion probe data were compared with conventional fluorination data on mineral separates and showed good agreement to within a permil or so following matrix corrections of $< 1 \, \%o$.

The main limitation of electron-multiplier measurements is the total number of counts that can be collected during the analysis time. Leshin et al. (1998) and Mahon et al. (1998) used ions with initial kinetic energies of 0-30 eV to increase count rates and allow a mixed detection mode for the analysis of carbonates whereby $^{16}\text{O}^-$ was measured on a Faraday cup (3 sec integration time) and $^{18}\text{O}^-$ was measured on the electron multiplier (5 secs per integration). In this configuration, $^{18}\text{O}^-$ count rates up to 250,000 c/s could be utilized enabling internal precisions of 0.5% for $^{18}\text{O}/^{16}\text{O}$. At the relatively low count rates for $^{18}\text{O}^-$, dead time corrections are not problematical. The Faraday cup measurements must be calibrated to the electron multiplier, which requires an additional measurement for accurate calibration. Once calibrated, any variability in the detector efficiencies will be reflected in a change in the measured fractionation. Engrand et al. (1999) also measured $^{17}\text{O}^-$ on the electron multiplier in a study of Antarctic micrometeorites.

Quite recently, the Cameca 1270 multiple collector has been used. Mojzsis et al. (2001) analyzed zircons from 4.3 billion year old zircons from Western Australia. Both $^{18}\text{O}$ and $^{16}\text{O}$ were collected on two Faraday cups at effective count rates of 2 GHz for $^{16}\text{O}^-$ and 4 MHz for $^{18}\text{O}^-$ allowing measurement precisions of 0.1 to 0.2 permil (2σ) to be obtained in less than 6 minutes. These data allow an evaluation of the SIMS O isotope technique for analyses at subpermil level.

Mojzsis et al. (2001) analyzed two standard materials, 91500 ($\delta^{18}\text{O} = 9.8 \pm 0.2 \, \%o$) and KIM5 ($5.04 \pm 0.05 \, \%o$) with 15-18 standard analyses presented for each of the two
sessions. Analytical uncertainties are better in the first session than in the second with mean uncertainties of 0.30 ‰ and 0.12 ‰ for 91500 and 0.20 ‰ and 0.12 ‰ for KIM5 respectively. The scatter of the data as determined from MSWD is 3.9 and 4.1 for 91500, and 24 and 8 for KIM5. Even with a higher analytical uncertainty in the first session, the MSWD values for the standards are no better in the first session than in the second. The scatter for 91500 is better than that for KIM5 and suggests that 91500 is better behaved than KIM5 at the microscale. If the excess scatter is assumed to be a Gaussian source of noise (errors inflated by \( \sqrt{\text{MSWD}} \)), the mean analytical uncertainties (per spot) are increased to 0.60 ‰ and 0.24 ‰ for 91500, and 0.94 ‰ and 0.33 ‰ for KIM5 (1σ). The errors in the means of the analyses are 0.10 ‰ and 0.05 ‰ for 91500, and 0.13 ‰ and 0.07 ‰ for KIM5. This treatment assumes all data are equal and no outliers have been excluded. In summary, the reproducibility of the standard data indicates a source of external variability is present. Even allowing for that variability, individual spots can be determined with precisions down to 0.4 ‰ (2σ) and errors in the mean down to 0.1 ‰ (2σ). These data suggest that 0.1 ‰ data are possible, but sufficient standards must be analyzed to ascertain the level of variability beyond that predicted from the measurement errors.

In the above example, KIM5 can be examined relative to 91500 to assess accuracy, i.e. we can use 91500 as the standard and examine the KIM5 composition. Using the augmented errors, the mean compositions for 91500 are 8.31 ± 0.10 ‰ and 7.99 ± 0.05 ‰, and for KIM5 are 4.01 ± 0.13 ‰ and 3.60 ± 0.07 ‰ (1σ). These data are offset from the absolute compositions noted above, but if the 91500 data is shifted back to \( \delta^{18}O \) of 9.80 ‰ for each session, the compositions for KIM5 are corrected to 5.50 ± 0.33 ‰ and 5.42 ± 0.09 ‰. The analyses for KIM5 agree well, but the composition is elevated above the 5.04 ± 0.05 ‰ reported as the KIM5 composition. This can be interpreted several ways but at this level of precision it is difficult to find a definitive interpretation. Possibly both of the compositions of the standards at the microscale do not agree with the bulk analyses or there are subtle heterogeneities within these samples. Reference to additional standard materials would be useful.

The Jack Hills zircons show a range of compositions and also show some variability within grains. The data presented by Mojzis et al. (2001) represents data combined for individual spots and grains. Analyses with higher uncertainties are quite likely due to sample heterogeneity (zones of metamict zircon for instance). The measured \( \delta^{18}O \) of the zircons ranged from 5.4 ‰ to 7.7 ‰ for optically continuous grains thus stressing the requirement of high precision for single measurements as well as high spatial resolution for these measurements. For comparison, similar systematics were determined by Wilde et al. (2001) in a similar study but in this case they used energy filtering (offset of 350 eV) and a total of 2 x 10^6 counts of \(^{18}O\) were counted to yield precision close to 0.7 permil (1σ). In this case the oxygen isotopic composition of the oldest zircon (at 4.4 Gyr) was resolved from the oxygen isotopic composition of zircons from direct mantle-derived rock by approximately 3σ (Figure 30.8). A number of the zircons with anomalously high \( \delta^{18}O \) are characterized by relatively young U-Pb ages (as opposed to Pb-Pb ages) and suggest that the zircons have exchanged with meteoric water, removing Pb and disturbing the O isotopes.
Figure 30.8 - Oxygen isotopic compositions in the world’s oldest zircons. The solid symbols are data from Mojzsis et al. (2001) while the open symbols are from Wilde et al. (2001).

(a) The zircons show a wide range in oxygen isotopic composition with $^{207}\text{Pb}/^{206}\text{Pb}$ age but all are above $\delta^{18}\text{O}$ of +5 ‰, the maximum level expected for derivation of magma from a primary mantle source. Rather these compositions are indicative of being sourced from material that has undergone low-temperature interaction with a liquid hydrosphere.

(b) Plotted against $^{206}\text{Pb}/^{238}\text{U}$, the heaviest zircons (in terms of $\delta^{18}\text{O}$) show the highest levels of discordance suggesting that late stage alteration is responsible for the more extreme $\text{O}$ isotopic compositions. Nevertheless, the most concordant zircons still lie above the limit for a mantle source.
30.4.2 Carbon and Nitrogen

The developments in analytical capability have also benefited carbon isotope analysis. Carbon is generally analyzed as negative ions with a Cs⁺ primary ion beam. A mass resolution of ≈3500 M/ΔM is required to separate ¹²CH⁻ from ¹³C⁻. Nitrogen is a difficult element to analyze by secondary ion mass spectrometry. It does not form N⁻ secondary ions and yields N⁺ ions a thousand times less productively than Si. However, Zinner et al. (1987) noted that nitrogen in the presence of carbon formed a very intense and stable CN⁻ beam.

The high ion yield of CN⁻ makes this species attractive in Biological SIMS where organic materials can be imaged (e.g. Larras-Regard & Mony, 1997). Furthermore, living materials (e.g. cells) can be doped with isotopically labeled (¹³C, ¹⁵N) drugs and the effects of these drugs on the cells can be directly imaged through the ¹³C and ¹⁵N abundances. The 50 nm spatial resolution of the Cameca NanoSIMS 50 allows an unprecedented view of intracellular structures.

Figure 30.9 - Correlated carbon and oxygen isotopic compositions in carbonate cements of differing composition from the San Joaquin Basin, California (Fayek et al., 2001). Early dolomite was precipitated soon after deposition (≈10 °C at ≈7 Ma), calcite between 4 and 5 Ma at 50 – 65 °C, and Fe dolomite near 100 °C in response to the pore-pressure reduction following exploitation of the gas cap.
(a) Balmat Pyrite

\[ \Delta^{33}S = -0.01 \pm 0.02 \text{ (2}\sigma) \]
(n = 20; MSWD = 3.7)

\[ \Delta^{34}S = 15.07 \pm 1.08 \text{ }^{\%\text{o}} \text{ (2}\sigma) \]

(b) 123 Pyrite

\[ \Delta^{33}S = 0.09 \pm 0.03 \text{ (2}\sigma) \]
(n = 12; MSWD = 2.6)

\[ \Delta^{34}S = 1.48 \pm 1.32 \text{ }^{\%\text{o}} \text{ (2}\sigma) \]
Similarly, evidence for biological fossils was found with in situ high precision C isotopic analyses of graphitic carbon inferred to be 3.9 Ga-old remnants of early life (Mojzsis et al., 1996). Mahon et al. (1998) measured carbon isotopes in carbonate cements with the same analytical setup for carbon as oxygen and using the electron multiplier as a single collector. Precision in the $^{13}$C/$^{12}$C better than 1‰ (2σ) could be obtained. Similar techniques are reported in Fayek et al. (2001)(Figure 30.9). Harte et al. (1999) describe techniques for carbon isotope analysis and nitrogen abundances in diamonds using a single collector Cameca ims-4f.

Figure 30.10 - S isotopic compositions of terrestrial standards measured with a multiple collector (Greenwood et al., 2000). Data from three standards are shown in plots of $\Delta^{34}$S (relative deviation of $^{34}$S/$^{32}$S from that in Cañon Diablo Troilite), against $\Delta^{33}$S, the fractionation-normalized $^{33}$S/$^{32}$S ratio (terrestrial = 0.0). The open stars indicate the conventional (bulk) compositions of the standards. Despite the high precision afforded by the multiple Faraday Cup measurements, all three standards show analytical precisions limited by reproducibility at the ca. 0.5-0.7 ‰ level. This indicates there are instrumental limitations to the measurement of the fractionation not related to signal intensity. The $\Delta^{33}$S measurements suggest the presence of non-linear fractionation or the possibility of analytical artifacts. Balmat pyrite shows the expected terrestrial ratio but with higher scatter than expected from the measurement errors. The other two standards show systematic deviations from the terrestrial composition at a level of 0.1 ‰. Mojzis et al. (in press) have used the same technique to document non-linear mass fractionation of $\Delta^{33}$S in Archean sedimentary sulfides at levels of −2 to + 2 ‰.
30.4.3 Sulfur and Selenium

The abundances of S isotopes are of great interest in economic geology where the origin of sulfide deposits can be addressed. In particular, biologic activity can cause quite extreme variability in S isotope ratios. Sulfur perhaps has the most varied range of possible primary and secondary ion species. Many combinations of primary O and secondary S polarities have been measured (e.g. O+/S-, Pimminger et al., 1984; O-/S+, Eldridge et al., 1987; O-/S-, Macfarlane & Shimizu, 1991). However, the high ion yield from Cs+ and S- makes this the preferred analytical setup.

Greenwood et al. (2000) studied S-isotopic compositions of Martian meteorites and were particularly interested in the abundance of 33S, which requires high precision and accurate determination of mass fractionation behavior. This study demonstrates the use of the Cameca 1270 with multiple collection in Faraday cups. The primary beam was ca. 2.5 nA Cs+ with low-energy electron charge compensation, and selection of secondary ions of 0-25 eV with respect to the accelerating potential. Under these conditions, individual δ34S analyses of standards (ca. 5 minute analyses) have 0.02 to 0.08 ‰ measurement uncertainties (2σ) with ca. 0.5 – 0.7 ‰ reproducibility (1 standard deviation of pooled analyses; Figure 30.10). Measurements of Δ33S yielded analytical uncertainties of 0.07 – 0.2 ‰ (2σ). These standards show excess scatter with an MSWD of 3.7. In this case the errors can be augmented by √MSWD thereby indicating measurement uncertainties of 0.1 to 0.2 ‰, or four apparent outliers can be rejected to yield a satisfactory MSWD. Without any indication of external influences, the former is the more robust method.

Greenwood et al. (2000) reported the detection of Δ33S anomalies in two separate ALH84001 pyrite grains (Δ33S = -0.74 ± 0.39 ‰ and -0.51± 0.38 ‰, 2σ); none were detectable in Nakhla pyrrhotite (total range in Δ33S =-0.4 ± 0.5 ‰ to -0.07 ± 0.5 ‰, 2σ). Mojzsis et al. (2003) used the same technique to determine a range of Δ33S in Archean sedimentary sulfides from –2 to + 2 ‰ and are well resolved from the analytical uncertainties.

Selenium is geochemically associated with sulfur and also shows isotope variability (Johnson et al., 1999; 2000b). Like S it can be efficiently ionized as a negative ion. However, Se typically remains as a trace element in most S-bearing minerals, but notably occurs as native Se which may be of interest in environmental geochemistry.

30.4.4 Hydrogen

Being the lightest element, the propensity for isotopic mass fractionation in D/H is the highest of any element (because of the large fractional mass difference between D and H). Hydrogen can be analyzed as either positive or negative ions: Hinton et al. (1983) used an O- primary beam with hydrogen isotopes measured as H+ and D+ while Zinner et al. (1983) used a Cs+ primary beam and collected negative secondary ions. Zinner et al. (1983) found that this technique has the advantage over using positive secondary ions of producing far less H2- and this species was less than 0.5 ‰ of the D- signal for all samples. They also found that the isotopic mass fractionation of
the hydrogen isotopes was far less than for positive ions. Deloule et al. (1991) were interested in measuring H isotopes in terrestrial samples and so high precision and accuracy is imperative. They used an O<sup>-</sup> primary beam and measured H<sup>+</sup> and D<sup>+</sup> at a mass resolution of 1300 M/DM to separate H<sub>2</sub><sup>+</sup> from D<sup>+</sup>. They took care to remove moisture from the sample surface by baking the sample and ion probe at 120°C and used a liquid nitrogen cold trap to fix residual water in the vacuum. Measurements commenced when the H<sub>2</sub><sup>+</sup>/H<sup>+</sup> ratio was lower than 8 x 10<sup>-4</sup>. Rather than simply comparing D/H ratios of standard and unknown, Deloule et al. (1991) found that the instrumental fractionation could be further calibrated by the measurement of Si<sup>+</sup>, Ca<sup>+</sup>, Ti<sup>+</sup>, and Mn<sup>+</sup> ion intensities on the same materials. The error of the best-fit calibration is around 7 ‰ and the δD can be measured to a precision of around ± 10 ‰.

Watson et al. (1994) used similar methodology as Deloule et al. (1991) and measured D/H ratios in hydrous amphibole, biotite, and apatite from SNC (Martian) meteorites. They found that the δD values in these minerals ranged up to +4,000 ‰, consistent with interaction with Martian crustal fluids having near atmospheric D/H. Leshin (2000) used the Cameca 1270 for D<sup>+</sup>/H<sup>+</sup> measurements of apatites from the Martian meteorite QUE94201. The water contents of the apatites were 0.2 – 0.6 wt %, as determined from H<sup>+</sup>/42Ca<sup>+</sup> comparison to a terrestrial apatite standard, and the D/H is strongly correlated with water content. This indicates the mixture of two pos-

![Figure 30.11](image_url)

**Figure 30.11** - Hydrogen isotopic composition and water concentration in apatites from the Martian meteorite QUE94201 (Leshin, 2000). The data suggest a mixture of water in the apatites between the Martian atmosphere at δD of +4200 ‰ and magmatic water at ca. +900 ‰.
sible endmembers on Mars: atmospheric water with $\delta D$ of ca. $+4,200 \%_\circ$, with water intrinsic to the Martian crust with $\delta D$ ca. $+900 \%_\circ$ (Figure 30.11).

30.4.5 Lithium, Boron

These elements are typically measured as positive ions with an $O^-$ primary beam. Some minerals occur with these elements as major constituents and so high precision analyses can be carried out quite quickly. For example, boron can be measured in tourmalines at ca. 10 wt % (e.g. Chaussidon & Uitterdijk Appel, 1997; Smith & Yardley, 1996; Nakano & Nakamura, 2001). In general however, in situ analysis of these elements requires long counting times because of low B concentrations in rock-forming minerals. Chaussidon et al. (1997) report methods for B isotope analysis in meteorites and mantle rocks with B concentrations less than 1 $\mu g/g$. Besides the low concentration, surface contamination and matrix effects also present major difficulties. Samples were rinsed in ultra-pure water and then sputter cleaned to reduce surface contamination to the level of 0.01 $\mu g/g$. Standard glasses showed reproducible analyses of less than 2 $\%_\circ$ over a period of several years. Chaussidon & Jambon (1994) measured B isotopic compositions and contents in oceanic basalts (Figure 30.12). Chaussidon & Robert (1998) used similar techniques to examine Li and B isotopes as well as Be concentrations in the Semarkona chondrite. Lithium isotopic compositions were measured from implanted solar wind in lunar soils by Chaussidon & Robert (1999). McKeegan et al. (2000) measured B isotopic compositions in a meteoritic refractory inclusion to infer the presence of live $^{10}Be$ in the early solar system. Williams et al.

![Figure 30.12 - Boron content and isotopic composition of Hawaiian basalt glasses show a strong correlation with MgO concentration of the magma that is interpreted as the result of assimilation – fractionation processes in seawater-rich oceanic crust (Chaussidon & Jambon, 1994).](image)
(2001b) used both SIMS and TIMS techniques to elucidate diagenetic reactions in marine sediments.

Decitre et al. (2002) describe Li isotope methodologies for characterization of serpentinitized peridotites. In the bulk samples determined by TIMS, Li concentrations range from 0.6 to 8.2 ppm, while whole rock $\delta^{6}$Li values range from -2.9 to -14‰. In situ analyses display a greater range in both Li concentration (0.1–19.5 ppm) and Li isotopic composition (-27 to +19‰), with the serpentinitized portions having higher Li concentrations than the associated relict phases.

30.5 State of the Art
30.5.1 Precision vs Accuracy vs Reproducibility

One of the main issues confronting SIMS analysis at present is the increasing analytical precision that can be obtained in a given analysis as opposed to the reproducibility of a given set of analyses. The pooled results may be accurate, but the scatter of analyses from a pool may not be commensurate with that expected from the measurement precision. The goal is to obtain reproducibility and accuracy commensurate with that precision.

This paper has not addressed in any detail the methods of combining data and obtaining reliable statistics for measurements. Data can be assessed at various levels for reliability indicators from the analytical error in a single measurement through to the final grand mean of the unknown referenced to the standard. In a truly robust method, the analytical scatter would be consistent at all these levels. SIMS analysis has made great strides in reducing analytical error in the past few years. In large part this is due to the use of Faraday cup analysis, particularly in multiple collector mode, allowing higher levels of analytical precision to be obtained from large ion beams. With that higher level of precision, scatter in pooled analyses becomes more apparent, as is seen in the S isotopic analyses in Figure 30.10. However, with this level of precision, the scatter of data can be quickly assessed from a given analytical protocol and will likely lead to commensurate improvements in achieving accurate and reproducible data.

At present, precisions (internal measurement error only) are achievable for O and S at a level of 0.1‰ with multiple faraday-cup collection. The accuracy of a given measurement is not quite as good with reproducibility indicating a level of ca. 0.5‰.

30.5.2 Standards

The ability to assess analytical precision and accuracy is dependent on having standards that are homogeneous to a sufficient level. Such a condition is very difficult to establish analytically, in large part because the ion probe samples such a small volume. Microscopic heterogeneity does not necessarily reveal itself in the substantially larger samples required for other techniques. The issues are important in terms of interpretation because scatter could be interpreted as due to a geological or biological phenomenon. Only when the level of homogeneity in a material can be reliably ascertained can the level of analytical reproducibility be established.
Good standards are therefore very valuable both in calibrating instrumental mass fractionation, but also in assessing measurement statistics. Obtaining standards is no easy task because most are based on single crystals where there is no guarantee that the next crystal from that source is as homogeneous as the previous one. As such, great care and effort is expended in calibrating and assessing standards for SIMS analysis.

### 30.6 Concluding remarks

Analytical protocols are improving such that highly precise and reproducible analyses are now readily forthcoming. However, the ease of placing a spot on a target is still mitigated by problems associated with determining instrumental mass fractionation for specific mineral compositions and other matrix effects that would otherwise be ascribed to a change in isotopic composition in the target. As such, ion microprobe analysis still requires careful measurement conditions and caution in interpretation of results where target chemistry and structure might be an issue.

Real advances in SIMS have been in stable isotope research allowing in situ negative ion analysis and these areas are only beginning to be exploited. SIMS offers an unparalleled capability for in situ analysis with high sensitivity and high spatial resolution. In the coming years, it can be expected that accuracy commensurate with precision will be obtained allowing in situ capability at a similar level to bulk methods. However, natural materials are seldom as homogeneous as we would like to believe and analysis at the microscale reveals the true complexity. The rapid feedback of data allows siting of analyses based on the observed characteristics of the material. As such SIMS allows real-time assessment of data and responsive control of the analytical program.

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