CHAPTER 1: AN INTRODUCTION TO SECONDARY ION MASS SPECTROMETRY (SIMS) IN GEOLOGY

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INTRODUCTION

The basis of the secondary ion mass spectrometry (SIMS) technique is the phenomenon where bombardment of a solid by a primary ion beam generates secondary ions. The secondary ions, analyzed for their mass-to-charge (m/z) ratios in a mass spectrometer, in turn reflect some compositional attribute of the solid (Fig. 1-1). In fact, as is the case for all mass spectrometric methods, it is the ratio of two secondary ion intensities (*e.g.*, $^{18}O^-/^{16}O^-$, $^{143}Nd^+/^{28}Si^+$) that is used for purposes of elemental or isotopic quantification. SIMS is an enormously widespread technique in the physical sciences and has many uses, including 'bulk' chemical or isotopic analysis from micro-volumes, imaging of element distributions, measuring compositional changes with depth, and surface molecular chemistry. The key advantages of SIMS are the ability to localize the analyses to the micro- and even nano-scale, the very low detection limits, and access to the entire periodic table. It is interesting to note that there exists a related technique called sputtered neutral mass spectrometry (SNMS), in which the large fraction of neutral sputtered species are ionized extrinsically (Benninghoven *et al.* 1987, Higashi 1999), but this has yet to be applied in geology.

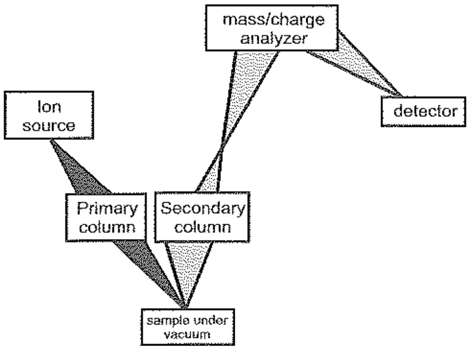

FIG. 1-1. Fundamental elements of a secondary ion mass spectrometer.

Although SIMS is a major technique employed in geochemistry and cosmochemistry, unfortunately no comprehensive treatments exist to guide geologists. A useful overview by Ireland (1995) remains relevant, and there are several texts and synopses for readers seeking details of the SIMS technique (Williams 1985, Benninghoven *et al.* 1987, Vickerman *et al.* 1989, Williams 1990). Readers seeking a broader understanding of mass spectrometry will find Becker's (2008) book useful. To understand SIMS applications in geology today, it is helpful to understand the basic analytical technique, and to become familiar with SIMS instrumentation, as they influence the approaches and capabilities to solve geochemical problems. Words in **bold** are defined in the glossary.

Brief Description of SIMS

The bombarding primary ions, typically of energies between 1 keV and 20 keV and either positively or negatively charged, become implanted within the uppermost atomic layers of the solid under **very high** to **ultra-high vacuum** (Fig. 1-2). The kinetic energy of the primary ions is transferred to target atoms by several generations of quasi-elastic collisions of the recoiling target atoms in a so-called '**collision cascade**' (Sigmund 1969). Recoil particles, both atoms and molecules (including molecular **fragments** or **clusters**), that have a component of motion toward the surface may escape (*i.e.*, are **sputtered**) if the kinetic energy of the recoiling atom exceeds the **surface binding energy** for the sputtered particle, typically <5 eV. Anywhere from one to tens of secondary particles may be sputtered for each incoming ion, termed the **total sputter yield**, and typical sputter rates are 1–5 nm/s. Most sputtered particles are neutral and simply fall back onto the sample, but the small fraction of particles that are ionized (typically <<10%, and highly variable) can be

Mineralogical Association of Canada Short Course 41, Toronto, May 2009, p. 1-18.

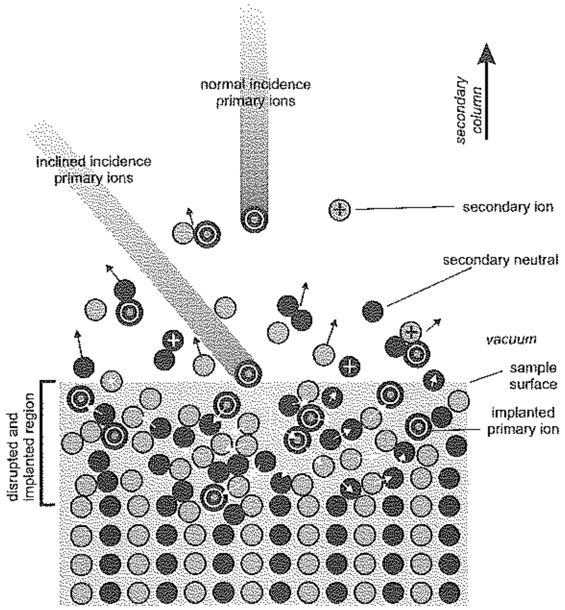

FIG. 1-2. Illustration of the sputtering process at the atomic scale. Shown are a normal incidence primary ion beam, utilized in some instruments, and the more common inclined incidence primary ions. The knock-on effects of the collision cascade are illustrated with the white arrows. Sputtered neutral and charged atoms and molecules are ejected from the implanted and structurally disrupted upper atomic layers. Ionization is generally considered to occur within the electrically and kinetically excited upper layers of the sample by processes still debated. Secondary ions are electrostatically drawn into the secondary column and then to the mass analyzer.

extracted into the secondary column and mass spectrometer (Figs. 1-1, 1-2). A figure of merit in SIMS is the **useful (ion) yield**, defined as the number of ions detected per atom of that species sputtered. Useful yields are highly variable, and depend on the element, the sample matrix, the instrument transmission (typically <0.5, but up to ~1.0 is possible) and the specific analytical conditions, but are generally 10^{-1} to 10^{-4} (*i.e.*, inefficient), which is typical of many other mass spectrometric techniques.

Although ion bombardment involves jostling of target atoms, the amounts of energy deposited are, compared with laser ablation, about five orders of magnitude lower, so *heating and vaporization are not the principal processes in SIMS.* Despite some success in describing the sputtering phenomenon in terms of the thermal behavior of the target, there is, in fact, no evidence that a plasma actually exists. The implantation of ions into the solid surface results in major changes to its electronic structure and bulk composition, as it momentarily becomes a mixture of the original target and the implanted ion species. Furthermore, the bombardment of the solid usually results in substantial damage to its crystalline structure, and the sputtered surface can be described as an 'amorphous selvedge' (Benninghoven *et al.* 1987). Sputtered particles are emitted mostly from the outer one or two atomic layers (<0.5 nm), whereas the primary ions penetrate several atomic layers, typically ~10 nm (Fig. 1-2). An ion that impacts a pristine surface will initially sputter some intact molecules from the uppermost atomic layer (**monolayer**), but subsequently the sputtered material will have been drastically altered by ion bombardment. The sputtered particles have a range of kinetic energies when they leave the surface, with most less than 10 eV and decreasing fractions up to 100s of eV. Atomic and molecular ions have distinct energy distributions, a fact that is often exploited in certain types of analyses.

A critical limitation of SIMS is relating secondary ion signal intensities to the actual (or relative, for isotopic analysis) abundances of the atoms of interest within the solid. In fact, the elemental specificity of ion yields is one of the defining characteristics of SIMS. Secondary ion signals are strongly dependent on the properties of the particular atom, such as its ionization potential, and its chemical and electronic environment, collectively termed **matrix effects**. We have seen, in fact, that bombardment itself changes the sample matrix, and therefore matrix effects are a combination of the nature of the undisturbed solid as well as the particular conditions employed during sputtering, including the type and energy of the primary ion. And despite the structural disruption induced by bombardment, secondary ion yields may also remain sensitive to the crystal structure of the original material. Secondary ions originate at or within the sample surface due to several interrelated factors, including the kinetic energy imparted by the implanted ions, and the chemical and electronic structure of the environment containing the **analyte** atom. Ion formation has, in fact, defied a theory of any practical significance in analytical chemistry of chemically complex targets (Williams 1985, Williams 1990). In general, matrix effects are less important for atomic ions of the same element (**isotopes**) compared with ions of different elements (*e.g.*, Hinton 1990).

Most types of quantitative analyses with SIMS, whether elemental or isotopic ratios, require empirical calibration of instrumental bias using **reference materials** that are assumed to be identical in composition to the unknown material, or bracket the unknown composition. Various types of analytical strategies have been adopted to reduce the matrix effects, such as measuring only high energy secondary ions (**energy filtering**). Additionally, secondary ion mass spectra are usually populated by numerous molecular ions, some of which may interfere with the ion of interest (*i.e.*, having nominally identical m/z (**isobars**)). The instrument type and conditions of analysis are important in reducing or resolving isobaric interferences and other potential analytical biases to an acceptable level. The efforts that practitioners take in calibration are directly related to the complexity of the target composition and the precision and accuracy desired, and most laboratories have developed unique reference materials and customized methods for their particular instruments and samples.

SIMS ORIGINS

SIMS has its roots in the development of mass spectrography (the recording of mass spectra on photographic film) and mass spectrometry (the electronic quantification of selected m/z signals) in the early part of the 20th century. Through to the middle part of the century, great improvements were made in the physics of designing better **mass analyzers**, and in the period 1945–1960 there was recognition of the potential for mass spectrometric techniques in analytical chemistry. New instruments were introduced and applications followed, particularly for the analysis of gases and liquids, which are relatively easy to ionize. However, producing ions directly from solids presented particular difficulties.

A significant advance in the analysis of solids was the development of an analytical platform that used (primary) ion bombardment and the resulting sputtering to generate (secondary) ions (Herzog & Viehböck 1949). The principle of secondary ion formation by sputtering had been recognized 40 years earlier by J.J. Thomson (1910), and received increasing attention just before and after WWII (for references, see Liebl 1974, Honig 1985). Instrumentation for SIMS comprises three distinct parts, the ion probe to generate the secondary ions, the secondary extraction column, and the mass analyzer (Fig. 1-1). We frequently refer to the 'ion (micro)probe' and imply that a mass analyzer is attached, although this is not necessarily the case. For example, ion microprobes nowadays can be used for micro-machining of solids in 'focused ion beam' (FIB) applications. In the case of SIMS instrument development, the concepts for mass analyzer design were generally well established, but the significant advance and foremost interest was in developing the ion probe as a source of secondary ions. It may come as a surprise that the initial motivation for SIMS development was not spatially controlled sampling, it was simply an improved method of generating ions from solids.

The first commercial SIMS instrument (IMS-101), initially called a 'solids mass spectrometer,' utilized Ar^+ primary ions to generate positive secondary ions (Liebl & Herzog 1963). The diameter of the probe was initially millimetres (*i.e.*, a 'macroprobe'). The development of the IMS-101, was, in fact, motivated by geology, as it was a NASA initiative related to the lunar program, and resulted in ground-breaking chemical and isotopic analyses of, amongst other things, meteorites (*e.g.*, Poschenrieder *et al.* 1965). The electronics industry quickly recognized SIMS as having low **detection limits** for many elements, and the unique ability to characterize the upper surface of solids, termed **in-depth** analysis. During the 1960s, the electronics industry developed their own SIMS instruments to analyze the chemical composition of semiconductors and thin-films (Honig 1985).

In parallel with the developments in SIMS to this point, another group had begun the journey towards using secondary ions from a slightly different angle. One of the pioneers in electron microscopy, R. Castaing, and his student, G. Slodzian, began exploring the possibility of using secondary ions to map the chemical composition of solid surfaces, *i.e.*, secondary ion *microscopy*. They sought a faster, more direct, and more sensitive method of producing chemical images than the existing approach of scanning an electron beam and quantifying secondary X-ray emission spectra. This work led to the design of the ion micro*scope* (Castaing & Slodzian 1962), an innovative concept and a remarkable instrument made possible with a novel, if unusual, mass analyzer design. A millimetre diameter Ar^+ ion beam sputtered the sample, and an image (~10^2 μm diameter) of the intensity and distribution of selected secondary ions was projected onto a fluorescent screen with micrometre-scale spatial resolution. The commercial version of the direct imaging ion microscope was introduced as the Cameca IMS 300 'ion analyzer,' claimed to have numerous advantages over the electron microprobe, including better sensitivity and speed (Rouberol *et al.* 1972).

In the 1960s, researchers began developing and exploiting the high surface sensitivity of ion bombardment techniques to characterize the molecular chemistry of organic samples and polymers. It was recognized that a primary ion beam maintained at a sufficiently low beam density (*e.g.*, <1 nA cm^{-2}), would, over several minutes, sputter a high proportion of atoms and molecules originating from the outer monolayer. The term 'statical analysis' was coined for conditions where the surface remained largely intact and free of the damaging effects of bombardment (Benninghoven 1969). Once the undisturbed surface layer was gone, subsequent sputtered particles would originate from the chemically and structurally modified solid. "Dynamical analysis' (Benninghoven 1969) was introduced to refer to the use of high density primary beam currents in which the surface was continuously being destroyed and regenerated. We now refer to the two main branches of SIMS as '**static SIMS**' and '**dynamic SIMS**' (Benninghoven *et al.* 1987), which can be equated with low primary current density and high primary current density, respectively. Initially, static SIMS instrumentation utilized quadrupole mass analyzers, but over the last decade, time-of-flight (TOF) mass analyzers have become popular (Van Vaeck *et al.* 1999, Vickerman & Briggs 2001). Readers should note that TOF–SIMS instruments can be operated in either a dynamic or static SIMS mode. TOF–SIMS also allows the collection of complete mass spectra, so a large number and mass range of secondary ion signals are determined simultaneously.

In the geosciences, the majority of applications and instruments use dynamic SIMS, however the last decade has seen increasing interest in characterizing mineral surfaces through the use of static SIMS (Mogk & Mathez 2000, Sjövall *et al.* 2008). The important point is to note that although SIMS is inherently a surface-sensitive analytical technique, only in static SIMS, and using the specific instruments designed for this purpose, can the intact surface monolayers be measured. In all other cases the sputtered particles originate from an amorphous mixture of the primary particles and the solid, and therein lies much of the complexity in dynamic SIMS. Nevertheless, dynamic SIMS is required for most geological studies. The outer monolayer of a mineral is typically of no interest, as it almost certainly comprises numerous environmental contaminants, such as hydrocarbons, and may be oxidized. Furthermore, residual gas molecules in the (imperfect) vacuum stick to and contaminate the surface of the sample, and for this reason static SIMS requires ultra-high vacuum to reduce the contamination to an acceptable level. Secondly, quantification requires the strongest and most stable secondary ion signals possible, and this requires the use of a high density primary beam species, not only to sputter as many particles as possible, but to change the chemistry of the surface deliberately in order to enhance and stabilize secondary ion yields (see below).

Returning to the development of (dynamic) SIMS instrumentation, ion *microprobes* (*i.e.*, micrometre diameter probes) emerged from predecessor macroprobes in the late 1960s, and were combined with suitable mass analyzers, largely of the **double-focusing**, magnetic sector type. An important instrument of this type was the commercially produced (ARL Corporation) 'ion microprobe mass analyzer (IMMA)' (Liebl 1967, Andersen & Hinthorne 1972a). The IMMA set the standard for many years to come, and included novel features such as a normal incidence, **scanning ion** beam for imaging, whereby a finely focused primary beam is incrementally moved across the target, and the secondary intensities at each point are determined.

The developers of the IMMA made key discoveries on the importance of surface electrical and chemical properties in generating secondary ions. In particular, the use of a chemically reactive primary ion species, such O_2^+ or O^-, with its high electron affinity, produced significantly stronger positive secondary ion signals compared with using inert gases (*e.g.*, Ar^+) as the primary ions (Andersen 1969, Andersen & Hinthorne 1972a). Similar findings were made in the yields of negative secondary ions using Cs^+ primary ions, which are strongly electropositive (Andersen 1970), and decrease the work function of the solid. The **duoplasmatron** ion source used in generating oxygen primary ions (Coath & Long 1995 and references therein), and the thermal ionization source for Cs^+ (Storms *et al.* 1977) eventually replaced the noble gas ion sources that were hitherto common, and remain the most important ion sources for geological SIMS applications. The IMMA instrument was used extensively for studying minerals, metals, and semiconductors, and became particularly well known for ground-breaking studies of lunar samples, including the first ion probe U–Pb geochronology (*e.g.*, Andersen & Hinthorne 1972b, Hinthorne *et al.* 1979).

Furthermore, the IMMA instrument inspired W. Compston at the Australian National University to embark on the design of the first ion microprobe designed especially for geology, the Sensitive High Resolution Ion MicroProbe, or 'SHRIMP.' The SHRIMP instruments were the first to incorporate very large magnetic and electrostatic sectors in the conventional double focusing design, allowing routine high mass **resolution**. During the 1980s, the prototype SHRIMP I and SHRIMP II (Fig. 1-3a) were introduced, and the SHRIMP II became commercially available in the early 1990s (De Laeter & Kennedy 1998, Ireland *et al.* 2008). There is little doubt that the SHRIMP instruments revolutionized the field of U–Pb geochronology of accessory minerals, by permitting spatially controlled dating (Williams 1998, Ireland & Williams 2003).

Meanwhile, Cameca continued on a parallel path to develop the ion microscope further, and introduced the IMS 3f in 1977. This newer instrument now used a conventional double focusing mass analyzer, and permitted both ion microscope and ion microprobe modes. Even though the Cameca 3f and successors (Fig. 1-3b) were not designed for geological applications *per se*, they nevertheless led the rapid expansion of SIMS applications in geochemistry and cosmochemistry in the 1980s, particularly trace element and stable isotope analyses of minerals (Shimizu *et al.* 1978, Zinner *et al.* 1983). The Cameca f-series remain the most commercially successful and widely used instruments in the geosciences, not to mention their dominance within materials sciences.

In the early 1990s, Cameca introduced a large geometry ion microprobe, the IMS 1270 (1280 currently), based upon the f-series (Fig. 1-3c), as a specialized instrument for geology and competitor to the SHRIMP II. It further added the capability of a multiple detector system, as well as maintaining Cameca's unique direct ion imaging optics (Conty *et al.* 1990, de Chambost *et al.* 1992, Harrison *et al.* 1995). Cameca also concurrently designed the NanoSIMS 50 (Fig. 1-3d) based upon a normal incidence, scanning ion probe with a working diameter for Cs^+ <0.1 μm (Slodzian *et al.* 1992, Hillion *et al.* 1994). The VG/Fisons Isolab 54 ion microprobe was also introduced during this period (England *et al.* 1992), although it was not commercially successful. The reverse geometry SHRIMP–RG is a prototype instrument designed for ultra-high (10,000–20,000 R) mass resolution (*e.g.*, Ireland & Bukovanska 2003), but it too has not been commercially successful. Currently, the SHRIMP II and Cameca magnetic sector type instruments dominate geoscience applications of dynamic SIMS. Recent applications of static SIMS in the geosciences have used time-of-flight mass analyzers, such as the German manufactured ION–TOF, employing primary beams of non-reactive species such as Ga^+ and Bi^+ (Fig. 1-3e). For various technical reasons, the TOF analyzers are not optimal for quantitative isotopic analysis, and therefore are not used in most dynamic SIMS applications in geology.

GEOLOGICAL (DYNAMIC) SIMS IN PRACTICE

Geological samples are usually chemically complex materials, and the elements and isotopes of interest may be at very low (*e.g.*, parts per million) concentrations. The compositional variability requires close attention to calibration, because to varying extents all SIMS element/element and isotopic ratios are biased from the true values in the solid, although generally less so for the latter. For element ratios, this fractionation is sometimes referred to as '**discrimination**,' and for isotopic ratios, **instrumental mass fractionation** (see below). Calibration in SIMS is done by analysis of matrix-matched reference materials, interspersed with the unknown samples. The more stringent the requirement for precision and accuracy, the more attention is placed upon the calibration scheme. Up to one third of analytical time may be spent in calibration. Most reference materials are natural minerals, with lesser use of natural or synthetic glasses (*e.g.*, SRM 610) or synthetic minerals. Use of ion-implanted reference materials is rare, although routine in materials science. It has been found that under conditions of extreme **energy filtering** (*i.e.*, selecting only very high energy ions), discrimination is less affected by matrix composition, which simplifies calibration in trace

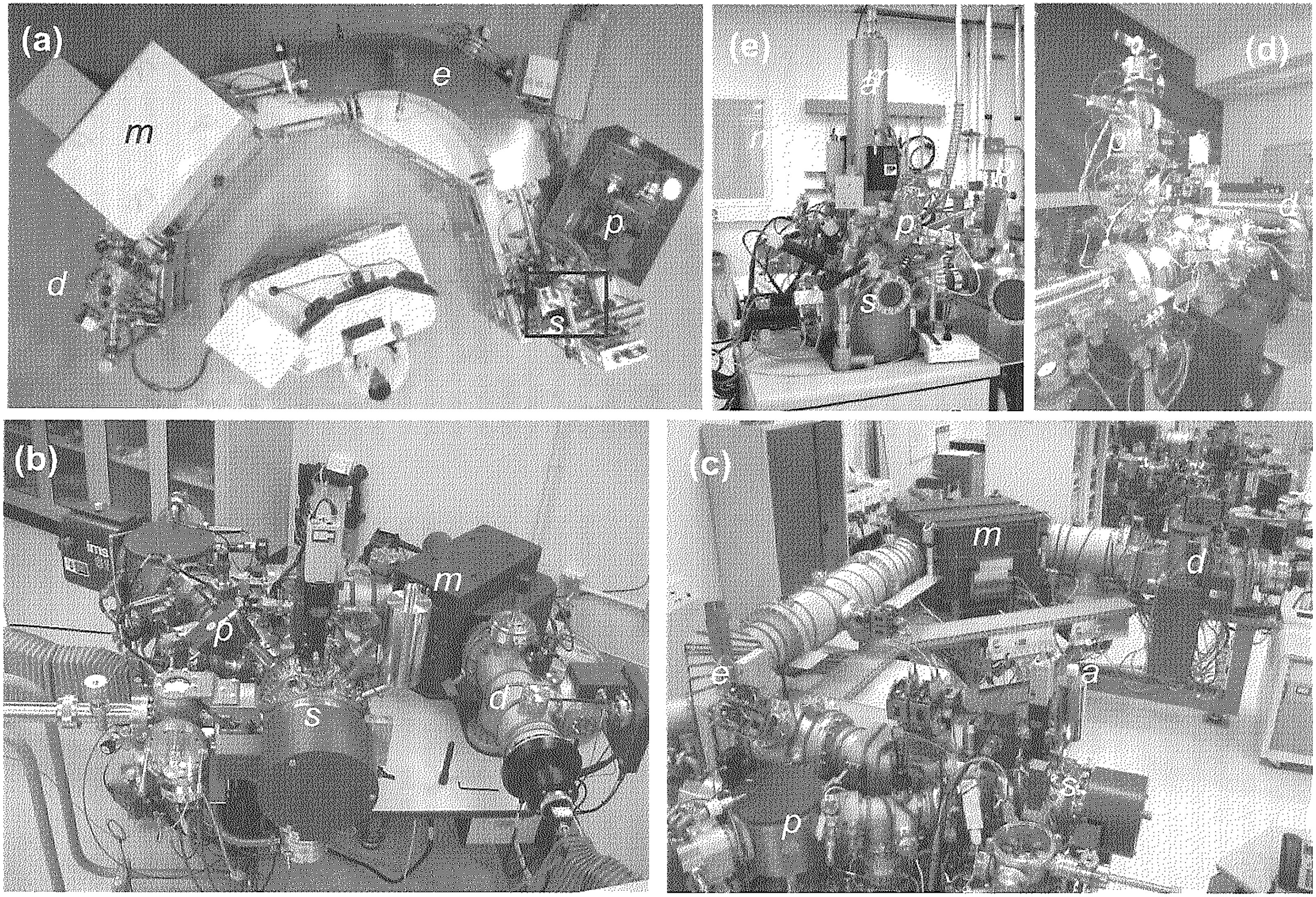

*FIG. 1-3. Photographs of various types of ion microprobes utilized in the analysis of geological samples: (**a**) SHRIMP II, ASI factory, Australia (image courtesy of ASI Pty Ltd); (**b**) Cameca IMS 6f, Arizona State University (image courtesy of L. Leshin); (**c**) Cameca IMS 1280, Paris; (**d**) Cameca NanoSIMS 50, The University of Western Australia (**e**) ION–TOF time-of-flight SIMS, University of Alberta. Symbols: a, analyzer; d, detector; e, electrostatic sector; m, magnetic sector; p, primary column; s, sample chamber. *For color version of this figure, see http://www.mineralogicalassociation.ca/index.php?p=160

element analysis. For example, synthetic glasses may be used to calibrate trace elements in minerals (*e.g.*, Hinton 1990). Furthermore, secondary ion mass spectra of natural materials are complex, and atomic and molecular (*e.g.*, oxides) isobars are frequently present (Fig. 1-4a). Isobars present a problem in accurately measuring secondary ion intensities, and must be eliminated in most cases, through the use of either high mass resolution (Fig. 1-4b) or energy filtering, or a combination of both.

In typical dynamic SIMS applications in geology, a 10–25 keV primary beam of $^{16}O^-$, $^{32}(O_2)^-$, or $^{133}C^+$ ions is focused onto the surface of the sample at 0° to 45° relative to normal (Fig. 1-2). As discussed previously, chemically reactive primary ions enhance the formation of secondary ions. Targets bombarded with oxygen become saturated in oxygen, a strongly electronegative element, to depths of ~10 nm, enhancing the environment for forming positive secondary ions of most metallic elements (*e.g.*, Ca^+, REE^+, Pb^+). Cesium saturation reduces the work function of the solid, enhancing the number of free electrons available to combine with non-metallic elements (*e.g.*, C^-, O^-). For **scanning ion imaging**, the region of interest (ROI) must be rastered for several minutes prior to imaging in order to saturate the near-surface with the chemically reactive primary ions. The use of chemically reactive primary species is a double edged sword, as it increases and stabilizes secondary ion yields, but also magnifies matrix-related discrimination. Electron flood guns are available to neutralize positive charging of the sample when analyzing insulating minerals with a Cs^+ beam (Ireland 2005). Negative charging with O^- ion bombardment is less problematic in general, but all surfaces must be inherently conducting or coated with a conducting film of Au or C.

The secondary ions, usually of opposite polarity to the primary ions, are extracted normally from the sputtering site into the secondary column, and in the process are accelerated through typically 4.5–10 keV (Fig. 1-1). The secondary column imposes an electrostatic field upon the sample surface to guide and focus secondary ions towards the entrance slit of the mass analyzer. The secondary mass analyzers in dynamic SIMS differ greatly between various instruments, depending on their design specifications, but all are of the magnetic sector, double focusing design (Roboz

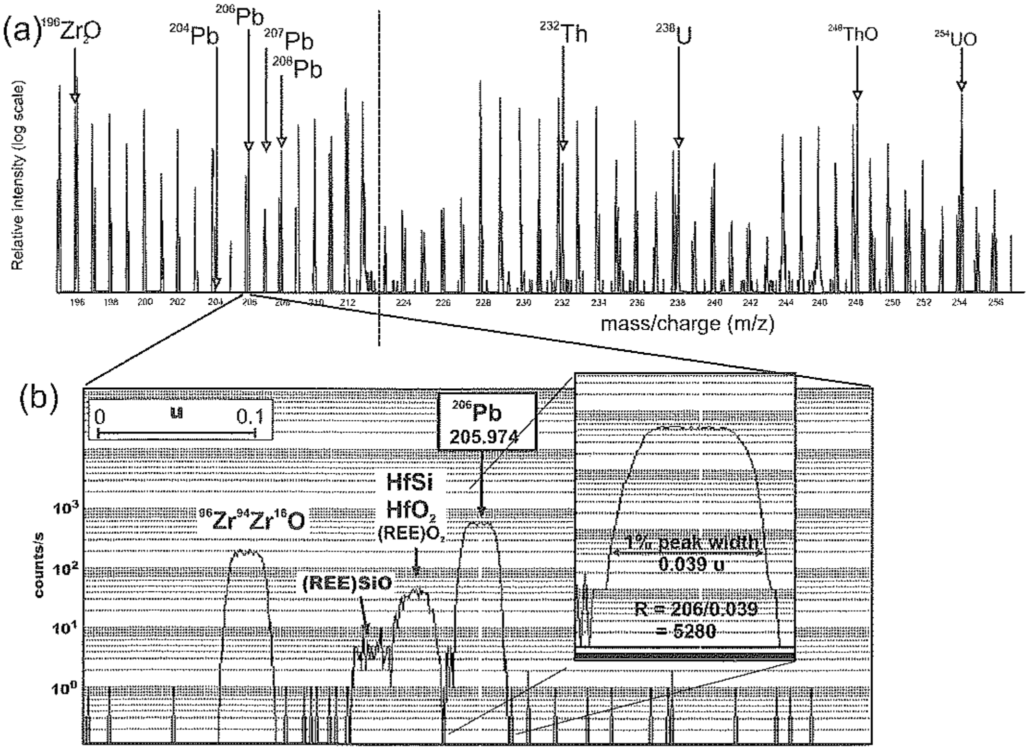

FIG. 1-4. Zircon ($ZrSiO_4$) positive secondary ion mass spectrum using primary $^{16}O^-$ (SHRIMP II ion microprobe). (**a**) 195–255 u, highlighting ions of interest in U–Pb geochronology; (**b**) detail of region near 206 u, adequately resolved from nearby isobars containing Zr, Si, REEs, and Hf.

1968). This analyzer includes the magnetic and electrostatic sectors, various electrostatic lenses, stigmators and deflection surfaces, and beam limiting slits and apertures, all in various complex ion optical arrangements. The device which does the 'heavy lifting' is the magnet sector, and as a general rule, the larger its radius, the higher will be the routine working mass resolution and usually also the transmission and sensitivity of the instrument. For example, magnet radii are 0.5–1.3 m for high resolution instruments and 0.1–0.2 m for low resolution instruments. The electrostatic sector, which precedes the magnetic sector in conventional designs and is used for energy dispersion, has a variable radius (0.1–1.2 m), depending on the ion optical design.

Most types of quantitative analyses occur with the secondary ion focusing being astigmatic, meaning that the relative lateral positions of the ions generated immediately at the sample surface within the footprint of the probe are not preserved at the detector. Astigmatic focusing allows for maximum ion transmission, and usually optimal mass resolution. Note that for scanning ion imaging, astigmatic focusing is used, but additional measures are taken to reduce spatially related variations in ion yields. For IMS instruments, the option exists to use direct ion imaging (stigmatic focusing), using a large diameter primary beam, with the advantage of 'live' ion images at about 1 μm spatial resolution, but this is generally at the expense of sensitivity and mass resolution. The field of view for SIMS imaging, whether direct or scanning, is typically <300 μm, but lateral variations in secondary ion signals due to instrument artifacts are difficult to avoid beyond a ~100 μm field of view.

Detection systems comprise one or more (in a multi-collector apparatus) electron multipliers and Faraday cups, and may include a microchannel plate, a spatially sensitive type of electron multiplier used in ion microscopy. Due in part to the low rate of sample consumption during sputtering, secondary ion signals are typically weak (*e.g.*, $<10^6$ counts per second), and the electron multiplier detector is preferred due to its high signal to noise ratio and fast dynamic response. In some instances of analyzing major isotope species in geological materials, secondary ion signals are sufficiently intense to warrant the use of a Faraday detector. The detection limits for electron multipliers are governed by the background count rate, which is a combination of the electronic noise ('dark counts') of the detection system, scattered ions within the mass spectrum, and tailing from other species. As an example, assuming a background count rate of $0.1\ c.s^{-1}$ for $^{206}Pb^+$ for a 1 nA primary beam, and a sensitivity of $20\ c.s^{-1}ppm^{-1}nA^{-1}$, this would calculate to a detection limit of about 15 ppb for Pb in the sample. Detection limits are highly variable depending on the element, target, and analytical conditions.

For all instruments, the desire is usually to collect, transmit, and detect as many secondary ions as possible within the given sputtering time interval selected, typically seconds, but varying widely. The high 'sensitivity' of the high resolution ion microprobes essentially refers to the high fraction of ions transmitted at a specified mass resolution (*i.e.*, elemental **sensitivity**), but these instruments also have relatively high **abundance sensitivity**. Abundance sensitivity refers to the ability to measure a faint isotope adjacent to an abundant one, and is a reflection of peak 'tailing' (broadening) caused by scattering of secondary ions. Abundance sensitivity (10^{-8} to 10^{-9}) can be optimized by the use of additional energy filters, including retardation lenses (De Laeter & Kennedy 1998) and electrostatic sectors (Saxton *et al.* 1996). In practical terms, ratios up to 10^6 are possible to measure with SIMS, largely determined by abundance sensitivity, prohibiting analysis of rare isotope isotopes such as ^{14}C or ^{36}Cl.

Small geometry, double focusing, magnetic sector ion microprobes/microscopes such as the Cameca f-series (*e.g.*, Fig. 1-3b) are highly versatile, all-purpose instruments suitable for many types of elemental and isotopic analyses in geology that require low to moderate mass resolution, or in high resolution applications in which the precision requirements are relatively modest. For some light isotopes (*e.g.*, $^{18}O/^{16}O$), uncertainties of about ±0.5‰ are possible. Analysis of ions of higher mass and lower abundance with such instruments becomes less favorable, particularly for metallic elements that have intrinsically low secondary ion yields (*e.g.*, Ti^+, La^+, Pb^+). Spectral interferences also tend to become more problematic with increasing mass. With the small geometry instruments, there may be need to employ the energy-filtering technique to remove the interferences from complex molecular ions and reduce matrix effects, but always with a significant reduction of secondary ion transmission (Shimizu *et al.* 1978, Zinner & Crozaz 1986, Benninghoven *et al.* 1987). A significant disadvantage with the small instruments is that the small radius magnetic sector severely limits the capabilities in parallel ion detection, despite newer instruments fitted with dual Faraday detectors. Despite these drawbacks, these instruments remain workhorses for geochemistry.

The limitations associated with small geometry ion microprobes are to a large extent removed with the SHRIMP and Cameca high resolution ion microprobes (Fig. 1-3a, c, d), which can routinely operate at a mass resolution up to 5000–8000 with flat-topped peaks, sufficient for a wide range of isotope ratio measurements in geology. As indicated, a significant advantage is the capability of multiple ion collection, with 5 or more detectors possible. The NanoSIMS instrument, for example is superbly suited to multicollection due to its Mattauch-Herzog ion optics, yielding a long focusing locus upon which the various detectors can be moved. In total there are about three dozen high resolution ion microprobes in various university and government laboratories around the globe, with two or three new ones sold annually. The disadvantages of such instruments are mainly their expense and complexity.

Samples

The one problematic aspect of SIMS compared with some other probe techniques is that there is usually more effort required to prepare the sample, as attention to detail can be quite important. Secondary ion yields are sensitive to local topographic and electrostatic features of the sample mount, and controlling these parameters is particularly important for high precision and high accuracy types of analysis and reducing imaging artifacts. Furthermore, for isotopic analyses, reference materials must be co-mounted with the unknowns in order to eliminate any potential differences between different mounts. This means that such reference materials are consumed in small amounts with each mount made, as they are seldom recovered.

An important consideration in conducting geological SIMS analysis is to determine whether it will occur *ex situ* or *in situ*. Most SIMS analyses are, in fact, *ex situ*, meaning that the mineral has been removed from the rock matrix. *In situ* analysis, although loosely used to refer to any type of probe analysis of a solid, is used here to refer to analysis of the mineral as it occurs in place within the rock matrix (*i.e.*, typically a polished thin section). Whether *ex situ* or *in situ* analysis, or both, is required principally depends on the nature of the scientific problem, but secondary factors such as cost effectiveness also play a role. Many people when first presented with the opportunity to conduct SIMS analysis assume that the easiest way to tackle the problem is *in situ*, as commonly done with the electron microprobe. Generally, *in situ* analysis is used only where context is critical or where the mineral cannot be easily removed from the rock matrix. The main disadvantage of *in situ* analysis is that one *in situ* mount may not provide a suitable number or type of the mineral being investigated. It is also more difficult to prepare *in situ* mounts with co-mounted reference materials, which is necessary for any work involving sub-percent level uncertainties.

Samples must be compatible with high to ultra-high vacuum and, if possible, be exposed as micrometre-flat surfaces. SIMS mounts are usually circular (1.0–2.5 cm diameter), and typically comprise either mineral separates embedded in epoxy, or grains pressed into a soft metal such as gold or indium (Fig. 1-5a). Thin sections may also be used, or cores from thin sections may be extracted from selected regions of thin sections and re-mounted in the more convenient circular forms. For some special samples, transmission electron microscope grids may be suitable, and even individual, ultra-small grains sprinkled onto a conducting surface are acceptable. As mentioned, samples are normally coated with conductive films, although for very weak primary beams it may not be necessary if the substrate is conductive.

The operator has a low resolution, magnified view of the sample surface in reflected light to permit accurate placement of the probe, aided in some of the Cameca instruments by secondary ion or (sputtering-induced) secondary electron imaging of the sample. In all circumstances, scanning electron microscope (SEM) characterization of the samples is essential, usually using backscattered or secondary electrons, and cathodoluminescence (Fig. 1-5b). The importance of thorough sample characterization prior to and after SIMS cannot be overstated.

Spatial Considerations

SIMS is currently the most powerful analytical tool for high spatial resolution geochemical and isotopic analyses. Examples of probe pits made in isotopic ratio analysis are shown in Figure 1-5 (b, c). Modern instrumentation is essentially reaching the theoretical limits of lateral spatial resolution during sputtering, which is about 10 nm, and depth resolution in dynamic SIMS is

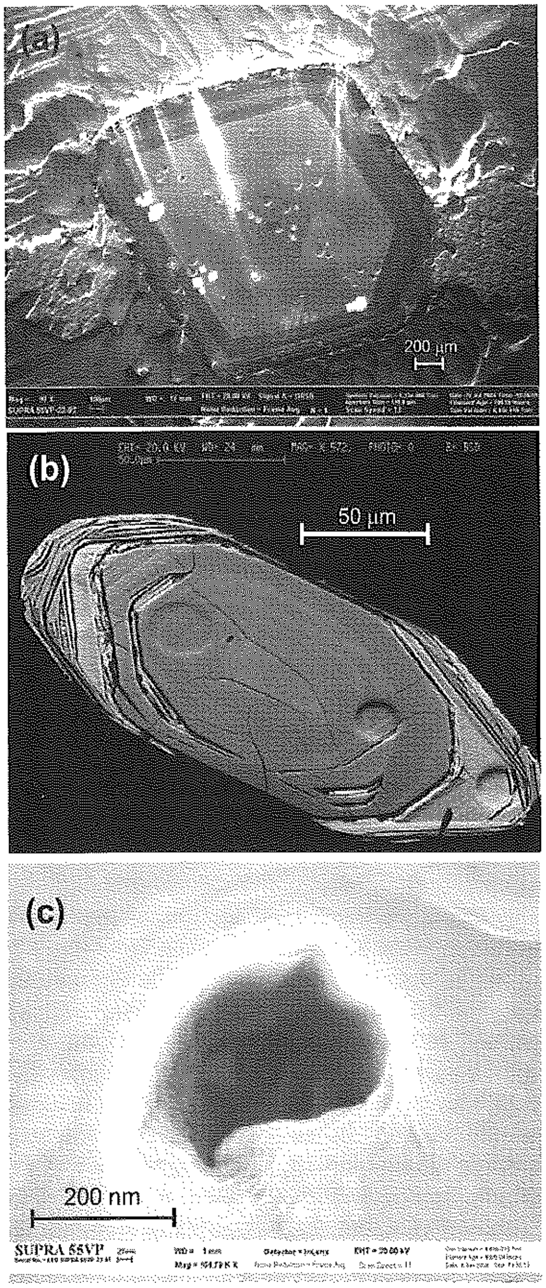

FIG. 1-5. Scanning electron microscope images of ion probe samples. (**a**) Backscattered electron image of a polished diamond embedded in indium and coated with gold for SIMS analysis. Circular ion probe analysis pits are visible. Bright areas are due to charging where Au has been removed. (**b**) Backscattered electron image of 15–25 µm x 1 µm pits in zircon sputtered with an $^{16}O^{-}$ probe; (**c**) ~200 nm diameter pit in diamond sputtered with a $^{133}Cs^{+}$ probe, secondary electrons.

similar but can literally be the thickness of an atomic layer under static SIMS conditions. However, higher spatial resolution comes at the price of analytical uncertainty, so in practice one selects the largest lateral and depth resolution that will suit the purpose, within the constraints of the instrumentation. For dynamic SIMS, typical working lateral spatial resolution would be 0.1–30 µm, and depth resolution <5 µm.

It is important to keep in mind the spatial dimensional options that may be available with the instrumentation:

a) Point source analysis, in which the primary beam is held on the target for seconds to minutes, sampling a disk-shaped volume of mineral (*e.g.*, Chapters 2–6, this volume). This is by far the most common type of analysis conducted in geology, and is used for determining elemental or isotopic compositions of minerals whose structural or compositional heterogeneity is exposed in cross-section. Because the total analysis depths are rarely more than a few micrometres, heterogeneity normal to the surface is usually undetectable. The analysis represents the average composition of the entire volume sputtered, which is typically 10^{-10} to 10^{-9} g (*i.e.* pg to ng).

b) Depth profiling (in depth) analysis, whereby the heterogeneity of the sample is parallel to the near-surface region (*e.g.*, Chapter 7, this volume). This type of analysis is a variation of the point source scheme whereby the data acquired during sputtering of a cylinder are subdivided during data processing into many small time (= depth) increments rather than integrating over the whole. Total depth may be greater than point source work, *e.g.*, 5–10 µm. This is the method employed when the highest spatial (depth) resolution is required for the analysis of grain outer surfaces that are too thin to be analyzed in section. The depth resolution is limited by the uniformity of the beam density of the probe and the amount of sample required to achieve the desired analytical precision.

c) Line scan analysis, in which the primary beam is moved in a straight line relative to the sample (or *vice versa*) for determining compositional variations across a suspected region of heterogeneity. For quantification, the line comprises closely spaced point source analyses. In fact, this type of analysis is not very common in geosciences applications.

d) Ion imaging, whereby compositional information is determined over a two dimensional region, either using a stationary and defocused primary beam (direct ion imaging) or a finely focused primary beam scanned across the region (scanning ion imaging). Scanning ion imaging is the technique of choice for quantitative analysis, and particularly isotopic ratio analysis.

e) 3-D imaging, is an extension of ion imaging, as a collection of discrete horizontal slices.

Data Essentials

The fundamental unit of data acquired during SIMS analysis is a measurement of the mean secondary ion count rate within a given sputtering time interval, essentially the point source analysis in the previous section. Raw count rates, or even simply counts, may be used for qualitative evaluations, such as in ion imaging of large compositional variations. But individual count rates are subject to many potential analytical artifacts, and so, for quantification, only pairs of isotope count rates are used. The secondary ions may be atomic or molecular species, and may belong to the same element (${}^{i}S_x/{}^{j}S_x$, *e.g.*, ${}^{13}C^-/{}^{12}C^-$) or different elements (${}^{i}S_x/{}^{j}S_y$, *e.g.*, ${}^{140}Ce^+/{}^{28}Si^+$, ${}^{140}Ce^+/{}^{172}YbO^+$). Data of the former are typically referred to as an 'isotope ratio' analysis, and the latter, an 'element ratio' analysis. Isotope ratios are considered the most powerful data for modeling and quantifying geological processes and reservoirs. Element ratio analyses, and derived absolute (*e.g.*, ppm Ce) or relative (*e.g.*, Ce/Yb) elemental abundances, typically provide complementary geochemical information.

For abundance determinations, quantification usually is based upon normalizing the element of interest (as an atomic or molecular secondary ion) to a matrix element, and comparing it to the same ratio in a reference material of known composition:

$$^{\mathrm{meas}}({}^{140}\mathrm{Ce}^+/{}^{28}\mathrm{Si}^+)_{\mathrm{unk}} \,/\, ^{\mathrm{meas}}({}^{140}\mathrm{Ce}^+/{}^{28}\mathrm{Si}^+)_{\mathrm{ref}} = {}^{\mathrm{true}}\mathrm{Ce}_{\mathrm{unk}} \,/\, {}^{\mathrm{true}}\mathrm{Ce}_{\mathrm{ref}}.$$

In the above case, solving for ${}^{\mathrm{true}}\mathrm{Ce}_{\mathrm{unk}}$ (*e.g.*, Ce $\mu g\ g^{-1}$) is straight forward, under the assumption that the matrix and analytical conditions for unknown and standard are the same, and the ${}^{140}Ce^+/{}^{28}Si^+$ is linearly related to Ce abundance. Similarly, for element ratios,

$$^{\mathrm{meas}}({}^{140}\mathrm{Ce}^+/{}^{172}\mathrm{YbO}^+)_{\mathrm{unk}} \,/\, ^{\mathrm{meas}}({}^{140}\mathrm{Ce}^+/{}^{172}\mathrm{YbO}^+)_{\mathrm{ref}} = {}^{\mathrm{true}}(\mathrm{Ce/Yb})_{\mathrm{unk}} \,/\, {}^{\mathrm{true}}(\mathrm{Ce/Yb})_{\mathrm{ref}}\,.$$

In the above case, the equation is solved for ${}^{\mathrm{true}}(\mathrm{Ce/Yb})_{\mathrm{unk}}$.

Elemental and isotope ratio data are affected by random and systematic errors. Random errors are dominated by counting statistics, which are constrained by the total number of ions detected in pulse-counted electron multiplier detector (EM) systems, or the signal/noise ratio in Faraday (FAR) detection. Many potential sources of systematic error may cause the measured elemental and isotopic ratios to be different than within the sample, (*e.g.*, discrimination and instrumental mass fractionation (IMF), respectively). Element discrimination can be relatively large, in comparison to IMF. In both cases, there is complete reliance upon independently characterized reference materials, matrix-matched and analyzed along with the unknown. In SIMS isotope ratio analysis, it is common to determine IMF by measuring the ratio of interest within a reference material and then apply a fractional correction to the unknown ratio. For example, for the reference material,

$$\alpha = {}^{\mathrm{meas}}({}^{13}\mathrm{C}^-/{}^{12}\mathrm{C}^-)_{\mathrm{ref}} \,/\, {}^{\mathrm{true}}({}^{13}\mathrm{C}/{}^{12}\mathrm{C})_{\mathrm{ref}},$$

where α is the fractionation factor. The IMF is commonly expressed as a % or ‰ deviation, as in:

$$\mathrm{IMF}\ (‰) = 1000 * (1 - \alpha).$$

To correct the unknown for IMF,

$${}^{\mathrm{true}}({}^{13}\mathrm{C}/{}^{12}\mathrm{C})_{\mathrm{unk}} = {}^{\mathrm{meas}}({}^{13}\mathrm{C}^-/{}^{12}\mathrm{C}^-)_{\mathrm{unk}} \,/\, \alpha$$

Only in a minority of cases in ion microprobe isotopic analysis the ideal case exist of assessing IMF by simultaneous measurement of another ratio of the same element that has a fixed (known) composition (*i.e.*, 'internal fractionation correction,' Stern 1998). For external fractionation correction, as described above, it is not necessary to know the detailed behavior of fractionation, only the magnitude, and make the assumption that it is identical to the unknown. Of course, this approach is only valid if the identical ratios are measured in the reference material and unknown, as any extrapolation to other mass ranges would require an understanding of the fractionation systematics. The IMF may range from undetectable for isotopes of heavy elements, to several % u^{-1} for lighter elements.

Most high precision ion microprobe isotope ratio analyses are limited not by counting errors, but by systematic errors, mainly estimating and controlling IMF. The IMF may have spatial and temporal components. It is often found that the standard deviation of replicate isotope ratio analyses of the reference material greatly exceeds the uncertainties of the individual analyses. In other words, the reproducibility (often termed 'external error', but unambiguously, 'spot-to-spot' uncertainty) is often much worse than the calculated uncertainties would lead us to believe. For SIMS, the spot-to-spot uncertainty is, under ideal conditions, no less than about ±0.1‰ (95% confidence level), and more typically it could be 2–10x times this value. It is very common for a number of individual SIMS analyses to be pooled to increase analytical precision. To some extent this defeats the spatial resolution of the analysis, in that one now effectively has sampled a greater total mass of material. Also, it is implicit in aggregate results that the analyses are from isotopically homogeneous material. Although such an interpretation may be consistent with statistical tests, such as the **mean square of weighted deviates**, the precision of the individual analyses may conceal isotopic heterogeneity. Further detail on statistical approaches to SIMS can be found elsewhere (*e.g.*, Fitzsimons *et al.* 2000).

Isotope ratio analysis is usually done with a stationary small probe to optimize counting statistics on specific regions of complex targets. Scanning ion imaging normally requires the presence of % level or higher abundances in the solid, as the counting statistics otherwise become unacceptable. For isotopic analysis, there may be lateral variations in IMF. Nevertheless, the ability to perform two-dimensional isotopic mapping is a relatively new and powerful capability in geological sample characterization.

Applications and Limitations

Applications of SIMS in geochemistry and cosmochemistry are extremely diverse, and involve determinations of elemental abundance, and elemental and isotope ratios. Most applications in geology tend to be in one or more of the following categories:

1. Trace element analyses
2. Light **stable isotopes** (u < 50)
3. U–Th–Pb geochronology
4. Geochemistry and geochronology of extra-terrestrial samples

SIMS is the technique of choice for the ability to conduct mass spectrometry at the finest lateral and vertical resolution possible (Fig. 1-5 b, c). An abundance or isotopic measurement is possible from a cylinder ~50 nm in diameter and depth, which is as little as 10^{-15}–10^{-16}g (1–0.1 fg) of material consumed. In some cases, statistically significant results can be achieved with as few as 100 counts, and with a typical useful yield of 10^{-3}, can be achieved by sputtering only 10^5 atoms. Point source analyses are the most common, followed by ion imaging and depth profiling.

SIMS is not a universal analytical tool for geochemistry, particularly in the context of complementary technologies that are now available, such as laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) and electron probe microanalysis (EMPA). For instance, although SIMS has particular strengths in trace element quantification due to its inherently low backgrounds and adequate sensitivity for many elements, it is seldom used for quantification of major and minor elements due to matrix effects. Nevertheless, major and minor elements are commonly analyzed in the course of ion imaging (*e.g.*, Fig. 1-6), where the spatial resolution of the ion probe can be superior to the X-ray based EPMA methods (Badro *et al.* 2007, Bland *et al.* 2007). The determination of rare earth elements (REE) and many others in minerals has historically been one of the strengths of SIMS, and remains an important technique using either the energy-filtering technique or high mass resolution (*e.g.*, Bebout *et al.* 2007, Grimes *et al.* 2007). Element abundances and ratios generally have uncertainties of the percent to tens of percent level, depending on many factors.

The greatest strength of SIMS is in isotope ratio measurements, and ion microprobes in various configurations can be utilized for applications covering a wide range of stable isotopes (*e.g.*, H, Li, B, C, N, O, Si, S, Cl, Ca, Cu) and others related to radioactive decay (parent–daughter) systems (*e.g.*, Al–Mg, Mn–Cr, Fe–Ni, U–Pb, Th–Pb, U–Th, Hf–W). The limitations of SIMS in isotopic analysis depend on a number of factors, including concentration in the sample, secondary ion yields, spatial resolution, presence of isobaric interferences, and analytical uncertainty desired. SIMS cannot be used to analyze materials where there exists a significant atomic isobar, such as ^{46}Ca at ^{46}Ti, ^{87}Rb at ^{87}Sr, ^{176}Lu at ^{176}Hf, ^{187}Re at ^{187}Os. Where there are minerals devoid of the parent isotope, then tracer isotopic measurements are possible (*e.g.*, Pb isotopes), as long as the application does not demand very high analytical precision (see Stern 1998).

The ability of SIMS to perform isotopic analyses on tiny quantities of matter introduces a major limitation, as it is not a method for applic-

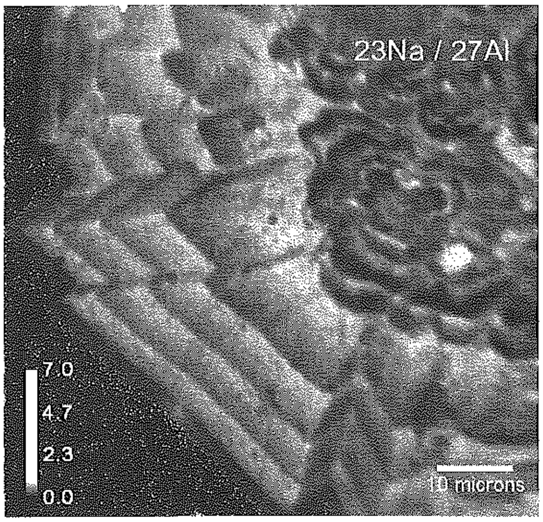

FIG. 1-6. Scanning ion image (NanoSIMS 50, with primary $^{16}O^-$) of an Al hydrate mineral (gibbsite), showing zoning in the minor element, Na, as represented using the raw $^{23}Na^+/^{27}Al^+$ ratio. The ratio has not been corrected for discrimination.

ations requiring the highest analytical precision and accuracy. Typically, SIMS secondary ion signals are relatively weak due to the small numbers of atoms actually sampled, requiring the use of electron multiplier detectors that introduce artifacts in the data that ultimately limit the achievable analytical uncertainties. Some high resolution ion microprobes with multiple Faraday detectors are capable of analytical uncertainties of ±0.1‰ (95% confidence) for individual measurements of some stable isotopes of major elements (*e.g.*, oxygen). Nevertheless, isotopic systems or applications routinely demanding uncertainties much less than 0.1‰ are impractical with SIMS, for example in measuring $^{143}Nd/^{144}Nd$, $^{176}Hf/^{177}Hf$, and "non-traditional" heavy stable isotopes (*e.g.*, Se, Fe, Cd, Zn). The limitation is related to the small ion currents typical of SIMS, difficulties resolving or peak-stripping isobaric interferences, and in controlling IMF.

SUMMARY

Geological applications were one of the motivations for the early development of the SIMS analytical technique, beginning more than 50 years ago, and now SIMS is routinely applied within a wide range of research areas. Over this period of time, numerous other probe technologies have emerged for the direct analysis of solids, especially electron- and photon-based methods, and in particular EPMA and LA–ICP–MS (*e.g.*, Sylvester 2008) have also become essential within the geochemical toolkit. Rather than the universal analytical instrument perhaps once envisioned, SIMS has a distinctly complementary role, as the technique of choice when the highest spatial resolution is demanded for trace element and isotopic analysis. Ion imaging, conceived very early on in SIMS development, is re-emerging as a powerful capability. Interest in mineral surface chemistry and the recognition of static (*e.g.*, TOF) SIMS as a molecular fingerprinting tool is also beginning to catch hold. In the chapters that follow, the analytical power of SIMS in geochemistry and cosmochemistry is amply demonstrated through a range of contemporary techniques and applications.

ACKNOWLEDGMENTS

The manuscript benefitted from a review by Mostafa Fayek.

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GLOSSARY

Definitions are the author's, and from various sources mentioned in the Introduction and elsewhere (ISO 1993, IUPAC, McNaught & Wilkinson 1997).

Abundance sensitivity: a measure of the ability of a **mass analyzer** to detect a small peak adjacent to a larger one.

Analyte: in the context of SIMS, the atom or molecule within the solid being analyzed.

Atomic mass unit: symbol, u, is equivalent to the mass of 1/12 the mass of the ^{12}C atom.

Cluster (ion): as used in SIMS, can also be referred to as a **molecular fragment**, generally implying molecular ions having an 'artificial' configuration, *i.e.*, not present originally in the target, as in $Zr_2Si_2^+$ in zircon ($ZrSiO_4$). The inference is often that the molecule has formed through some process of ion generation, either by combination or fragmentation. For **dynamic SIMS**, all molecular ions are presumably of this type, whereas for **static SIMS**, there may be intact molecules. On the whole, the term **molecular ion** is sufficient for most purposes without implying a genetic mechanism.

Collision cascade: the 'billiard ball' process of transferring kinetic energy from an impacting atomic or molecular ion to the atoms of a target via a succession of elastic atomic displacements. See Figure 1-2.

Depth profiling: also referred to as 'in-depth' analysis, in which the composition of a target is progressively measured with time, *i.e.*, normal to the sample surface.

Detection limit: the minimum level that can be distinguished from background, which is typically taken as 3 standard deviations of the background count rate; in physics and materials science applications of SIMS, detection limit units are atoms cm^{-3}, and the range is generally 10^{12} to 10^{16} atoms cm^{-3} (roughly ppb to ppm range).

Dimer: a molecule that includes only two of the same element, as in Si_2^+; monomer, trimer, and tetramer have also been used. As an adjective, has been used to describe more complex molecules, *e.g.*, dimeric niobium pentoxide $Nb_2O_5^+$.

Direct ion imaging: the technique of stigmatic focusing of secondary ions onto a spatially sensitive detector for live imaging of the distribution of secondary ions across a surface. Compare with **scanning ion imaging**.

Discrimination: often used to refer to the effect of SIMS analysis in biasing the element/element ratios from the true values in the sample, due to inherent differences in secondary ion yields and the specific analytical conditions employed.

Double focusing (mass analyzer): permits focusing of an ion beam of single mass/charge that has initially inhomogeneous angular (beam spread) and chromatic (= velocity) aberrations. Requires appropriately configured magnetic and electrostatic sectors to allow the directional and velocity loci of the mass analyzer to coincide.

Duoplasmatron: a device for generating primary ions, comprising a two-stage, magnetically confined plasma discharge.

Dynamic SIMS: a branch of SIMS conducted with a high density primary beam, whereby the upper layers of the target are continuously and thoroughly saturated with primary ions, and the sputtered material is a highly structurally and chemically modified version of the original.

Energy filtering: an analytical technique whereby ions are selected on the basis of kinetic energy; in many cases, high energy ions are preferentially selected to reduce matrix effects and isobaric interferences.

Fragment (ion): see **cluster**.

Instrumental Mass Fractionation (IMF): bias in an isotope ratio measurement (in ‰ or %), related to the isotope species, the sample, and the analytical method, determined from comparing a measured value to its independently determined ('true') value; often, it is assumed that IMF is systematically mass-dependent (*e.g.*, $\%\ u^{-1}$), but this may not be correct in all cases.

In-depth analysis: equivalent to **depth profiling.**

Ion: an atom or molecule having a net positive or negative charge, as in atomic ion or **molecular ion.**

Ion Yield: number of ions of a particular type sputtered per primary ion impact; may also refer to the ratio of two secondary ions; may also refer qualitatively to the relative intensity of the ion signal.

Isobars: nuclides having nominally equivalent mass numbers (within the resolution of the instrument); strictly speaking isobars are atoms, although in SIMS it is also often used to refer to a molecule.

Isotopes: nuclides having the same number of protons (atomic number), but different number of neutrons, as in ^{12}C and ^{13}C.

Matrix effects: the combined influences of the sample and the sputtering conditions on secondary **ion yields**. Important factors relating to the atom(s) of interest include ionization potential, and chemical, electronic, and structural environment during sputtering.

Mean square of weighted deviates (MSWD): a statistic where the value quantifies the overall extent to which the individual values used to calculate a mean are actually likely to be measurements of that mean. Also termed the 'reduced chi-squared value.' A value near 1.0 is ideal. Values much less than unity usually indicate that individual uncertainties are too large, while values much greater usually indicate the sample is heterogeneous, or the individual uncertainties are underestimated.

Mass analyzer: an assembly that permits ions of uniform mass/charge (m/z) ratio to be separated from others of slightly different m/z.

Molecular ion: a molecule with one or more electrons lost or gained; see **cluster**, **fragment**.

Monolayer: a single layer of atoms or molecules, often referring to the topmost layer of a surface under vacuum.

Nuclide: a type of atom characterized by its mass number, atomic number, and nuclear energy state.

Primary (ion) beam: an electrostatically focused beam of **ions** that form the probe in SIMS.

(mass) Resolution: R, is *the inverse fractional mass separation of resolved peaks*, that is, the peaks are sufficiently separated such as not to influence a count rate determination. It is quantified from the observed mass spectra. There are several methods of calculating R. The mass-to-base-width ratio (*i.e.*, $M\,\Delta M^{-1}$ in atomic mass units, u) at a specified fraction of peak intensity is common, *e.g.*, at R = 5000, isotopes differing in mass by 1/5000 = 0.02% are considered resolved. Qualitatively, resolution can be described as low (<1000), medium (1000–3000), and high (>3000).

Radiogenic isotope: a nuclide derived from a **radionuclide**; it may be stable, or itself be a radionuclide.

Radionuclide: a radioactive nuclide (*i.e.*, undergoes nuclear decay).

(mass) Resolving power: equivalent to **mass resolution**, however some commercial SIMS software may use this term according to a different definition; check definitions when comparing performance.

Reference material (RM): in SIMS, a solid in which elemental or isotopic composition has been determined by independent analytical methods to specified limits, and is used for calibrating instrumental bias, assessing a measurement procedure, or assigning measurement uncertainties to the procedure. Ideally for SIMS, the RM is homogeneous at the micrometre scale, but many do not comply or have not been proven. The term 'standard' is commonly used in geology, but the term is imprecise, ambiguous, and is not equivalent to RM (ISO 1993), as a 'measurement standard' is for calibration only.

Scanning ion imaging: refers to the technique of incrementally moving a finely focused primary ion beam across the surface of the target in two dimensions, in order to determine spatially related secondary ion intensity variations; this is the imaging technique preferred for quantitative ion microscopy.

Secondary (ion) beam: the electrostatically and/or magnetically focused beam of ions derived from sputtering.

(elemental) Sensitivity: a figure of merit in SIMS relating the count rate of a particular secondary ion normalized to the abundance in the target and the primary beam current. See also **abundance sensitivity**.

SIMS: secondary ion mass spectrometry

Sputtering: ejection of atoms and molecules (often referred to as 'clusters' in dynamic SIMS) from a surface bombarded by a flux of ions. The particles may be neutral, positive, or negatively charged.

Stable isotope: a nuclide that is not radioactive, *i.e.*, not decaying to form another nuclide. Note that stable isotopes may also be **radiogenic isotopes**, but in isotope geochemistry, stable isotope normally refers to ones that are not part of any radioactive decay series.

Static SIMS: a branch of SIMS conducted with an extremely low density primary beam that permits sputtering of the undisturbed monolayer at the surface; the local environment of the sample is impacted by only one primary ion, and the total ion dose over a region is $< 10^{13}$ cm^{-2}.

Surface binding energy: the energy required to remove an atom from the top surface layer in vacuum during sputtering.

Total sputter yield: total number of all particles sputtered per primary ion impact (atoms/ion).

Useful Yield: the number of measured secondary ions of a particular atom per second, normalized to the total number of sputtered atoms (of the same type) per second (ions/atom); in some usages, it is defined as the number of detected atoms per atoms in target.

Ultra-high vacuum: an arbitrary range of gas pressure conditions, generally 10^{-12} < pressure < 10^{-9} mbar (1 mbar = 100 Pa = 0.75 Torr).

Very high vacuum: an arbitrary range of gas pressure conditions, generally 10^{-9} < pressure < 10^{-6} mbar.