Laser ablation ICP-MS with 157 nm laser, a new way to analyze solid samples.

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ABSTRACT :

An excimer 157nm laser ablation multiple-collector inductively coupled mass spectrometry (LA-MC-ICP-MS) has been used for the isotopic measurements of solid materials. Elements of geological interest with different volatilities such as Pb and U (e.g. zircon dating) and Cu and Zn (e.g. geochemical/biochemical tracers) were analyzed. The range of ablation rates of 20 - 150 nm/s enabled us to burn the sample down to a depth of 45 µm for a 50 µm diameter pit. The Cu and Zn isotopic measurements, the values were very stable with on average 0.01% standard error, which is comparable with what is achieved in liquid mode measurements.

INTRODUCTION :

For the past 20 years, laser ablation ICP-MS has widely been used for a wide variety of solid sample analyses. Fields concerned range from semi-conductor to geochemistry or specific industrial applications (Gray, 1985). One of the most important problems reported by many authors, was the differential removal of chemical species from a single sample during laser ablation (Feng *et al.*, 1993). Different laser wavelength can be used from 1064 nm (Infra Red) to

157 nm (Vacuum UV). After several experiments with the entire range of different laser (Bruguier *et al.*, 2001; Jefferies *et al.*, 1998; Günther *et al*., 1998; Z. X. Chen, 1999) a few conclusions were drawn. (1) It became clear that the shorter the wavelength, the more reproducible the ablation rate and the lower the fluence in order to initiate the ablation (Russo, 2000). (2) The shorter the wavelength, the lower the particles size distribution and then the higher the plasma ionization efficiency.

Over the last two years, two new lasers have been used, a 157 nm excimer laser (F_2 laser) and a femtosecond laser. The only work using 157 nm laser (Russo, 2000) is a test of a modified 193 nm to 157 nm laser. Their results were quite ambiguous due to a poor 157 nm beam profile from the laser and very low power. Nevertheless, the authors only reported smaller elemental fractionation than with the 213 and 266 nm laser. Only scarce data are available for femtosecond laser and ablation rate below a few hundreds of nm/pulse is hard to obtain (Margetic, 2002). This drawback can be a problem in geology studies in the case of mineral analysis in a thin section (on average 30-50 μm thick).

This work reports experiments on a low wavelength laser. We have developed a home made 157 nm laser which is based on a native 157 nm laser from Lambda-Physiks with a very good beam profile and a high-energy beam. 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 age dating (tests on U, Pb) or stable isotope measurements (tests 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 is 50 mJ at 157 nm (compare to 400 mJ at 193 nm) with a pulse width of 9 - 10 ns. This is

an excimer laser which uses 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 must be 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 for the laser purge and 1 l/min in the ablation cell. The configuration of the laser was defined to obtained two values for the demagnification, 6 and 20. The first configuration, just at the limit of the ablation fluence thresholds is used for very low ablation rate (configuration 1) and the second one (configuration 2) is used for higher ablation rate. The lowest ablation rate, in configuration 1, was about 20 nm/s at 10 Hz. In the standard configuration for ICP-MS analysis (configuration 2) the ablation rate is a factor of ten higher, with 150 nm/s for 10 Hz laser frequency. The pit size can vary from 30 µm to 500 µm and the entire system is controlled by a computer. The beam is focused onto the sample with a CaF_2 plano-convexe lens. CaF_2 window on the ablation cell minimize energy loss. Both NIST 612 and 610 glass standards were tested for elemental fractionation in the two configurations to compare which one 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, multicollector 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 configuration are summarized in table 2. The scanning electron microscope picture (picture 1) clearly shows a clean ablation of the glass standard NIST 612. No fusion is visible around the 50 or 100 µm diameter crater unlike what has been reported in other study upon ablation at the 193nm wavelength (Horn *et al*., 2000). The flat bottom of the pit is a sign of a well-focussed homogeneous beam and high ablation efficiency. When defocusing the beam on NIST 610, the pit loses its flatness and cracks are observed on the walls as shown by a zoom on picture 2. Nevertheless the walls of the pit still show no trace of fusion. At 157nm, the laser behaves likes a photonic hammer and removes material from the solid sample leading to a real ablation of the sample but no fusion. This is crucial to test before any analysis because any

physical process (such as material being melted) happening during the ablation could lead to additional elemental fractionation (Hirata and Nesbitt, 1995) and may require heavy corrections on the analytical results.

With the laser tuned at 10Hz and 30mJ, the average ablation rate on glass material was 150 nm/s which corresponds to a depth of ablation of 45 μm, for a 50 μm diameter pit. This represents an aspect ratio of ≈1 ideal for depth profiling analysis for example. After 30 minutes, the pit has reached a depth of 270 μm for an unchanged diameter (aspect ratio of 5.5). This very slow beam penetration in the sample prevents 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 like NIST 610 and a pyroxene. An ideal distribution of particle would be a mono-modal narrow distribution around a mean size as small as possible. Otherwise a mechanism which differentially transports bigger particles (such as clustered smaller particles for example) and smaller particles to the ICP-MS may cause elemental fractionation (e.g. Longerich *et al*., 1996, Mank *et al*, 1999). The inherent risk of having too big particles is 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 633nm He-Ne laser tube. On this instrument the detector is an avalanche photo diode (APD) at a fixed 90º angle. The deconvolution of the signal was achieved with the cumulant method in the case of a glass sample with a narrow range of the size distribution and with the Contin method in the case of a pyroxene sample with a wider range of size distribution (e.g. Malvern Instrument publication) in accordance with the ISO13321 analytical quality requirements. In both cases, the particle distribution was mono-modal. The NIST 610 produced particles on average of 162.4 nm and in the same conditions the pyroxene produced particles on average of 355.9 nm size. The particle size distribution is log-normal. The mean particle size is at least 10 to 50 times smaller than previously described in the literature with laser with higher wavelength (Sparks, 1993). The collection of particles in a vial filled with deionised water were collected over several days during several laser ablation sessions. The mono-modal results demonstrate therefore the stability in time of the laser for a given frequency and energy conditions and the reproducibility of the ablation between sessions. Considering that

some pits were made by leaving the beam in the same pit between 15 to 30 minutes, defocusing of the beam does seem to not interfere with the narrow particle size distribution.

The elemental fractionation:

The laser was coupled to a VG PQ2+ ICP-MS to compare the ablation efficiency between the two NIST standards (610 and 612) and the elemental fractionation. The standards are two soda-lime glass matrix spiked with sixty-one trace elements to nominal concentrations of 500 and 50µg/g, respectively. The ICP-MS operating parameters are described in table 1.

For lead and uranium analysis, the average measured values for the Pb/U ratio for the two standards are in the same range with 1.31 (8 % rsd) for NIST 612 and 1.27 (5% rsd) for NIST 610 (figure 1). 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 standards. No certified value exists for the absorption of NIST standards at 157 nm but it can be inferred with these results that the absorption coefficients for both glasses are similar. Therefore at this wavelength a strong absorption can be assumed for a wide range of samples and little variation between different type of samples are indistinguishable during laser ablation operation. After 300 seconds ablation at 10Hz, the Pb/U ratio is constant, which demonstrates that the elemental fractionation is very limited during ablation and that stable ratios can be measured precisely quite rapidly. It indicates the very good coupling of this laser with this type of sample and, the remarkable efficiency of this technique for the elemental composition measurement. However, after 30 minutes, the intensity measured on the PQ2+ started decreasing and the noise increasing without however changing the average value of the Pb/U ratio (within rsd).

Example of geological applications:

The laser was coupled to a multicollector instrument (Plasma 54) for isotope measurement which is, in our laboratory, the motivation of the laser ablation ICP-MS technique. This time we focussed on the analysis of NIST 610 to assess the overall performances of the complete system (LA-ICP-MS) for zircon age dating applications compare to other configuration (Feng *et al.*,

1993; Hirata and Nesbitt, 1995; Horn *et al*., 2000). The Plasma 54 was then configured to measure at the same time Hg, Pb, Tl and U. Hg was used for interference correction on 204 and Tl for mass bias correction. The off-axis Faraday collector was used to measure the uranium peaks. The low dispersion possibility of the Plasma 54 does not allow the U and Hgto be measure simultaneously at the same time on the focal plane Faraday detectors. The isotopic measurements were done during 8 minutes at 10 Hz for craters diameter size of 50 and 100 µm (figure 2 and 3). The loss of signal intensity by a factor of two is due to beam defocusing with increasing depth but after the first 20 seconds, the Pb/U ratio stabilized and remains constant during the rest of the acquisition (figure 2). Measurements of $^{208}Pb/^{238}U$ are reproducible within 1% (figure 2 and 3). The $^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{238}U$ isotopic ratios remained stable and the corrected values of the ratios agree with the certified NIST values (figure 3). Table 3 summarizes all the results. For the 50µm crater, the standard error was a little higher due to a lower intensity (less ablated material) but the results for the 50µm and 100µm are very consistent and there is no evidence of different ablation behavior between the two craters. The standard error for the Pb/U measured ratios was ten to twenty times higher than for the same measurements in liquid mode (mixed Tl, Pb, U liquid standard). This is the evidence of an 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 permit the use of this new LA-ICP-MS for uranium-lead dating with better precision than before (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 results contrast with previous study (Longerich *et al.*, 1996) at different wavelength.

A brass nut sample was tested for copper and zinc isotope ratios (both elements are geochemical and biochemical tracers). The Plasma 54 was configured to measure simultaneously the two copper isotopes and the four zinc isotopes. The $^{63}Cu/^{65}Cu$ 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 $^{63}Cu/^{65}Cu$. The figure 4 shows the ratios obtained during 8 minutes measurement and the table 4 summarizes the results. The values were very stable with 0.01% standard error which is comparable with what is achieved in liquid mode measurements. These results show that there is no isotopic fractionation on a single element

during laser ablation at 157 nm, even for low mass elements. It is then possible to use zinc to mass bias correct for copper and vice versa. Helium as carrier gas in the sample chamber is expected to lower the fractionation (Gunther, 1999) and will be tried.

CONCLUSIONS :

A completely new laser ablation system at 157 nm was developed. It uses 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 for two very different elements, uranium and lead. This leads us to expect the increasing use of such instrument in geology for example in zircon dating.

There is also no detectable single element fractionation during laser ablation even in the case of a lighter element. This suggests that excimer laser can be successfully used for isotopic analysis of non-radiogenic elemental fractionation analysis like 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 step to improve the detection limit.

Table 1: ICP-MS parameters summary

ICP-MS type	VG Plasmaquad 2+, 1989	VG Plasma 54,
Analysis mode	-Time resolving acquisition, 3pts/peak -Peak jumping for Hg, Pb, Th and U	Static
Acquisition time	10 to 20 min	-1 or 2 sec each points -background measurement at half mass
Dwell time	10 ms	
Sensitivity	25 Mcps for In at 1 mg/l (solution), Background ~ 50 cps	2,5 Gcps for Hf at 1 mg/l
High voltage for the interface		6000 Volts
Pumps	Diffusion	Turbo
Multi-collection setting	no	-Standard focal plane faradays for 202Hg, 204, 206, 207, 208Pb, 203, 205Tl (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 (238U)
Plasma parameters	Standard configuration	Standard configuration

Table 2 : 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 a volume of 5 cm^3 internal volume, CaF_2 window
Focussing : plano-convex lens with 40 mm focal length
Argon flow rate in the ablation cell at 1 l/min

Table 3 : Plasma 54 measurements on NIST 610

Ratios on NIST 610	**Average**	**Rsd (%)**	**%SE**
^{207}Pb / ^{206}Pb mass bias corrected (50 µm spot)	0.9105	0.2212	0.0140
^{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)	0.7420	3.0824	0.1951

Table 4 :

	$^{65}Cu/^{63}Cu$ corrected for mass bias with 66/64Zn	$^{65}Cu/^{63}Cu$ corrected for mass bias with 68/64Zn	$^{65}Cu/^{63}Cu$ corrected for mass bias with 68/66Zn	$^{66}Zn/^{64}Zn$ corrected for mass bias with 65/63Cu	$^{67}Zn/^{64}Zn$ corrected for mass bias with 65/63Cu	$^{68}Zn/^{64}Zn$ corrected for mass bias with 65/63Cu
Mean	0.44523	0.44541	0.44560	0.56891	0.08304	0.37922
RSD %	0.11667	0.12765	0.16955	0.11477	0.20123	0.24759
SE %	0.007	0.008	0.011	0.007	0.013	0.016

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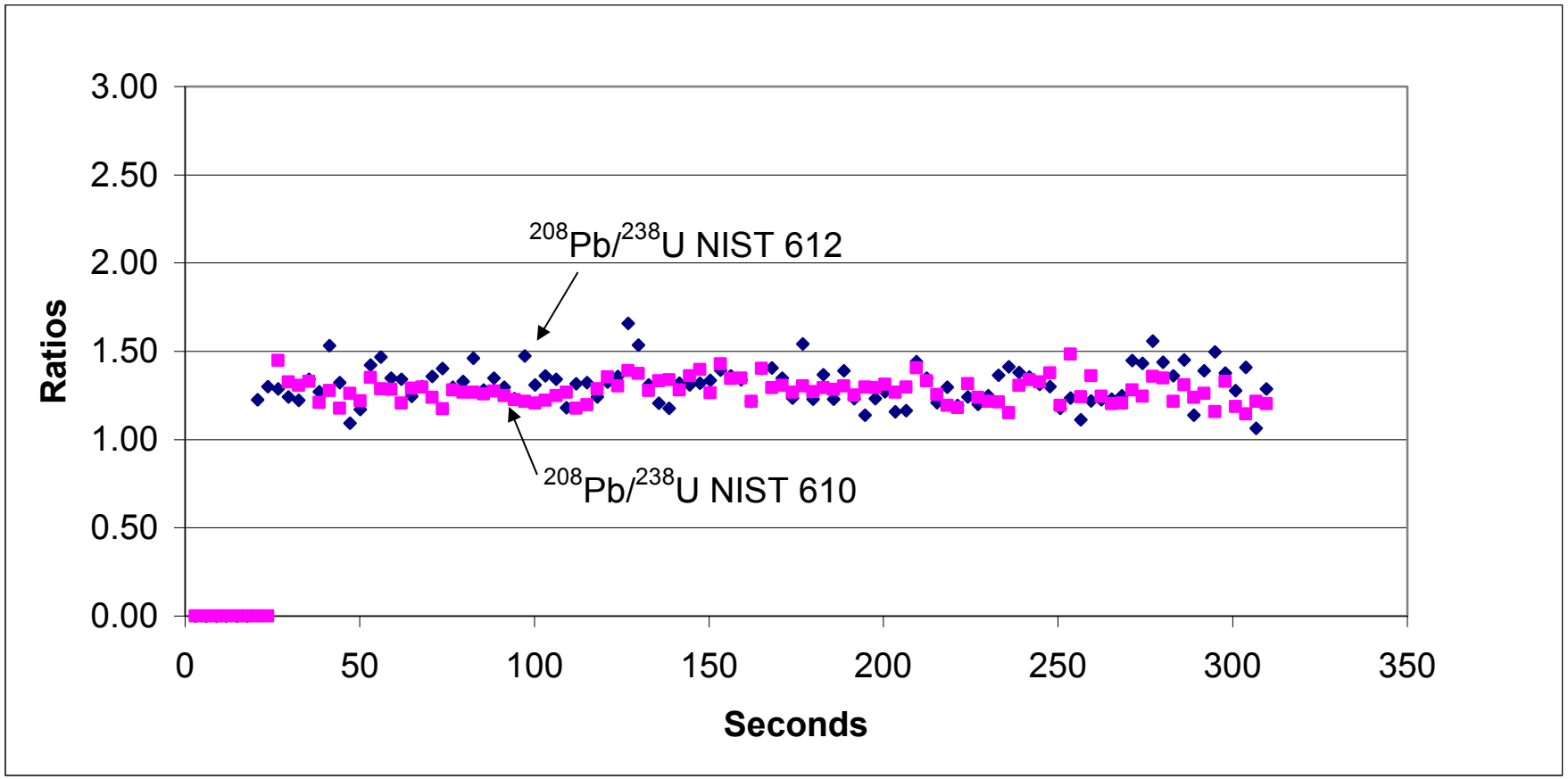


Figure 1 : $^{208}Pb/^{238}U$ ratios measured with 157 nm laser and VG PQ2+ (ratios for NIST 610 were corrected to a same NIST 612 Pb/U ratio)

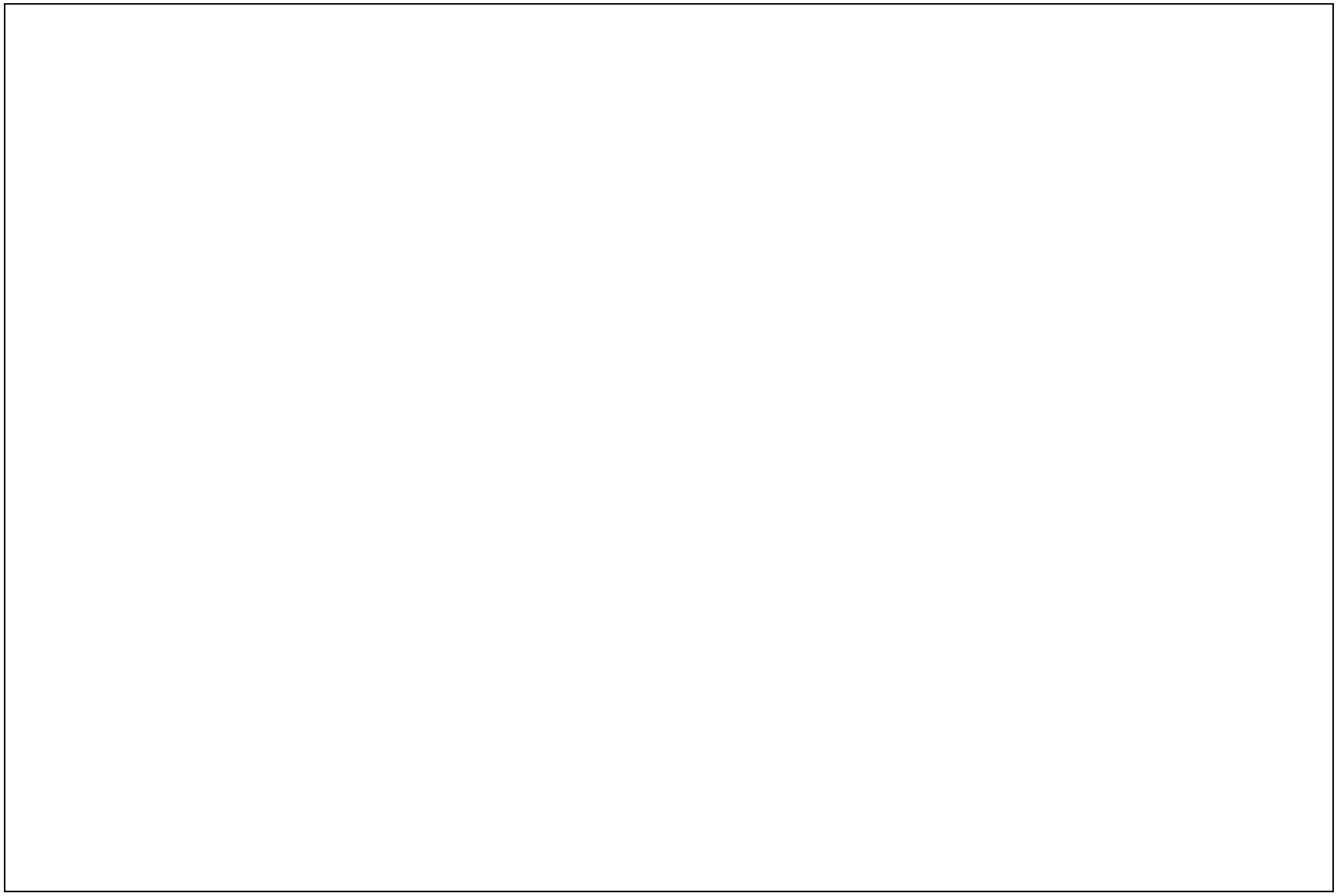


Figure 2 : Plasma 54 measurements on NIST 610 for a 100 µm crater at 10 Hz. Each symbol represents 2 seconds. The total acquisition time is 8 minutes.

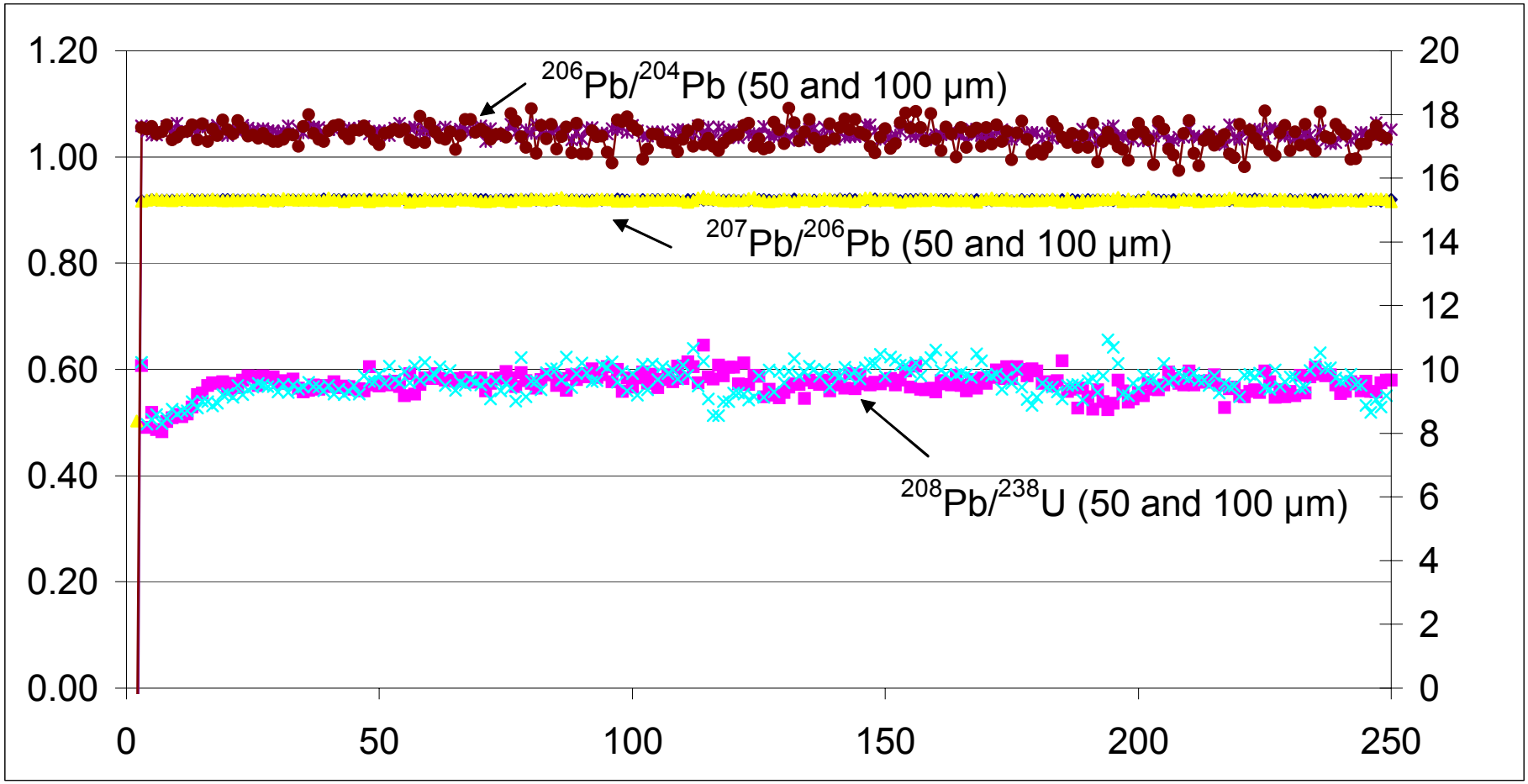


Figure 3 : NIST 610 measurements for 50 and 100 µm crater with the Plasma 54 ICP-MS. Each symbol represents 2 seconds. The total acquisition time is 8 minutes.

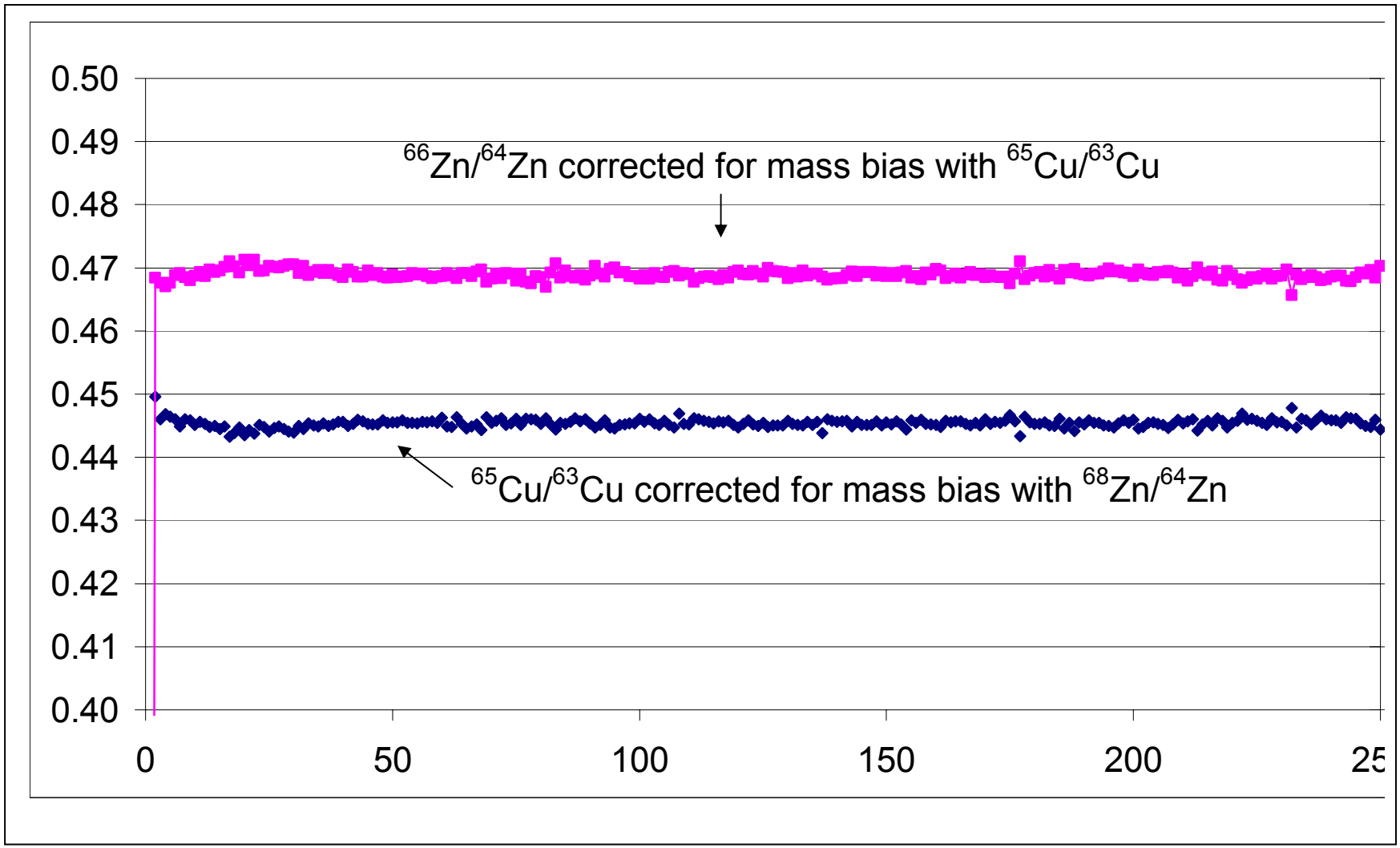
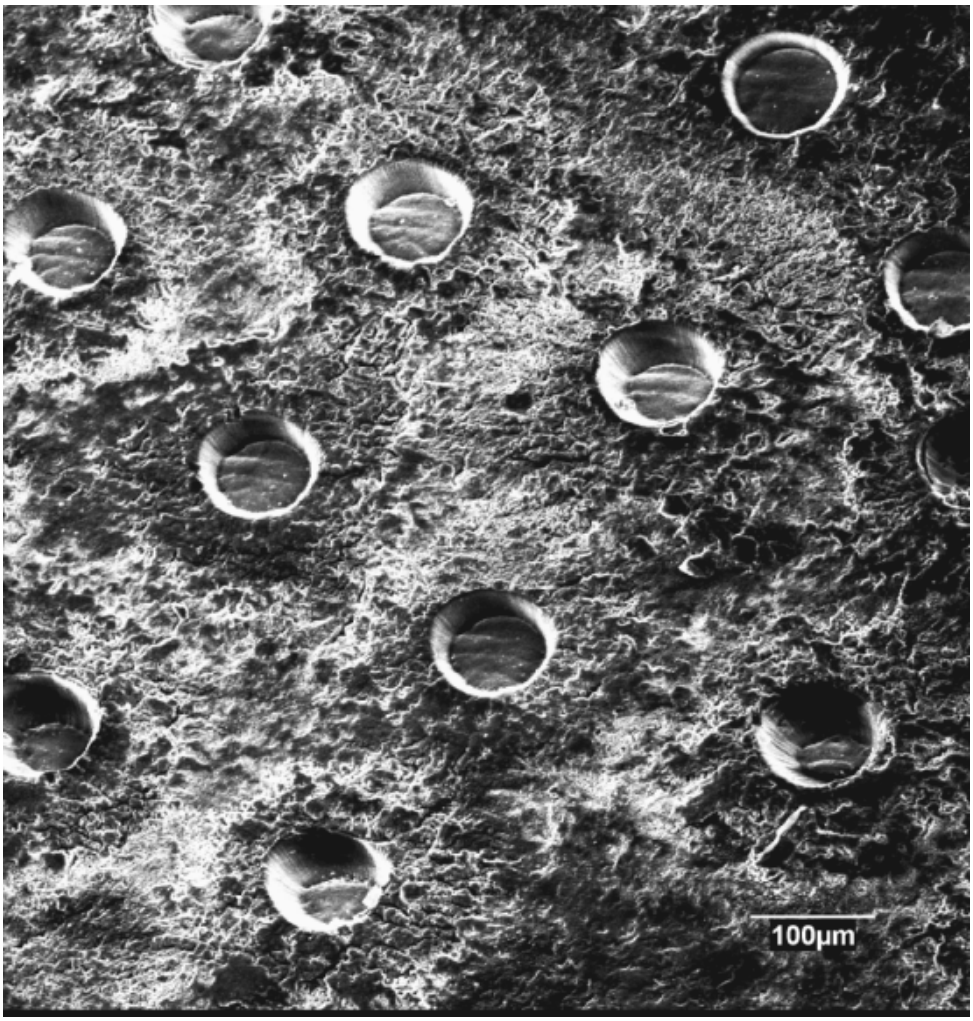
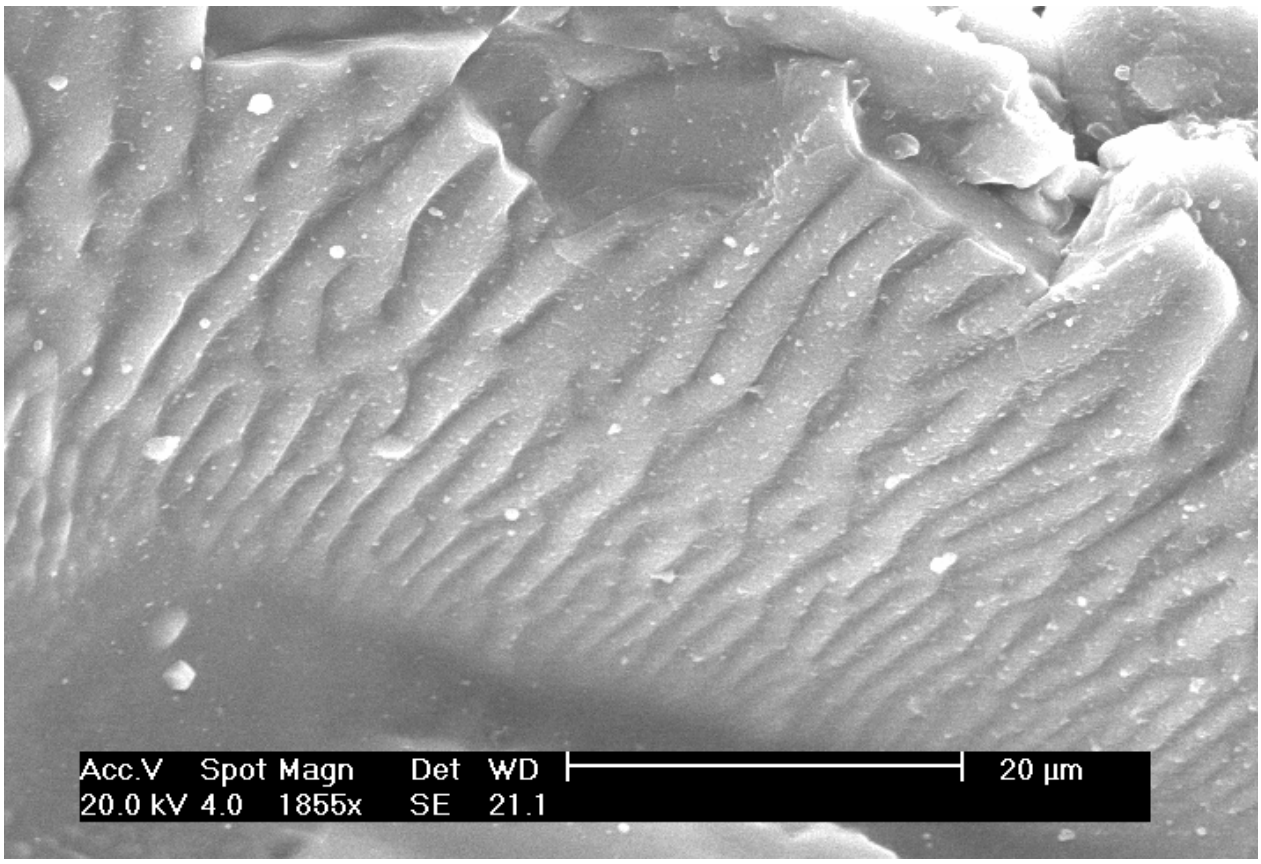


Figure 4 : Cu and Zn measurements on a brass nut sample (Plasma 54)



Picture 1 : Laser impact on NIST 612



Picture 2 : Cracks on NIST 610