SECONDARY-ION MASS SPECTROMETRY 
AND GEOLOGY

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ABSTRACT

Secondary-ion mass spectrometry (SIMS) is the marriage of traditional mass spectrometry with microanalytical in situ surface analysis. Ions produced by selective sputtering of the topmost layers of a sample by a focused primary beam of particles may be areally mapped or quantitatively analyzed. In the absence of a general workable model for sputtering and ionization, quantification is empirical, based upon isotopes implanted for calibration or, more generally, upon homogeneous and well characterized mineral and glass standards. Nevertheless, sensitivity for most elements is in the low ppb range. The early part of this review presents the salient features of the technique, notes the limitations of each mode of use, and provides references to the literature for further reading. In the latter pages, a number of geological applications are briefly described. With their selection, the intent has been to "whet the appetite" of potential users and not to attempt an exhaustive account of the many excellent applications to problems in geochemistry and cosmochemistry.

Keywords: secondary-ion mass spectrometry, ion microprobe, micro-analysis, geochemistry.

INTRODUCTION

The term "secondary-ion mass spectrometry" (SIMS) subsumes a variety of methods, all of which are based upon the analysis of ions emitted from the surface layers of a sample by the in situ bombardment with energetic primary particles. Mass spectrometry has long been successfully applied to the analysis of bulk samples. However, by being coupled with a mechanism to selectively volatilize or sputter small volumes of sample, it has also become a surface analytical technique.

In 1975, John Lovering wrote: "Clearly the elegant capabilities of the SIMS microanalytical technique, when fully developed, should provide the chemical geologist with a single instrument which approaches the concept of an "ultimate weapon" as far as in situ microanalytical capability is concerned."

Primarily owing to the chemical complexity of geological samples, geochemical applications have lagged far behind those in the semiconductor industry. Nevertheless, the potential to supply very low currents of secondary ions without background noise and quantitative elemental data to low ppm and ppb levels for virtually all the elements of the periodic table, to provide isotopic compositions for age dating or diffusion studies, and to produce high-resolution isotopic-distribution images of geological samples has kept SIMS a rapidly developing analytical technique.

It is not the aim of this paper to review the historical development of SIMS or to fully describe the various configurations of the instrument. Whereas some
aspects of the topics are included, it is my primary aim to highlight current geological applications of SIMS.

**Sputtering and Ionization**

In SIMS, the primary particles may be neutral, protons or electrons, but most commonly are ions. Bombardment of a sample by energetic atoms or ions initiates a complex sequence of events, many of which are not yet quantifiable. Primary among them is the simple "billiard ball" or "knock-on" type of collision, in which some energy is lost by electrostatic excitation, but most is transferred from the primary particle to the impacted surface. Sputtering is the process of particle emission from the bombarded sample (Fig. 1). The sputtering activity may be schematically pictured as a succession of individual events, and the time to complete each event is in the order of $10^{-14}$ to $10^{-12}$ s (Shimizu & Hart 1982). Thus, the sputtering produced by one primary ion is completed prior to the next primary ion hitting the sample surface. The induced activity of particles, which can take various forms, extends to about 10 nm into the sample surface. An excellent listing of the observed processes of sputtering is given by Betz & Wehner (1983). The existence of ionized particles in the sputtered products was first documented by J.J. Thomson (1910), but it was nearly four decades before SIMS instruments were built to measure these "secondary ions" (Ilerzog & Viebiick 1949).

As SIMS depends upon the analysis of sputtered ions, an understanding of the sputtering process is important. The simplest approach is the bond-breaking model, introduced by Slodzian (1975) and since extended by many workers (e.g., Wittmaack 1977, Slodzian 1982, Yu 1988, Williams 1990). This model was developed to illustrate ion emissions from ionic solids, based upon the premise that ground state and ionic state are equivalent. As a secondary ion moves, the distance between the ion and a ground state (or neutral) surface determines the probability of observing that atom (Vickerman 1989b). The bond-breaking model is too simple to express the true mechanism, but it is useful to illustrate the possible interactions.

Computer-simulation models (Gay & Harrison 1964, Harrison et al. 1966, Harrison & Delaplain 1976, Harrison et al. 1978) give us a better understanding of the dynamics of sputtering. Inherent to computer-simulation models to date are the assumptions that only atoms or atomic ions interact, and that only classical mechanics apply (Vickerman 1989b). Whereas the results prove very interesting and helpful, they are limited by the inability to illustrate electronic properties.

The local thermal equilibrium (LTE) model (Andersen & Hintborne 1973) takes a different approach. It is not based upon any specified mechanism of sputtering, but assumes that sputtering generates a plasma in thermodynamic equilibrium. Although supporting physical evidence is tenuous, their approach can semiquantitatively predict the yield of secondary ions from simple samples (Steele et al. 1981, Newbury 1980).

Progress in the development of theoretical models to predict sputtered-ion yields has been considerable, but the more accurate analyses are still based upon empirical comparison of data from unknowns and standards. Comprehensive reviews of models and processes by which particles are ionized are given by Vickerman (1989a), Sigmund (1984) and Williams (1979).

**Instrumentation**

Detailed reviews of the historical development of SIMS and detailed descriptions of SIMS instrumentation are given by Benninghoven et al. (1987), Evans (1972), Lodding (1988) and Lovering (1975). The first commercial SIMS instruments were built at GCA Corporation (Liebl 1967, 1974, Herzog & Vieböck 1949, Leibl & Herzog 1963), but not until after the development of a microanalytical capability (Castaing & Slodzian 1962) did they generate much interest. The choice of determined analytical conditions (density and energy of the primary ion current) allows the investigation of different depths within the sample area. For example, if it is the intent to examine only the surface monolayer, then a combination of a high vacuum and low primary-ion impact energy to produce a very gentle etching and minimal mixing of deeper layers is essential. Today's instruments are based primarily on the following two modes of operation.

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**Fig. 1.** Simplified illustration of the sputtering process showing emission of secondary particles induced by the collision of primary particles (from Vickerman 1987).
Static SIMS

Static SIMS (SSIMS) uses a beam of primary ions of sufficiently low current-density that the lifetime of a surface monolayer is of the order of hours. "Time-of-flight" mass spectrometry has been adapted to SSIMS very successfully. TOF–SIMS has the advantage of nearly simultaneous analysis of an unlimited mass-range, while retaining very high mass-resolution and spectrometer transmission. To date, this technique has been used mainly to examine polymers and peptides (e.g., Schwieters et al. 1992), but application to surface chemistry will increase in the coming years.

Dynamic SIMS

Dynamic SIMS uses a primary ion-current of sufficient density to rapidly erode the sample; the current density denoting the division between static and dynamic modes is $10^{-8}$ to $10^{-9}$ A/cm$^2$ (Benninghoven et al. 1987, Metson 1990). Most analytical studies in geochemistry use dynamic SIMS, as this produces quantitative bulk-analyses of minerals and glasses. Because the rate of erosion of the sample surface may be high, one obvious application of dynamic SIMS is depth profiling of element concentration.

The demand for data of both high resolution and high sensitivity in geological research has resulted in the choice of dynamic instruments incorporating a magnetic-sector mass spectrometer rather than a quadrupole analyzer. The principle is simply to pass ions through a region of constant magnetic field and thus separate them according to different masses. Whereas that basic arrangement has some capability of focusing, better resolution is obtained by incorporating an electrostatic analyzer ahead of the magnetic sector, thus achieving a "double-focusing" spectrometer (Benninghoven et al. 1987, Eccles 1989). The electrostatic field disperses ions of different energies, but not different masses, resulting in a spectrum with none of the degradation in resolution that is produced by simple energy-spread.

The popular CAMECA ion microscopes, and specifically their IMS series, are typical examples of double-focusing dynamic SIMS instruments available commercially (Fig. 2); despite the IMS designation,

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**Fig. 2** Schematic of the CAMECA IMS 3f ion microprobe–microscope (from Migeon et al. 1992).
these units may be operated in either microscope or microprobe mode.

Many types of particles are generated at the sample surface by the sputtering process, but it is the emitted (secondary) ions that are mass-analyzed. These typically constitute only 1% of the secondary particles (Metson 1990), and it is important to have as large a proportion of these as possible transmitted to the mass spectrometer. Documentation of transmission capability is difficult to obtain; however, Migeon et al. (1992) noted that the immersion-lens design of the CAMECA IMS–5f is capable of transmitting between 40 and 50% of the secondary ions.

**Quantitative Trace-Element Analysis**

The principal use of dynamic SIMS has never changed: the high-sensitivity analysis of a sample for elements present at ppm and ppb levels of concentration. The usual mode of operation is to raster a well-focused beam of primary ions over the sample, then accept for analysis only those secondary ions from a central area of the sputter crater. By reducing the scan area to "spot mode", bulk analysis of small sample volumes may be done. Coordinated erosion of the sample and collection of data over time produce a depth profile.

Contamination of the sample surface from careless handling is removed by sputter-cleaning immediately prior to analysis. Mass filtering of the primary beam removes any source impurities. Adsorption of molecules on the sample surface can be prevented with a well-maintained vacuum; residual hydride ions can be removed from the vacuum gasses with a "cold finger" inserted adjacent to the sample surface.

The use of positively charged primary ions to sputter an insulating target, such as a silicate mineral, will usually cause the surface of the sample to charge positively. The main consequence is that positive secondary ions are given sufficient energy to accelerate them past the acceptance energy of the analyzer (Vickerman 1989a). In the case of negative secondary ions, positive surface-charging can completely suppress them. Remedies include the use of negatively charged primary ions, neutral primary particles (called "fast-atom bombardment" or FAB), and flooding the surface with low-energy electrons (Vickerman 1989b, López et al. 1992, Blanchard et al. 1988).

There are several reasons why initial analyses will not represent the sample's bulk composition: (1) some elements are more readily sputtered than others (preferential sputtering), (2) isotope fractionation can occur during sputtering, and (3) particles from the primary beam are implanted into the sample. Some period of sputtering (normally of very short duration) is required before steady-state conditions are attained. These problems do not adversely affect bulk analysis, but may make the interpretation of very near-surface depth-profile data quite difficult.

Quantitative interpretation of secondary-ion intensities must deal with three problem areas: (1) the freedom from interferences of the measured peaks, (2) the sensitivity of ion yield to matrix composition, and (3) calibration procedures.

**Molecular Interferences**

The overlap of ionic species with the ion peak to be determined is a major problem, particularly with chemically complex geological samples. Early attempts to minimize the effects of multiply charged, polyatomic and complex molecular-ion overlaps in the spectra centered mainly upon peak-stripping routines (e.g., Colby 1975, Andersen & Hinthorne 1974). If the ion desired is roughly of the same order of intensity or greater than that of the overlapping molecular ion, the method is reasonably successful.

For the separation or elimination of mass interference, two methods are generally emphasized: (1) high mass-resolution, and (2) kinetic-energy filtering.

**High Mass-Resolution**: The aim of high-mass-resolution analysis is to measure sufficiently small differences in masses that nearly coincidental peaks are resolved. As examples, \(^{58}\text{Ni}^+\) may be resolved from the \(^{42}\text{Ca}^{16}\text{O}^+\) interference with a mass resolution \((M/\Delta M)\) of 3200, whereas 7500 is required to resolved \(^{153}\text{Eu}^+\) from \(^{137}\text{Ba}^{16}\text{O}^+\). To accomplish high mass-resolution, mass spectrometer slits or "windows" must be narrowed, thus greatly reducing the number of secondary ions processed (i.e., the recorded intensity), and thus sensitivity. Except for those instruments with very large mass spectrometers and efficient secondary-ion capture, the higher the resolution required, the lower the sensitivity.

**Kinetic-Energy Filtering**: All ions leave the sputtered surface of the sample with a certain kinetic energy. In most SIMS instruments, an additional potential difference is added to accelerate the ions from the sample surface. Figure 3 shows the intensities of a typical elemental ion and a typical molecular ion distributed about an accelerating potential of +4500 eV (relative to ground). An acceptance window of ±50 eV would thus admit all secondary ions with initial kinetic energies up to 50 eV.

Oxide (and other dimer) molecular ions (which would be particularly abundant in the case of a silicate or oxide sample bombarded with a primary beam of oxygen ions) have distinctively narrower energy-distributions than elemental ions (Fig. 3). By offsetting the accelerating potential from +4500 to +4200 eV (for example), only ions with initial kinetic energies between +250 and +350 eV will be admitted. As very few molecular ions fall in this range, they are effectively filtered out. However, secondary-ion intensities...
Fig. 3. Typical relative intensities of elemental ions and dimer molecular ions distributed about a 4500 eV extraction voltage, with an acceptance window of ±50 V. An identical acceptance window centered at 4200 eV (i.e., with an offset of 300 V) would effectively filter contributions from the molecular ions.

(and thus sensitivities) are decreased by this method, and it is recommended that distribution plots be constructed such that optimal accelerating voltage and windows be chosen. Effective removal of trimers (but not dimers) from the spectrum is accomplished with as little as -80 to -100 eV offset.

Whereas a moderate voltage-offset (termed CEF, or “conventional energy filtering”; see Shimizu et al. 1978, Crozaz & Zinner 1986) of -80 eV or -100 eV is normally adequate to eliminate most molecular-ion overlaps, it is not always sufficient, as in the case of heavy rare-earth elemental ions overlapped by the oxide ions of light REEs (Metson 1990). Computerized peak-stripping methods (Crozaz & Zinner 1986) or an extreme form of energy filter may then have to be used. One such filtering technique, called “specimen isolation” (SI), develops an offset of 500–600 eV through the use of a special specimen holder that keeps uncoated and insulating samples electrically isolated from the holder (Metson et al. 1983, McIntyre et al. 1985). The result is that a very large negative potential difference will quickly develop on the sample surface (under a beam of negative primary ions), filtering out virtually all molecular interferences. Intensities are maintained by using higher primary-ion currents.

Removal of molecular ion interferences by either kinetic-energy filtering or by high mass-resolution results in significant loss in intensity. A comparison of the two methods to find the option yielding least loss for a required resolution was done by Shimizu & Hart (1982). They developed a general rule of thumb, which recommends removal of molecular interferences by kinetic-energy filtering for elements above number 70; for lower masses, the use of high mass-resolution of 4500 or less results in higher sensitivity, and many instruments have that capability.

Matrix effects and calibration of ion yield

Yields of sputtered secondary ions of the same element are not necessarily linearly related to concentration in different matrices (Deline & Evans 1978, Shimizu et al. 1978, Steele et al. 1981, Shimizu 1986). A wide variety of crystal-chemical factors, atomic interactive processes and effects induced specifically by the bombarding particles are responsible. Matrix effects are well documented for major elements (e.g., Ray & Hart 1982, Shimizu et al. 1978, Steele et al. 1977, 1981), but for trace elements, they seem much less significant (Bottazzi et al. 1992, MacRae et al. 1993, Shimizu & Hart 1982).

As the secondary-ion intensity of an element must be a function of specific ionization process as well as concentration, several attempts to systematize matrix effects have been made (Havette & Slodzian 1980). As yet, theoretical models do not effectively predict ion yields for complex samples; most calibrations are thus an empirical process in which standards and unknowns
are very similar in composition.

The empirical approach suffers from a lack of standards. One solution is to implant or add to the sample's near-surface region a known quantity of the element(s) desired (Gries 1992). Implants may be done with the SIMS primary ion source (Smith et al. 1986), but these are of low energy and thus very shallow. More commonly, high-energy remote ion-accelerators are used to provide peak concentrations of dopant of about 100 nm into the sample (Leta & Morrison 1980). During subsequent analysis, the secondary-ion signal from the implanted quantity is readily distinguished from the quantity originally present on the basis of the characteristic shape (more or less Gaussian) of ion implantation (Leta & Morrison 1980). Although time-consuming and expensive, the technique has been applied to the analysis of lunar samples (Zinner & Walker 1975, Zinner et al. 1976) and to the determination of Au and Ag in sulfides (Chryssoulis 1990, Chryssoulis & Weisener 1990); it is a widespread practice in semiconductor work.

A number of difficulties are apparent in developing suitable standards among natural minerals, primary among them being sample inhomogeneity. One result has been extensive discussion and testing of secondary-ion yields from homogeneous glasses versus crystals of the same chemistry (MacRae et al. 1993, Bottazzi et al. 1992, Hinton 1990, Muir et al. 1987, Ray & Hart 1982). MacRae et al. (1993) tested secondary-REE-ion yields from crystalline and fused material of two amphiboles and three clinopyroxenes. Under conditions of CEF to suppress molecular-ion interferences by kinetic-energy filtering, the crystal/glass ion yields were approximately unity, consistent with the results for other materials and other elements (Hinton 1990, Bottazzi et al. 1992). MacRae (1987) also studied REE-ion yields for both crystal and glass in SI mode and concluded there was no significant difference; Muir et al. (1987) came to the same conclusion after a study of glass, crystal and ceramic for a variety of major and minor elements in both SI and CEF modes.

Whether by ion implantation, selection of homogeneous crystals or fusion of natural material, acquisition of accurate standards is essential to empirical calibration.

The precision of absolute ion-intensity measurement in a particular sputter crater by SIMS is subject to some variations with time, caused by such phenomena as sample flatness (Deng & Williams 1989). However, by measuring the ratio of the peak intensity of the element of interest to that of a major species in the matrix (such as $^{30}$Si$^{+}$ in silicates), precisions of a per mil or greater are expected. Certainly, precisions from ratio measurements rather than absolute intensities of secondary ions will be greater, although the ease of ionization of an element, the abundance of the analyte in the unknown, and the time spent counting will be important variables.

Reduction of ion-intensity ratios to concentration may be achieved by construction of “working curves” based upon a series of standards. However, most analysts prefer to use sensitivity factors [Fig. 4; data from Wilson et al. (1992) for RSFs of 50 elements]. A relative sensitivity factor (RSF) for element X relative to the matrix reference element R in a standard, for
which both $X$ and $R$ are expressed in atomic concentrations (i.e., $C_{XR}$), is defined as $F_{XR} = C_{XR}/I_{XR}$, where $I_{XR}$ is the ratio of ion-current intensity (in counts per second) corrected for respective natural abundance. Subsequent use of the factor to obtain the content of element $X$ in an unknown assumes knowledge of matrix composition, at least with respect to element $R$. Calibration by relative sensitivity factors has the advantage of making some measure of compensation for matrix variations. However, one concern with the use of RSFs is evidence that they are also a function of crater depth (Smith 1990).

**DEPTH PROFILING**

Continuous sputtering of surface atoms makes SIMS an ideal tool to define surface reactions, such as weathering, and diffusion. As with any SIMS quantitative analysis, mass interferences and surface charging must all be dealt with. Distinctive to the technique is the added problem of secondary-ion source; even with uniform sputtering of a smooth sample, the craters that develop will show sloping walls (Eccles 1989). If all secondary ions were processed, there would thus be a mix of those from the walls and those from the crater floor. To eliminate this "edge effect", most SIMS instruments are capable of electronic or physical gating such that only those ions produced from the center of the crater floor are processed.

Analysis of those monolayers closest to the sample surface is nearly impossible, even for a low-energy sputtering beam, because it requires some period of time to establish steady-state conditions. Nevertheless, for the remainder of a profile, using ion-implanted standards and crater-depth measurements correlated to sputtering time, quantification is commonly at the 5% level down to the lower ppm range for many elements (McPhail 1989).

Further improvements in depth profiling depend upon our ability to resolve two problems: (1) mixing of sample atoms by sputtering, and (2) crater-floor topography.

**Ion-beam mixing**

The problem of target-atom mixing or randomization during sputtering is well expressed by McPhail (1989): "If we could freeze the depth profile at any moment in time and identify all the atoms at the bottom of the crater, we would discover atoms that were originally several nanometres above that level and had been mixed downwards, together with atoms originally several nanometres below that level and had been mixed upwards (and of course atoms incorporated from the primary ion beam)". The effect of such mixing is to blur monolayer resolution.

Successful depth-profiling depends upon the formation and maintenance of an altered surface layer in dynamic equilibrium with the activity of sputtered sample atoms and the primary beam. For a discussion of sputter-induced artefacts, see Hues & Williams (1986). In cases where the profile obviously does not reflect the true distribution of an element, consideration should be given to the potential of its redistribution (either toward the advancing crater floor or away from it) by the primary beam (Dowsett et al. 1992).

**Ion-beam-induced topography**

Particularly from the study of craters developed in semiconductors, it is well known that even a perfectly flat surface will develop topography under ion bombardment (Stevie et al. 1988, Ishitani et al. 1992, Kilner et al. 1992, Nakagawa et al. 1992, Karen et al. 1992). It is also well known that yields of secondary ions vary as the roughness of the crater floor develops. Early studies suggested that lattice defects, microimpurities and other original features of the sample surface were responsible (Nelson & Mazey 1973, Hermanne 1973). More recently, the regularity of the topography and its process of development point primarily to characteristics of the primary ion beam. Suppression of ridge or ripple development on crater floors, and thus recovery of depth-profiling resolution, are best accomplished with sample rotation (Ishitani et al. 1992, Stevie et al. 1992, Cirlin & Vajo 1992, Hatada et al. 1992).

Kilner et al. (1992) studied topography developed by Cs+ and O2+ on natural calcite and fluorapatite. Both samples were coated with gold and exposed to nearly identical run-conditions. Interestingly, whereas the O2+ results were found to compare generally with those reported for semiconductor experiments (see above) and for Cs+ bombardment of calcite, the Cs+ beam produced no discernable roughness on fluorapatite.

**SIMS IMAGING**

Chemical mapping of high sensitivity for elements or molecules present may be done with submicrometer resolution. In ion-microscope mode, a large area of the sample surface is illuminated by a stationary primary beam, and chemical data are extracted from central circular areas. In this mode, information of all points in the field of view is collected simultaneously. In the microprobe mode, images are constructed line-by-line by a rastering beam. Introduction of liquid-metal primary-ion sources has increased popularity of the scanning beam configuration because spatial resolutions of the order of 20 nm can be attained; resolution for the ion microscope is approximately 200 nm (Humphrey 1989).

Just as the destructive aspect of SIMS was utilized for depth profiling, so it can be used to produce three-dimensional element-distribution maps (Patkin & Morrison 1982, Rüdenauer 1984). Image-processing
software can restack the images collected at different depths, maintaining vertical alignment through the use of perpendicular line-scans.

The optical viewing facility of many SIMS instruments is of poor quality; one feature of ion-microprobe scanning is thus particularly welcome. The process of particle bombardment not only produces secondary ions, but also secondary electrons in sufficient numbers that an electron image of the sputter area may be formed (Humphrey 1989). Whereas image quality does not match that produced by scanning electron microscopes, it is a means of accurate beam-location.

Quantification of SIMS images is difficult. The normal treatment is to compare the intensity of implanted standards with those from the analysis area, thus obtaining a qualitative estimate of compositions. More rigorous methods require treatment of enormous volumes of data. Nevertheless, SIMS is one of the few analytical techniques with sufficient sensitivity and resolution to produce trace-element maps in geological materials, and is unique in its capability to combine those properties with depth profiling.

**EXAMPLE APPLICATIONS**

**Analysis of samples for the rare-earth elements**

Routine *in situ* microanalysis to ppm and ppb levels in chemically complex materials was recognized by Lovering (1975) as the ultimate goal of SIMS applications by chemical geologists. Because of their distinctive behavior in geochemical processes, the abundances and distributions of the rare-earth elements (*REE*) among common minerals and glasses are used as petrogenetic indicators. As both lithophile and refractory elements, the *REE* are present in such common silicate minerals as calcic pyroxene, amphibole and plagioclase. Abundance levels are normally below the detection limit of the electron microprobe for most minerals.

Lovering (1975) reported that preliminary SIMS work on two synthetic high-*REE* glasses was generally unsatisfactory because of the inadequate correction-procedures then available. A significant improvement was reported by Shimizu *et al.* (1978), who used the process of kinetic-energy filtering to remove many of the molecular ion interferences that had proven problematic for Lovering (1975).

Even with energy filtering sufficient to clear molecular interferences from the lower masses, heavy-*REE* peaks are overlapped by the molecular ion oxides of the light *REE*. MacRae & Metson (1985) overcame the problem by using the SI (specimen isolation) technique. The same process was successfully applied by MacRae & Russell (1987) to obtain approximate partition-coefficients of the *REE* for clinopyroxene in komatiitic liquids, showing that, within the limits of error, partition values for komatiitic systems match those of basaltic systems.

Crozaz & Zinner (1986) and Zinner & Crozaz (1986) took the approach of combining conventional energy-filtering (CEF) with peak stripping; their method has been widely adopted, producing data at the 1 ppm level with an accuracy of approximately 10%. MacRae *et al.* (1993) and Muir *et al.* (1987) compared *REE* data obtained using both SI and the Zinner & Crozaz (1986) methods, and concluded that both are equally accurate.

Snyder *et al.* (1993) conducted an elegant SIMS study of coexisting glasses, apparently representing two immiscible liquids, together with two rare very small grains of zircon hosted by the glass in a lunar sample brought back from the Appolo 14 mission. From a combination of electron- and ion-microprobe analyses, they calculated apparent liquid/liquid partition coefficients for the *REE*, as well as other elements, for the lunar environment. More particularly, from the *REE* zircon analyses and partition coefficients developed by Hinton & Upton (1991), they calculated liquid compositions that could have been in equilibrium with the lunar zircon. Interestingly, they showed that the zircon could not have precipitated from the glass hosts, but only from a considerably more primitive liquid, the best probability being a magma similar to that which formed the plagioclase-poor rocks of the lunar highlands.

Nesbitt *et al.* (1990) and MacRae *et al.* (1992) analyzed cored sediments from the Amazon deep-sea fan for the *REE* (Fig. 5). They concluded that the light-*REE*-enriched character of the sediments does not represent either diagenetic fractionation nor direct evidence of source rocks, but the extreme chemical weathering of soils formed in the Amazon drainage basin, combined with particle sorting during transportation. In addition, the unexpected positive Eu-anomaly could be explained only by remobilization of Eu across a reduction–oxidation boundary within the sediment pile.

**Analysis for the light elements**

A major strength of SIMS is the ability to quantitatively analyze samples for the light elements (below atomic number 10). Whereas they are difficult to determine by the electron microprobe, concentrations of the light elements can be determined with ease and with very few interferences by SIMS.

Ottolini *et al.* (1993) developed calibration curves applicable over wide ranges of concentration for Li, Be and B in silicates (Fig. 6). Reference samples used in the construction were a mix of minerals and glasses; a set of interlaboratory samples was used for testing. They reported sensitivities (cps per ppm per nA of primary-beam current) of approximately 8 for Li and Be, and 3 for B. These numbers translate to approximately 10 ppb for Li and Be, and 25 ppb for B for their
operating conditions. Whereas relative standard deviations for intensity ratios were found to be higher in minerals than in glasses, they nevertheless estimated overall analytical uncertainty in their SIMS procedure at about 20% for Li but better than 10% for Be and B in the tens of ppm range.

Invisible gold: quantification and imaging

Bürg (1930) introduced the term "invisible gold" to denote trace gold either incorporated in solid solution in a mineral, or as inclusions of pure gold smaller than 1000 Å in size. A controversy concerned with whether or not sulfide and arsenide minerals incorporate trace levels of gold in only one or both of these states has been stalled by the technical difficulty of examination (Harris 1989, Gasparrini 1983, Wagner et al. 1986, Marion et al. 1986).

Using a CAMECA IMS-3f ion microscope, voltage offset for energy filtering, and implanted $^{197}$Au for standardization, Chryssoulis and coworkers (Chryssoulis 1990, Cook & Chryssoulis 1990, Chryssoulis & Weisener 1990) have established a quantitative technique to analyze sulfides, arsenides and Fe-oxides for Au, the results are considered accurate to 15% at the 1 ppm level, with detection limits of 0.4 ppm Au in pyrite, 0.2 ppm in arsenopyrite and 0.5 ppm in Fe-oxide. In addition, Chryssoulis & Weisener (1990) imaged submicroscopic gold, with detection limits between 1 and 10 ppm, depending upon the matrix.

Mumin (1993), Fleet et al. (1993) and Mumin et al. (1994) have used SIMS to image "invisible gold" contained by arsenian pyrite from a group of well-studied gold deposits. Figures 7A and 7B are SIMS maps of the $^{75}$As and $^{197}$Au ions in a grain of arsenian pyrite from the Dumassie deposit, Ashanti Gold Belt, Ghana. The arsenian pyrite is partly replaced by pure pyrite (FeS$_2$). The images show that gold in solid solution is restricted to the arsenian pyrite (content established at 78 ppm by the quantification method noted above). In the replacement process, As recrystallizes as small grains of arsenopyrite, but Au leaves the system to precipitate elsewhere as microscopic particles of gold.

Depth profiling

Studies of thin layers, interfaces, and implantations in semiconductors have accounted for most of the SIMS depth-profiling work. One problem in applying the method to minerals is resolution of the threedimensional inhomogeneity to be expected of natural materials.

Hofmann et al. (1974) were first to apply the technique to minerals, in a study of the diffusion of $^{39}$K and $^{41}$K through biotite in which they had previously induced isotopic exchange under hydrothermal conditions. Cunningham et al. (1983) used depth profiling to study lithium diffusion in silicate melts. Whereas both studies proved successful, neither addressed major
problems of quantification.

Nesbitt & Muir (1988), Muir et al. (1989) and Nesbitt et al. (1991) used the SI mode of SIMS operation to define the character of surface reactions of feldspars exposed to various weathering solutions. Depth profiles showed that, of the solutes dissolved in the test solutions (i.e., Na, K, Ca, Al, Si), Al had the greatest effect on composition of the near-surface altered layer, and Si had the least effect. Variation in the ratio of Al/Si with depth thus clearly defined the extents of alteration (Fig. 8). Subsequent modeling of the data led to the prediction that Si-rich residual layers should not form on feldspars exposed to natural soil and weathering conditions. SIMS studies of feldspars exposed to natural weathering confirms this conclusion (H.W. Nesbitt, pers. comm.).

Isotope ratios

SIMS offers the exciting possibility of in situ isotope analysis of very small mineral grains, from which one may glean geochronology, fractionation and diffusion history, or information on the environment of formation. However, early studies showed that the isotope ratios obtained always differed from the ratios determined by other methods; the differences are due to fractionation within the instrument, and little was known of the factors that control this process. A comprehensive review of the principles and applications of isotopic ratio measurements compiled by Zinner (1989) is recommended reading for potential users.

Deloule et al. (1991, 1992) analyzed D/H from amphiboles and micas for which δD values were known with a reproducibility of better than 10‰. In their study of amphiboles from mantle xenoliths, Deloule et al. (1991) found such large but small-scale variations in hydrogen ion concentration that hydrogen transport immediately prior to eruption was considered the only reasonable explanation. In addition, they clearly indicated that the various mantle reservoirs presumed to have interacted must have different D/H ratios.

Clues to the nucleosynthesis of materials of stellar origin may be found in anomalies of isotopic abundances in meteoric samples. The SIMS is uniquely suited to such studies, as neatly illustrated by Zinner et al. (1991). Their study of the abundances of ²⁶Mg, produced from the decay of ⁶⁰Al, in graphite and in grains of SiC recovered from the Murchison meteorite, showed that (1) Al is correlated with N, suggesting that the aluminum condensed as AlN, (2) the ²⁶Al decayed inside the SiC or graphite grains, confirming the
sequence of condensation obtained by thermodynamic calculation, and (3) the radiogenic $^{26}\text{Mg}$ apparently is presolar, thus the $^{26}\text{Al}/^{27}\text{Al}$ ratios obtained reflect production ratios in stars.

Valley & Graham (1991, 1992) used SIMS to analyze magnetite grains and reported the first routinely reproducible oxygen isotope ratios in the precision range of 1% with a spatial resolution of 2–8 μm. Their study, while contributing information about the cooling histories of the granulite-facies rocks tested, raised serious questions about the conventional use of oxygen isotope thermometry, in which bulk samples are analyzed. The magnetite grains were found to be sufficiently isotopically zoned ($^{18}\text{O}$-depleted rims) as a result of late-stage fluid activity having nothing to do with the mineral equilibrium system used for thermometry (magnetite – calcite), that the significance of the bulk data must be questioned. It is important, they pointed out, to note that such disequilibrium could only be recognized from microbeam analyses.

Pioneering work by Andersen & Hinthorne (1972) (using a low-resolution ARL instrument) showed the

![Image](image-url)
potential of SIMS for U–Pb dating, but accurate measurements were then not feasible owing to lack of sufficient mass-resolution and low intensity of signals. Subsequently, a sensitive high-mass-resolution ion microprobe (SHRIMP) was constructed at the Australian National University (Clement et al. 1977) specifically to produce accurate in situ geochronological data.

One problem of general interest to earth scientists, and which is being clarified primarily by SHRIMP data, is accurate placement on the time scale of the Precambrian–Cambrian boundary. Prior to 1982, an age of approximately 610 Ma was accepted; however, reconsideration of all available data in 1982 resulted in a suggested age of 520–540 Ma (Odin 1986). A variety of studies since then have produced as many dates. SHRIMP-derived U–Pb dates of zircon from material known to be deposited in the very latest Precambrian (Tentudia Group, southwestern Spain) support the 540–530 Ma age for the base of the Cambrian (Schöfer et al. 1993).

Typical references are included in Table 1 for a number of elements for which SIMS has been used to obtain isotopic ratios for geological problems.

**TABLE 1. ELEMENTS FOR WHICH SIMS HAS BEEN USED TO OBTAIN ISOTOPIC RATIOS**

<table>
<thead>
<tr>
<th>Isotopic Ratio</th>
<th>Typical Reference</th>
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</thead>
<tbody>
<tr>
<td>D/H</td>
<td>Delano et al. (1991, 1993)</td>
</tr>
<tr>
<td>12C/13C</td>
<td>Delano et al. (1993)</td>
</tr>
<tr>
<td>15N/14N</td>
<td>Harte &amp; Oster (1992)</td>
</tr>
<tr>
<td>13C/12C</td>
<td>Zimmer et al. (1991)</td>
</tr>
<tr>
<td>15O/16O</td>
<td>Valley &amp; Graham (1991)</td>
</tr>
<tr>
<td>18O/16O</td>
<td>Zehner et al. (1991), Ireland et al. (1986)</td>
</tr>
<tr>
<td>18O/16O</td>
<td>Zimmer et al. (1991)</td>
</tr>
<tr>
<td>16O/18O</td>
<td>Eddington et al. (1987)</td>
</tr>
<tr>
<td>16O/18O</td>
<td>Hutchinson et al. (1984)</td>
</tr>
<tr>
<td>16O/18O</td>
<td>Simon et al. (1994)</td>
</tr>
<tr>
<td>16O/18O</td>
<td>Morita (1991)</td>
</tr>
<tr>
<td>182W/184W</td>
<td>Conpton et al. (1984)</td>
</tr>
<tr>
<td>206Pb/235U</td>
<td>Conpton et al. (1984), Maebotokota et al. (1991)</td>
</tr>
<tr>
<td>204Pb/234U</td>
<td>Holliger (1992), Maebotokota et al. (1991)</td>
</tr>
</tbody>
</table>

**Fig. 8.** SIMS depth profile of 27Al/28Si of the experimentally leached layer of labradorite, expressed as percent change from the unleached sample. Profiles labeled “Dist. Water” and “HCl” mark the two extremes; the profiles labeled #1 to #4 indicate the results from solutions to which various solutes were added (see Nesbitt *et al.* 1991).
TABLE 2. SIMS LABORATORIES WITH INTERESTS IN THE GEOSCIENCES

<table>
<thead>
<tr>
<th>Canada</th>
<th>CANMET</th>
<th>568 Booth Street</th>
<th>Ontario, Ontario K1A 001</th>
<th>[P. Rae]</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.L.A.</td>
<td>SP Research</td>
<td>4440 Wrennsville Center Road</td>
<td>Cleveland, OH 44128</td>
<td></td>
</tr>
<tr>
<td>Arizona State University</td>
<td>Arizona State University</td>
<td>1700 University Drive</td>
<td>Tempe, AZ 85287-1600</td>
<td>[R. Harper, P. Williams]</td>
</tr>
<tr>
<td>Charles A. Beams &amp; Associates</td>
<td>The State University of New York</td>
<td>University of Illinois</td>
<td>Chicago, IL 60607</td>
<td></td>
</tr>
<tr>
<td>Advanced Research Laboratories</td>
<td>Woods Hole Oceanographic Institute</td>
<td>Department of Geology &amp; Geophysics</td>
<td>Woods Hole, MA 02543</td>
<td>[N. Blochus]</td>
</tr>
<tr>
<td>McDonnell Center for the Space Sciences</td>
<td>Cornell University</td>
<td>Department of Chemistry – BAKER Lab.</td>
<td>Ithaca, NY 14853</td>
<td></td>
</tr>
<tr>
<td>California Institute of Technology</td>
<td>RECO Research</td>
<td>Clinton Townshhip</td>
<td>Ames, IA 50010</td>
<td></td>
</tr>
<tr>
<td>University of California</td>
<td>North Carolina State University</td>
<td>Engineering Research Services</td>
<td>Raleigh, NC 27693</td>
<td></td>
</tr>
<tr>
<td>Pennsylvania State University</td>
<td>University of Wisconsin</td>
<td>Materials Science Center</td>
<td>Madison, WI 53706-1697</td>
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</tr>
<tr>
<td>Materials Chemistry Laboratory</td>
<td>McCombs Associates</td>
<td>830 Paugashill Drive</td>
<td>Westport, CT 06883</td>
<td></td>
</tr>
<tr>
<td>Sartorius National Laboratory</td>
<td>Advanced Materials Laboratory</td>
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<td>University of New Mexico</td>
<td></td>
</tr>
<tr>
<td>2125 Research Park</td>
<td>1500 Johnson Drive</td>
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<td></td>
</tr>
<tr>
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<td>University of Illinois</td>
<td>Materials Research Laboratory</td>
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<td></td>
</tr>
<tr>
<td>390 Claude Drive NE</td>
<td>Urbana, IL 61801</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>University of Chicago, Lewis-Sigler Group</td>
<td>California Institute of Technology</td>
<td>Materials Science Center</td>
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<td>[E. Libowitz]</td>
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<tr>
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<td></td>
</tr>
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<td>[L. Onofri]</td>
</tr>
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<td>School of Physics</td>
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<td>[J. Graham]</td>
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<tr>
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<td>Centre de Recherches Pitaugogiques</td>
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<td>Philadelphia, PA 19114-2495</td>
<td>[C. Armitage]</td>
</tr>
<tr>
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<td>University of Paris-Sud</td>
<td>1114 College Street</td>
<td>New York, NY 10027</td>
<td>[J. L. Bunting]</td>
</tr>
<tr>
<td>University of Antwerp</td>
<td>Institute of Materials Science</td>
<td>Centro de Investigaciones</td>
<td>5-9800 Leuven, Belgium</td>
<td>[J. L. Bunting]</td>
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<tr>
<td>University of Antwerp (U.I.A.)</td>
<td>University of Cambridge</td>
<td>Department of Earth Sciences</td>
<td>Cambridge CB2 3QZ, U.K.</td>
<td>[J. L. Bunting]</td>
</tr>
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</tr>
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<td>[J. L. Bunting]</td>
</tr>
</tbody>
</table>

Australasia

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| The Australian National University | 104 South Goodwin Street | Urbana, IL 61801 | [S. Layon] |
| G.P.O. Box 4, Canberra, A.C.T. 2601, Australia | | | | |

Japan

<table>
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<tr>
<th>Institute of Geoscience</th>
<th>College of General Education</th>
<th>Osaka University</th>
<th>1-1 Midosuigaoka-cho</th>
<th>Toyonaka, Osaka 560, Japan</th>
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<tr>
<td>Chemical Analytical Center</td>
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<td></td>
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<tr>
<td>The University of Tokyo</td>
<td></td>
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<tr>
<td>Tohoku, Sendai 980, Japan</td>
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**REFERENCES**


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