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APPLICATIONS OF LAM–ICP–MS ANALYSIS TO MINERALS

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ABSTRACT

Laser-ablation microprobe ICP–MS (LAM–ICP–MS) is rapidly emerging as an exciting new analytical tool in the earth sciences. Here we present the results of a series of isotopic and trace-element studies of various minerals; we used a commercially available Fisons-VG Laserprobe and PQ2+ ICP–MS capable of ablation at spot-sizes of 20 to 60 µm. Results are presented for Pb/Pb dating of zircon, for which an accuracy of <1% is attainable. For carbonate and mafic minerals of igneous origin, detection limits of 100 ppb and precisions of 2–5% are attained for many trace elements. In general, calibration is possible using synthetic or natural standards; as elemental responses are controlled by the efficiency of the ionization of ablated material in the ICP-plasma, matrix-matched calibrations are not as important as for ion-probe analysis, owing to the efficiency of ionization in the plasma torch. In the future, new high-sensitivity ICP – mass spectrometers, coupled with high-spatial-resolution UV laser microprobes, should provide detection limits at the ppt level and spatial resolution comparable with that attained with an ion microprobe.

Keywords: laser ablation, inductively coupled plasma – mass spectrometry, ICP–MS, trace elements, Pb isotopes, minerals.

SOMMAIRE

L'ablation au laser couplée à la technique de plasma à couplage inductif avec spectrométrie de masse (ICP–MS) est devenue rapidement un outil analytique performant dans les sciences de la terre. Nous présentons ici les résultats de plusieurs études sur les compositions isotopiques et les teneurs en éléments traces de divers minéraux. Ces résultats ont été obtenus à partir d'une sonde laser Fisons-VG couplée à un appareil ICP–MS PQ2+; avec ce système nous pouvons produire des points d'ablation par laser de l'ordre de 20 à 60 µm. Les quelques données géochronologiques sur cristaux de zircon nous permettent de calculer des âges Pb/Pb d'une précision inférieure à 1%. Pour les carbonates et les minéraux mafiques, les seuils de détection des éléments traces sont de l'ordre de 100 ppb, et les précisions, de 2 à 5%. En général, le calibrage est possible à partir d'étalons synthétiques et naturels. Par rapport aux analyses obtenues par sonde ionique, les effets de matrice sur l'analyse sont moins importants. Ceci est dû à l'efficacité d'ionisation dans la torche à plasma. A l'avenir, l'augmentation de la sensibilité des spectromètres de masse et de la performance des sondes lasers à résolution spatiale élevée devrait permettre d'atteindre des seuils de détection de l'ordre du ppt, et une résolution spatiale comparable à celle d'une microsonde ionique.

Mots-clés: ablation au laser, plasma à couplage inductif – spectromètre de masse, ICP–MS, éléments traces, isotopes de Pb, minéraux.

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INTRODUCTION

Laser-ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS) is a highly sensitive technique capable of direct elemental and isotopic measurements in solid samples at the scale of 100 μm or less (Gray 1985, Arrowsmith 1987, Hager 1989, Denoyer *et al.* 1991, Pearce *et al.* 1992, Perkins *et al.* 1993, Longerich *et al.* 1993). Focusing an incident Nd:YAG (1064 nm) laser results in crater sizes of 20–60 μm, depending on target material and ablation time. Provided that sufficient material can be transported to the plasma torch of the ICP–MS, quantitative analysis is possible for these small-volume craters (*i.e.*, Jackson *et al.* 1992, Feng *et al.* 1993, Feng 1994). Frequency quadrupling of the Nd:YAG laser to produce a wavelength of 266 nm can result in craters of <10 μm (Longerich *et al.* 1993), but the significant reduction in the volume of material carried to the plasma torch results in signals that are commonly at the current limits of detection of the ICP–MS. Improvements in the sensitivity of the ICP–MS, the efficiency of ionization in the plasma torch, and the means of transport of the ablated materials are required in order to analyze such small volumes of sample.

The processes of mechanical and chemical fractionation that occur during the interaction of the incident laser-beam and the sample are poorly understood. Some of the processes have been summarized by Ready (1971), Moenke-Blankenburg *et al.* (1990), Hager (1989) and Remond *et al.* (1990). Experiments involving focused lasers of different energy, different carrier gases and sample volumes for specific groups of elements (*i.e.*, Feng *et al.* 1993, Ludden *et al.* 1995) are required in order to provide quantitative analysis by LAM–ICP–MS. Nonetheless, the available data suggest that mass fractionation, matrix effects, and the mechanical transport of the ablated material are controlable, and LAM–ICP–MS can thus produce quantitative trace-element and isotope data with ablation craters 20–60 μm in size (Jackson *et al.* 1992, Feng *et al.* 1993, Fryer *et al.* 1993).

In this paper, we present a summary of results for minerals using a commercially available Fisons-VG LaserProbe and PQ2+ ICP–MS. Initial experiments centered on (1) the analysis of zircon for U, Pb and Th, with potential applications in geochronology (Feng *et al.* 1993, Ludden *et al.* 1995), (2) analysis of carbonate minerals and foraminiferal tests (Feng 1994, Wu & Hillaire-Marcel 1995), and (3) analysis of mafic minerals in igneous rocks for trace elements and the establishment of minerals as reference standards.

INSTRUMENTATION

A Fisons-VG PQ2+ ICP mass spectrometer and a Fisons-VG LaserProbe were used for this work. The LaserProbe uses a Spectron 300 mJ Nd:YAG laser operating at 1064 nm with a 5-nanosecond half-pulse duration for Q-switched mode. The laser is attenuated by inserting circular ceramic apertures into the beam path to reduce beam divergence, resulting in an output energy of 2–10 mJ per pulse, about 1–5% of the uncollimated laser output. However, power density at the target is maintained at the same level as (or higher than) the uncollimated laser by reducing the area of ablation to <100 μm in diameter in Q-switched mode (*e.g.*, Pearce *et al.* 1992). The LAM–ICP–MS is optimized for maximum count-rates by ablating NBS

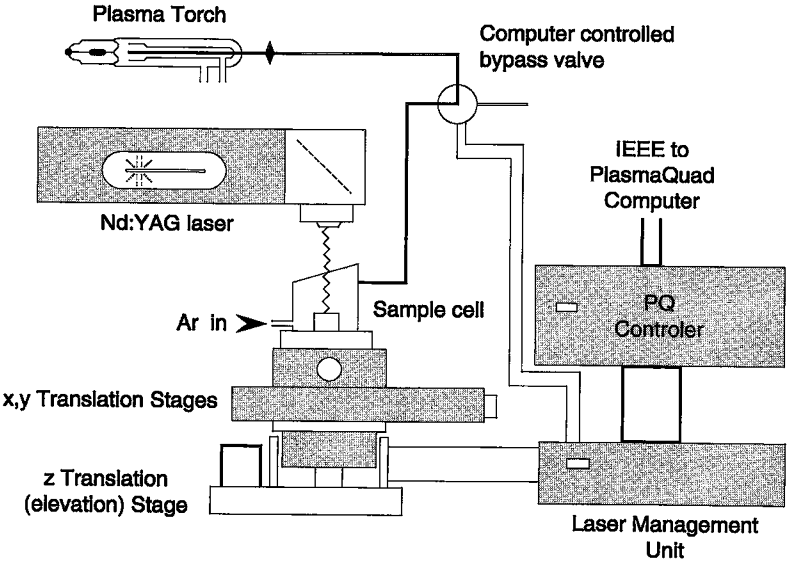

FIG. 1. Schematic of the Fisons-VG laser microprobe system (adapted from Fisons-VG brochure).

TABLE 1. LAM-ICP-MS OPERATING CONDITIONS

LASER MICROPROBE	
Laser mode	Q-switched
Flashlamp voltage	700-750 v
Laser repetition rate	4-10 Hz
Approximate laser output	4-6 mJ/pulse
Laser power density	$2*10^{12}$ to $3*10^{10}$ W/cm^2
Sample pit size	20 - 80 µm diameter
Pre-ablation time	20 s
Focus condition	On sample surface
ICP - MASS SPECTROMETER	
Extraction lens	0.6 - 1 v
Collector lens	variable
Nebuliser flow	1.1 - 1.3 L/min
Coolant gas	1.4 L/min
Auxilary gas	1 - 1.2 L/min
Resolution (amu)	approx. 1 amu peak width
Measuring points	3 points with DAC step of 1
Dwell time	20 - 30 ms

(now NIST) silicate-glass reference material 612 (NIST 612); the usual operating conditions are listed in Table 1. A simplified diagram of the instrument is shown in Figure 1. The instrument is optimized differently depending on the isotopes of interest (*e.g.*, ^{208}Pb for zircon, ^{88}Sr and ^{140}Ce for carbonate, and ^{140}Ce for mafic minerals).

During ablation, the laser beam passes through the top of a silica-glass sample cell and is focused onto the sample, which is either an individual grain of a mineral mounted in resin, or a thin section. The carrier gas flows through the sample cell, transporting the ablated material through approximately 1.5 m of 3 mm (i.d.) polyurethane tube to the injector tube of the standard ICP torch. The sample is held in an argon atmosphere, and as no vacuum is required, changing the sample is rapid. These operating conditions result in sample pits of 20 to 60 µm, depending on the

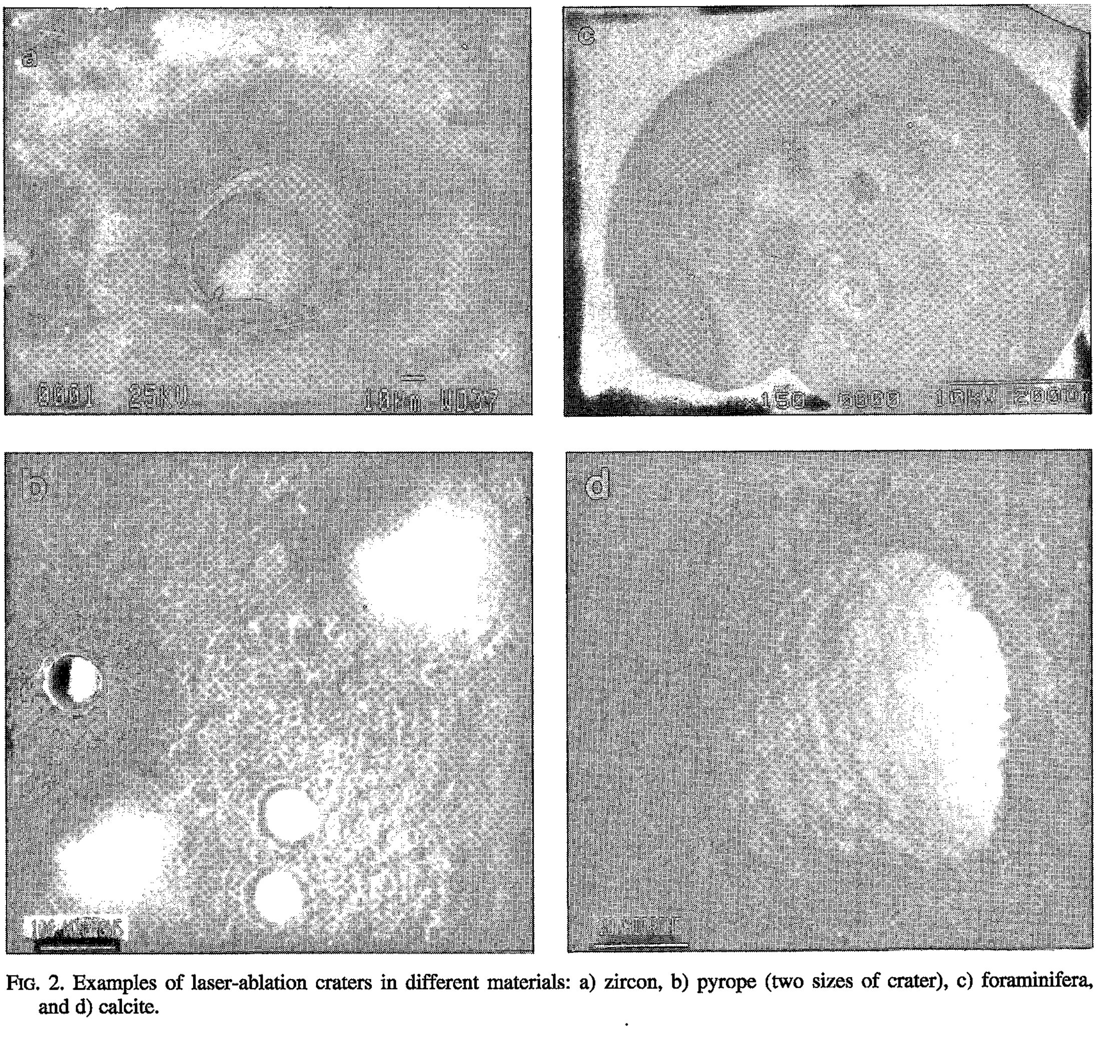

FIG. 2. Examples of laser-ablation craters in different materials: a) zircon, b) pyrope (two sizes of crater), c) foraminifera, and d) calcite.

TABLE 2. BLANK VALUES AND LIMITS OF DETECTION IN LAM-ICP-MS

ELEMENT	BLANK VALUE	LIMIT OF DETECTION
Li, Be	50 - 100 cps	0.1 - 0.2 ppm
Sc, V, Cr, Co, Ni	500 - 3000	0.5 - 6.0
Rb, Sr, Y	50 - 100	0.1 - 0.2
Y, Zr	50 - 200	0.1 - 0.3
Ba, REE	15 - 20	0.01 - 0.02
Hg	500 - 700	1.0 - 2.0
Pb	30 - 40	0.02 - 0.04
U, Th	15 - 20	0.01 - 0.02

material ablated and the duration of the ablation. Examples of sample pits in zircon, NIST glass, calcite and a foraminiferal test are shown in Figure 2. Ablation rates at a pulse energy of 5–6 mJ (750 V), for an instrument operated at 4–6 Hz, are estimated at 20–40 μm/min. for zircon crystals and up to 100 μm/min. for glass samples. In most materials analyzed, these conditions are required to maintain an adequate signal in the ICP–MS. Lowering the laser energy and repetition rate results in slower rates of drilling and less material ablated, degrading sensitivity and detection limits. However, improvements in ICP–MS sensitivity should allow ablation of smaller volumes using lower-energy UV and IR lasers in the future.

Sensitivities of the instrument operated in laser-ablation microprobe mode vary from 200 to 700 cps/ppm based on results from NIST 612 glass. Detection limits in ppm are estimated at three times the "gas blank" (analysis of argon carrier gas); for <50 μm sample pits, limits of detection (l.o.d.) for NIST–612 glass vary from 0.01 ppm to 2–3 ppm (Table 2). It is possible to operate the laser in a "bulk-sampling mode", producing craters of 150 to 250 μm. In this mode, sensitivity increases to 2000 – 10000 cps/ppm, with a resultant 5- to 10-fold decrease in the limit of detection. Although useful for the analysis of glass and powder samples (Fedorowich *et al.* 1993, Pearce *et al.* 1992), this mode is of limited use in studies of minerals owing to the poor spatial resolution of the laser.

TREATMENT OF DATA

Signal stability

Because of the transient nature of the LAM–ICP–MS signals, the ICP–MS is operated in a peak-jumping mode. The detection system scans individual peaks for at least 40 ms (30 ms on peak and 10 ms on background) on low-abundance isotopes and 20 ms acquisition time for abundant or mono-isotopic species. In our early experiments for U, Pb and Th, we used a 5-s acquisition-time repeated 15–30 times for each laser-sampling spot (Feng *et al.* 1993). A statistical routine was used to eliminate spurious (outside 95% confidence level) blocks of data, and average isotope and elemental ratios were taken over the same time-interval for different samples [see section on zircon analysis, and also Feng *et al.* (1993)]. For U, Th and Pb isotopes, a zircon crystal was used as a standard (CN–92–1); the change in the signal with time after a 20-s pre-ablation period is shown in Figure 3a. Several factors may cause variation in the amount of sample ablated by the laser, with consequent variation in the observed signal. These include pulse-to-pulse variation in laser energy, defocusing of the laser beam during ablation, and differences in physical properties between samples (*e.g.*, Arrowsmith 1987). To further evaluate these variations, Ludden *et al.* (1995) did a series of tests under different laser-ablation conditions on NIST 610 glass and zircon (CN–92–1). As shown in Figures 3a–c, the relative fractionation for different isotopes of an individual element (^{206}Pb, ^{207}Pb, ^{208}Pb) is similar, and the ratios can be measured at a precision of <1% (see section on zircon analysis). However, substantial fractionation occurs among differing elements (*e.g.*, U, Pb and Th), as shown by the maximum for the Th signal after 25-μm profiling, and for U at 60–70 μm. This results in element ratios that change in the ablation process. This relative fractionation during prolonged ablation is contrary to what would be predicted from the vaporization energies of the elements: Pb > U > Th. However, these elements seem to fractionate according to their vaporization energies in the 20-s pre-ablation stage of the analysis (Ludden *et al.* 1995). Once a high-temperature plasma is established above the crater, it appears that other factors (such as Pb diffusion into the crater) control the relative abundance of the elements in the plasma. Despite these problems, measurement on standards show that it is possible to measure ^{232}Th/^{206}Pb and ^{238}U/^{206}Pb with a precision of 2–5%. Preliminary studies show that elements of similar character [*i.e.*, the rare-earth elements (*REE*), highly charged elements, alkaline earths] do not exhibit this type of decoupling during ablation.

Mass fractionation

For isotopes of the same element, mass discrimination may be caused by a bias in measurement due to Coulombic collision during ion transmission; generally, the heavier isotope is enhanced relative to the lighter isotope (Hieftje 1992). For an element with two or more stable isotopes, a mass-fractionation correction can be done by internal normalization, and it is usually less than 1%. For elements where there are no stable pairs of isotopes (*i.e.*, Pb), mass-fractionation corrections must be done by using an external standard. A similar method is used

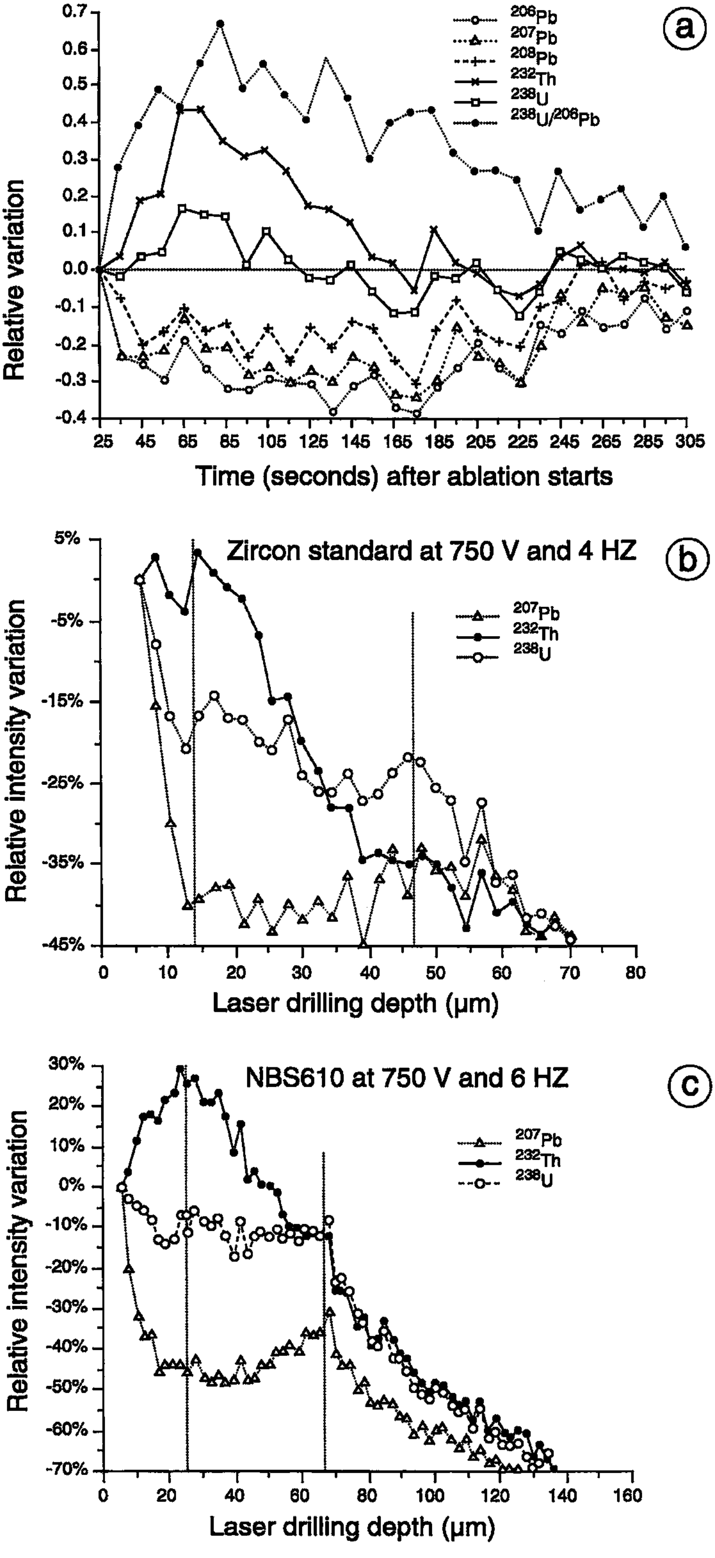

FIG. 3. Variations in laser-ablation signal with time and profiling depth: a) relative variation in the signal for U, Th and Pb isotopes in standard zircon (CN–92–1) (from Feng *et al.* 1993); b) relative intensity variation in the signal for standard zircon (CN–92–1), both from Ludden *et al.* (1995), and c) relative variation in the signal for NIST 610 glass relative to profiling depth (calculated at a rate of 0.05 µm per pulse at 750 V).

for correcting mass fractionation in ICP–MS analysis of solutions (Hinners *et al.* 1987). In laser ablation, if an external standard is used to calculate the mass-discrimination factor, we must assume that this factor remains constant for the standard and the unknown. This may not be the case if the standard and the unknown have different elemental concentrations and different absorption characteristics of IR and UV light. In LAM–ICP–MS Pb/Pb zircon geochronology, the mass-fractionation factors applied are generally less than 1%.

Matrix-matched calibration and internal standards

Unlike electron-microprobe analysis, for which theoretical calibration procedures are well established, techniques such as SIMS and LAM–ICP–MS analysis depend upon empirical methods. These usually consist of external calibrations using well-established, matrix-matched standards, coupled with the use of an internal standard to correct for variable yields during the sampling (Perkins *et al.* 1992, 1993). The choice of internal standard is based on the following considerations: (1) proximity in mass to the trace elements of interest, (2) proximity in concentration to the unknown samples, (3) accurate abundances of sufficient concentration to produce high count-rates. In our studies, low-abundance isotopes of major elements (generally ^{29}Si, ^{44}Ca or ^{43}Ca, and ^{57}Fe) are used as internal standards, the major-element concentrations having been determined prior to laser ablation by electron-microprobe and X-ray fluorescence analyses.

For single standard calibrations, NIST–612 is used for a suite of elements, as this standard has been doped with many geologically interesting trace elements ranging in concentration from 15 to 78 ppm (Jackson *et al.* 1992, Fedorowich *et al.* 1993). This standard has been used to analyze for trace elements in diverse matrices such as glass, amphibole, and carbonate, generally using ^{29}Si and ^{44}Ca as internal standards. NIST–612 seems to produce more accurate results when ^{44}Ca is used as the internal standard for mafic glasses and for minerals with calcium contents similar to that of NIST–612 (Fig. 4). In this case, one potential problem is that the standard and the unknowns are not matched in terms of overall major-element contents (*e.g.*, Si, Al, Mg). This may cause problems in accuracy under certain conditions. For felsic glasses calibrated with NIST–612, it is generally necessary to use ^{29}Si as the internal standard, as silica contents are matched, and other elements are either at low concentrations (Ti, Mg, Ca, Fe) or have high gas-blanks (Na, Al).

In minerals, internal standardization can be done by obtaining an estimate of the proportion of an element in the mineral and monitoring this element during LAM–ICP–MS analysis. A correction for the Relative Sensitivity Function (RSF) of an unknown element relative to an element of known concentration can be made using the following formula:

$$(C_x)_{\text{samp.}} = \frac{[I_{(m,x)}/I_{(m,Is)}]_{\text{samp.}} * (C_{Is})_{\text{samp.}} * (C_{m,x})_{\text{std.}}}{[I_{(m,x)}/I_{(m,Is)}]_{\text{std.}} * (C_{Is})_{\text{std.}}}$$

where (Is) is an internal standard of choice, $I_{(m,x)}$ is the intensity at mass x of the element being sought, and $C_{(m,x)}$ is the concentration of the element of mass x in the standard.

The concentration of the internal standard can be determined by (1) assuming a stoichiometric concentration in a mineral (*e.g.*, Ca in calcite, Zr or Si in zircon), or (2) by electron-microprobe analysis of spots in the mineral to be analyzed by LAM–ICP–MS. The accuracy of the analysis depends on the accuracy of the determination of the internal standard, and on accurately monitoring drift in the RSF. The results presented in this paper have been acquired using ^{29}Si and ^{43}Ca or ^{44}Ca as the internal standard.

The accuracy of the results presented here and in other studies (*i.e.*, Jackson *et al.* 1992, Fedorowich *et al.* 1993) suggests that matrix effects are relatively unimportant in the laser-ablation process. Experiments in progress with multiple glass standards of differing Fe, Ca and Si composition indicate some dependence on the matrix, particularly for samples with high Fe contents (Stix *et al.* 1995). Both Y and Zr display incoherent behavior in glasses of different composition (see results for NIST 612, Fig. 4), suggesting that matrix effects may play a significant role for some elements. This observation may partly explain the common difficulty of obtaining accurate Y and Zr concentrations by laser-ablation analysis of mafic glasses when using NIST–612 as a standard, since the iron content is significantly different between the standard and the unknown samples.

Interference corrections

Oxide formation is a significant problem in determining *REE* concentrations by solution-mode ICP–MS (*e.g.*, Jarvis *et al.* 1992). However, in laser-ablation mode, the absence of a solvent entering the ICP torch results in much less oxide formation. Jackson *et al.* (1992) observed that oxide formation is typically around 1.5%, and, even for light-*REE*-enriched minerals, the difference between the results by oxide-corrected and oxide-uncorrected calibrations are generally less than 1%. Accordingly, no oxide corrections were applied in the trace-element studies reported here. However, at levels of 1% oxide formation, interferences may be a problem in isotope-ratio determinations. During the experiments on zircon crystals, possible interferences due to *REE* dioxide were evaluated by analyzing solutions of Yb, Lu and

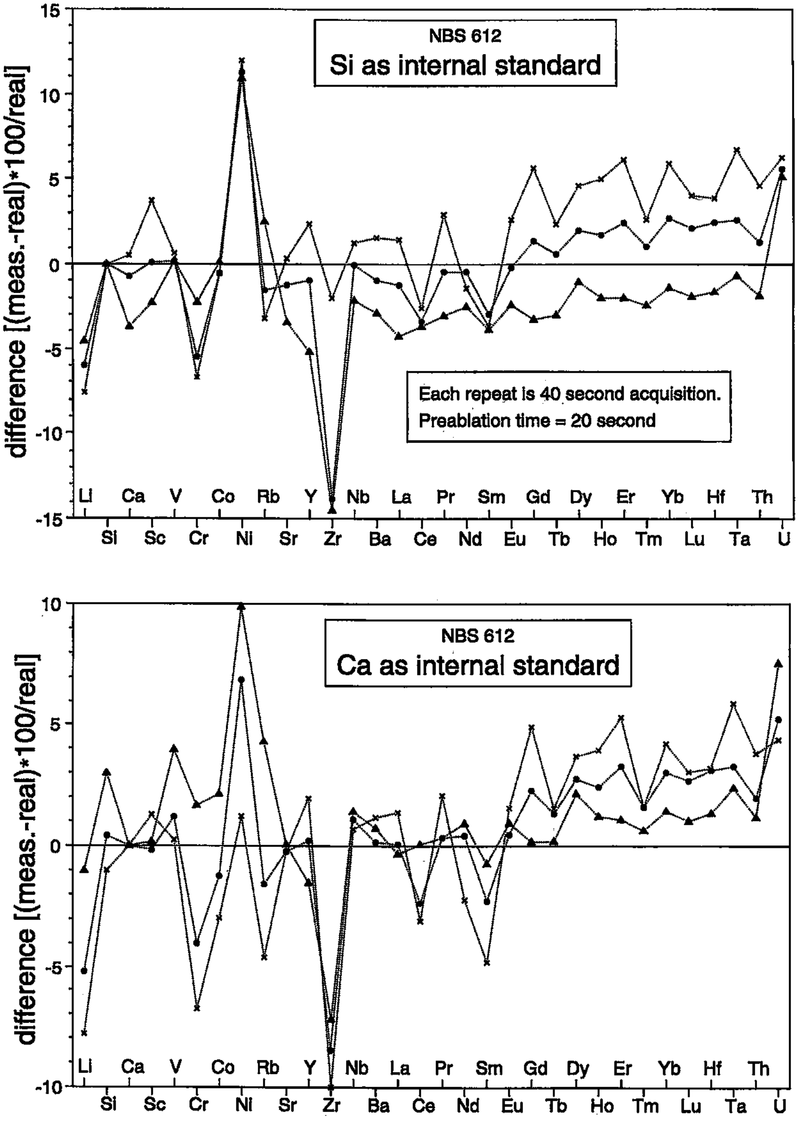

FIG. 4. Relative accuracy of NIST 612 determinations by laser-microprobe analysis: a) using Si as an internal standard; b) using Ca as an internal standard.

Hf; no interferences were detected. Monoxide interferences on U or Pb may come from platinum-group elements, which are at low concentrations in minerals of interest in geochronology.

Blank corrections are a more significant problem. High blanks will degrade detection limits, and it is in the operator's interest to limit the gas blanks across the mass spectrum. As is evident from Table 2, the gas blank is highly variable. High blanks are caused by a poorly sealed instrument, glow discharge in the mid-mass range, and memory from earlier samples. The blanks in the middle masses result from glow-discharge and complex ionization of gases, whereas the high Hg blank (similar blanks may be present for light masses) results from contamination in the instrument and can only be lowered by a complete cleaning of the sampling area and the lens stack.

Data acquisition and calibration

In our early work on zircon crystals, the data-collection philosophy closely followed that used for thermal-ionization mass spectrometry. As individual blocks of data could be obtained over a 5 to 10-second counting period with precisions of 1–3% (Feng *et al.* 1993), statistical compilation of 15–30 data blocks should lead to improved precisions. However, as is evident from the signals displayed in Figure 3, significant changes in relative intensity occur that probably result from the sampling process. These variations can be averaged by sampling over a longer period. However, increasing the sampling interval may lead to inclusion of spurious data caused by sample heterogeneity. In Figure 5, the results for variation in ^{207}Pb/^{206}Pb and ^{238}U/^{206}Pb are shown for fewer blocks with longer durations. The decrease in RSD and its convergence to the theoretical value indicate that Poisson counting statistics dominate the sources of error. The lack of convergence to the correct U/Pb ratio confirms the problematic behavior of U and Pb, discussed elsewhere in the paper. As a general procedure, longer counting-times and higher-intensity signals will lead to higher precision. If a single spot can be ablated for several minutes, precisions in isotope ratios of single elements of less than 0.5% and in interelement ratios of less than 1% are attainable.

For a 30-s acquisition for 10 isotopes, the measurement time for each isotope is about one second; the raw count-rate is therefore equal to the integrated rate of counting (cps). The 30-s acquisition is repeated three times to give a total time of ablation of 90 seconds for each laser-sampling pit. The mean intensity measured from the three repeat analyses is extracted off-line and calculated using a spreadsheet program.

A typical analytical routine includes analyzing six sampling pits of the reference standard (NIST 612; zircon crystal CN–92–1; "in house" mineral standard), twelve unknown samples and five gas-blanks in between the standard measurements. The mean intensity of the five gas-blank measurements is taken as the background level of the instrument and subtracted from the mean intensity of each measurement. The relative instrument response factors (RSF) are established by using the glass standard. The concentrations for NIST 612 were taken from Jackson *et al.* (1992) and our own analyses in solution mode. Ideally, "in house" mineral standards are analyzed in solution mode by ICP–MS and in several laboratories by multiple techniques. The RSF is used to correct for relative ablation-yield, transportation efficiency and matrix effects. As the RSF may drift over time, it is monitored by repeat analysis of the standards. The effectiveness of the drift correction was confirmed by analyzing the standard as an unknown. As shown in Figure 5, with few exceptions, the LAM–ICP–MS results for NIST 612 matched with solution mode and reported values.

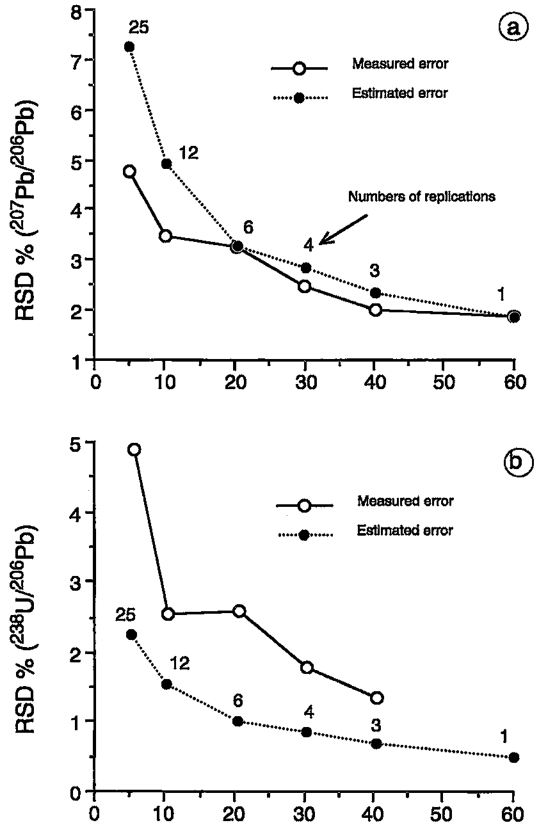

FIG. 5. Changes in relative standard deviation (RSD, 1 sigma) using different data-collection times and repeats. Taken from Ludden *et al.* (1995): a) example for Pb/Pb variation; b) example for U/Pb variation; estimated error: RSD for (7a+7b+...n)/(6a+6b+...n); measured error RSD for $[(7/6)_a+(7/6)_b+....]/n$.

Pb GEOCHRONOLOGY

Conventional U–Pb geochronology involving mechanical separation, abrasion and dissolution of U-enriched minerals and analysis by thermal-ionization mass spectrometry (TIMS: Krogh 1973, 1982) remains the technique of choice to obtain high-precision (<0.1%) ages. Kober (1987) and Kröner & Todt (1988) have developed a single-zircon method of analysis by TIMS that involves mounting a zircon grain on a filament to produce sequential evaporation of Pb to obtain ^{207}Pb/^{206}Pb radiogenic ages. This method is relatively rapid but does not have the precision of conventional TIMS analysis and does not provide U/Pb ratios required to prove zircon concordance; stepwise evaporation moves the ^{207}Pb/^{206}Pb value toward that of zircon on the concordia.

Grains of zircon and other minerals of interest in U/Pb geochronology may have a core and overgrowths; analysis by conventional TIMS is possible on mineral fractions of abraded cores, *etc.*, but *in situ* analysis of grains is the only realistic means of resolving these complicated growth-histories. The SHRIMP (Sensitive High Resolution Ion Microprobe) technique has pioneered this area (Compston *et al.* 1986) by using a focused ion-beam to sputter craters of about 20–30 µm. This ablated material is transported into a high-resolution mass spectrometer that produces ages of 1–2% precision and provides both Pb- and U-isotope data. Despite the potential of the SHRIMP, the high price and operating costs have hampered the widespread use of this technique. As discussed above, with the LAM–ICP–MS, it is possible to measure isotope ratios of the same element with a precision of <1%. The technique thus presents an exciting possibility for Pb/Pb geochronology in zircon and other minerals (Feng *et al.* 1993, Fryer *et al.* 1993); at a precision of 1%, ages of Precambrian zircon can be determined to ±30–40 Ma. Obviously, the precision of the technique does not allow the high-resolution stratigraphy required in unraveling the evolution of Precambrian terranes (*e.g.*, Corfu *et al.* 1989). However, the SHRIMP also does not provide the age resolution to solve many stratigraphic problems. However, both laser-microprobe ICP–MS and the SHRIMP provide *in situ* ages that can be used to decipher the history of zircon crystals, to analyze populations of detrital zircon, and to provide regional geological information in relatively unknown terranes. Both *in situ* techniques should be used in concert with the conventional method of U/Pb analysis.

Pb geochronology

To evaluate the Pb/Pb laser-ablation technique, we analyzed a series of zircon crystals by conventional U/Pb techniques and by Pb/Pb LAM–ICP–MS. The ^{207}Pb/^{206}Pb ratios were determined relative to a standard zircon, CN–92–1, from a skarn in the Grenville Province, Canada. This zircon standard was used to monitor mass fractionation. No optical zonation was observed in CN–92–1. However, examination in different spots indicates variations in Pb, U, and Th abundances and ^{208}Pb/^{206}Pb ratios, but homogeneous ^{207}Pb/^{206}Pb ratios. Four analyses of different fragments of CN–92–1 by the conventional TIMS U–Pb method give ^{207}Pb/^{206}Pb = 0.07784 ± 6, and the average of ^{207}Pb/^{206}Pb from ten individual sampling pits can be reproduced within 0.5% of the TIMS data with a 0.6% (1 sigma) RSD (Feng *et al.* 1993).

In cases of high-quality transparent zircon with a relatively simple history, ages are within 1% of the U/Pb (TIMS) age (Fig. 6). From these results and for the present configuration of the instrument, we can define the limits for accurate analysis as follows: approximately twice the sample-pit size (*i.e.*, 80 µm, or 200 mesh) and abundances exceeding 5 ppm ^{207}Pb (Fig. 7).

Application of this technique to a population of detrital zircon crystals from the Amazon Precambrian shield in Brazil (Fig. 8) indicates a bimodal population, 3.2 and 2.9 Ga. The eastern Amazon shield is thus underlain by rocks much older than hitherto known, and distinct source-rocks were eroded to fill the basins. These data provide an invaluable background to single-grain conventional geochronology, as following laser ablation, the grains can be removed from the mount, dissolved and analyzed.

The limitations of LAM–ICP–MS Pb geochronology can be reduced by using a higher-sensitivity mass spectrometer, smaller spot-size, and a UV laser. The destructive nature of laser ablation relative to the SHRIMP technique is disadvantageous in terms of our ability to collect data for long times, although the higher sensitivities (5–10 times those of the SHRIMP for Pb) partly overcome this problem. However, profiling through a zircon grain does provide important information that would otherwise be unobtainable on core–rim history (Feng *et al.* 1993).

CARBONATES

We have examined three types of carbonate material: calcite, dolomite, and benthic foraminiferal tests. In the studies of calcite and dolomite, the aim was to establish a routine trace-element package for carbonate analysis, and to evaluate the possibility of using NIST glasses as standards. In the foraminiferal-test study, we determined key element-ratios that are dependent on the temperature of formation of the foraminifers, with the aim of circumventing laborious cleaning and separation of these foraminiferal tests for routine solution-analysis.

Analysis of calcite and dolomite

Feng (1994) presented results for calcite and dolomite samples for which we had completed both LAM–ICP–MS and solution ICP–MS determinations using standard addition (Jenner *et al.* 1990). LAM–ICP–MS analysis followed the general procedures outlined in this paper, with ^{43}Ca as an internal standard. There is excellent agreement between solution analyses and laser analyses for most samples, but significant disparities in some cases (Fig. 9). For sampling pits of <50 µm, the limits of detection are about 15 ppb for the light *REE*, 10 ppb for the heavy *REE*, and 200 ppb for Sr, Y and Ba. For homogeneous mineral samples, based on sensitivities of about 500 cps/ppm, the counting-statistics uncertainty for an isotope of 1 ppm concentration is approximately 5% RSD; relative accuracy for the same elements in NIST glass 612 is generally <2% (Fig. 4).

In some minerals, there are considerable differences between results of the bulk analysis in solution and spot analysis by laser. In general, these differences are attributable to trace-element inhomogeneity within crystals. Figure 9 shows results for igneous dolomite

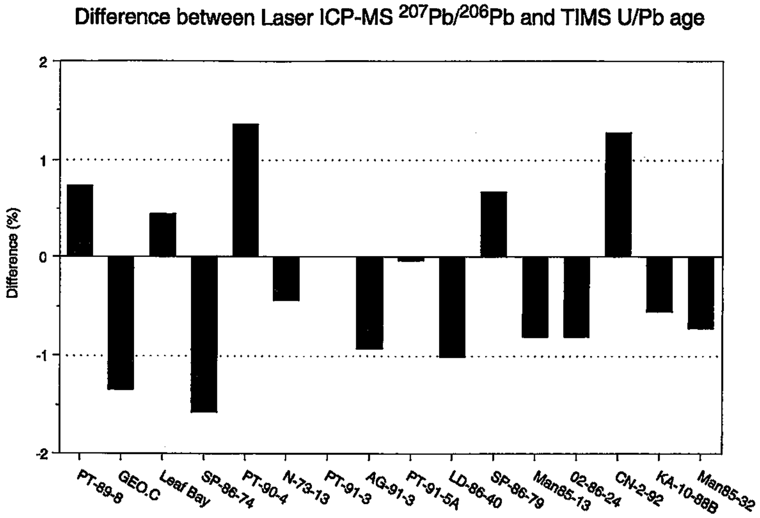

FIG. 6. Pb/Pb age results by laser-ablation microprobe ICP–MS: comparison of differences relative to U/Pb TIMS determinations (sample descriptions in Feng *et al.* 1993).

from a carbonatite, which is very rich in light *REE* and poor in heavy *REE*. The relative variation for the three different sampling pits from a single grain was from 2–10%, whereas the variation among all grains sampled was as much as 40% for the light *REE* and approximately 10% for the heavy *REE*. The most reasonable explanation for this variation is primary differences in concentrations of the light *REE* in these

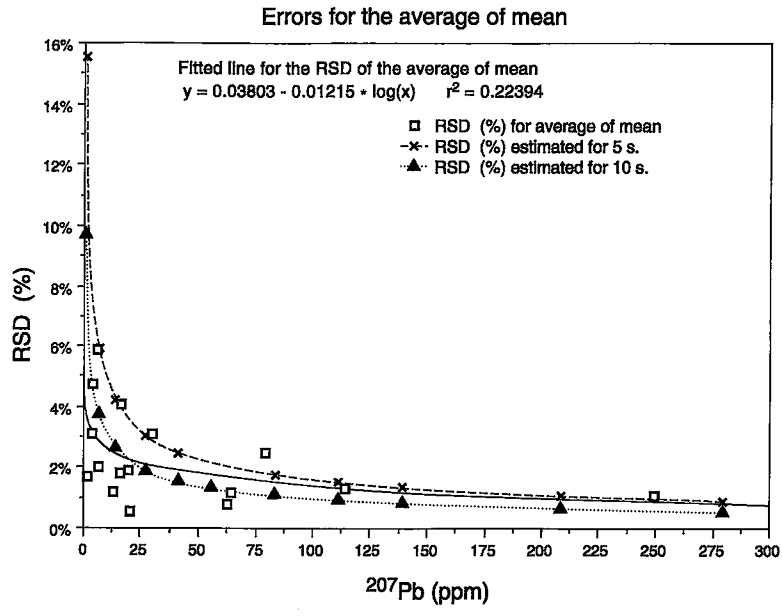

FIG. 7. Changes in analytical error (1 sigma) relative to the ^{207}Pb concentration of the mineral.

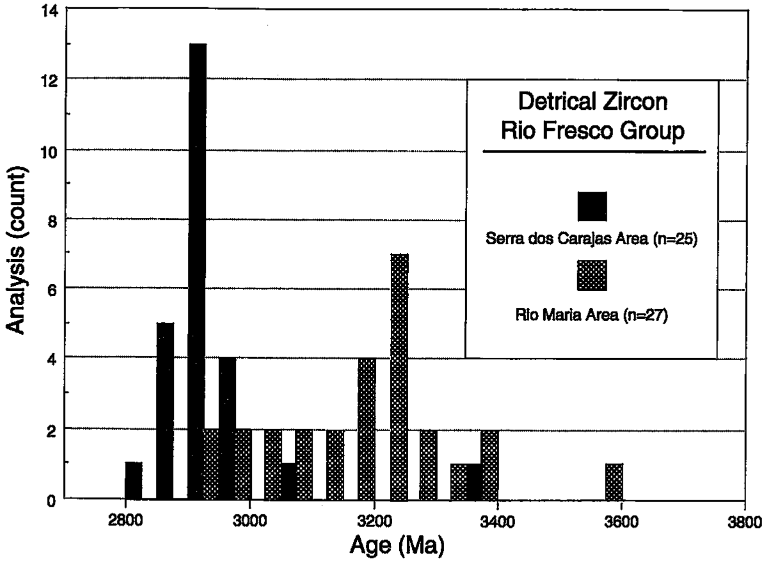

FIG. 8. Pb/Pb ages from detrital zircon from the Rio Fresco Group in the Amazon Shield.

minerals. Nonetheless, the excellent coherence of the solution-ICP–MS results and the composite of all grain analyses by LAM–ICP–MS is proof of the accuracy of the LAM–ICP–MS technique. Two calcite samples with <2 ppm for all *REE* (Fig. 9) show fractionation of the heavy *REE* and reasonably good correspondence between results of laser-ablation and solution analyses despite the very low abundances.

The results for carbonates show that it is possible to obtain quantitative analyses of calcite and dolomite using LAM–ICP–MS with non-matrix-matched standardization, even though calcite and dolomite have poor absorption of the IR-laser energy used in this study. As discussed by Feng (1994), the success of the non-matrix-matched standardization is related to a stable and reproducible laser-coupling process. In particular, the laser beam used in this study can be focused to about 10 μm, forming craters 30–50 μm across; the power density of the focused beam (*i.e.*, 10^{11} W/cm^2) is higher than an unfocused beam [*e.g.*, 10^9 W/cm^2, forming a crater of >200 μm: Denoyer *et al.* (1991)]. As suggested by Abell (1992), under this high-power density, the dominant absorption of laser light and the resulting processes of thermal vaporization at lower power (Ready 1971) give way to direct ablation due to laser-induced plasma-plume expansion. The induced plasma is the major source of energy for the ablation, not the absorption of laser light. Thus, this secondary coupling process allows ablation even when the material is transparent to the laser (*e.g.*, calcite).

Analysis of benthic foraminiferal tests

The trace-element composition of foraminiferal tests has received much attention from marine geochemists as a means of inferring the physical and chemical conditions of the seawater in which the foraminiferal tests grew (Bender *et al.* 1975, Boyle 1981, Lea & Boyle 1991). Current techniques require several cleaning and leaching steps before analysis in solution by ICP–MS, graphite-furnace atomic absorption or other techniques. Commonly, several foraminiferal tests are required to provide sufficient material for analysis. The LAM–ICP–MS technique offers the advantage of being able to analyze single foraminifera tests for several elements simultaneously. In a pilot study, Wu & Hillaire-Marcel (1995) analyzed large (approximately 250 μm) benthic foraminifera for four minor cations (Sr, Mg, Mn and Ba) that are relatively concentrated in benthic samples (generally >10 ppm). The instrument was optimized at maximum sensitivity for ^{88}Sr, ^{43}Ca was used as an internal standard, calibration was done using NIST 612 glass, and the ratios Sr/Ca, Mn/Ca, Mg/Ca and Ba/Ca were determined (Fig. 10); ablation craters are shown in Figure 2. In general, the ratios can be reproduced to <10%. The *in situ* analysis shows that Sr is present primarily in the carbonate of the benthic foraminifera and not in the Fe–Mn coatings, Mg and Mn are concentrated in the coatings, and Ba is associated either with the coatings or with barite crystals.

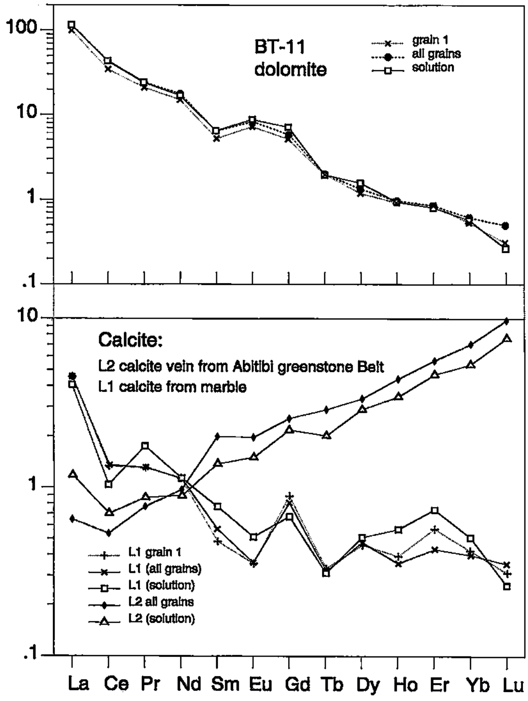

FIG. 9. Comparison of chondrite-normalized concentrations of rare-earth elements in carbonates by LAM–ICP–MS and by solution-mode ICP–MS: a) igneous dolomite; b) vein calcite from an Archean metavolcanic rock and from a Grenvillian marble.

MAFIC MINERALS AND STANDARDS

As matrix matching is not as strict a requirement as in ion-probe analysis, the fact that the calibration for LAM–ICP–MS can be done using synthetic glasses is extremely encouraging. Whereas more tests are required, particularly in comparing coupling between transition-metal-rich samples and transition-metal-poor samples (*i.e.*, Stix *et al.* 1995), the use of synthetic glasses provides a significant advantage, as minerals that are homogeneous within the detection limits of the LAM–ICP–MS are rare. At current limits of detection, repeat LAM–ICP–MS analyses of NIST glasses indicates homogeneity at least at the 1–2% level of precision.

Minerals equilibrated at high temperatures and pressures commonly are homogeneous for major elements. However, these minerals are commonly poor in many trace elements of interest; in terms of advantages for use as standards, their homogeneity is therefore offset by the low abundances of some elements. To test the feasibility of analyzing mantle minerals and to create working standards, we selected a kaersutite and a diopside megacryst from Kakanui, New Zealand. Repeat electron-microprobe analyses for the major elements define an RSD of <2%, including K (1.5%) and Na (1.8%) for the amphibole and Na (1.5%) for the clinopyroxene; Ti has an RSD less than 1%, and the RSD of Si is approximately 0.5% for both minerals. Given the detection limits of the electron microprobe, these minerals are therefore homogeneous. The results from a LAM–ICP–MS sampling traverse across the amphibole and the clinopyroxene are given in Table 3; included are the limits of detection based on three times the gas blank (see earlier discussion). These data illustrate the homogeneity of these minerals, as concentrations of elements such as Ba, La and Sr are reproduced at better than 2% in many cases.

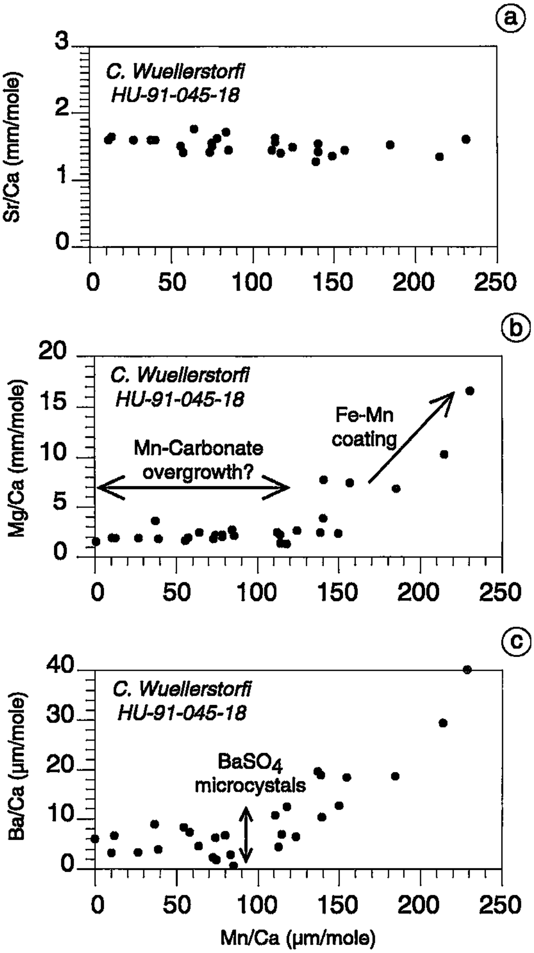

FIG. 10. Ratios of Sr/Ca, Mg/Ca and Ba/Ca in benthic tests of *C. wuellerstorfi*, showing the effects of Fe–Mn-coating and Mn-carbonate overgrowth; data from Wu & Hillaire-Marcel (1995).

The data of Table 3 were calculated using ^{44}Ca as an internal standard (Fig. 11). For the *REE*, significant differences exist in the absolute values depending on which major element is used for normalization; in this example, both Ca and Si were used. These differences seem constant, at least across the *REE* spectrum, with the Ca-normalized results being higher and invariably closer to the values determined for dissolved samples (Fig. 11). For several elements, the laser reproduces the solution data within error. The LAM–ICP–MS data presented here show lower (by about 5%) absolute values relative to results of solution analyses from the Université de Montréal and the Memorial University laboratories. In most cases, the ratios of the elements are constant between LAM–ICP–MS and solution ICP–MS analyses. The integrity of the trace-element profiles produced by LAM–ICP–MS, in particular the relative fractionation of high-field-strength elements and the heavy *REE*, can be used to provide important constraints on magma genesis.

TABLE 3. RESULTS OF REPLICATE LAM-ICP-MS ANALYSES OF KAKANUI MEGACRYSTS

	Diopside[1]		Kaersutite		Blank[2]
	N = 12	RSD%	N = 9	RSD%	
Sc	38 ppm	2	19.5 ppm	13	5 ppm
V	304	7	339	6	1
Rb	0.10	>20	14.8	10	0.4
Ba	0.09	>20	252	1	0.3
Th	0.06	>20	0.08	>20	0.04
Ta	0.07	>20	1.66	6	0.05
U	0.01	>20	0.01	>20	0.02
Nb	0.34	18	26.1	2	0.1
La	1.81	7	4.7	4	0.05
Ce	8.02	15	16.8	4	0.05
Pr	1.37	5	2.78	4	0.05
Sr	68.30	2	454	1	0.2
Nd	8.16	6	15.78	3	0.2
Sm	2.49	14	4.18	6	0.2
Zr	27.80	5	54.4	4	0.2
Hf	1.46	4	2.4	8	0.1
Eu	0.89	6	1.44	6	0.05
Gd	2.67	11	3.44	10	0.3
Tb	0.34	1	0.48	12	0.03
Dy	2.10	7	2.35	5	0.04
Y	8.50	6	7.55	5	0.1
Ho	0.38	8	0.33	12	0.04
Er	0.83	9	0.61	19	0.1
Tm	0.09	17	0.05	>20	0.03
Yb	0.52	15	0.33	>20	0.2
Lu	0.06	18	0.01	>20	0.0

[1] Data were calculated using Ca as an internal standard.

[2] Blank values are based on an average for the two data-sets.

THE FUTURE

The encouraging results summarized here for Pb/Pb analysis of zircon crystals, carbonates and mafic minerals, in addition to data presented elsewhere, in particular by Jackson *et al.* (1992), Jenner *et al.* (1993), and Fryer *et al.* (1993), have established the LAM–ICP–MS technique as a powerful new analytical tool. The technological advances in LAM–ICP–MS analysis are evolving rapidly. ICP–MS instruments are now capable of producing in excess of 200 million cps/ppm for solutions; the instrument used for the work discussed here has a sensitivity of about 40 million cps/ppm. The results given here were collected using a finely tuned Nd:YAG laser at low power (4–5 Hz), which operates in the IR region at 1064 nm and can produce ablation pits of 20–40 μm depending on the material analyzed. Quadrupling (fourth harmonic) the laser beam produces a UV laser of 266 nm, capable of ablating pits one quarter the size of the IR Nd:YAG, and results in better coupling between the laser and transparent minerals (Jenner *et al.* 1993, Fryer *et al.* 1995). However, the amount of ablated material ejected from the pit is directly related to the volume of the crater. To maintain count rates equivalent to those reported here for NIST glasses, the sensitivity of the ICP–MS instrument must be increased by an order of magnitude, through a combination of enhanced plasma-ionization efficiency (*i.e.*, using mixed carrier gases), modified geometry of the ICP–MS – plasma interface, and more efficient transport of ions in the mass analyzer. High-sensitivity analysis of 30–50 μm craters should result in an order-of-magnitude increase in count rate, and the ability to attain detection limits of tens of ppb. However, the requirement to monitor a minor isotope of a major element in a mineral and attain these detection limits requires a linearity of the detection system of at least 10^9 orders of magnitude.

Most of the applications described here require refinement, and are in the development stage. In particular, we emphasize the importance of studies relating matrix affects, coupling processes and variation in elemental yield. The accuracy of the results obtained for carbonate analysis is good, and the results presented reflect a bulk analysis of a pit of 30–40 μm in diameter and depth. Most low-temperature minerals are finely zoned, and variation in the results from repeated ablations reflects this. Higher spatial resolution and ablation traverses using time-resolved collection are required in these studies and will become an important part of LAM–ICP–MS applications. Nonetheless, sampling at a scale that may average some of these heterogeneities, (*i.e.*, in studies of partitioning of an element in mantle minerals) provides fundamental constraints on mantle melting and the evolution of magmatic systems.

As the resolution and sensitivity of the LAM–ICP–MS increase, standardization will become increasingly important. The NIST standards now used may well be heterogeneous at lower spatial resolution. The technique is destructive and hence requires a continuous supply of mineral or glass standards; the future supply of high-quality standards is an important constraint on LAM–ICP–MS analysis.

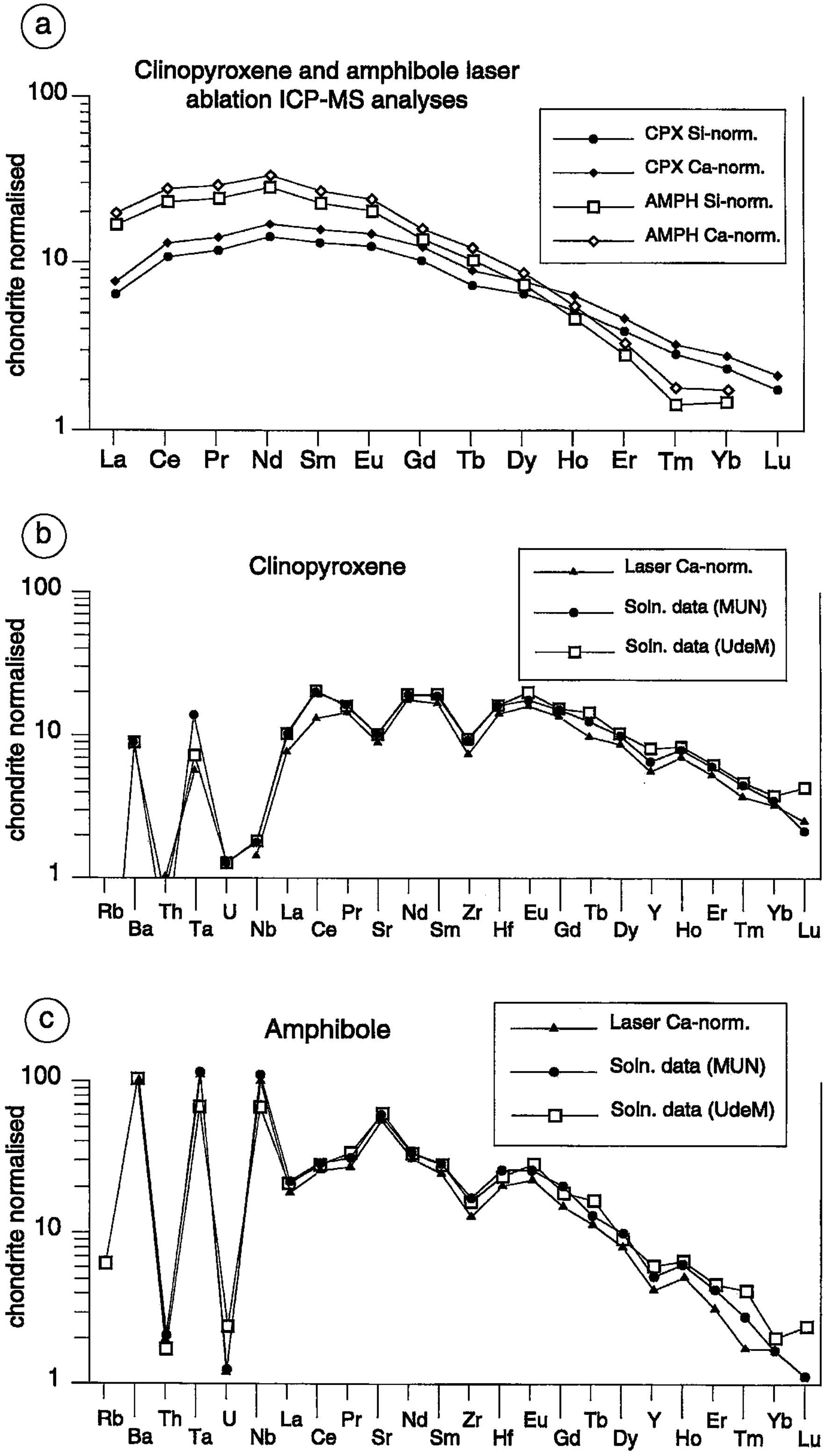

FIG. 11. Results of LAM–ICP–MS analysis of amphibole and clinopyroxene megacrysts from Kakanui, New Zealand: a) comparison of Ca-normalized *versus* Si-normalized data; note the crossover in heavy *REE*, which is maintained in both normalizations; b) and c) illustrate results for clinopyroxene and amphibole megacrysts, respectively displayed relative to solution data on cleaned mineral fractions. All data are chondrite-normalized using values given in Sun & McDonough (1989).

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