Vol. 27 – N°1 03 03 p.5-11

GEOSTANDARDS NEWSLETTER
The Journal of Geostandards and Geoanalysis

Preliminary Results from a New 157 nm Laser Ablation ICP-MS Instrument: New Opportunities in the Analysis of Solid Samples

Philippe **Telouk***, Estelle F. **Rose-Koga** and Francis **Albarede**

Ecole Normale Supérieure de Lyon (ENS-Lyon), Laboratoire de Sciences de la Terre, 46 Allée d'Italie, 69364 Lyon Cedex 07
* Corresponding author, e-mail: telouk@ens-lyon.fr

Preliminary results are given from an excimer 157 nm laser ablation multiple-collector inductively coupled plasma-mass spectrometer (LA-MC-ICP-MS), used for the isotopic measurements of solid materials. Elements of geological interest with different volatilities such as Pb and U (e.g. zircon geochronology) and Cu and Zn (as examples of geochemical/biochemical tracers) were analysed. The range of ablation rates of 20-150 nm s^{-1} enabled us to ablate the sample down to a depth of 45 μm for a 50 μm diameter pit. The Cu and Zn isotopic measurements gave values that were very stable with, on average, a 0.01% standard error, comparable with that achieved in liquid mode measurements.

Keywords: laser ablation, ICP-MS, 157 nm, excimer, elemental fractionation, NIST SRM 610, 612.

Des résultats préliminaires d'analyses isotopiques sur des matériaux solides ont été obtenus en utilisant un système d'ablation laser de type Excimer 157 nm couplé à un spectromètre de masse avec source à plasma induit (LA-MC-ICP-MS). Des éléments d'intérêt géologique ayant des volatilités très différentes, tels que Pb, U (applications en géochronologie sur zircon) Cu et Zn (représentatifs de traceurs bio-géochimiques) ont été analysés. La vitesse d'ablation, de l'ordre de 20 à 150 nm s^{-1} nous a permis de travailler sur des cratères d'une profondeur de 45 μm et 50 μm de diamètre. Les mesures de rapports isotopiques de Cu et Zn donnent des valeurs très stables, avec une erreur standard moyenne de 0.01%, ce qui est comparable avec ce qui est obtenu en analysant des solutions.

Mots-clés : ablation laser, ICP-MS, 157nm, excimer, fractionnement élémentaire, NIST SRM 610, 612.

For the past twenty years, laser ablation inductively coupled plasma-mass spectrometry has been widely used for a considerable variety of solid sample analyses. Fields of application range from the semiconductor industry to geochemistry to specific industrial applications (Gray 1985). One of the most important problems reported by many authors, has been the differential removal of chemical species from a single sample during laser ablation (Feng *et al.* 1993). Different laser wavelengths can be used, from 1064 nm (infrared) to 157 nm (vacuum UV). After several experiments with the entire range of different laser frequencies (Jefferies *et al.* 1998, Günther *et al.* 1998, Chen 1999, Bruguier *et al.* 2001) several conclusions can be drawn. (1) It is clear that the shorter the wavelength, the more reproducible the ablation rate and the lower is the required fluence to initiate ablation (Russo *et al.* 2000). (2) The shorter the wavelength, the lower the particle size distribution and, as a consequence, the higher the plasma ionisation efficiency.

Over the last two years, two new lasers have become available, a 157 nm excimer laser (F_2 laser) and a femtosecond laser. The only work using the 157 nm laser to date (Russo *et al.* 2000) was a test of a 157 nm laser, modified from a 193 nm laser. The results were quite ambiguous due to a poor 157 nm beam profile from the laser and very low power. Nevertheless, the authors reported smaller elemental fractionation when compared with the 213 and 266 nm lasers. Only scarce data are available for the femtosecond laser and an ablation rate below a few hundreds of nm/pulse is hard to obtain (Margetic pers. comm.). This drawback can be a problem in geological studies when analysing minerals in a thin section (on average 30-50 μm thick).

Received 05 Dec 02 — Accepted 27 Jan 03

This present work reports experiments using a low wavelength laser. We have developed an in-house constructed 157 nm laser which is based on a native 157 nm laser from Lambda-Physiks with a sharp beam profile and a high-energy beam. A few preliminary results from micromachining were reported at this wavelength (Lambda Physiks 1999). In this study we have connected the laser to two different types of ICP-MS, (1) a standard quadrupole PQ2 machine and (2) a Plasma 54 multicollector ICP-MS. We demonstrate that no elemental fractionation can be detected and that this new LA-ICP-MS laser is potentially a powerful tool for geological applications, for example in age dating (experiments on U, Pb) or stable isotope measurements (experiments on Cu, Zn).

Experimental

The laser used in this study was a Lambda Physiks, LPF 202. It can be used at 157 nm and 193 nm by changing mirrors and the gas filling the laser cavity. The maximum power of the laser was 50 mJ at 157 nm (compared to 400 mJ at 193 nm) with a pulse width of 9-10 ns. This was an excimer instrument that used a F_2/He mixed gas in the laser cavity to operate at 157 nm. Because of strong absorption at this wavelength by oxygen, care was taken to confine the beam path from the output of the laser to the sample in a box purged by argon or nitrogen. We used an argon flow of 10 l min^{-1} for the laser purge and 1 l min^{-1} in the ablation cell. The configuration of the laser was defined to obtain two values for the demagnification, of 6 and 20. The first configuration, just at the limit of the ablation fluence threshold, was used for very low ablation rates (configuration 1) and the second (configuration 2) was used for higher rates of ablation. The lowest ablation rate, in configuration 1, was about 20 nm s^{-1} at 10 Hz. In the standard configuration for ICP-MS analysis (configuration 2) the ablation rate was a factor of ten higher, at 150 nm s^{-1} for a 10 Hz laser frequency. The pit size could be varied from 30 μm to 500 μm and the entire system was controlled by a computer. The beam was focused onto the sample with a CaF_2 plano-convex lens. A CaF_2 window on the ablation cell minimised energy loss. Both NIST SRM 612 and 610 glass reference materials were tested for elemental fractionation in the two configurations to evaluate which was best suited for different applications. Two ICP-MS were used for the experiments, the first one was a standard quadrupole instrument (VG Plasmaquad 2+) and the second was a VG Plasma 54 multi-collector instrument.

Results and discussion

The ablation

The first test required for laser ablation is the ability to make a clean round flat-bottom pit. Laser setting and tuning in both configurations are summarized in Table 1. The scanning electron microscope image (Figure 1) clearly shows a clean ablation of the glass reference material NIST SRM 612. No fusion is visible around the 50 or 100 μm diameter crater, unlike that which has been reported in another study based upon ablation at the 193 nm wavelength (Horn *et al.* 2000). The flat bottom of the pit is a sign of a well-focused homogeneous beam and high ablation efficiency. When defocusing the beam on NIST SRM 610, the pit lost its flatness and cracks were observed on the walls, as shown in close-up (Figure 2). Nevertheless, the walls of the pit still showed no trace of fusion. At

Table 1.
Laser parameters

Lambda Physiks LPF 202	
Wavelength	157 nm
Power	40 mJ
Repetition rate	10 Hz
Ablation mode	Single spot
Pulse width	9 ns
Ablation cell	Round Teflon cell with an internal volume of 5 cm^3, CaF_2 window
Focusing	Plano-convex lens with 40 mm focal length
Argon flow rate in ablation cell	1 l min^{-1}

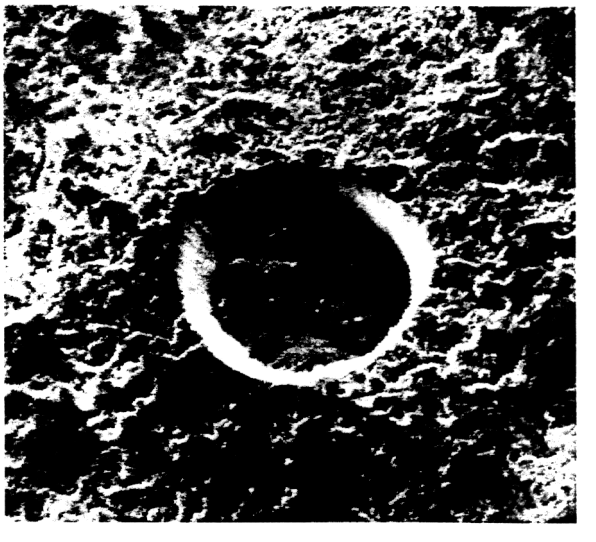

Figure 1. SEM photograph showing laser impact crater on NIST SRM 612 glass reference material. The crater shown had a diameter of 100 μm.

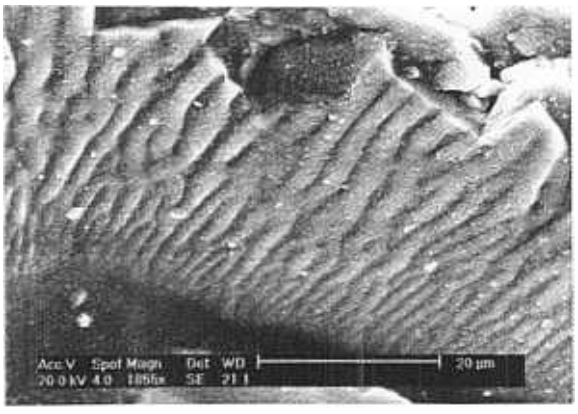

Figure 2. SEM photograph showing cracks on NIST SRM 610 glass reference material.

157 nm, the laser behaved like a photonic hammer and removed material from the solid sample leading to a real ablation of the sample without fusion. This is a crucial test before any analysis, because any physical process (such as material being melted) that occurs during ablation could lead to additional elemental fractionation (Hirata and Nesbitt 1995) and may require large corrections to the analytical results.

With the laser tuned at 10 Hz and 30 mJ, the average ablation rate on glass material was 150 nm s^{-1}, which corresponds to a depth of ablation of 45 µm, for a 50 µm diameter pit. This represents an aspect ratio of ~ 1, which is ideal for depth profiling analysis (Mank and Mason 1999). After 30 minutes, the pit reached a depth of 270 µm with an unchanged diameter (aspect ratio of 5.5). This very slow beam penetration in the sample prevented laser defocusing.

Another important parameter to investigate in laser ablation processes is the size of the ablated particles. We have determined the particle size distribution, on two different samples, NIST SRM 610 and a pyroxene. An ideal size distribution would be a single narrow distribution with as small a mean particle size as possible. Otherwise, any mechanism that differentially transports larger particles (such as clustered smaller particles, for example) compared with smaller particles to the ICP-MS may cause elemental fractionation (e.g., Longerich *et al.* 1996, Mank and Mason 1999). The inherent risk of having particles that are too large is the extent to which they affect the efficiency of the plasma to destroy them. The particle size distributions were measured at the Malvern Parc-Club annex in Lyon, France with a Zetasizer 3000 Hsa with a 633 nm He-Ne laser tube. On this instrument the detector was an avalanche photo diode (APD) at a fixed 90° angle. The deconvolution of the signal was achieved with the cumulative method for a glass sample having a narrow size distribution range and with the Contin method for the pyroxene sample with a wider size distribution range (e.g. Malvern Instruments 1996) in accordance with the ISO 13321 analytical quality requirements. In both cases, the particle size distribution displayed only one group of particles. The NIST SRM 610 glass produced particles with an average diameter of 162.4 nm and, under the same conditions, the pyroxene produced particles of average size 355.9 nm. The particle size distribution was log-normal with a size variation of ± 100 nm around the average value. The mean particle size was at least 10 to 50 times smaller than that previously described in the literature using a laser with a higher wavelength (Sparks *et al.* 1993). Particles were collected in a vial filled with deionised water over several days during several laser ablation sessions. The uni-modal results obtained from these samples demonstrate, therefore, the stability in time of the laser for given frequency and energy conditions and the reproducibility of the ablation process between sessions. Considering that some pits were made by leaving the beam in the same pit for between 15 to 30 minutes, defocusing of the beam does not seem to interfere with the narrow particle size distribution.

Elemental fractionation

The laser was coupled to a VG PQ2+ ICP-MS to compare the ablation efficiency between the two NIST reference materials (SRM 610 and 612) and corresponding elemental fractionation. These reference materials comprise two soda-lime glass matrices spiked with sixty one trace elements at nominal concentrations of 500 and 50 µg g^{-1}, respectively. The ICP-MS operating parameters are described in Table 2.

For lead and uranium analysis, the average measured values for the Pb/U ratio for the two reference materials are in the same range, that is 1.31 (8% RSD) for NIST SRM 612 and 1.27 (5% RSD) for NIST SRM 610 (Figure 3). These values are not the accepted average value (NIST 1970), due to a non-flat transmission curve of the PQ2+, but the ablation efficiency is the same for the two reference materials. No certified value exists for the absorption of the NIST reference materials at 157 nm, but it can be inferred from these results that the absorption coefficients for both glasses

Table 2.
ICP-MS parameters summary

ICP-MS type	VG Plasmaquad 2+, 1989	VG Plasma 54
	- Time resolving acquisition, 3pts/peak - Peak jumping for Hg, Pb, Th and U	Static
Acquisition time	10 to 20 min	- 1 or 2 for each point - Background measurement at half mass
Dwell time	10 ms	
Sensitivity	25 Mcps for In at 1 mg l^{-1} (solution), Background ~ 50 cps	2.5 Gcps for Hf at 1 mg l^{-1}
High voltage for the interface	-	6000 V
Pumps	Diffusion	Turbo
Multi-collection setting	no	- Standard focal plane Faradays for ^{202}Hg, $^{204, 206, 207, 208}Pb$, $^{203, 205}Tl$ (all isotopes on Faraday) for Pb/U measurement and $^{63, 65}Cu$, $^{64, 66, 67, 68}Zn$ for the brass nut sample - Off-axis Faraday for uranium measurement (^{238}U)
Plasma parameters	Standard configuration	Standard configuration

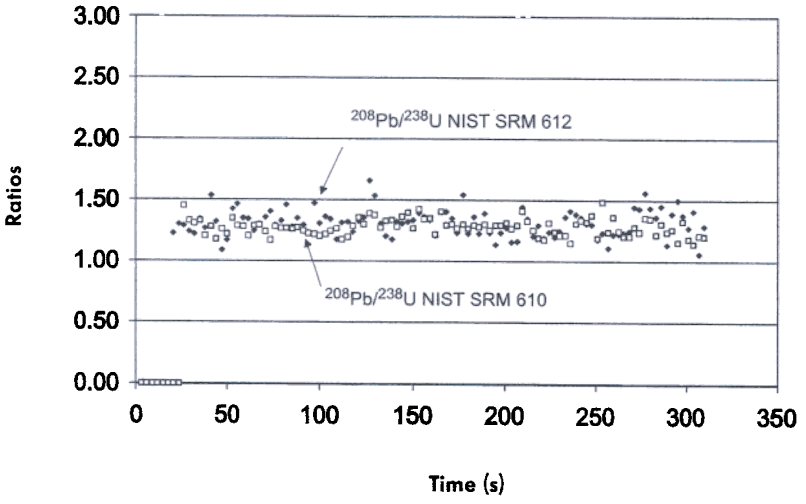

Figure 3. $^{208}Pb/^{238}U$ ratios measured with the 157 nm laser and VG PQ2+ ICP-MS. Ratios for NIST SRM 610 were corrected to the same Pb/U ratio as NIST SRM 612.

are similar. Therefore, at this wavelength, a strong absorption can be assumed for a wide range of samples, and variation between different types of sample is distinguishable during laser ablation operation. After 300 seconds ablation at 10 Hz, the Pb/U ratio remained constant, demonstrating that the elemental fractionation was less than ~ 3% during ablation and that stable ratios could be measured both precisely and quite rapidly (Figure 3). This observation indicates the stable coupling of this laser with this type of sample and the remarkable efficiency of this technique for elemental composition measurement. However, after 30 minutes, the intensity measured on the PQ2+ started to decrease and the noise increased without, however, changing the average value of the Pb/U ratio (within RSD).

Examples of geological applications

The laser was coupled to a multi-collector instrument (Plasma 54) for isotope ratio measurement which is, in our laboratory, the motivation for using the laser ablation ICP-MS technique. This time, we focused on the analysis of NIST SRM 610 to assess the overall performance of the complete system (LA-ICP-MS) for zircon age dating applications in comparison with other configurations (Feng *et al.* 1993, Hirata and Nesbitt 1995, Horn *et al.* 2000). The Plasma 54 ICP-MS

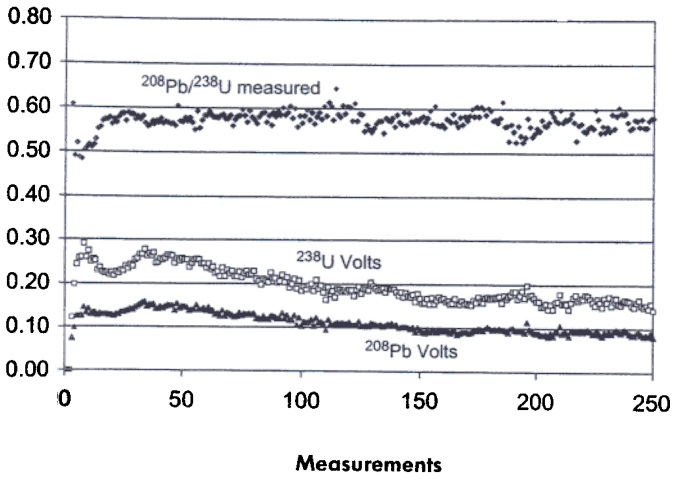

Figure 4. Plasma 54 ICP-MS measurements on NIST SRM 610 for a 100 μm crater at 10 Hz. Each symbol represents 2 seconds. The total acquisition time was 8 minutes.

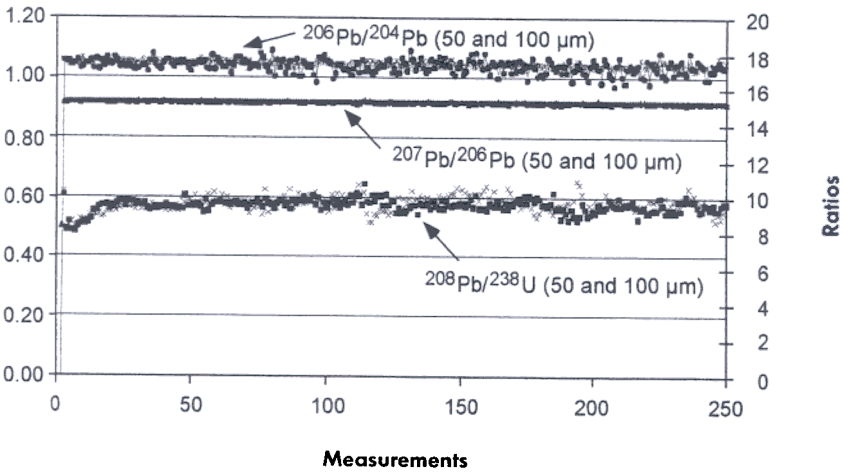

Figure 5. NIST SRM 610 measurements for 50 and 100 μm craters with the Plasma 54 ICP-MS. Each symbol represents 2 seconds. The total acquisition time was 8 minutes.

was then configured to measure simultaneously Hg, Pb, Tl and U. Mercury was used for interference correction on m/e 204 and Tl for mass bias correction. The off-axis Faraday collector was used to measure the uranium peaks. The low dispersion capability of the Plasma 54 did not allow U and Hg to be measured simultaneously on the focal plane Faraday detectors. The isotopic measurements were undertaken over 8 minutes at 10 Hz for crater diameter sizes of 50 and 100 μm (Figures 4 and 5). The loss of signal intensity by a factor of two is due to beam defocusing with increasing depth; however, after the first 20 seconds, the Pb/U ratio stabilized and remained constant for the rest of the acquisition (Figure 4). Measurements of $^{208}Pb/^{238}U$ were reproducible within 1% (Figures 4 and 5). The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{238}U$ isotopic ratios remained stable and the corrected values of these ratios agree with the certified NIST values (Figure 5). Table 3 summarizes all the results. For the 50 μm crater, the standard error was two times higher due to the lower intensity (corresponding to less ablated material), but the results for the 50 μm and 100 μm ablations are consistent and there is no evidence of different ablation behaviour between these two craters. The standard error for the Pb/U measured ratios was ten to twenty times higher than that for the same measurements in liquid mode (mixed Tl, Pb, U solution standard). This is taken as evidence of elemental fractionation between uranium and lead during ablation, but it is clear that this fractionation is very stable and is small enough (i.e. below 2-4%) to allow the use of this new LA-ICP-MS instrument for uranium-lead dating with better precision than has previously been reported (Hirata and Nesbitt 1995, Horn *et al.* 2000). With an excimer laser in the present configuration, no inter-element fractionation was observed during the ablation processes and these preliminary results contrast with a previous study (Longerich *et al.* 1996) that was undertaken at a different wavelength.

A brass nut sample was tested for copper and zinc isotope ratios (both elements can be used as geochemical and biochemical tracers). The Plasma 54 was configured to measure simultaneously the two copper

Table 3.
Plasma 54 ICP-MS measurements on NIST SRM 610

Ratios on NIST SRM 610	Average	% RSD	Standard error (%)
$^{207}Pb/^{206}Pb$ mass bias corrected (50 µm spot)	0.9105	0.2212	0.014
$^{207}Pb/^{206}Pb$ mass bias corrected (100 µm spot)	0.9107	0.0839	0.0053
$^{206}Pb/^{204}Pb$ (corr Hg) mass bias corrected (50 µm spot)	16.992	2.1524	0.1363
$^{206}Pb/^{204}Pb$ (corr Hg) mass bias corrected (100 µm spot)	17.099	0.8085	0.052
$^{208}Pb/^{238}U$ Pb mass bias corrected (50 µm spot)	0.7506	4.1386	0.2619
$^{208}Pb/^{238}U$ Pb mass bias corrected (100 µm spot)	0.742	3.0824	0.1951

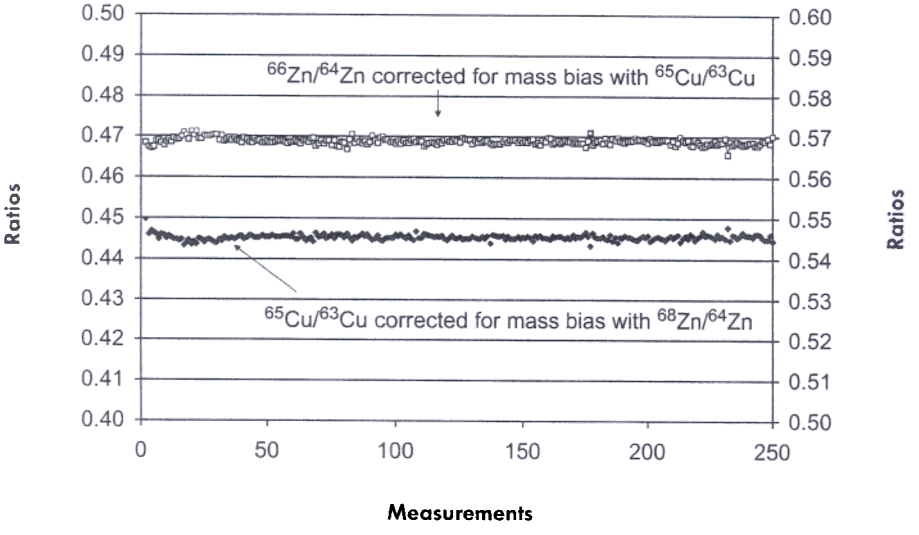

Figure 6. Cu and Zn measurements, made with the Plasma 54 ICP-MS, on a brass nut sample.

Table 4.
Plasma 54 ICP-MS measurements of stable isotopes from a brass nut sample

	Mean	% RSD	Standard error (%)
$^{65}Cu/^{63}Cu$ corrected for mass bias with $^{66}Zn/^{64}Zn$	0.44523	0.11667	0.007
$^{65}Cu/^{63}Cu$ corrected for mass bias with $^{68}Zn/^{64}Zn$	0.44541	0.12765	0.008
$^{65}Cu/^{63}Cu$ corrected for mass bias with $^{68}Zn/^{66}Zn$	0.4456	0.16955	0.011
$^{66}Zn/^{64}Zn$ corrected for mass bias with $^{65}Cu/^{63}Cu$	0.56891	0.11477	0.007
$^{67}Zn/^{64}Zn$ corrected for mass bias with $^{65}Cu/^{63}Cu$	0.08304	0.20123	0.013
$^{68}Zn/^{64}Zn$ corrected for mass bias with $^{65}Cu/^{63}Cu$	0.37922	0.24759	0.016

isotopes and the four zinc isotopes. The $^{63}Cu/^{65}Cu$ ratio was measured and corrected for mass bias with the $^{64}Zn/^{66}Zn$ ratio (Maréchal *et al.* 1999). For Zn, another ratio ($^{68}Zn/^{64}Zn$) was measured and corrected for mass bias with the $^{63}Cu/^{65}Cu$ ratio. Figure 6 shows the ratios obtained over an 8 minute measurement time and Table 4 summarizes the results. The values were very stable with a 0.01% standard error, which is comparable with that which can be achieved in liquid measurements. These results show that there is no detectable isotopic fractionation on a single element during laser ablation at 157 nm, even for low mass elements. It is then possible to use zinc isotope ratios to mass bias correct for copper and *vice versa*. Helium as the carrier gas in the sample chamber is expected to lower the fractionation (Günther and Heinrich 1999) and will be tested. More work is being undertaken to further characterise the performance of this system.

Conclusions

A new laser ablation system operating at 157 nm has been developed. It uses a F_2/He gas mixture and Ar as a carrier gas in its present configuration. The results we have obtained show a very low elemental fractionation (< 3%) in the measurement of isotope ratios of two very different elements, uranium and lead. This leads us to expect the increasing use of such instruments in geology, for example in zircon dating. No detectable single element fractionation was observed during laser ablation, even in the case of lighter elements. This suggests that an excimer laser can be successfully used for the analysis of stable isotopes of elements such as copper, zinc, magnesium or iron. The ablation is very clean and there is no evidence of fusion or redeposition of the ablated material. An optimisation of the system by using helium as a carrier gas and a new ablation cell will be the next steps taken to improve the detection limit.

Acknowledgements

The authors thank Dr B. Beaugiraud at the Ecole Centrale de Lyon, Department of IFOS, for his help with the scanning electron microscope and G. Diraison at Malvern Lyon for the grain size distribution measurements. We acknowledge the Institut National des Sciences de l'Univers and Centre National de la Recherche Scientifique for financial support.

References

Bruguier O., Télouk P., Cocherie A., Fouillac A.M. and Albarède F. (2001)
Evaluation of Pb-Pb and U-Pb laser ablation ICP-MS dating using matrix matched calibration samples with a frequency quadrupled (266 nm) Nd:YAG laser. Geostandards Newsletter: The Journal of Geostandards and Geoanalysis, 25, 361-373.

Chen Z.X. (1999)
Inter-element fractionation and correction in laser ablation-inductively coupled plasma-mass spectrometry. Journal of Analytical Atomic Spectrometry, 14, 1823-1829.

Feng R., Machado N. and Ludden J.N. (1993)
Lead geochronology of zircon by laser probe inductively coupled plasma-mass spectrometry, Geochemica et Cosmochimica Acta, 57, 3479-3486.

Gray A. (1985)
Solid sample introduction by laser ablation for inductively coupled plasma-source mass spectrometry. The Analyst, 110, 551-556.

Günther D. and Heinrich C.A. (1999)
Enhanced sensitivity in LA-ICP-MS using helium-argon mixtures as aerosol carrier. Journal of Analytical Atomic Spectrometry, 14, 1363-1368.

Hirata T. and Nesbitt R.W. (1995)
U-Pb isotope geochronology of zircon: Evaluation of the laser probe-inductively coupled plasma mass spectrometry technique. Geochimica et Cosmochimica Acta, 59, 2491-2500.

Horn I., Rudnick R.L. and McDonough W.F. (2000)
Precise elemental and isotope ratio determination by simultaneous solution nebulization and laser ablation. Chemical Geology, 164, 281-301.

Horn I., Guillong M. and Günther D. (2001)
Wavelength dependant ablation rates for metals and silicates glasses using homogenized laser beam profiles: Implications for LA-ICP-MS. Applied Surface Science, 182, 91-102.

Jefferies T.E., Jackson S.E. and Longerich H.P. (1998)
Application of a frequency quintupled Nd:YAG source (213 nm) for laser ablation ICP-MS analysis of minerals. Journal of Analytical Atomic Spectrometry, 13, 935-940.

Lambda Physiks Highlights (1999)
Material processing using 157 nm radiation. No. 55, 3pp.

Malvern Instruments (1996)
Particle size analysis. Photon correlation spectroscopy. 20pp.

Mank A.J.G. and Mason P.R.D. (1999)
A critical assessment of laser ablation ICP-MS as a tool for depth profiling in glass samples. Journal of Analytical Atomic Spectrometry, 14, 1143-1153.

Maréchal C.N., Télouk P. and Albarède F. (1999)
Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chemical Geology, 156, 251-273.

NBS (1970)
Trace elements in glass SRMs: SRM 610 through 619, inclusive. National Bureau of Standards (Certificate), 4pp.

Russo R.E., Mao X.L., Borisov O.V. and Liu Haichen (2000)
Influence of wavelength on fractionation in laser ablation ICP-MS. Journal of Analytical Atomic Spectrometry, 15, 1115-1020.

Sparks C.M., Holcombe J. and Pinkston T.L. (1993)
Particle size distribution of sample transported from an electrothermal vaporizer to an inductively coupled plasma-mass spectrometer. Spectrochimica Acta, Part B, 48, 1607-1615.