Comment on Barboni et al. (2025), 'Pervasive impact modification of pristine lunar clasts'

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In a recent contribution, Barboni et al. (2025)[1] present an experimental calibration relating the aluminium content of zircon and its parent melt under lunar conditions. This calibration is then used to argue that lunar zircons are not in equilibrium with their host silicate melts, and that caution is required when interpreting zircon-derived U-Pb dates in evolved lunar rocks. Their contribution includes an Excel spreadsheet that allows users to calculate a predicted equilibrium melt composition for lunar zircons to test whether they are in equilibrium with their host melt. While this study addresses important questions in lunar petrology, several methodological issues limit the reliability and applicability of the current proposed model. These include (1) a mismatch between experimental and natural compositions, (2) analytical data quality, and (3) the regression approach used to derive the calibration. Here, we examine each issue and discuss its implications for the interpretation of lunar zircon petrogenesis.

Mismatch Between Experimental and Natural Conditions

The experimental calibration range does not overlap with that of the natural dataset (*Fig. 1*). Experimental zircon Al concentrations span 70–640 μg.g^{-1}, whereas lunar zircons contain only 3.30–38.7 μg.g^{-1} Al (median of 10.8 μg.g^{-1}). Similarly, the experimental glass compositions have generally higher aluminium index values (Al_I), ranging from 0.28 to 0.65 (median of 0.43), whereas the lunar glasses have Al_l values ranging from 0.25 to 0.30 (median of 0.28). These discrepancies indicate that the regression model is being extrapolated beyond its experimental calibration range, which reduces confidence in using it for quantitative predictions for natural lunar samples.

Analytical Conditions and Data Quality

Upon request, the authors provided the raw calibration data: experimental glass and zircon analyses, measured using electron probe microanalysis (EPMA) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), respectively. Inspection of these datasets revealed two major issues. First, several repeat analyses that were inconsistent with the analysed glasses were included in the published averages, resulting in large uncertainties in calculated glass Al-indices (Fig. 1a). Second, multiple zircon analyses show strongly non-stoichiometric zirconium abundances (many yielding calculated ZrO_2 and SiO_2 abundances > 100 wt.%), inconsistent with ideal zircon compositions or have excessive Al counting statistics. Of 190 glass analyses (5 repeats per experimental charge), 16 were discarded, and of 327 zircon analyses, 29 were discarded. Figure 1b presents new weighted averages and standard deviations calculated after excluding poor-quality analyses, which yield substantially smaller uncertainties on each datapoint. However, this filtering does not resolve the consistently low analytical totals observed for multiple experimental glass analyses (Fig. 1b).

EPMA analytical totals for the experimental glasses range from 77.4 to 99.9 wt.%, with many below 90 wt.% (Fig. 1). Totals of this magnitude are unlikely to reflect elevated water contents, as silicate melts containing more than ~9 wt.% H_2O typically do not quench to homogeneous glass[2]. Moreover, one of two anhydrous experiments has a similarly low total (~92 wt.%; Fig. 1), further indicating that unmeasured water alone cannot explain the deficit. The incorporation of capsule material (e.g., Pt or Au) is also improbable, as these native metals are generally inert under experimental conditions and would appear as discrete blebs in back-scattered electron images. Therefore, the low totals are most plausibly attributed to analytical artefacts such as mixed-phase signal averaging (e.g., from microlites within the quenched melt)[3], or inadequate standard–sample matrix matching[4]. Barboni et al. calibrated their EPMA analyses using basaltic glass standards (VG2 and A99[5]), which are not matrix-matched to several of the evolved experimental glasses. No data for secondary standards are reported, preventing assessment of analytical accuracy, instrumental drift, or matrix effects. The cause(s) of these low analytical totals should be investigated, and glasses remeasured to ensure that they are not a symptom of wider issues with the experimental glass EPMA analyses.

Finally, distinct analytical protocols were applied for the experimental and natural samples, resulting in visibly larger uncertainties for the experimental glasses (Fig. 1a). Consistent analytical conditions are essential when combining datasets in a joint calibration; their absence reduces the comparability and reliability of the regression.

Regression Approach and Model Bias

Barboni et al (2025) treat the relationship between zircon and melt Al contents as a linear regression problem, with errors in both *x* (glass Al content index) and *y* (measured zircon Al abundance). The authors employ a weighted least squares approach, that accounts only for uncertainty in the zircon Al contents. Figure 1a shows their preferred fit through the published data, where the regression is constrained to pass through the origin. This fit has poor goodness-of-fit metrics (R^2 of 0.365, reduced $\chi^2 >> 1$), indicating either substantial data scatter, an inappropriate regression equation, or both[6].

Figure 1b presents the same regression equation fitted to the less noisy, filtered dataset. This fit was performed using Orthogonal Distance Regression, which accounts for uncertainty in both variables[7]. This resulting improvement in goodness-of-fit metrics in marginal, which suggests that the chosen regression model (forced through the origin) does not adequately describe the calibration data. In both cases, the calibration data deviate systematically from the fitted model, implying that the model does not adequately describe the experimental relationship.

The consequences of this regression choice become clear when extrapolating to natural compositions (Fig. 2). Following the approach of ref[8], we rigorously propagate both analytical and regression uncertainties into the predicted glass compositions. Forcing the calibration through the origin leads to predicted melt compositions that deviate markedly from the measured coexisting melts and yields artificially low uncertainties (Fig. 2a,b). In contrast, allowing the intercept to vary freely produces a substantially better fit ($R^2 = 0.662$, reduced $\chi^2 = 6.78$) and yields predicted melt compositions that coincide with the measured values (Fig. 2c,d).

Although more complex models tend to produce smaller residuals, the substantial reduction in Bayesian and Akaike information criteria (BIC and AIC; from ~700 to ~500; Fig. 2a,c), which explicitly penalise increased model complexity, indicates the improved fit of the unconstrained model is statistically justified. Collectively, these results demonstrate that constraining the regression through the origin systematically biases the calibration and, consequently, leads to the erroneous conclusion that lunar zircons are not in equilibrium with their host melts.

Neglected Role of Water in the Calibration

Barboni et al. justify the use of a regression model that is forced through the origin with the assertion that it would be unphysical for zircon to exhibit negative aluminium contents when its host glass contains aluminium. Here we propose a potential reason why the experimental data are better represented by a regression with an unconstrained y-intercept. The substitution reaction proposed they consider is:

$$\mathrm{ZrSiO_4}(zircon) + \frac{1}{2}\mathrm{Al_2O_3}(melt) + \frac{1}{2}\mathrm{H_2O}(melt) \rightleftharpoons \mathrm{Zr[AlHO_4]}(zircon) + \mathrm{SiO_2}(melt)$$

which implies that:

$$[\mathrm{Al}]_{\mathrm{zircon}} \propto \left(\frac{a_{\mathrm{Al_2O_3}}^{0.5}\, a_{\mathrm{H_2O}}^{0.5}}{a_{\mathrm{SiO_2}}}\right)$$

Barboni et al. assume that the water activity (a_{H2O}) is constant among their experimental glasses and, therefore, omit this term when constructing their regression. They justify this assumption with the observation that zircon Al contents from nominally anhydrous experimental runs overlap those from water-bearing experiments (Fig. 1). However, in high-temperature capsule experiments, H_2O abundance can vary substantially due to loss or redistribution during the run or quench[9]. As H_2O influences melt structure and the activities of Al and Si, and thus the partitioning of Al into zircon, neglecting variable water activity will bias both the slope and intercept of the regression, and may contribute to the observed scatter.

Indeed, unaccounted variation in H_2O provides a plausible explanation for the negative intercept suggested by the trend of the experimental data (Figures 1 and 2). Even under simple assumptions, such as Henry's law behaviour, reasonable variations in melt H_2O content would lower the aluminium index, effectively flattening the experimental trend and reducing the intercept toward zero. Incorporating measured post-run H_2O contents of both experimental and natural glasses is, therefore, essential to establish a physically meaningful calibration.

Implications and Recommendations

The concerns outlined above collectively reduce confidence in the robustness of the proposed calibration and its applicability to natural systems. We acknowledge the importance of investigating whether dates derived from lunar zircons represent the formation ages of their host evolved rocks, as these ages underpin our understanding of the role of evolved lunar magmatism in the Moon's geological history[10,11]. However, several refinements are required before the model is applied to lunar mineral-melt systems by other researchers:

- Expand the calibration dataset to encompass the compositional range of natural samples.

- Reassess analytical protocols to ensure the accuracy glass and zircon analyses, supported by rigorous calibration and standardisation procedures.
- Investigate and address the cause(s) of low analytical totals in experimental glass analyses.
- Quantify the water contents of both experimental and natural glasses and incorporate these into the regression model.

Until these revisions are implemented, the application of the proposed calibration to interpret the petrogenesis of lunar zircon should be undertaken with caution.

References

1. Barboni, M., Needham, E., Trail, D., Bell, E. A. & Chen, H.-Y. Pervasive impact modification of pristine lunar clasts. *Nat. Commun.* **16**, 2485 (2025).
2. Gavrilenko, M., Krawczynski, M., Ruprecht, P., Li, W. & Catalano, J. G. The quench control of water estimates in convergent margin magmas. *Am. Mineral.* **104**, 936–948 (2019).
3. Kuehn, S. C., Froese, D. G. & Shane, P. A. R. The INTAV intercomparison of electron-beam microanalysis of glass by tephrochronology laboratories: Results and recommendations. *Quat. Int.* **246**, 19–47 (2011).
4. Hughes, E. C. *et al.* Low analytical totals in EPMA of hydrous silicate glass due to sub-surface charging: Obtaining accurate volatiles by difference. *Chem. Geol.* **505**, 48–56 (2019).
5. Jarosewich, E., Nelen, J. A. & Norberg, J. A. Reference Samples for Electron Microprobe Analysis. *Geostand. Newsl.* **4**, 43–47 (1980).
6. Tellinghuisen, J. & Bolster, C. H. Using R2 to compare least-squares fit models: When it must fail. *Chemom. Intell. Lab. Syst.* **105**, 220–222 (2011).
7. Boggs, P. T. & Rogers, J. E. Orthogonal distance regression. in *Statistical analysis of measurement error models and applications: Proceedings of the AMS-IMS-SIAM joint summer research conference, june 10–16, 1989* vol. 112 186–194 (American Mathematical Society, 1990).
8. Tellinghuisen, J. A simple, all-purpose nonlinear algorithm for univariate calibration. *The Analyst* **125**, 1045–1048 (2000).
9. Truckenbrodt, J. & Johannes, W. H_2O loss during piston-cylinder experiments. *Am. Mineral.* **84**, 1333–1335 (1999).
10. Seddio, S. M., Jolliff, B. L., Korotev, R. L. & Zeigler, R. A. Petrology and geochemistry of lunar granite 12032,366-19 and implications for lunar granite petrogenesis. *Am. Mineral.* **98**, 1697–1713 (2013).
11. Meyer, C., Williams, I. S. & Compston, W. Uranium-lead ages for lunar zircons: Evidence for a prolonged period of granophyre formation from 4.32 to 3.88 Ga. *Meteorit. Planet. Sci.* **31**, 370–387 (1996).

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Competing Interests The authors declare no competing interests.

Data Availability Experimental data are from the original paper[1]. Filtered data and code to replicate the fitting and recreate Figures 1 and 2 is available at Github: *https://github.com/fboschetty/natCom_LunarClast_Commentary*

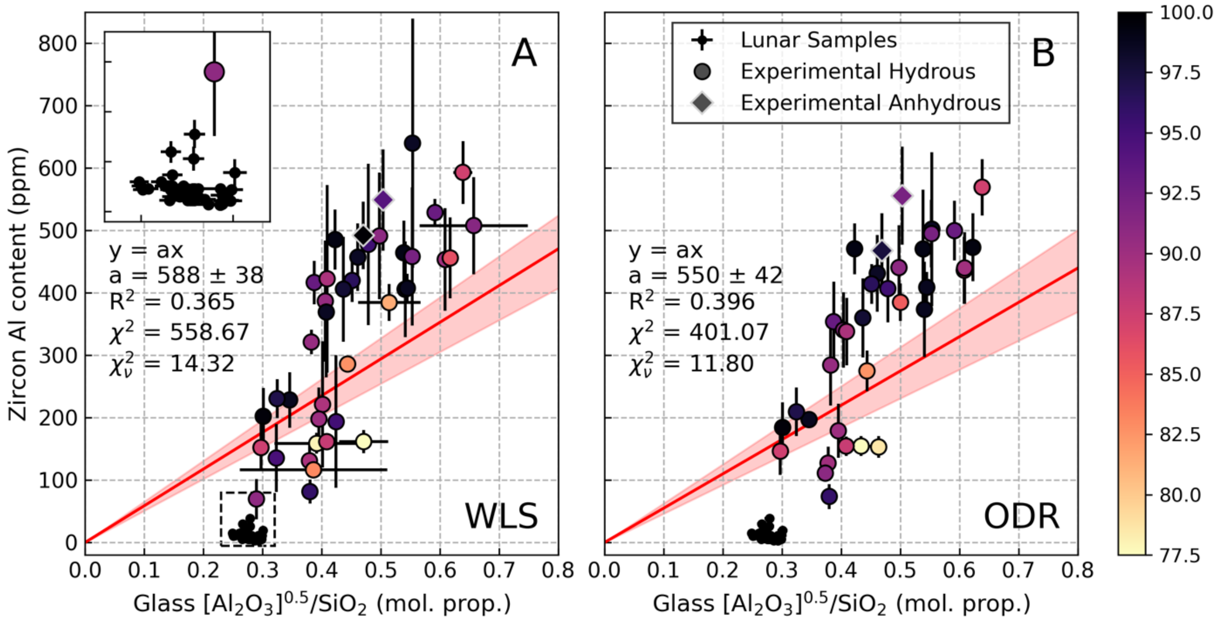

Figure 1 | Calibration of experimental zircon Al content vs. melt composition (AlI_{glass}).

(A) published experimental and lunar datasets from Barboni et al. (2025). (B) the same experimental dataset filtered to remove mixed-phase analyses as best as we could. Large circles denote hydrous experimental glass-zircon pairs, diamonds are the two anhydrous experiments. Symbols are coloured according to glass analytical totals. Small black circles indicate natural lunar zircon-glass pairs. Error bars reflect 1σ uncertainties; *x*-error bars are propagated from analytical uncertainties in glass Al_2O_3 and SiO_2 contents. In (A) the red line shows the preferred regression from Barboni et al. (2025), constrained to pass through the origin. In (B), the same regression model refitted to the filtered dataset. The red shaded region indicates the 95% confidence interval. The calculated gradient and its 1σ uncertainty, together the calculated goodness-of-fit statistics. The inset highlights the region containing all lunar data, outlined in the main plot by a black dashed rectangle.

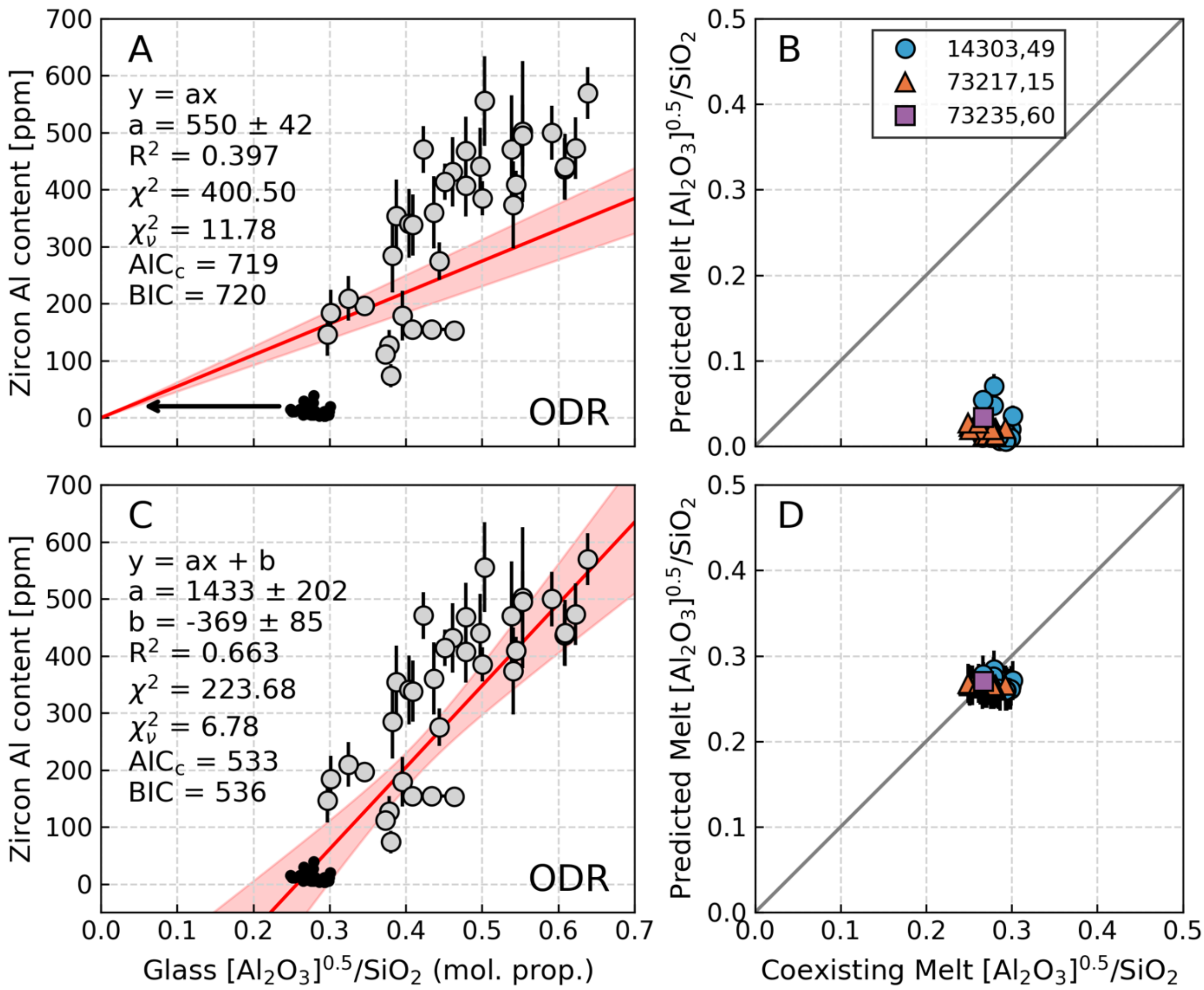

Figure 2 | Effect of regression choice on predicted melt compositions.

Experimental zircon–glass pairs (grey circles) and lunar samples (black circles) are shown. Panels A and C illustrate alternative regression models used to calibrate zircon Al content as a function of melt composition: (A) regression constrained to pass through the origin, and (C) regression with a freely varying intercept. Each panel reports the best-fit equation, 1σ parameter uncertainties, and associated goodness-of-fit metrics. The black arrow in (A) highlights the systematic offset between the lunar zircon data and the origin-forced model. Panels (B) and (D) compare predicted versus measured melt compositions for lunar zircons, derived from the regressions in (A) and (C), respectively. The grey line denotes the 1:1 relationship. Forcing the fit through the origin (A–B) produces a systematic deviation from the

1:1 line, whereas allowing an intercept (C–D) yields predictions consistent with measured melt compositions.