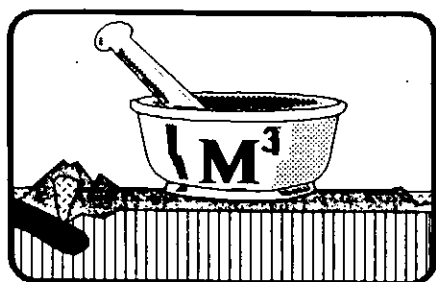


Feature



Machinations

The Laser Ablation Microprobe-Inductively Coupled Plasma-Mass Spectrometer

Henry P. Longerich, Simon E. Jackson, Brian J. Fryer and David F. Strong
*Department of Earth Sciences and
 Centre for Earth Resources Research
 Memorial University of Newfoundland
 St. John's, Newfoundland A1B 3X5*

INTRODUCTION

The fundamental building blocks of rocks are the 83 naturally occurring elements which have half-lives greater than a few million years. Elemental and isotopic analysis of rocks and minerals have thus taken on increasing importance in studies of the solid earth. One of the important recent breakthroughs in instrumentation was the coupling of the efficient ionizing ability of an atmospheric pressure argon inductively coupled plasma (ICP) source with the selectivity and sensitivity of a quadrupole mass spectrometer (MS). The resulting ICP-MS instrument has the ability to determine a large number of elements and isotopes at a speed and sensitivity that have generally superseded previous analytical techniques.

The delivery of commercial ICP-MS to the geo-analytical community, starting in 1984 (Strong and Longerich, 1985), has contributed significantly to the ease, cost and accuracy of the determination of a large number of less abundant elements, including the precious metals (Jackson *et al.*, 1990) and many other trace elements, including the rare earths (*e.g.*, Longerich *et al.*, 1990; Jenner *et al.*, 1990). Furthermore, this instrument has extended the ability to analyze extremely small mineral separates. Conventional sample preparation, however, necessitates painstaking separation of the mineral from its matrix and, more importantly, cannot give information on spatial distribution of elements within minerals. To extend the capability of ICP-MS to perform direct *in situ* sampling of solids, the authors have recently linked a laser ablation microprobe (LAM) sample introduction system to the ICP-MS at Memorial (Jackson *et al.*, 1992). With demonstrated limits of detection as low as 0.01 ppm and a probe diameter as small as 25 μm , it promises great advances in the area of mineral analysis.

HISTORY OF WHOLE ROCK ELEMENTAL ANALYSIS AT MEMORIAL UNIVERSITY

In the 1960s, elemental analysis of whole rocks at Memorial University was initiated using flame Atomic Absorption (AA). The procedure of Langymhyr and Paus (1968) and Abbey (1968) was adopted for the routine determination of the major elements (mean crustal abundances >0.1%) Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe). Installation of an automated X-ray Fluorescence (XRF) instrument in the mid-1970s made possible routine determination of a suite of trace elements (mean crustal abundances >1 ppm), V, Cr, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th and

U). These elements were determined using a pressed powder pellet sample preparation procedure with limits of detection of 5 ppm for the light elements (V through Nb), 30-60 ppm for Ba, La, and Ce, and 15 ppm for Pb, Th, and U. The most recent advance in whole rock elemental analysis at Memorial University started in late 1984, with the installation of a SCIEX ICP-MS. In an earlier Machinations paper (Strong and Longerich, 1985), it was predicted that this instrument would allow "an entirely new array of studies which are not realistically possible without the ICP-MS". The predicted revolutionary potential of the ICP-MS has been fulfilled, as methods have been developed for the routine determination of a suite of 33 trace elements in rocks and minerals, including all the REE, with limits of detection as low as 0.01 ppm for the less abundant mono-isotopic elements and near 0.1 times chondrite values for all of the REE. Chemical separation and concentration techniques lower these limits of detection by more than one order of magnitude (Jarvis, 1989; Longerich *et al.*, 1990; Shabani *et al.*, 1990). At the same time, a routine NiS collection-Te precipitation procedure for the precious metals with mean limits of detection for the 6 platinum group metals in the range of 0.1 and 0.4 ppb (Jackson *et al.*, 1990) has been developed, extending the use of PGE geochemistry to basaltic and mantle systems. In addition, ICP-MS has been used to determine highly radiogenic Pb isotope ratios (Longerich *et al.*, 1992) and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (Longerich, in press).

MICROPROBE ELEMENTAL ANALYSIS

With the advancement of geological science built upon elemental analysis of whole rocks, the geochemist began to request the analysis of the individual

mineral grains which make up the whole rock. As well, determination of elemental concentrations within grains (zoning) became increasingly important in ascertaining the growth and reaction history of minerals. While analysis was (and continues to be) carried out using mineral separates, labour-intensive separation procedures were required to minimize the inclusion of contaminant mineral phases with potentially high elemental concentration of some elements. Hence, there was an evident need for probe techniques which could analyze samples in standard petrographic sections, while allowing microscopic examination of the samples before and during analysis. The most successful and widespread of the probe techniques is the Electron Microprobe (EMP) with either wavelength- or energy-dispersive X-ray analyzers. With limits of detection of <0.1% and resolution of a few microns, the EMP revolutionized the analysis of major elements in rock-forming minerals and, for the first

time, allowed routine study of zoned minerals. Memorial University installed a wavelength-dispersive EMP in 1976 which performs routine determination of 11 major elements in minerals. The EMP has established itself as an essential instrument for the geochemist, and its moderate capital and low operating costs ensure its continuing importance to the earth scientist for the determination of major and minor elements.

The diverse geochemical behaviour of trace elements during geochemical processes was the driving force for the development of microprobe techniques capable of elemental determinations at trace levels. The most important of these techniques is Secondary Ion Mass Spectrometry (SIMS). A recent review by Reed (1989) covers geological applications and instrumental capabilities. Whereas the EMP measures X-ray emission from a target stimulated by an electron beam, the ion probe employs an ion beam probe with mass spectrometric detection of the sample

ions produced. Usually Ar or O ions are used to create a probe with a diameter of approximately 10 μm , which removes sample to a depth of a few atomic layers. Limits of detection are often <1 ppm. While progress is being made in solving the technique's major difficulties of calibration and oxide and other polyatomic ion interferences (e.g., the rare earth oxides), the high capital costs associated with the instrument's ion source and high resolution mass spectrometer will continue to inhibit widespread development and adoption of SIMS.

Another microprobe technique, Proton Induced X-ray Emission (PIXE), utilizes a megavolt proton accelerator to excite characteristic X-rays of the elements in the sample. A report by Ryan *et al.* (1990) discusses some of the recent accomplishments of this instrumentation in the analysis of geological materials using exciting beams of 10-20 μm diameter and producing limits of detection approaching 1 ppm. While these

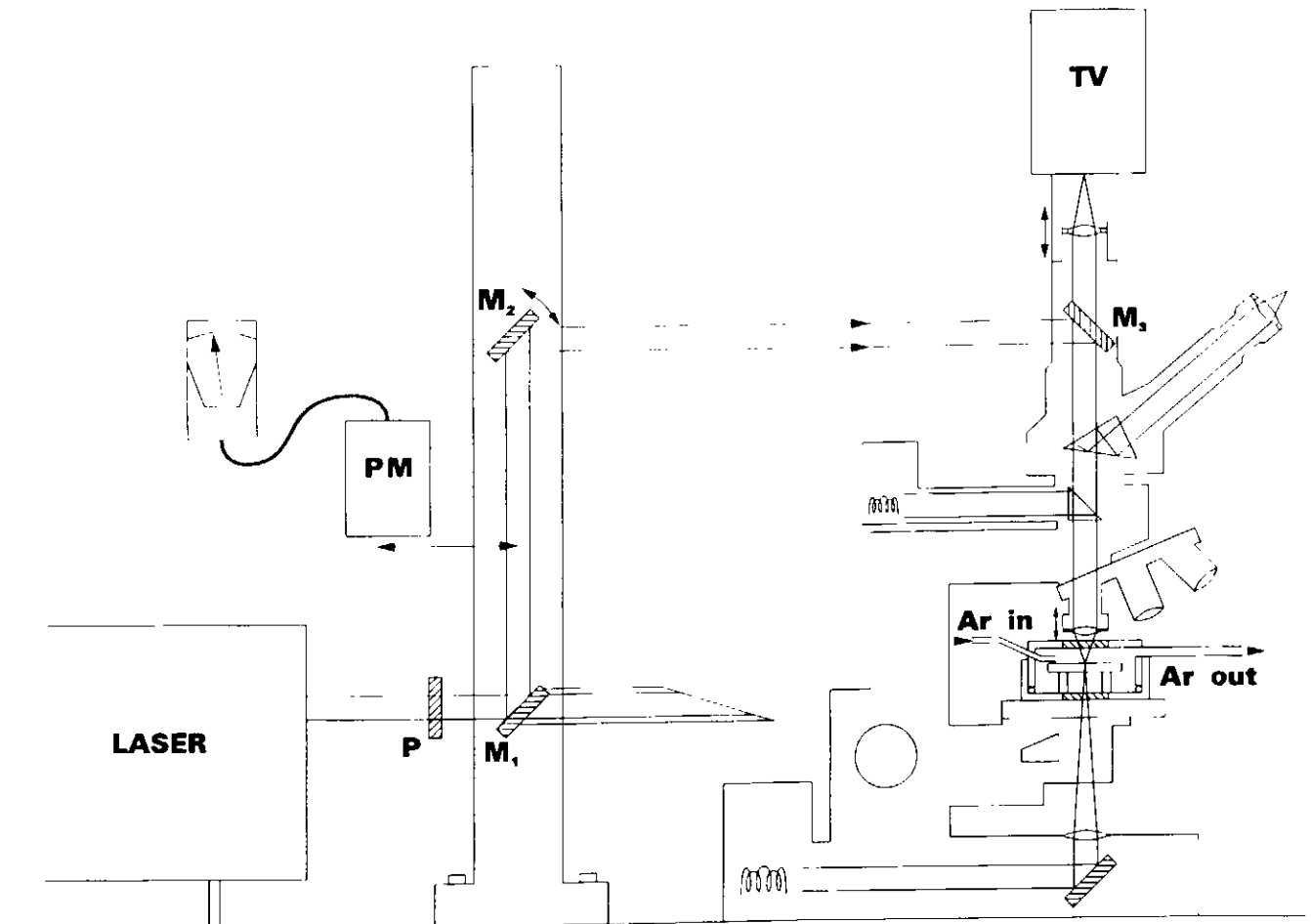


Figure 1 Laser Ablation Microprobe solid sample introduction system. The ablated sample is carried from the sample cell to the ICP by the Ar nebulizer gas using 1-2 m of flexible tubing. M_1 is a beam sampler, M_2 and M_3 are mirrors, P is a half wave plate, and PM is the power meter.

applications demonstrate PIXE's exciting capability, high capital cost will again limit its routine application to geological problems.

LASER ABLATION MICROPROBE-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETER (LAM-ICP-MS)

The history and recent developments of laser ablation sample introduction systems have been extensively reviewed by Moenke-Blankenburg (1989). Chapter 10 of this book gives a summary of the work that has been carried out using ICP-MS, and cites 12 references, including the first laser ablation ICP-MS report of Gray (1985). Laser ablation has been studied since the production of the first lasers and has been applied to geological analysis, especially with the use of ICP-Optical Emission Spectrometry (ICP-OES) systems. Some of the fundamentals of laser ablation are, therefore, well established. Presently, two manufacturers, VG in England and Perkin Elmer-SCIEX in Canada, are offering a laser ablation sample introduction system as an option to their ICP-MS instruments. Some applications of these systems have been recently described by Broadhead *et al.* (1990) and Denoyer *et*

al. (1991), with a focus on bulk sampling of solids. Remond *et al.* (1990) have characterized the ablation behaviour of minerals, using high-energy laser sampling.

Commercial systems were under development but not commercially available when the authors constructed a LAM sample introduction system at a cost of less than \$100,000 to interface to the existing ICP-MS. The LAM system, shown schematically in Figure 1, consists of a Q-switched 1064 nm Nd:YAG laser, the output of which is steered down the phototube of a petrographic microscope and focussed into a sample cell using mirrors (M1, M2 and M3). To attenuate laser power, a half-wave plate (P) and beam sampler (M1) are used. A power meter (PM), which can be moved into and out of the laser path, monitors the laser power. When a laser pulse is focussed onto a sample, material is ablated from the sample surface and is flushed, using argon ($\sim 1 \text{ L}\cdot\text{min}^{-1}$), into the ICP-torch. There, the sample is volatilized and ionized in a manner similar to using standard solution nebulization-ICP-MS. The ablation process can be monitored visually by a TV camera and monitor. Unlike the current commercial systems, the emphasis in the design of

the system at Memorial was microsampling of geological materials in petrographic sections, and not bulk sampling of solids or sampling of powdered geological samples.

The entire laser beam path prior to entrance into the sample cell is at ambient pressure and, thus, requires no expensive vacuum system. The resulting system is not only relatively inexpensive to construct (compared to SIMS and PIXE), but easily incorporates a petrographic microscope to provide the user with the full range of visible light petrographic observation techniques (transmitted and reflected light, polarized light, various magnification objectives, *etc.*) essential for geological applications.

The operation of the laser path at atmospheric pressure also allows ready modification of the system as the need arises. For example, the work of Arrowsmith and Hughes (1988) clearly demonstrates the importance of sample cell design on sample transport. In addition, the authors are in the process of adding a translation stage to allow automated traverses. More significantly, a harmonic generator is being incorporated into the laser to provide lower wavelength (532 nm and 266 nm) laser radiation, which is more strongly absorbed by transition element-poor minerals such as quartz and the common feldspars and carbonates.

It must be noted that there is a need for very stringent safety in the operation of lasers due to the use of high energies, especially when using 1064 μm radiation, which is just outside the visible spectrum in the near infrared. The use of safety glasses with high absorbency of 1064 nm radiation is imperative for all personnel and visitors in the room.

INSTRUMENT PERFORMANCE

One of the fundamental advantages of a LAM-ICP-MS system is that the separation of the ablation and excitation processes allows each to be individually optimized. The ablation process produces melt droplets (Fig. 2) and vapour phase products (some of which are excited). The sample material, regardless of its physical state (vapour or solid), is efficiently transmitted to the ICP torch where the high temperature (6000°C) produces predominately singly charged ions for most elements at high efficiencies. A further advantage of solid sample introduction over solution nebuliza-

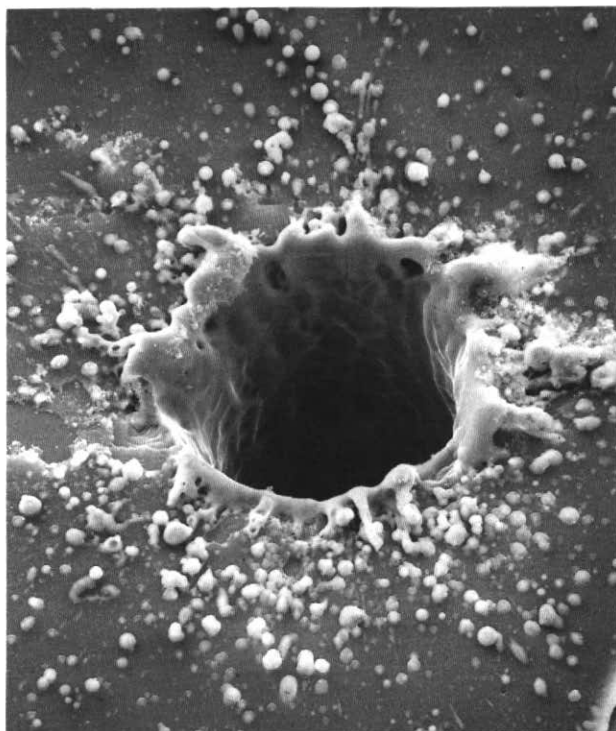


Figure 2 Scanning Electron Micrograph (SEM) of a 30 μm ablation pit in Zircon, showing ejected melt droplets.

tion is the absence of solvent water, resulting in a significantly reduced amount of oxygen in the plasma. This reduces oxide polyatomic ion interferences, which can be significant in the middle rare earth region of the spectra.

While for many geological analyses the limit of quantification is an important figure of merit of an analytical technique, the limit of detection is more widely used. In LAM work, many compromises have to be made according to the requirements of the analysis, which will result in a wide range of limits of detection. For example, increasing the amount of material ablated, either by use of higher power or more pulses, gives a lower limit of detection at the expense of a degraded spatial resolution (larger pits). Similarly, an increase in the number of elements determined in a given volume of sample will increase individual element detection limits.

An example of the low detection limits which can be obtained using the LAM system are presented using the determination of Tm in NBS 616 glass. This is a synthetic silicate glass with a nominal composition of 72% SiO₂, 12% CaO, 14% Na₂O, and 2% Al₂O₃, spiked with 61 trace elements at a nominal concentration of 0.02 ppm. There is no NBS certified value for Tm. Using our standard 33 trace element procedure (Jenner *et al.*, 1990), however, it has been determined that the Tm concentration is 0.019 ppm (reagent blank corrected) with a standard deviation of 0.002 ppm.

Figure 3 shows the Tm signal resulting from a 10-second ablation of the glass (centred at about 40 seconds) using a laser repetition rate of 10 Hz. A well-defined signal for Tm with an average intensity of 10 counts per second in the interval 30-50 seconds is clearly observed above the background of 4 counts per second. The calculated limit of detection is 0.007 ppm. It should be noted that the broadening of the signal to almost 20 seconds, caused largely by dilution of the sample in the gas volume of the sample transport system, is not an undesirable effect, as it allows the MS, a sequential analyzer, time to peak jump many isotopes during normal multi-element analyses.

Multi-element analysis of minerals can be performed, using the quadrupole mass analyzer, by sequentially integrating the ion intensities of a number of isotopes of different elements, using individual isotope dwell times as short as 1 msec. The data for the garnet shown in Figure 4 was acquired using an integration (dwell) time of 10 ms, which was repeated 100 times for each of 19 elements (masses), giving a total data acquisition time of 1 second per element. These parameters allow quality elemental analyses to be produced, as shown in Figure 5. These data were acquired using an external reference material for calibration and the known concentration of Si as an internal standard to correct for differences in ablation yield.

SPATIAL RESOLUTION

For the analysis of small or finely zoned mineral grains, the best spatial resolution possible is required, even with an increase in limits of detection. Although the calculated diffraction limit of focus for the system at Memorial (6 mm diameter Nd:YAG beam focussed through a 25 mm focal length objective) is 10 μm (Moenke-Blankenburg, 1989, p. 21, equation 6), this pit diameter is a minimum, since it neglects thermal energy transfer in the sample and other optical effects. The authors have obtained 25 μm diameter pits (Fig. 6) in selected minerals using approximately 100 laser shots. This resolution can be used to determine element zonation in minerals (Fig. 7). The vigor of the ablation and the size of the ablation pit, however, vary significantly between minerals as a function of mineral composition, and consequent absorptivity and tenacity. The use of shorter wavelengths, obtained by frequency doubling of the fundamental 1064 nm Nd:YAG wavelength to 532 nm and frequency quadrupling to 266 nm, is expected to allow smaller pits (Moenke-Blankenburg, 1989). As well, the use of apertures in the system can also reduce pit size.

APPLICATIONS

The ability to quantitatively determine low ppm trace elements (rare alkalis, rare earths, high field strength, and other incompatible elements) in minerals by a simple and relatively inexpensive

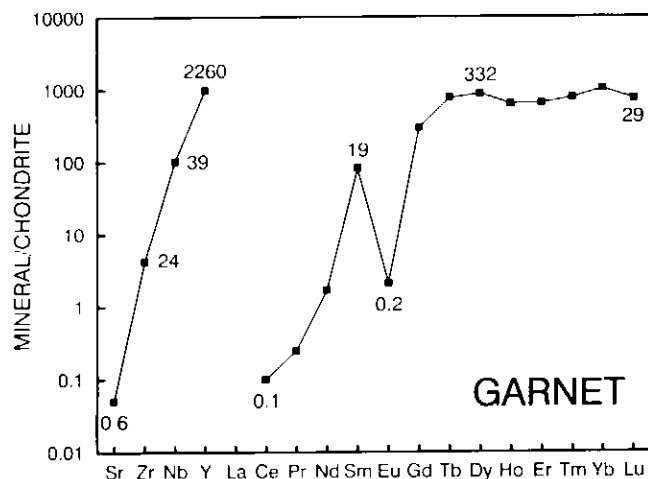


Figure 3 LAM-ICP-MS spectra of Tm (0.019 ppm) in NBS 616 glass obtained using 100 laser shots at 10 Hz. The signal of Tm was measured at 1 second per data point using the SCIEX multi-element data acquisition mode, and was then smoothed using a 7 point Savitzky and Golay (1964) quadratic/cubic smoothing filter. The calculated limit of detection is 0.007 ppm.

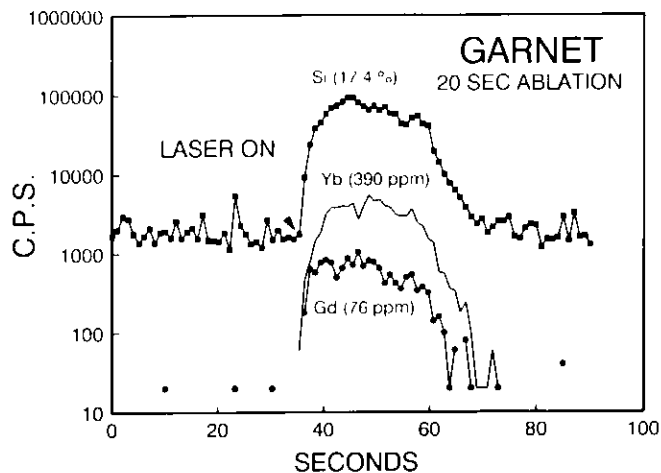


Figure 4 Time variation of the signal (counts per second, C.P.S.) of Si, Yb, and Gd in a garnet. Integration of the signal allows quantification. The high background count rate for Si (mass 29) is from ¹⁴N₂¹H⁺ and other polyatomic ions present in the Ar ICP.

sive tool opens Pandora's Box for the geologist. In igneous and metamorphic rocks, the partitioning of elements between minerals could be extensively

used for geobarometry and geothermometry. In metamorphic petrology, very little work using trace elements has been reported, primarily due to the diffi-

culty of obtaining extremely pure mineral separates in sufficient quantities for traditional analytical methods. The study of trace element distributions in

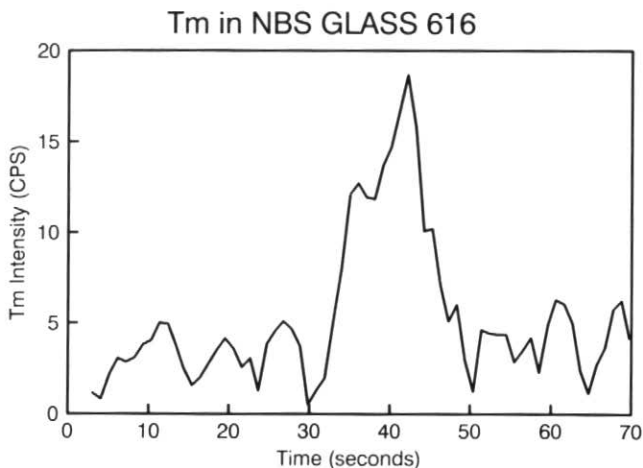


Figure 5 (above) Extended chondrite normalized rare earth element diagram of a garnet using LAM-ICP-MS. Concentrations (ppm) of a diverse set of selected elements are shown demonstrating the wide dynamic range of the technique.

Figure 6 (right) SEM image of a 25 μm ablation pit in titanite, demonstrating cylindrical geometry and a lack of significant splattered material.

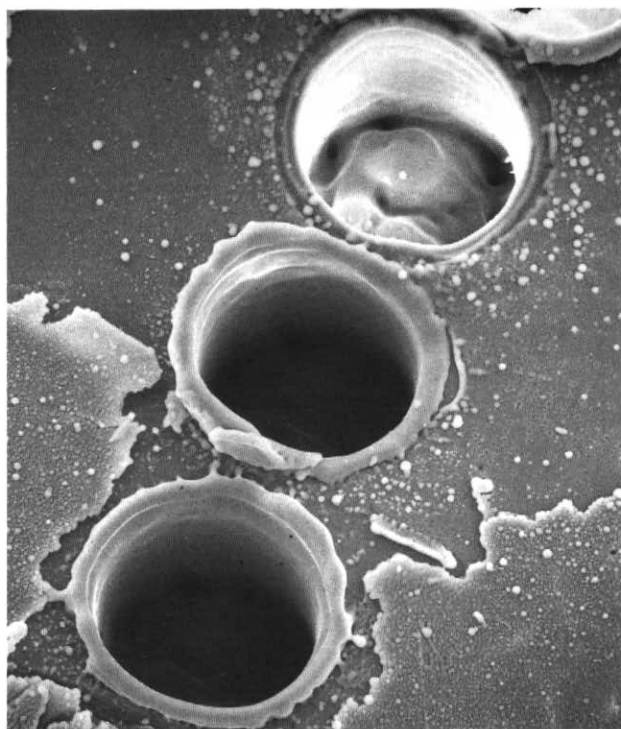
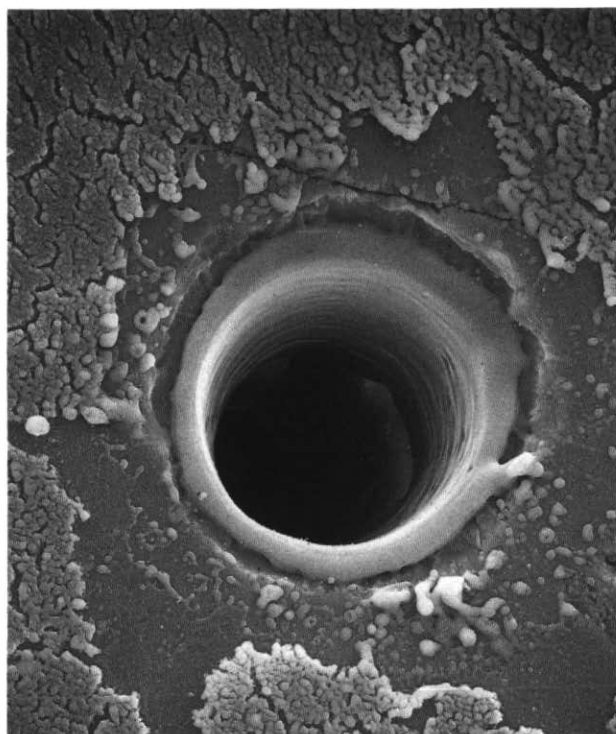


Figure 7 SEM image of a traverse producing a series of 50 μm ablation pits in a zoned garnet.

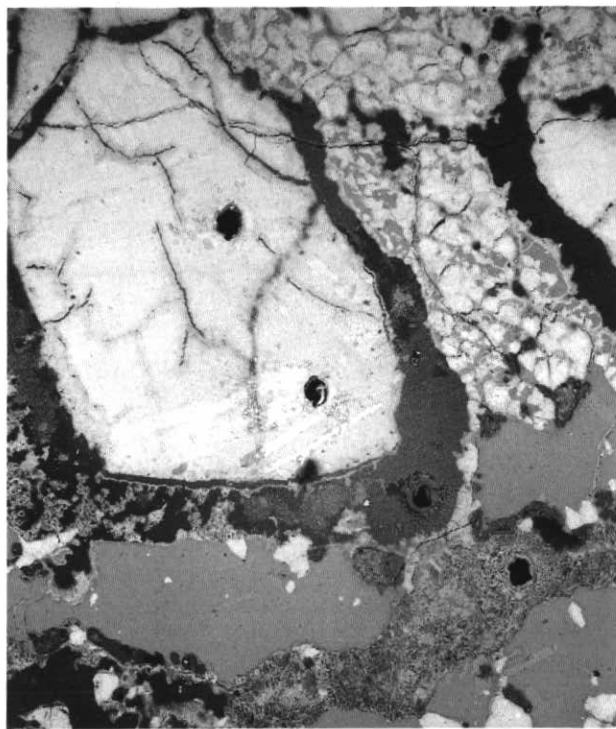


Figure 8 SEM image showing ablation sampling of primary uraninite (light gray), coffinite rim on the uraninite (dark gray), and secondary uraninite (mottled vein) from the Collins Bay deposit, Saskatchewan.

growth and reaction zones could help elucidate the chemical evolution of melts and the subsequent reaction history of minerals, which may not be well recorded in their major element chemistry. LAM-ICP-MS could also provide information on the distribution (crystal chemistry *versus* grain boundary phenomena) of fugitive elements in lower crustal rocks, to decipher lithophile element depletion models. The technique can also be applied to diverse studies of sedimentary rocks, including characterization of the origin of detrital grains, diagenetic cements and overgrowths, and authigenic phases.

A LAM sample introduction system also has potential major applications in the area of mineral deposits research. It can be used as a new exploration tool through the trace element characterization of ores and their genesis. For example, in exploration, variations in the trace element content of cumulate minerals in large layered intrusions can be used to determine PGE-bearing magma-mixing horizons. Analysis of growth zones in hydrothermal minerals could be used to monitor evolving mineralizing fluids, while element partitioning will provide data on temperature and pressure of deposition. In addition, the technique allows sampling of complex hydrothermal mineral assemblages (see Fig. 8) for either trace element distribution studies or isotopic analysis (e.g., $^{207}\text{Pb}/^{206}\text{Pb}$ dating of U-rich phases). In mineral processing, the ability to determine the distribution of the elements in the ore, especially the precious metals, and of toxic or metallurgically damaging elements (Fig. 9), could lead to developing more efficient and less environmentally hazardous recovery procedures.

CONCLUSIONS

The LAM-ICP-MS has profound potential as an economical analytical instrument for the *in situ* determination of trace elements in minerals. Accurate, quantitative results have been produced by calibration of the instrument using synthetic glass standards with major element internal standards to correct for differing ablation yields. In addition, the instrument has a demonstrated potential to make useful isotope ratio determinations. The data that this technique provides will lead to a better understanding of how rocks and minerals form, and open new areas of research into ore genesis and petrogenetic stud-

ies in igneous, metamorphic and sedimentary systems.

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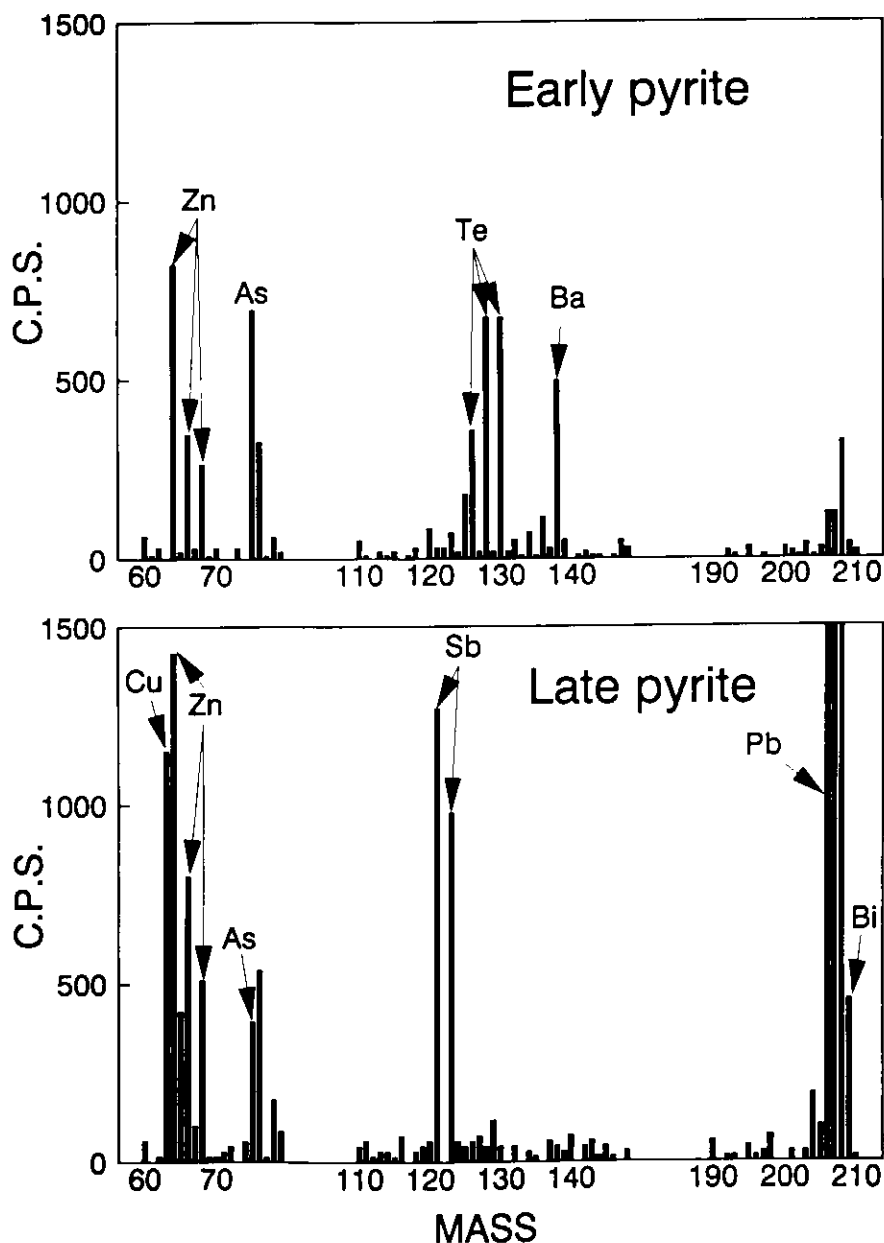


Figure 9 Partial mass spectra of different pyrite generations in thin section from a gold-base metal ore. Signals (counts per second, C.P.S.) for both analyses normalized to average $^{57}\text{Fe}^+$ intensity.

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