

Geochemical analysis of small samples: Micro-analytical techniques for the nineties and beyond

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Introduction

As technology becomes more sophisticated, the number and type of tools available to the geochemist continue to grow and the amount of data collected from a single sample is dramatically increased. Micro-analytical techniques developed over the last 20-30 years allow the geochemist to obtain an almost overwhelming wealth of data from single samples. Not only can bulk analysis be routinely conducted, but detailed major- and trace-element determinations, as well as isotopic analysis of individual components from geological, metallic, ceramic, and plastic materials are opening up a whole new avenue of research and petrogenetic interpretation. *In situ* measurements have become an important aspect of many geoscience applications, following the realization that much of the information relating to the origin and evolution of rock systems is retained at the scale of individual mineral grains [e.g., Reed, 1989, 1990, 1993]. The new generation of high resolution ion probes has furthered our ability to perform trace element and isotope analyses at the micron (μm = micron = 10^{-3} mm) scale. Laser ablation techniques, coupled with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses have opened up a parallel capacity for trace element analysis, while laser fluorination oxygen extraction is fast becoming the tool of choice for silicate oxygen isotope geochemistry. With these analytical techniques available, a detailed data base on a single sample or suite of samples can be quickly built up. For major and minor element analyses, the electron microprobe is normally used and as this has generally become a routine analytical technique and has recently been extensively reviewed by Reed [1993], it will not be discussed here.

This paper is concerned with the analysis of geologic materials on a sub-mm scale allowing the recognition of major and trace element, as well as isotopic zonation across individual mineral grains. The primary concentration is on work conducted in laboratories in the United States, although reference to work conducted in other countries is made where deemed appropriate. Three analytical techniques will be discussed: 1) *In situ* microsampling for isotopic analysis; 2) Secondary Ion Mass Spectrometry (SIMS); and 3) Laser Ablation Inductively Coupled Plasma - Mass Spectrometry (LA-ICP-MS). The object of the paper is to give the reader a current overview of the applications of each of the three analytical techniques as well as a detailed description of the newer LA-ICP-MS procedure.

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1. *In Situ* Microsampling

Introduction

Despite tremendous advances in our ability to perform trace element and isotope analyses at the micron scale using high resolution ion probes, the capabilities of these approaches do not extend to isotopic analysis for elements such as Sr and Nd. Thus, in order to obtain adequate precision and satisfy stringent resolution requirements (e.g., resolving ^{87}Rb from ^{87}Sr), researchers have turned to *in situ* microsampling coupled with bulk analysis using Thermal Ionization Mass Spectrometry (TIMS - see Faure, 1986 for a review of this technique).

The technique is as its name suggests: a small amount of material is extracted via mechanical microdrilling and prepared using standard dissolution and ion exchange techniques to isolate Sr and Nd [and any other element that can be analyzed for isotope ratio, or for concentration by isotope dilution - e.g., Richard *et al.*, 1976] for TIMS analysis. Some additional care over normal bulk rock chemistry must be observed. The reduction in sample size commonly requires reduction in blanks so that they do not significantly affect the measured ratios. Sample masses typically contain $< 10\text{ng}$ of the element of interest. The most important advance in mass spectrometry that has enabled such small sample sizes to be measured with relative ease is the multicollector, which allows a number of masses to be simultaneously measured (i.e., each collector is fixed on a desired mass) rather than with a single collector which scans over the masses of interest. The advance is not so much one of improved precision through collector or amplifier design, but rather one of optimizing data collection, by being able to collect a much larger fraction of ions arriving at the collector than had been possible with a peak switching single collector. Clearly with the limited number of ions available from microsamples, precision can be best achieved by using as much of the ion inventory as possible for analysis. Ionization efficiency can also be improved by using modified loading techniques - arguably an important avenue to pursue as we refine microsampling techniques, since standard ionization efficiencies for elements such as Nd and Sr are only of order 1%.

Advantages and Disadvantages of *In Situ* Microsampling

The microsampling itself is mechanical, usually involving sampling by fine diamond tipped or coring bits. The sample is taken from thin or thick sections, controlled by observation through an optical microscope. There are several factors of this technique which could be termed disadvantages: 1) laborious sample prep (potentially higher blank, more time expenditure, more preparation cost per sample); 2) Much larger spot size [limited by the physical size of the drill bit balanced by a

realistic mass requirement for ≈ 1 nano-gram ($\text{ng} = 10^{-6}$ grams) or more of the element of interest; and 3) Limitations on diversity of analysis (only a few isotope ratios or spiked isotope dilution analyses can be derived from a given sample, compared with a whole suite of potential trace-element concentrations from ICP-MS). However, the technique offers the advantage of being able to characterize the sample in advance by less destructive analysis, such as with the electron microprobe. The major advantage of *in situ* microsampling and standard TIMS over LA-ICP-MS and SIMS is the much greater precision (it is the only way to measure isotope ratios to better than $\sim 0.01\%$).

Applications

Microsampling technology has been utilized for several years to investigate problems of diagenesis and records of temperature fluctuations during crystal growth [e.g. *Given and Lohmann*, 1985]. The carbonate materials analyzed in these studies are easy to drill, and contain high abundances of carbon and oxygen - analysis for which the material is separated. This contrasts with the ppm level of Sr, Nd, and Pb tracers. As a consequence, much smaller samples can be separated for C and O isotopic analysis, and spatial resolution is superior to microsampling for Sr, Nd, and Pb isotopes. *Dettman and Lohmann* [1993] reported carbon and oxygen isotopic analyses of 10-20 mg samples from individual growth layers from fresh water bivalves. These data were used to infer temperature variations and mixing relationships between water reservoirs. A similar study of microlayering in mollusk shells was used to estimate bottom temperature variations in the north Atlantic [Weidman *et al.*, 1994]. For such applications, fine scale milling techniques were employed, controlled by computer rather than a human operator.

The utility of microsampling in igneous petrology is clear. Isotopic disequilibrium between crystals and groundmass glass has been demonstrated by many studies [e.g. *Christensen and DePaolo*, 1993; *Ruiz and Duffield*, 1994]. *In situ* microsampling enables us to further identify inter-crystal and intra-crystal variability, and investigate quantitatively isotopic gradients within crystals and between groundmass and xenocrysts, xenoliths or magmatic inclusions. Isotopic gradients can be used to infer crystal growth rates [as demonstrated for metamorphic garnets by *Christensen et al.*, 1989] or to track the evolution of differentiating magma systems [e.g., *Davies et al.*, 1994].

An elegant study from the University of Michigan laboratory shows how isotopic variability in crystal phases from the Tuscan rhyolites is related to precipitation from a magma evolving by assimilation of wallrock material (i.e., open system evolution) [Feldstein *et al.*, 1994]. A number of studies reported at the recent International Conference On Geochronology, Cosmochronology, and Isotope Geology in Berkeley, CA, also attest to the growing interest in microanalytical approaches. Strontium isotopic zonation within single feldspar crystals has been identified, and used to investigate growth rates in high Rb/Sr magmas [e.g. *Heumann et al.*, 1994] or diffusion time scales in xenocrysts [Tepley *et al.*, 1994]. Disequilibrium melting of crustal rocks during assimilation has been identified [Tommasini *et al.*, 1994] via microsampling of plagioclase crystals. The less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ signature of the feldspars relative to the source rock were interpreted as being consistent with the feldspars not having undergone equilibration with the bulk rock during melting. This observation will surely force us to re-evaluate our assumption that contaminants are characterized by the isotopic ratios of the bulk rock. *Churikova and Kostitsyn* [1994] on the basis of core-rim $^{87}\text{Sr}/^{86}\text{Sr}$ variations in plagioclase phenocrysts (increasing from 0.7034 to ≈ 0.7037 core to rim) have reported that the effects of combined assimilation and fractional crystallization can be recorded in single crystals.

Baker et al. [1994] drew similar conclusions from Nd-Sr-O isotope analysis of zoned clinopyroxene crystals in a high MgO basalt from Yemen flood basalts. Such observations should stimulate caution in the interpretation of bulk rock geochemistry in the context of mantle sources and processes. The effects of crustal differentiation can be faithfully recorded in individual crystal phases, and would otherwise be missed adopting a bulk chemistry approach.

It is evident that *in-situ* micro-sampling techniques to the investigation of geological processes has the potential to provide details of geochemical signatures and processes that would have been overlooked using a bulk rock analytical approach. Expansion of this technique is expected over the next four years which will allow the petrologist to obtain an intimate picture of geological processes. Use of *in-situ* microsampling with other micro-analytical techniques will enable the refinement of many petrogenetic models and possibly negate others.

2. Secondary Ionization Mass Spectrometry (SIMS)/ Ion Microprobe

Introduction

In studies requiring determinations of isotopic and/or trace-element abundances with very high spatial resolution, the ion microprobe remains the premier tool for the geochemist and cosmochemist. In SIMS analysis, a focused beam of "primary" ions (a few μm in diameter) bombards a solid sample in order to obtain a localized analysis. The bombardment or "sputtering" removes atoms from the polished surface of the specimen, some of which are ionized and can be accelerated into the entrance slit of a mass spectrometer [see *Reed*, 1989]. Both custom-built and commercial ion microprobes have been employed in geo/cosmochemical research for approximately 15 years.

The ion microprobe's capabilities for *in situ* quantification for many elements at sub-ppm concentrations, including those with $Z < 11$, are complementary to, and provide a natural extension of, the kind of analytical data obtained via the electron microprobe. Many applications have involved REE abundances and experimental measurement techniques in this field have become rather mature [see *MacRae et al.*, 1993 and references therein]. The present quadrennium has seen a continuation of instrumental and technique developments, particularly in the design of new high-sensitivity ion microprobes and in the area of stable isotope measurements (e.g., VG ISOLAB, SHRIMP II, and CAMECA ims 1270). There has also been a gradual shift in emphasis toward applications. "Experimental techniques" sections, which formerly constituted a large part of geo/cosmochemical papers that utilized SIMS analyses, are now often rather terse. Ion microprobes are in routine use for U-Pb zircon dating, measurements of trace element abundances, and stable isotope measurements - especially in interstellar dust, but increasingly also in terrestrial igneous and metamorphic rocks. Given the large number of papers published in the last 4 years that contain ion microprobe data from labs worldwide, the reader is referred to *Ireland* [1994] for a global SIMS review.

Advantages of SIMS

The relatively high ionization probability for many elements during sputtering, combined with localization of the secondary ions either by the use of a focused primary ion beam (ion microprobe) or by a direct ion imaging system (ion microscope), allows measurements of isotope ratios for both major and minor elements in small (nanogram) particles as well as *in situ* mapping of isotopic and trace element abun-

dances in thin sections or individual grains. While the lateral spatial resolution can be sub-micron for major element mapping, it is more typically in the few to ~25 μm range for most isotopic and trace element measurements. However, since the vast majority of sputtered ions originate from the instantaneous sample surface (which is continually eroded during analysis), spatial resolution in the vertical dimension can be very good (tens of nm), enabling depth profiling of tracer isotopes or elements in natural samples and experimental run products (e.g., diffusion studies).

Applications - Geochemical Analysis

The application of SIMS analysis to geological materials has mushroomed over the last four years. The measurement of isotopic ratios of the low-mass elements which undergo significant mass fractionation during many geochemical processes, the so-called 'stable isotopes' of H, C, O, S, etc., has been a continuing interest of ion microprobe applications in both cosmochemistry and geochemistry for the past decade. Carbon isotopes have been measured in numerous meteoritic samples, but so far not many terrestrial studies have been performed. An exception is provided by studies of diamond [Harte and Otter, 1992] which may be analyzed with sub-permil [permil (‰) as opposed to percent (%)] precision by negative SIMS since it becomes semiconducting under Cs^+ bombardment. Sulfur isotopes have been analyzed in a variety of mineral phases (e.g., chalcopyrite, pyrite, galena, sphalerite) from different geologic environments ranging from sulfide ores [Macfarlane and Shimizu, 1991] to sedimentary sulfide deposits [e.g., Eldridge et al., 1993] to small inclusions in diamond [Eldridge et al., 1991]. In every case, an extremely large range in $\delta^{34}\text{S}$ [usually spanning several percent - see Faure, 1986 for definition of delta notation] was found reflecting the complex geochemical behavior of sulfur. These isotopic heterogeneities, which are largely averaged out by conventional bulk analyses, are highly diagnostic for sources of sulfur and hence processes for ore formation, etc., and therefore we can expect further application of ion microprobe measurements in this area.

The natural variability of oxygen isotope ratios and their well-established utility in thermometry and as monitors of fluid-rock interactions has made the *in situ* measurement of $^{18}\text{O}/^{16}\text{O}$ at the 10 μm spatial scale an important goal of ion microprobe technique development. Several laboratories have approached the problems of sample charging and the control of instrumental mass discrimination differently, and remarkable progress has been made. Valley and Graham [1991, 1992, 1993] have used high mass resolution (~2000 channels per atomic mass unit) and exploited the fact that magnetite is sufficiently conducting in order to measure $\delta^{18}\text{O}$ to a precision of 1 permil (‰). These authors also employed depth profiling to determine very fine-scale isotopic gradients that cause a shift in $\delta^{18}\text{O}$ of up to ~1‰ over a distance of ~10 μm from rim to core of individual crystals. From such data they were able to constrain possible cooling histories and isotopic exchange with fluids in this granulite-facies marble following regional metamorphism [Valley and Graham, 1991]. Further detailed analyses of $\delta^{18}\text{O}$ across a large (few mm) magnetite grain showed evidence for fluid transport along healed cracks, and led the authors to urge caution in modeling bulk-mineral oxygen isotope data in terms of thermometry or diffusive processes without knowledge of the microscale variations in $\delta^{18}\text{O}$ [Valley and Graham, 1993]. For the analysis of electrically insulating samples (such as silicates), Hervig and colleagues attacked the charging problem by developing a focused high-energy electron gun in order to balance incoming and outgoing positive and negative currents during an analysis, and also employed extreme energy filtering to discriminate against

molecular interferences [Hervig, 1992]. The method was used to correlate oxygen isotopic zoning (measured in 30 μm spots) across a hydrothermal garnet with other indicators of changing fluid chemistry, such as fluorine and REE content [Jamtveit and Hervig, 1994].

The proportion of ion microprobe studies devoted to terrestrial, as opposed to meteoritic, samples has been increasing during the present quadrennium and this trend will undoubtedly continue. Many terrestrial applications concern geochronology, where the SHRIMP has been employed with great success to date thousands of zircons ranging from the oldest terrestrial minerals and rocks [Nutman and Collerson, 1991; Liu et al., 1992; Mueller et al., 1992] to some of the youngest tectonically active regions on Earth [e.g., Zeitler et al., 1993]. Ancient materials can provide unique geochemical information regarding differentiation processes in Earth's early evolution. For example, Maas et al. [1992] concluded, based on extensive morphological, mineralogical, and elemental (including trace element) characterization, that these tiny grains of ancient zircon provide good evidence for a 'differentiated continental crust of substantial thickness' as their source. Kinny et al. [1991] used the SHRIMP to measure the Hf isotopic compositions of some of these zircons demonstrating concordance of Hf-model ages with U/Pb up to 4.2 Ga.

One of the most exciting applications of SIMS has been in the study of discrete relict interstellar dust grains in primitive meteorites [Anders and Zinner, 1993, and references therein]. Trace amounts of tiny grains of diamond, SiC, and graphite were identified from chondrites by virtue of their unique chemical properties (relative to the silicate host) and their correlations with concentrations of various exotic (*i.e.*, non-solar system) noble gas components. Since the isotopic abundance patterns in each presolar grain were fixed in specific, and potentially unique, stellar sources, it is essential to measure isotope ratios on individual particles. While the diamonds, with a typical grain size of only 10's of nanometers, are far too small to permit any isotopic measurements on individual grains, fortunately SiC and graphite can often range up to several microns in diameter, ideal for SIMS analysis. Only the ion microprobe has the sensitivity to perform this task; moreover in many cases it has proven possible to measure C, N, and Si isotopes, as well as the isotopic composition of several minor elements on SiC and graphite particles. The isotopic correlations have been used to distinguish groups of grains that may derive from similar stars and these data provide strong experimental constraints on theories of nucleosynthetic processes in various stellar environments [e.g., Anders et al., 1991; Amari et al., 1992; Alexander, 1993; Hoppe et al., 1993a,b]. Correlated isotopic measurements of C and N have also been performed on many individual graphite grains [Amari et al., 1993]. Carbon isotopic compositions are exceedingly anomalous, with both depletions and excesses of ^{13}C by more than a factor of 20 relative to the solar $^{13}\text{C}/^{12}\text{C}$ ratio. However, nitrogen isotopic ratios are relatively close to the terrestrial value and do not correlate with N abundance which varies by more than a factor of 100 among graphite grains.

Zinner et al. [1991a] documented huge ^{26}Mg excesses in SiC and graphite particles which they interpreted as "fossil" anomalies due to the decay of now-extinct ^{26}Al . The inferred $^{26}\text{Al}/^{27}\text{Al}$ at the time the grains condensed ranges up to 0.06 in graphite and 0.2 in SiC; this is much higher than the value of $\sim 5 \times 10^{-5}$ found in many refractory oxide inclusions in carbonaceous chondrites. The signatures of the short-lived nuclides ^{44}Ti and ^{49}V may also have been found by Amari et al. [1992] in the calcium and titanium isotopes of SiC grains. Based on their major element isotope systematics, these grains are considered to be possible supernova ejecta, although there are difficulties in modeling their high ^{26}Al abundances from a supernova source. The Ba and Nd isotopic

compositions of aggregates of SiC particles were also demonstrated to have a distinct "s-process" (supernova) signature by Zinner *et al.* [1991b].

The incorporation of short-lived isotopes, especially ^{26}Al (half life = $t_{1/2}=0.7\text{Ma}$), into mm to cm sized refractory inclusions (i.e., objects that formed in the early solar nebula) in meteorites has important implications for the evolution of this phase of solar system formation. Disturbances of the Al-Mg system, which affect the use of ^{26}Al as a high-precision relative chronometer, have been studied by Podosek *et al.* [1991] and MacPherson and Davis [1993]. In addition to Mg, isotopic anomalies in O, Ca, and Ti in refractory phases from primitive meteorites have been investigated [e.g., Davis *et al.*, 1991; Ireland *et al.*, 1991, 1992; Lundberg *et al.*, 1994].

The role of physical processes, such as diffusion, melting, and distillation by evaporation, in determining isotopic and trace element abundance patterns in refractory inclusions and chondrules has been receiving increased attention by ion microprobe analyses of natural samples [Simon *et al.*, 1991; Ireland *et al.*, 1992] and experimental run-products [e.g., Kennedy *et al.*, 1993; Ryerson and McKeegan, 1994; Simon *et al.*, 1994]. Sheng *et al.* [1992] determined self-diffusion rates for Mg in spinel and co-existing melts and were therefore able to use the existence of natural isotopic heterogeneities in spinel to constrain possible cooling rates, and hence formation mechanisms, of plagioclase-olivine inclusions. Similarly, Ryerson and McKeegan [1994] attempted to constrain thermal histories of a certain class of Ca-Al-rich inclusions (CAI) by comparing ion probe measurements of self-diffusion rates for oxygen in the minerals ankerite, anorthite, diopside, and spinel with known patterns of oxygen isotopic anomalies in these phases. They concluded that existing O isotopic data cannot be explained by simple gas-solid or gas-melt diffusive exchange processes, but probably require multiple thermal events including alteration and recrystallization of some CAI minerals.

Extra-terrestrial samples other than primitive meteorites have also been scrutinized by the ion microprobe, principally trace element studies. For example, Floss and Crozaz [1991, 1993] investigated rare earth element (REE) distributions in reduced meteorites. Igneous activity on the Moon has been examined by Shearer and co-workers [1990a,b] as well as Snyder *et al.* [1993] and Jolliff *et al.* [1993], with results demonstrating a complex source mixing and metasomatism for lunar magmas. Igneous meteorites thought to be derived from Mars have been measured for REE contents [Lundberg *et al.*, 1990] as well as hydrogen isotopes [Watson *et al.*, 1994]. The minor and trace element trends in pyroxenes, as well as the calculated compositions of parent melts, are consistent with formation of the shergottites by closed-system fractional crystallization [Wadhwa *et al.*, 1994]. High deuterium to hydrogen (D/H) ratios measured in hydrous phases of these meteorites are best explained by post crystallization isotopic exchange with crustal fluids having D/H values similar to the present Martian atmosphere (about five times the terrestrial atmospheric value) [Watson *et al.*, 1994]. These results have implications for the extent of hydrogen loss from the Martian atmosphere and its interaction with a fluid phase present in that planet's crust.

Applications - Geochemical Mapping

Although much harder to find because of the enormous background of local (solar system) material, a few interstellar oxide grains have recently been identified by ion microprobe measurements of oxygen and magnesium isotopes in meteorites [Hutcheon *et al.*, 1994; Huss *et al.*, 1994]. Nittler *et al.* [1994] employed a CCD ("Charge Coupled Device") camera to quantify ion microscope images in order to identify grains with highly anomalous $^{18}\text{O}/^{16}\text{O}$ ratios. Although the method has the drawback of missing interstellar grains which have

anomalous ^{17}O abundances but relatively normal $^{18}\text{O}/^{16}\text{O}$, it does permit an automated survey of a large number of separated dust grains thereby enabling the rapid identification of particles worthy of further detailed investigation. With the increasing use of powerful computers for ion microprobe data acquisition and analysis, it is likely that the next few years will see refinement of techniques and an expansion of applications for isotopic mapping at the few micron spatial scale.

New areas of interest that are driving SIMS technique development are measurements of fluid inclusions [Diamond *et al.*, 1990, 1991] and of melt inclusions [Sobolev and Shimizu, 1991; Dunbar and Hervig, 1992a,b; Lu *et al.*, 1992; Metrich *et al.*, 1993]. Because of sample heterogeneities and typically small sizes, inclusions in diamond, and mantle xenoliths in general, are good subjects for investigation by ion microprobe methods [e.g., Johnson *et al.*, 1990; Moore *et al.*, 1991; Rampone *et al.*, 1991; Jerde *et al.*, 1993a,b]. Finally, the same techniques that apply to the measurement of natural samples may be used to quantify the results of laboratory experiments, such as trace element partitioning [e.g., Jolliff *et al.*, 1993; La Tourette *et al.*, 1993] and dissolution [Muir *et al.*, 1990]. The latest machines incorporate features such as high sensitivity at high mass resolving power, high abundance sensitivity, and multicollection at high mass resolution, among others, that promise to open up new areas for investigation by SIMS.

3. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Introduction

Inductively coupled plasma - mass spectrometry is an analytical technique which requires the sample to be introduced to a high temperature plasma, commonly argon, which dissociates molecules and ionizes atoms. The ions are passed into vacuum via a sample and skimmer cone interface, where a lens stack focuses the ion beam into a quadrupole mass spectrometer. Here, the ions are sorted by mass and detected using a scanning electron multiplier. The use of a laser in ICP-MS has allowed the geochemical analysis of small, solid samples to be accomplished. In order to give an insight to the potential of LA-ICP-MS, reference to work published by non-US labs up to the present day is made in outlining the theory and development behind this new and exciting analytical technique.

Advantages of LA-ICP-MS

Laser ablation ICP-MS is incredibly versatile. In theory, any solid material can be analyzed provided the laser can couple with the material, external standards are available, and internal standards are known. The advantages of LA-ICP-MS over conventional solution nebulization ICP-MS have been reported by many authors [e.g., Denoyer *et al.*, 1991; Jarvis and Williams, 1993; and Longerich *et al.*, 1993]: (A) Analysis of solid samples is direct and requires no lengthy dissolution processing which may be incomplete and can also potentially introduce contamination to the sample; (B) Analysis of solid samples by LA-ICP-MS requires little preparation (a flat surface may be required if the entire sample is to be probed, but it need not be parallel to better than 200 μm provided that the focus of the laser does not change from one part of the sample to another, resulting in different ablation characteristics); (C) a dry sample is introduced to the plasma with a resulting lack of polyatomic interference species produced by the interaction of water and acid species with the argon plasma.

Compared to other microsampling analytical techniques, LA-ICP-MS has several distinct advantages: 1) Laser probing utilizes light rather than charged particles and can, therefore,

analyze both conducting and non-conducting material without the need for a conductive coat and/or other charge balancing techniques, as in SIMS and electron microprobe techniques; 2) no vacuum is required in the sample chamber, although an airtight seal is; 3) LA-ICP-MS, unlike Atomic Emission Spectroscopy, separates the ionization step from the sampling step - the laser is used to ablate the sample only and the material is transported to the secondary plasma source in the torch of the ICP. Therefore, both steps can be independently controlled and optimized; 4) the high sensitivity of the ICP-MS allows small samples to be quantified, which is ideal for LA-ICP-MS in that spatial resolution can be used to investigate compositional gradients across a sample, even though the laser sampling area is 5-10 times greater than that obtained for the electron or ion microprobes [Reed, 1989, 1990]. However, the spatial resolution and detection limit of LA-ICP-MS is being constantly reduced for *in-situ* analysis of solid samples [e.g., Jackson *et al.*, 1992; Pearce *et al.*, 1992a; Neal, 1993; Feng, 1994]. For example, Gray [1985] reported a pit diameter of 700 μm , whereas Jackson *et al.* [1992] and Neal [1993] reported pit diameters of 20-30 μm - a 96% decrease over 7-8 years. Finally, trace-element analysis using LA-ICP-MS does not require involved interference corrections inherent in SIMS analysis and the hardware is considerably cheaper. Given this proviso, it has been found that a larger number of elements can be accurately quantified by LA-ICP-MS over SIMS, provided well characterized standards are available, with a detection limit similar to that of SIMS [Denoyer *et al.*, 1991].

Analytical Technique

The laser light emitted using a Nd:YAG laser is generally at 1064 nm in the infra-red range. This wavelength couples easily with samples containing significant quantities of the transition elements. Longerich *et al.* [1993] incorporated a harmonic generator into the laser apparatus which allowed shorter wavelength (532 nm and 266 nm) laser radiation to be generated. Jenner *et al.* [1994] determined crystal-matrix partition coefficients for a variety of trace elements using 266 nm wavelength laser radiation and reported a fourfold decrease in the diameter of the ablation pit from that produced at 1064 nm on this particular LA-ICP-MS system. This is important for controlled ablation of transition-element-poor materials (e.g., the minerals calcite and feldspar). However, Abell [1990] noted that materials which are transparent to laser light could be ablated using the 1064 nm wavelength if the laser pulse has sufficient energy. Feng [1994] used this *modus operandi* to undertake controlled ablation and analysis of carbonates using 1064 nm laser radiation.

The laser may be operated in two modes: (a) "Q-Switched" where a short laser pulse (≈ 10 ns) contains practically all of the energy; and (b) "Fixed-Q" or "Free-Running" where the laser pulse is much longer (120-150 μs) and the power delivered is considerably less [see Denoyer *et al.*, 1991, for detailed descriptions]. The resulting ablation characteristics are very different and produce very different ablation pits, thus affecting the size of the sample analyzed. In Q-switched mode, the laser energy is higher (relative to the free-running mode), and much of the ablation occurs through total vaporization and mechanical ablation. Calculated Relative Sensitivity Factors (RSFs) are relatively uniform across the mass range [e.g., Denoyer *et al.*, 1991]. In Fixed-Q or Free-Running mode, the power of the laser is lower, the laser interacts with the sample for a longer period of time and is conducted more deeply into the sample. This produces a deeper crater of smaller diameter relative to Q-switched mode, but the elements are ablated selectively on the basis of their vaporization energies [e.g., Thompson *et al.*, 1990]. This fractionation produces variable RSFs across the mass range relative to those produced in Q-

switched mode. Generally, the laser is operated in Q-switched mode.

By its very nature, the signal induced by the laser pulse is a transient one, thus making tuning difficult even in Q-switched mode. Hollocher [1993] reported a technique involving the by-pass of the argon carrier from the sample chamber over a crystal of iodine held in a glass tube. Iodine is evaporated at room temperature, is monoisotopic having an atomic weight of 127 which is in the middle of the mass range, and is relatively resistant to forming polyatomic species (i.e., ArI^+). While the memory of iodine may be long in the system, if this element does not need to be quantified and is only used for tuning, such a set up would seem ideal for LA-ICP-MS.

Detection limits are intimately related to the signal intensity, counting time per element for the ablation mass, and on the sample cell design which affects the size and configuration of the ablation pit and, thus, on the amount of material ablated. The precision of LA-ICP-MS is dependent on signal fluctuations as a result of pulse-to-pulse variations in the amount ablated and hence the amount reaching the plasma [van de Weijer *et al.*, 1992]. A quantitative analysis of both major and trace elements in geological samples can be obtained by normalizing the intensities of the observed peaks to either the weight of the sample removed or a true internal standard [e.g., Imai, 1990; Denoyer *et al.*, 1991]. Determining the accurate weight of sample removed is an extremely involved process, especially as not all of the material ablated reaches the plasma or collector [e.g., Remond *et al.*, 1990]. Internal standardization removes the need of knowing an accurate volume of material ablated and amount transported to the ICP torch. Also, normalizing signals from the unknown sample to an internal standard concentration removes any change in response with time between analyses [e.g., Pearce *et al.*, 1992 a,b]. However, this requires a knowledge of matrix composition and if it has an isotopic abundance which is less than 1% of the total matrix [van de Weijer *et al.*, 1992]. Choice of an internal standard is critical in that its behavior during ablation must be representative of the unknown elements being quantified [c.f., Jarvis and Williams, 1993]. If knowledge of the matrix is known, then such data can be used as internal standards. This is of particular significance for geological applications, where major and minor elements are usually determined via other methods (i.e., electron microprobe for minerals and XRF or INA for bulk samples).

The requirement of careful matrix matching in order to obtain quantitative analyses of small samples via LA-ICP-MS is well documented in the recent literature [e.g., Denoyer *et al.*, 1991; Jarvis and Williams, 1993; Williams and Jarvis, 1993]. In a study of pressed powder standard reference materials, Williams and Jarvis [1993] concluded that geological standards for LA-ICP-MS should not only be matched in chemistry, but more importantly in mineralogy. This is a particularly critical observation for the analysis of small geological samples which will tend to be individual minerals. However, it has been demonstrated that if the laser pulse has sufficient energy to ablate the sample via plasma plume expansion and not from absorption of the laser beam with resulting thermal vaporization (and matrix-dependent element fractionation), then non-matrix matched standards may be used [e.g., Abell, 1990; Jackson *et al.*, 1992; Jenner *et al.*, 1994; Feng, 1994]. Note that all procedures using nonmatrix matched standards are conducted in Q-switched mode which produces a more intense but shorter duration laser pulse (see above).

Applications

One major limitation of the present state-of-the-art is that LA-ICP-MS cannot rival SIMS or TIMS for the determination of isotopic ratios across the mass range, nor in spatial resolution. Factors such as ablation characteristics, transient sig-

nal, peak resolution, and counting statistics using a scanning electron multiplier do not produce isotopic ratios to the degree of accuracy required for petrogenetic interpretation. However, LA-ICP-MS has been used to accurately determine the heavier isotopes [e.g., U/Pb - Feng et al., 1993; Walder et al., 1993; Ludden, 1995] providing Pb is present in sufficient quantities (i.e., > 3 ppm) and the unstable ablation of U can be reconciled [e.g., Hirata and Nesbitt, 1995]. Furthermore, LA-ICP-MS does offer a cheaper alternative for trace element analyses without as many interference problems.

By optimizing the laser operating parameters, the amount of material ablated can be controlled such that depth profiling through a sample is possible [e.g., Denoyer et al., 1991] with comparison of surface and bulk compositions possible. Generally, depth penetration can be controlled to 1-10 μm per laser pulse. This is of particular significance to the semiconductor industry where impurities in high purity quartz have been identified [e.g., Denoyer and Wallace, 1989], although it is recognized that for most purposes, the scale of 1 μm depth resolution is still too coarse.

Perhaps one of the most advantageous applications of LA-ICP-MS is semi-quantitative analysis which allows a compositional fingerprint of unknown materials to be obtained, as well as fingerprinting compositional variations across a sample, although sample throughput is enhanced at the expense of accuracy. Critical in semi-quantitative LA-ICP-MS analyses is determining RSFs. By determining RSFs across the mass range, a calibration or response curve is generated using a multi-element standard which can be applied to all elements (from atomic mass 4 to 240) by reference to a single internal standard. Van de Weijer et al. [1992] demonstrated that for each matrix, a different set of RSF values need to be calculated, depending upon where the elements are located in a given matrix [cf., Jarvis and Williams, 1993]. The accuracy of the procedure depends upon the RSF values used, updating as necessary, and also upon the number of internal standards.

Applications of LA-ICP-MS to a number of different areas have been reported primarily from laboratories outside the United States. For example, several studies have been reported where LA-ICP-MS has been used to analyze sea shells for trace-element fluctuations, recording major pollution events [Fuge et al., 1993]. Marshall et al. [1991] used LA-ICP-MS to determine the trace elements in solid plastic materials. A defocused beam was used to analyze polyester, polyethylene, nylon, polyvinyl chloride, and polypropylene which contained a variety of fillers and other additives. Semi-quantitative and quantitative analyses were undertaken using ^{13}C as an internal standard. Results demonstrated that LA-ICP-MS can be used to explore the spatial distribution of trace elements in polymeric materials.

The application of LA-ICP-MS to the analysis of whole-rock geological materials (i.e., pressed powder pellets, lithium metaborate fusions) has been described by several authors [e.g., Perkins et al., 1991, 1993]. A recent development has been in the direct fusion of whole-rock samples using a tungsten strip heater cell under an Ar atmosphere to suppress volatile loss and minimize oxidation [Fedorovich et al., 1993]. By producing glass matrices in this way, dilution due to flux addition (and a potential source of contamination) is eliminated and matrix-matched glass standards are available (e.g., NIST 610, 612 glasses) for quantitative analyses.

Mineral analyses have been reported either analyzing grains [e.g., calcite, aragonite, zircon, olivine, plagioclase, and K-feldspar - Pearce et al., 1992a] or in thin section [e.g., titanite, zircon, uraninite, apatite, and garnet - Jackson et al., 1992; garnet and clinopyroxene - Neal, 1993]. The potential of LA-ICP-MS to the analysis of thin sections is seen in these studies, although spatial resolution, detection limits, and reproducibility need to be improved.

The application of LA-ICP-MS to the analysis of small samples is continually being developed. Furthermore, the area required for a fully quantitative analysis is constantly being reduced. Optimization of ablation and transportation of material will further enhance the sensitivity of this technique and expansion of the LA-ICP-MS analytical technique to geological samples and beyond is anticipated over the next quadrennium.

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