Comment on 'The magmatic architecture and evolution of the Chang'e-5 lunar basalts'

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This comment was submitted to Nature Geoscience. However, it was rejected on the basis that '*we do not feel the comments raised sufficiently advance or clarify understanding of the paper by Luo et al…* We encourage you to post your comment on an appropriate preprint server.*'*. **We disagree that showing the vast majority of P spread is within error is not important. We are looking for an alternative home – any suggestions welcome!**

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Luo et al.[1] present exciting new data on lunar basalt samples erupted at ~2 Ga, and brought to Earth by the Chang'e-5 (CE-5) mission. These samples offer important new opportunities to understand lunar magmatic systems. Luo et al.[1] use Clinopyroxene-Liquid (Cpx-Liq) thermobarometry and pMELTS modelling of mineral compositions to determine the pressures (P) and temperatures (T) of magma storage on the moon. Specifically, they iterate the barometer of Neave and Putirka[2] and the thermometer of Putirka (eq33)[3], yielding pressures spanning ~1-12.9 kbar, which are strongly correlated with calculated temperatures (Fig. 4a). They also compare the measured Na_2O and Al_2O_3 contents of lunar Cpx and pigeonites to the phase compositions predicted in a pMELTS calculation path. Most measured pyroxene compositions overlap with pMELTS calculations at 0-7 kbar, although a few overlap with calculations at 8-12 kbar. Using these two constraints, Luo et al. suggest that '*multiple magma reservoirs could have been distributed throughout the upper part of the lunar lithospheric mantle, feeding magmas into shallower levels, and ultimately to the surface*' (Fig. 5c). In their schematic Fig. 5b, they draw what has become a rather typical representation of 'trancrustal' (or in this case, translithospheric) storage, with 5 different magma reservoirs distributed across 100s of km depth.

Recent advances in understanding the sources and magnitudes of error associated with Cpx barometry reveal that the majority of studies utilizing Cpx barometry in the literature neglect to (1) propagate analytical uncertainty into P and T estimates[4], and (2) ensure that the composition space of the studied magmas is similar to that of the barometer's calibration dataset[5]. Luo et al.[1] allude to point 1 with their sentence '*For this purpose, high-quality concentration data on clinopyroxenes in equilibrium with the host basaltic melts are required*'.

The Cpx-Liq barometer used by Luo et al.[1] relies on the exchange of the jadeite ($NaAlSi_2O_6$) component between Cpx and liquid. Although Jadeite in Cpx can be calculated from Na or Al, almost all (75/76) of the lunar Cpx used to calculated pressures and temperatures have major element chemistry such that the jadeite component is calculated from the Na content. This is problematic because of the very low abundances of Na_2O in Cpx from the CE-5 samples (median=0.06 wt%), reflecting the overall volatile-depleted nature of the moon. When analysed by electron probe microanalyser (EPMA) at the chosen conditions (15 kV, 20nA, 10s), these low concentrations mean that a small number of Na x-rays arrive at the detector, so the measurement is imprecise. This low precision in Na propagates into a large uncertainty in the calculated Jadeite component, and thus the calculated pressure. By compiling the stated errors from Luo et al.[1] and Che et al. [6], we determine that the mean precision for Na_2O in Cpx used to calculate pressures using thermobarometry (N=76) is 26% (range=7-53%, opaque symbols, Fig. 1a). Precision for all analysed pyroxene (which are used to compare to pMELTS calculations) show an even greater range (in some instances exceeding 100%, Fig. 1a, transparent symbols). We were not able to obtain errors for the other two studies from which Cpx analyses for thermobarometry were obtained[7,8]. However, as a first order approximation, we estimate the possible % error based on a best fit line through the data that is available (black line, Fig. 1a). Given these two studies used different EPMA, it is very possible the errors could be significantly larger (or slightly smaller, see[4]).

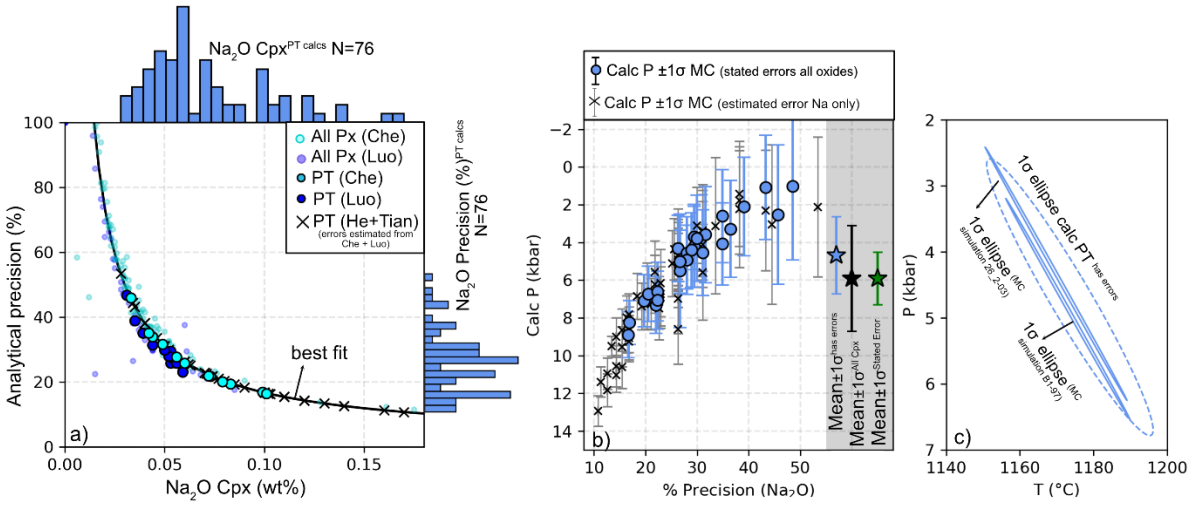

Figure 1. a) EPMA-outputted estimates of analytical precision for all Cpx analysis presented by Luo et al.[1] and Che et al. [6], with Cpx used to calculate P and T shown as opaque circles. As precision estimates were not available for the Cpx from He et al. [8]and Tian et al.[7] used by Luo et al.[1], we estimate errors for just Na_2O from a best fit line through the available data (black crosses). b) 1σ of MC simulation for each Cpx vs. the precision of Na_2O analyses (%). The 1 σ variation of the published pressures for Cpx with precision data (blue star and bar, N=25), all Cpx (N=76, black bar and star) , and the stated error of Luo et al.[1] (green bar and star) is shown in the grey box for comparison. c) 1σ ellipse of all published pressures and temperatures with precision data (N=25) vs. two representative ellipses for MC simulations from individual Cpx.

We use Monte Carlo methods to investigate the effect of these large analytical uncertainties on calculated P and T[4,9]. For each Cpx with published error data, we simulate N=1000 synthetic compositions. For each element, the simulated oxide follows a normal distribution, centred on the stated value, with 1σ derived from the EPMA-calculated estimates of precision for that specific oxide during that specific Cpx analysis. We calculate P and T for each of these N=1000 Cpx when paired to the single liquid composition used by Luo et al. The mean 1σ of these Monte Carlo simulations for Cpx with published precision values is 2.1 kbar (range=1.2-3.6 kbar), and the 1σ of published pressures for these same Cpx is 2.05 kbar (blue star and error bar, Fig. 1b). Thus, analytical precision alone can account for the range of P calculated from the Cpx of Luo et al.[1] and Che et al. [6]. Additionally, it is noteworthy that the spread in pressure generated just from analytical precision is much greater than the error stated by Luo et al.[1] (1σ=1.4 kbar). For Cpx without published precision values, we use the predicted Na_2O precision only (Fig. 1a) to estimate a minimum 1σ value (grey bars). The 1σ for all Cpx (black star and error bar, Fig. 1b) is only 2.8 kbar, which isn't that much larger than our Monte Carlo simulations, particularly considering we do not estimate errors for other elements. Importantly, analytical uncertainty can also account for the distinctive negative array defined by the P and T estimates of Luo et al.[1]. We demonstrate this by overlaying error ellipses calculated for Monte Carlo simulations for two randomly selected Cpx on the error ellipse for all calculated P and T determined for Cpx with precision data. Not only do these three ellipses show a very similar P-T span, they also show a very similar slope (Fig. 1c).

Overall, these simulations show that analytical uncertainty alone can account for the vast majority of the translithospheric spread in pressures and temperatures shown by Luo et al.[1], with the possible exception of a relatively small number of more Na_2O-rich Cpx. Without precision data for these literature measurements, it is hard to assess the uncertainty in calculated pressure robustly. We suggest that the

observed distribution of Cpx chemistry could easily be accounted for by storage in just two distinct reservoirs (a shallower reservoir supplying the majority of Cpx, and a deeper reservoir supplying <10% of Cpx), rather than requiring true translithospheric storage. Substantially more analyses of these higher Na_2O Cpx with estimates of analytical precision are clearly required to have confidence in the depth of this deeper storage region.

When considering the overall error on a barometer, it is important to consider accuracy as well as precision. Accuracy is of particular concern when conducting thermobarometry on lunar basalts, because the experimental Cpx and Liq compositions used to calibrate the barometer of Neave and Putirka[2] show little to no overlap with the compositions of Chang'e-5 basalts (Fig 2a). Comparison of experiments conducted at relevant pressures and bulk compositions[10,11] show a systematic offset between calculated and experimental pressure, which increases at increasing pressure. Assuming the same relationship applies to the natural samples, the iterated barometer may underestimate P by 1 kbar at P=5kbar, and ~3.5-4 kbar at P=15 kbar (blue dots show extrapolated offset for each Cpx calculation, Fig. 2c). This makes the calculated pressures of the most Na_2O-rich Cpx even more uncertain (and again, far outside the stated 1.4 kbar error).

Finally, we assess whether pMELTS can be used to reliably predict Na_2O and Al_2O_3 contents in Cpx, to obtain pressure information. We run equilibrate calculations using experiment liquid compositions at experimental P and T conditions for the Lunar experiments discussed above, as well as the calibration dataset of the Neave and Putirka[2] barometer. We compare calculated mineral compositions to those precipitated in the experiments. We note that there is a very large amount of scatter between predicted and measured Cpx Al_2O_3 contents, with MELTS tending to overpredict Al_2O_3 (except for the experimental pigeonites, Fig. 2d). MELTS drastically overpredicts Na_2O for the Lunar Cpx and the barometer calibration dataset (Fig 2e-f). Thus, we do not believe this method can provide useable pressure information.

Having the ability to retrieve samples from the Moon through missions such as CE-5 is game changing for understanding the petrological evolution of other bodies in our solar system. The availability of such unique samples will result in great advances in understanding lunar magmatic systems. However, we highlight some distinct challenges associated with establishing the P and T of magma storage, which also apply to many terrestrial studies. We hope this response spurs the community to evaluate and publish precision data estimated by EPMA software based on the actual counts for each individual analysis (rather than using secondary standards), and propagate these uncertainties through thermobarometry calculations. The low Na_2O contents of CE-5 Cpx mean that efforts to increase analytical precision (e.g., longer count times, higher beam currents) will be vital to distinguish true translithospheric magma storage from analytical uncertainty blurring together distinct storage reservoirs. Targeted experiments to determine the relationship between Cpx-Liq equilibria and pressure in systems would also greatly reduce systematic uncertainty (Fig. 2c). Large (and highly correlated) pressure and temperature ranges which result from analytical imprecision are common in published studies employing Cpx-Liq barometry, a realization that presents an opportunity for the community to revisit the importance of propagating analytical uncertainties in geothermobarometric calculations prior to making geological interpretations[4,9].

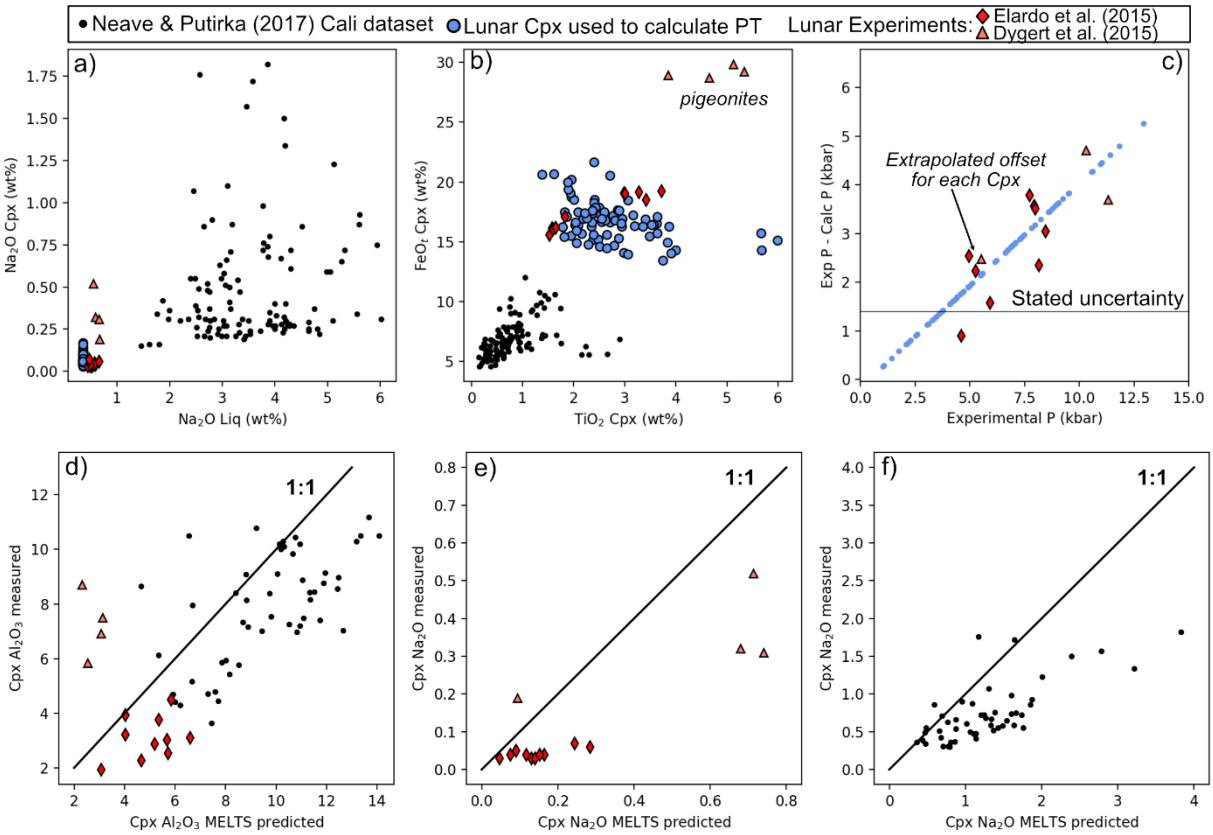

Figure 2. a-b) Calibration dataset of the Neave and Putirka (2017) barometer relative to the Cpx and Liq compositions in this study (which are extremely Na-poor, Fe and Ti-rich), and available lunar experiments with similar bulk compositions[10,11]. c) Offset between calculated and experimental pressure shows an offset which increases relatively coherently with increasing pressure, allowing an estimate of the systematic error to be estimated for each published Cpx pressure. d-e) Comparison of measured Cpx compositions in experiments and those calculated from the coexisting liquid composition in pMELTS.

Data Availability

All Jupyter Notebooks to reproduce the plots shown in this paper are available on Penny Wieser's Github. https://github.com/PennyWieser/Supplement_Comment_on_Luo23_LunarCpx

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