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Representative sampling using single-pulse laser ablation with inductively coupled plasma mass spectrometry

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Abstract

Single pulse laser ablation sampling with inductively coupled plasma mass spectrometry (ICP-MS) was assessed for accurate chemical analysis. Elemental fractionation (e.g. Pb/U), the quantity of ablated mass (crater volume), ICP-MS intensity and the particle contribution (spike signal) during single pulse ablation of NIST 610 glass were investigated. Pb/U fractionation significantly changed between the first and second laser pulse and showed strong irradiance dependence. The Pb/U ratio obtained by the first pulse was usually higher than that of the second pulse, with the average value close to the representative level. Segregation during laser ablation is proposed to explain the composition change between the first and second pulse. Crater volume measurements showed that the second pulse produced significantly more ablated mass. A roll-off of the crater depth occured at ~750 GW/cm^2. The absolute ICP-MS intensity from the second pulse showed no correlation with crater depth. Particle induced spikes on the transit signal showed irradiance and elemental species dependence.

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I. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) with laser ablation (LA) sampling offers high sensitivity, *in situ* spatial resolution, and minimal sample preparation, making this technology ideal for direct solid chemical analysis. A continuous pulsing mode with laser repetition rates ranging from 1 to 20 Hz is commonly used [1,2], in which long duration steady state signals improve analytical precision. To achieve accuracy, one must ensure that the laser ablation process generates a chemically representative vapor from both standards and unknown samples. For continuous pulsing, a chemically representative ablated mass can be achieved at certain laser irradiances. However, time dependent elemental fractionation can be induced by continuous pulsing when the laser beam spot size is small and the irradiance is high. [3,4,5]. To achieve good spatial resolution for inhomogeneous samples, a small laser beam spot size is essential. Previous work has shown that this kind fractionation was related to the aspect ratio of the crater depth and diameter [4,5]. Methods have been tried to overcome or correct crater induced fractionation, such as active focusing [6] , and increasing the laser power during repetitive pulsing [7]. Horn et. al. found that there is a correlation between fractionation and the number of laser pulses for each beam size and a correction can be applied using this correlation [5].

In comparison to the continuous pulsing mode, single pulse ablation avoids crater effects on fractionation. Also the single pulse mode is more suited for spatial resolution or depth-profile analysis, such as analysis of inclusions, chemical zoning, and thin film analysis. There are several concerns with single pulse ablation, including signal

fluctuation or poor measurement reproducibility, small quantity of ablated mass inducing weak ICP-MS intensity, sample representation, and fractionation. Due to the transit nature of single pulse ablation and sequential collection by quadrupole mass filters which are commonly used in ICP-MS, signal may be lost during multi-element analysis causing poor measurement precision[8, 9]. The time of flight mass spectrometer (TOF-MS) is suited for the measurement of fast transit signals [10] and there is increasing interest in using such an instrument for single pulse laser ablation sampling [11] due to its simultaneous signal collection for all isotopes. Quadrupole mass spectrometer detection is still suitable for single pulse ablation if the data acquisition parameters and number of elements are reasonably arranged [8,9]. Sensitivity is currently better for the quadrupole MS system.

In this work, we assessed how single pulse laser ablation sampling can be used for accurate chemical analysis. Elemental fractionation, quantity of ablated mass, ICP-MS intensity, contribution of large particles to the ICP-MS intensity (spike signal), and crater characteristics were investigated to determine suitable conditions for single pulse ablation as a representative sampling method for ICP-MS analysis. Possible mechanisms that influence fractionation and mass removal processes are discussed. The behavior of the first and second pulse at the same area on a sample was studied. Pb and U were selected to demonstrate fractionation behavior due to their distinct thermal properties, as well as the significance for precise Pb/U measurements in geochronology.

II. Experimental Section

A quadrupled Nd:YAG laser at wavelength of 266 nm (Coherent, Infinity) with pulse duration of 3 ns was used. Single-pulse laser ablation was used. The laser-beam spot size was 18μm in diameter. The diameters and depths of the ablated crater were measured using a white-light interferometric microscope (New View200, Zygo Corporation). An ablation chamber with 7 cm^3 inner volume made of quartz was fixed on an XYZ translation stage, so the ablated area could be changed after each measurement. The sample surface was polished using silicon-carbide paper (>600grit) and cleaned repeatedly by methanol before the single pulse experiments. The ablated mass was entrained into a 0.3 L/min Ar gas flow through the ablation chamber via a 1 m long and 4.3mm i.d. polyethylene tube. The gas flow through the chamber was controlled by a separate mass flow controller (Matheson, 8217). The flow from the ablation chamber was mixed with a nebulized solution in a " T " section before entering the ICP touch. With this configuration the same plasma conditions can be maintained for both solution and laser ablation sampling[13,14]. After ICP-MS optimization, a solution of dissolved NIST 610 glass was measured without firing the laser to determine the ICP-MS response curve. When the laser was fired and the ablated mass was transported into the ICP, a 2% HNO_3 blank solution was introduced simultaneously by a spray chamber to maintain constant ICP conditions. Therefore, the ICP-MS response including mass discrimination and ionization efficiency can be corrected using this approach. The Pb/U values shown in this paper are corrected by using the digested NIST 610 solution.

NIST 610 glass with certified Pb and U concentrations of 426±1 ppm and 461.5±1.1, respectively was used as the sample. Based on the Pb isotopic composition reported by Walder et al [12], the $^{206}Pb/^{238}U$ ratio of 0.2249 [6] in this glass can be

calculated. Pb and U was chosen as a example in this study to show fractionation behavior due to the differences in thermal properties, because of its significance in geochronology. We can evaluate if the sampling is representative because of the certified values of these two elements in NIST 610. It is more difficult to evaluate representative sampling for the other isotope pairs such as Ho/U and the two REE due to the lack of well certified concentration values for these elements. A standard solution was prepared by digesting a portion of the NIST 610 glass. 20mg of glass powder was weighed into a Teflon vessel and dissolved into 0.5mL 1:1 (v/v) HNO_3 and 1mL HF. The vessel was vibrated in an ultrasonic water-bath for 30 min. and evaporated to dryness on a hot plate to remove the silica. An additional 0.5mL 1:1 HNO_3 and 1mL HF acid mix was added and the vessel was left to digest at 120 °C on an hot plate for five days. The final sample was treated with 2mL HNO_3 and diluted to 500 mL solution in 2% HNO_3. A blank was also prepared with the same procedure, except without the powder. The ICP-MS response discrimination was corrected using the digested NIST 610 solution.

A PQ3 (VG Elemental) inductively coupled plasma mass spectrometer (ICP-MS) was used. Data were acquired in the time-resolved mode. A 1.5ms quadrupole settling time and a 8.33ms dwell time were selected to keep approximately 85% of the total time for the data acquisition [8]. Five isotopes (i.e., ^{165}Ho, ^{205}Tl, ^{206}Pb, ^{232}Th, ^{238}U) were measured. The effect of spectral skew (spectral information lost) due to the sequential nature of the quadrupole mass filter can be neglected within the inherent precision of laser ablation ICP-MS[9].

Spikes are commonly observed in the temporal profiles of laser ablation sampling as shown in Figure1-a. These spikes originate from ablated particles and are not due to

instrumental noise [15]. Since the particle residence time in the ICP is approximately 1 ms, and 8.33ms dwell time was selected for quadrupole mass filter, only one particle signal can be detected in one element isotope sweep. These particle spikes will give a large error when determining the ratio of two different elements. The particle signals could be sufficiently high that one or two inadvertently analyzed particles would obscure the composition of the ablated mass. A program was developed to remove such spike signals (as showed in Figure1-b) during signal integration. The contribution of spike signal to the total integrated signal was also calculated. The error bars in experiments are the standard deviation for individual measurements that represent the variation of the 5 measurements.

III. Results and Discussion

1. Pb/U fractionation versus laser pulses:

Fractionation has been found to increase with the number of laser pulses (ablation time) due to the development of a crater [16]. In previous work using continuous ablation, the Pb/U ratio was found to decrease initially and then increase with the number of laser pulses [3]. This effect was especially dramatic when the laser focus was at the target surface. However, the initial laser pulses generally produce representative Pb/U values, although the error can be large [3]. Shot by shot analysis at the same spot was performed in this work to study fractionation on an individual pulse basis (**Figure 2).** The 10 data points in **Figure 2** were obtained by averaging two successive pulses, representing the Pb/U change during the initial 20 ablation pulses with an irradiance of 535±24 GW/cm^2 (4.08 ± 0.18 mJ with 18 μm beam diameter) at the same spot. The

measured Pb/U ratio by laser ablation is initially close to the representative value, decreases gradually to a lowest value, and afterwards increases with successive laser pulses. This Pb/U fractionation behavior is similar to that observed using continuous pulsing [3]. The initial few pulses provide a close representative analysis. To find the best laser conditions for representative sampling, we investigated the influence of laser irradiance on this fractionation behavior.

2. Pb/U fractionation versus laser Irradiance

The average Pb/U value for the first pulse obtained by 5 repeat measurements at seven fixed energy value is showed in Figure 3. The Pb/U ratios decrease with increasing laser irradiance. The Pb/U value is higher than the representative value and the errors are larger at lower laser irradiances (< 750 GW/cm^2). However, the Pb/U values approached the representative value and the errors were relatively small at higher laser irradiances (> 750 GW/cm^2). The experiments show that representative Pb/U sampling can be achieved with single pulse laser ablation sampling if the laser irradiance is properly chosen.

When the irradiance was relatively low, the Pb/U ratio from the first laser pulse was higher than the representative value. The higher ratio leaves U rich in the bottom of the crater. For the second laser pulse, the Pb/U ratio may be less than that of the original material. By averaging the value of the first and second pulse, the measurement was closer to the representative value. Figure 4 shows the ^{206}Pb/^{238}U normalized data of first and second pulses from 20 measurements on NIST 610 at a fixed irradiance of 616±21 GW/cm^2. The first pulse gave a relatively higher Pb/U value and the second pulse gave a relatively lower Pb/U value. The average Pb/U value of the first and second pulse varied

statistically close to the representative value. The average of these 20 Pb/U mean ratios was 0.2251, which is very close to the NIST 610 certificate Pb/U value of 0.2249. Two successive single pulses at the same location provided better representative Pb/U sampling.

This phenomenon also was found in a wide range of irradiance from 100 to 2500 GW/cm^2 (figure 3). For irradiance less than 500GW/cm^2 , the average Pb/U value was higher than the representative value. However, once the irradiance exceeded 500 GW/cm^2, the average Pb/U values of the first and second pulse approached the representative value. Previous studies have shown that for laser with nanosenond pulse widths, thermal effects are the main mechanism for elemental fractionation. Generally, surface temperature has a positive correlation with the extent of fractionation, although exact fundamental relation does not exist for nanosecond laser heating/ablation. Pb and U are two elements with significantly different thermal properties, so the irradiance has an important control over Pb/U fractionation. The surface temperature is difficult to measure. However, we believe the significant difference in the thermal properties for Pb and U (e.g. letent heat of Pb and U are 177KJ/mol and 477KJ/mol) could explain the change in the ratio by more than 30%.

The inset of Figure 4 shows changes in the difference of Pb/U ratios between the first and second pulses as a function of laser irradiance. The difference was calculated by $\frac{Pb/U_{2nd} - Pb/U_{1st}}{Pb/U_{mean}}$, where the Pb/U_{1st} , Pb/U_{2nd} and Pb/U_{mean} represent the $^{206}Pb/^{238}U$ value of first, second pulse and average value of the first and second pulses,

respectively. The calculated $\frac{Pb/U_{2nd} - Pb/U_{1st}}{Pb/U_{mean}}$ changes in the inset of Figure 4 are negative except for a few data points, meaning that the Pb/U values obtained by the second pulse are lower than those of first pulse. The difference in Pb/U ratios changes from 35% in the low irradiance of 100~200 GW/cm^2 to less than 10%, once irradiance exceeded ~ 750GW/cm^2. High irradiance (>500GW/cm^2) was beneficial for representative sampling and good precision of analysis using two successive single pulses.

Elemental segregation is a possible source of the Pb/U fractionation between the first and second pulses. There is extensive evidence supporting the presence of a molten phase during laser ablation at lower laser irradiances [2, 15,16]. Because of the lower melting temperature (both metal and oxide state) of Pb compared to U (see Table I), segregation during laser ablation may lead to an enrichment of the near-surface in Pb, and a corresponding depletion of Pb in the reminder of the melted volume. Therefore, a relatively Pb enriched mass is sampled by the first pulse, and a relatively Pb depleted mass is measured by the second pulse (Figure 4). The irradiance effect on the Pb/U values between the first and second pulses can be explained in two ways. As the irradiance increases, the surface temperature increases and the segregation between Pb and U reduces. Also, in the low irradiance range there are more larger particles [17]. There is evidence for enrichment of elements in larger particles [15]. To confirm the influence of large particles, we studied the spike signals in the temporal profile of the ICP-MS intensity.

3. Particle induced spikes versus irradiance:

The high Pb/U ratio at relatively low laser irradiance might be related to the particle size distribution. When a large particle passes through the ICP, a spike appears in the ICP-MS intensity temporal profile. The ratio of the particle induced spike signal intensity to the total intensity represents the percentage of mass from large particles to the total mass. This ratio as a function of laser irradiance is plotted in Figure 5. Both Pb and U particle intensity decreased as laser irradiances increased. The error bar represents the standard deviation (SD) of five repeat measurements.

Similar to that observed using continuous ablation [**15**], the frequency and magnitude of these spikes by single pulse ablation also was found to be element dependent, as shown in the inset of Figure 5. The particle contribution decreased with the sequence Tl, Pb, U and Th, which has a correlation with elemental thermal properties such as melting temperature (MT) , boiling temperature (BT) and oxide melting temperature (**Table I)**. Such phenomenon could be directly related with the particle generation mechanism during laser ablation. Outridge et al [**15**] discussed the presence of particles which were significantly enriched in certain elements during the ablation of NIST 610 glass and mammal tooth, using scanning electron microscopy (SEM). The enriched elements in the particles included Pb, Bi, Zn, Au and Ag, which were found to produce frequent spikes in the ICP-MS signal. There was an inverse exponential relationship between the number of spikes and their oxide melting points. A likely mechanism for enriched particle generation is segregation and migration within the melted portion of the sample, followed by shock-wave ejection of element-enriched molten droplets. Another feature illustrated in **Figure 5** is that both Pb and U particle contributions decreased with increased irradiance (Tl and Th showed the same trend, but

were not plotted here); the contribution of segregation during mass removal decreased as laser irradiance increased.

4. Crater properties:

The different composition of ablated mass from the first and second laser pulse indicates that the laser modified the sample. The influence of the surface modification to the amount of ablated mass was studied by measuring crater characteristics using a white light interference microscope. The measured crater depth created by a single pulse and two pulses as a function of laser irradiance is plotted in Figure 6-a. The irradiance used for the second pulse was the same as that of the first pulse. The ablation depth by the first pulse changed from 0.5 μm to 3.7 μm when the irradiance changed from of 100 to 2000 GW/cm^2. For the second pulse over the same irradiance range, the crater depth increased from 1μm to ~18 μm. There is a dramatic increase in the ablation depth by the second pulse compared to the first pulse. And, the increase in the second pulse ablation rate was not linear with irradiance; it rolled off at ~750 GW/cm^2. The reason for the dramatic increase in the ablation rate by the second pulse is not clear and needs further investigation. One possibility is that the ablated region undergoes a phase change such as melting and re-solidification after the first pulse. Because the composition of the surface layer changed after re-solidification, the bonding energy between the atoms could be different. The ablation depth roll-off by the second pulse at ~750 GW/cm^2 is believed to be related to phase explosion [18,19]. Measurements of the crater area produced by the first pulse also show a roll-off at ~750 GW/cm^2 (figure 6b).

5. ICP-MS sensitivity

There is concern of small quantity of ablated mass inducing weak ICP-MS intensity in single pulse ablation sampling. The applications might only be carried out for major elements in single pulse mode. The study of single pulse LA-ICP-MS sensitivity shows that it is not only for major elements but also for trace element analysis. The detection limits defined by 3 times standard deviation of background signal for heavy elements is in the 0.2 ppm level.

Crater measurements can be related the total mass removed by the ablation process. The ICP-MS intensity is proportional to the mass entering the ICP, which depends on transport efficiency. Comparison between the ICP-MS sensitivity and crater measurements can provide transport efficiency information. The integrated Pb and U intensities by first and second pulses as a function of irradiance are plotted in Figure 7. Although the crater depth measurements showed a dramatic increase in the ablation depth by the second pulse, the ICP-MS intensity from first and second pulses did not show a significant difference; they were the same within experimental error (Figure 7). In the irradiance range below 500 GW/cm^2, both Pb and U intensity increased slowly with irradiance. When irradiance was greater than 500 GW/cm^2, the ICP-MS intensity rapidly increased with irradiance. The absolute ICP-MS intensities from the second pulse were not crater depth dependent. The reason might be that the deep crater was formed by ejecting larger particles (>10 μm); these large particles cannot be transported to the ICP. Energy needed to eject a small molten particle is less than that needed to evaporate the same quantity of mass [20]. Since only particle size less than 1~2 μm can be transported and ionized in the ICP [17], the ICP-MS signal is mainly determined by the amount of

small particles transported to the ICP. Although the second pulse makes a deep crater, the absolute ICP-MS intensity was not greatly enhanced because of the production of large particles.

IV. Conclusion

Single pulse laser ablation sampling with the ICP-MS can be used for representative Pb/U analysis at higher laser irradiances. Accuracy was improved by averaging the Pb/U ratio from the first and second laser pulses. The Pb/U ratio by the first pulse was higher than that from the second pulse and the difference decreased with increasing irradiance. The average Pb/U values of first and second pulse approached the representative value after the irradiance exceeded ~500 GW/cm^2. For irradiance > 750 GW/cm^2, the Pb/U differences obtained by first and second pulses was small and the first pulse was enough to get reproducible analytical results. Segregation during the laser ablation process was proposed to explain the Pb/U behavior.

The spikes on the transit signal showed both element and irradiance dependence, supporting the existence of segregation. The percentage of mass from larger particles to the total mass decreased with increasing irradiance. Although the crater measurements showed that there was dramatically more ablated mass by the second pulse compared to the first pulse, most of mass was not transported into the ICP. With increasing laser irradiance, there were fewer larger particles. The ratio of Pb/U also achieved a representative value at high irradiance.

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Table I. Elemental thermal properties

Element	Melting Temperature (^oC)	Boiling Temperature (^oC)	Oxide Melting Temperature (^oC)
Tl	303.5	1457	300 (Tl_2O)
Pb	327.5	1740	370 (Pb_2O_3)
U	1132	3818	2878 (UO_2)
Th	1750	4790	3220 (ThO_2)

CRC Handbook of Chemistry and Physics, D.R. Lide, Eds.

(75th ed., CRC Press, Boca Raton, 1995).

Figure captions:

Figure 1. Transit signals of Pb by single pulse ablation on NIST 610 glass with particle induced spikes (**a**) and after spike removal (**b**).

Figure 2. Pb/U fractionation as a function of laser pulses at fixed laser irradiance of 535±24 GW/cm^2. Each data point represent the averaged Pb/U value of two single pulse.

Figure 3 The Pb/U ratio by first pulse , second pulse and their mean value as a function of irradiance. The results were obtained by five repeat measurements under same laser condition The error bar represent the standard deviation.

Figure 4. Difference of Pb/U fractionation between first and second pulse at fixed laser irradiance of 616±21 GW/cm^2, i.e., the Pb/U value by first pulse (■) is higher than that by second pulse (□). Their mean value (●) are statistically close to the representative value 0.2249. The data are after ICP-MS response correction using NIST 610 solution value. The inset shows the extent of Pb/U difference between first and second pulse versus irradiance.

Figure 5. The particle contribution (spike signal) to the entire ICP-MS signal as a function of laser energy. The particle contribution has a close correction with the elemental thermal properties. As the energy increase the particle contribution to the entire ICP-MS signal decrease.

Figure 6. (a) The crater depth produced after first pulse (■)and second pulse (□) as a function of laser irradiance. The crater depth by second pulse has a dramatic increase and roll-off when irradiance >750 GW/cm^2. **(b)** The measured crater

area by first pulse as a function of irradiance. A roll-off of crater area at 750 GW/cm^2 was also observed.

Figure 7. The integrated ICP-MS intensity of Pb (**a**) and U (**b**) obtained by first pulse (■)and second pulse (□) as a function of laser irradiance. There is an rapid increase of the ICP-MS signal when irradiance > 500 GW/cm^2.