

TRACE-ELEMENT ANALYSIS OF GARNET BY LASER-ABLATION MICROPROBE ICP-MS

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ABSTRACT

Samples of pyrope were analyzed by a variety of methods in order to test the laser-ablation microprobe (LAM) ICP-MS method for *in situ* trace-element analysis of garnet. In this study, LAM-ICP-MS calibration employs NIST 612 glass as an external calibration standard, and either ^{29}Si or ^{43}Ca is used as an internal standard. Three other techniques were used in the cross-comparison: electron microprobe (EMP), nebulizer-mode ICP-MS, and proton-induced X-ray emission (PIXE). Comparisons of major-element compositions on an in-house garnet standard were carried out between EMP and LAM-ICP-MS, and indicate that all major elements except Fe and Mg provide 87–100% comparability, and precision better than $\pm 8\%$. Between LAM-ICP-MS and nebulizer-mode ICP-MS, the elements Sc, V, Ni, Ga, Y, Zr, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Hf provide 87–100% comparability. In comparing LAM-ICP-MS and PIXE data on trace elements, Ni, Ga, Y, and Zr provide comparability of 92–100% and precisions of better than $\pm 11\%$, but the rest of the above suite of trace elements are below the limit of detection by PIXE. A suite of five pyrope samples with a significant range in trace-element concentration also has been analyzed, and provides results similar to those stated above. The LAM-ICP-MS method is unmatched for rapidity, ease of sample preparation, and flexibility in the selection of external calibration standards. In the analysis of mounted grains with a minimum diameter of 250 μm , it gives accurate and reproducible concentrations. However, efforts are at present underway to decrease the 50- μm spot size. Such a reduction will be required before multi-element analysis can be carried out on typical polished thin sections.

Keywords: garnet, pyrope, provenance, inductively coupled plasma – mass spectrometry, ICP-MS, laser ablation, diamond exploration.

SOMMAIRE

Nous avons analysé des échantillons de pyrope par une variété de techniques afin d'évaluer les mérites d'un plasma à couplage inductif avec spectrométrie de masse, et avec prélèvement de matière par ablation au laser (LAM-ICP-MS), pour la caractérisation des teneurs en éléments traces. Dans cette étude, nous nous sommes servis de l'étalon vitreux NIST 612 pour calibrage externe, et soit ^{29}Si , soit ^{43}Ca pour calibrage interne. Trois autres techniques ont fourni les données nécessaires pour une comparaison des mérites relatifs: analyse par microsonde électronique, technique ICP-MS sur solutions, et émission de protons due à un faisceau de protons (PIXE). Une comparaison des teneurs en éléments majeurs d'un échantillon de grenat de référence a été entreprise avec les résultats de microsonde électronique et de LAM-ICP-MS; pour tous les éléments sauf le Fe et le Mg, il y a concordance (à 87–100%) et une précision supérieure à $\pm 8\%$. Entre les techniques LAM-ICP-MS et ICP-MS sur solutions, les concentrations des éléments Sc, V, Ni, Ga, Y, Zr, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, et Hf concordent à 87–100% près. Entre les techniques LAM-ICP-MS et PIXE, les teneurs en Ni, Ga, Y et Zr concordent à 92–100%, avec une précision supérieure à $\pm 11\%$, mais les teneurs des autres éléments sont inférieures au seuil de détection de la technique PIXE. Une suite de cinq échantillons de pyrope ayant un intervalle important de concentrations a aussi été analysée, et les résultats de la comparaison sont semblables aux autres. La technique LAM-ICP-MS n'a pas d'égal pour sa rapidité, la facilité du protocole de préparation des échantillons, et la flexibilité dans le choix des étalons pour le calibrage externe. Dans le cas de l'analyse de cristaux sertis dans une monture appropriée, d'un diamètre minimum de 250 μm , la méthode donne des résultats précis et reproductibles. Toutefois, nous tentons de réduire la taille du faisceau laser, présentement de 50 μm de diamètre, afin de permettre une analyse chimique complète des minéraux dans une lame mince polie typique.

(Traduit par la Rédaction)

Mots-clés: grenat, pyrope, provenance, plasma à couplage inductif avec spectrométrie de masse, ablation au laser, LAM-ICP-MS, exploration pour le diamant.

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INTRODUCTION

Garnet has found widespread use in igneous and metamorphic studies of a wide variety of rock types, but is especially useful in provenance studies intended to locate and assess kimberlite and lamproite pipes during exploration for diamond. In diamond exploration, large numbers of grains of pyrope, chromite, spinel, and other minerals are routinely collected from heavy-mineral concentrates that are obtained from soil, till, or rock samples. On the basis of major-element compositions, a number of criteria have been developed that separate pyrope into a number of groups or classes pertinent to kimberlites and lamproites. For example, Dawson & Stephens (1975) have subdivided pyrope compositions into ten groups (G1–10). Griffin *et al.* (1992, 1993) have suggested a reduction to six “classes” by combining some of the above groups. Of the ten groups of pyrope compositions, one group, subcalcic pyrope (G10 or Class 5 and 6), has been found as inclusions in diamond and is considered to be cogenetic with diamond (Dawson 1980, Leighton & McCallum 1979, Gurney 1984); group-9 (G9) garnet also is commonly found in diamond-producing pipes (Griffin *et al.* 1992). In contrast, other groups of garnet found in kimberlites can be indicative of barren, *i.e.*, non-diamondiferous pipes (Dawson 1980, Griffin *et al.* 1989).

In addition to the major-element compositions, rare-earth element (*REE*) patterns have been used to study the origin of garnet in kimberlitic rocks (Shimizu 1975, Shimizu & Richardson 1987, Jones 1987, Nixon *et al.* 1987, Boyd *et al.* 1993, Olson *et al.* 1993). Such patterns have also been found useful in studies that attempt to determine metamorphic protoliths, and the origin of some metamorphosed mineral deposits (Irving & Frey 1978, Hickmott *et al.* 1987, Schwandt *et al.* 1993). Other trace elements, such as Ni, Ti, Sc, Y, Ga, and Zr, also have been found useful as garnet discriminators (Shimizu & Richardson 1987, Griffin *et al.* 1992, 1993).

General requirements of any analytical technique used to study the trace-element geochemistry of garnet are small sample-size and low detection-limits. Inhomogeneities within garnet are common; such features as solid inclusions or exotic minerals along grain boundaries and within transgranular fractures are not easily avoided by a non-*in situ* method. Also, *in situ* microsampling can be useful in determining patterns of mineral zoning, and in assessing trace-element zonation. The trace-element contents of garnet are currently established by various methods, including proton-induced X-ray emission (PIXE), secondary-ion mass spectrometry (SIMS), atomic absorption spectrophotometry (AAS), instrumental neutron-activation analysis (INAA), and nebulizer-mode inductively coupled plasma – mass spectrometry (ICP–MS). Each of these methods has its advantages and particular

shortcomings. The most widespread methods currently used are spot analysis by PIXE, and SIMS. PIXE is not without disadvantages, particularly in the relatively high detection-limits for certain elements of interest (Fig. 1). For example, concentrations of the *REE* in garnet are generally <10 ppm, and other elements of interest such as Ni, Y, Ga, and Zr are in the 10–120 ppm range for typical samples of pyrope (Griffin *et al.* 1989), but the detection limits for these elements by PIXE are generally around 5–10 ppm. Nebulizer-mode ICP–MS gives much better limits of detection (sub-ppm to high ppb), but is not an *in situ* technique, and has the disadvantage that a population of garnet grains must be used. For example, 25-mg samples are commonly required in order to provide good detection of low-concentration elements. Also, the samples must undergo a cleaning procedure, followed by dissolution, both of which contribute to increased turnaround time per sample, because leaching and handpicking are necessary steps in the preparation procedures. INAA has the advantage of low to sub-ppm detection limits, but does not yield information on all *REE*, Y and Zr, cannot analyze individual ~250 μm grains of garnet, and also suffers from high turnaround time. SIMS analysis has the advantages of sub-ppm detection limits, and superior *in situ* performance (5- to 20- μm spot size), but the disadvantage of overall limited availability of this instrument, and the necessity of matching the matrix of the calibration standard with that of the sample.

The first reconnaissance study of a number of silicates by laser-ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS), including one zoned grain of garnet, was carried out by Jackson *et al.* (1992), and much of their analytical protocol has been adopted here. LAM–ICP–MS has been tested in this study as a rapid, accurate, *in situ* method of obtaining concentrations of some major elements, *REE* and Sc, V, Ni, Zn, Ga, Y, Zr, Cs, Hf, Ta, and U, which can be used to help determine the origin of detrital grains of garnet. We compare trace-element data on garnet by four methods: LAM–ICP–MS, nebulizer-mode ICP–MS, electron-microprobe (EMP) analysis, and PIXE. Some of the criteria used in the evaluation, besides *REE* patterns, are the empirical interelement relationships Zr–Ti, Sc–Ti (Shimizu & Richardson 1987), and the Ga–Y, Zr–Y relationships of Griffin *et al.* (1993). Another method available, not used in this study, is the contentious Ni-geothermometer (Griffin *et al.* 1989, Kjarsgaard 1992), which has recently been revised by Canil (1994).

SAMPLE DESCRIPTIONS

There is currently no available International Reference Standard pyrope with a well-characterized composition in terms of trace elements. Therefore, in

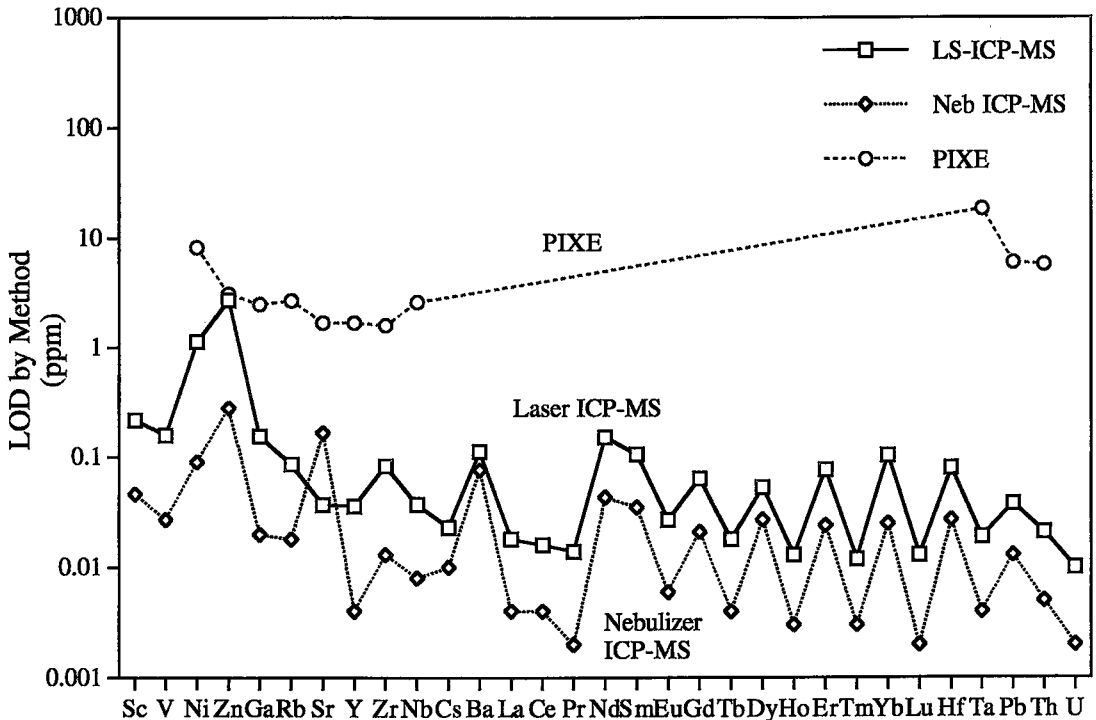


FIG. 1. Comparison of the limit of detection for analyses carried out in this study, listed by analytical method.

developing a scheme for routine trace-element analysis of garnet at the University of Saskatchewan, we first set out to establish an in-house reference standard by multimethod analysis. A relatively homogeneous megacryst of pyrope (STAG) from the Schaffer kimberlite in southern Wyoming was kindly provided by Dr. D. Schulze, University of Toronto; it has been characterized in this study for further use as an in-house reference standard. The megacryst is reddish brown, roughly 4 cm in diameter, has no visible solid inclusions, but is cross-cut by sets of narrow transgranular fractures. A dark gray coating of oxides (ilmenite, magnetite, spinel) is present along with minor carbonate and silicates on some of the fracture surfaces (Figs. 2a, b), which probably are the result of secondary kelyphitic alteration. This is a resorption phenomenon that commonly produces a rim of oxides on garnet in kimberlite [see Dawson (1980) for a description]. A second megacryst (Amalia) is a red-brown crystal one cm in diameter from the Frank Smith kimberlite pipe and diamond-producing mine in South Africa. Four coarse grains of garnet (2–4 mm in diameter), KM1P to KM4P, were obtained from heavy-mineral concentrates of soil samples that were collected in a current diamond-exploration programme in north-central Saskatchewan. These samples consist of burgundy-colored (KM1P, KM2P), violet (KM3P) and red brown

(KM4P) garnet; they were chosen for this study both for their optical homogeneity under the binocular microscope, and for their variation in color, which can reflect variation in composition (Jackson *et al.* 1992).

ANALYTICAL TECHNIQUES

Electron-microprobe method

Quantitative major element analyses of the garnet grains were carried out using a JEOL JXA 8600 Superprobe in wavelength-dispersion spectrometry (WDS) mode, with an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 10 μm . The maximum counting times for each element were 20 seconds on the unknown and 40 seconds on the standard. Analyses were made of ten widely spaced points throughout the grains of garnet. A ZAF correction program was used to calculate the concentrations. Oxide concentrations determined by this method have mean instrument-imposed limits of detection ranging from 0.04 to 0.22 wt.%, and analytical reproducibilities among ten closely spaced points generally ranging from 1 to 15% RSD (Table 1). The suite of minerals (Structure Probe Inc. standards) selected for calibration of unknowns includes: pyrope for Si and Mg, rutile for Ti, almandine for Fe and Al, bustamite for Mn and Ca,

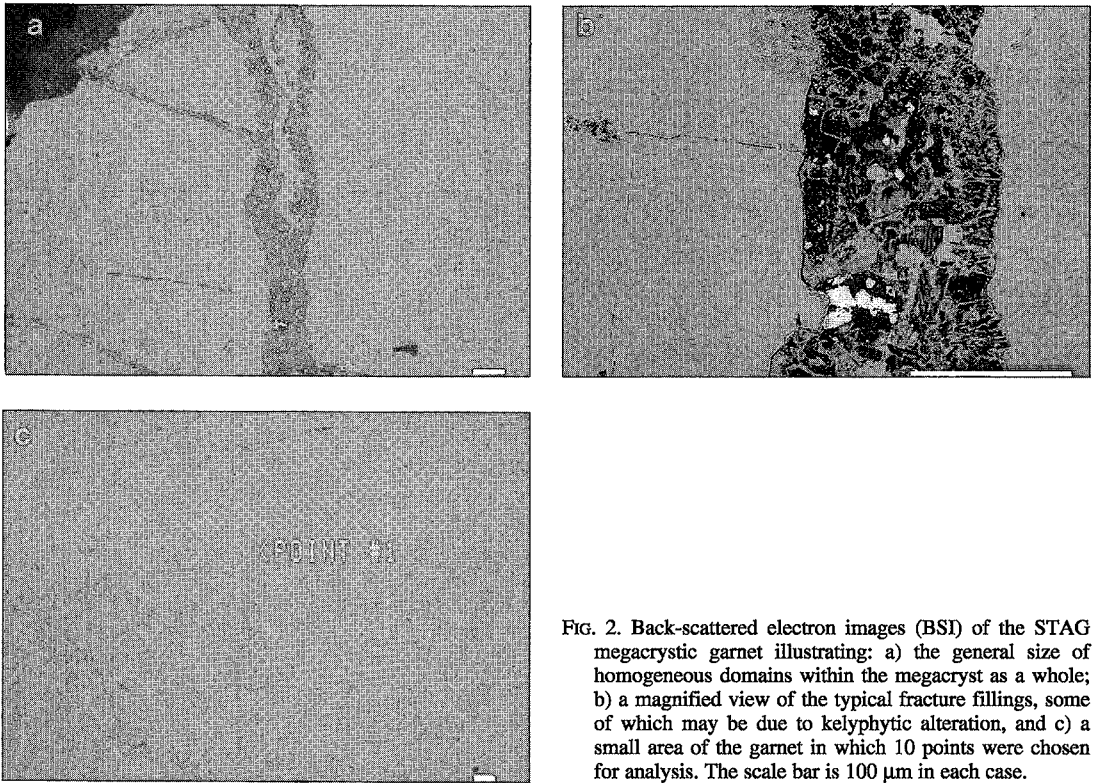


FIG. 2. Back-scattered electron images (BSI) of the STAG megacrystic garnet illustrating: a) the general size of homogeneous domains within the megacryst as a whole; b) a magnified view of the typical fracture fillings, some of which may be due to kelyphytic alteration, and c) a small area of the garnet in which 10 points were chosen for analysis. The scale bar is 100 μm in each case.

jadeite for Na, and chromite for Cr. EMP analysis by back-scattered electron image (BSI) analysis and spot wavelength-dispersion X-ray analyses (WDS) of all grains of garnet were carried out as a preliminary step to an assessment of compositional homogeneity.

LAM-ICP-MS instrumentation and analytical methods

A Perkin-Elmer Sciex[®] Elan 5000 ICP-MS and a model 320 laser sampler were used for this work. This

laser sampler utilizes a Spectra-Physics Quanta-Ray[®] DCR-11 pulsed Nd:YAG laser source with a wavelength of 1064 nm. It was operated in Q-switched mode, with pulse energy of 144 mJ, a pulse repetition rate of <10 Hz, and a 240 μs delay. Delivery of laser light to the sample is through a highly transparent quartz singlet lens, and a sample-cell window of borosilicate glass oriented 10° from normal to the laser beam. Sample positioning is controlled by computerized motor, and position of the incident beam was observed through a video monitor.

TABLE 1. CHEMICAL COMPOSITION OF GARNET SAMPLES, AS DETERMINED BY ELECTRON-MICROPROBE ANALYSIS

	STAG n=10 close		STAG n=10 wide		KM1P n=10		KM2P n=10		KM3P n=10		KM4P n=10		Amalia n=3		INSTR
	Avg	STD	Avg	STD	Avg	STD	Avg	STD	Avg	STD	Avg	STD	Avg	STD	MDL
SiO ₂	42.3	0.4	42.2	0.3	43.4	0.4	43.6	0.5	42.8	0.4	43.1	0.2	41.2	0.3	0.06
TiO ₂	0.97	0.04	0.99	0.03	0.03	0.02	0.02	0.01	0.01	0.01	0.23	0.02	1.10	0.03	0.04
Al ₂ O ₃	20.8	0.1	20.8	0.1	21.6	0.4	21.6	0.4	18.0	0.2	21.9	0.3	20.9	0.3	0.09
Cr ₂ O ₃	0.82	0.06	0.79	0.09	2.26	0.08	2.84	0.07	7.37	0.09	1.35	0.07	1.65	0.07	0.11
FeO	10.4	0.2	10.4	0.2	5.6	0.1	5.8	0.1	6.0	0.1	8.5	0.2	9.8	0.2	0.21
MnO	0.32	0.05	0.31	0.02	0.22	0.02	0.26	0.03	0.32	0.02	0.37	0.05	0.31	0.01	0.22
MgO	18.9	0.1	18.9	0.1	21.4	0.1	21.8	0.2	22.8	0.3	19.8	0.2	20.0	0.2	0.09
CaO	4.90	0.06	4.90	0.05	4.50	0.05	4.04	0.09	1.66	0.05	4.33	0.04	5.24	0.01	0.13
Total	99.4	0.5	99.3	0.5	99.1	0.8	99.9	0.6	99.0	0.5	99.6	0.6	100.2	0.8	

All concentrations are in wt percent. Abbreviations: Avg = average; STD = standard deviation; INSTR MDL = instrumental mean detection limit

Sample aerosol transport to the ICP-MS occurs *via* an Ar carrier gas with a flow rate of 0.8 litres per minute, through 4 m of polyvinyl chloride tubing 6.0 mm in inside diameter. Multi-element data were acquired using the rapid peak-hopping multichannel mode of the ICP-MS, with three replicates and 25 sweeps per replicate, for total analysis time of 50 seconds. The instrument was operated at a power setting of 1000 W, nebulizer flow-rate of 0.80 L/min, B, P, E1, and S2 lens settings of 45, 45, 25, and 38 respectively, and argon supply of 375 kPa. The measurement time per mass was 1.0 s, and the dwell time was 0.01 s, which was found to be the optimum condition during the one-minute ablation and analysis time. Optimization of the LAM-ICP-MS was carried out by varying the laser energy and ICP-MS settings for test ablations on NIST-612 glass standard until a steady signal was obtained for a 1.5-minute ablation.

In this study, NIST 612 glass is used as an external calibration standard. It is a synthetic standard reference material originally prepared for use in electron-microprobe analyses, and was first used by Jackson *et al.* (1992) as an external calibration standard for LAM-ICP-MS. It has nominal concentrations of 50 ppm for over 61 elements [see Fedorowich *et al.* (1993) for a summary] and works well as a calibration standard because it is sufficiently homogeneous for the scale of analysis of LAM-ICP-MS. Cautions as to the matching of matrices are advised by Stix *et al.* (1995). However, mineral standards with well-characterized trace-element concentrations are generally not available. Therefore, the use of a standard reference material such as NIST 612 is a very good alternative. Analyses of a wide variety of materials (*i.e.*, widely differing matrices) by Jackson *et al.* (1992), Fedorowich *et al.* (1993), and Jenner *et al.* (1993) indicate that good calibration *can* be obtained for concentrations that range over several orders of magnitude using NIST 612 and other synthetic glasses for external calibration.

Along with NIST 612, the garnet grains analyzed as unknowns were mounted within the laser sampling cell at approximately the same height. All surfaces were only lightly polished using a 25- μ m lapidary wheel, to provide a relatively even surface for focusing the laser beam. The laser beam was focused as precisely as possible upon the sample surface, and no down-focusing procedure was used in this study.

The ablation lasted for 80 seconds, of which the last 50 seconds was analysis time. Each spot analysis on garnet was paired with an analysis of the external calibration standard. The pit sizes that resulted were generally about 150 μ m in diameter, and the pits were found to be cone-shaped, commonly with a central projection at the base of the pit. A measurement of the background counts for the Ar carrier gas was made for 1.3 minutes before ablating the next sample.

Instrumental limits of detection are obtained in the

conventional manner. For LAM-ICP-MS, they represent three times the standard error of three consecutive measurements of background on aliquots of argon carrier gas (argon supplied at 34.5 kPa for 1.3 minutes each). The trace-element concentrations of these are obtained by external standard calibration using NIST 612, and are generally in the high ppb to low ppm range, depending on the element (Fig. 1, Table 2).

Raw intensities acquired from the ICP-MS were downloaded to an off-line computer for data reduction and plotting. Background counts were subtracted from the standard and unknown in order to subtract ions contributed from the argon carrier gas. Internal standardization, as outlined by Arrowsmith (1987), was used to correct for variations in the signal for individual ablations, which result from differences in ablation efficiency among elements owing to their absorption of fundamental Nd:YAG laser radiation. The internal standard is an element of known concentration within the garnet, as determined using an independent analytical technique; here, EMP analysis was used. The signals of all elements are normalized to the internal standard. In selecting the internal standard, the calibration curves showed that Si worked best for four samples, and Ca gave better working curves for the other two (KM4P and Amalia). Since concentrations of only eight elements were available by EMP analysis, the choice was somewhat limited. Jackson *et al.* (1992), Fedorowich *et al.* (1993), and Jenner *et al.* (1993) have also demonstrated that one-element internal standards work reasonably well for a large suite of elements, but an assessment for each individual mineral or material must be made prior to the selection. Several investigators (Moenke-Blankenburg *et al.* 1992, Walsh 1992, Ramsey & Coles 1992) have used multi-element internal standards, wherein the elements used as internal standards are close to the analyte in atomic number.

Nebulizer-mode ICP-MS

As a preliminary step to LAM-ICP-MS analysis, trace-element analyses of STAG and other samples of garnet were carried out by nebulizer-mode ICP-MS. An intense leaching procedure was performed in order to remove oxides, and possibly REE minerals (*e.g.*, Schwandt *et al.* 1993), that reside along fracture surfaces and in the kelyphitic rim. Samples were leached overnight in concentrated HNO₃, followed by a further 12 hours in aqua regia, and finally a two-minute leaching in concentrated HF. This procedure removed approximately 75% of the impurities, as verified using a binocular microscope. The final step in the procedure was the picking of 100- to 300- μ m inclusion-free grains, again using a binocular microscope. Final purity of the sample was >99%. Garnet samples, 25 mg each, were then dissolved in HF-HNO₃ in Saville[®] screw-top bombs for 48 hours. The solutions were

TABLE 2. NEBULIZER AND LASER ICP-MS CONCENTRATIONS AND REPRODUCIBILITY FOR STAG, AND COMPARISON WITH PIXE ANALYSES

	Five laser spot analyses				Three Nebulizer analyses			8 PIXE analyses CSIRO			15 PIXE analyses Guelph		
	Avg	Std	LOD	LA/EMP	Avg	Std	LOD	Avg	Std	LOD	Avg	Std	LOD
SiO ₂ %	42.26	IS	0.04	100.00									
TiO ₂ %	1.09	0.04	0.001	112.79									
Al ₂ O ₃	22	1	0.001	106									
Cr ₂ O ₃	0.76	0.06	0.000	92.73				0.77	0.07	0.09	0.7	0.1	0.2
FeO%	3	1	0.002	31				10.88	0.04	0.01	10.70	0.03	0.03
MnO%	0.32	0.01	0.000	100.88							0.32	0.04	0.01
MgO%	32	16	0.002	167									
CaO%	4.9	0.2	0.03	99.1									
ppm													
Sc	114	3	0.2		101	20	0.05						
V	333	10	0.2		359	5	0.03						
Ni	59	1	1		56	2	0.09	57	2	10	69	5	8
Zn	33	12	3		20.9	0.6	0.3	21	3	4	21	2	3
Ga	18	2	0.2		18.4	1.0	0.02	18	2	3	18	1	3
Rb	0.06	0.05	0.09		0.07	0.06	0.02						
Sr	0.38	0.08	0.04		0.9	0.1	0.2	3	3	3	2	1	2
Y	23	2	0.04		25	2	0.004	26	1	3	28	2	2
Zr	98	7	0.08		95	4	0.01	90	3	4	97	4	2
Nb	0.26	0.07	0.04		0.35	0.04	0.008						
Cs	0.01	0.01	0.02		0.01	0.01	0.01						
Ba	0.8	0.6	0.1		1.6	0.8	0.08						
La	0.03	0.01	0.02		0.10	0.04	0.004						
Ce	0.29	0.03	0.02		0.46	0.08	0.004						
Pr	0.13	0.02	0.01		0.15	0.02	0.002						
Nd	1.2	0.3	0.2		1.3	0.1	0.04						
Sm	1.1	0.1	0.1		1.1	0.1	0.04						
Eu	0.51	0.08	0.03		0.55	0.05	0.006						
Gd	2.3	0.3	0.06		2.5	0.2	0.02						
Tb	0.49	0.05	0.02		0.52	0.03	0.004						
Dy	4.1	0.5	0.05		4.3	0.3	0.03						
Ho	1.0	0.1	0.01		1.03	0.07	0.003						
Er	3.0	0.4	0.08		3.3	0.2	0.02						
Tm	0.46	0.05	0.01		0.53	0.05	0.003						
Yb	3.1	0.5	0.1		3.5	0.2	0.03						
Lu	0.48	0.04	0.01		0.56	0.06	0.002						
Hf	2.5	0.2	0.08		2.8	0.2	0.03						
Ta	0.01	0.01	0.02		0.05	0.03	0.004						
Pb	0.02	0.03	0.04		0.2	0.2	0.01						
Th	0.01	0.02	0.02		0.09	0.04	0.005						
U	0.01	0.01	0.01		0.02	0.01	0.002						

Laser spot analyses calibrated with sequential NIST 612 samples as external standard, and Si as internal standard (IS). Abbreviations: Avg=average; Std=standard deviation; LOD=limit of detection; LA/EMP=LA-ICP-MS vs EMP.

evaporated to dryness, and taken up in 1 mL of concentrated HNO₃, evaporated and taken up again in HNO₃ to remove any residual fluorides, and after the final evaporation, taken up in 3 mL of 8 N HNO₃. Samples were then transferred to 60-mL polypropylene bottles and diluted with water gravimetrically to 25 g (*cf.* Jenner *et al.* 1990). The dilution factor for the method is 0.1%.

For nebulizer-mode analysis, the ICP-MS instrument settings were essentially the same as for laser sampling, except that total counting times of 10 s per mass, with dwell times of 0.05 s per mass, were used. The calibration strategy employed was that of Jenner *et al.* (1990), wherein pure elemental standards are used for calibration (supplied by Inorganic Ventures Inc.). The instrumental limit of detection for a run is determined by analysis of six regularly spaced reagent blanks (0.2 N HNO₃) calculated to three times standard error. The chondritic values of Taylor & McLennan

(1985) are used to normalize the concentrations of REE reported here.

Proton probe

Garnet samples were sent to two different laboratories for proton-induced X-ray emission (PIXE) analysis: the Department of Physics at the University of Guelph, and the Commonwealth Scientific and Industrial Research Organization (CSIRO), Division of Exploration Geoscience, HIAF Laboratory, North Ryde, Australia. Sample-preparation procedures for PIXE analysis are essentially the same as for EMP. Analytical conditions for both Guelph and CSIRO analyses were: beam current of 2.5 nA at 3.0 MeV, and beam size of 30–80 μm in spot mode. A Link Si(Li) detector was used for a counting time of five minutes. Data reduction was performed at each of the respective laboratories, at the University of Guelph using the

GUPIX software program developed by Maxwell *et al.* (1989), and at CSIRO using the calibration procedure described by Ryan *et al.* (1990).

RESULTS AND INTERPRETATION

STAG

Major-element homogeneity of the in-house standard STAG is indicated by the reproducibility of 20 EMP points taken both in one small domain (10 points), and throughout a 2 cm × 1 cm area of the megacryst (Table 1). Homogeneity in major-element concentrations is also exhibited by back-scattered electron imaging (BSI), as shown in Figure 2c. According to the classification scheme of Dawson & Stephens (1975), this sample consists of Group-2 high-Ti pyrope. A few microvein minerals (Figs. 2b, c) were analyzed by EMP, as well as the composition of altered garnet within 100 µm of vein or fracture surfaces. The latter were found to exhibit greater variability in Ca, Al, and Fe concentrations.

A comparison of major- and trace-element data for STAG is shown in Table 2. These include results of five LAM-ICP-MS spot analyses (39 elements), three separate dissolutions and nebulizer-mode

ICP-MS analyses (31 elements), and eight and 15 PIXE points from the two different labs (eight elements each). Reproducibility and the detection limits (LOD) for each set of results are given. Comparisons of major-element concentrations as determined by EMP and LAM-ICP-MS methods indicate that all major elements except Fe and Mg provide 87–100% comparability, and precision better than ±8%. Problems are evident in LAM-ICP-MS data for Fe, which is only 30% of the value obtained by EMP, and Mg, which yielded a concentration 167% higher than with EMP (Table 2). Both of these elements also show rather poor analytical reproducibility. Significant differences in ablation efficiency for these elements (Fedorowich *et al.* 1993) compared with that of other elements analyzed here may be at the root of these problems. Fe and Mg clearly require internal standards other than Si for a better calibration. However, of the elements amenable to routine EMP analysis, none of the alternative internal standards has given significantly better results. Between LAM-ICP-MS and nebulizer-mode ICP-MS, the elements Sc, V, Ni, Ga, Y, Zr, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Hf provide 87–100% comparability in their respective concentrations. In comparing LAM-ICP-MS and

TABLE 3. COMPARISON OF NEBULIZER-MODE AND TRIPPLICATE LASER-ABLATION ICP-MS DATA ON TRACE ELEMENTS IN GARNET

	KM1P			KM2P			KM3P			KM4P			AMALIA			Mean LOD	
	Nebulizer	Laser	Std	Nebulizer	Laser	Std	Nebulizer	Laser	Std	Nebulizer	Laser	Std	Nebulizer	Laser	Std		
CaO%		4.3	0.3		4.08	0.08		1.6	0.2		IS			IS		0.008	
TiO ₂ %		0.04	0.002		0.02	0.001		0.01	0.002		0.21	0.01		1.03	0.04	0.001	
Cr ₂ O ₃ %	1.93	1.9	0.2	2.30	2.4	0.2	5.81	6.0	0.6	1.20	1.08	0.06	1.65	1.4	0.1	0.001	
MnO%		0.16	0.02		0.20	0.03		0.27	0.03		0.41	0.04		0.26	0.07	0.001	
Sc		71	80	7	68	95	5	154	185	19	96	112	2	102	110	2	0.07
V		177	165	14	170	181	13	187	192	20	184	179	3	333	306	11	0.03
Co			35	3		36	3		37	4		44.1	0.3		47	2	0.06
Ni		57	46	11	48	54	3	55	39	7	76	42	6	90	61	13	0.04
Zn		11	13	3	10	14	3	15	10	1	14	23	3	25	27.0	0.6	0.3
Ga			5.6	0.6		3.6	0.4		1.8	0.2		11.4	0.1		13.9	1.0	0.03
Ge			1.1	0.2		1.2	0.4		1.6	0.4		1.8	0.5		2.5	0.4	0.001
Y		6	6.4	0.5		4	4.7	0.3		1	0.62	0.04		8	6.8	0.6	0.002
Zr		23	20	2		16	20.3	0.5		21	20	2		28	21	2	0.03
La	0.16	0.03	0.01	0.17	0.03	0.004	0.64	0.55	0.08	0.11	0.02	0.003	0.66	0.3	0.3	0.004	
Ce	0.50	0.37	0.02	0.36	0.35	0.01	7.97	8.3	0.9	0.30	0.15	0.02	1.63	0.8	0.4	0.001	
Pr	0.20	0.18	0.004	0.20	0.16	0.01	2.89	2.8	0.4	0.11	0.07	0.01	0.63	0.19	0.03	0.002	
Nd	2.1	2.0	0.4	2.2	2.60	0.09	17.6	18	2	1.1	0.7	0.2	2.8	1.9	0.3	0.03	
Sm	0.9	0.9	0.1	1.2	1.36	0.04	3.4	3.4	0.3	0.7	0.64	0.06	1.9	1.6	0.1	0.001	
Eu	0.27	0.22	0.02	0.35	0.45	0.05	0.54	0.56	0.07	0.33	0.27	0.01	0.85	0.8	0.1	0.004	
Gd	0.7	0.7	0.1	0.9	1.0	0.1	1.0	0.84	0.08	1.1	0.8	0.1	3.7	3.8	0.3	0.02	
Tb	0.11	0.11	0.02	0.08	0.10	0.01	0.06	0.05	0.01	0.18	0.14	0.02	0.83	0.75	0.05	0.002	
Dy	0.9	0.80	0.09	0.5	0.51	0.02	0.2	0.17	0.02	1.4	1.04	0.09	6.5	6.2	0.2	0.008	
Ho	0.2	0.23	0.04	0.1	0.15	0.01	0.0	0.02	0.01	0.3	0.22	0.02	1.5	1.4	0.1	0.002	
Er	1.0	0.8	0.2	0.6	0.75	0.09	0.1	0.05	0.01	1.1	0.74	0.08	4.6	4.4	0.2	0.02	
Tm	0.15	0.15	0.01	0.13	0.14	0.004	0.02	0.01	0.004	0.16	0.11	0.02	0.74	0.63	0.04	0.002	
Yb	1.2	1.19	0.09	0.1	1.2	0.1	-0.1	0.13	0.05	1.2	0.9	0.2	4.3	4.3	0.5	0.001	
Lu	0.21	0.20	0.02	0.21	0.25	0.03	0.04	0.03	0.01	0.19	0.13	0.01	0.64	0.63	0.06	0.002	
Hf	8.2	0.33	0.04	0.3	0.31	0.03	0.4	0.37	0.03	1.1	0.26	0.06	2.9	2.8	0.2	0.02	
Ta	0.13	0.03	0.01	0.26	0.03	0.01	0.19	0.04	0.01	0.12	0.02	0.01	0.06	0.02	0.004	0.005	
U	0.02	0.03	0.01	0.09	0.05	0.01	0.36	0.32	0.08	0.04	0.01	0.01	0.26	0.07	0.04	0.003	

Garnets spot analyses were calibrated with sequential NIST 612 samples (blank subtracted). Abbreviations: Avg=average, Std=standard deviation, LOD=limit of detection, IS=internal standard. KM1P, KM2P, and KM3P were calibrated using Si as internal standard, whereas for KM4P and Amalia Ca was used.

PIXE measurements of trace-element concentrations, Ni, Ga, Y, and Zr provide 92–100% comparability and a precision of better than $\pm 11\%$, but the rest of the above suite of trace elements are below the limit of detection by PIXE. Other elements in this sample of garnet, such as U, Th, Pb, Ta, Ce, La, and Ba, appear to have concentrations at or near the detection limit for LAM-ICP-MS. Minor differences in trace-element concentrations may be attributed to slight variations in trace-element abundances within each of the spots analyzed, although the reproducibilities in Table 2 are within the general limits of precision for each of the techniques.

Amalia and KM1P–KM4P samples

On the basis of major-element concentrations, the Amalia megacryst consists of Group-2 high-Ti pyrope,

KM1P and KM2P consist of Group-9 chromian pyrope, KM3P consists of Group-10 low-Ca (sub-calcic) chromian pyrope, and KM4P consists of Group-1 titanian pyrope, according to the criteria of Dawson & Stephens (1975). Among these, the Group-10 subcalcic chromian pyrope is the typical garnet found as an inclusion in diamond, and may therefore be cogenetic with diamond from kimberlite (Dawson 1980), but it is not the only garnet associated with diamond-bearing pipes (Griffin *et al.* 1992, 1993).

Concentrations of 30 elements were obtained by LAM-ICP-MS for five samples of pyrope, with NIST 612 glass as an external calibration standard (Table 3). The average concentrations and reproducibility for three laser spot-analyses and one nebulizer-mode ICP-MS analysis are all shown in Table 3, along with the instrumental limits of detection for each run. Analytical reproducibility and comparability to

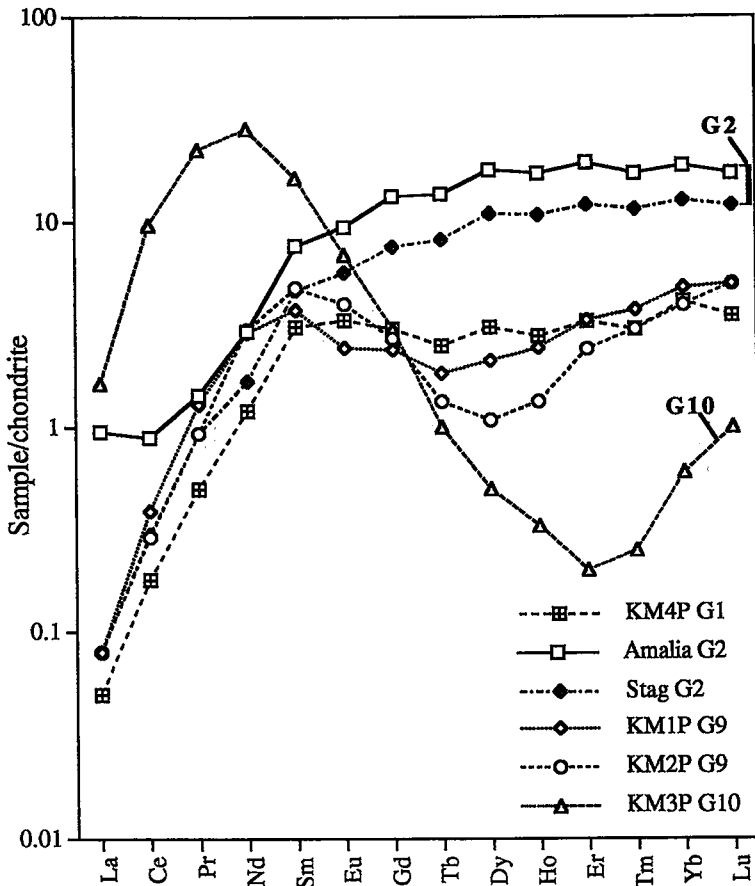


Fig. 3. Chondrite-normalized REE patterns of garnet as analyzed by LAM-ICP-MS. Patterns are grouped according to the type of garnet.

nebulizer-mode ICP-MS concentrations are similar to those obtained for STAG. Note that 18 of these elements fall well below the detection limits for PIXE.

REE patterns

The most significant overall differences among the pyrope samples analyzed are found in the concentrations of REE, and especially in the ratio of light rare-earths LREE (La-Sm) to heavy rare-earths HREE (Gd-Lu). Three types of patterns are illustrated in the chondrite-normalized plots shown in Figure 3. The REE patterns obtained by LAM-ICP-MS seem to be

comparable to patterns for garnet from kimberlitic rocks, obtained using SIMS. For example, STAG and Amalia Group-2 megacrysts have a HREE-enriched pattern typical of megacrysts from kimberlite, which are interpreted to have had a peridotitic parent magma (Shimizu 1975, Jones 1987). The G10 garnet (KM3P) has a sinusoidal REE pattern (Fig. 3), with Ce-Sm enrichment and HREE depletion, typical of subcalcic chromian pyrope (*cf.* Shimizu & Richardson 1987, Nixon *et al.* 1987, Boyd *et al.* 1993, Olson *et al.* 1993). The LREE enrichment observed in Group-10 garnet is unusual, and is not consistent with an equilibrium relationship between garnet and any known silicate

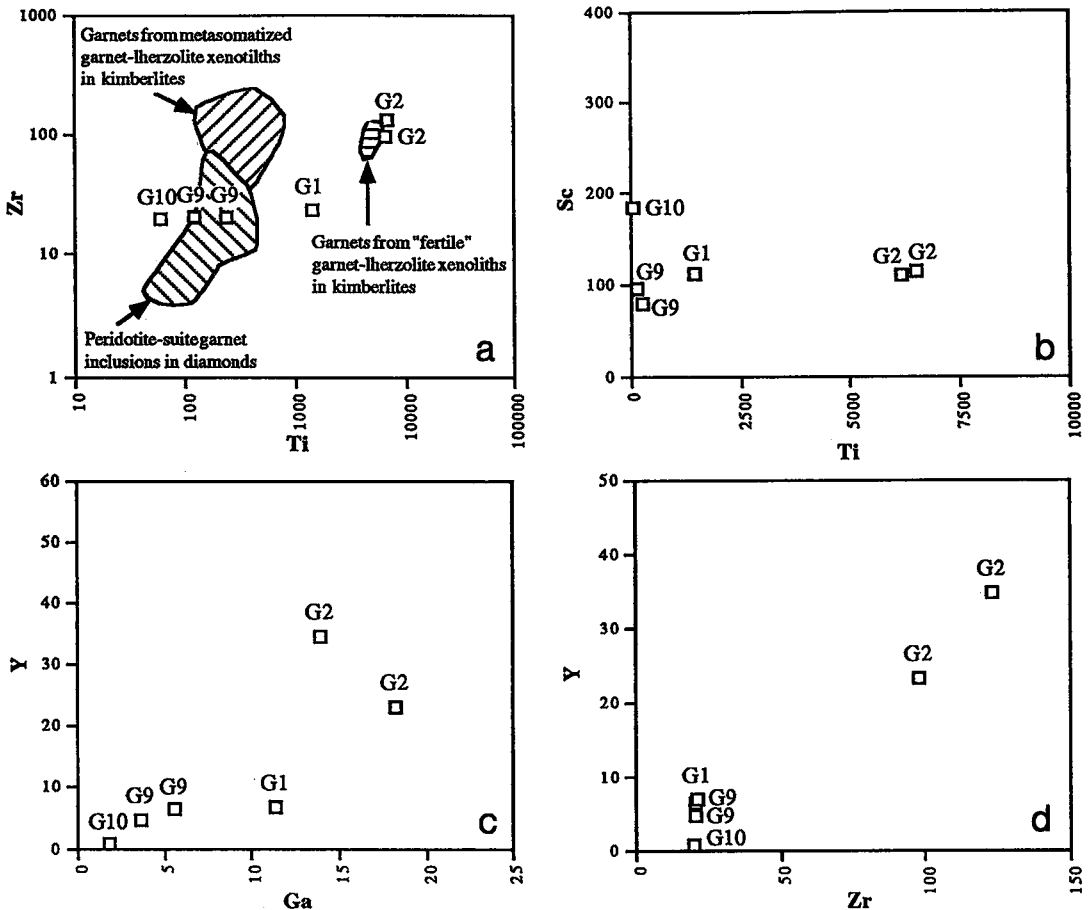


Fig. 4. a) A plot of the concentration of Ti versus that of Zr (ppm) for the six samples of pyrope analyzed. The various fields as labeled are from Shimizu & Richardson (1987), and help in assessing possible origins for the pyrope samples. b) A plot of the concentration of Ti versus that of Sc illustrates a similar general trend. c) Plots of Ga versus Y and d) of Zr versus Y (after Griffin *et al.* 1993) both illustrate a strong trend toward depletion of these elements in G10 garnet as compared with enrichment in G2.

liquid or hydrous fluid (Shimizu & Richardson 1987). Therefore, two-stage models involving early metasomatic events are commonly put forward to explain these patterns. For example, an early metasomatic event may have been superimposed on a garnet + Mg-rich olivine + orthopyroxene \pm diamond assemblage, with the bulk of the REE incorporated into garnet (Shimizu & Richardson 1987); alternatively, equilibration may have been incomplete between a refractory garnet and mantle-derived liquid in which the LREE more readily adjusted to changes in composition brought about by large-ion lithophile elements (LILE) and LREE-enriched metasomatic fluids (Olson *et al.* 1993). Unusual, slightly sinuous (*i.e.*, LREE-enriched, HREE-depleted) patterns with minor enrichment in Nd–Eu are displayed by the G1 and G9 samples of pyrope (Fig. 3). This pattern may indicate some intermediate stages between the above two cases.

Other trace-element patterns

Shimizu & Richardson (1987) and Griffin *et al.* (1992, 1993) have demonstrated the usefulness of other trace elements in comparing samples of garnet and in establishing their origin. For example, in a plot of Ti–Zr (after Shimizu & Richardson 1987), shown in Figure 4a, the samples of G9 garnet plot within the field of peridotite-suite garnet inclusions in diamond, and therefore are certainly of interest for diamond exploration. In comparison, the samples of G2 garnet plot with garnet from fertile garnet lherzolite xenoliths in kimberlite, and thus are of less interest in the context of exploration for diamond. Shimizu & Richardson (1987) suggested that a similar discrimination is possible on the basis of Ti–Sc, and Figure 4b shows that an overall similar pattern is exhibited. Griffin *et al.* (1992, 1993) suggested the use of Ga–Y and Zr–Y plots to discriminate various populations of garnet. In Figures 4c and 4d, a general trend of trace-element depletions is evident for the G9 and G10 (and G1?) garnets, which are more typical of diamond-producing pipes than any of the other pyrope grains analyzed. Qualitative criteria, such as the relative depletions in these important trace elements, may prove useful in assessment of large suites of garnet samples.

CONCLUSIONS

How can one obtain *in situ* trace-element analyses of a suite of garnet samples having a wide range of compositions, without using matrix-matched standards (since none are available)? Comparison of the concentrations obtained by LAM–ICP–MS with those obtained by other analytical methods are given and assessed. The method has the distinct advantage of sub-ppm limits of detection, which are necessary for accurate determination of the concentration of the REE

in garnet. Generally, good analytical reproducibility for concentrations above 0.5 ppm is found. The method is unsurpassed in rapidity of analysis (5 minutes per sample), in simplicity of sample preparation, and in the flexibility of analytical procedure.

The work has resulted in the development of a new in-house reference standard (STAG) characterized by a number of analytical techniques; we plan further tests to compare NIST 612 and our in-house standard for calibration of unknowns. From preliminary runs, we believe that other problems, such as drift in laser energy (Fedorowich *et al.* 1993) and variable efficiency of ablation for different elements, regardless of the matrix, may contribute more to some of the problems of comparability and analytical reproducibility found in this study than do the differences in matrices. In this study, the comparability of concentrations of 19 elements ranging across the mass spectrum indicates that the differences in matrix between the external calibration standard (NIST 612) and the unknown samples of garnet do not constitute a serious problem.

One of the shortcomings of LAM–ICP–MS is the average 150- μ m pit size obtained in typical 30-element runs. This is 5 to 10 times larger than a typical spot-size in SIMS analysis, but only about twice the diameter of a PIXE spot-size. Smaller sizes of pit can be obtained, especially for small suites of elements. However, a tradeoff always remains between sensitivity and amount of sample (*i.e.*, pit size). Use of frequency quadrupling (to a wavelength of 266 nm) by other researchers (Fryer *et al.* 1995) has brought about a significant reduction in laser-spot diameters, and is the subject of ongoing research and improvements.

Despite these shortcomings and possibilities for future improvements, the LAM–ICP–MS technique is at present capable of providing rapid and reproducible results on grains of the size commonly available from heavy-mineral concentrates, such as are routinely obtained in exploration for diamond.

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