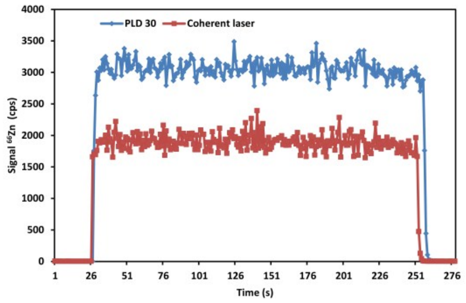
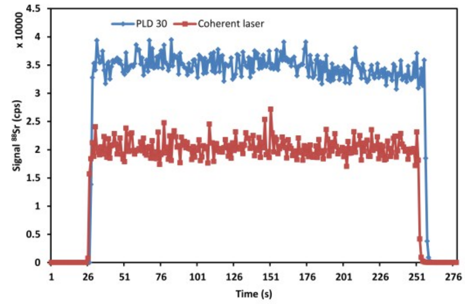
Transient signals of the modified RESOlution M50 laser ablation system

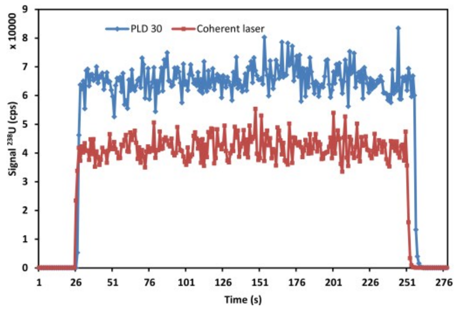
The transient time signals of three isotopes detected ranging from low to high mass (^{66}Zn, ^{88}Sr, ^{238}U) using the new PLD 30 excimer gas laser based LA-ICP-MS are displayed, and for comparison the corresponding transient time signals using the COMPEXPRO 102 excimer gas laser based LA-ICP-MS are shown in Fig. S1 (a-c). The line-scan mode for both laser ablation cases results in approximately constant signal during the whole four minutes ablation process, and the comparison of three time-resolved LA-ICP-MS signal shapes using the two laser based ablation setups shows no differences. It is thus suggested that there is negligible difference in the time resolved LA-ICP-MS signals for typical isotopes on account of the modification of RESOlution M50 due to the replacement of PLD 30 gas laser source.



a



b



c

Fig. S1 ICP-MS signal intensity of low to high mass (^{66}Zn, ^{88}Sr, ^{238}U) vs. time for ns-LA-ICP-MS analysis of NIST 610 in line-scan laser ablation mode (a, b, c), using laser wavelength of 193 nm and width with 20 ns at 80 mJ for Coherent laser and 130mJ for PLD 30 laser.

Elemental fractionation

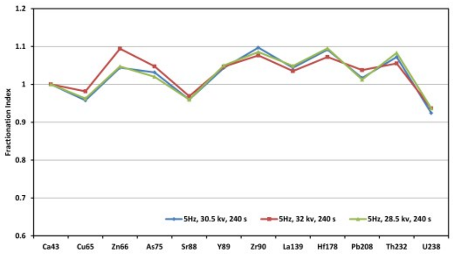
Due to the possible alteration of the stoichiometric compositions within the laser-generated aerosol when experiencing the formation by laser ablation, the transport into the ICP, and the conversion into ions within the ICP, the occurrence of non-stoichiometric effects in the transient signals of LA-ICP-MS are evidenced. It is the elemental fractionation that can explain the determined approach of matrix-matched calibration necessary for quantitative elemental analysis. Elemental fractionation effects can be quantitatively evaluated in terms of the fractionation index (FI), which shows how the intensity ratios of elements change in particles generated by the LA. FI is defined by dividing a second half time-resolved transient signal of a measurement by a first half as in the following formula.[16,17]

$$\frac{\sum cps(E_{second\Delta})/\ cps(Ca_{second\Delta})}{\sum cps(E_{first\Delta})/\sum cps(Ca_{first\Delta})} \quad (1)$$

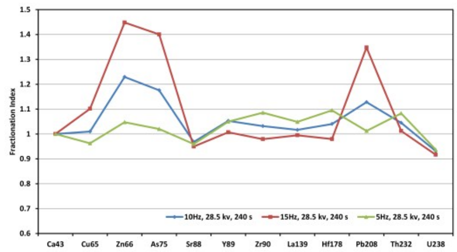
Where $E_{second\Delta}$ and $Ca_{second\Delta}$ are the second half time transient signals for given element and element Ca, and $E_{first\Delta}$ and $Ca_{first\Delta}$ are the first half time transient signals for given element and element Ca.

The modified laser ablation due to the replacement of excimer gas laser source in this work might result in more or less different elemental fractionation behavior in comparison with original RESOlution M50. NIST 610 glass sample was selected for evaluating the elemental fractionation of ICP-MS signals in our modified LA-ICP-MS setup. Fig. S2 (a-c) shows the fractionation index (FI) of twelve isotopes Ca, Zn, Cu, As, Sr, Y, Zr, La, Hf, Pb, Th, U under the conditions of varied energy, repetition rate and spot size of laser parameters given. It is shown that the pulse energy increase ranging from 130 mJ (high voltage: 28.5 kv), 212 mJ (high voltage: 30.5 kv) to 300 mJ (high voltage: 32 kv) does not result in significant variations of fractionation index (fig. S2a). In contrast, higher variations of fractionation index calculations, deviation from fractionation index of (1), are observed, and the most affected elements are Zn, Pb, As, Cu, when the laser parameter of repetition rate increases from 5 Hz to 15 Hz (fig. S2b). Although the laser ablation mode was single-site for measurements in fig. S2a and fig. S2b, these phenomena are quite different from as described in the case of line scan mode using ultrafast laser ablation.[11] The different mechanism in fs-LA and ns-LA laser ablation process might determine the effects of energy and repetition rate on the elemental fractionation. Furthermore, contrary to the description in the literature,[18] there are negligible differences of the spot size effects on elemental fractionation although the 285 μm spot size lead to less than 8% reduction of the FIs for elements Cu, Zn, As, and Pb (fig. S2c). It is thus suggested that the selection of laser conditions of spot size less than 155 μm, repetition rate of less than 10 Hz and energy of 300 mJ (high voltage: 32 kv) is preferred for negligible laser-induced elemental fractionation in our new PLD 30 based LA-ICP-MS.

Another way to measure elemental fractionation is through evaluating how elemental ratios change as laser parameters vary. The U/Th and U/Pb ratios in particular are a measure of laser- and transport-induced elemental fractionation.[19] Fig. S2(d-e) shows the differences of time-resolved variations in U/Th and U/Pb ratios due to the replacement of PLD 30 in RESOlution M50 laser ablation unit based LA-ICP-MS. The slopes (0) and intercepts of around (1) in both trend lines can be recognized, which suggests that neither ratio in U/Pb nor U/Th changes significantly due to the replacement of laser source. Fig. S2(f-g) shows the three combined measurements of time-resolved variations of Zn/Ca, Pb/Ca ratios under the conditions of the same laser pulse fluence but three various repetition rates given. Both Zn/Ca ratio and Pb/Ca ratio show the same pattern, in which the ratios keep unchanged during the first half laser ablation time period and changes significantly during the second half laser ablation time period. In other words, as the repetition rate increase from 5 Hz to 15 Hz, the variations of both ratios in the second half time series increase. In contrast, the laser pulse fluence changes due to increase of high voltage from 28.5 kv to 32 kv cannot result in Zn/Ca and Pb/Ca ratios variations as much as under the condition of repetition rate changes(fig. S2h-S2i). These phenomena support the elemental fractionation index calculations in fig. S2a and fig. S2b.



a



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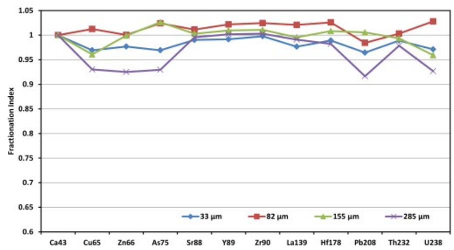

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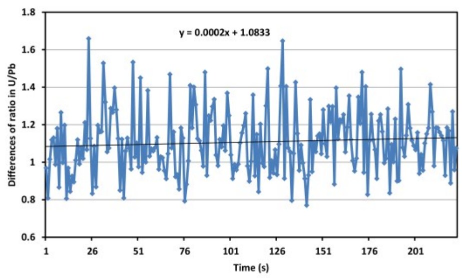
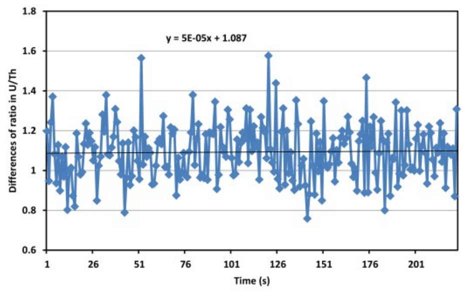
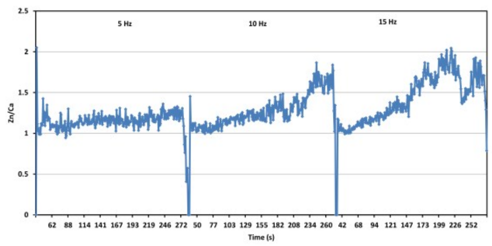


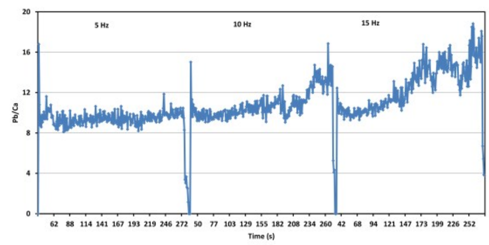
d



e



f



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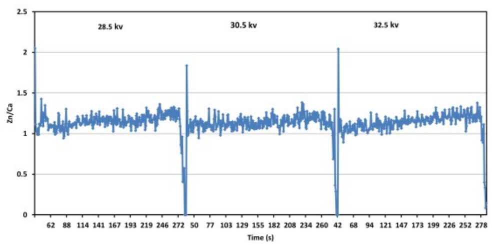
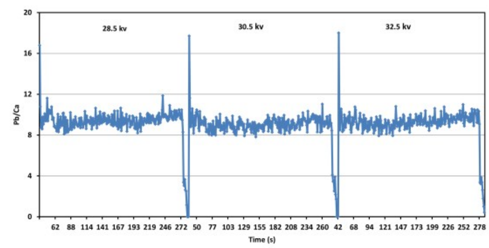


h



i

Fig. S2 The elemental fractionation (FI) calculation for isotopes Ca, Y, Zr, La, Hf, Pb, Th, U, Cu, Zn, As, Sr in single-site mode using laser PLD 30 in modified RESOlution M50 (a), (b), but line-scan laser ablation mode for (c), the laser parameter details see the text; Differences of variations in ratio of U/Pb was obtained by dividing ratios of U/Pb under the condition of PLD 30 excimer gas laser by ratios of U/Pb under the condition of Coherent excimer gas laser, line-scan mode for laser ablation process (d), the same of U/Th (e). The slopes and intercepts of lines are calculated for showing the tendency of time-resolved variations of ratios given (d), (e). Time-resolved Zn/Ca and Pb/Ca ratios during laser ablation periods in single-site mode under the laser parameters given, repetition rate increase from 5 Hz ,10 Hz to 15 Hz for (f) and (g), pulse energy increase from 130 mJ (28.5 kv), 212 mJ (30.5 kv) to 300 mJ (32 kv) for (h) and (i).

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18. Zhen Li, Zhaochu Hu, Yongsheng Liu, Shan Gao, Ming Li, Keqing Zong, Haihong Chen and Shenghong Hu, *Chemical Geology*, 2015, **400**, 11-23.
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