We sincerely thank both reviewers for their detailed comments. Our manuscript addresses a complex problem that we all struggle to understand on the basis of limited experimental evidence. Reviewer 1 is correct that our original account was unclear and apologize for the resulting confusion. We greatly appreciate the technical expertise of Reviewer 2, which has helped us to better understand the physics.

As suggested by both reviewers and the editor, we have omitted the sections discussing instrument bias (previous section 3.1) and focussed the work on ablation bias. We have added a paragraph near the end (new sub-section 3.2.6 at line 611) where we summarize our views on how the ablation process drives Pb/U fractionation.

RC1-1: The manuscript entitled, “Causes and mitigation of U-Pb fractionation during LA-ICPMS analyses of zircon using nanosecond excimer laser systems” investigates the fractionation behavior of Pb from U during successive pulses of a laser on (primarily) both crystalline and metamict zircon, and offers possible explanations for these observations that are ubiquitous in laser-ablation geochronologic analyses. Further to explain possible causes of fractionation, the authors present code to correct for this behavior, but in the end, recognize that it has many of the same shortcomings of other data reduction schemes when it comes to zircon that has undergone radiation damage. The data and ideas presented in the manuscript are useful to the geochronologic community with a few caveats. Though the paper was organized fairly well, it lacked a thorough explanation of instrument conditions for each experiment that was performed in the study, was commonly worded ambiguously, and there was insufficient detailed explanation of the ideas and presentation of the data, including figures, to live up to its potential. Many concepts are discussed but not shown (e.g., pit morphology during ablation is discussed early on, but only shown in a figure later on), and others are shown but not discussed (the images of the melted zircon in the laser pits is a complete unknown), but nevertheless, the data and reasoning (which is often hard to follow) are sound, and, if modified, the presentation of this study will be quite useful to those who perform or collect laser-ablation data, whether it be geochonologic data or otherwise.

One concern I have for the study is that it is lacking in repeatability. As someone who collects considerable laser-ablation data, instrument conditions can commonly dictate day-to-day behavior of ablated material analyzed by an ICPMS. Data presented herein appears to be done on multiple occasions, though it is commonly unspecified, and the authors (correctly) point out that one run cannot be compared to another that was run on a different day. Most of the experiments shown indicate trends rather than absolute value corrections and thus do not necessarily need to be repeated, but differences in down-hole fractionation between one day and the next begs a question about how much we can rely on conclusions based on a data from a single session. That said, most of the conclusions do not require that the experiments be repeated, however, I see a good reason to compare datasets that were collected in a single session rather than multiple sessions, and given that the time to repeat some of these experiments is not extreme, I encourage the authors to conduct at least the experiment shown in Figure 11 on the same day, and possibly comment on why they might be different from day to day. In the case of understanding the processes, this would be an important focus area.

AC1-1: Following suggestions by both reviewers we have omitted parts of the manuscript that are not relevant to laser ablation and rewritten other parts to make them easier to understand. As explained at new line 497, the experiment shown in the old Fig 11 (now Fig 10) involves two sessions during each of which measurements were made on 3 standards. Results on each represent averages of 4 to 6 measurements. Instrument biases should be comparable for results from each session after within session retuning so Y-axis intercepts of different standards within the same session are the only relevant parameters. The sessions are different only in that the first was run with the laser firing at 0.2 Hz, allowing resolution of results from the earliest pulses, while the second was run at 10 Hz.

RC1-2: A second main comment I would make refers to this and several LA fractionation studies: pulses analyzed in this study seem to go well beyond the number of pulses used in a typical ablation. I don’t know how deep the pits were, but they were only performed on ‘standards,’ which are much bigger than typical grains. I suspect that many unknown grains would not withstand 250 pulses at 3.5 j/cm2. Though it is interesting to see the behavior beyond a typical depth, it should be mentioned what a typical depth is

and what part of the profile one should pay most attention to. I am also not sure that the authors ever make an attempt to explain why the slope of the fractionation curve changes at a specific depth or pulse count. I would be interested to know if they have any ideas.

AC1-2: Since the purpose was to study and model Pb/U fractionation profiles, we needed ablation pits to be as deep as possible before signal attenuation seriously compromised the data. One of the conclusions of the study is the unreliability of data while the pit is shallow (section 3.2.4). We summarize our view of the fractionation process in a new section (3.2.5).

RC1-3: At times, I feel that the reference list is rather small. Many researchers have looked at laser induced elemental fractionation (LIEF, which is not mentioned here), and many others have discussed the physical coupling between the incident radiation and crystal structure which created the ablation plume. Though including this background material is not strictly necessary, it would add a lot of insight into the processes investigated *herein.*

AC1-3: We have added several new references for which we are indebted to suggestions by both reviewers.

RC: Though I have many comments below that I think could add to the clarity and significance of the manuscript, I commend the authors on tackling a difficult problem, the solution to which could have a rather large impact on our ability to solve geologic problems.

Line item comments:

RC1-4: 73. Need more instrument information. What kind of cell?

AC1-4: The NWR193UC ablation system includes both the laser and the ablation cell. We have added a link to the brochure describing the ablation cell in detail at new line 63.

RC1-5: 74. I belive this is meant to be j/cm2

AC1-5: Corrected at new lines 65 and 176.

RC1-6: 77. Where is the table of instrument conditions? See Horstwood et al., 2016 for suggestions.

AC1-6: The work describes a number of experiments that were performed at different times and that generally aimed to identify patterns rather than determine exact numerical results. We tried to keep the laser and plasma conditions the same, as described in section 2 where we have added additional information on the plasma conditions.

RC1-7: 120. If the idea is increased turbulence entraining oxygen, then moving the torch closer to the cones should not be the same as increasing the Ar flow, no? Please explain.

AC1-7: Following reviewer comments, we have omitted this section.

RC1-8: 146. Another possibilty is that it is an interference. Please explain why you think O is increased during the ablation of calcite over zircon. I imagine the spots are larger, for one.

AC1-8: Following reviewer comments, we have omitted this section.

RC1-9: 147. Monazite is a phosphate, but you just said there was no detectable change for monazite.

AC1-9: Following reviewer comments, we have omitted this section.

RC1-10: 180. A picture is worth 1000 words. Not everyone has this system, so use of "normally" isn't really appropriate. The newest designs tend to have a fixed cup and a stage enclosed in the cell. Somewhat surpisingly, these also have differences in apparent oxide production from one location to another.

AC1-10: Following reviewer comments, we have omitted this section.

RC1-11: 190. But earlier it was noted that oxidation decreases through time?

AC1-11: Following reviewer comments, we have omitted this section.

RC1-12: 212. Is this your data or someone else's conclusion?

AC1-12: Following reviewer comments, we have omitted this section.

RC1-13: 244. What study are the 206/238 ratios of the NIST glasses from?

AC1-13: We have added the Jochum et al (2005) reference at new line 106.

RC1-14: 266. I believe you mean TRA?

AC1-14: Now corrected at new line 126.

RC1-15: 270. Ambiguous. Does this fs laser have a shorter wavelength too? Please expand.

AC1-15: Our mistake. We have removed reference to wavelength in new line 130. The picosecond laser actually has a longer wavelength.

RC1-16: 298. And elswhere: micron is usually abreviated μm.

AC1-16: This has been corrected throughout the text and figure captions.

RC1-17: 300. How many pulses?

AC1-17: See reply to next comment.

RC1-18: 302. What were the conditions of this pass?

AC1-18: "200 pulses at 10 Hz, 3.5 J/cm^2" added at new line 176.

RC1-19: 304. An order of magnitude reduction from an uneven surface? How deep was the pit? Was the laser out of focus at the bottom of the pit? Why does the pit look so strange?

AC1-19: As explained at new line 178, the floor of the pit is covered in congealed melt. The important point of the experiment is not the variation of intensity but rather the decrease in 206Pb/238U, which shows that the melt is depleted in Pb. It therefore represents part of the complimentary component to the Pb/U enriched signal as now discussed more thoroughly in new section 3.2.5. There seems to be some confusion about the melt phase, perhaps partly as a result of showing a pit generated by a rotating laser beam in Fig. 2B and C. We now explain in lines 172-175 and the figure caption that this was done to clearly show the presence of melt. We have removed the old Fig 5D, which is redundant.

RC1-20: 306. It is unclear how this experiment was performed. Also, why would you expect lower ratios at the bottom of the pit? Don't we expect the analyses from the bottom of the pit to have higher ratios? Please elaborate on these points.

AC1-20: A paragraph has been added at new line 156 giving some experimental background. The rationale for this experiment: that the basal melt should represent at least part of the Pb-depleted reservoir complementary to the Pb-enriched enriched signal, is now more clearly explained in lines 168-170. The role of this reservoir is discussed further in the section on modelling.

RC1-21: 310. This is not clear, and not explained in the text. What was done to create these laser pits, and why does it represent a typical ablation?

AC1-21: This ablation is of course not typical. As now explained at lines 172-174 laser rotation was done to disturb the surface and show that it was liquid.

RC1-22: 324. Same question here about the pit - is there an intention to create a different style of ablation and pit? It isn't clear in the text.

AC1-22: See AC1-19.

RC1-23: 398. Why not just use 90Zr? Why use an oxide?

AC1-23: We have added: ‘Zr or Si oxide species must used so as not to overload the detector.’ At line 323.

RC1-24: 407. Pulses, not passes.

AC1-24: ‘Pass’ is the term used in the NWR software to represent the laser warm-up time plus ablation. This is now defined at line 334.

RC1-25: 427. Are there any other possible reasons? Possibly a change in the coupling of the laser with the material, or other? Is there anyway to test this?

AC1-25: Good point. We have expanded the sentence at line 354 to read: ‘This might be a result of increased coupling of the laser but if not it suggests that fallback is a major source of signal loss for the earliest pulses…’

RC1-26: 431. This is where an explanation such as that given in figure 12 is necessary.

AC1-26: We agree and now introduce this figure and its discussion earlier as Fig 4.

RC1-27: 448. This is confusing. Are you saying that the radius of the base of the pit reduces is reduced by 20% at the bottom than the top? What do you mean that the emission (emission of what?) is reduced to half with a 20% reduction in area? If the mass of the ablation plume is proportional to area, then a 30% reduction leads to half the area (0.7^2 = 0.49).

AC1-27: This section discussed factors that might change the ablation volume with pit depth but was poorly explained. It has been revised in the paragraph at line 288. Ablation volume per pulse is also discussed at lines 305-308.

RC1-28: 450. This sentence makes a claim that forcing an analytical change would create a physical change which is impossible, and is one of the reasons that this section is confusing.

AC1-28: The wording has been changed in line 401.

RC1-29: 452. It is strange that rather than examine pit shape, depth change per pulse, etc., with the instrumentation used within this study that the authors refer to a study 30 years prior, when instrumentation would have been significantly different. Why not make and measure pits in this study?

AC1-29: The Eggins et al. (1998) study contains a great deal of information that was not thoroughly discussed in the original publication. These authors carefully bisected a piece of NIST610 glass, fitted the pieces tightly together and ablated pits parallel to the plane of bisection. This cannot have been easy and would be more difficult with most zircon, where grains are small. It could have been done with KL, and this might be a good topic for another manuscript but we have no reason to expect that ablation of NIST glass would be qualitatively different from zircon.

RC1-30: 458. It seems magical that the first pulses have only plasma-biased effects. Are you implying that there is no laser-induced fractionation during the first pulse?

AC1-30: This is discussed in the paragraph at line 262 of the revised version. We are not implying that the first pulses have only plasma-biased effects but we need to normalize measured results to the best estimate of the plasma bias when the measurement was taken. That is why all the profiles start at 1 but there is no expectation that results of the first measurement will give 1.

RC1-31: 484. What was the spot size? Did you perform any experiments with a different spot size? It would be interesting to know if these trends are related to the aspect ratio or just the first 10 pulses.

AC1-31: Reference to the spot sizes is now given in lines 499-500.

RC1-32: 486. Why? Doesn't the previous statement imply that the first several pulses are the most important? Fig 11 shows early pulses in 11A but seems to start at 5 in 11B. There needs to be more explanation.

AC1-32: Revised at line 496 to mention that signals from the first five pulses at 10 Hz have not stabilized so we cannot determine accurate ratios.

RC1-33: 487. Why did you do this? If the Y-axis can't be compared, how do we know the slopes can be compared? Is it possible that the tuning conditions are partly responsible for the change in signal during ablation? Can you repeat the experiment and show that the patterns look the same between sessions?

AC1-33: This is explained in AC1. The 0.2 Hz and 10 Hz runs were done during different sessions in part because of limited time on the instrument. The purpose of the experiment was to compare results from 3 standards within the same session to see if they would be different, which they are in both cases. Comparison of results obtained at different laser pulse frequencies was not considered relevant.

RC1-34: 492. Do you mean pulses 5-15?

AC1-34: As now stated at line 496 and 503 of the revised manuscript, we refer to data from the 0.2 Hz runs where ratios based on the earliest pulses could be calculated.

RC1-35: 493.This wording is ambiguous. It looks to me that the trend in the first several pulses can not be distinguished in the latter pulses. This is different than was stated earlier, which was that the first several pulses were unchanging.

AC1-35: Now line 504. The Y-axis intercepts of the average regression lines are discussed here, which are calculated from all the data not just the earliest pulses.

RC1-36: 508. The wording here is confusing. The authors speak of the base and the wall of the pit, but the deposition shown in the figure is both on the base (only at the edge) and the wall of the pit. There is a disconnect between the language used and the conception of the process which needs to be changed/improved.

AC1-36: The conceptual model is now introduced earlier in the manuscript at line 279. We don't see an ambiguity. The ablation pit has a base and a wall along which some of the excavated material could be deposited. The slope of the wall is reduced (<90^{o}) after deposition but it is still considered as a wall.

RC1-37: 513. "unrealistic": Is is just that the angle of the deposit on the figure is exaggerated?

AC1-37: We now specify at line 291 that we used recursive modelling to determine the rate of narrowing of the pit.

RC1-38: 515. Interesting that a moat at the base of the pit is ubiquitous. One might assume that laser energy is uneven across the beam (highest at edges), but the process described here would put that assumption into question, or at least imply that the deposition and reablation at the wall is different than its aspect ratio might suggest.

AC1-38: We presume that Fig 6 of Eggins et al. (1998) is referred to. This shows that the base of the pit in NIST610 is not flat but shows a convex shape. Our experience is that the defocussed laser beam does not seem to become larger but the radial energy density is not uniform so the convex shape might be a result of downhole defocussing. Another possibility is that low-angle reflection of beam off the sides of the pit might focus energy near the corner of the base as we suggest in line 306.

RC1-39: 518. I don't believe it is explicitly stated here, but I think the authors are implying that the amount of deposition on the walls of the laser pit increases with depth. Possibly because the height of the wall increases with depth, yielding more surface area for deposition and less space for the ablation plume to escape the pit. Would be nice to state this more clearly. An image similar to that of figure 12, but with a more thorough explanation, would be rather helpful in doing so.

AC1-39: This is now summarized in section 3.2.5 at line 512 of the revised manuscript.

RC1-40: 526. Show this figure earlier in the manuscript and either expand on it here or where it is earlier.

AC1-40: We now introduce the figure in section 3.2.1 instead of 3.2.5.

RC1-41: 533. Should be labeled B1?

AC1-41: This is now corrected on Fig 4A of the revision.

RC1-42: 546. This can't be seen in any of the diagrams. Why include it?

AC1-42: This refers to the paragraph now at line 416. The progressive decrease in recycling of basal melt refers to the model which is in an Excel file that is now referenced.

RC1-43: 547. What does 1 refer to?

AC1-43: This is now explained in at line 423 of the revision.

RC1-44: 552. Are you implying that we shouldn't expect any recycling? Did you model it with some recycling? What are the results from that?

AC1-44: This is now discussed in more detail in lines 430-433.

RC1-45: 558. Why not point to all these phenomena in the figure? It is difficult to follow with text only.

AC1-45: We now make references to the figures and ranges of pulse counts in lines 434-440, which should make the discussion easier to follow.

RC1-46: 560. Better to say U signal than U concentration.

AC1-46: This done at line 442.

RC1-47: 561. This discussion goes back and forth between discussing one sample and both samples. It needs to be rewritten for clarity.

AC1-47: We have specified the sample more clearly at line 441.

RC1-48: 583. Fix subscript.

AC1-48: The subscript is meant to be ‘i’ (pulse number), not 1, as now explained in line 464.

RC1-49: 593. I recall this recommendation, however, it is hard for me to believe that Gehrels was ablating his sample for 250 pulses. Please check this work to make sure it is correct.

AC1-49: This has been clarified at line 537. The number of pulses used by Gehrels and others for dating zircon is smaller than in this experiment but it is useful to push the range of pulses beyond that normally used.

RC1-50: 598. Normalized to another reference material? To expected plasma bias? Is the the 68 ratio? This is also confusing.

AC1-50: We have carefully reworded the explanation in lines 542-552 of the revision.

RC1-51: 601; What do you mean by this? The explation has to be here in the text, not in a supplement.

AC1-51: We hope that our rewrite in lines 542-552 will be more comprehensible. We refer to the supplementary data file for the detailed calculations.

RC1-52: 606. This isn't much different from just the average of of the data points (0.2 vs 0.15%). Are you assuming that the intercept is correct or some other part of the curve?

AC1-52: See AC1-51.

RC1-53: 624. Please state here whether this approach is applied to large datasets or just single data points.

AC1-53: See AC1-51.

RC1-54: 635. What are the analytical conditions here? Same as all the other experiments? Is 250 pulses typical for an experiment run on a quadrupole? How deep are these holes? Describing the analytical conditions and showing and describing laser pits, etc. in each of these experiments would go a long way.

AC1-54: The analytical conditions are now specified at line 577. ‘Standard’ conditions are defined at lines 65-66. Line 573 mentions that the results in Supplementary Data File 7 include raw data. This can be processed using other software packages.

RC1-55: 645. Above it states that the ZrO decays more rapidly in metamict zircon, but here it says the the average is the same, so it must mean that ZrO in metamict zrn starts out at a higher value, but the decay rate is faster, leading to a similar average. This must say something about the difference in interaction of the laser with metamict vs crystalline zrn.

AC1-55: See AC1-56.

RC1-56: 647. Were the pits deeper? Showing profiles of the data (ZrO, 68, U) of the different metamict zircon vs pristine zircon would be helpful to make predictions here.

AC1-56: The reviewer raises some good questions. Unfortunately, we do not have the ability to precisely measure pit dimensions, beyond focussing with a petrographic microscope, which we find gives rough and somewhat subjective results.

RC1-57: 654. What is meant here by discordance - the different between the measured 68 and 76 or between 68 and the accepted value? The former would have a larger uncertainty.

AC1-57: Discordance is a term commonly used by U-Pb geochronologists to quantify the separation between a U-Pb datum and the concordia curve. It is the percent difference above (negative) or below (positive) of the datum with respect to a point on concordia having the same 207Pb/206Pb age. This has now been explained at lines 579-581.

RC1-58: 715. This is highly confusing. It would appear that there are 3 different fractionation terms: cloud, deposit, signal. The "0" explanation is for deposit; this is understandable. The second explanation is for a cloud?? The third would be for a signal, but how can one discuss the signal of a pulse relative to the following ablation cloud?

AC1-58: We have revised the first part of the Appendix to improve clarity (new lines 645-684).

RC1-59: DR Tables. These are fairly raw and could be organized with the reader in mind.

AC1-59: We presume that this refers to the Supplementary Data Excel files for the modelling, regressions and data processing. These are necessarily complex but we have included detailed instructions in text boxes for the most ambitious readers.

Citation: https://doi.org/10.5194/egusphere-2026-2779-RC1

RC2
This text aims to elucidate the origin of the bias, or- more precisely - the difference between the mass abundance ratio and the measured intensity ratio in U–Pb LA-ICP-MS analysis of zircon. This difference, commonly expressed as the relative sensitivity factor, is the principal calibration parameter in LA-ICP-MS and is therefore critical to the accuracy of U–Pb age determinations. This text also offers a computational method to compensate for the laser ablation-induced component of that bias. I believe that this text, particularly the sections dealing with the ablation-induced bias and its computational correction, is valuable and should eventually be published, subject to substantial revisions and, potentially, a reorganisation of the manuscript, including the possibility of spliRng it into two or more separate manuscripts.

RC2-1 CONCEPTUAL COMMENT:
(1) This long manuscript covers a range of topics that can be broadly divided into three groups:
• Plasma-related biases (biases associated with the operation of the mass-spectrometer);
• Ablation-induced biases (Pb-U fractionation);
• Computational correction of ablation-induced biases.
Each of these topics could be developed into a dedicated manuscript. Moreover, they are approached using different methodologies. The plasma- and ablation-related biases are addressed from a technical perspective, which requires a thorough understanding of ICP-MS and access to additional instrumentation, including a transmission electron microscope. In this part of the manuscript, I find several gaps, as well as unsubstantiated or speculative statements. At this stage, the computational part appears to be the most robust and may be worth separating from the rest of the manuscript, together with only the minimum discussion of the ablation-related biases that is necessary to provide the required context. I would recommend publishing it as a separate manuscript.
The oxidation-related bias represents another topic that could be developed into a separate manuscript. Finally, the physical and chemical meaning of the ablation-related bias could serve as the foundation for yet another manuscript. Given that both of these topics require substantial further work before they are ready for publication, I recommend setting them aside for the time being. Developing them into publishable manuscripts is likely to require some amount of additional work and time.

AC2-1 Following suggestions by both reviewers we have omitted parts of the manuscript that are not relevant to laser ablation.

SPECIFIC COMMENTS:
Introduction:

RC2-2 "The analytical precision is limited to about 1% for a single analysis" This statement is somewhat misleading because it refers only to the *measured uncertainty* and does not account for the long-term (systematic) uncertainty. The latter may be significant but is difficult to quantify deterministically, particularly for individual spot analyses.

AC2-2 This is now specified as being internal precision in line 33 of the revised manuscript.

RC2-3 (2) "Because of the complexity of the analytical processes, LA-ICPMS is often treated like a 'black box¨by the users (including the authors)." In my view, the present manuscript illustrates this issue rather well, which is regrettable. In addition, I suggest considering whether a hyphen should be used in 'ICP-MS'. The ICP-MS literature contains many articles that omit the hyphen and even more that include it. Still, there are good reasons to use the hyphenated form.

The 1st reason is technical. When we deal with a branch of optical spectroscopy or mass spectrometry, one consideration is the degree of integrity between the signal source and the spectroscope / spectrometer. For example, in optical emission ICP spectroscopy (ICP-OES) and in ICP-MS, the source is rather easy to disconnect or reconnect to the ion channel of the spectrometer. On the Element 2/XR, it is even placed in a compartment that you can open and move away from the spectrometer for inspection and repair. The same applies to electrospray mass spectrometry (ESI-MS) and MALDI mass spectrometry. All these techniques have one feature in common. Their signal sources operate under

atmospheric pressure and it is difficult to do otherwise. For example, the analytical ICP is an argon plasma maintained by resistive heating by eddy currents induced in the plasma body by fast changing magnetic field. Eddy currents cannot circulate *in vacuo*. So, we need some pressure, often it is just 1 atm. In glow discharge MS (GD-MS), it is below 1 atm, but is still substantial. But the ion channel must be kept under vacuum, otherwise no ion transmission, collimation, mass discrimination is possible and the detection becomes complicated. Thus, we naturally come to an instrument made of two separate and rather easily separable parts – the source and the spectrometer itself, with an interface between them. Such techniques are sometimes called 'hyphenated techniques', emphasizing that it is better to hyphenate between the source and the mass spectrometer: ESI-MS, MALDI-MS, ICP-MS, GD-MS. Interestingly, ICP and GD can be combined with the same ion channel, mass discriminator and detection system. Consequently, we find two instruments on the market: Element 2 and Element GD. They share the same spectrometer, the interface uses the same principle but is not identical, and the ion sources are different: ICP vs GD. How not to hyphenate under such circumstances? Full-vacuum techniques, e.g., TIMS or SIMS, have ion sources operating under vacuum and more deeply integrated in the spectrometer design. Consequently, we do not hyphenate.

The 2nd reason has to do with the authors' rights. Robert Samuel Houk, who is a founder of the ICP-MS technique, has once expressed his opinion as follows: 'There are even some heretics who brazenly want to remove the hyphen from ICP-MS, put there by me in 1978, and without my permission', R.S. Houk, J. Chem. Ed., 77, 2000, 598-607). I am not sure what the personal opinion of Velmer A. Fassel on this interesting topic was, but, as the supervisor of R.S. Houk, he apparently agreed that the technique could go out into the world as 'ICP-MS', with a hyphen separating 'ICP' and 'MS'. Admittedly, there are researchers who repeated in obstinacy that there is no need for a hyphen. They did so mainly because they had not used the hyphen in their early articles and later thought it was already too late to change. Many of them eventually changed their minds. Unfortunately, the very first lines of this manuscript immediately reveal that its authors still hold heretical views.

AC2-3 The first author is old enough to remember a time when mass spec. analysts built their own instruments and had to be experts in all aspects of the field. Most instruments at present are supplied commercially and users have become more specialized. We therefore very much appreciate having an expert on the instrumentation review the manuscript and regret that we did not have access to such expertise earlier. A hyphen has been added to the ICP-MS acronym in the title and throughout the text as well as relevant references.

RC2-4 (3) ¨The most significant sources of Pb/U measurement bias are mass fractionation, ionization efficiency, oxidative loss of U and ablation bias. The first three occur in the plasma while the forth…¨ Mass fractionation does not occur exclusively in the plasmati it also occurs in the ion beam inside the mass spectrometer, where ions are subject to space-charge-related losses that are more pronounced for lighter ions.

AC2-4 'The first three occur in the plasma (as well as the MS for mass fractionation)' is now added at line 44.

RC2-5 (4) ¨A common procedure in analyzing calcites and phosphates is to correct for the first three biases using a glass standard… but these are also affected by ablation bias, which can only be corrected using a 'matrix-matched' standard…¨. I recommend removing this statement. A wide range of trace elements in calcite and phosphate minerals can be analysed accurately by LA-ICP-MS using the NIST SRM 610 or 612 glass standards as primary calibrants. It is true that the Pb/U ratio in these minerals is generally determined using matrix-matched standardisation. Still, this is not universally the case for U–Pb dating of all U-rich minerals. For example, non-matrix-matched approaches have also been reported for minerals such as allanite and titanite, although they are rarely used in practice. There is no need to discuss all this here. In fact, there is no need to discuss calcite and phosphate minerals at all. I recommend keeping the discussion focused on zircon.

AC2-5 The phrase: 'in analyzing calcites and phosphates' has been removed from line 46.

RC2-6 (5) ¨Working hypotheses will be advanced to explain… Even if these explanations are not all strictly valid, they may provide a starting point for understanding the causes of bias… We hope that our observations and arguments will at least provide some insights to the community and inspire further efforts.¨ In my opinion, this approach is not appropriate for a research paper. The manuscript should present only those data and interpretations that are reasonably well supported by the available evidence. Speculative ideas and insufficiently substantiated interpretations should be set aside until they can be supported more convincingly.

AC2-6 While we understand the reviewer's point of view, one of the objectives of this manuscript is to stimulate further research efforts by the community towards a more thorough understanding of biases so that robust correction methods can be developed. We do not see why informed speculation should not be part of a scientific manuscript.

RC2-7 (6) What remains of the Introduction after these revisions? I recommend expanding it by including a brief review of the previous literature on the biases that the manuscript ultimately chooses to address. For example, the Introduction should familiarize the reader with the literature on laser-induced Pb–U fractionation in zircon, including its physical and chemical origins, instrumental approaches to minimizing it, and the available mathematical methods for its correction (e.g. the ratio-of-means vs. intercept and related approaches). At this stage, it would also be appropriate to identify the principal sources of inaccuracy and possibly long-term uncertainty, again backed by the literature.

AC2-7 We have expanded the background review, especially as a result of both reviewer's comments and suggestions.

Instrumentation and methods:

RC2-8 What RF power was applied to the load coil? Did you attempt to optimise this parameter?

AC2-8 This is now specified in line 64. We used standard plasma conditions specific to the instrument.

RC2-9 Was nitrogen added to the sample gas? It appears from the description that nitrogen was not used.

AC2-9 As now stated in line 70, N2 gas was not added. We have experimented with this but found that it did not improve sensitivity with our instrument.

RC2-10 The original NWR193 is a very old laser ablation system. I assume that you used a more recent version of it, such as the NWR193UC or perhaps the NWR193HE. Please specify the exact model.

AC2-10 It is NWR193UC, now specified at line 66.

RC2-11 (4) Please provide here a reasonably detailed description of the ablation cell used in this study.

AC2-11 A link to the technical description is now given at line 62.

RC2-12 (5) "…with a fluence of 3.5 mJ/cm2…" and the later statement in line 94, where the fluence is explicitly given as 3.5 millijoules/cm2, require clarification. Please specify the correct value. Did you mean a laser pulse energy of 3.5 mJ (measured immediately downstream of the laser cavity output coupler), or an onsample fluence of 3.5 J/cm2? An on-sample fluence of 3.5 mJ/cm2 that you report would be unrealistically low for laser ablation. Please also explain the rationale for the chosen on-sample fluence, as this parameter is directly relevant to laser-induced Pb–U fractionation in zircon. The published literature reports on-sample fluences ranging from 1.5 to 19.5 J/cm2, although more recent studies have generally favoured values between 1.5 and 3.0 J/cm2. I would therefore expect your experimental conditions to be broadly consistent with current practice, corresponding to an on-sample fluence of approximately 2-2.5 J/cm2.

AC2-12 The unit for fluence was mistaken and has been corrected to J/cm2 at lines 65 and 176.

RC2-13 (6) Uranium has relatively low first and second ionisation potentials (comparable to those of calcium) and therefore forms an appreciable fraction of doubly charged ions in the ICP (up to ca. 0.5%, I assume). Please specify the abundance of U++ ions under your operating conditions and, perhaps, in the following consider their formation as one of the potential sources of plasma-induced bias.

AC2-13 Discussion of instrument bias has now been removed from the manuscript.

RC2-14 (7) Please consider adding a table listing all important operating parameters for the both laser ablation system and ICP-MS (it is sometimes called ‘metadata table’).

AC2-14 Most labs operate using a fixed set of operating (standard) parameters that have been adjusted for maximum sensitivity of their instruments. Some parameters vary from day to day. Other labs may have different instruments with different standard settings. We think that such information is not critically important for the reader beyond the conditions of fluence, frequency and beam size for the laser as well as plasma power and oxidation. Our project investigates broad influences on measurement biases in order to better understand their mechanisms. We do not seek to establish or reproduce precise numerical results.

RC2-15 (8) Regarding the Keuhl Lake (KL) zircon standard: please explicitly specify whether it has been dated by ID-TIMS. Treating it as equivalent to the 91500 standard without direct ID-TIMS dating is not an appropriate approach. I recently discussed this issue with Jiři Slama, who previously attempted to date by ID-TIMS a zircon megacryst "from the same deposit" as the 91500. The resulting age differed by approximately 100 Ma from the accepted value (!), highlighting the importance of independent age verification by ID-TIMS.

AC2-15 As now mentioned at line 77, the KL sample has been cross-calibrated against other ID-TIMS dated zircon standards and given ages within error of 91500.

RC2-16 (9) In this section, please also describe all additional equipment (profilometers, electron microscopes, Raman microprobes?) that you used in your study.

AC2-16 The scanning electron microscope is now specified at line 79.

Plasma-induced biases, generals aspects, oxidation:

RC2-17 (1) Unlike ablation-induced biases, which are, at a particular wavelength and pulse length, mainly controlled by the fluence, repetition rate, pit size, and the physical and chemical properties of the zircon matrix, plasma-induced biases - and the oxidation bias in particular - depend enormously on the spectrometer settings and the way we prepare the spectrometer for work, and may be specific to a particular LA-ICP-MS facility. For example, in laser ablation mode, an Element XR can readily be tuned to achieve a $^{248}ThO^+/^{232}Th^+$ ratio of <0.05, while providing a sensitivity at least 1.5 times higher than that of an Agilent 8900 in the heavy-mass range. At a $^{248}ThO^+/^{232}Th^+$ ratio of 0.03–0.04, which is routinely achievable for the Element XR with the addition of 1 mL/min N_2 to the sample gas, the oxidation-related bias is unlikely to be significant. Also, not all two-volume ablation cells permit a helium leak. Cells with a fixed extraction funnel and a movable sample holder do not have this potential leak path. Therefore, the observations reported in this section are unlikely to be generally applicable, which limits their broader significance. Ultimately, most, if not all of these biases can be readily corrected by external standardisation. This is the main reason why I recommend removing this section from the present manuscript. After further revision and completion, it could form the basis of an interesting technical note suitable for submission elsewhere (e.g., as a JAAS Technical Note).

AC2-17 Discussion of instrument bias has now been removed from the manuscript.

RC2-18 (2) Irrespective of the eventual fate of this section, please clarify your position regarding the spectrometer settings. Nowadays, nitrogen is very frequently added to the sample gas to increase sensitivity and, particularly importantly, to reduce oxide production. Its use with recent Agilent ICPMS instruments has been well studied and documented. It was recognised during the earliest experiments with atmospheric ICP discharges in the 1940s that nitrogen readily reacts with oxygen to form NO-species. It was even initially proposed that atmospheric ICP discharges might ultimately be used for nitric acid production. By binding oxygen as NO, less free oxygen remains available to oxidise other elements, thereby reducing oxide formation for the analytes. Your manuscript contains no indication that nitrogen was added to the sample gasti I therefore assume that it was not used. If so, please explain why. Please also clarify your choice of RF power. Traditionally, Agilent ICP-MS instruments are operated at relatively high RF powers (e.g. around 1500 W), but this is an important TUNABLE parameter that influences oxide productionti on ICP-MS instruments of other brands commonly used for U–Pb geochronology, it is typically optimised over a range of approximately 1200–1600 W. After all, both nitrogen addition and increased RF power generally promote ionisation and may therefore influence the component of the plasma-induced bias associated with the degree of ionisation.

AC2-18 As now mentioned at line 70, we did not add N2 gas. We have experimented with adding a small flow of N2 gas to the mixing chamber. Signal strength and U oxidation increased because of increased flow into the plasma but after reducing the makeup Ar flow to achieve ThO/Th of 0.5% as before, signal strength remained the same. We do not know why this was so, when an increase has been reported by others. If the reason for the increase is N oxidation, we would very much like to try it with H2 as suggested by Guillong and Heinrich, 2007. One of the problems with writing a long manuscript is that at the end of it one thinks (or is made to think) of many things that should have been tried earlier.

RC2-19 (3) ¨The plasma is maintained within normal atmosphere and cooled by air flow around it.¨ This description is imprecise. The plasma within the torch is maintained within argon and cooled primarily by the tangentially injected cool gas (argon at a flow rate of approximately 16 L/min), which both confines and cools the discharge and also cools the torch. The plasma is, of course, also cooled as it dissipates after emerging from the torch towards the sampler cone. However, this cooling is of limited importance for the analyte zone of the plasma, where sample ionisation and extraction takes place. It is, however, true that the surrounding atmosphere may penetrate as far as the orifice of the sampler cone. This is illustrated, for example, by the elevated silver background observed on instruments containing silver-plated components in the interface region. I assume that this is the point you intended to convey to the reader. If so, please express it more clearly.

AC2-19 This part has been removed from the manuscript.

RC2-20 (4) You observe a gradual decrease in oxide production over several hours after the ICP is switched on. I can confirm this observationti moreover, it is not limited to Agilent instruments but is also observed on PerkinElmer and Thermo ICP-MS systems. A complementary drift may likewise be observed in the ++/+ ratio. I do not consider this drift to be of major significance for U–Pb dating by LA-ICP-MS, since the primary standard is routinely reanalysed throughout an analytical session and the calibration is updated accordingly. However, I can see that this drift substantially complicates the optimisation of the gas flows (auxi or He) in your experiments and makes the resulting observations and interpretations more difficult to follow. Please note that this drift largely disappears after 1–2 days of continuous ICP operation. My recommendation would therefore be not to overcomplicate the data by introducing additional corrections, but instead to allow the instrument to stabilise with the ICP-MS operating continuously for approximately 36 hours before beginning experiments on oxidation and, potentially, doubly charged ion production.

AC2-20 We thank the reviewer for his comments on this important problem. An instrument warm-up time of 36 hours would require a lot of Ar but might be possible in a lab that runs continuously. Eliminating the oxidation problem by some technical means would be an important improvement.

RC2-21 (5) Please exercise caution when using the 16O18O+ dimer intensity as a proxy for the oxygen activity in the analytical zone of the ICP during laser ablation. Depending on the load imposed by the sample matrix on the plasma, some part of the plasma energy is consumed, thereby promoting the formation of molecular ions such as 16O18O+ in the less energetic plasma. This effect is unrelated to the oxygen abundance in the sample itself. To be more conclusive on this point, I suggest ablating an oxygen-free material, such as a silicon wafer.

AC2-21 These comments refer to the paragraph at line 122 of the original manuscript. We removed the detailed discussion of instrument bias, which includes background oxygen monitoring.

RC2-22 (6) *A priori*, changing the He flow rate may not be the most appropriate way to extrapolate the plasma bias to zero oxygen. Actually, changing the He flow significantly shifts the whole system. For example, He is an excellent heat conductor, while the ICP plasma, as an inductively coupled heat source, is heated primarily in the auxiliary zone (skin effect), from which energy is transferred to the sample channel by conduction, radiation, and convection. A lower He flow rate in the sample channel results in less efficient heat transfer, while Pb and U have different first ionisation potentials. I do not claim that your approach is necessarily inaccurateti nevertheless, I encourage you to reassess its validity.

AC2-22 This refers to lines 161-170 of the original manuscript . This is part of the discussion of instrument bias, which has been removed.

RC2-23 (7) Regarding the potential presence of a position effect in two-volume ablation cells equipped with a movable extraction funnel, this phenomenon cannot be regarded as universal. We are satisfied users of the S-155 cell, which has a fixed extraction funnel. It appears, however, that most twovolume cells, including the HelEx II from Teledyne Photon Machines and your NWR-ESI cell, use a movable extraction funnel with sliding parts around the stainless-steel tube through which the ablated material is extracted from the cell. You may therefore be correct that helium leakage through these sliding parts is responsible for changes in the signal. The important point, however, is that this hypothesis should be supported by experimental evidence rather than presented as speculation. Specifically, you should demonstrate that the proposed leakage results in a measurable pressure drop within the cell and that any resulting position effect is reflected in the U/Pb dates obtained for an appropriate secondary standard. Otherwise, this explanation - despite its potential practical importance - remains unsubstantiated, providing one more reason to omit the entire section discussing the plasma-induced biases from this manuscript.

AC2-23 (line 171-185 and line 12 of the original manuscript). This is part of the discussion of instrument bias, which has been removed.

RC2-24 (8) Regarding the idea of placing the entire torch assembly in a nitrogen atmosphere, I quite agree that this is an interesting idea. Moreover, depending on the source of argon supplied to your laboratory, you might even consider using argon instead of nitrogen for this purpose, as it could prove to be more economical. The only question is whether this manuscript is the most appropriate place to present this idea in its current form, as it is not supported by experimental data and therefore remains a pure conceptual exercise. In my opinion, this concept would be better developed and presented in a dedicated manuscript focusing on plasma-induced biases in U/Pb LA-ICP-MS.

AC2-24 This refers to lines 186-192. This is part of the discussion of instrument bias, which has been removed.

Plasma-induced biases, differential ionisation and mass fractionation:

RC2-25 (1) ¨As shown below, calibration using a matrix-matched standard should correct both plasma and ablation bias… if ablation bias proved to be identical…(then) knowing the plasma bias would eliminate the need to measure a standard¨ Exactly. Matrix-matched standardisation should correct for both plasma- and ablation-induced biases. However, based on extensive experience, the idea

that different zircon samples can be assumed to exhibit the same ablation bias appears hopeless, even if the zircons are annealed. Consequently, knowing the plasma bias alone does not eliminate the need to measure a standard. This is another reason to remove the discussion of plasma induced biases from this text and use the related data as the basis for a dedicated manuscript.

AC2-25 This refers to the first paragraph of old section 3.1.2. We have changed 'plasma bias' to 'instrument bias' and followed the reviewer's suggestion by removing detailed discussion of it.

RC2-26 (2) ¨The plasma in an ICP torch is maintained by the transfer of radio frequency energy from the surrounding coil to electrons…¨ Still, the plasma channel, where the sample aerosol is injected, vaporised, atomised and ionised, is heated primarily by conduction, radiation, and convection from the hotter outer zone (see above). Direct heating by eddy currents induced by the rapidly oscillating magnetic field generated by the load coil is minimal in the analytical zone of the ICP.

AC2-26 This refers to the paragraph at old line 200, now line 87. It our statements should be true no matter the mode of heat transfer within the plasma.

RC2-27 (3) ¨Levels of ionisation … are much higher (>80% for most elements) than would be expected from the temperature of the plasma (Saha equation)…¨ Ionisation efficiencies most commonly reported in the ICP literature come from R.S. Houk (1986): *Mass Spectrometry of Inductively Coupled Plasmas*. Analytical Chemistry, 58(1), 97A–105A. His estimates are based on the Saha equation. Please explain your position on this in greater detail.

AC2-27 old lines 204-206. This part has been largely removed from the manuscript but we have added the Houk (1986) reference.

RC2-28 (4) ¨The extraction efficiency is dependent on atomic or molecular weight, favouring heavier species¨.
As a standalone phrase, it may be acceptable, but in the context, it appears somewhat misleading. As far as I remember, in the differentially pumped interface typically used in ICP-MS, ion transport between the sampler and skimmer cones is dominated by viscous flow effects (viscous drag), with the sample ions entrained in a dense plasma plume consisting of argon atoms, ions, and electrons. Mass-dependent fractionation at this stage is generally small because the ions are transported collectively with the expanding plasma (like a man in a moving crowd), rather than moving independently according to their individual masses. More significant mass discrimination can occur downstream, during ion extraction and transmission through the ion optics, where the ion beam fractionation becomes space-charge dominated. Space-charge effects indeed favour the transmission of heavier ions, though their magnitude depends on the details of the ion optics / instrument tuning. Here, as well as in many other places in the manuscript, there is a need for more citations, e.g., Niu, H. & Houk, R. S. (1996). *Fundamental aspects of ion extraction in inductively coupled plasma mass spectrometry*. Spectrochimica Acta Part B, 51, 779–815. In brief, here we are dealing with a bias induced during ion transfer through the ion channel of the instrument, rather than with a plasma-induced bias in the strict sense.

AC2-28 This refers to the discussion at old line 210. We thank the reviewer for his detailed insight. This part has been largely removed from the manuscript but we have added the Niu & Houk reference.

RC2-29 (5) Regarding the last four paragraphs of this section, which describe the exponential fractionation model and provide an estimate of 93% for the ionisation efficiency of lead: the final result is inconclusive and of limited practical value. Is it worth presenting in the manuscript? Moreover, the estimated lead ionisation efficiency of 93% appears rather low and may be inconsistent with the previous literature. Please provide a thorough analysis of the available literature and present a well-supported conclusion. Are you certain that the inferred 206Pb/238U plasma bias of 30% is attributable solely to processes occurring within the ICP? Could part of this bias arise from ion losses during ion extraction and transmission through the mass spectrometer (i.e., the interface and ion optics), rather than from the plasma itself? That would explain the relatively low apparent

ionisation efficiency of 93% that you derive here.

AC2-29 This refers to old section 3.1.2. which was a detailed discussion of instrument bias that has now been removed.

RC2-30 (6) ¨The most convenient approach is to use laser scans but these are not free of ablation bias…¨ The entire paragraph beginning with this phrase would fit more naturally in the subsequent section dedicated to the ablation bias. ¨The edge of each individual pulse has a relatively high brightness under BSE…As noted by Nasdala et al. (2006) for zircon, the brightness of the BSE response increases with the degree of atomic disorder. This suggests deposition of Pb-depleted melt around the edge of the ablation footprint or the removal of melt that had previously formed within it.¨ This statement is too strong and would not generally be considered correct. A more accurate statement would be: "Radiation-damaged (metamict) zircon may appear brighter in BSE images than well crystallized zircon, partly because atomic disorder reduces electron channeling." From this observation, however, it is a long way to the conclusion that the ablation footprint contains Pbdepleted glass. Please use transmission electron microscopy (TEM), and possibly Raman microspectroscopy and other surface analytical techniques, to demonstrate that this material is indeed a Pb-depleted glass (melt) formed during laser ablation.
Ablation bias

AC2-30 This refers to old line 243 now at line 105. The scans show a clear and consistent difference between total Pb/U bias measured on NIST glasses and zircon. Both were measured in the same session so have the same instrument bias so the difference is due to ablation bias. Since the bias is higher (less negative) for glass than for zircon the glass must have preferentially lost more Pb than zircon. We assume that amorphous zircon is congealed melt and must be a glass. Even if it is not all glass, it seems to us to be reasonable evidence that the original zircon had melted.

RC2-31 Fig. 4. ¨These should be deleted in Pb…¨ vs. ¨…depleted in Pb¨.

AC2-31 This is now Fig. 1. We corrected the spelling and changed the phrase to ‘These may be depleted in Pb…’.

RC2-32 (1) ¨The bias increases as a function of the aspect ratio of the pit with an early rapid rise changing to a slower linear rise, eventually levelling off…¨ This behaviour is typical of old zircons subjected to aggressive ablation. However, for most Paleozoic zircons, using a repetition rate of 5 Hz, an onsample fluence of 2 J/cm2, and a beam diameter of 30 µm - a set of ablation settings typical for sensitive sector-field spectrometers - only the initial, approximately linear part of the trend is typically observed during the first 15 s of ablation. A more appropriate description would be: "The dependence of the measured intensity ratio on time can be empirically described by the sum of linear and exponential components:
Intensity Ratio(time) = a + b × time + c × exp(−d × time).
For younger zircons and slow ablation rates (e.g., 5 Hz rep. rate and 2-2.5 J/cm2 fluence), the linear component dominates. As the ablation rate increases, particularly at higher fluences, the exponential component becomes increasingly important¨.

AC2-32 This refers to old line 267. Having rarely analyzed Phanerozoic zircon using LA-ICP-MS, we find the reviewer’s comments to be very informative. All work here has been done on Precambrian zircon, where fractionation profiles typically (though not always) show the characteristics described at lines 370-372.

RC2-33 (2) ¨…shows the appearance of a melt, consisting of ZrO2 and liquid SiO2, …¨ the phase diagram predicts the formation of a Si-rich liquid rather than pure liquid SiO_2. Unless supported by direct structural and compositional evidence, it is not appropriate to describe the phase as liquid SiO_2.

AC2-33 This refers to old line 283. We have changed the phrase to ‘SiO_2 rich liquid’ at new line 143.

RC2-34 (3) ¨However, this does not explain why minimal ablation bias is seen at the start…¨ Please first introduce that ¨minimal bias¨ to the reader appropriately, otherwise, the logical flow is disrupted.

AC2-34 This refers to old line 287. We are not sure of the intended meaning here but have changed the wording from 'minimal ablation bias' to 'the least ablation bias' at new line 147.

RC2-35 (4) ¨Melt should boil off during irradiation down to a depth at the base of the pit where temperature falls below the boiling point. Zircon ablation pits typically show a layer of solidified melt at the base and along the walls…¨ Unless demonstrated by transmission electron microscopy (TEM) or another high-resolution analytical technique, these considerations remain speculative. Please bear in mind that a phase diagram describes equilibrium relationships, whereas laser ablation is a highly nonequilibrium process. What can be stated with confidence is the presence of particles and their agglomerates – this is very common with any LA experiments. The presence of a Si-rich melt phase (glass), as well as crystalline ZrO_2, should be demonstrated independently of the phase diagram using a high-resolution technique capable of phase identification. Please note that the presence of crystalline ZrO_2 has already been demonstrated by TEM. The corresponding TEM images have been presented and discussed within the LA-ICP-MS community on several occasions - for example, by Jan Košler at WCPS 2013 in Florida and, more recently, by Simon Jackson at EWLA 2026 in Milan. However, these researchers focused on the presence of ZrO_2 rather than on the melt phase.

AC2-35 This refers to old line 296. What we presume to observe is solidified melt (glass). We have revised the paragraph at new line 168 to discuss this. The scan line is clearly visible in Fig. 3A.

RC2-36 (5) Regarding the idea to ablate the bottom of a wide (130 µm) ablation pit with a smaller beam to qualitatively characterize the composition of the melt (glass) presumably coating the bottom of the wide pit and to demonstrate that this melt has a low Pb/U ratio, I find the results inconclusive. What is known for sure is that crystalline ZrO_2 is present within the ablation pit. As this phase readily accommodates U in its crystal structure while excluding Pb, it is expected to have a low Pb/U ratio. Consequently, it will lower the Pb/U ratio of the bulk material sampled during the second ablation, irrespective of whether that material consists of ZrO_2, glass, pristine zircon, or a mixture of these phases. Therefore, the experiment does not uniquely demonstrate the presence of a Pb-depleted glass phase. If you maintain that such a glass forms within the ablation pit - which is possible - please provide convincing structural and compositional evidence to support this claim. Please also clarify whether you scanned across or around the bottom of the wide pit. In this respect, the legend of Fig. 5 contradicts the main text.

AC2-36 This refers to the paragraph at old line 296. The reviewer is correct that we make the assumption that the rounded globs seen at the base of the ablation pit consist of glass and not baddeleyite. We think that this is a safe assumption but now qualify our statement at new line 178: ' the base is partly floored by an irregular layer of what appears to be solidified congealed melt lying on top of a smooth surface'

RC2-37 (6) ¨A potential approach to correcting ablation bias… A possible candidate is Yb…¨ I suggest removing this paragraph, as it presents inconclusive information and the manuscript is already quite lengthy.

AC2-37 This refers to the paragraph at old line 316. We have kept this small paragraph because it describes an interesting negative result, which could save others the time and effort of repeating the experiment.

RC2-38 (7) ¨The usual way to correct for ablation bias is to measure a standard…¨ This conventional approach accounts for all types of bias discussed in your text, not solely for the ablation bias.

AC2-38 This refers to line old 330. We have replaced 'ablation bias' with 'all biases' at new line 209.

RC2-39 (8) ¨A complication with zircon is that, although most natural zircon is of similar composition, the crystal structure may be damaged by alpha recoil… … … younger zircons should generally have less

damage, especially if samples are annealed before being ablated.¨ This observation raises an important concern. The magnitude of the ablation bias can be influenced by annealing, whereas the standard zircons used in this study do not appear to have been annealed. However, annealing of both samples and standards prior to LA-ICP-MS U–Pb dating is now common practice. Please clarify the significance of annealing in the context of your results. Would it be appropriate to also present laser-induced fractionation patterns for annealed zircon standards?

AC2-39 This refers to old line 333 (new line 209). A principal aim of this work is to understand what drives ablation bias so it can somehow be corrected, not establish a sample treatment procedure that minimizes it. We therefore intentionally chose samples with as wide a range of properties (age, U) as possible to see how this affects the fractionation profiles.

RC2-40 (9) Regarding the raster ablation (¨Taking data from line scans¨). Please consider that the ablation process may be influenced by laser pre-irradiation of the sample. High-energy UV photons penetrating beyond the bottom of the ablation pit may induce defects in the underlying zircon, potentially modifying the laser–material coupling and, consequently, the particle-size distribution of the generated aerosol. Spot ablation may benefit from this effect more than raster ablation, as the same region is irradiated repeatedly.

AC2-40 Refers to old line 346. This is an interesting detail, but if scans are compared between samples and standard these effects should largely cancel. Even if they don't, scans have the advantage of giving a constant result, rather than a variable one as with spots. Provided ablation conditions are they same, they should give reproducible results.

RC2-41 (10) The famous "split NIST 612" experiment of Eggins et al. (1998). I have two concerns. First, I am not sure that your interpretation of the ablation pits presented by Eggins et al. is correct. From Fig. 6 of Eggins et al., I cannot determine whether the bright features along the crater walls represent two distinct coatings, a single coating with two interfaces, SEM edge effects, or charging/detector contrast. I would therefore describe the observations more cautiously as follows: *"The BSE images appear to show two bright rims along the crater wall. However, Eggins et al. do not discuss these features as two distinct coatings, and the available SEM images do not permit a unique interpretation. Confirmation would require high-resolution TEM together with compositional mapping (e.g. STEM-EDS) to determine whether the bright rims represent separate deposited layers, interface contrast, or imaging artefacts."* Second, I am not convinced that the conclusions drawn from the "split NIST 612" experiment can be directly applied to the mineral zircon. That experiment does not establish whether the same mechanisms operate during zircon ablation, where additional phases may be present, including crystalline ZrO_2 and possibly a Si-rich glass whose composition may differ substantially from that of the parent zircon. Nor can the "split NIST 612" experiment be used to infer the existence or composition of a Pb-depleted melt in zircon. Addressing these questions requires direct structural and compositional characterization of the ablation products from zircon itself. In my opinion, the lack of reliable original experimental evidence on this point is one of the major shortcomings of the manuscript.

AC2-41 Refers to old line 335. We see the reviewer's point about the ambiguities in interpreting cross-section images the ablation pits in the Eggins et al (1998) paper. We have modified the text accordingly at new line 238.

RC2-42 (11) Finally, I recommend that the authors consult the recent literature on laser-ablation-induced fractionation. As a possible starting point, I suggest the following paper: Adamson, M.N., Cottle, J.M. & Kylander-Clark, A.R.C. (2026). *A Mechanistic Study of Matrix Effects in Zircon U–Th/Pb Geochronology Using Single-Particle Laser Ablation Time-of-Flight Mass Spectrometry*. *Chemical Geology*, 707, 123325. I do not necessarily agree with all of the conclusions presented in this paperti however, it provides a reasonable introduction to the current state of the literature and to some (not all) of the modern experimental approaches for investigating the ablation behaviour of zircon. Measuring and correcting ablation bias

AC2-42 This is an important paper that we somehow missed. It is now referenced and we are grateful to the reviewer for drawing our attention to it.

RC2-43 I am sorry, but at this point I feel that I no longer have enough energy or patience to continue reviewing your manuscript paragraph by paragraph. However, unlike the previous sections, I would like to stress that I rather liked your understanding of how the ablation bias might be corrected, and I think that this part may be publishable, provided that several aspects are revised.

(1) Remove the speculative discussion regarding the melt and the proposed causal relationships responsible for laser-induced fractionation or, preferably, replace it with direct observations obtained by transmission electron microscopy. Unfortunately, much of the speculative content from the *Ablation Bias* section is repeated here. I suggest retaining only those fractionation mechanisms that are convincingly supported by experimental evidence.

(2) Irrespective of the exact causes of laser-induced fractionation, keep on insisting that the intercept definition of the intensity ratio does not necessarily ensure accurate U/Pb dates. This point is fundamental, is consistent with the recent literature, and is fully confirmed by at least a decade of experience with regression-based data processing. Indeed, a significant long-term uncertainty still persists (typically <2%), as well as inaccuracies. Ironically, as you point out yourself, calculating the $^{206}Pb/^{238}U$ ratio from mean signals is not the source of that inaccuracy !

(3) Be cautious when interpreting the first few seconds of the ablation signal. Your observations concerning this part of the signal are interesting and potentially important, but they do not permit a unique interpretation. One plausible alternative is the formation of relatively large particles at the very beginning of the ablation process. Such particles may not be completely vaporized and ionized in the ICP, resulting in the preferential release of lead. After several seconds of ablation, the particle size decreases, causing the measured $^{206}Pb/^{238}U$ intensity ratio to drop. Subsequently, however, the ratio begins to increase again because of the accumulation of ZrO_2 in the ablation pit. I am sorry to say this, but I find this interpretation to be more thoroughly supported by the experimental evidence available in the literature than the one you propose.

AC2-43

(1) Reiterating AC2-35 and 36, we do not think that it is necessary to employ TEM to demonstrate the presence of a solidified melt. An amorphous residue from a brief high temperature event most likely was a melt given that it was exposed to energy sufficient to vapourize part of the sample and the liquid reside would not have had time to crystallize. We agree with the reviewer that some of our interpretations are speculative. We disagree that speculation is inappropriate for a scientific publication. A theory is, by definition, speculative. As is well known, theories can never be proved right, they can only be proved wrong. Our interpretation of the role of early melt in the fractionation process (paragraph at line 262 and section 3.2.5) is a theory that needs to be tested, but it is consistent with what be think should be happening during the early stages of ablation. This is something that might be tested in a future study.

(2) We have added a sentence at line 635 emphasizing the reviewer's point.

(3) We hope that we have conveyed a sense of caution with all of our interpretations. The reviewer presents another speculation on early ablation. It is not incompatible with ours but is more complex, which is not a reason to ignore it. This again illustrates to us the necessity of speculation to point the way toward future testing.

Although we do not always agree, we thoroughly appreciate the reviewer's comments and, we hope, have complied with the most important ones. Both reviews have greatly improved the manuscript.

In response to the editor's comments, we have explained how discordance was calculated in lines 578-580.