

Spatially resolved and bulk trace element analysis by laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS)

MAURIZIO PETRELLI*, DIEGO PERUGINI, KELGAN E. ALAGNA, GIAMPIERO POLI and ANGELO. PECCERILLO

Dipartimento di Scienza della Terra, Università degli Studi di Perugia, Piazza Università, 1, 06123 Perugia, Italy

Submitted, February 2007 - Accepted, October 2007

ABSTRACT. — In this contribution, the analytical capabilities of the Laser Ablation - Inductively Coupled Plasma - Mass Spectrometer (LA-ICP-MS) instrumentation installed at the Earth Sciences Department of Perugia University are evaluated. The instrumental set up and the analytical protocols for single-phase spatially-resolved and bulk trace-element analyses are presented.

Spatially-resolved analysis allow 'in situ' trace element determinations with lateral resolutions ranging from less than 20 μm to more than 80 μm . Precision (expressed as relative standard deviation) is better than 10% with the only exception of Cs (14% with a 20 μm laser beam diameter) whereas accuracy (expressed as relative deviation from the reference value) is better than 11%. Precision and accuracy increase as increasing the laser beam diameter. The extreme versatility of the instrument permits to analyze with excellent results compositions of crystals, melt inclusions, ceramics, archaeological, and environmental samples.

Bulk configurations are utilized to perform whole-rock trace-element determination on samples prepared as fusion beads. Both flux-free and lithium tetraborate fusion sample preparation for whole rock trace element determination are investigated. **Results**

show that the lithium tetraborate fusion produces beads with higher degrees of homogeneity compared to the flux-free method, resulting in more precise and accurate trace-element determinations. In detail, for the lithium tetraborate fusion precision is better than 10% for elements with concentrations above 2 $\mu\text{g/g}$ with the only exception of Pb (~15%). For elements with concentrations below 2 $\mu\text{g/g}$ the precision decreases to about 15%. Accuracy values are always better than 10% with the only exception of Pb.

RIASSUNTO. — Nel presente lavoro vengono messe in evidenza le potenzialità analitiche del sistema di ablazione laser accoppiato ad uno spettrometro di massa (Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry, LA-ICP-MS) installato nel Dipartimento di Scienze della Terra dell'Università degli Studi di Perugia. In particolare vengono discussi i protocolli analitici utilizzati per le analisi di fasi singole e roccia totale.

Le analisi di fasi singole possono essere effettuate con risoluzioni spaziali che variano da meno di 20 micron a più di 80 micron. La precisione (espressa come deviazione standard relativa) è migliore del 10 % per tutti gli elementi con la sola eccezione del Cs (14% utilizzando una risoluzione spaziale di 20 micron), mentre l'accuratezza (espressa come deviazione relativa dal valore di riferimento) è sempre migliore dell' 11 %. Precisione e accuratezza

* Corresponding author, E-mail: maurip@unipg.it

migliorano aumentando la dimensione del fascio laser. La versatilità dello strumento permette di analizzare con ottimi risultati la composizione chimica di cristalli, inclusioni vetrose, ceramiche, reperti archeologici e campioni per analisi ambientali.

Le analisi di roccia totale vengono eseguite su perle di vetro ottenute fondendo le polveri dei campioni. Per quanto riguarda la preparazione delle perle, sono stati valutati due metodi: la fusione senza fondente e quella con fondente. I risultati mostrano che le perle realizzate senza l'utilizzo di un agente fondente risultano meno omogenee di quelle realizzate aggiungendo una miscela di borati di litio alla polvere del campione al fine abbassare la temperatura di fusione e diminuire la viscosità del fuso. In particolare, le analisi eseguite sulle perle realizzate con l'ausilio dell'agente fondente mostrano precisioni migliori del 10% per gli elementi chimici presenti in concentrazioni superiori a 2 µg/g con la sola eccezione del Pb. Per gli elementi presenti in concentrazioni inferiori a 2 µg/g la precisione è dell'ordine del 15 %. L'accuratezza per le analisi di roccia totale è sempre migliore del 10% con la sola eccezione del Pb.

KEY WORDS: *ICP-MS, laser ablation, trace-elements, bulk analysis, spatially-resolved analysis, figures of merits.*

INTRODUCTION

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) has become a powerful tool for trace element and isotope ratio determination in geological samples (e.g. Norman *et al.*, 1996; Horn *et al.*, 2000; Jeffries *et al.*, 1998; Becker and Dietze, 1999; Durrant, 1999; Günther *et al.*, 1999; Sylvester, 2001; Tiepolo, 2003; Tiepolo *et al.*, 2003; Jeffries *et al.*, 2003; Rusk *et al.*, 2004; Pettke *et al.*, 2004). The operating principles of the technique are practically unchanged since their introduction (Gray, 1985), but recent developments in ICP-MS instrumentation significantly improved the performance of the new generation mass spectrometers, allowing ultra-trace element determinations (down to ppb level) with excellent precision and accuracy.

Parallel progress in new ICP-MS analyzers, laser ablation systems were also developed. Early Nd-YAG ablation systems utilized the laser fundamental wavelength (1064 nm), which did

not perform satisfactory, especially in the case of highly transparent materials (Günther *et al.*, 1999). The introduction of laser ablation systems that utilize fifth Nd-YAG harmonic (wavelength equal to 213 nm; Jeffries *et al.*, 1998) or excimer lasers (wavelengths equal to 193 or 157 nm; Günther *et al.*, 1997; Telouk *et al.*, 2003) greatly improved ablation performances resulting in more accurate and reproducible determinations, particularly when small laser beam diameters are employed and highly transparent materials are analyzed.

Among the different applications (e.g. Sylvester 2001 and references therein), laser ablation ICP-MS is also commonly used in bulk and spatially-resolved trace-elements determinations.

In bulk analysis, spot diameters are typically equal or larger than 80 µm and under these conditions sub-ppb concentrations levels can be achieved coupling good precision and accuracy (Günther *et al.*, 1999). An example of the application of LA-ICP-MS bulk configuration in the geological field is the analysis of trace elements in whole rock samples.

In spatially-resolved LA-ICP-MS analysis, spot diameters typically range from 15 to 80 microns; under these conditions, precision reported as Relative Standard Deviation (RSD), and accuracy, expressed as relative deviation from reference values, are typically of the order of 10% for all elements, whereas detection limits vary as a function of several parameters including the laser beam diameter, the repetition rate, the background signal, and the instrumental sensitivity (Longerich *et al.*, 1996; Norman *et al.*, 1998; Gao *et al.*, 2002; Tiepolo *et al.*, 2003). The application fields of spatially-resolved trace-elements determinations in Earth Sciences are very large and examples are the analysis of trace-elements in natural and synthetic crystals, melt and fluid inclusions.

In this contribution, the capabilities of the LA-ICP-MS equipment installed at the Earth Sciences Department of the Perugia University are evaluated in detail. Developed analytical protocols for bulk and spatially-resolved analysis are carefully described and figures of merits are evaluated by comparison with international reference materials.

EXPERIMENTAL SETUP

The Laser Ablation-Inductively Coupled Plasma-Mass Spectrometer (LA-ICP-MS) system installed at the Earth Sciences Department of Perugia University [belonging to Scientific Methodologies Applied to Archaeology and Art (SMAArt) Centre] is composed by a commercial New Wave UP213 (New Wave, UK) LA system coupled with a Thermo Electron X7 (Thermo Electron Corporation, Waltham, USA) ICP-MS.

The laser ablation system is a frequency quintupled Nd:YAG laser, whose fundamental wavelength of 1064 nm is converted into 213 nm by means of three harmonic generators. The commercial ablation cell (New Wave, UK), capable to support both thin sections and cylindrical resin chips, has been modified in order to mount together both reference materials and unknown samples. In addition, special adjustments have been developed on the ablation cell for the lodging of 'large' samples (up to c.a. 5 cm). Helium is preferred over argon as a carrier gas to enhance the transport efficiency of ablated aerosol (Eggins *et al.*, 1998). The helium carrier gas exiting the ablation cell is mixed with argon make-up gas before entering the ICP torch; this configuration permits the maintenance of stable and optimum excitation condition. LA-ICP-MS measurements are carried out using time resolved analysis operating in a peak jumping mode (Table 1). The laser repetition rate and the laser energy density are fixed to 10 Hz and ~ 10 J/cm², respectively (Table 1).

The LA-ICP-MS system is optimized for dry plasma conditions prior to each analytical session on a continuous linear ablation of NIST SRM 612 glass standard by maximizing the signals for selected masses (La⁺ and Th⁺) and reducing oxide formation by minimizing the ThO⁺/Th⁺ ratio.

For the operating conditions outlined above, background intensities are typically 20-200 cps for Sc, V, Cr and Ga, 10-20 cps for Rb, Sr and Pb, and <10 cps for all other elements. Analyte sensitivities vary as a function of the amount of material reaching the torch, the ionization efficiency, isotope abundance, and mass. For the operating conditions outlined above and for a laser beam of 40 μ m sensitivities range between 690 and 6230 cps/ μ g g⁻¹ (Table 2).

Data are collected in discrete runs of 15-24 analyses, each run comprising 6-15 unknowns and 1 quality control standard analyzed as an unknown, bracketed by 8 analyses of the external standard. External calibration is performed using NIST SRM 610 and 612 glass standards in conjunction with internal standardization using a major element, generally ²⁹Si or ⁴²Ca (Fryer *et al.*, 1995), previously determined by an independent technique (e.g. EPMA or XRF) following the method proposed by Longerich *et al.* (1996).

Unknown samples are mounted together with standards in order to avoid changes in instrumental conditions due to continuous opening of the ablation cell interface. A typical analysis consists of acquiring 60 s of background followed by 60 s of the signal produced by the ablated aerosol. Data reduction is performed on the time-resolved signals by carefully selecting homogeneous portion of background and signal intensity. Data reduction is performed by using the Glitter software (van Achterbergh *et al.*, 2001) and in-house written codes.

SPATIALLY RESOLVED CONFIGURATION

Spatially resolved applications allow analyzing 'in situ' trace-elements using lateral resolutions ranging from less than 20 μ m to more than 80 μ m. A total of 30 elements are routinely analyzed ranging from Sc to U and including V, Cr, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, REEs, Hf, Ta, Pb and Th.

Three different analytical configurations are considered here: (i) 20 μ m spot diameter, (ii) 40 μ m spot diameter and (iii) 60 μ m spot diameter. These configurations cover the entire range of laser beam diameters routinely utilized in the laboratory. Laser beam diameters smaller than 20 μ m can be also used and the reader interested in high spatial resolution applications can refer to Petrelli *et al.* (2007a) for full details.

Figures of merit (limits of detection, precision and accuracy) are evaluated on the USGS BCR2G basalt glass (USGS; 2006). This reference standard is well characterized (Norman *et al.*, 1998; Gao *et al.*, 2002; Eggins, 2003; Tiepolo *et al.*, 2003) and, therefore, suitable for the determination of long term stability, precision, and accuracy.

TABLE 1
ICP-MS and Laser Ablation (LA) operating conditions

ICP-MS	
Instrument	Thermo Electron X7
Plasma conditions	
RF Power	1200-1300 W
Plasma Gas Flow	13-14 l min ⁻¹
Auxiliary Gas Flow	0.8-1.0 l min ⁻¹
Helium Carrier Gas Flow	0.5-0.8 l min ⁻¹
Argon Make Up Gas Flow	0.5-0.8 l min ⁻¹
Data Acquisition Parameters	
Scanning Mode	time resolved
Background Acquisition Time	~ 60 s
Signal Acquisition Time	~ 60 s
Wash out	~ 60 s
Laser Ablation	
Laser Ablation device	New Wave UP213
Laser Type	Nd-YAG
Wavelength	213 nm
Mode	Q-Switched
Shot Repetition Rate	10 Hz
Energy Density on Sample Surface	~ 10 J cm ⁻²
Spot Size	Spatially-resolved 12 - 60 µm
	Bulk 80 µm

Limits Of Detections (LODs) are estimated by using the formulation reported by Longerich *et al.* (1996). LODs are complex function of background, instrumental sensitivity, and counting statistics (Longerich *et al.*, 1996; Günther *et al.*, 1999); when all other parameters are fixed, LODs decrease with increasing laser beam diameters. In particular, LODs range from 0.005 to 4 µg/g for

the 20 µm configuration, from 0.002 to 2 µg/g for the 40 µm configuration, and from 0.001 to 1 µg/g for the 60 µm configuration (Table 2 and Fig.1).

Precision values are given at one Relative Standard Deviation (RSD); average values are reported in Table 3 and also displayed in Figs 2a, 2c and 2e. Precision values are always better than 10% for the 20 µm laser spot configuration (Fig.

TABLE 2
Limits of detection (LODs) for spatially-resolved analysis at 20, 40, and 60 micron laser beam diameter on the USGS BCR2G basalt glass reference standard

Element	40 μm Sensitivity (cps/ $\mu\text{g g}^{-1}$)	Detection limits ($\mu\text{g g}^{-1}$)		
		20 μm	40 μm	60 μm
Sc	690	3	2	0.8
V	940	1	0.2	0.03
Cr	620	4	2	1
Ga	1140	1	0.4	0.1
Rb	1260	0.8	0.3	0.08
Sr	2280	0.3	0.1	0.06
Y	1840	0.3	0.1	0.03
Zr	1060	0.8	0.3	0.1
Nb	2160	0.2	0.1	0.03
Cs	3550	0.5	0.1	0.06
Ba	1400	1	0.4	0.1
La	2600	0.1	0.04	0.02
Ce	3200	0.07	0.03	0.01
Pr	3500	0.06	0.02	0.01
Nd	1100	0.2	0.09	0.04
Sm	990	0.2	0.1	0.03
Eu	2300	0.08	0.03	0.02
Gd	1330	0.3	0.10	0.08
Tb	2180	0.04	0.01	0.007
Dy	1450	0.1	0.05	0.02
Ho	3390	0.04	0.01	0.008
Er	1950	0.06	0.03	0.02
Tm	3690	0.03	0.01	0.005
Yb	2900	0.2	0.07	0.02
Lu	4480	0.03	0.01	0.004
Hf	1570	0.08	0.03	0.01
Ta	4110	0.03	0.009	0.001
Pb	2900	0.2	0.04	0.01
Th	4480	0.01	0.006	0.003
U	6230	0.005	0.002	0.001

2a) with the only exception of Cs (14%). Precision values are better than 10% and 8% for the 40 μm (Fig. 2c) and the 60 μm (Fig. 2e) configuration, respectively.

Accuracy is expressed as the relative difference from reference values of USGS BCR2 (USGS 2006). The results of LA-ICP-MS analysis on the USGS BCR2G obtained by Norman *et al.* (1998), Gao *et al.* (2002) and Tiepolo *et al.* (2003) are also reported in Table 3. Average values for accuracy, displayed in Figs 2b, 2d and 2f, are always better than 10% for the 20 μm (Fig. 2b) and the 40 μm (Fig. 2d) configurations with the only exception of Yb (11%) in the 20 μm configuration. Accuracy is always better than 8 % for the 60 μm configuration (Fig. 2f).

BULK CONFIGURATION

Bulk configurations (laser beam $\geq 80 \mu\text{m}$) allow making trace element whole rock analyses. The analyses can be performed without any sample preparation if the starting material is homogeneous, whereas heterogeneous samples need always to be homogenized to obtain accurate and reproducible results. Examples of sample preparation utilized in bulk LA-ICP-MS analyses include powdering (e.g. Imai, 1990), strip flux-free fusion (Fedorowich *et al.*, 1993; Norman *et al.*, 1996), Pt-crucible flux-free fusion (Chen *et al.*, 2000), Pt-capsule flux-free fusion (Kurosawa *et al.*, 2006) and lithium borate fusion (Günther *et al.*, 2001; Ødegård *et al.*, 1998; Eggins, 2003). We did not test LA-ICP-MS analysis on powdered samples because, in these targets, the ablation process is not easily controllable and it is strongly influenced by matrix effects (Motelica-Heino and Donard, 2001). The other preparation procedures can be grouped in two categories: flux-free and lithium borate fusions. The flux-free method is evaluated on beads produced by graphite electrode fusion, whereas the lithium borate fusion is tested on beads made by both commercial automated fusion machines and graphite electrode fusion.

The graphite electrode fusion device consists in a 12V (400 A) power source (Fedorowich *et al.*, 1993; Ødegård, 1999; Petrelli *et al.*, 2007b) coupled with a fusion chamber similar

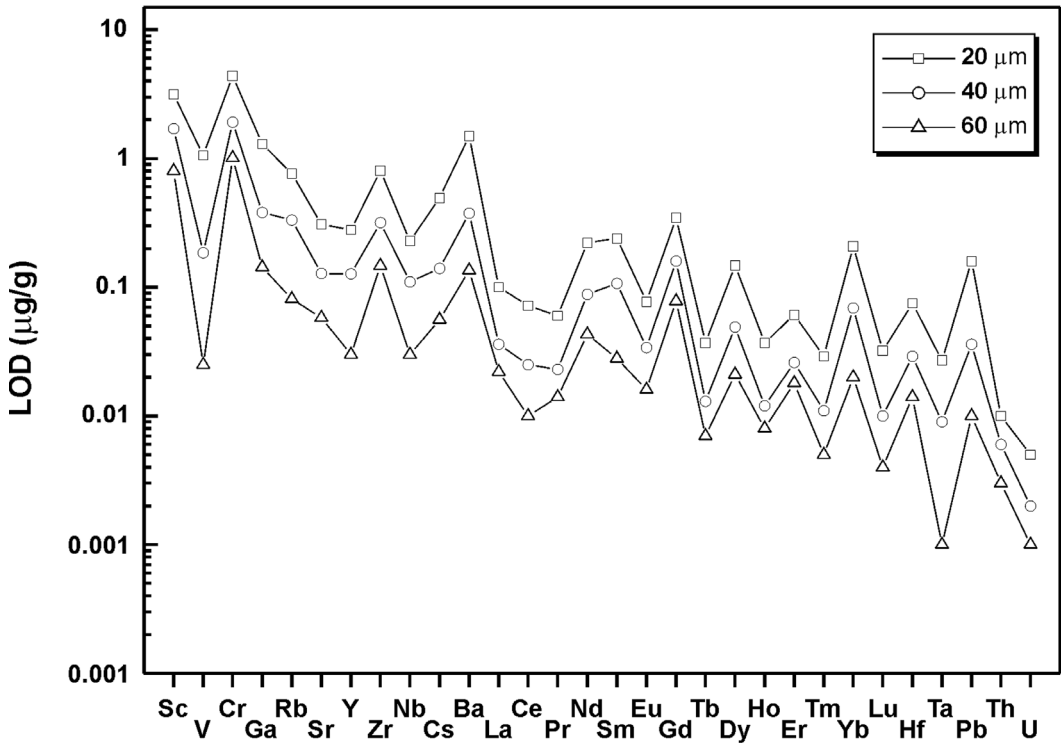


Fig. 1 – Limits of detection (LOD) on spatially-resolved analysis measured for 20, 40, and 60 micron laser beam sizes on the USGS BCR2G basalt glass reference standard.

to that proposed by Fedorowich *et al.*, (1993). The fusion chamber is maintained in Argon atmosphere in order to reduce oxidation effects. Graphite electrodes are clamped across the pole of the electrical source and temperature is varied by resistance heating (e.g. Ødegård, 1999). No direct temperature measurement is performed and the current intensity vs temperature calibration is carried out by fusing 20 mg of pure elements and oxides. In particular, Iron ($T_f \sim 1535$ °C) and electrolytic Copper ($T_f \sim 1080$ °C) are utilized to identify the current intensity required to perform the fusion in the flux-free and lithium borate fusion respectively.

The automated fusion machines are a commercial Claisse instrument (University of Pisa, Department of Earth Sciences) and a Breitländer Autofluxer (University of Perugia,

Department of Earth Sciences), where fusion is performed in Pt-crucibles.

In flux-free experiments, about 20 mg of powdered sample is poured in cylindrical cavities drilled in the graphite electrodes and the fusion is made at ~ 1535 °C for 5 min. Such an elevated fusion temperature is employed in order to induce the melting even of refractory minerals.

In lithium borate experiments carried out by graphite electrode fusion, about 50 mg of powdered sample is weighted and subsequently mixed and homogenized with lithium tetraborate using 1:3 ratio. The fusion of 20 mg of the homogeneous mixture is performed, using the graphite electrode fusion device previously described, at ~ 1080 °C for 5 min (Petrelli *et al.*, 2007b).

TABLE 3 – LA-ICP-MS analyses for the USGS BCR2G glass performed at 20, 40 and 60 μm . For each laser beam diameter the average of 9 determinations (“This Study” column), the absolute standard deviation (1σ column) and the relative standard deviation (RSD column) are reported. Analysis performed by Gao *et al.* (2002), Norman *et al.* (1998), Tiepolo *et al.* (2003) on the USGS BCR2G and reference values from USGS (2006) and Govirindaraju (1994) are also reported

Element	20 μm (n=9)			40 μm (n=9)			60 μm (n=9)			REFERENCE VALUES ($\mu\text{g/g}$)			
	This Study ($\mu\text{g/g}$)	1σ ($\mu\text{g/g}$)	RSD (%)	This Study ($\mu\text{g/g}$)	1σ ($\mu\text{g/g}$)	RSD (%)	This Study ($\mu\text{g/g}$)	1σ ($\mu\text{g/g}$)	RSD (%)	Gao <i>et al.</i> , (2002)	Norman <i>et al.</i> , (1998)	Tiepolo <i>et al.</i> , (2003)	USGS (2006) Govirindaraju (1994)
Sc	31	3	10	35	1	4	34.7	0.6	2	32	33	34.7	33
V	395	12	3	420	18	4	425	10	2	425	414	451	416
Cr	20	2	9	16	1	7	18	1	7	17	-	18.4	18
Ga	21	1	6	22	1	5	23.6	0.3	1	24	22.7	-	22
Rb	46	2	4	46	1	3	46.0	0.8	2	51	49	51.3	48
Sr	323	6	2	334	5	2	335	5	1	321	342	352	346
Y	36	3	8	34	2	7	36	2	6	31	35.3	34.3	37
Zr	171	13	8	177	7	4	190	6	3	167	194	197	188
Nb	14.2	0.7	5	13.5	0.5	4	13.5	0.3	2	10.9	12.8	14.8	13.1
Cs	1.1	0.1	14	1.0	0.1	9	1.07	0.04	3	1.17	1.13	1.1	1.1
Ba	719	31	4	668	24	4	694	20	3	641	660	717	683
La	26.5	0.9	3	25.7	0.6	2	25.1	0.6	2	25	24.5	25.1	25
Ce	55	2	4	52	1	3	52.1	1.2	2	52	50.5	56.1	53
Pr	6.5	0.3	4	6.6	0.3	4	6.6	0.2	3	6.3	6.8	7	6.8
Nd	29	3	10	29	1	4	28	1	4	27	29	29.6	28
Sm	7.3	0.6	9	6.6	0.4	6	6.3	0.2	4	6.3	6.6	6.7	6.7
Eu	1.9	0.1	6	1.93	0.07	3	1.95	0.06	3	1.91	1.92	2.1	2
Gd	6.3	0.4	6	6.4	0.4	5	6.5	0.3	4	6.5	6.5	6.3	6.8
Tb	0.99	0.05	5	0.97	0.04	5	1.00	0.04	4	0.95	-	1	1.07
Dy	6.3	0.4	6	6.3	0.4	6	6.0	0.3	5	6	6.5	6.3	6.38
Ho	1.2	0.1	10	1.26	0.09	7	1.31	0.09	7	1.2	1.31	1.3	1.33
Er	3.4	0.2	5	3.7	0.2	5	3.5	0.2	4	3.3	3.6	3.6	3.66
Tm	0.50	0.04	7	0.52	0.03	5	0.52	0.03	5	0.46	-	0.5	0.54
Yb	3.1	0.3	9	3.6	0.2	4	3.4	0.1	4	3.2	3.5	3.4	3.5
Lu	0.47	0.03	6	0.51	0.02	5	0.47	0.02	4	0.47	0.51	0.5	0.51
Hf	4.39	0.30	7	4.6	0.3	6	4.5	0.2	5	4.5	5	4.8	4.8
Ta	0.74	0.06	8	0.82	0.03	4	0.84	0.01	1	0.63	0.78	0.8	0.78
Pb	10.1	0.6	6	10.4	0.4	3	11.2	0.3	3	11	11.5	11.5	11
Th	5.7	0.2	3	6.2	0.2	3	5.9	0.2	3	5.5	6.1	6.2	6.2
U	1.6	0.1	8	1.59	0.06	4	1.63	0.04	2	1.7	1.73	1.9	1.69

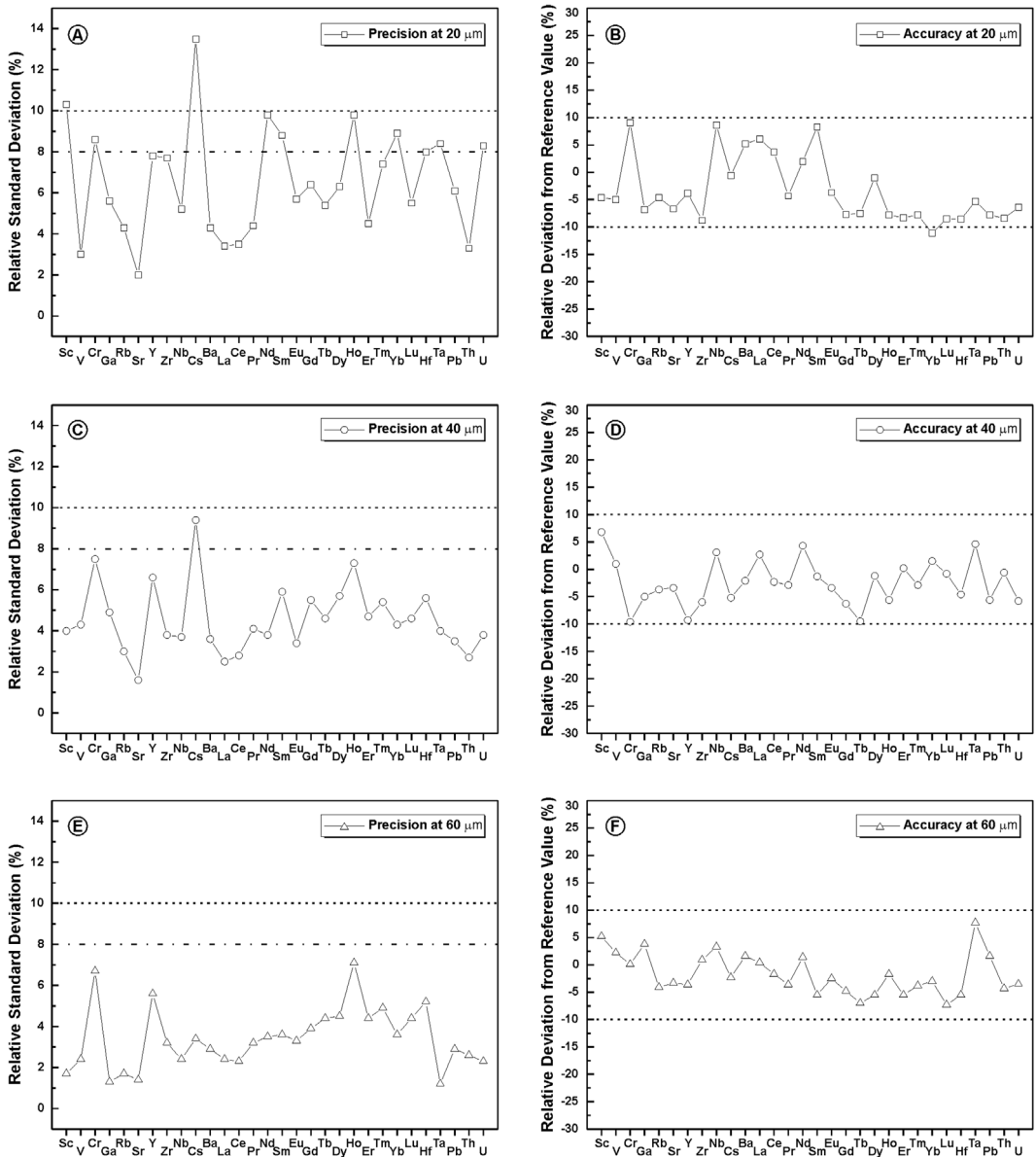


Fig. 2 – Precision and accuracy expressed as Relative Standard Deviation (RSD) and deviation from the reference values respectively for spatially-resolved analysis. (A) Precision with 20 μm laser beam diameter; (B) accuracy with 20 μm laser beam diameter; (C) precision with 40 μm laser beam diameter; (D) accuracy with 40 μm laser beam diameter; (E) precision at 60 μm laser beam diameter; (F) accuracy with 60 μm laser beam diameter.

Two different sample to flux ratios are used in lithium borate fusion experiments achieved using commercial automated fusion machines. In particular, 1:7 (e.g. Tamponi *et al.*, 2003) and 1:5 (e.g. Eggins., 2003) sample to flux ratios are employed with the Claisse and the Autofluxer instruments, respectively.

A laser beam of 80 μm is utilized for all the analysis and three replicates are performed in each unknown sample. The software *Plasmalab* (Thermo Electron, Waltham, USA) that controls the ICP-MS allows developing automated analytical protocols in the ACL scripting language. It also allows to control the laser ablation device and therefore automated LA-ICP-MS analytical protocols can be readily developed. The automated analytical experiment consists in discrete runs of 21 analyses, comprising 12 determinations on unknown samples (three spots for each sample) plus 1 quality control standard analyzed as unknown sample, bracketed before and after by 4 analyses of the external standard (NIST SRM 612). As a consequence, four samples are analyzed during each experiment. Up to five experiments can be loaded in sequence and therefore 20 samples can be analyzed for each analytical session.

Determination of several elements results problematic in flux-free fusion experiments. In particular Pb systematically shows lower values than expected due to volatilization and loss of this element during the fusion. Acidic samples give frequently heterogeneous glasses (RSD ~20%) probably due to the high viscosity of felsic melts that inhibited efficient mixing. In addition, high degree of inhomogeneity is often encountered for Zr and Hf in felsic rocks suggesting a not complete melting of the zircon phase. A typical analysis performed on granite (CRPG GSN) is reported in Table 4. Precision is worse than 10% for most elements resulting in scarcely reproducible analyses. In addition, accuracy is not satisfactory (within 10%) for several elements. For example, obtained values for Y, Zr, REE, Hf, Pb and Th are systematically lower than expected values suggesting a loss of these elements (e.g. Pb) or an incomplete melting of Y, Zr, REE, Hf, and Th rich phases (e.g. zircon and monazite) during the fusion.

TABLE 4 – Typical LA-ICP-MS analyses of a felsic rock (CRPG GSN, granite) prepared as flux-free graphite electrode fusion

Element	CRPG GSN (n=3)			
	This study ($\mu\text{g/g}$)	1 σ ($\mu\text{g/g}$)	RSD (%)	REF.
V	69	8	11	65
Ga	22.2	0.7	3	22
Rb	181	8	4	185
Sr	524	27	5	570
Y	14	2	13	16
Zr	93	25	27	235
Nb	30	5	18	21
Ba	1344	78	6	1400
La	66	7	10	75
Ce	131	13	10	135
Pr	12	1	11	14.5
Nd	44	5	12	49
Sm	6.4	0.9	14	7.5
Eu	1.4	0.1	7	1.7
Gd	4.6	0.6	12	5.2
Tb	0.50	0.06	11	0.6
Dy	2.7	0.3	11	3.1
Ho	0.49	0.06	12	0.6
Er	1.3	0.2	14	1.5
Tm	0.18	0.02	10	0.2
Yb	1.3	0.1	11	1.4
Lu	0.18	0.02	12	0.2
Hf	2.6	0.7	28	6.2
Ta	2.9	0.5	18	2.6
Pb	41	7	17	53
Th	30	4	14	41
U	6.4	0.6	9	7.5

TABLE 5 – *Limits of detection (LOD) for samples prepared as lithium borate fusion*

Element	Limits of Detection ($\mu\text{g/g}$)		
	Graphite electrode fusion	Automated fusion machine (Univ. Perugia)	Automated fusion machine (Univ. Pisa)
sample/flux	1/3	1/5	1/7
V	-	0.3	0.6
Ga	0.07	0.1	0.3
Rb	0.1	0.2	0.4
Sr	0.02	0.03	0.07
Y	0.01	0.03	0.06
Zr	0.04	0.07	0.2
Nb	0.009	0.01	0.03
Ba	0.07	0.1	0.2
La	0.006	0.008	0.02
Ce	0.003	0.005	0.01
Pr	-	0.005	0.01
Nd	0.01	0.02	0.05
Sm	0.01	0.02	0.05
Eu	0.006	0.008	0.02
Gd	0.03	0.04	0.09
Tb	0.003	0.004	0.01
Dy	0.007	0.01	0.03
Ho	0.002	0.004	0.007
Er	0.005	0.01	0.02
Tm	0.002	0.005	0.01
Yb	0.01	0.02	0.05
Lu	0.002	0.005	0.01
Hf	0.007	0.02	0.03
Ta	0.002	0.005	0.01
Pb	0.01	0.01	0.02
Th	0.0008	0.003	0.006
U	0.0007	0.003	0.006

Figures of merit (limits of detection, precision, and accuracy) related to the lithium borate fusion experiments are estimated on several international reference materials and reported in Table 5, 6, 7 and 8. The average LODs, reported in Table 5, range from c.a. 0.006 $\mu\text{g/g}$ to 0.6 $\mu\text{g/g}$ (1:7 sample to flux ratio), from c.a. 0.003 $\mu\text{g/g}$ to 0.3 $\mu\text{g/g}$ (1:5 sample to flux ratio) for the samples prepared by using the automated fusion machines and from c.a. 0.0007 $\mu\text{g/g}$ to 0.1 $\mu\text{g/g}$ (1:3 sample to flux ratio) for the samples prepared by graphite electrode fusion. The discrepancies in terms of LODs obtained for the three distinct fusion experiments and the fact that LODs for the bulk configuration are of the same order of magnitude of those in 40-60 μm spatially resolved applications are not surprising and are strictly related to the used sample to flux ratios (1:7, 1:5, and 1:3). Obtained LODs are fully suitable for the analysis of the selected suite of elements in the concentrations commonly encountered in silicate samples. If lower detection limits are required, larger spots and/or higher laser repetition rates could be used since LODs are cubic function of the laser spot diameter and a linear function of the laser repetition rate. However, the use of large laser beams (c.a. 150-200 μm) coupled with elevated repetition rates (e.g. 20 Hz) should be avoided since it could result in an excessive amount of material reaching the ICP-MS and possibly destabilizing the ICP-torch (Jeffries *et al.*, 2003).

Precision values, given at one RSD (%), are reported in Table 6-7-8 and also displayed in Figs 3a, 4a and 5a. Independently on the adopted fusion method, RSDs are always better than 10% for elements in concentration above 2 $\mu\text{g/g}$ with the only exception of Pb (~15%). For elements in concentration below 2 $\mu\text{g/g}$ the RSD rise to about 15%. In detail, RSDs are 14%, 13%, 11% for Tm (0.3 $\mu\text{g/g}$), Yb (1.7 $\mu\text{g/g}$) and Lu (0.2 $\mu\text{g/g}$) in the GSP2 bead obtained by graphite electrode fusion (Fig. 3a) with a 1:3 sample to flux ratio. RSDs are 12% for Tm (0.4 $\mu\text{g/g}$) and 14% for Lu (0.4 $\mu\text{g/g}$) in the RGM1 sample fused with the Autofluxer machine using a 1:5 sample to flux ratio (Fig. 4a) and are 14% for Tm (0.3 $\mu\text{g/g}$) in the GSP2 and 16 % for Lu (0.2 $\mu\text{g/g}$) in the GSN

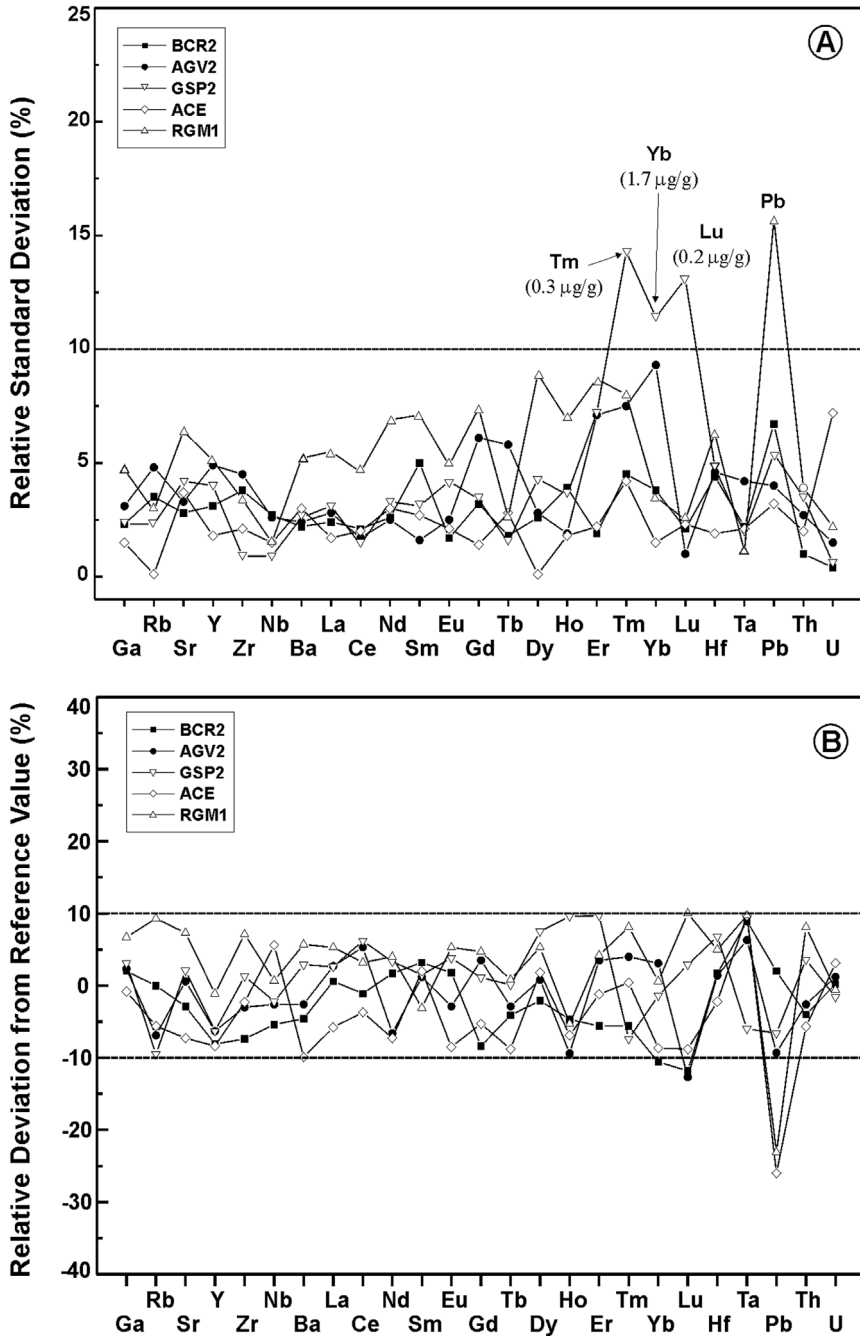


Fig. 3 – Precision and accuracy expressed as Relative Standard Deviation (RSD) and deviation from the reference values respectively for whole rock analysis on lithium borate fusion beads prepared with the graphite electrode device using a 1:3 sample to flux ratio: (A) precision; (B) accuracy.

TABLE 6 – LA-ICP-MS analyses of reference materials prepared as lithium borate glasses with the graphite electrode device (1:3 sample to flux ratio)

Element	USGS BCR2 -basalt (n=3)				USGS AGV2 -andesite (n=3)				USGS GSP2 - granodiorite (n=3)			
	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.
Ga	22	1	2	22	20	1	3	20	24	1	2	23
Rb	48	2	3	48	63.8	3.1	5	68.6	222	5	2	245
Sr	336	9	3	346	666	22	3	662	245	10	4	240
Y	34	1	3	37	18.8	0.9	5	20	26	1	4	28
Zr	174	7	4	188	223	10	5	230	557	5	1	550
Nb	12.4	0.3	3	13.1	14.6	0.4	3	15	26.4	0.2	1	27
Ba	651	14	2	683	1111	27	2	1140	1348	35	3	1310
La	25.2	0.6	2	25	39	1	3	38	185	6	3	180
Ce	52	1	2	53	72	1	2	68	435	6	1	410
Nd	28.5	0.7	3	28.0	30.8	0.8	2	33	203	7	3	196
Sm	6.9	0.3	5	6.7	5.97	0.09	2	5.9	27.4	0.9	3	27
Eu	2.04	0.03	2	2.0	1.55	0.04	2	1.6	2.4	0.1	4	2.3
Gd	6.2	0.2	3	6.8	4.9	0.3	6	4.7	12.2	0.4	3	12.1
Tb	1.03	0.02	2	1.07	0.62	0.04	6	0.6	1.30	0.02	1	1.3
Dy	6.25	0.16	3	6.38	3.63	0.10	3	3.6	5.9	0.3	4	5.5
Ho	1.27	0.05	4	1.33	0.64	0.01	2	0.7	1.04	0.04	4	1.0
Er	3.5	0.1	2	3.66	1.85	0.13	7	1.8	2.4	0.2	7	2.2
Tm	0.51	0.02	4	0.54	0.27	0.02	7	0.3	0.27	0.04	14	0.3
Yb	3.13	0.06	2	3.5	1.75	0.02	1	1.7	1.7	0.2	13	1.7
Lu	0.45	0.02	4	0.51	0.22	0.02	9	0.3	0.24	0.03	11	0.2
Hf	4.9	0.2	4	4.8	5.2	0.2	5	5.1	15.0	0.7	5	14.0
Ta	0.86	0.02	2	0.79	0.95	0.04	4	0.9	0.91	0.02	2	1.0
Pb	11.2	0.8	7	11	11.8	0.5	4	13.0	39	2	5	42
Th	6.0	0.06	1	6.2	6.3	0.2	3	6.5	110	4	4	106
U	1.69	0.01	1	1.69	1.90	0.03	1	1.9	2.46	0.02	1	2.5

beads obtained with the Claisse fusion machine using a 1:7 sample to flux ratio (Fig. 5a).

Average values for accuracy, given as relative deviation from reference values, are displayed in Figs 3b, 4b and 5b. Obtained results are in good agreement with the reference values within 12% for the graphite electrode fusion products

(Fig. 3b) and within 10% for beads produced by the automated fusion machines (Fig. 4b and Fig. 5b) with the only exception of Pb.

The obtained values of precision and accuracy are fully suitable for quantitative routine analysis in many geological applications. On this regard, it is important to stress that LA-ICP-MS samples

TABLE 6 – continued...

CPNR ACE - granite (n=3)				USGS RGM1 - rhyolite (n=3)			
This study ($\mu\text{g/g}$)	1σ ($\mu\text{g/g}$)	RSD (%)	REF.	This study ($\mu\text{g/g}$)	1σ ($\mu\text{g/g}$)	RSD (%)	REF.
38.7	0.6	1	39	16.0	0.8	5	15
143	1	1	152	164	5	3	150
2.8	0.1	4	3	116	7	6	108
169	3	2	184	25	1	5	25
762	16	2	780	235	8	3	219
116	2	1	110	9.0	0.1	1	8.9
50	1	3	55	853	44	5	807
55.6	0.9	2	59	25	1	5	24
148	3	2	154	49	2	5	47
85	3	3	92	20	1	7	19.0
24.7	0.7	3	24	4.2	0.3	7	4.3
1.83	0.04	2	2	0.69	0.03	5	0.7
24.6	0.3	1	26.0	3.9	0.3	7	3.7
4.4	0.1	3	4.8	0.67	0.02	3	0.7
30	1	3	29.0	4.3	0.4	9	4.1
6.1	0.1	2	6.5	0.90	0.06	7	1.0
17.5	0.4	2	17.7	2.71	0.24	9	2.6
3	0.1	4	2.6	0.40	0.03	8	0.4
16	0.4	2	17.4	2.62	0.07	3	2.6
2.2	0.03	1	2.5	0.44	0.02	3	0.4
27.3	0.5	2	27.9	6.5	0.4	6	6.2
7.0	0.1	2	6.4	1.04	0.01	1	1.0
29	0.9	3	39	18	3	16	24
17.4	0.3	2	19	16.3	0.6	4	15
4.7	0.3	7	4.6	5.8	0.1	2	5.8

prepared as lithium borate glasses could provide a solution to the problem of achieving complete sample digestion encountered with the chemical treatment required by solution nebulisation ICP-MS analysis.

Regarding the observed inaccuracy related to Pb analysis, as already reported by Eggins

(2003), obtaining accurate determination of this element has been proved to be problematic in LA-ICP-MS analysis of lithium borate glasses. Eggins (2003) explained this occurrence as a Pb contamination related to Pb sequestration into and subsequent release from Pt crucibles in which samples were prepared.

TABLE 7 – LA-ICP-MS analyses of reference materials prepared as lithium borate glasses with the Autofluxer fusion machine (1:5 sample to flux ratio)

Element	USGS BCR2 - basalt (n=3)				CRPG AGV2 - andesite (n=3)				CRPG RGM1 - rhyolite (n=3)			
	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.
V	436	4	1	416	123	3	2	121	12	1	8	13
Ga	20.8	0.5	3	22	19.9	0.2	1	20	15.5	0.9	6	15
Rb	46.0	0.5	1	48	67.0	0.1	1	68.6	160	13	8	150
Sr	377	6	1	346	690	2	1	662	101	1	1	108
Y	40	1	3	37	20.8	0.2	1	20	23	2	8	25
Zr	200	4	2	188	245	3	1	230	220	5	2	219
Nb	14.0	0.3	2	13.1	16.3	0.2	1	15	9.4	0.6	7	8.9
Ba	711	9	1	683	1136	14	1	1140	731	6	1	810
La	27.0	0.5	2	25	41.1	0.6	1	38	22	2	7	24
Ce	53.8	0.4	1	53	68.7	0.9	1	68	43.0	0.5	1	47
Pr	7.2	0.3	4	6.8	7.9	0.1	2	8.3	4.59	0.09	2	4.7
Nd	30	1	4	28	33.5	0.5	2	33	18	2	10	19
Sm	7.1	0.3	4	6.7	5.76	0.07	1	5.9	3.90	0.07	2	4.3
Eu	2.16	0.05	2	2	1.73	0.09	5	1.6	0.61	0.05	8	0.7
Gd	7.2	0.5	7	6.8	4.9	0.4	9	4.7	4.0	0.3	8	3.7
Tb	1.08	0.04	4	1.07	0.63	0.05	7	0.6	0.64	0.05	8	0.7
Dy	6.9	0.2	3	6.38	3.9	0.2	6	3.6	3.8	0.4	10	4.1
Ho	1.40	0.07	4	1.33	0.69	0.06	9	0.7	0.86	0.07	8	1
Er	3.9	0.4	9	3.66	1.8	0.2	9	1.7	2.40	0.08	4	2.6
Tm	0.585	0.007	1	0.54	0.24	0.02	7	0.3	0.37	0.05	12	0.4
Yb	3.8	0.1	3	3.5	1.9	0.2	9	1.8	2.5	0.2	9	2.6
Lu	0.56	0.03	4	0.51	0.29	0.03	9	0.3	0.44	0.06	14	0.4
Hf	5.2	0.2	4	4.8	5.6	0.1	2	5.1	6.18	0.04	1	6.2
Ta	0.80	0.08	9	0.78	0.99	0.06	6	0.9	1.0	0.1	10	1
Pb	9.4	0.7	7	11	12	1	9	13	24	4	14	24
Th	6.8	0.3	4	6.2	6.7	0.4	5	6.5	14	1	7	15
U	1.59	0.02	1	1.69	1.9	0.1	6	1.9	6.2	0.2	3	5.8

TABLE 8 – LA-ICP-MS analyses of reference materials prepared as lithium borate glasses with the Claisse fusion machine (1:7 sample to flux ratio)

Element	USGS BCR2 - basalt (n=3)				CRPG BR - basalt (n=3)				CRPG GSP2 - granodiorite (n=3)				USGS GA - granite (n=3)				CRPG GSN - granite (n=3)			
	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.	This study (µg/g)	1σ (µg/g)	RSD (%)	REF.
V	393	8	2	416	248	3	1	235	53	3	5	53	41	2	4	38	62	3	5	65
Ga	23.5	0.7	3	22	17.2	0.5	3	19	23	1	5	23	17.0	0.6	4	16	23.3	0.8	3	22
Rb	51	1	3	48	44.1	0.9	2	47	250	9	4	245	182	3	1	175	200	8	4	185
Sr	346	11	3	346	1363	29	2	1320	230	8	3	240	282	6	2	310	588	18	3	570
Y	34	1	4	37	28.0	0.7	3	30	26.6	0.9	3	26	19.9	0.5	3	21	16.7	0.8	5	16
Zr	177	7	4	188	246	7	3	260	562	14	2	550	146	5	3	150	234	10	4	235
Nb	11.9	0.3	2	13.1	105	2	2	98	24.9	0.9	4	27.0	11.6	0.3	2	12	23.0	0.4	2	21
Ba	681	19	3	683	1046	19	2	1050	1262	36	3	1310	784	17	2	840	1444	42	3	1400
La	24.5	0.9	4	25	78	1	2	82	178	5	3	180	38	1	3	40	72	3	4	75.0
Ce	54	2	3	53	154	2	1	151	417	14	3	410	72	1	2	76	138	3	2	135
Pr	6.6	0.2	4	6.8	16.2	0.2	1	17	50	2	4	52	7.7	0.3	4	8.3	13.7	0.5	4	14.5
Nd	28.4	0.9	3	28	63	1	2	65	191	7	4	196	26.7	0.7	3	27	47	2	5	49
Sm	6.6	0.4	6	6.7	11.3	0.4	4	12.2	25.1	0.9	4	27.0	5.1	0.3	6	5	7.4	0.4	6	7.5
Eu	2.1	0.1	5	2.0	3.69	0.05	1	3.7	2.12	0.09	4	2.3	1.10	0.08	7	1.1	1.57	0.09	5	1.7
Gd	6.7	0.2	2	6.8	9.2	0.3	3	9.5	11.7	0.6	5	12.1	4.0	0.2	4	3.8	4.7	0.3	7	5.2
Tb	1.04	0.05	5	1.07	1.20	0.04	3	1.3	1.21	0.03	2	1.3	0.64	0.05	7	0.6	0.65	0.06	10	0.6
Dy	6.4	0.2	4	6.38	5.86	0.02	0	6.4	5.7	0.2	4	5.5	3.2	0.1	5	3.3	3.4	0.3	9	3.1
Ho	1.30	0.08	6	1.33	1.02	0.03	3	1.1	0.95	0.05	5	1	0.63	0.04	7	0.7	0.62	0.01	2	0.6
Er	3.5	0.2	6	3.66	2.3	0.1	5	2.5	2.40	0.07	3	2.2	2.08	0.07	4	1.9	1.49	0.08	6	1.5
Tm	0.50	0.02	4	0.54	0.33	0.02	7	0.3	0.33	0.05	14	0.3	0.28	0.02	7	0.3	0.24	0.02	10	0.2
Yb	3.4	0.3	9	3.5	1.67	0.05	3	1.8	1.7	0.1	7	1.7	1.8	0.2	10	2	1.26	0.09	7	1.4
Lu	0.50	0.04	7	0.51	0.24	0.02	9	0.3	0.22	0.02	8	0.2	0.27	0.03	10	0.3	0.20	0.03	16	0.2
Hf	4.7	0.3	6	4.8	5.0	0.2	4	5.6	14.5	0.7	5	14.0	3.9	0.2	5	4	6.5	0.4	6	6.2
Ta	0.71	0.04	5	0.8	5.60	0.09	2	6.2	0.96	0.03	3	1	1.20	0.05	4	1.3	2.4	0.1	5	2.6
Pb	10.6	0.4	4	11	5.4	0.3	5	5	33	2	5	42	22.7	0.3	1	30	44	2	4	53
Th	6.0	0.2	4	6.2	10.1	0.3	3	11	103	3	3	106	16.1	0.7	4	17	41	2	5	41
U	1.82	0.04	2	1.7	2.6	0.1	5	2.5	2.36	0.03	1	2.5	4.6	0.1	3	5	8.0	0.4	4	7.5

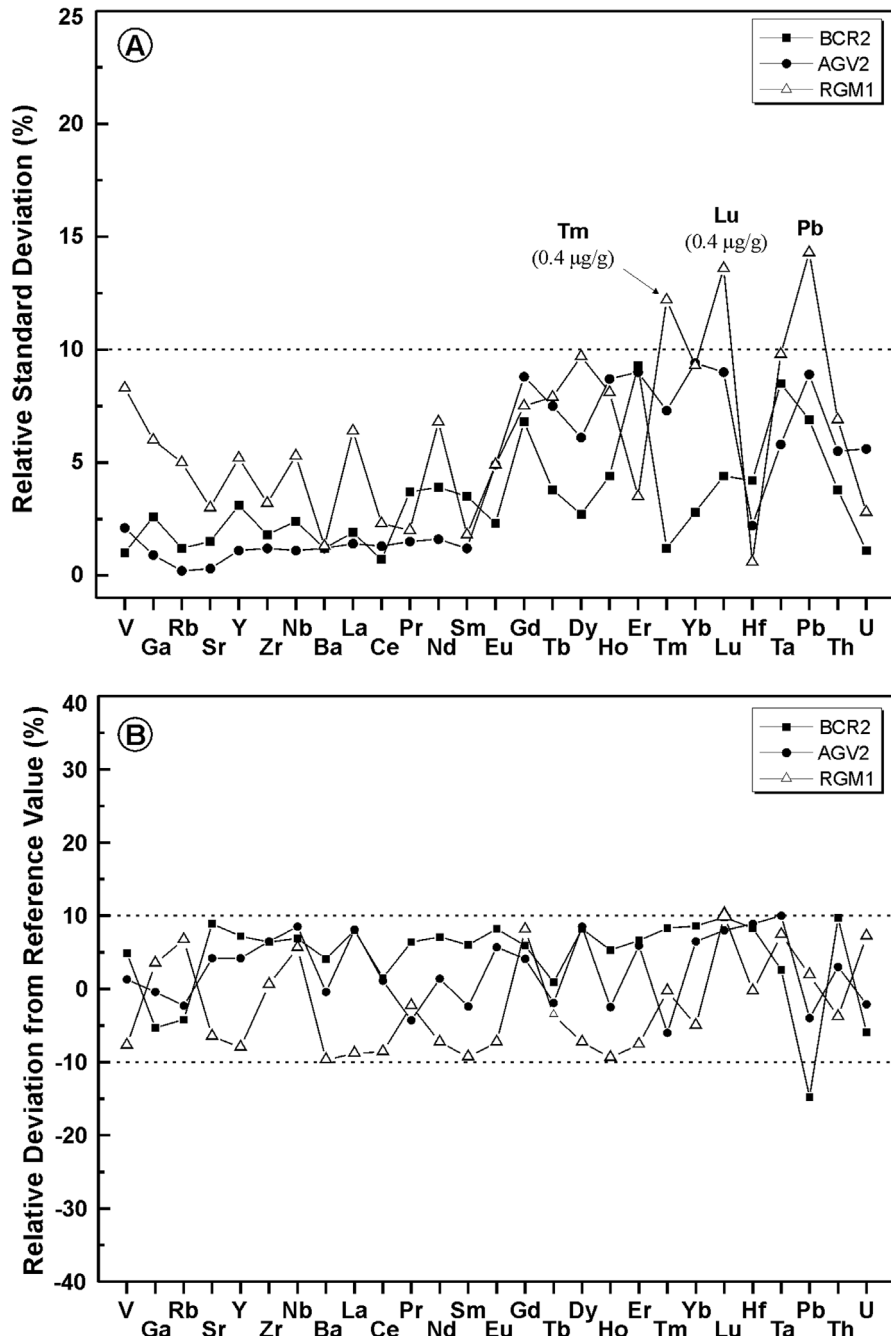


Fig. 4 – Precision and accuracy expressed as Relative Standard Deviation (RSD) and deviation from the reference values respectively for whole rock analysis on lithium borate fusion beads prepared with the Autofluxer fusion machine (University of Perugia) using a 1:5 sample to flux ratio: (A) precision; (B) accuracy.

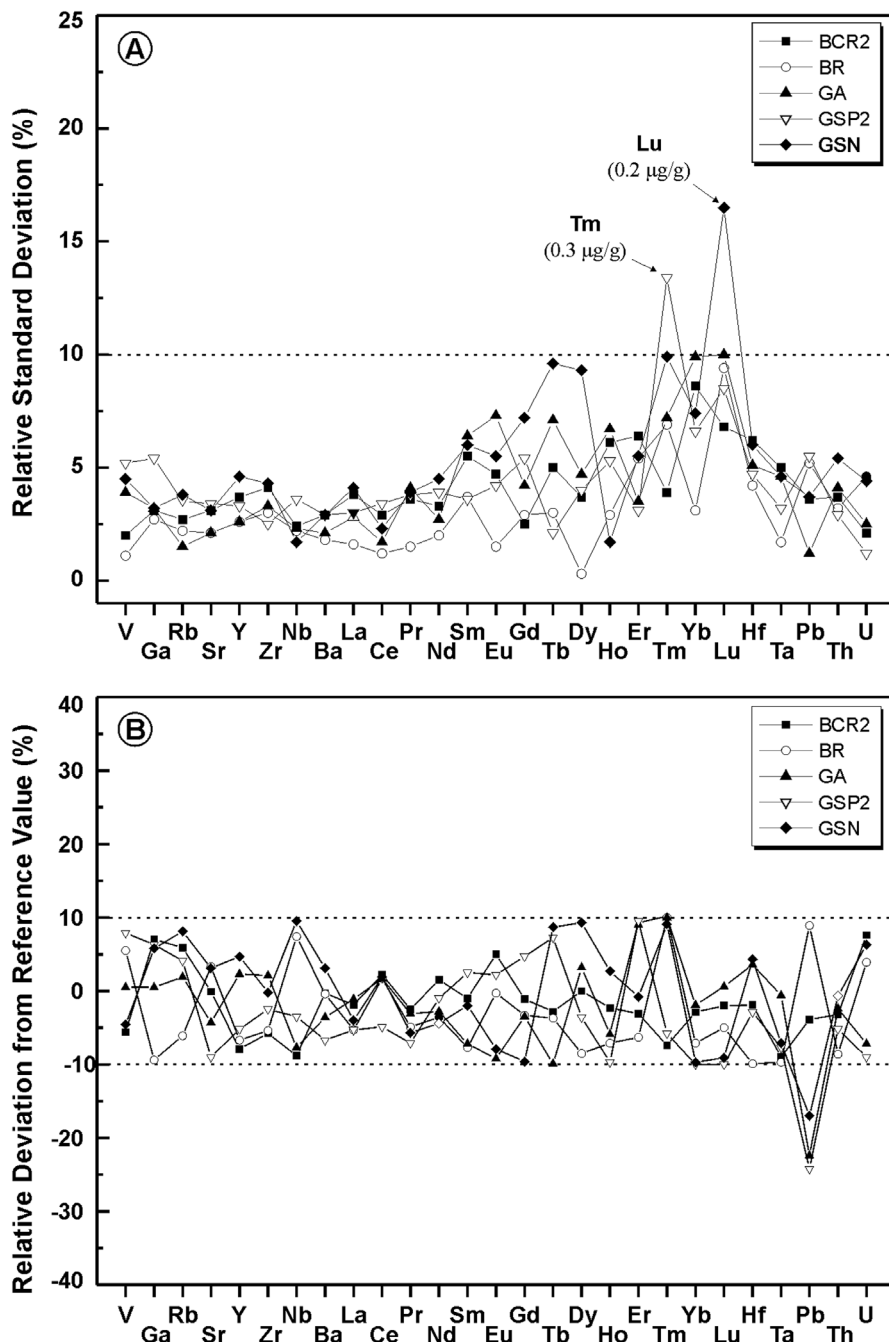


Fig. 5 – Precision and accuracy expressed as Relative Standard Deviation (RSD) and deviation from the reference values respectively for whole rock analysis on lithium borate fusion beads prepared with Claissé fusion machine (University of Pisa) using a 1:7 sample to flux ratio: (A) precision; (B) accuracy.

CONCLUDING REMARKS

The Thermo Electron X7 quadrupole mass spectrometer coupled with commercial New Wave UP213 laser ablation system allows high quality quantitative trace element determinations coupling good precision and accuracy for both spatially-resolved and bulk applications. The use of laser beams ranging from less than 20 μm to about 80 μm have been successfully tested demonstrating the extreme versatility of the instrument. Results shows that, operating in spatially resolved trace-element configuration, precision is better than 10% whereas accuracy are better than 11%. Precision and accuracy increase as increasing the beam diameter. The field of possible application of spatially resolved trace elements determinations is extremely large and include analysis of minerals, glasses, melt inclusions, ceramics, metals and environmental samples. Operating in bulk configuration, the complete whole rock-trace elements characterization is achievable obtaining high-quality data.

In addition, the limited time required for each trace element determination allows to analyze a large number of samples during each analytical session.

ACKNOWLEDGMENTS

We thank P. Armenti e M. Tamponi (University of Pisa) for having provided some of the fusion beads analyzed in this work. Constructive comments of A. Zanetti and D. Barca are gratefully acknowledged. This work was funded by MIUR (Ministero dell'Istruzione, dell'Università e della Ricerca), INGV (Istituto Nazionale di Geofisica e Vulcanologia), and University of Perugia grants.

REFERENCES

- BECKER J. S. and DIETZE H. J. (1999) - *Determination of trace elements in geological samples by laser ablation inductively coupled plasma mass spectrometry*. *Fres. J. Anal. Chem.*, **365**, 429-434.
- DURRANT S. F. (1999) - *Laser ablation inductively coupled plasma-mass spectrometry: Achievements, problems, prospects*. *J. Anal. Atom. Spectrom.*, **14**, 1385-1403.
- CHEN Z., CANIL D. and LONGERICH H. P. (2000) - *Automated in situ trace element analysis of silicate materials by laser ablation inductively coupled plasma mass spectrometry*. *Fres. J. Anal. Chem.*, **368**, 73-78.
- EGGING S. M. (2003) - *Laser ablation ICP-MS analysis of geological materials prepared as lithium borate glasses*. *Geost. Newsl.*, **27**, 147-162.
- EGGING S. M., KINSLEY L. P. J. and SHELLEY J. M. G. (1998) - *Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS*. *Appl. Surf. Sci.*, **127-129**, 278-286.
- FEDOROWICH J. S., RICHARDS J. P., JAIN J. C., KERRICH R. and FAN J. (1993) - *A rapid method for REE and trace-element analysis using laser sampling ICP-MS on direct fusion whole-rock glasses*. *Chem. Geol.*, **106**, 229-249.
- FRYER B. J., JACKSON S. E. and LONGERICH H. P. (1995) - *The design, operation and role of the Laser-Ablation Microprobe coupled with an Inductively Coupled Plasma - Mass Spectrometer (LAM-ICP-MS) in the Earth Sciences*. *Canad. Mineral.*, **33**, 303-312.
- GAO S., XIAOMIN L., YUAN H., HATTENDORF B., GÜNTHER D., CHEN L. and HU S. (2002) - *Determination of forty two major and trace elements in USGS and NIST SRM glasses by laser ablation-inductively coupled plasma-mass spectrometry*. *Geost. Newsl.*, **26**, 181-196.
- GOVINDARAJU K. (1994) - *1994 compilation of working values and sample description for 383 geostandards*. *Geost. Newsl.* **18**, 1-158.
- GRAY A. L. (1985) - *Solid Sample introduction by laser ablation for inductively coupled plasma source mass spectrometry*. *Analyst*, **110**, 551-556.
- GÜNTHER D., FRISCHKNECHT R., HEINRICH C. A. and KAHLERT H. J. (1997) - *Capabilities of a 193 nm ArF excimer laser for LA-ICP-MS micro analysis of geological materials*. *J. Anal. Atom. Spectrom.*, **12**, 939-944.
- GÜNTHER D., JACKSON S. E. and LONGERICH H. P. (1999) - *Laser ablation and ark/spark solid sample introduction into inductively coupled plasma mass spectrometers*. *Spectrochim. Acta*, **54B**, 381-409.
- GÜNTHER D., QUADT A. W., WIRZ R., COUSIN H. and DIETRICH V. J. (2001) - *Elemental analyses using laser ablation-inductively coupled mass spectrometry (LA-ICP-MS) of geological samples fused with Li₂B₄O₇ and calibrated without matrix-matched standards*. *Microchim. Acta*, **136**, 101-107.
- HORN I., RUDNICK R. L. and McDONOUGH W. F. (2000) - *Precise elemental and isotope ratio determination by simultaneous solution nebulization and laser ablation ICP-MS: Application to U-Pb geochronology*. *Chem. Geol.*, **167**, 405-425.
- IMAI N. (1990) - *Quantitative analysis of original and powdered rocks and mineral inclusions by laser ablation inductively coupled plasma mass spectrometry*. *An. Chim. Acta*, **235**, 381-392.
- JEFFRIES T. E., JACKSON S. E. and LONGERICH H. P. (1998) - *Application of a frequency quintupled Nd:YAG source*

- ($\lambda=213$ nm) for laser ablation inductively coupled plasma mass spectrometric analysis of minerals. *J. Anal. Atom. Spectrom.*, **13**, 935-940.
- JEFFRIES T. E., FERNANDEZ-SUAREZ J., CORFU F. and GUTIERREZ ALONSO G. (2003) - *Advances in U-Pb geochronology using a frequency quintupled Nd:YAG based laser ablation system ($\lambda = 213$ nm) and quadrupole based ICP-MS*. *J. Anal. Atom. Spectrom.*, **18**, 847-855.
- KUROSAWA M., SHIMA K., ISHII S. and KIMIKAZU S. (2006) - *Trace element analysis of fused whole-rock glasses by laser ablation-ICP-MS and PIXE*. *Geost. Geoanal. Res.*, **30**, 17-30.
- LONGERICH H. P., JACKSON S. E. and GÜNTHER D. (1996) - *Laser ablation-inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation*. *J. Anal. Atom. Spectrom.*, **11**, 899-904.
- MOTELICA-HEINO M. and DONARD O. F. X. (2001) - *Comparison of UV and IR laser ablation ICP-MS on silicate reference materials and implementation of normalisation factors for quantitative measurements*. *Geost. Newsl.* **25**, 345-359.
- NORMAN M. D., PEARSON N. J., SHARMA A. and GRIFFIN W. L. (1996) - *Quantitative analysis of trace elements in geological materials by laser ablation ICP-MS: Instrumental operating conditions and calibration values of NIST glasses*. *Geost. Newsl.*, **20**, 247-261.
- NORMAN M. D., GRIFFIN W. L., PEARSON N. J., GARCIA M. O. and O'REILLY S. Y. (1998) - *Quantitative analysis of trace elements abundances in glasses and minerals: a comparison of laser ablation inductively coupled plasma mass spectrometry, solution inductively coupled plasma mass spectrometry, proton microprobe and electron microprobe data*. *J. Anal. Atom. Spectrom.*, **13**, 477-482.
- ØDEGÅRD M. (1999) - *Preparation of synthetic calibration materials for use in the microanalysis of oxide minerals by direct fusion in high-purity graphite electrodes: Preliminary results for quartz and rutile*. *Geost. Newsl.*, **23**, 173-186.
- ØDEGÅRD M., DUNDAS S. H., FLEM B. and GRIMSTVEDT A. (1998) - *Application of a double-focussing magnetic sector inductively coupled plasma mass spectrometer with laser ablation for the bulk analysis of rare earth elements in rocks fused with Li₂B₄O₇*. *Fres. J. Anal. Chem.*, **362**, 477-482.
- PETRELLI M., CARICCHI L. and ULMER P. (2007A) - *Application of High Spatial Resolution Laser Ablation ICP-MS to Crystal-Melt Trace Element Partition Coefficient Determination*. *Geost. Geoanal. Res.*, **31**, 13-25.
- PETRELLI M., PERUGINI D., POLI G. and PECCERILLO A. (2007B) - *Graphite electrode tetraborate fusion for automated trace element determination in bulk samples by laser ablation ICP-MS*. *Microchim. Acta.*, **158**, 275-282.
- PETTKE T., HALTER, W. E., WEBSTER J. D., AIGNER-TORRES M. and HEINRICH C. A., (2004) *Accurate quantification of melt inclusion chemistry by LA-ICPMS: A comparison with EMP and SIMS and advantages and possible limitations of these methods*. *Lithos*, **78**, 333-361.
- RUSK B. G., REED M. H., DILLES J. H., KLEMM L. M. and HEINRICH C. H. (2004) - *Composition of magmatic hydrothermal fluids determined by LA-ICP-MS of fluid inclusions from the porphyry copper-molybdenum deposit at Butte, MT*. *Chem. Geol.*, **210**, 173-199.
- SYLVESTER P. (2001) - *Laser ablation ICP-MS in Earth sciences: Principles and applications*. Mineral. Ass. Canada Short Course Series, **29**, 243 pp.
- TELOUK P., ROSE-KOGA E. F. and ALBAREDE F. (2003) - *Preliminary results from a new 157 nm laser ablation ICP-MS instrument: New opportunities in the analysis of solid samples*. *Geost. Newsl.*, **27**, 5-11.
- TAMPONI M., BERTOLI M., INNOCENTI F. and LEONI L. (2003) - *X-ray fluorescence analysis of major elements in silicate rocks using fused glass discs*. *Atti Soc. Tosc. Sci. Nat., Mem.*, **108**, 73-79.
- TIEPOLO M. (2003) - *In situ Pb geochronology of zircon with laser ablation-inductively coupled plasma-sector field mass spectrometry*. *Chem. Geol.*, **199**, 159-177.
- TIEPOLO M., BOTTAZZI P., PALENZONA M. and VANNUCCI R. (2003) - *A laser probe couplet with ICP-double focusing sector-field mass spectrometer for in situ analysis of geological samples and U-Pb dating of zircon*. *Canadian Mineral.*, **41**, 259-272.
- USGS (2006) - *Geochemical Reference Materials and Certificates*. http://minerals.cr.usgs.gov/geo_chem_stand/
- VAN ACHTERBERGH E., RYAN C. G., JACKSON S. and GRIFFIN W. L. (2001) - *Data reduction software for LA-ICP-MS*. In: Sylvester, P. (Ed.), *Laser-Ablation-ICPMS in the Earth Sciences, Principles and Applications*. Mineral. Ass. Canada Short Course Series, **29**, 239-243 pp.

