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THE DESIGN, OPERATION AND ROLE OF THE LASER-ABLATION MICROPROBE COUPLED WITH AN INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETER (LAM–ICP–MS) IN THE EARTH SCIENCES

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ABSTRACT

The coupling of a laser-ablation microprobe (LAM) to an Inductively Coupled Plasma – Mass Spectrometer (ICP–MS) has produced a relatively simple and inexpensive multi-element, high-sensitivity trace-element microbeam analytical system with characteristics ideally suited to research in the Earth Sciences. The LAM should be designed to allow for flexibility in sampling a wide variety of materials of various physical sizes and shapes, at variable, but small-scale, spatial resolution. The data aquisition and processing protocols of the LAM–ICP–MS system must allow the use of time-resolved analytical data for routine analytical work. Raw analytical data must be acquired and stored for processing on a time-scale appropriate to the rate of laser sampling and the scale of chemical variation in the sample (normally, integrated data for each mass, at least each second, during sample ablation). Robust calibrations, with reference materials (NIST trace-element glasses) and suitable internal standards contained in both the sample and reference material, allow quantification of the concentrations of many petrogenetically important trace elements. Relative fractionation of elements does occur during the analysis, and understanding of these phenomena is required before the full potential of LAM–ICP–MS can be realized. Despite this current limitation, the method is now capable of unique applications in mineralogical and geological research. Of particular importance is its ability to characterize, not only the chemical concentration of trace elements at ppm to ppb levels in minerals, but also the nature of their distribution. Time-resolved analysis of the analytical data allows distinction between trace elements incorporated in the host crystal-structure and those located in other phases (inclusions, *etc.*).

Keywords: laser-ablation microprobe, inductively coupled plasma – mass spectrometry, ICP–MS, high sensitivity, *in situ* analysis, trace element, microbeam, Earth Sciences, design criteria.

SOMMAIRE

L'utilisation d'une microsonde conçue pour ablation par rayon laser avec un plasma à couplage inductif et la spectrométrie de masse a produit un système analytique (LAM–ICP–MS) relativement simple et peu coûteux, permettant l'analyse à sensibilité élevée de matériaux géologiques pour plusieurs éléments traces. Le système laser devrait être conçu pour en maximiser la flexibilité pour l'échantillonage d'une grande variabilité de matériaux de toutes dimensions et de toutes formes, avec variabilité dans la résolution spatiale à petite échelle. L'acquisition des données et les protocoles pour leur manipulation doivent permettre l'utilisation routinière de données analytiques prélevées en fonction du temps. Les données de base doivent être stockées pour traitements à un rythme approprié en fonction du taux de prélèvement par le faisceau laser et l'échelle de variations compositionnelles dans l'échantillon (en mode normal, données intégrées pour chaque masse, au moins à chaque seconde, pendant l'ablation de l'échantillon). Des calibrages robustes, impliquant des étalons de référence (les verres NIST dopés avec éléments traces), et des étalons internes présents dans l'échantillon et les matériaux de référence, permettent la quantification des concentrations d'éléments d'importance pétrogénétique. Il y a un fractionnement relatif des éléments pendant l'analyse; ces phénomènes devront être expliqués avant de pouvoir réaliser le plein potentiel de cette technique. Malgré cette limitation, la méthode est déjà pleinement en mesure d'applications uniques dans des projets de recherche minéralogique et géologique. Sa capacité de caractériser non seulement les concentrations des éléments traces dans les minéraux, à des seuils de détection du ppm au ppb, mais aussi la nature de leur distribution, en fait un outil important. L'analyse des données en fonction du temps permet de distinguer les éléments incorporés dans une structure cristalline des éléments logés dans des micro-inclusions.

(Traduit par la Rédaction)

Mots-clés: microsonde avec ablation au laser, plasma à couplage inductif – spectrométrie de masse, ICP–MS, sensibilité élevée, analyse in situ, élement trace, microfaisceau, sciences de la terre, critères de conception.

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TABLE 1. PRIMARY SAMPLING BY LASER ABLATION

	Microbeam	Solid Sampling
Spot diameter	1 to 100 μm	100 μm to >1 mm
Volume sampled[1]	1 to 1,000,000 μm^3	0.001 to >1 mm^3
Weight sampled[2]	2 pg to 2 μg	2 μg to >2 mg

[1] Diameter assumed equal to depth. [2] Calculated for a solid density of 2.5 g/cm^3.

INTRODUCTION

Coupling of a laser-ablation sampling device with an Inductively Coupled Plasma – Mass Spectrometer (ICP–MS) has produced a relatively simple and inexpensive instrument with which to determine elemental and isotopic ratios in solid samples with extremely low limits of detection (Gray 1985, Arrowsmith 1987, Moenke-Blankenburg *et al.* 1990). The appropriate design and control of a laser-ablation microprobe (LAM) sample-introduction system allow high-spatial-resolution sampling of most geological materials. Methods of calibration are relatively simple and straightforward, and currently protocols for calibration use both internal standards and external glass-based reference materials.

Controlled high-spatial-resolution microsampling requires a focused laser beam of low pulse-energy. Most modern LAM sampling systems use a Q-switched Nd:YAG laser capable of producing sampling pits with diameters from 10 to 100 μm. The ablated material is flushed from the sample cell through one to two meters of tubing to the ICP torch by a continuous flow of argon. The ablated material is broken into atoms and ionized in the argon plasma before extraction into the mass spectrometer for analysis.

Current LAM–ICP–MS systems are capable of rapid multiple-element determination, with detection limits down to a few parts per billion. The ability of LAMs to bore near-cylindrical pits in a controlled fashion enables measurement of vertical (as well as horizontal) chemical profiles in minerals (Jackson *et al.* 1992). Isotope-ratio determinations of modest precision (0.5 to 1% RSD) also are possible and have led to some interesting preliminary results on isotopic dating (Feng *et al.* 1993, Fryer *et al.* 1993) using the U–Pb system.

This paper describes the relation between LAM sampling and ICP–MS instrumentation. Procedures are rapidly evolving as more laboratories become involved, and as rapid technical changes are made to both LAM capabilities and to ICP–MS instrumentation.

LASER SAMPLING OF SOLIDS

Two main approaches are currently used in the laser sampling of solids to supply material to ICP–MS analyzers for analysis: (1) bulk sampling (representative of the bulk material), and (2) spatially resolved sampling. In the earliest work on laser-ablation sampling for ICP–MS (Gray 1985), relatively high lasing powers were used to create sampling pits of 0.5 to 0.7 mm diameter. This work has been extended by a number of investigators (Denoyer 1990, Fedorowich *et al.* 1993, Jarvis & Williams 1993, Perkins *et al.* 1993) in order to use laser-ablation bulk sampling to eliminate the need to dissolve materials prior to analysis by ICP–MS. The principal challenge with this approach as a bulk sampling technique in the Earth Sciences is to ensure that the material being analyzed is representative of the geological sample. Heterogeneity is a ubiquitous problem, and preparing a representative and homogeneous solid material at the scale at which it will be sampled by the laser (Table 1) is difficult for most natural materials. Approaches to date include preparation of pressed-powder pellets as used for X-ray-fluorescence (XRF) analyses (Denoyer 1990, Perkins *et al.* 1993) and fusions of solid powders, both with (Perkins *et al.* 1993, van Heuzen 1991) and without (Fedorowich *et al.* 1993) the use of fluxes.

A laser-sampling system specifically designed to sample solids at high spatial resolution and coupled to an ICP–MS analyzer for analysis of geological materials was first reported by Jackson *et al.* (1992). This type of facility and more recent developments (Longerich *et al.* 1993, Jenner *et al.* 1993) show great potential for providing a new microbeam analytical tool for the study of the distribution of elements at trace (ppm) and ultratrace (ppb) levels in natural solids. The laser-ablation microprobe (LAM) of Jackson *et al.* (1992) consisted of a Q-switched Nd:YAG laser, components to control laser energy, optics to steer and focus the laser beam, a standard petrographic microscope, and a sample cell connected to the ICP–MS analyzer by flexible plastic tubing. This system is capable of producing controlled ablation of near-cylindrical sampling sites with pit diameters in the range of 30–40 μm in a variety of minerals rich in transition elements.

LAM design

Successful LAM systems (as opposed to bulk sampling devices) require the ability to control ablation geometry, size and position. Laser-ablation sampling behavior is a function of a number of variables, including the laser focus, laser-pulse power, the sampling rate, and the sample's absorptivity at the specific wavelength of the laser. The most commonly used Nd:YAG laser, operating in the infrared (IR), at the fundamental wavelength of 1064 nm, is strongly absorbed by many transition-element-rich materials at low power. However, minerals can be

TABLE 2. DIAMETER OF ABLATION PIT (μm) FOR DIFFERENT Nd:YAG LASER WAVELENGTHS

	1064 nm	532 nm	266 nm
Calculated from diffraction theory	22	11	5
Titanite - 10 shots	38	21	15
Titanite - 100 shots	48	21	12
Glass - 10 shots	25	15	12
Glass - 100 shots	25	15	12

Focal length of lens: 50 mm; diameter of laser beam: 6 mm.

difficult to ablate controllably with the 1064 nm wavelength owing to their low absorptivity at this energy, as well as unpredictable effects of cleavage, defects and inclusions (Jackson *et al.* 1992). Recently, Nd:YAG-based LAMs have been modified by the introduction of frequency-quadrupling, allowing use of the fourth harmonic (266 nm), which is in the ultraviolet (UV) region (Longerich *et al.* 1993, Jenner *et al.* 1993). Most minerals and glasses absorb 266 nm radiation strongly, resulting in more controlled ablation over a wide range of solids, with higher-resolution sampling (better geometry and smaller predicted and achieved ablation pits: Table 2, Fig. 1). Use of UV laser radiation requires significant modification to the optical components of a LAM system.

In addition to controlling the geometry and position of the ablation site, one must be able to control and vary the rate of sampling (mass ablated per unit time), which is related to the diameter of the ablation pit. The sensitivity of the LAM–ICP–MS system is a function of the mass of material supplied to the ICP–MS per unit time. Where information on fine-scale distribution of elements is required without high sensitivity, the LAM should be capable of being optimized for sampling at high spatial resolution [*e.g.*, 10 μm or smaller spots to study zoning of the rare-earth elements (*REE*) in accessory minerals such as titanite]. For other applications, such as analysis of ultratrace elements in

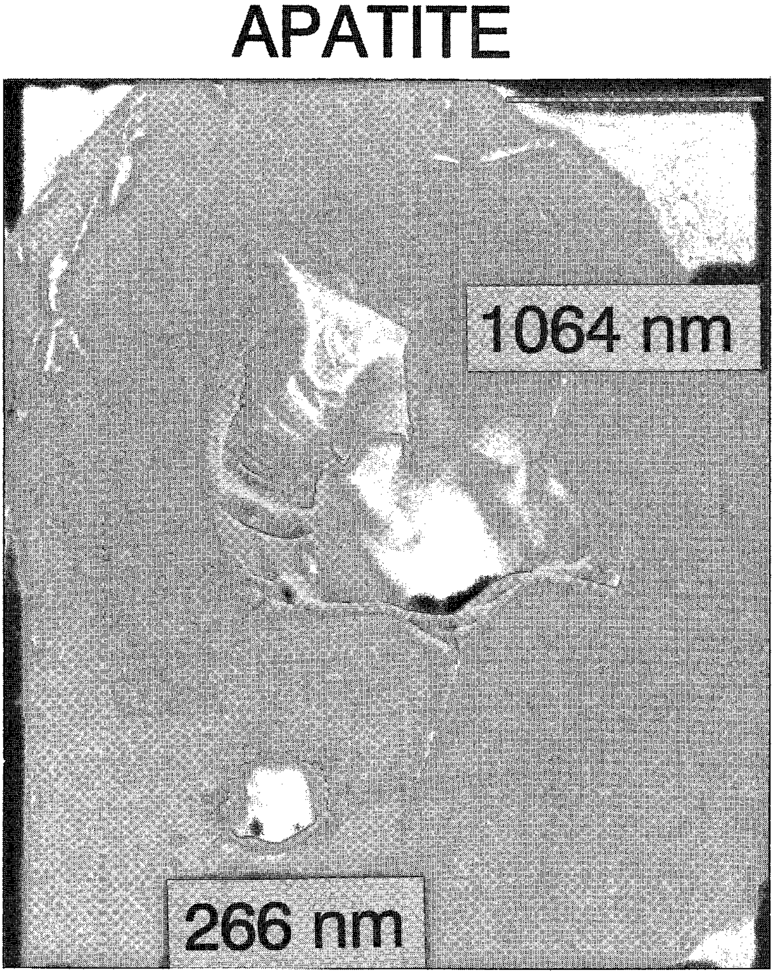

FIG. 1. Scanning electron micrograph of laser-ablation pits in apatite made with laser radiation of wavelength 1064 nm (IR) and 266 nm (UV). Laser-ablation sampling of many minerals is more easily controlled using laser radiation in the UV rather than in the IR, and provides higher spatial resolution (smaller pits). Scale bar: 48 μm.

common minerals, where sensitivity must be maximized with an accompanying loss of spatial resolution, the LAM must be capable of high sampling-rates to lower the detection limits of the system (*e.g.*, 100 μm, or larger spots, to study low concentrations of the *REE* in large grains of coexisting olivine and orthopyroxene).

As with all microprobe systems, it is important to have the best capabilities for optical viewing incorporated into the LAM design. The location of the LAM several meters from the ICP–MS analyzer allows the incorporation of more sophisticated optical systems than are found in other microprobe systems. Indeed, incorporation of a high-quality petrographic microscope into the LAM optical system (Jackson *et al.* 1992) allows full use of both low- and high-power transmitted- and reflected-light optics to locate features to be analyzed. During ablation, relevant optical components of the system are removed from the laser path to prevent damage. The ablation process can be viewed using a TV monitor incorporated into the system.

Building flexibility into a LAM designed for coupling with an ICP–MS is crucial. In a LAM–ICP–MS system, the capabilities of the ICP–MS are largely fixed, whereas flexibility built into the LAM device provides for the orders of magnitude variation in the integrated analytical sensitivity, which are possible by varying the rate of material provided to the ICP–MS (Table 1).

Design of the sample cell

The interaction of the laser with the solid must take place in a sample cell (Fig. 2) that allows the laser to be focused on the sample. The cell must have an inlet and exit for Ar gas (at slightly above atmospheric pressure and at a flow rate of approximately 1 L/min) to enter the cell and sweep the ablated material to the ICP. Successful designs of sample cells are numerous, and almost all cell designs work reasonably well.

The cell must have a window above the sample that is transparent to the laser wavelength used. Optical-quality glass is suitable for IR wavelengths (1064 nm, Nd:YAG primary radiation), but materials such as fused silica are required with UV wavelengths, as produced by a frequency-quadrupled Nd:YAG laser (266 nm). Because of the possibility of laser damage to the cell window, it should be designed for ease of replacement. For transmitted-light viewing of transparent samples, an additional window below the sample is used.

The cell must be closed and reasonably air-tight so that the Ar (Fig. 2) can efficiently sweep the ablated sample to the ICP. The cell also must allow easy change of samples and provide for the efficient flushing of residual atmospheric gases occluded during sample changeover, otherwise an undesirable "mixed gas" plasma may result in an ICP with different analytical characteristics. Small leaks in the cell may

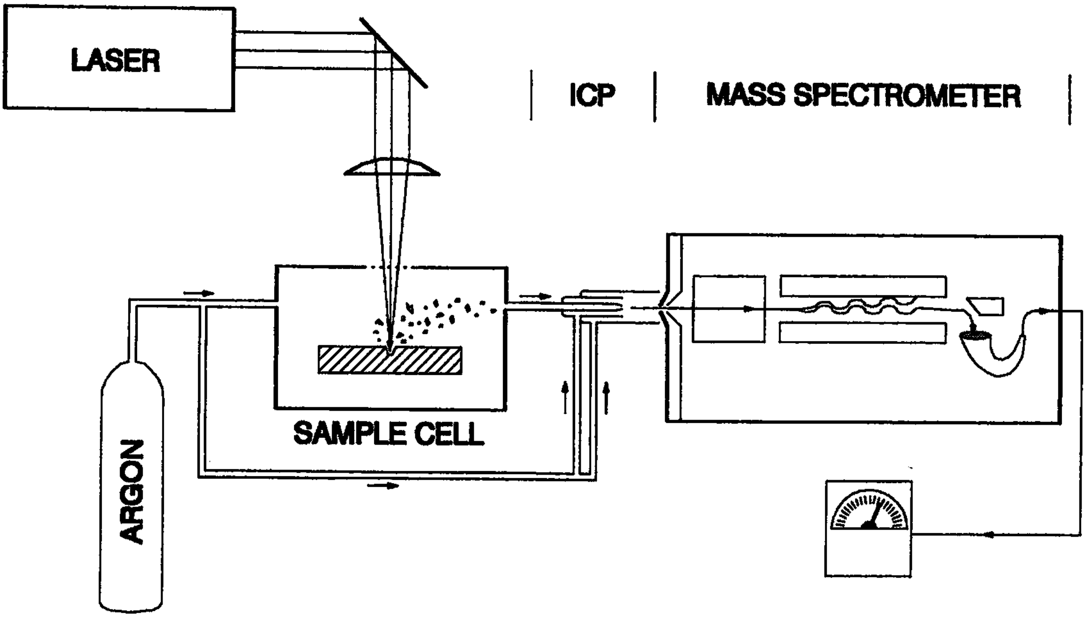

FIG. 2. Schematic diagram of the components of a laser-ablation sampling device connected to an ICP–MS.

not be a problem, as the working cell is normally slightly above atmospheric pressure. Indeed, Arrowsmith (1990) has used "leaks" to allow some of the Ar to be vented to the atmosphere in order to optimize gas-flow dynamics.

The cell must be able to contain the samples and reference materials used during the analysis. Specimens to be analyzed come in all sizes and shapes, from grain mounts to standard petrographic sections to slabs. LAM sampling does not need the stringent preparation of samples required by most microprobe techniques, although the need to optically locate petrographic features for sampling, or to obtain prior or subsequent quantification of internal standard or other elemental concentrations by electon microprobe, may require a good-quality polish of the specimen surface(s). For petrographic thin sections, thicker sections than normal (100 μm rather than 30 μm) are recommended to allow sampling at higher rates to improve detection limits or to enable deeper chemical profiling.

Cell design is a compromise between what is convenient and what is practical. Cell design may also be influenced by the calibration protocols of the LAM–ICP–MS system (*i.e.*, requirements for efficient switching between reference materials and samples without disruption of the plasma). Cells that can contain several samples with reference materials allow efficient production of data with a continuity of analytical conditions. Given the variability in size, shape and nature of natural solid specimens in research in the Earth Sciences, use of a range of sample cells is a distinct advantage.

Ablation products and transfer to the ICP–MS

The nature of the material that has been ablated is not completely understood (Darke & Tyson 1993). What is known is that transport of the ablated material to the ICP by the Ar carrier gas is surprisingly efficient, even through narrow (inside diameter in millimeters) transfer tubing several meters long. Either plastic or metal tubing can be used, but the use of inflexible metal tubing inhibits cell movement relative to the fixed path of the laser, during both analysis of various points on the sample(s) in the cell and disconnection of the sample cell during sample change.

Geometrical considerations for efficient transport of the ablation products through the tubing have been studied (Moenke-Blankenburg 1993). A large diameter is desirable, as it increases the ratio of gas volume to wall area and minimizes loss of sample by deposition on the wall. Conversely, a small diameter is desirable to increase the gas velocity and minimize the time for transport of the sample from the cell to the ICP. Although a minimum volume in the transfer tubing would seem desirable (minimum length for a constant diameter), a volume sufficient to produce a relatively stable supply of material to the ICP is required in practice. Most mass spectrometers used in ICP–MS analysis are sequential mass analyzers that require the measurement of each mass sequentially (typically 10 to 30 masses per sweep of the required mass-range), and therefore require some smoothing of the sample input into the analyzer for accurate quantification of element concentration.

LAM–ICP–MS analysis

The LAM provides the material to be analyzed by the ICP–MS. The ICP–MS itself is composed of an inductively coupled plasma (ICP), which dissociates and ionizes the transported ablated material from the LAM sample cell, and a mass spectrometer (MS), which measures the ion-beam intensity of the charged masses produced in the plasma. Thus, unlike other trace-element microbeam techniques such as SIMS (Secondary-Ion Mass Spectrometer) and LAMMA (LAser-Microprobe Mass Analyzer), the sampling process is not required to produce the ions that are ultimately measured by the MS. With the sampling process separate from the analyzer, the two main parts of the analytical system can be independently adjusted to optimize the performance of the LAM–ICP–MS system.

Calibration of LAM–ICP–MS analysis

Calibration and quantification of LAM–ICP–MS analysis are not fundamentally different than for standard ICP–MS solution analysis or from any determinative method for specific elements. Techniques used to date involve combinations of internal standards, external reference-materials, matrix matching, and the use of surrogate calibration. The most significant differences between solution ICP–MS and LAM–ICP–MS calibrations are related to the practical difficulties of supplying a constant or homogeneous sample to the ICP–MS analyzer from a LAM sampling system.

External calibration by matrix matching of major-element compositions has been used (van Heuzen 1991) with success to analyze pressed-powder pellets, but this procedure is impossible to use for *in situ* LAM–ICP–MS studies. With external calibration, reproducibility of the rate of laser sampling must be closely controlled to provide a constant and homogeneous supply of material to the ICP–MS. This method of calibration is of principal use for bulk sampling of solids rather than for *in situ* microprobe applications.

The most successful method of microbeam calibration, as developed by the Memorial University group (see Jackson *et al.* 1992) and independently duplicated by the Université de Montréal group (Ludden *et al.* 1995), involves the use of elements of known concentration, in the sample, as internal standards in combination with external reference materials. The addition of internal standards to both samples and standards, although theoretically possible, is very difficult. In most cases, "naturally occurring" internal standards are used, *i.e.*, elements for which the concentration is known in both the sample and the reference material. Calibration is normally done by reference to the spiked-glass reference material NBS (now NIST) 612, with correction for difference in ablation yield between sample and reference material by use of naturally occurring internal standards in each solid. The concentration of the internal standard can be obtained by an analysis of the material, or may be sufficiently accurately known from the stoichiometry of the phase being analyzed. In our experience with the analysis of very small volumes of minerals, there are significant differences in the ablation behavior among suites of elements. The alkaline-earth elements, the rare-earth elements, Zr, Hf, Th and U are ablated and transported to the MS detector with approximately the same efficiency. Thus Ca is a very good internal standard for the quantification of this suite of elements. It is also present in most rock-forming minerals and is present at similar concentrations in reference materials. For some sets of elements (*e.g.*, Pb and U), difficulties have been reported (Fryer *et al.* 1993, Ludden *et al.* 1995) in the determination of relative concentrations at the accuracy required for many studies.

Fractionation of elements in laser-ablation sampling and transport is neither understood nor well documented. An experiment to document the relative fractionation of elements (Fig. 3) shows the integrated signals obtained from the second two minutes (minutes 2–4) of a continuous ablation of NBS 610, ratioed to the signals from the first two minutes (minutes 0–2), for a wide variety of elements (60), and normalized to an internal standard, Ca. The fractionation factors calculated are thus a measure of the fractionation of each element during ablation, relative to Ca.

The fractionation factors shown in Figure 3 demonstrate the possible occurrence of extremely large interelement fractionations during laser ablation and transport, which have profound implications for accurate calibration. Similar experiments with a variety of natural minerals produce relative fractionations similar to those for the NIST glass, suggesting that fractionation is substantially independent of sample matrix. No single physical or chemical property of the elements correlates with, or explains, the pattern of fractionation factors. However, it is evident that most lithophile elements generally behave similar to each other, with factors near 1. Likewise, many chalcophile elements show similar behavior during ablation, with factors of 2 or more, whereas siderophile elements have intermediate fractionation factors.

The initial success of the Jackson *et al.* (1992) calibration technique for the *in situ* determination of trace-element concentrations was due to the specific

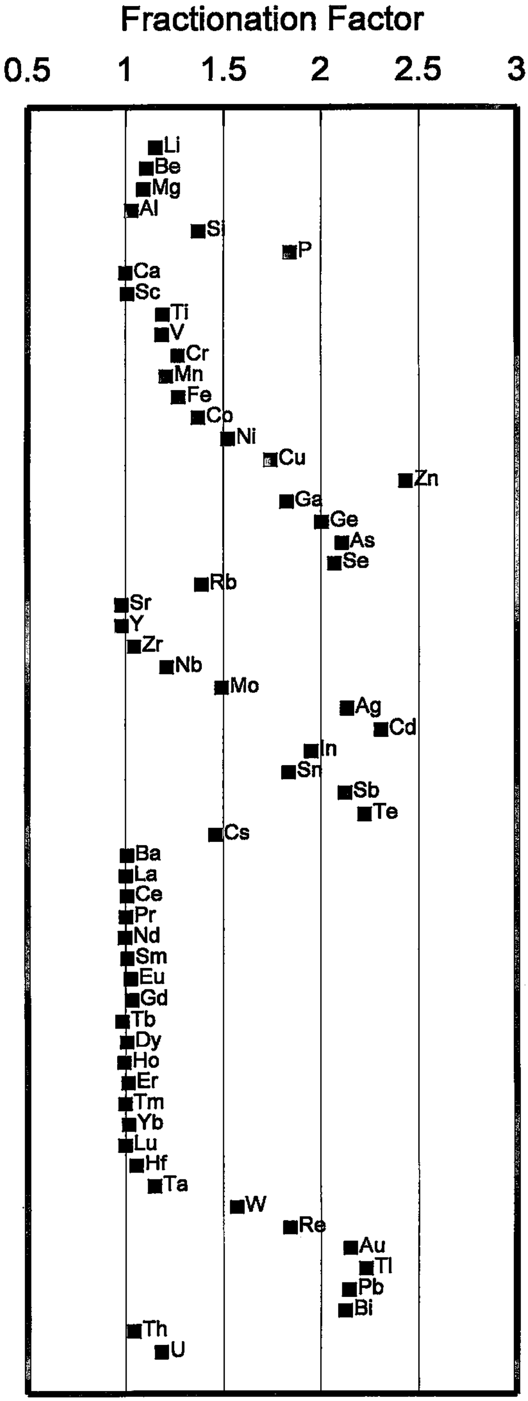

FIG. 3. The relative fractionation of 60 elements during a continuous prolonged laser-ablation sampling of NBS 610 glass. The fractionation factor is the ratio of the integrated signal obtained for the second two minutes (minutes 2–4) of the continuous ablation to the signal for the first two minutes (minutes 0–2), normalized to Ca as the internal standard.

elements determined and the internal standards (*i.e.*, Ca, Zr, U) used. All of these elements have fractionation factors close to one (Ca = 1). Successful quantification of elements with fractionation factors dissimilar from the internal standard (*e.g.*, Pb using Ca, Zr or U as internal standards) is not yet viable. Successful determination of concentrations of these elements could be done by careful matching with internal standards with similar behavior during ablation, or by the development of procedures that minimize inter-element fractionation. Clearly, much work on the systematics of the ablation process is required to maximize the applicability of LAM–ICP–MS to all elements. Although Figure 3 suggests widely varying behavior of elements during ablation, we should recognize that almost all lithophile metals (exceptions are the alkalis, Si and W) have similar (±15%) fractionation-factors, and most minerals contain suitable internal standards (*i.e.*, Mg, Al, Ca, Zr, Th, U) for quantitative calibration of the majority of lithophile elements. The use of Si as an internal standard, however, could lead to significant bias, relative to concentrations determined using Ca as an internal standard (see also Ludden *et al.* 1995).

LAM–ICP–MS signals and data processing

The ICP–MS receives a transiently variable input from the sampler (LAM) *via* a significant length (normally several m) of tubing. The need to deal with the transient nature of the signals (intensity as a function of time) produced by a LAM–ICP–MS requires the capability to record the raw data and to evaluate these data prior to processing. The complexity of the transient signals requires data-processing capabilities that are normally not provided by commercial software for the analysis of solutions. Indeed, the protocols for data acquisition and storage for some commercial instruments have precluded the collection of data required for characterization of the compositional zoning as observed in the garnet crystal of Jackson *et al.* (1992, Fig. 15). Where the difference in elemental concentrations is detectable over a few micrometers (typical rates of boring by the laser are 1 μm/s), protocols for data acquisition must allow the isolation and processing of analytical data with integrations on the order of one second (Jackson *et al.* 1992). It must be recognized that all ICP–MS systems with general multi-element capabilities currently available use sequential mass-analyzers (generally quadrupoles). Even the rapid peak-switching capability of a quadrupole MS requires, in practice, approximately 10 ms per mass analyzed. An analysis involving 20 different masses per sweep collects a full mass-spectrum every 0.2 second. Data collected in each mass-sweep may be significantly different. The ability to analyze this variation in signal (which is a function of the spatial chemical variation being studied) is essential for successful use of the LAM–ICP–MS technique. The appropriate time-scale to integrate the analytical mass sweeps can only be determined after the data are inspected and the nature of the signals has been determined.

Information contained in LAM–ICP–MS signals

An appropriately configured LAM–ICP–MS system can collect and process time-resolved data at a physical scale of a few μm^3, and provides a unique microbeam capability for crystal-chemical studies. The data contain significant additional information about the nature of the sample being analyzed as a function of time. Jenner *et al.* (1993) reported studies of K_d on synthetic crystals that were of marginal size for analysis, and used the time-resolved signal to determine when the laser was sampling the crystalline phase, as opposed to mixtures of both glass and crystal. In the determination of trace-element distributions, it is important to determine not only the concentration of each element in each phase, but also the type of element distribution. Figure 15 of Jackson *et al.* (1992) documents a smooth change in Lu concentration of the garnet crystal, from approximately 75 (core) to 5 ppm (rim). These data indicate not only that there is a concentration gradient, but also that it is systematic. This smoothly zoned example can be contrasted with the distribution of trace elements contained in phenocrysts of clinopyroxene (Fig. 4) and phlogopite (Fig. 5) from a lamprophyre. Within the clinopyroxene (Fig. 4), the Ce and Zr signals correlate with the signal of the internal standard (Ca), indicating homogeneous distribution of these two trace elements in the crystal. In contrast, the Ba signal indicates that the Ba, in the material sampled by the laser, is contained in submicroscopic inclusions within the clinopyroxene, and not in the clinopyroxene structure. Ba in the clinopyroxene itself is below the detection limit of this LAM–ICP–MS analysis. However, if the entire data had been integrated before calculation of element concentrations for the crystal, as with some microbeam protocols, a low concentration (but above detection limit) would have been determined. For the phlogopite phenocryst from the same sample, good correlation of the Sr and Nb signals relative to the internal standard Ti is observed (Fig. 5), but the signals for Ce are erratic. The Sr and Nb signals are consistent with the incorporation of these elements at crystallographic sites in the mineral during growth. The Ce signal indicates that, like the Ba in the clinopyroxene, Ce does not occur in the phlogopite structure. The observation that the Ce signal persists much longer than the Ba signal (generally a single data-block of one second), however, suggests that the Ce is contained in zones that have vertical dimensions that are sampled by the laser over several seconds (several μm depth). The Ce-rich zones also seem to be sampled more regularly in the

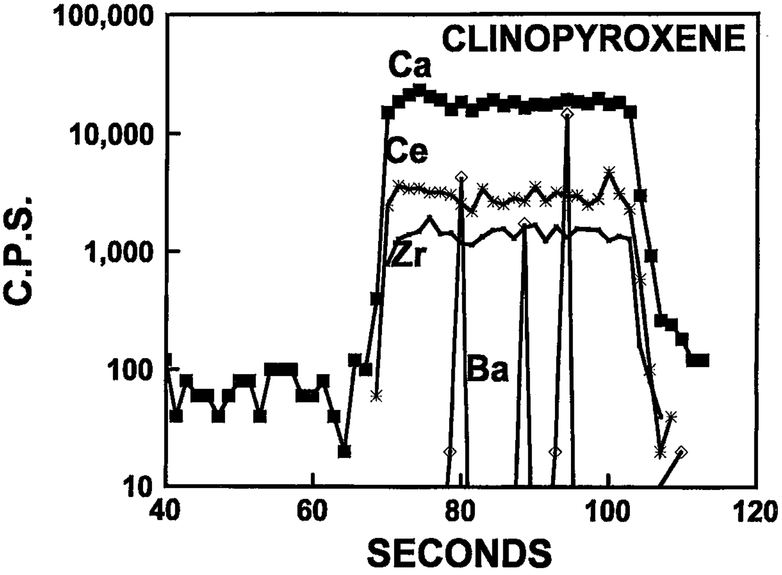

FIG. 4. LAM–ICP–MS data from a 30-s laser ablation of a clinopyroxene phenocryst in a petrographic thin-section of a lamprophyre. The signals for the trace elements Ce and Zr track the Ca internal standard signal, indicating their homogeneous distribution within the phenocryst. The sporadic, short-lived Ba signal is indicative of submicrometric inclusions or zones in the host clinopyroxene.

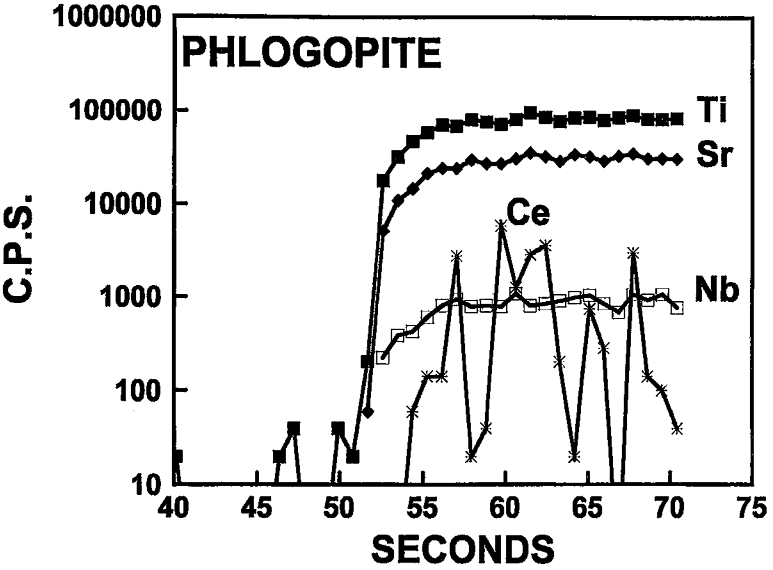

FIG. 5. LAM–ICP–MS data from a laser-ablation sampling of a phlogopite phenocryst from the same petrographic section shown in Fig. 4. The signals for the trace elements Sr and Nb follow the signal for the internal standard Ti, indicating their incorporation into the structure of the phlogopite during the mineral's growth. The irregular, but persistent, Ce signal indicates the presence of zones of significant size in the phlogopite, *i.e.*, sampled over several µm (inclined cleavage planes?) that contain high concentrations of Ce.

phlogopite than Ba was in the clinopyroxene. The data indicate that although Ce is below the limit of detection for the LAM–ICP–MS in phlogopite, the zones in which it is contained (on cleavage planes?) are a recurring feature in the mineral. These examples provide a powerful demonstration of the capabilities of the use of time-resolved LAM–ICP–MS analytical signals to provide new information on the nature of element distribution in minerals.

THE FUTURE OF LAM–ICP–MS FOR RESEARCH IN THE EARTH SCIENCES

LAM–ICP–MS is a new technique that is undergoing rapid development, and its role relative to other microbeam trace-element techniques still needs to be established. A LAM–ICP–MS system, appropriately configured for work on Earth materials, has some unique capabilities. The reader is referred to the recent review of Koppenaal (1992) on AMS (Atomic Mass Specrometry) for comparisons of the capabilities of other similar systems.

As shown above, the ability to extract information on the spatial as well as chemical distributions of elements within minerals will allow better evaluation of the significance of trace-element concentrations in natural solids. For example, in studies of partition coefficients, we will no longer have to assume that trace elements are contained within the mineral structure, if they are measured reliably and regularly in physical separates by bulk analytical techniques, or by *in situ* microbeam techniques that integrate analytical signals over large (tens of μm^3) volumes of sample. Studies on the distribution of trace constituents in rocks also will be able to pinpoint the location of elements in bulk samples and more accurately determine what proportion of trace elements is contained in the major phases rather than in accessory minerals and along grain boundaries. Advances can also be anticipated in studies of crystal-growth mechanisms and the variation in the physicochemical nature of the environments in which they grew.

The fact that a LAM–ICP–MS microbeam facility is relatively inexpensive to install and operate will facilitate its rapid adoption by the research community. Although much work still is required to fully develop its capabilities, the current state of development is such that it is now ready for applications, even though the first microbeam data were published in 1992 only. There are robust protocols for calibration of most of the petrogenetically important trace elements, and they use the readily available NIST trace-element-doped glasses. The major drawback to the widespread use of the LAM–ICP–MS in the Earth Science community will be the requirement for investment of much time and skill in the understanding of (and in working with) the raw analytical data.

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